

Variations in chemical speciation and reactivity of phosphorus between suspended-particles and surface-sediment in seasonal hypoxia-influenced Green Bay

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## Abstract

Water, suspended-particles, and surface-sediment samples were collected from Green Bay for the measurements of phosphorus (P) species, including dissolved/particulate-P, inorganic/organic-P, and five different forms of particulate-P, namely exchangeable- or labile-P (Ex-P), iron-bound-P (Fe-P), biogenic-apatite and/or CaCO<sub>3</sub>-associated-P (CFA-P), organic-P (Org-P) and detrital-apatite-P (Detr-P) to elucidate their reactivity and transformation pathways in the water column. Suspended particles contained mainly Ex-P (25±15%), Fe-P (28±12%) and Org-P (29±7%). In contrast, Detr-P (34±10%) and Org-P (36±12%) were the predominant P species in surface sediment. Contents of Ex-P, Fe-P, Org-P and CFA-P decreased consistently from suspended-particles to surface-sediment, but an increase was observed for the Detr-P, indicating a net loss of Ex-P, Fe-P, Org-P and CFA-P from particulate into dissolved phase. Such active regeneration of P in the water column between particulate and dissolved phases may serve as an internal phosphate source in Green Bay, especially under hypoxic conditions. Degradation of organic matter in south central bay areas seemed to promote hypoxia and enhance the reductive-dissolution of Fe-P and preservation of Org-P under low-oxygen conditions in the central bay. Overall, Ex-P, Fe-P, CFA-P and Org-P species, which comprised up to 50-90% of total particulate-P, can be collectively considered as potentially-bioavailable-P (BAP). Under low-phosphate (0.022±0.014 μM in Green Bay) and summer low-oxygen/hypoxic conditions, suspended-particles may release up to 71% of their BAP before deposited in sediment although the BAP regeneration decreased along the south-north transect in Green Bay.

Key words: Phosphorus cycling; Particulate Phosphorus; Chemical Speciation; Coastal Hypoxia; Green Bay Sediment; Lake Michigan

## **Introduction**

As an essential and often limiting nutrient, phosphorus (P) plays a critical role in the ecosystem function and biogeochemical cycling of bioactive elements in freshwater and marine environments (Filippelli, 2010; Slomp et al., 2013; Marko et al., 2017; Orihel et al., 2017). However, excess P can also cause eutrophication and hypoxia in aquatic environments, including the Great Lakes (Scavia et al., 2014; Zhou et al., 2015). Due to its particle-reactive nature (Santschi, 1995; Lin et al., 2016), P can partition preferentially onto suspended particles and sediment in addition to uptake and assimilation by phytoplankton (Coelho et al., 2004; Lin et al., 2013). Phosphorus in both suspended particles and sediment contains different chemical species with distinct exchangeability, reactivity and bioavailability, which can play different roles in regulating water quality and the biogeochemical cycling of P and other bioactive elements in aquatic environments (Zhang et al., 2004; Lopez, 2004; Wang et al., 2009; Lin et al., 2012a). Therefore, knowledge of the partitioning and transformation of P among different particulate phases and chemical forms is essential to understanding the role of P in controlling water quality and the development of eutrophication and hypoxia, especially in anthropogenically influenced aquatic environments.

Recently, eutrophication and hypoxia have been shown to enhance coastal acidification and CO<sub>2</sub> production (Cai et al., 2011; Semiletov et al., 2016). However, linkages between hypoxic conditions and changes in chemical speciation and reactivity of P are not well understood, especially in the context of environmental and climate change. For example, phosphate enrichments have been shown to have dramatic impacts on the development of re-eutrophication and hypoxia in estuarine and coastal environments, such as Lake Erie, the northern Gulf of Mexico, Chesapeake Bay and the Baltic Sea (Elsbury et al., 2009; Rabalais et al., 2009; Reed et al., 2011; Diaz et al., 2012; Baker et al., 2014), but the role of particulate- and organic P species is less clear (Lin et al., 2016). The response of biogeochemical cycling of different P species to eutrophication and hypoxia remains poorly understood, especially the particulate and sedimentary P species. Within the water column or near the sediment-water interface, the degradation of organic P can consume dissolved oxygen. Active redox transformation of iron-bound P and the dissolution of CaCO<sub>3</sub>-bound P can occur due to hypoxia-derived pH changes (e.g., Conley et al., 2002; Hou et al., 2009; Joshi et al., 2015). All these processes could result in internal cycling and transformation of dissolved and particulate P species under different extents

of hypoxia. Therefore, in addition to dissolved P species, systematic studies considering the dissolved-particulate-organic-inorganic continuum should provide insights into the role of different P species in the development of hypoxia in estuarine and coastal environments, and, in turn, the influence of hypoxia on chemical speciation and cycling pathways of P in the water column.

Green Bay is the largest freshwater estuary in the Laurentian Great Lakes, comprising approximately 7% of surface area of Lake Michigan (Klump et al., 2009). Increased urbanization, industrial activities, and agricultural fertilization on the Fox River basin have resulted in hypereutrophic water quality conditions in the southern Green Bay (Valenta, 2013; Qualls et al. 2013; Hamidi et al., 2015; Klump et al. 2018). Even though the nutrient loading from the Fox River has been regulated and significantly reduced during past decades (Klump et al., 1997; Bunnell et al., 2014), sporadic and seasonal hypoxic conditions in Green Bay remained frequent (Klump et al. 2018). Our hypothesis is that, in addition to riverine P loading, the active internal regeneration of P species from particulate to dissolved phase may play an important role in the development of hypoxia in Green Bay.

During summer 2014, water samples and surface sediments were collected from Green Bay, including stations from the Fox River plume to northern Green Bay for the measurements of P species in both suspended particles and surface sediment. Our major objectives were to: 1) quantify the abundance, distribution and chemical speciation of P in suspended particles and surface sediment; and 2) examine the potential bioavailability of particulate P species and their possible regeneration/transformation in the water column with seasonal hypoxia in Green Bay.

## **Materials and methods**

### *Sampling*

During August (25<sup>th</sup> – 26<sup>th</sup>) 2014, field sampling was conducted onboard the R/V Neeskay with sampling stations across a trophic gradient from the southern to northern Green Bay (GB) (Fig. 1). Additionally, four end-member river stations were sampled, including the Fox River (FR), Oconto River (OR), Peshtigo River (PR) and Menominee River (MR) that discharge into Green Bay (Fig. 1 and Electronic Supplementary Material (ESM) Table S1). Surface waters (~2 m depth) and selected vertical profile samples in central Green Bay were collected directly into acid-cleaned HDPE plastic bottles using a submersible pump or taken from Niskin bottles.

Specific conductivity, concentrations of dissolved oxygen (DO) and chlorophyll-a fluorescence (Chl-*a*) were measured via *in situ* sensors (YSI Sondes). Samples were stored in a cooler with ice and filtered within 12-24 h. Data of DO and Chl-*a* have been published elsewhere (Lin et al., 2016; DeVilbiss et al., 2016).

Sediment samples were also collected from stations along the trophic gradient from the southern to northern Green Bay (Fig. 1) using a box-corer (Klump et al., 1997). Box cores were immediately subsampled using 10 cm diameter polycarbonate core tubes and the top 0-1 cm layer was sampled, kept in a plastic box, and freeze-dried for measurements of different P species. Suspended particles were collected through the filtration of water samples onto a 0.4  $\mu\text{m}$  Nuclepore membrane (Whatman, 47 mm). Filter samples were kept frozen for the measurements of different particulate P species. For surface sediments, samples were freeze-dried, homogenized, and ground to a fine powder (<200 mesh or <74  $\mu\text{m}$ ) with an agate pestle and mortar prior to the analysis of P species using SEDEX sequential extraction (see details below).

#### *Measurements of dissolved inorganic and organic P species*

The acid persulfate method with modification was used for the measurements of total dissolved phosphorus (TDP, Koroleff, 1983; Huang and Zhang, 2009). The filtrate samples (<0.4  $\mu\text{m}$ ) were digested with acid persulfate solution in an oven at 95 °C for 24 h, followed by analysis using the standard phosphomolybdenum blue method with a UV-vis spectrophotometer (Agilent 8453) in 5 cm cuvettes at 882 nm (Hansen and Koroleff, 1999). Concentrations of dissolved inorganic phosphorus (DIP) were directly measured without digestion and concentrations of dissolved organic phosphorus (DOP) were calculated from the difference between TDP and DIP. The detection limit for the conventional DIP method was 8 - 10 nM based on replicate blank sample measurements. Using MAGIC method with a concentration factor of ~15 for low DIP samples, the detection limit was 0.8 - 1.0 nM (Lin et al., 2016).

Data on concentrations of dissolved P species in the Fox River and Green Bay during the sampling period have been published elsewhere (Lin et al. 2016). Additional dissolved P data from other end-member river samples (ESM Table S1) will be discussed along with particulate and sedimentary P species.

#### *Sequential extraction and measurements of particulate P species*

Phosphorus in suspended particles and sediments was chemically fractionated into five operationally defined P species, namely (1) P adsorbed onto particulate surfaces here called exchangeable P (Ex-P), extracted by 1 M MgCl<sub>2</sub> solution, (2) P associated with easily reducible iron and manganese oxides and/or oxyhydroxides (Fe-P), extracted by BD solution containing 0.11 M NaHCO<sub>3</sub> and 0.11 M Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> with pH adjusted to 7.0, (3) authigenic carbonate fluorapatite, biogenic apatite and CaCO<sub>3</sub>-associated P (CFA-P), extracted by acetate buffer solution with a pH of 4, (4) detrital apatite P (Detr-P), extracted by 1 M HCl solution, and (5) organic P (Org-P), extracted through ashing at 550°C followed by 1 M HCl extraction. The extraction procedures were mostly based on SEDEX sequential extraction technique developed by Ruttenberg (1992) and revised by Zhang et al. (2004, 2010).

Briefly, depending on sample's P contents, about 0.2 g of freeze-dried sediment were extracted with 20 mL of the extraction solution in polyethylene centrifuge tubes, while filter samples were extracted with 10 mL of the extraction solution (Sutula et al., 2004; Lin et al., 2012b, 2013). After each extraction, the sample was centrifuged and the supernatant containing the extracted P was analyzed by the standard phosphomolybdenum blue method (Hansen and Koroleff, 1999) on an Agilent 8453 UV-Vis spectrophotometer. An aliquot of each initial extraction solution was used as blanks during sample analysis. Samples with acid or extraction solution were first neutralized prior to the analysis of P using the phosphomolybdenum blue method. Concentrations of total particulate P (TPP) of suspended particles and total P (TP) of surface sediment samples were calculated from the sum of five different particulate P species defined by the SEDEX procedures (Lin et al., 2012b). The sedimentary P concentrations are reported in terms of µg-P/g-dried sediment. Based on a 10 mL extraction solution for particulate samples (20 mL for sediment samples) and a 50 mm quartz cuvette, the detection limit was 0.1 or 0.2 nano-mole-P for particulate-P samples.

#### *Measurement of suspended particulate matter concentrations*

To determine the concentration of total suspended particulate matter (SPM), a predetermined volume (0.4 - 1.0 L) of raw water was filtered on pre-weighed 0.4 µm Nuclepore filters. After freeze-drying, the filter samples were weighed until a constant weight was achieved. Concentrations of SPM were then calculated from net particle weights and sample volumes.

### *Statistic analysis*

GoldenSoftware Surfer was used to plot surface contours and distributions of different P species and other parameters (e.g., DO and Chl-*a*). Statistical analysis was performed using SigmaPlot software to derive the vertical profile and statistical parameters such as values of  $R^2$  and  $p$ -value. A One-way ANOVA analysis was performed for the significance in differences between values or sample sets.

## **Results and Discussion**

### *Variations in chemical speciation of particulate P*

Concentrations of different particulate P species, including the exchangeable (Ex-P), Fe-bound (Fe-P), authigenic (CFA-P), detrital (Detr-P), and organic P (Org-P) in surface waters are given in Table 1. Their concentrations were highly variable between species and sampling locations. For the first two particulate-P species, concentrations of Ex-P varied from undetectable (or below detection-limit, b.d.) to 606 nM with an average of  $96 \pm 140$  nM ( $\pm$ SD, standard deviation for all samples), while Fe-P had an average concentration of  $68 \pm 58$  nM varying from 16 to 283 nM. In general, concentrations of CFA-P were lower than those of Ex-P and Fe-P phases, ranging from b.d. to 138 nM with an average of  $36 \pm 30$  nM, and concentrations of Detr-P varied from undetectable to 88 nM with an average of  $14 \pm 20$  nM in Green Bay. Contents of Org-P were relatively high, ranging from 14 to 310 nM with an average of  $83 \pm 76$  nM. For the partitioning of P among the five particulate P phases in surface waters, contents of Ex-P, Fe-P and Org-P were somewhat comparable and were higher than those of CFA-P and Detr-P in Green Bay. On average,  $25 \pm 15\%$  of the TPP was partitioned in the Ex-P,  $28 \pm 12\%$  in the Fe-P, and  $29 \pm 7\%$  in the Org-P, while only  $14 \pm 7\%$  of the TPP were associated with CFA-P and  $4 \pm 3\%$  with Detr-P. Although the abundance of all particulate P species decreased in general from southern to northern bay, the percentage of different P species in the TPP pool showed a contrasting pattern along the south-north transection (Fig. 2), suggesting different transport and transformation pathways among different particulate-P species in Green Bay. For instance, %Ex-P decreased from the highest value (51%) in southern bay to undetectable in northern bay. On the other hand, %Fe-P had the lowest abundance in southern bay (3%), and two apatite species (i.e., CFA-P and Detr-P) both had the highest percentage near Sturgeon Bay.

The greatest spatial variability in these particulate P species occurred in the Fox River plume during estuarine mixing (ESM Fig. S1), due to input of P from the Fox River and the mixing with low-P bay waters. Indeed, a positive relationship between specific conductivity and concentration of P species was evident for most of particulate P species in eastern portion of the bay, except for CFA-P (Fig. S2). This suggested a significant contribution of terrestrially and/or biologically derived particulate P from the river since the Fox River plume is a negative estuary with a higher specific conductivity in river water and lower specific conductivity in bay water (Xu et al., 2017). Moreover, Sturgeon Bay seemed to serve as another source of CFA-P for the east coast of Green Bay, as shown by its elevated abundance in the region (ESM Fig. S1). In contrast to eastern coastal regions, stations in western portion of the bay had higher specific conductivity (although low during June, DeVilbiss et al., 2016) but lower concentrations of particulate P, likely due to the influence of small rivers with low TPP concentrations (e.g. 256 nM for the OR, 214 nM for the PR and 164 nM for the MR compared to 2480 nM for the Fox River, Table 1 and ESM Fig. S3).

#### *Transformation of particulate P species in hypoxic water column*

In order to further examine the transformation of particulate P species in the water column that was affected by seasonal hypoxia, two vertical profiles were sampled in central Green Bay, as shown in Fig. 3 and Table 1. At stations GB17 and GB32 in central Green Bay, most of the particulate P species varied with depth in the water column. However, the Detr-P showed little change with water depth, for example, varying from 5 nM in surface to 7 nM in bottom waters at station GB32 (Table 1). This is consistent with its inert nature and less exchangeable potential (Ruttenberg, 1992; Lin et al., 2012b, 2013). Among the other four particulate-P species, concentrations or percentage of Ex-P, CFA-P and Org-P had a similar vertical variation trend. For instance, Ex-P decreased from 95 nM in surface water to 19 nM in the middle water column (8 m) and then increased to 56 nM in bottom water at station GB17 (Table 1). In general, higher abundance of these three species were observed in surface and subsurface waters where a DOP- and/or Chl-*a* maximum was also found (Fig. 3) although there were some exceptions especially in bottom waters related to evident elevated SPM concentrations from sediment resuspension at station GB17 (Table 1). In addition, both Ex-P and Org-P had a significant positive correlation with Chl-*a* concentrations in the water column (Fig. 4). Together, this suggested a source for Ex-



P and Org-P from *in situ* biological production, as also shown in their surface water distribution in southern Green Bay (Fig. 2). It also implied that Ex-P was predominantly derived from the adsorption of DIP onto plankton cell surfaces, but less from inorganic mineral surfaces in Green Bay. Similar observations have been documented in other aquatic environments (e.g., Sañudo-Wilhelmy et al., 2004; Lin et al., 2012b; Lin and Guo, 2016). In comparison, CFA-P also increased with increasing Chl-*a* concentrations (Fig. 4) and showed similar vertical profiles with Ex-P and Org-P (e.g., station GB32, Fig. 3). Nevertheless, its relationship with Chl-*a* was less significant (Fig. 4), consistent with the fact that only a portion of CFA-P, like biogenic apatite and/or calcareous plankton cell surface adsorbed P, is of biological origin in the water column.

In contrast to Ex-P, CFA-P and Org-P species, Fe-P concentrations demonstrated more variability in the deeper water column (> 10 m, Fig. 3). The decrease in Fe-P in the lower water column was also accompanied with the evident change in the DIP and dissolved oxygen (DO). For instance, at station GB17, when DO concentrations began to decrease at 8 m, Fe-P% in suspended particles decreased dramatically from 44% at 8 m to 14% in bottom water where a quasi hypoxic condition (i.e.,  $DO < 3$  mg/L) and ~10-fold increase in DIP concentrations were observed (also see Lin et al., 2016). Similarly, two low-DO water layers at station GB32 (~4 mg/L at 12.5 m and ~6 mg/L at 20 m) were found to be related to the significant decrease in Fe-P abundance (e.g., very low Fe-P was detected in bottom water at station GB32, Fig. 3). However, the increase in DIP concentrations in bottom water at station GB32 was not so evident compared to that at station GB17, likely resulting from the intrusion of higher DO water between the 14-17 m layer. These observations were all suggestive of the triggering impact of hypoxia/low-DO on accelerating the release of phosphate from the reductive dissolution of Fe-oxyhydroxide and thus the release of Fe-bounded P, as observed in other hypoxia-influenced estuaries (e.g., Reed et al., 2011; Diaz et al., 2012). Similarly, low percentage of Fe-P was also observed in surface waters in southern Green Bay (Fig. 2) where low DO concentrations co-existed (~5 mg/L, ESM Fig. S4). Therefore, the reductive-dissolution of Fe-P occurred not only in surface sediments (e.g., Conley et al., 2002; Hou et al., 2009; Joshi et al., 2015), but also in hypoxic and low-DO water column, which should enhance particle regeneration and serve as a source of phosphate.

#### *Variations in chemical speciation of sedimentary P*

In surface sediment, total phosphorus (TP) concentrations ranged from 460 to 1794  $\mu\text{g-P/g}$ -dried sediment, with an average of  $943\pm344$   $\mu\text{g-P/g}$  and highest values in the northern bay (Table 2 and ESM Fig. S5). Among the five particulate-P species in surface sediment, Org-P had the highest concentration, with an average of  $334\pm133$   $\mu\text{g-P/g}$ , followed by the Detr-P ( $288\pm47$   $\mu\text{g-P/g}$ ), Fe-P ( $177\pm176$   $\mu\text{g-P/g}$ ) and CFA-P ( $110\pm90$   $\mu\text{g-P/g}$ ), while the Ex-P had the lowest abundance ( $33\pm29$   $\mu\text{g-P/g}$ ) in sediment. Clearly, the partition of P among the five chemical phases in surface sediment is distinct compared to that in suspended particles (Fig. 2). For example, while the Ex-P was the most abundant particulate-P species in the water column, the Org-P and Detr-P became the most abundant species, comprising, on average,  $36\pm12\%$  and  $34\pm10\%$  of the total P in surface sediment, respectively, followed by the Fe-P ( $17\pm10\%$ ), CFA-P ( $10\pm5\%$ ) and Ex-P ( $3\pm2\%$ ).

In terms of  $\mu\text{g-P/g}$ -sediment, most of the inorganic sedimentary P species, including Ex-P, Fe-P and CFA-P, had higher abundances in northern Green Bay, especially in the areas close to the Chamber Island and the northwest of Sturgeon Bay (ESM Fig. S5). Moreover, the Detr-P ( $288\pm47$   $\mu\text{g-P/g}$ ) also had relatively high concentrations in southeast coast of Green Bay in addition to high deposition in northern Green Bay. Thus, while the Fox River is the main source of inorganic P species to the southern Green Bay, P-containing inorganic species including the Detr-P may partly originate from coastal erosion from the Chamber Island and nearby coastal line in the northern Green Bay. In contrast to inorganic P species in surface sediment, organic P generally had higher abundance in central Green Bay and lower concentrations in southern Green Bay (ESM Fig. S5).

#### *Environmental fate of particulate P under hypoxic conditions*

Comparing data between suspended particulate and sedimentary P pools, a dynamic change in the partitioning of P from suspended particles to surface sediment was evident (Figs. 2 vs. 5). On average, major P species in suspended particles were Org-P, Fe-P and Ex-P, collectively contributing over 80% of the TPP, leaving CFA-P and Detr-P as the minor P species. However, the Detr-P became one of the predominant P species ( $33\pm10\%$ ) in surface sediment, second to Org-P ( $36\pm12\%$ ), followed by Fe-P, with Ex-P and CFA-P being the minor P species (Fig. 6). Interestingly, the percentage of Org-P remained high in sediment ( $36\pm12\%$ ) compared to  $29\pm7\%$  in suspended particles, while the relative percentage of Ex-P, Fe-P and Detr-P decreased

significantly from suspended particles to sediment, especially for Detr-P (from  $5\pm 4\%$  in suspended particles vs.  $33\pm 10\%$  in surface sediment). The relative abundance of CFA-P also remained somewhat unchanged between suspended particles and surface sediment (Fig. 6). Overall, these variation trends clearly demonstrated the release/decomposition of particulate P into dissolved phosphate (i.e., regeneration) in the water column, resulting in an enormous decrease in %Ex-P, a moderate decrease in %Fe-P, but a substantial increase in %Detr-P in sediment (Fig. 6). However, both %Org-P and %CFA-P changed little on average during the regeneration of particulate P in the water column. The enrichment of Org-P in sediment relative to suspended particles likely resulted from the occurrence of hypoxic conditions and time scales in the shallow water column. Indeed, diagenetic and stoichiometric models of P cycling imply that  $>80\%$  of the P deposited is permanently buried (Klump et al. 1997). Presumably this residual P consists of a large fraction of Detr-P, which is relatively inert in this system on these time scales.

In order to evaluate the loss or deposition of individual P species from suspended particles to sediments, normalized P concentrations (in  $\mu\text{g-P/g}$ ) in both suspended particles and surface-sediment were used to compare their differences, although bias may exist due to differences in particle size and mineral composition between suspended particles and sediment. As shown in Fig. 6, there existed a significant difference in P concentrations for all species between suspended particle and sediment ( $p < 0.05$ , One-Way ANOVA). The abundance of Ex-P, Fe-P, CFA-P and Org-P species (all in  $\mu\text{g-P/g}$ ) all decreased significantly from suspended particles to surface sediment, showing an intensive regeneration of these particulate P species in the water column. In contrast, contents of Detr-P increased from suspended particles in the water column ( $135\pm 137 \mu\text{g-P/g}$ ) to surface sediment ( $286\pm 47 \text{ g-P/g}$ ), showing its preferential accumulation in sediment. Based on changes in P abundance between suspended particles and surface sediment (Fig. 6), the loss of four P species, shown as the mean value, during particle regeneration was estimated to be  $505 \mu\text{g-P/g}$  for Ex-P,  $519 \mu\text{g-P/g}$  for Fe-P,  $235 \mu\text{g-P/g}$  for CFA-P, and  $443 \mu\text{g-P/g}$  for Org-P, which accounted for a loss of 93%, 70%, 65% and 59% of their average abundance in surface waters, respectively. Lake Michigan is highly oligotrophic and a P-limited freshwater ecosystem (Cuhel and Aguilar, 2013; Lin and Guo, 2016), and low concentrations of phosphate in Green Bay have also been observed ( $22\pm 14 \text{ nM}$ , Lin et al., 2016). Under relatively high TPP concentrations ( $297\pm 287 \text{ nM}$ ) and seasonal hypoxic conditions in Green Bay, it is not

surprising to observe a huge loss of the four potentially active particulate-P species (Fig. 6) and an intensive regeneration of particulate-P in the water column, as also reported in other environments (Zhang and Huang, 2011; Lin et al., 2013).

For discussion purposes, Green Bay was operationally divided into four segments along the south-north transect based on previous studies (Dolan and Chapra, 2012; Maccoux et al., 2013). As shown in Fig. 7, the difference in Ex-P concentrations between suspended particles and sediment were consistently high along the south-north transect, with a loss extent of >90% in all segments in the bay, consistent with its labile and exchangeable characteristics. The other noticeable feature was that contents of Org-P increased from southern to central bay in both suspended particles and surface sediment, with the extent of Org-P losses generally decreased from southern bay (~78%) to central bay (~24%), indicating an accumulation or deposition of Org-P in sediment in the central bay region. This is consistent with the observations of Klump et al. (2009) which show a focusing of organic matter in sediments in the central bay reaching in excess of 10% organic carbon by weight coupled to a tight stoichiometric relationship between organic carbon and total sedimentary P. In contrast, contents of Fe-P in surface sediment decreased slightly in central bay, showing the highest extent of Fe-P loss in central bay (~86%). For CFA-P, its difference in concentration between suspended particles and surface sediment were similar along the south-north transect (Fig. 7). Because seasonal hypoxic conditions in Green Bay are usually observed in deeper waters of the central bay (> 10 m, Fig. 3 and ESM Fig. S4, Conley, 1983; Klump et al., 2009; Qualls et al., 2013), the quasi-negative relation between Fe-P and Org-P implied a different feedback between Fe-P and Org-P to hypoxic conditions in Green Bay.

It can be speculated that the decomposition and remineralization of terrestrial and/or biological-produced organic matter are relatively intense in southern-central Green Bay (or segment GB-II, Fig. 7), which consumed considerable DO in the water column and promoted the development of hypoxic conditions. With the consumption of DO, the oxidation and degradation of particulate Org-P were depressed in the central bay, especially in segments GB-III and GB-IV areas (ESM Fig. S5), enhancing the preservation of Org-P in the water column and sediment (Fig. 7). In the meantime, low-DO conditions will promote the reductive-dissolution and the loss of particulate Fe-P in the water column (Fig. 3), resulting in lower Fe-P contents in surface sediment as observed at segment GB-III in central Green Bay (Fig. 7). Therefore, our

observations on the dynamic changes in chemical speciation and partitioning of P in suspended particles and surface sediment along the south-north transect in Green Bay pointed to a coupling of hypoxic conditions with the regeneration and internal cycling of different particulate P species in the water column-sediment continuum. Furthermore, the high regeneration extent of different particulate P species observed here also pointed to their potential bioavailability and positive feedback to eutrophication and algal bloom in coastal environments.

#### *Potentially bioavailable particulate P in suspended particles and sediment*

In P-limited ecosystems, algal growth is largely limited by the bioavailable P species (Ruttenberg, 1992; Sutula et al., 2004). However, the bioavailability or reactivity of particulate P is largely unknown. Because P can exist in different chemical forms in both suspended particles and sediments and not all particulate-P species are bioavailable, an experimental approach using sequential extraction methods is thus indispensable to elucidating the reactivity of P in the particulate phase. Potentially bioavailable P can be defined as the upper limit of P that can be released into the water column from suspended particles and/or sediment in the form of phosphate and/or DOP which may become available for algal growth (Sonzogni et al., 1982; Andrieux-Loyer and Aminot, 1997; Yang et al., 2016). Among the five particulate P species, the Ex-P, Fe-P and Org-P have been recognized as the potentially BAP in aquatic environments (Jensen and Thamdrup, 1993; Coelho et al., 2004; Hou et al., 2009; Prasad and Ramanathan, 2010). Indeed, our observations here clearly showed a strong regeneration of these three P species (Figs. 6 and 7) and both Ex-P and Org-P also had a close relationship with Chl-*a* (Fig. 4). On the other hand, the two apatite species (CFA-P and Detr-P) are usually considered to be insoluble and not a potential source of phosphate in the water column since the kinetics of apatite formation and dissolution is slow (Andrieux-Loyer and Aminot, 2001). As shown in Fig. 6, the accumulation of Detr-P from the overlying water column to sediment further confirmed its inert nature or low reactivity. However, the positive correlation between CFA-P and Chl-*a* (Fig. 4) suggested its biological origin in Green Bay. In addition, the decrease in CFA-P with water depth (Fig. 3) suggested that CFA-P could be partially dissolved and regenerated especially in hypoxic water column and at the sediment-water interface (Cai et al., 2011; Lin et al., 2016). Therefore, the sum of Ex-P, Fe-P, CFA-P and Org-P can be considered as the potentially BAP in Green Bay.

At the river end-member stations, the contribution of BAP to the TPP pool was typically higher than 90% for all rivers draining into Green Bay (Table 1 and ESM Fig. S3). For example, BAP concentrations reached 2321 nM in the Fox River, which corresponded to 94% of the TPP and was much higher than the phosphate concentration (Table 1). Similarly, the BAP fraction in the TPP pool was also consistently higher than 90% in different segments of Green Bay (Fig. 8, Table 1), with an average of  $283 \pm 272$  nM (or  $2398 \pm 1103$   $\mu\text{g-P/g}$ ) and comprising up to  $96 \pm 3\%$  of the TPP in the study area. Compared with the abundance of BAP in surface sediment along the south-north transect (Fig. 8), the extent of loss of BAP in suspended particles could reach up to 75% in southern bay (i.e., segment GB-I) but decreased to 50% in northern bay (or segment GB-IV), resulting in higher BAP preserved in northern bay sediment (Table 2 and Fig. S6). On average, 71% of BAP in suspended particles were estimated to be regenerated in the water column during their transport in Green Bay, which was much higher than previous observations in other marine estuarine environments (e.g., Sutula et al., 2004; Yang et al., 2017). Because the phosphate concentrations were low (averaged  $22 \pm 14$  nM) in Green Bay (Lin et al., 2016) and rivers draining into the bay (all  $< 25$  nM, ESM Table S1 and Fig. S3) except for the Fox River, high BAP abundance in suspended particles may contribute significant amounts of phosphate to the water column as an internal source for biological production in Green Bay, especially in central bay area, in addition to riverine dissolved phosphate input.

## Conclusions

Different particulate-P species were quantified and compared between suspended particles and surface sediment when seasonal hypoxia occurred during summer 2014. In addition to the particulate Ex-P, Fe-P and Org-P species which have been shown to have measurable exchangeability with surrounding water, the CFA-P was also found to contribute bioavailable phosphate to the water column in Green Bay. Therefore, potentially-bioavailable-P from all four particulate-P species may comprise up to 90% of TPP in suspended particles. Under depleted phosphate conditions, the BAP, as an internal DIP source, could contribute significant phosphate to the water column for biological production in Green Bay. The regeneration of particulate-P was enhanced in low-DO and/or hypoxic bottom waters. Based on the difference in P speciation between suspended particles and surface sediment, about 71% of the particulate BAP could be regenerated into the water column prior to their deposition onto sediment in Green Bay. Indeed,

degradation of organic matter and the development of hypoxia were accompanied by reductive dissolution of Fe-P and regeneration of particulate-P species in bottom waters in central Green Bay. In turn, low-DO conditions seemed to enhance the preservation of Org-P in sediment although contents of all particulate-P species, except for Detr-P, decreased from suspended particles to surface sediment. Because P dynamics and regeneration in the water column may change with season and hydrodynamic conditions, future studies are needed to examine the seasonality and controlling factors in P biogeochemical cycling, the relative importance between the internal regeneration fluxes from particulate P and total external P inputs, and the role of biological processes such as invasive quagga mussels, plankton biomass and foodweb structure in Green Bay.

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## References

- Andrieus-Loyer, F., Aminot, A., 2001. Phosphorus forms related to sediment grain size and geochemical characteristics in French coastal areas. *Estuar. Coast. Shelf Sci.* 52(3), 617-629.
- Allen, H.E., 1973. Seasonal variation in nitrogen, phosphorus and chlorophyll a in Lake Michigan and Green Bay. U.S. Bureau of Sport Fisheries and Wildlife Technical Papers 70, 1-23.
- Baker, D.B., Confesor, R., Ewing, D.E., Johnson, L.T., Kramer, J.W., Merryfield, B.J., 2014. Phosphorus loading to Lake Erie from the Maumee, Sandusky and Cuyahoga rivers: The importance of bioavailability. *J. Great Lakes Res.* 40, 502-517.
- Bunnell, D.B., Barbiero, R.P., Ludsin, S.A., Madenjian, C.P., Warren, G.J., Dolan, D.M., Brenden, T.O., Briland, R., Gorman, O.T., He, J.X. and Johengen, T.H., 2014. Changing ecosystem dynamics in the Laurentian Great Lakes: bottom-up and top-down regulation. *BioScience*, 64(1), 26-39.
- Cai, W.J., Hu, X., Huang, W.J., Murrell, M.C., Lehrter, J.C., Lohrenz, S.E., Chou, W.C., Zhai, W., Hollibaugh, J.T., Wang, Y. and Zhao, P., 2011. Acidification of subsurface coastal waters enhanced by eutrophication. *Nature Geoscience* 4(11), 766-770.
- Coelho, J.P., Flindt, M.R., Jensen, H.S., Lilebo, A.I., Pardal, M.A., 2004. Phosphorus speciation and availability in intertidal sediments of a temperate estuary: relation to eutrophication and annual P-fluxes. *Estuar. Coast. Shelf Sci.* 61, 583-590.
- Conley, D.J., 1983. Limnological characteristics of Green Bay, Lake Michigan, May–October, 1980. M.S. Thesis. Univ. Wisconsin-Green Bay.
- Conley, D.J., Humborg, C., Rahm, L., Savchuk, O.P., Wulff, F., 2002. Hypoxia in the Baltic Sea and basin-scale changes in phosphorus biogeochemistry. *Environ. Sci. Technol.* 36, 5315-5320.
- DeVilbiss, S.E., Zhou, Z., Klump, J.V., Guo, L., 2016. Spatiotemporal variations in the abundance and composition of bulk and chromophoric dissolved organic matter in seasonally hypoxia-influenced Green Bay, Lake Michigan, USA. *Sci. Total Environ.* 565, 742-757.
- Diaz, J.M., Ingall, E.D., Snow, S.D., Benitez-Nelson, C.R., Taillefert, M., Brandes, J.A., 2012. Potential role of inorganic polyphosphate in the cycling of phosphorus within the hypoxic water column of Effingham Inlet, British Columbia. *Global Biogeochem. Cycles* 26, GB2040. doi:10/1029/2011GB004226.

- Dolan, D.M., Chapra, S.C., 2012. Great Lakes total phosphorus revisited: 1. Loading analysis and update (1994-2008). *J. Great Lakes Res.* 38, 730-740.
- Elsbury, K.E., Paytan, A., Ostrom, N.E., Kendall, C., Young, M.B., McLaughlin, K., Rollog, M.E., Watson, S., 2009. Using oxygen isotopes of phosphate to trace phosphorus sources and cycling in Lake Erie. *Environ. Sci. Technol.* 43(9), 3108-3114.
- Filippelli, G.M., 2010. Biogeochemistry: Phosphorus and the gust of fresh air. *Nature* 467, 1052-1053.
- Hamidi, S.A., Bravo, H.R., Klump, J.V., Waples, J.T., 2015. The role of circulation and heat fluxes in the formation of stratification leading to hypoxia in Green Bay, Lake Michigan. *J. Great Lakes Res.* in press. doi:10.1016/j.jglr.2015.08.007.
- Hansen, H.P., Koroleff, F., 1999. Determination of nutrients. In *Methods of Seawater Analysis*, Third Edition; Grasshoff, K., Kremling, K., Ehrhardt, M., Eds.; Wiley-VCH Verlag GmbH: Weinheim Germany. doi:10.1002/9783527613984.ch10.
- Hou, L., Liu, M., Yang, Y., Ou, D., Lin, X., Chen, H., Xu, S., 2009. Phosphorus speciation and availability in intertidal sediments of the Yangtze Estuary, China. *Applied Geochem.* 24(1), 120-128.
- Huang, X.-L., Zhang, J.-Z., 2009. Neutral persulfate digestion at sub-boiling temperature in an oven for total phosphorus determination in natural waters. *Talanta* 78, 1129-1135.
- Jensen, H.S., Thamdrup, B., 1993. Iron-bound phosphorus in marine sediments as measured by bicarbonate-dithionite extraction. *Hydrobiologia* 253, 47-59.
- Joshi, S.R., Kukkadapu, R.K., Burdige, D.J., Bowden, M.E., Sparks, D.L., Jaisi, D.P., 2015. Organic matter remineralization predominates phosphorus cycling in the mid-bay sediments in the Chesapeake Bay. *Environ. Sci. Technol.* 49(10), 5887-5896. doi:10.1021/es5059617.
- Klump, J.V., Edgington, D.N., Sager, P.E., Robertson, D.M., 1997. Sedimentary phosphorus cycling and a phosphorus mass balance for the Green Bay (Lake Michigan) ecosystem. *Can. J. Fish. Aquat. Sci.*, 54(1), 10-26.
- Klump, J.V., Fitzgerald, S.A., Waples, J.T., 2009. Benthic biogeochemical cycling, nutrient stoichiometry, and carbon and nitrogen mass balances in a eutrophic freshwater bay. *Limnol. Oceanogr.* 54(3), 692-712.

- Klump, J.V., S.L. Brunner, B. Grunert, J. Kaster, K. Weckerly, E. Houghton, J. Kennedy, T. Valenta. 2018. Evidence of persistent, recurring summertime hypoxia in Green Bay, Lake Michigan. *J. Great Lakes Res.* (This issue).
- Koroleff, F., 1983. Determination of phosphorus. In *Methods of Seawater Analysis*; Grasshoff et al., Eds; Verlag Chemie pp. 167-173.
- Lin, P., Chen, M., Guo, L., 2012a. Speciation and transformation of phosphorus and its mixing behavior in the Bay of St. Louis estuary in the northern Gulf of Mexico. *Geochim. Cosmochim. Acta* 87, 283-298. doi:10.1016/j.gca.2012.03.040.
- Lin, P., Guo, L., Chen, M., Tong, J., Lin, F., 2012b. The distribution and chemical speciation of dissolved and particulate phosphorus in the Bering Sea and the Chukchi-Beaufort seas. *Deep-Sea Res. II* 81/84, 79-94. <http://dx.doi.org/10.1016/j.dsr2.2012.07.005>.
- Lin, P., Guo, L., Chen, M., Cai, Y., 2013. Distribution, partitioning and mixing behavior of phosphorus species in the Jiulong River estuary. *Mar. Chem.* 157, 93-105.
- Lin, P., Klump, J.V., Guo, L., 2016. Dynamics of dissolved and particulate phosphorus influenced by seasonal hypoxia in Green Bay, Lake Michigan. *Sci. Total Environ.* 541, 1070-1082.
- Lin P., Guo L., 2016. Dynamic changes in abundance and chemical speciation of dissolved and particulate phosphorus in southwest Lake Michigan. *Limnol. Oceanogr.* 61(2), 771-789. doi:10.1002/lno.10254.
- Lopez, P., 2004. Spatial distribution of sedimentary P pools in a Mediterranean coastal lagoon 'Albufera d'es Grau' (Minorca Island, Spain). *Mar. Geol.* 203(1-2), 161-176.
- Maccoux, M.J., Dolan, D.M., Chapra, S.C., 2013. Chloride and total phosphorus budgets for Green Bay, Lake Michigan. *J. Great Lakes Res.* 39, 420-428.
- Marko, K.M., Rutherford, E.S., Eadie, B.J., Johengen, T.H., Lansing, M.B., 2013. Delivery of nutrients and seston from the Muskegon River Watershed to near shore Lake Michigan. *J. Great Lakes Res.* 39(4), 672-681.
- Yang, B., Song, G.D., Liu, S.M., Jin, J., 2017. Phosphorus recycling and burial in core sediments of the East China Sea. *Mar. Chem.* 192, 59-72.
- Nausch M., Nausch, G., 2006. Bioavailability of dissolved organic phosphorus in the Baltic Sea. *Mar. Ecol. Prog. Ser.* 321, 9-17.

- Orihel, D.M., Baulch, H.M., Casson, N.J., North, R.L., Parsons, C.T., Seckar, D.C., Venkiteswaran, J.J., 2017. Internal phosphorus loading in Canadian fresh waters: a critical review and data analysis. *Canadian J. Fisheries Aquatic Sci.* 74(12), 2005-2029.
- Prasad, M.B.K., Ramanathan, A.L., 2009. Characterization of phosphorus fractions in the sediments of tropical intertidal mangrove ecosystem. *Wetlands Ecol. Management* 18(2), 165-175.
- Qualls, T.M., Harris, H.J., Harris, V.A., 2013. *The State of the Bay: The condition of the bay of Green Bay/Lake Michigan 2013*. Univ. Wisconsin Sea Grant Institute.
- Rabalais, N.N., Turner, R.E., Diaz, R.J., Justic, D., 2009. Global change and eutrophication of coastal waters. *ICES J. Mar. Sci.* 66(7), 1528-1537. <http://doi.org/10.1093/icesjms/fsp047>.
- Reed, D.C., Slomp, C.P., Gustafsson, B. G., 2011. Sedimentary phosphorus dynamics and the evolution of bottom-water hypoxia: A coupled benthic-pelagic model of a coastal system. *Limnol. Oceanogr.* 56(3), 1075-1092. doi:10.4319/lo.2011.56.3.1075.
- Ruttenberg, K.C., 1992. Development of a sequential extraction method for different forms of phosphorus in marine sediments. *Limnol. Oceanogr.* 37, 1460-1482.
- Ruttenberg, K.C., Sulak, D.J., 2011. Sorption and desorption of dissolved organic phosphorus onto iron (oxyhydr)oxides in seawater. *Geochim. Cosmochim. Acta* 75, 4095-4112.
- Santschi, P.H., 1995. Seasonality in nutrient concentrations in Galveston Bay. *Mar. Environ. Res.* 40, 337-362.
- Sañudo-Wilhelmy, S.A., Tovar-Sanchez, A., Fu, F.-X., Capone, D.G., Carpenter, E.J., Hutchins, D.A., 2004. The impact of surface-adsorbed phosphorus on phytoplankton Redfield stoichiometry. *Nature* 432, 897-901.
- Scavia, D., Allan, J.D., Arend, K.K., Bartell, S., Beletsky, D., Bosch, N.S., Brandt, S.B., Briland, R.D., Daloglu, I., DePinto, J.V., Dolan, D.M., Evans, M.A., Farmer, T.M., Goto, D., Han, H., Hook, T.O., Knight, R., Ludsin, S.A., Mason, D., Michalak, A.M., Richards, R.P., Roberts, J.J., Rucinski, D.K.L., Rutherford, E., Schwab, D.J., Sesterhenn, T.M., Zhang, H., Zhou, Y., 2014. Assessing and addressing the re-eutrophication of Lake Erie: Central basin hypoxia. *J. Great Lakes Res.* 40(2), 226-246. doi:10.1016/j.jglr.2014.02.004.
- Semiletov, I., Pipko, I., Gustafsson, Ö., Anderson, L. G., Sergienko, V., Pugach, S., Dudarev, O., Charkin, A., Gukov, A., Broder, L., Anderson, A., Spivak, E., Shakhova, N., 2016.

- Acidification of East Siberian Arctic Shelf waters through addition of freshwater and terrestrial carbon. *Nature Geoscience* 9, 361-365. doi:10.1038/ngeo2695.
- Slomp, C.P., Mort, H.P., Jibert, T., Reed, D.C., Gustafsson, B.G., Wolthers, M., 2013. Coupled dynamics of iron and phosphorus in sediments of an oligotrophic coastal basin and the impact of anaerobic oxidation of methane. *PLOS One* 8(4), e62386.
- Sonzogni, W.C., Chapra, S.C., Armstrong, D.E. Logan, T.J., 1982. Bioavailability of phosphorus inputs to lakes. *J. Environ. Quality* 11(4), 555-563.
- Sutula, M., Bianchi, T.S., McKee, B.A., 2004. Effect of seasonal sediment storage in the lower Mississippi River on the flux of reactive particulate phosphorus to the Gulf of Mexico. *Limnol. Oceanogr.* 49(6), 2223-2235.
- Valenta, T.J., 2013. Oxygen depletion in Green Bay. MS Thesis, Univ. Wisconsin-Green Bay.
- Wang, Y., Shen, Z., Niu, J., Liu, R., 2009. Adsorption of phosphorus on sediments from the Three-Gorges Reservoir (China) and the relation with sediment compositions. *J. Hazardous Materials* 162(1), 92-98.
- Xu, H., Houghton, E.M., Houghton, C.J., Guo, L., 2017. Variations in size and composition of dissolved organic matter in a negative freshwater estuary. *Sci. Tot. Environ.* 615, 931-941.
- Zhang, J.-Z., Fischer, C.J., Ortner, P.B., 2004. Potential availability of sedimentary phosphorus to sediment resuspension in Florida Bay. *Global Biogeochem. Cycles* 18(4), GB4008. doi:10.1029/2004GB002255.
- Zhang, J.-Z., Huang, X.-L., 2011. Effect of temperature and salinity on phosphorus sorption on marine sediments. *Environ. Sci. Technol.* 45(16), 6831-6837. doi:10.1021/es200867p.
- Zhang, J.-Z., Guo, L., Fischer, C., 2012. Abundance and chemical speciation of phosphorus in sediments of the Mackenzie River Delta, the Chukchi Sea and the Bering Sea: Importance of detrital apatite. *Aquat. Geochem.* 16, 353-371.
- Zhou, Y., Michalak, A.M., Beletsky, D., Rao, Y.R., Richards, R.P., 2015. Record-Breaking Lake Erie Hypoxia during 2012 Drought. *Environ. Sci. Technol.* 49, 800-807.

### Figure captions:

Fig. 1. A map showing the sampling locations for suspended particulate matter (left panel) and surface sediment (right panel) in Green Bay, Lake Michigan, during summer 2014. Stations 17 and 32 (star symbols) were the two vertical profile sampling stations. Contour lines are depth contours or bathymetry in Green Bay. Red lines (from the south, Segment GB-I, to the north, GB-IV) separate the Green Bay into different geographic segments from the south to the north based on Maccoux et al. (2013).

Fig. 2. Surface distributions of the percentage of different particulate P species in the total particulate P pool (TPP) of suspended particulate matter, as well as the concentrations of Chl-*a* (in  $\mu\text{g/L}$  and data from DeVilbiss et al., 2016) in Green Bay during August 2014.

Fig. 3. Vertical distributions of different P species (in nM) and dissolved oxygen (DO, in mg/L) concentrations at stations GB17 and GB32 in central Green Bay during August 2014. Data of the dissolved P phases, including phosphate (DIP) and dissolved organic P (DOP) concentrations are taken from Lin et al. (2016).

Fig. 4. Relationship between Chl-*a* concentration ( $\mu\text{g/L}$ ) and different particulate P species in surface waters of Green Bay during August 2014.

Fig. 5. Distributions of the percentage of different particulate P species in the total P (TP) pool in surface sediment in Green Bay.

Fig. 6. Comparison in the average concentrations ( $\mu\text{g-P/g}$ ) and their relative percentage (pie charts) in the total P between suspended particulate matter (SPM) ( $n = 40$ ) and surface sediment ( $n = 27$ ) in Green Bay. “\*” denotes the difference ( $p < 0.05$ ) is significant in P concentration between SPM and surface sediment.

Fig. 7. Variations in the average concentration ( $\mu\text{g-P/g}$ ) of different P species between suspended particulate matter (SPM) and surface sediment in different geographic segments along the south-north transect in Green Bay.

Fig. 8. Variations in the average concentration ( $\mu\text{g-P/g}$ ) and percentage of potentially bioavailable P (BAP) between suspended particulate matter (SPM) and surface sediment in Green Bay.

Table 1. Concentrations and partitioning of different P species in suspended particulate matter (SPM) in surface waters of Green Bay and the Fox River during August 2014. Other small rivers were also collected during August 2015. BAP = potentially bioavailable phosphorus. “b.d.” denotes concentrations lower than detection limit.

Station ID	Ex-P (nM)	Fe-P (nM)	CFA-P (nM)	Detr-P (nM)	Org-P (nM)	%Ex-P	%Fe-P	%CFA-P	%Detr-P	%Org-P	BAP (nM)	SPM (mg/L)
<b>Rivers</b>												
Fox River	782	701	114	158	725	32	28	5	6	29	2321	88.0
Oconto River	42	87	65	b.d.	63	16	34	25	b.d.	24	256	4.2
Petshigo River	41	118	12	14	29	19	55	6	6	13	201	4.9
Mem River	25	82	33	b.d.	24	15	50	20	b.d.	15	164	2.7
<b>Green Bay</b>												
GB01	124	196	73	21	184	21	33	12	3	31	577	7.5
GB2S	479	176	93	b.d.	192	51	19	10	b.d.	20	940	27.5
GB2E	183	199	138	88	286	21	22	15	10	32	807	13.9
GB2W	322	105	61	19	217	44	15	8	3	30	706	23.7
GB05	145	36	23	26	115	42	10	7	8	33	318	5.9
GBSC	606	283	32	80	241	49	23	3	6	19	1162	44.4
GB6E	503	25	114	62	310	50	3	11	6	31	953	36.5
GB07	97	167	64	21	164	19	33	12	4	32	491	4.5
GB8	106	68	45	b.d.	113	32	20	14	b.d.	34	333	4.0
GB09	89	43	18	6	42	45	22	9	3	21	191	3.6
GB11	77	104	58	17	95	22	30	16	5	27	333	4.6
GB12	81	75	63	16	63	27	25	21	5	21	281	2.5
GB14B	110	85	19	14	87	35	27	6	5	28	301	2.9
GB16B	48	53	39	14	82	20	22	17	6	35	221	2.7
GB17	95	64	43	22	75	32	21	14	7	25	277	3.3
GB18	4	46	23	1	36	3	42	21	1	33	109	2.0
GB18B	73	54	67	12	92	25	18	22	4	31	285	3.5
GB19	93	64	61	4	104	29	20	19	1	32	322	3.3
GB20	69	42	b.d.	6	73	36	22	b.d.	3	38	184	2.0
GB22	58	38	11	12	66	31	21	6	7	35	173	2.6
GB25	35	31	26	12	56	22	19	17	7	35	148	1.4
GB26S	15	74	19	b.d.	43	10	49	12	b.d.	28	151	2.8
GB30E	31	38	53	7	37	19	23	32	4	22	159	2.0
GB30	20	27	17	b.d.	29	22	29	18	b.d.	31	93	2.5
GB30B	58	16	21	2	28	47	13	17	1	23	122	1.2
GB31	11	42	16	5	32	11	40	15	5	30	101	2.6



GB32	64	47	28	10	29	36	27	16	6	16	168	2.3
GB38	17	46	20	4	29	15	40	17	4	25	111	1.4
GB39	20	36	22	5	48	15	27	17	4	37	126	2.4
GB39-Pump	53	33	4	3	31	43	26	3	3	25	121	1.6
GB42	b.d.	46	18	7	17	b.d.	52	21	8	19	82	1.6
GB43	9	38	11	1	14	12	52	15	2	19	73	0.9
GB44	b.d.	51	13	3	53	b.d.	43	11	2	44	117	0.9
GB45	34	22	25	6	40	27	17	20	5	31	121	1.1
GB47	b.d.	39	23	13	22	b.d.	40	24	13	23	84	0.5
GB48	13	27	23	3	18	16	32	28	3	21	81	1.2
GB48W	b.d.	59	19	10	26	b.d.	52	17	9	22	104	1.7
GB54	b.d.	38	4	5	35	b.d.	46	4	6	43	77	0.4
GBcondos	85	24	47	3	32	45	13	25	2	17	188	3.6
GBMR	20	49	b.d.	7	54	16	38	b.d.	5	42	123	1.5
<b>Green Bay</b>												
<b>Average</b>	109.9	67.65	38.26	15.19	82.75	28.29	28.15	15.05	4.89	28.53	282.9	5.86
<b>±SD</b>	144.5	57.82	30.06	20.16	75.65	13.12	12.30	6.73	2.64	7.25	271.6	9.79

Table 2. Concentrations and partitioning of different P species, as well as potentially bioavailable P (BAP) in surface sediments of Green Bay.

Station ID	Ex-P (µg-P/g)	Fe-P (µg-P/g)	CFA-P (µg-P/g)	Detr-P (µg-P/g)	Org-P (µg-P/g)	%Ex-P	%Fe-P	%CFA-P	%Detr-P	%Org-P	BAP (µg-P/g)
GB73	21.9	165.8	74.5	279.1	391.1	2	18	8	30	42	653.3
GB67	14.3	185.7	91.8	269.4	135.5	2	27	13	39	19	427.2
GB64	14.2	337.6	177.4	320.5	272.9	1	30	16	29	24	802.1
GB59B	24.4	327.9	173.0	219.1	183.0	3	35	19	24	20	708.3
GB53	61.5	503.8	321.2	256.1	291.4	4	35	22	18	20	1177.9
GB52	81.0	534.8	365.6	450.7	362.2	5	30	20	25	20	1343.5
GB48	12.6	43.0	68.5	286.9	417.0	2	5	8	35	50	541.0
GB47	93.9	593.4	260.6	264.1	478.5	6	35	15	16	28	1426.4
GB42	13.6	49.4	92.0	258.1	428.8	2	6	11	31	51	583.8
GB39	132.8	629.5	277.7	273.9	444.5	8	36	16	16	25	1484.5
GB30	29.7	59.7	83.5	239.7	381.0	4	8	11	30	48	553.9
Condos	27.1	111.4	40.1	228.0	249.8	4	17	6	35	38	428.5
GB26S	9.5	40.7	61.6	275.3	384.5	1	5	8	36	50	496.3
GB17	20.8	213.0	70.9	286.0	385.8	2	22	7	29	40	690.5
GB9	20.2	139.4	100.2	300.3	306.1	2	16	12	35	35	565.9
GB6E	20.1	53.6	25.4	254.3	106.4	4	12	6	55	23	205.6
GB6	35.6	79.2	27.8	292.4	141.0	6	14	5	51	24	283.6
GB2S	32.8	85.7	43.1	273.8	163.0	5	14	7	46	27	324.5
GB2E	74.1	168.4	63.6	259.7	245.6	9	21	8	32	30	551.7
GB10	24.7	74.4	30.5	274.4	203.2	4	12	5	45	33	332.8
GB34	13.4	117.6	164.2	287.5	537.0	1	11	15	26	48	832.2
GB27	26.7	54.5	92.8	295.1	531.0	3	5	9	30	53	704.9
GB32	12.9	52.0	96.3	277.6	441.3	1	6	11	32	50	602.4
GBEL-B	20.9	51.0	34.4	285.5	168.4	4	9	6	51	30	274.7
GB08	35.8	126.2	72.2	374.2	355.8	4	13	7	39	37	590.0
GB31	10.9	152.0	99.0	245.9	501.8	1	15	10	24	50	763.8
GB20	16.0	62.3	81.1	361.7	468.1	2	6	8	37	47	627.6
GB21	16.1	59.6	70.8	313.4	518.1	2	6	7	32	53	664.6
<b>Average</b>	32.77	181.1	112.9	285.8	339.0	3.36	16.75	10.57	33.14	36.25	665.8
<b>±SD</b>	29.42	178.3	90.7	46.9	133.1	2.09	10.54	4.75	10.00	12.04	332.2

Figure 1

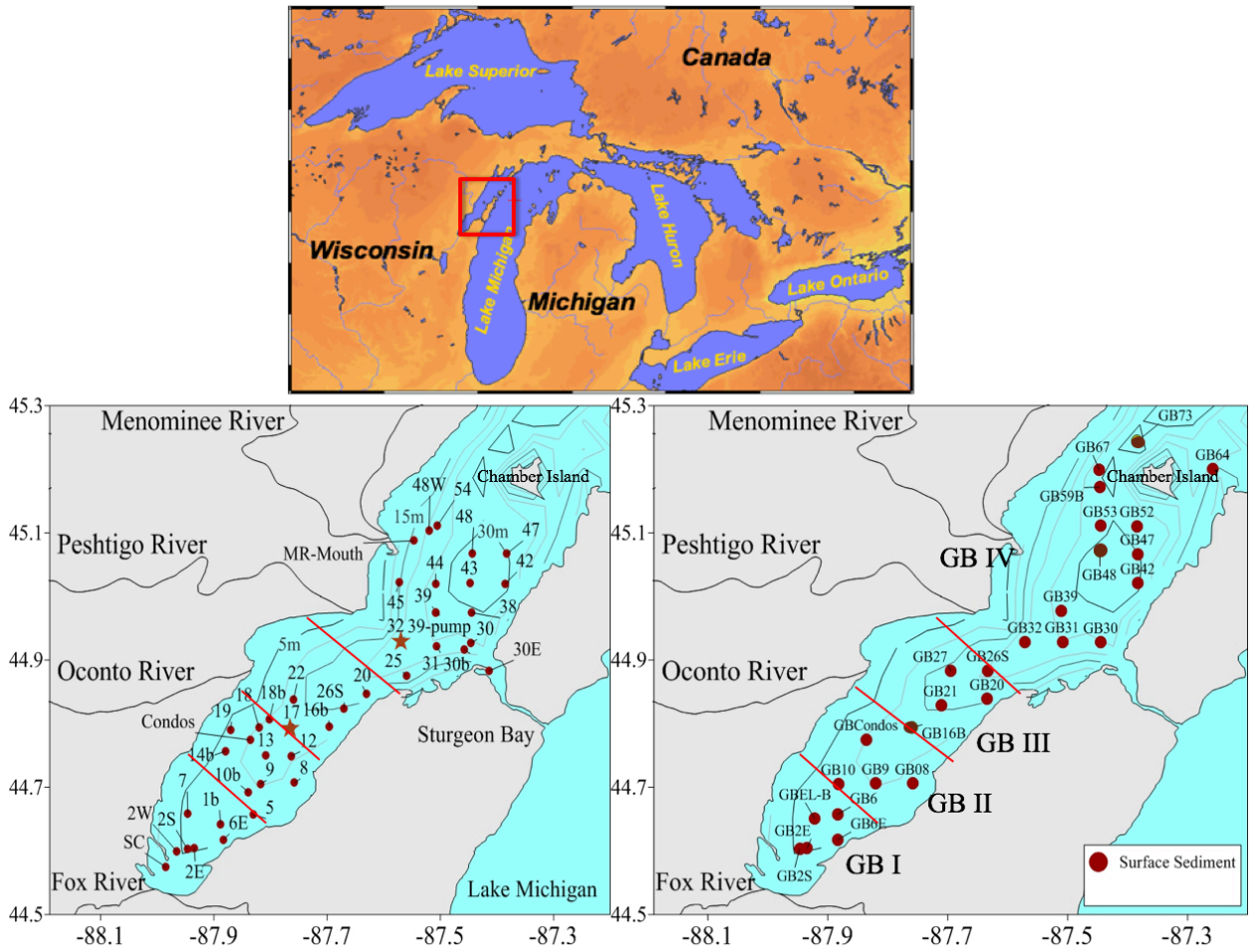


Figure 2

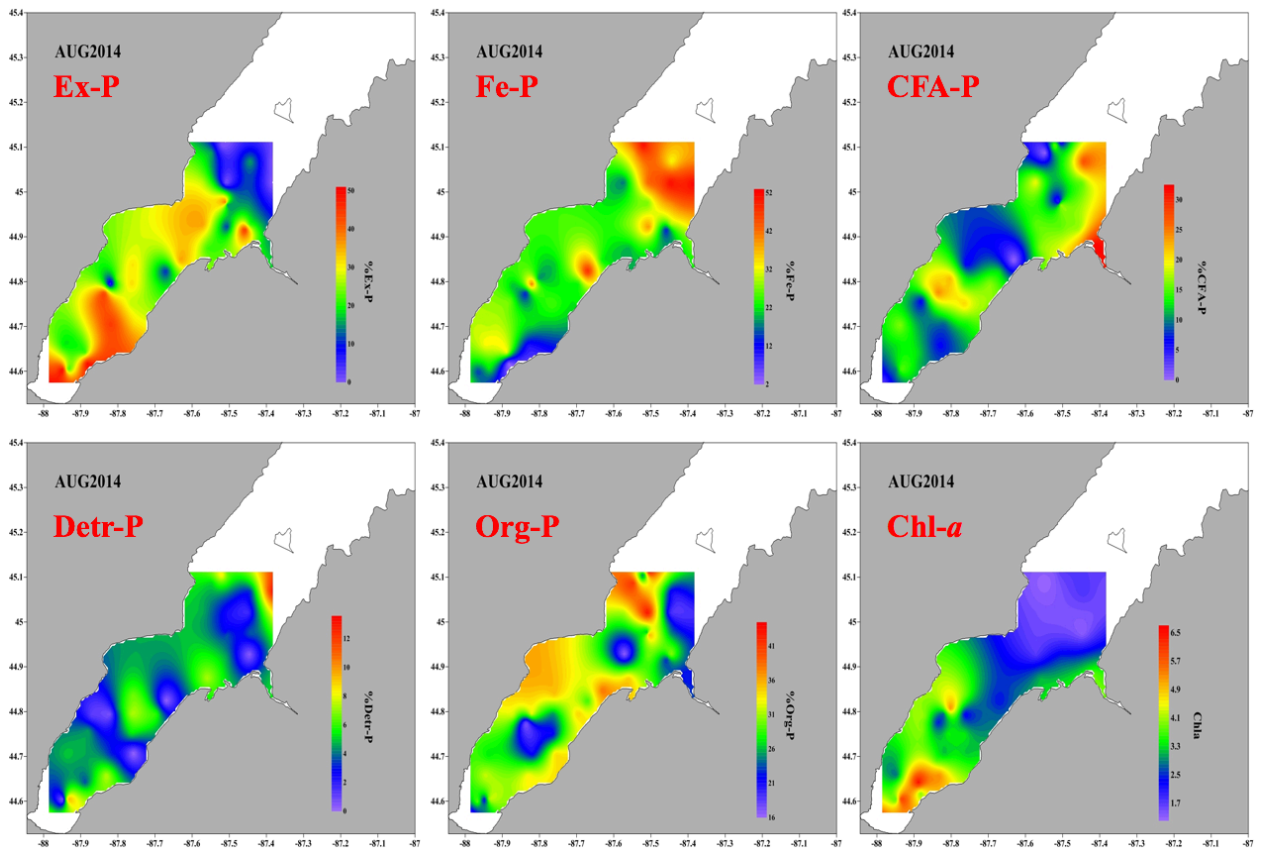


Figure 3

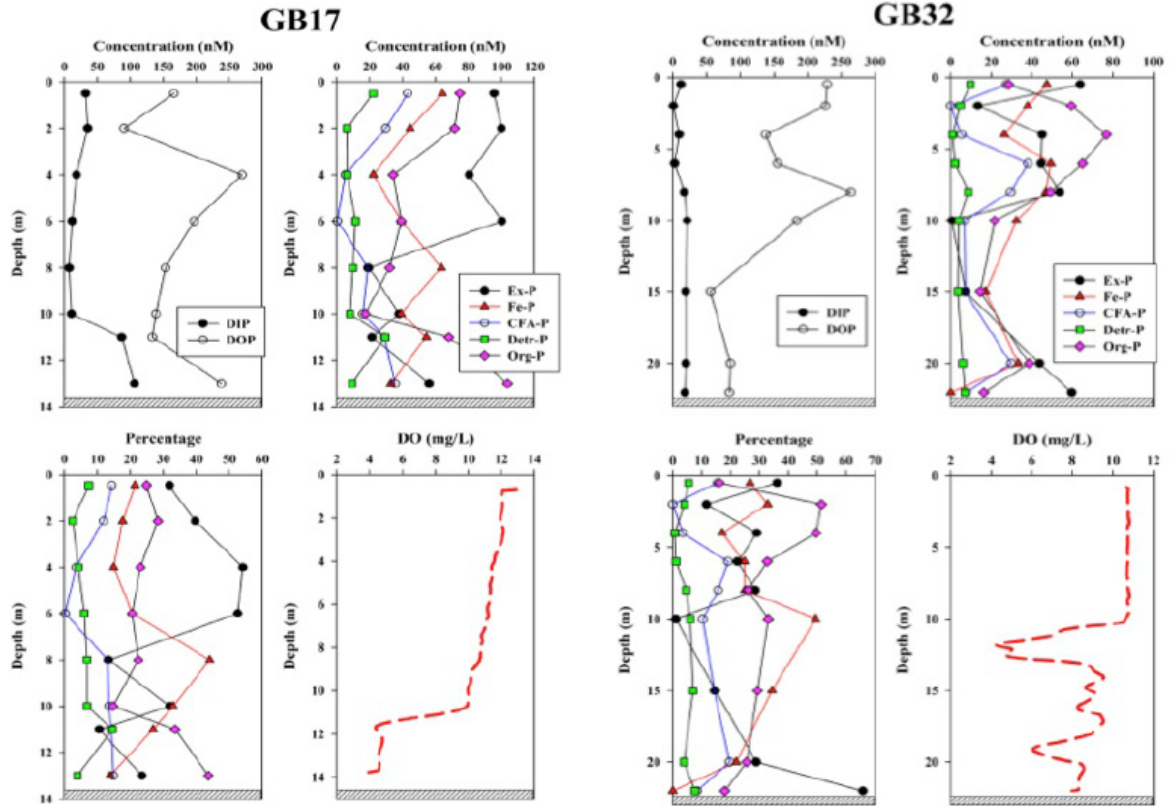


Figure 4

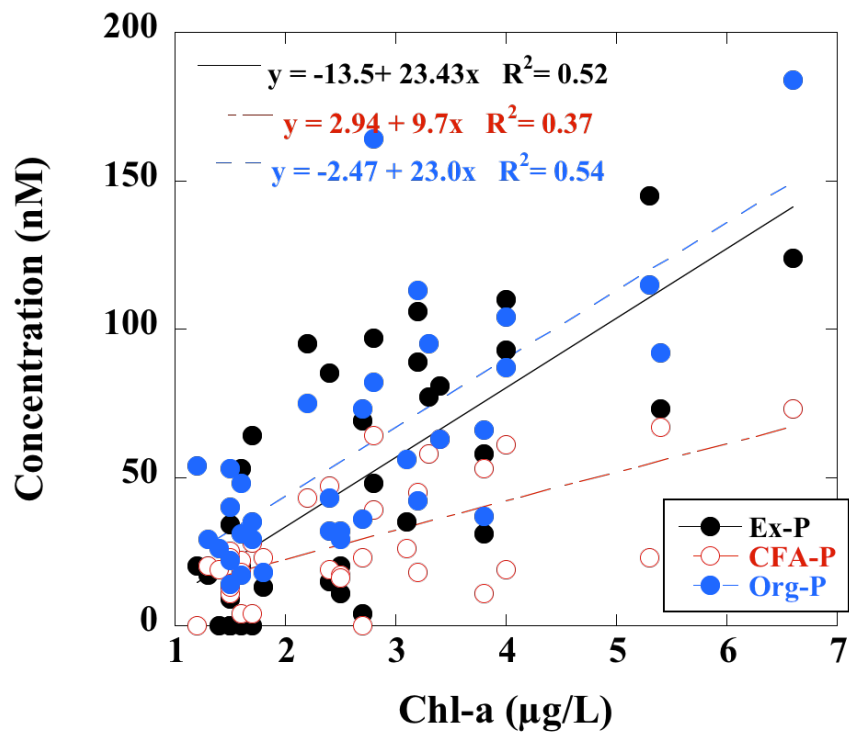


Figure 5

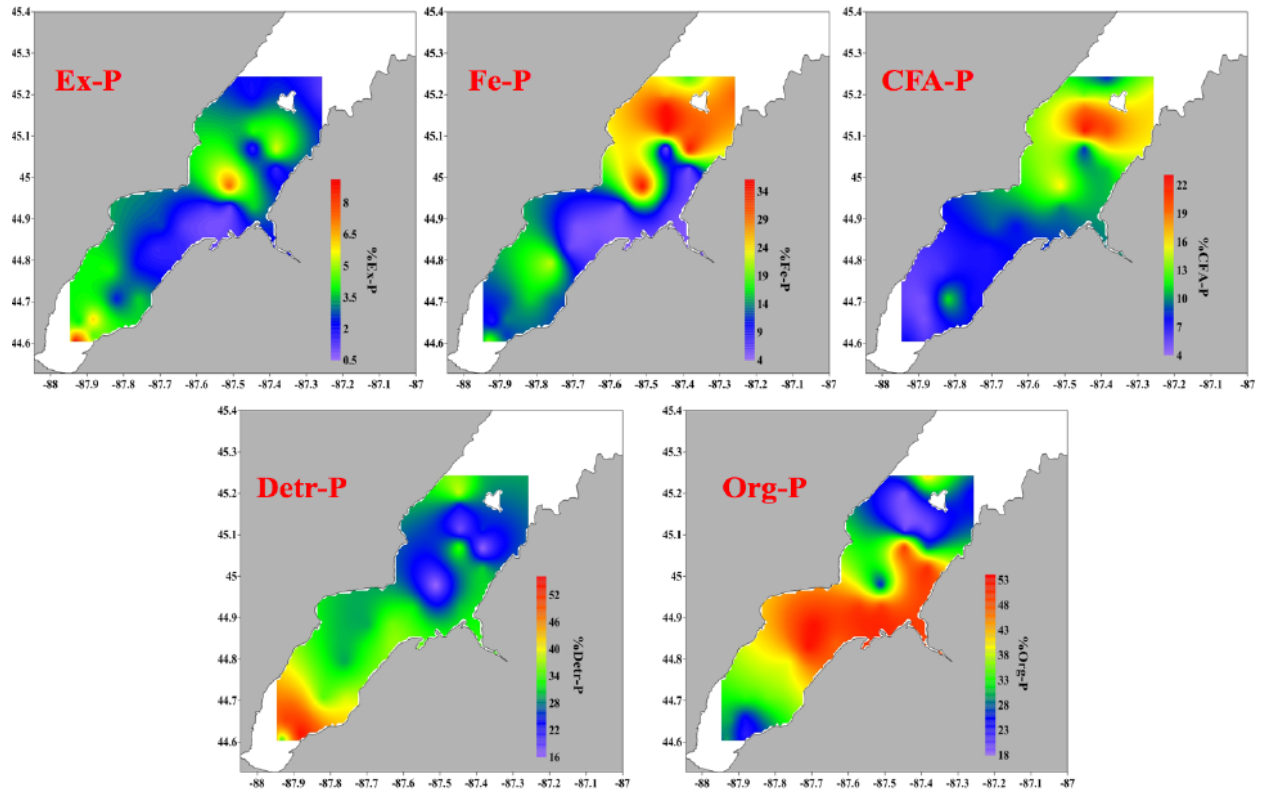


Figure 6

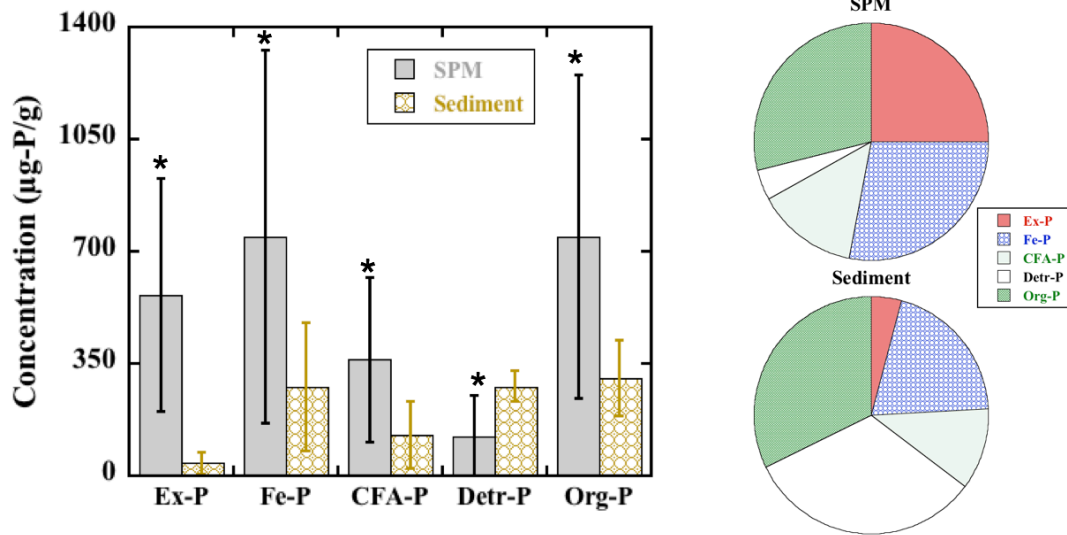




Figure 7

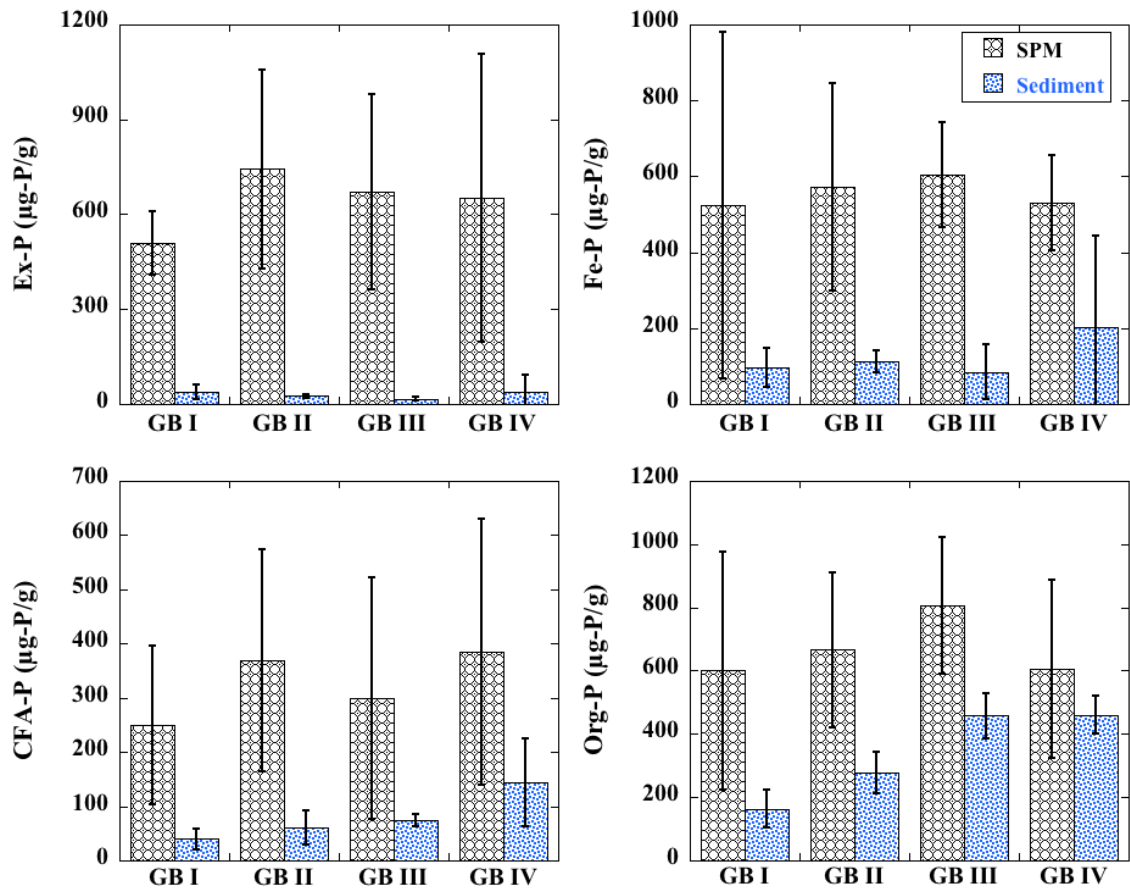


Figure 8

