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Chemical speciation, reactivity, and long-term burial of sedimentary phosphorus in Green Bay, a seasonally hypoxia-influenced freshwater estuary

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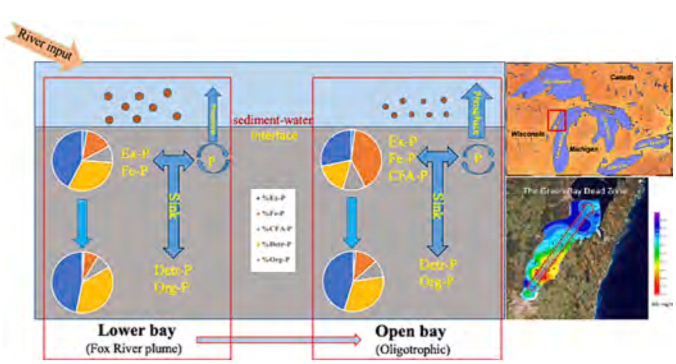
HIGHLIGHTS

- Post-depositional behavior of sedimentary P species was examined.
- Organic-P and detrital apatite were the main sedimentary P sink in Green Bay.
- P-regeneration occurred mostly from internal cycling of potentially bioavailable P.
- Estimated fluxes of regenerated P increased along the river-lake transect.
- Variations in detrital apatite may serve as an indicator of anthropogenic impact.

GRAPHICAL ABSTRACT



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ABSTRACT

Sediment cores were collected along a trophic gradient in Green Bay, a seasonally hypoxia-influenced freshwater estuary in Lake Michigan, to measure various phosphorus (P) species, including exchangeable-P (Ex-P), iron-bound-P (Fe-P), biogenic-apatite and/or $CaCO_3$-associated-P (CFA-P), organic-P (Org-P) and detrital-apatite-P (Detr-P). Although total phosphorus (TP) decreased with increasing depth, different P species exhibited distinct vertical distribution patterns with different post-depositional behaviors. The Ex-P, Fe-P and CFA-P species were identified as potentially bioavailable-P (BAP). Little variation was observed for Org-P and Detr-P species, especially below the upper-active-layer, both serving as the primary sink for P in sediment. Detr-P% decreased consistently from the near river plume station to the open bay in the north. P accumulation rates were estimated at 25.1 mmol-P/m^2/yr (779 mg-P/m^2/yr) in the south, 10.9 mmol-P/m^2/yr (338 mg-P/m^2/yr) in the central region, and 8.1 mmol-P/m^2/yr (252 mg-P/m^2/yr) in the north of Green Bay, showing a decrease in the depth of the upper active layer for P regeneration along the south-north transect. The overall potential P regeneration back into the water column increased from 2.8 mmol-P/m^2/yr (87 mg-P/m^2/yr) in the south, and 3.3 mmol-P/m^2/yr (101 mg-P/m^2/yr) in the central region to 5.6 mmol-P/m^2/yr (173 mg-P/m^2/yr) in the north of the bay, corresponding to P burial efficiencies of ~89 %, 70 % and 31 % along the trophic gradient. The recent decrease in Detr-P and thus the increase in BAP over the last 2–3 decades could be related to anthropogenic

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activities, such as damming and implementation of agricultural conservation practices. Conversely, a recent increase in TOC/TOP ratios may reflect the increased extent of trophic status and seasonal hypoxia in bottom waters and enhanced regeneration and recycling of particulate P in Green Bay since the 1960s. New results from this study provide an improved understanding of the linkage between sources, internal cycling, and long-term burial of P in the basin.

1. Introduction

As a common limiting nutrient, phosphorus (P) plays an essential role in ecosystem function in freshwater and coastal marine environments (Filippelli, 2010; Slomp et al., 2013; Orihel et al., 2017). Nevertheless, excess P can enhance eutrophication and algal blooms in aquatic environments, potentially leading to seasonal hypoxia especially during warm and stratified conditions (Zhang et al., 2010b; Scavia et al., 2016; Klump et al., 2018; Tellier et al., 2022). For example, nutrient enrichments have been shown to have dramatic impacts on the development of seasonal hypoxia in the Great Lakes regions, such as Lake Erie and Green Bay (Zhou et al., 2013; Klump et al., 2018), freshwater lakes (Nürnberg et al., 2013a, 2013b), and estuarine and coastal marine environments like the northern Gulf of Mexico, Chesapeake Bay and the Baltic Sea (e.g., Elsbury et al., 2009; Rabalais et al., 2009; Reed et al., 2011; Diaz et al., 2012). In the Great Lakes region, efforts have been made over several decades to regulate nutrient loadings and point sources with the aim of reducing nutrient levels in lake waters especially on phosphate or dissolved reactive P (Dolan and Chapra, 2012; Finlay et al., 2013; Dove and Chapra, 2015). Despite these regulations, there have been increasing reports of re-eutrophication, algal blooms, and increased extent of seasonal hypoxia in the Laurentian Great Lakes, including Lake Erie, Green Bay in Lake Michigan, and western Lake Superior (Scavia et al., 2014; Klump et al., 2018; Sterner et al., 2020; Tellier et al., 2022). Therefore, knowledge about sources, chemical speciation, reactivity/bioavailability, and biogeochemical cycling pathways of P in aquatic environments is needed to better understand P dynamics and its role in the development of seasonal hypoxia in estuarine and coastal environments (Yang et al., 2019; Liu et al., 2020; Yang et al., 2021).

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 in the Fox River basin have resulted in hypereutrophic water quality conditions in southern Green Bay (Qualls et al., 2013; Hamidi et al., 2015; Harris 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; Robertson et al., 2018), sporadic and seasonal hypoxic conditions in Green Bay remained frequent (Bartlett et al., 2018; Klump et al., 2018). Our previous studies on the dissolved-particulate-organic-inorganic continuum in the water column (Lin et al., 2016, 2018) have demonstrated the active internal regeneration of P from particulate to dissolved phases in the water column, which was greatly enhanced under hypoxia or anoxic conditions in bottom waters.

In addition to being a limiting nutrient, P has been found to preferentially partition or adsorb onto particle surfaces in the water column (Coelho et al., 2004; Lin et al., 2013), owing to its highly particle-reactive nature (Santschi, 1995; Lin et al., 2016; Yang et al., 2021). Since suspended particles usually contain diverse chemical compositions, including biogenic, inorganic, and detrital components, the deposited particulate P or sedimentary P also includes different chemical species. These sedimentary P species may have distinct reactivity, bioavailability, and post-deposition behaviors, potentially being regenerated into dissolved P through internal processes prior to their permanent burial and consequently regulating nutrient status and environmental quality (Klump et al., 1997; Wang et al., 2010; Lin et al., 2012a). Indeed, Lin et al. (2018) demonstrated the distinction in the chemical speciation of particulate P between suspended particulate matter in the water column and surface sediment, implying active P regeneration from certain P species prior to their burial. Moreover, post-depositional regeneration and diagenetic reactions could be enhanced by diffusion and sediment resuspension. Based on sedimentary total P and porewater phosphate profiles, Klump et al. (1997) first reported the recycling, burial and mass balance of P in Green Bay, and Zorn et al. (2018) observed increased dissolved phosphate in the overlying water associated with episodes of oxygen depletion. However, the linkages between the chemical speciation of sedimentary P, the reactivity or regeneration, and long-term deposition of different P species, environmental change, and anthropogenic activities in Green Bay watersheds remain to be explored.

To fill this knowledge gap, three sediment cores along a trophic gradient from southern to northern Green Bay were collected and sectioned at 1–2 cm intervals for the measurement of five operationally defined P species using sequential extraction methods (SEDEX). Our major objectives were to 1) quantify the variations in abundance and chemical speciation of P with depth in sediment and with stations along the trophic gradient in Green Bay; 2) estimate the active P regeneration depth in sediments and corresponding annual efflux of P to the overlying water column; and 3) uncover the main sedimentary sink and the depositional history of different P species based on sediment chronology derived from radionuclides. Our hypothesis is that among different forms of sedimentary P, only the potentially bioavailable P fractions within the upper active layer would actively interact with the overlying water column, contributing to the sediment P diffusive efflux, with an increasing trend along the river-lake transect in Green Bay.

2. Materials and methods

2.1. Study area and sample collection

The Lower Green Bay was designated as an Area of Concern (AOC) by the International Joint Commission of Canada and the United States in 1980s due to various environmental issues, including legacy nutrient pollution (Harris et al., 2018). Significant efforts have been made to address remedial actions and the maxima daily loads of nutrient and suspended sediment (e.g., Environmental, U.S., 2012; Robertson et al., 2018; Robertson et al., 2023). Despite these efforts, the lower Green Bay remains on the EPA's list of AOCs. Inputs of nutrients from the Fox River basin resulted in a trophic gradient along the south-north transect from the river plume (828 $\pm$ 216 nmol-P/L) to southern bay (298 $\pm$ 21 nmol-P/L) and then to open northern Green Bay (19 $\pm$ 6 nmol-P/L, Lin et al., 2016; Yang et al., 2021; Lin et al., 2023). In addition, re-eutrophication and seasonal hypoxia have been increasingly observed (Valenta, 2013; Harris et al., 2018; Klump et al., 2018).

Three sediment cores were collected along a trophic gradient from Green Bay onboard the R/V Neeskay using a gravitational sampler during August (25th–26th) 2014 (Fig. 1). The sampling sites were located in southern (GB16B), central (GB48) and northern Green Bay (GB73). Note that the limited number of sediment cores at each sampling site may not adequately represent the heterogeneous sedimentation environments, particularly in the river plume region.

The upper portion of the core (<10 cm) was sectioned at 1 cm intervals, while the rest was sectioned at 2 cm intervals. Sediment samples were freeze-dried and grounded to a fine powder (<200 mesh, 74 μm) with an agate pestle and mortar. Aliquots of the grounded samples were taken for the measurement of total organic carbon (TOC) and different sedimentary P species.

2.2. Sequential extraction of sedimentary P

The extraction procedures were mostly based on SEDEX sequential extraction technique developed by Ruttenberg (1992) and revised by Zhang et al. (2004, 2010a). The SEDEX procedure has been widely used to evaluate the chemical speciation and potentially bioavailable forms of P in sediments in aquatic environments (Parsons et al., 2017). To facilitate comparisons with previous studies, the same extraction technique was utilized in the present study.

Specifically, sedimentary P was chemically fractionated into five operationally defined P species: (1) P adsorbed onto grain surfaces or exchangeable P (Ex-P) extracted by 1 M $MgCl_2$ solution; (2) P associated with easily reducible iron and manganese oxides and/or oxyhydroxides (Fe-P), extracted by BD solution containing 0.11 M $NaHCO_3$ and 0.11 M $Na_2S_2O_4$ with pH adjusted to 7.0; (3) authigenic carbonate fluorapatite, biogenic apatite and $CaCO_3$-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) refractory organic P (Org-P) extracted through ashing at 550 °C followed by 1 M HCl extraction. It should be noted that during sample extraction, some easily degraded or leachable organic P may contribute to the P contents in Ex-P and CFA-P.

About 0.2 g of freeze-dried sediment were extracted with 20 mL of the extraction solution in polyethylene centrifuge tubes. All extraction was conducted in duplicate. 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 P (TP) in surface sediment were calculated from the sum of five different P species defined by the SEDEX procedures (Lin et al., 2012b). The sedimentary P concentrations are reported in μg-P/g-dried sediment.

2.3. Measurement of total organic carbon

Sediment samples were decalcified by reacting with diluted HCl (2 M) in amber glass bottles (Gao et al., 2018). After subsequent rinses with ultrapure water, the decalcified samples were dried and homogenized. Aliquots of the decalcified samples (~20 mg) were measured for total organic carbon (TOC) on an elemental analyzer (Guo et al., 2004). The precision of the TOC analysis was ≤1 % in terms of coefficient of variation (cv) as determined by replicate analysis of standards or samples (Gao et al., 2018).

2.4. Measurement of ^{137}Cs

Cesium-137 (^{137}Cs) is an anthropogenic radionuclide primarily introduced to the environment through nuclear weapon tests during the cold war era and accidents at nuclear power plants. The peak of the ^{137}Cs activity concentration in sediment columns usually indicates the particles deposited during the height of global nuclear bomb testing in 1963, thus serving as a useful tracer for determining sedimentation rates or the age of sediment layers. For measurements of ^{137}Cs, the dried sediment samples of different layers were placed into counting vials and counted on a high-purity germanium well gamma detector (Canberra Industries) at 661 keV. All samples were prepared with the same geometry and counted until a counting error of <10 % was achieved. Counting efficiencies were calibrated using different masses of marine sediment standard (NIST-4357). Activity concentrations of ^{137}Cs were decay-corrected to the sampling date. The sedimentation rates derived from ^{137}Cs profiles are comparable with those from ^{210}Pb dating reported previously (Klump et al., 1997).

2.5. Estimation of P accumulation rate and burial efficiency

Based on Ingall and Jahnke (1997) and Schenau and De Lange (2001), the averaged TP accumulation rate (PAR) was estimated using the following equation (Eq. (1)):

$$PAR = C_p \times MAR \quad (1)$$

where C_p is the averaged concentration of TP in each sediment core, MAR is the sediment mass accumulation rate calculated from the sedimentation rate derived from ^{137}Cs profiles and the averaged dry bulk sediment density of the sediment core. The dry bulk sediment density was calculated from the dried sediment weight and the wet volume (Dadey et al., 1992).

Following methods in Bala Krishna Prasad and Ramanathan (2010), Yang et al. (2017), and Liu et al. (2020), the P burial efficiency (PBE) was calculated using the following equation (Eq. (2)):

$$\%PBE = \%100 \times \frac{PAR}{PAR + P_{efflux}} \quad (2)$$

where the P_{efflux} is the efflux of dissolved P released from sediment at each sampling site (in mmol-P/m^2/yr); PAR is the averaged P accumulation rate (in mmol-P/m^2/yr). In the present study, the sum of Ex-P, Fe-

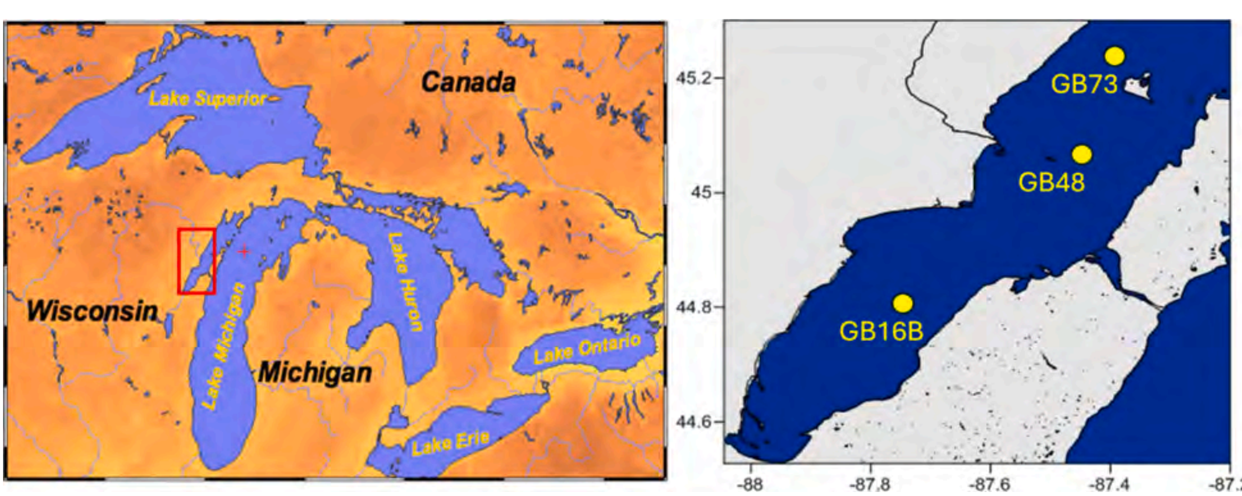

Fig. 1. Map showing the location of Green Bay in the Laurentian Great Lakes (left panel) and sampling locations of three sediment cores along a trophic gradient from an estuarine station near the plume in the south (GB16B) to an open water station in the north (GB-73) of Green Bay, Lake Michigan.

P and CFA-P contents was used to access the fraction of potentially bioavailable P (BAP) in the TP pool. The potential P efflux from sediment (P_{efflux}) was estimated from the difference in average BAP concentrations between the upper active layer and the deeper sediment layer, which may represent the upper limit of efflux compared to those measured from porewater profiles (Ingall and Jahnke, 1997; Schenau and De Lange, 2001).

3. Results and discussion

3.1. Chemical speciation of sedimentary phosphorus

Vertical distributions of the total phosphorus (TP) and different sedimentary P fractions (in μg-P/g-dried sediment) in different sediment cores from stations GB16B, GB48, and GB73 are shown in Table S1 and Fig. 2. Concentrations of TP ranged from 920 to 1494 μg-P/g at station GB16B, from 855 to 1759 μg-P/g at station GB48, and from 866 to 1779 μg-P/g at station GB73, which are comparable to the previously reported TP concentrations in Green Bay (900–1500 μg-P/g, Klump et al., 1997; Lin et al., 2018). In general, all sediment cores showed peak TP values in surface or subsurface layers and a decreasing trend with increasing depth, especially in the shallower layers (<5 cm), followed by minor changes in TP concentrations within the deeper sediment column.

Among the five sedimentary P species, Ex-P was generally a minor fraction of the TP pool, typically representing <5 % of TP in all sediment cores (Fig. 3) with a significant decreasing trend within the top 10 cm layer. Below this depth, concentrations of Ex-P were relatively constant at ~10 μg-P/g. On the other hand, Fe-P was one of the most abundant P species in the top 10 cm core (>30 %, Fig. 3), showing similar vertical distributions as Ex-P for all sediment cores (Fig. 2). Such observations for both Ex-P and Fe-P indicated a labile nature of these two P species in the upper sediment column and the release of dissolved P into the overlying water column, resulted from the reductive-dissolution of Fe-oxides/hydroxides and their associated particles (Fang et al., 2007; Lin et al., 2018). In contrast, concentrations of Detr-P varied little with depth in all cores (Fig. 2), consistent with its inert characteristics and association with terrestrially derived apatite. However, the peak value of Detr-P in the subsurface layers (e.g., GB16B, Fig. 2) and the increasing percentage in the TP pool with depth (GB48 and GB73, Figs. S2 and S3) suggested changes in terrestrial inputs from land to the bay over the past decades (see detailed discussion below).

Another apatite species, CFA-P, which usually exists as authigenic carbonate fluroapatite, biogenic apatite or $CaCO_3$-associated P, also showed distinct vertical profiles along with Detr-P, except for GB16B (Fig. 2). For both GB48 and GB73 cores, CFA-P abundance decreased rapidly with depth in the subsurface section and remained relatively

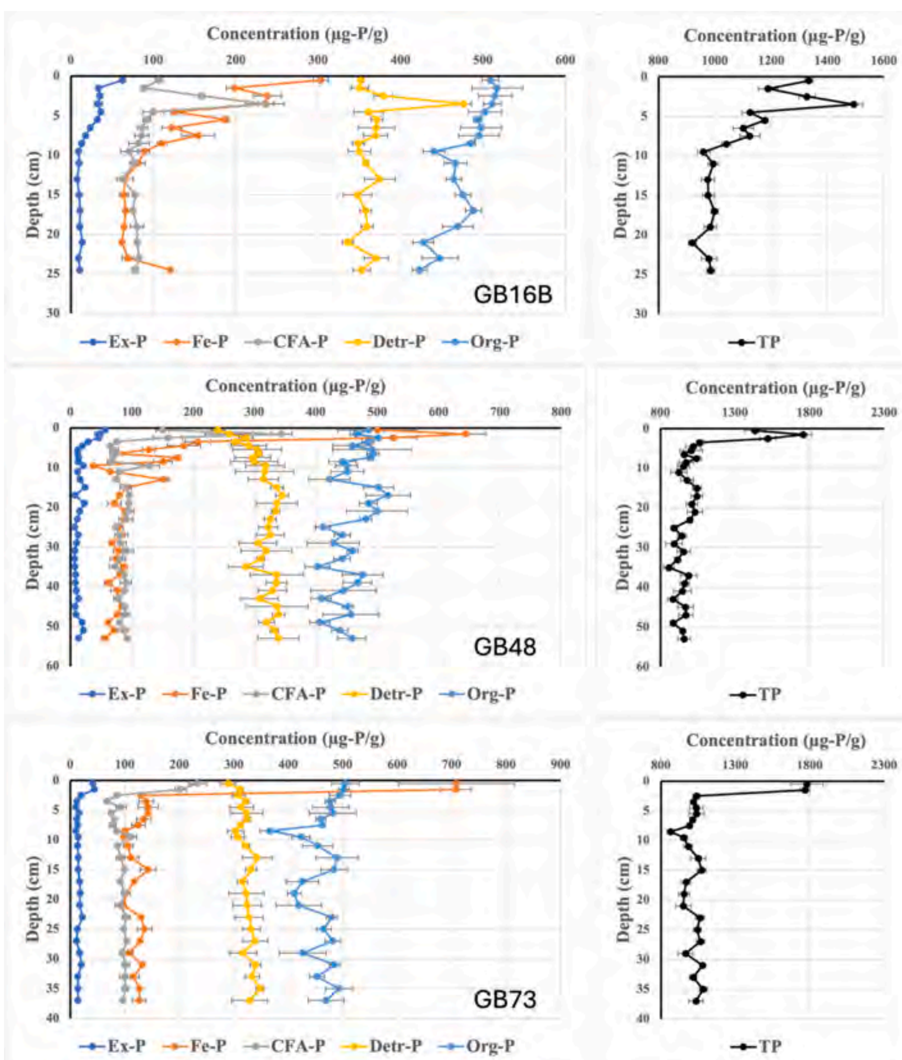

Fig. 2. Vertical profiles of different sedimentary P species, including labile- or exchangeable-P (Ex-P), iron-bound-P (Fe-P), biogenic-apatite and/or $CaCO_3$-associated-P (CFA-P), organic-P (Org-P), detrital-apatite-P (Detr-P) and total P (TP) (all in μg-P/g-dried sediment), at stations GB16B (upper panel), GB-48 (middle panel), and GB-73 (lower panel) in Green Bay.

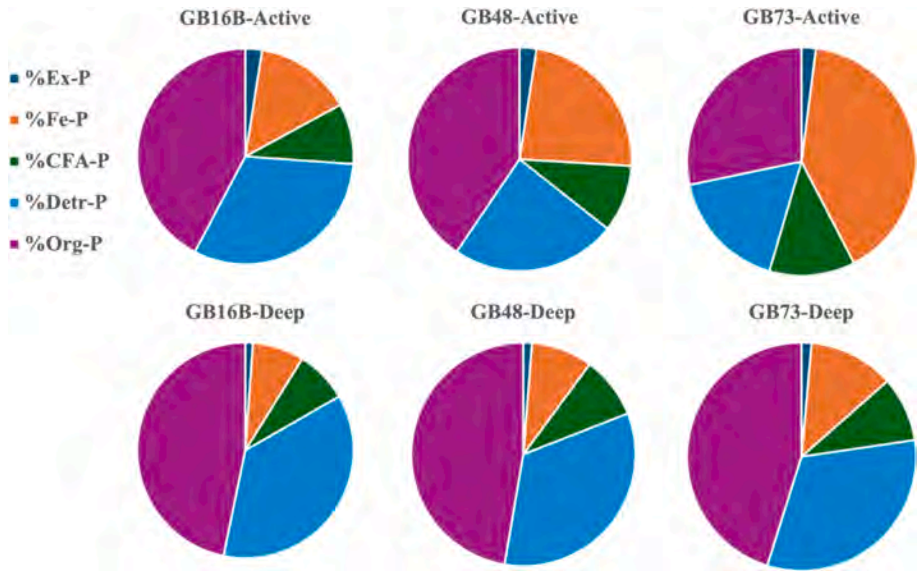

Fig. 3. Comparisons in the partitioning of sedimentary P species between the upper active regeneration layer (<10 cm at GB16B, <7 cm at GB48, and <3 cm at GB73) shown in upper panels and the deeper sediment column (lower panels) at stations along the trophic gradient from the south to the north in Green Bay, showing an increase in both Detr-P and Org-P and a decrease in Fe-P and CFA-P from the upper active layer (upper panels) to the lower sediment core (lower panels) as well as a significant increase in Fe-P and a decrease in both Detr-P and Org-P from the south to the north of the bay.

constant in the deeper sediment column, similar to Ex-P and Fe-P (Fig. 2). These variations suggested certain CFA-P components were relatively labile and can potentially be regenerated into dissolved P during early diagenetic processes in central and northern Green Bay (i.e., GB48 and GB73), but not in southern Green Bay (i.e., GB16B), as observed in a previous study in the water column of Green Bay (Lin et al., 2018). Among all the sedimentary P species, Org-P was typically the most abundant fraction in all three sediment cores, especially in the deeper sediment layers, that accounted for >50 % in the TP pool (Fig. 3). The depth profile of Org-P concentrations (in terms of μg-P/g) was more variable compared with those of other P species (Fig. 2), showing minor variations at GB48, somewhat decreasing with depth at GB16B, and more fluctuation at GB73. Nevertheless, in terms of percentage in the TP pool, it increased with depth to a constant value in the deeper sections of the three sediment cores (Fig. 3 and Table S1).

As shown in Figs. 2, S1, S2 and S3, different sequentially extracted sedimentary P species clearly exhibited distinct post-depositional behaviors compared to the bulk TP. Generally, two groups of P species with different post-deposition behaviors could be identified based on their vertical distributions: 1) Labile P species showing evident decreasing trends in the upper sediment column (Table 1) and potentially being regenerated back into the overlying water column; and 2) Relatively more refractory and well-buried P species (i.e., Detr-P and Org-P), showing minor vertical variations throughout the sediment column, especially below the upper active layer.

The labile P species include Ex-P, Fe-P and CFA-P. As a fraction loosely adsorbed on particle surfaces (Bala Krishna Prasad and Ramanathan, 2010; Lin et al., 2012a, 2012b), it is not surprising to observe Ex-P from sediments actively interacts with surrounding waters and generates dissolved P into the overlying water column. In addition, Fe-P, a redox sensitive species, can release phosphate from reductive dissolution of Fe-oxyhydroxide (Reed et al., 2011; Diaz et al., 2012). Similar processes were observed in bottom water under seasonal hypoxia/low-DO conditions in Green Bay (Lin et al., 2018). In comparison, P regeneration from CFA-P has not been commonly reported in aquatic environments. Lin et al. (2018) observed a significant correlation between CFA-P in suspended particles and Chl-a concentration, suggesting the occurrence of biogenic apatite and/or calcareous-plankton adsorbed P in addition to $CaCO_3$-associated P. Compared with other CFA-P components (e.g., authigenic apatite), these biogenic CFA-P phases are relatively readily to be regenerated, especially under hypoxic conditions and/or at the sediment-water interface (e.g., Cai et al., 2011). Thus, Ex-P, Fe-P and CFA-P could be considered as the BAP in Green Bay, especially in the upper sediment layer.

Table 1
Averaged concentrations of different P species, total phosphorus (TP), and bioavailable phosphorus (BAP), in terms of μg-P/g-dried sediments, in regeneration-active layer and deep layer of three sediment cores in Green Bay.

	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)	TP (μg-P/g)	BAP (μg-P/g)
GB16B							
Active layer (0–10 cm)	30	177	111	373	497	1187	207
Deep layer (>10 cm)	10	74	77	357	458	977	85
GB48							
Active layer (0–7 cm)	32	324	134	279	483	1251	489
Deep layer (>7 cm)	12	85	86	323	454	959	183
GB73							
Active layer (0–2 cm)	43	709	218	301	503	1774	970
Deep layer (>2 cm)	15	122	93	325	458	1013	230

The relatively more refractory and well-buried P species include Detr-P and Org-P. As depicted in Fig. 3, both Detr-P and Org-P are the predominant P species, comprising about 85 % of the TP pool and serving as the main P sink in Green Bay sediment, especially below the surface-active layer. Such observations in the sediment differ from our previous study of the water column in Green Bay, which categorized the Org-P in suspended particles as the BAP in the water column (Lin et al., 2018). Particulate Org-P in the water column may contain more freshly produced biomasses, making it potentially more easily decomposable compared to the more refractory sedimentary Org-P, that has undergone a series of oxidation and regeneration cycles before being permanently buried in sediment. The distinct phase distributions of particulate P between the water column (Lin et al., 2018) and sediment especially deeper sediment (Fig. 3) suggest that most labile particulate organic P in the overlying water column could degrade either prior to its deposition or within the surface-active layer, with an active internal P cycling in Green Bay.

3.2. Sedimentary bioavailable phosphorus and its potential efflux

Based on the post-deposition behavior of P species discussed above, the BAP was operationally defined as the sum of Ex-P, Fe-P and CFA-P in sediment. Vertical distributions of BAP contents and its percentage in

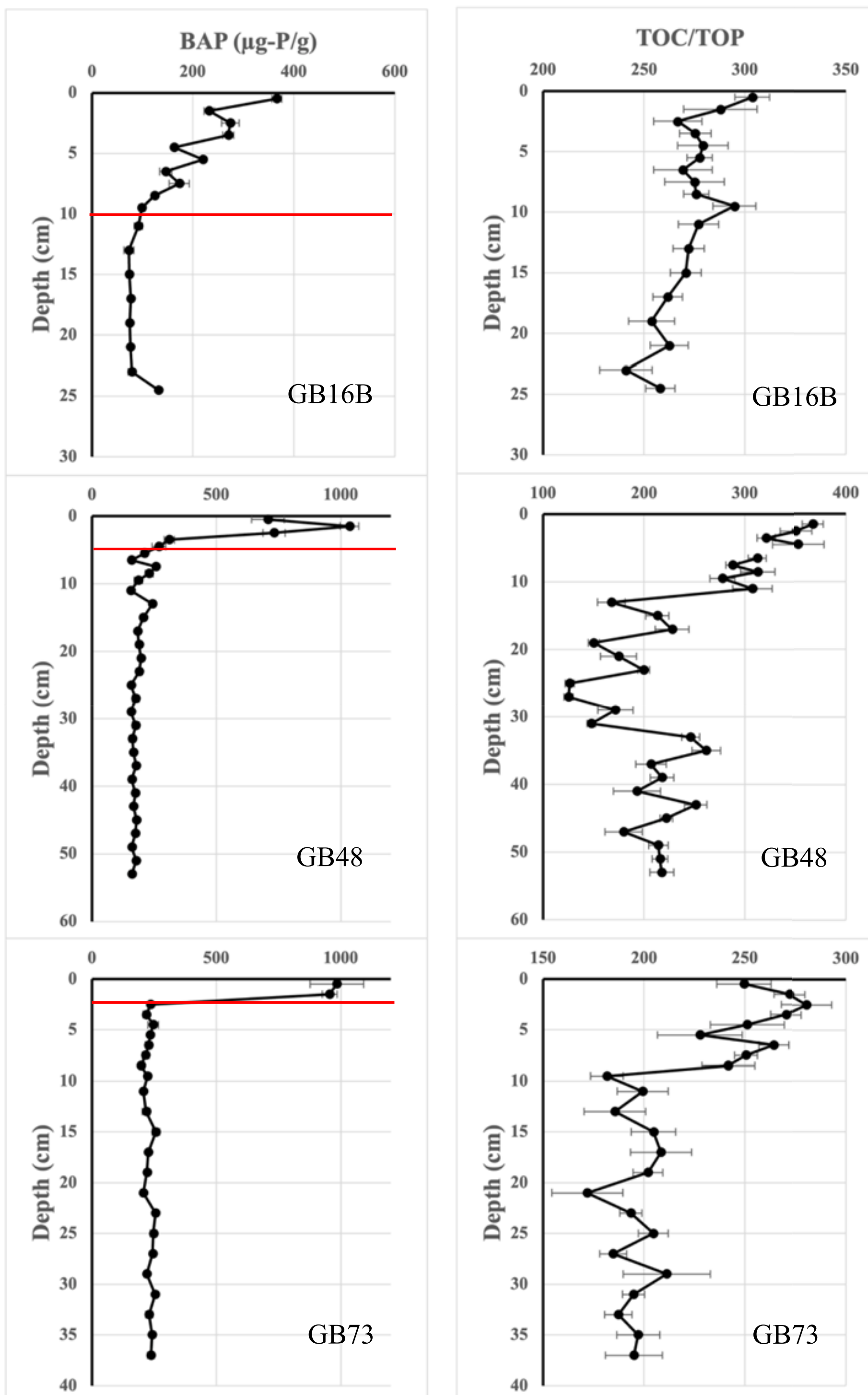

Fig. 4. Depth profiles of potentially bioavailable phosphorus (BAP, in µg-P/g) and total organic carbon to total organic phosphorus ratio (TOC/TOP) in different sediment cores. The red lines denote the depth of active regeneration layer.

the TP pool are shown in Fig. 4 and Fig. S4, respectively. It should be noted that the vertical profile of CFA-P at GB16B demonstrated that CFA-P may be insoluble and have low lability to be regenerated into the overlying water column. This implies the predominance of inert authigenic carbonate fluorapatite in the CFA-P pool at GB16B, consistent with its proximity to the river mouth. Thus, the BAP pool in the GB16B core was mostly composed of Ex-P and Fe-P. The concentration of BAP varied from 73 to 366 μg-P/g at GB16B, from 156 to 1035 μg-P/g at GB48, and from 197 to 984 μg-P/g at GB73, respectively, representing 8–27 %, 17–59 % and 21–55 % of the TP in the three sediment cores (Table S1, Fig. 4). Generally, the peak concentration and percentage of BAP were observed in surface and subsurface layers, with a significant decrease with depth in the upper sediment (Fig. 4). Together with the generally low dissolved phosphate conditions in Green Bay (<20 nM, Lin et al., 2018), the high BAP in the upper sediment layers suggested that a significant portion of surface/subsurface sedimentary BAP in Green Bay had a strong tendency to release dissolved P into the overlying water column. Moreover, this P regeneration mostly occurred in the upper sediment cores, with varying active regeneration depths observed among different stations along the trophic gradient from south to north. According to the vertical distributions of BAP (Fig. 4), the depth of active P regeneration layers typically decreased along the south-north transect in Green Bay, from 10 cm in depth at GB16B to 7 cm at GB48 and then to 2–3 cm at GB73 (Table 1, see their locations in Fig. 1), probably due to the shallow water depth and more intense sediment resuspension in southern Green Bay.

High abundance of BAP in the active regeneration layer of sediments should lead to the release of dissolved P from BAP across the sediment-water interface, which may serve as an internal source of P to the overlying water column in Green Bay (e.g., Zorn et al., 2018). Based on the variation in BAP in the upper active regeneration layer and the estimated sediment mass accumulation rate (MAR), the potential regeneration of P released from sedimentary BAP to the overlying water column can be estimated. The sedimentation rates at GB48 and GB73 were estimated from their corresponding ^{137}Cs profiles (Fig. S5), assuming a steady state depositional environment in Green Bay. Based on the sediment layer containing peak ^{137}Cs values that were associated with the year of global nuclear bomb testing (i.e., 1963), the average sedimentation rates at GB48 and GB73 sites were 0.22 cm/yr and 0.11 cm/yr, respectively. As the ^{137}Cs peak values at GB16B site cannot be detected due to its higher sedimentation rate or short sediment core, a sedimentation rate of 0.54 cm/yr reported by Klump et al. (1997) for the same sampling site was utilized to estimate the MAR. Together with the averaged dry bulk sediment density of each core, the MAR was estimated to be 71 mg/cm^2/yr at GB16B, 33 mg/cm^2/yr at GB48, and 23 mg/cm^2/yr at GB73. Using Eq. (1), the total P accumulation rate (PAR) was estimated to be 25.1 mmol-P/m^2/yr (or 779 mg-P/m^2/yr) at GB16B, 10.9 mmol-P/m^2/yr (338 mg-P/m^2/yr) at GB48, and 8.1 mmol-P/m^2/yr (252 mg-P/m^2/yr) at GB73.

Based on the difference in average BAP concentrations between the upper active regeneration layer (i.e., 10 cm at GB16B, 7 cm at GB48 core, and 3 cm at GB73 sites, Fig. 4) and the deeper sediment layer (Ingall and Jahnke, 1997; Schenau and De Lange, 2001), the potential regenerative effluxes of P (P_{efflux}) from sediment were estimated to be 2.8 mmol-P/m^2/yr (or 87 mg-P/m^2/yr) at GB16B, 3.3 mmol-P/m^2/yr (101 mg-P/m^2/yr) at GB48, and 5.6 mmol-P/m^2/yr (173 mg-P/ m^2/yr) at GB73. These P effluxes may represent the potential or upper limit of fluxes out of the sediment and could contribute majority of internal P loading to the Green Bay water column, ranging from ~10 % in the southern and central bay (GB16B and GB48) to ~20 % of the external P loading from the Fox River (~1000 mg-P/ m^2/yr, Klump et al., 1997; Larson et al., 2020). Considering that the external P loading from terrestrial and riverine inputs may have been consumed and deposited in the southern bay (see discussion below), such sediment diffusive effluxes may act as the predominant P source to the open northern Green Bay (e.g., 173 mg-P/m^2/yr of P_{efflux} to GB73). Our estimated sediment P effluxes (87–173 mg-P/m^2/yr) are comparable to the P internal loading/sediment P diffusive fluxes observed in other Laurentian Great Lake systems that also experience seasonal hypoxia/anoxia conditions. For example, P internal loading in western Lake Erie ranged from 157 to 332 mg-P/m^2/yr (Matisoff et al., 2016) and P diffusive flux during summer in the Bay of Quinte, Lake Ontario, ranged from 548 to 1314 mg-P/m^2/yr (Doan et al., 2018). Similarly, relatively higher internal P loading but with a similar magnitude has been observed in other freshwater systems, such as Lake Winnipeg (259–468 mg-P/m^2/yr, Nürnberg and LaZerte, 2016) and Lake Taihu (552 mg-P/m^2/yr, Qin et al., 2006), although different methods were used for estimation.

Compared to coastal marine environments, our estimated P effluxes in Green Bay are also comparable to estimated P diffusive fluxes in the East China Sea (e.g., 31–651 mg-P/m^2/yr, Fang et al., 2007) and at a permanently oxic site in the Baltic Sea (~217 mg-P/m^2/yr, Mort et al., 2010). However, they are lower than the estimated fluxes at the seasonally hypoxic sites in the Baltic Sea (2108–8990 mg-P/m^2/yr, Conley et al., 2002; Mort et al., 2010).

Our observed potential effluxes of P provided the first dataset of P internal loading derived from the sedimentary BAP pool, instead of from Fe-P and TP in sediment and/or porewater phosphate, for Green Bay. However, more comprehensive and seasonal studies covering broader areas of the bay are needed to better understand the contribution of P internal loading to the P mass balance in Green Bay.

The P burial efficiency (PBE) in Green Bay was calculated using Eq. (2), with values varying from 89 % at GB16B to 70 % at GB48, and then to 31 % at GB73, exhibiting a consistent decrease along the trophic gradient from the south/central to the north of Green Bay. The relatively higher PBE value at site GB16B may be partially attributed to its lower abundance of BAP in the TP pool (27 % at GB16B vs. 49 % at GB48 and 55 % at GB73) due to the lower participation of CFA-P in active transformation into dissolved P, coupled with relatively higher contents of detrital apatite and a faster sedimentation rate (0.54 cm/yr at GB16B vs. 0.22 cm/yr at GB48 and 0.11 cm/yr at GB73). In contrast, the slower sedimentation rate and relatively higher abundance of BAP in the upper section of the GB73 core allowed for more efficient exchange of sedimentary BAP with the overlying water column, particularly under the prevalent oligotrophic conditions in northern Green Bay, which is adjacent to the oligotrophic Lake Michigan known for its low phosphate levels (Lin et al., 2016, 2018).

3.3. Variations in detrital apatite and organic carbon/phosphorus ratio

As shown in Fig. 2, the abundance of detrital apatite (i.e., Detr-P) clearly increased with depth, reaching a relatively constant value below the upper active layer in all three sediment cores. Since the Detr-P is mostly derived from terrestrial sources (e.g., riverine particles) and is resistant to biogeochemical processes (Zhang et al., 2010), variations in Detr-P abundance may elucidate temporal changes in the terrestrial/riverine input of detrital apatite to Green Bay. According to the estimated sedimentation rate, the Detr-P content in all three sediment cores increased with depth until the sediment layer deposited around 1993 (~11 cm at GB16B, ~5 cm at GB48, and ~2.5 cm at GB73, see Figs. 2 and 5). The decrease in the input of riverine and terrestrial particles and thus the content of Detr-P in sediment after 1993 likely resulted from changes in agricultural practices and anthropogenic activities in the river basin. This impact is clearly manifested in sediment cores from the central and northern Green Bay (GB48 and GB73). However, most terrestrial particles from the Fox River may be predominantly deposited in southern Green Bay, further implying that regeneration and internal cycling (with 589 mg-P/m^2/yr of P_{efflux} at GB73, Section 3.2), instead of external terrestrial inputs, may be the predominant P source in central and northern Green Bay (e.g., Klump et al., 1997), similar to other study areas such as Lake Taihu (e.g., Xu et al., 2021).

Moreover, the ratios between TOC and reactive P ($P_{reactive}$, including Ex-P, Fe-P, CFA-P and Org-P) and between TOC and total organic P

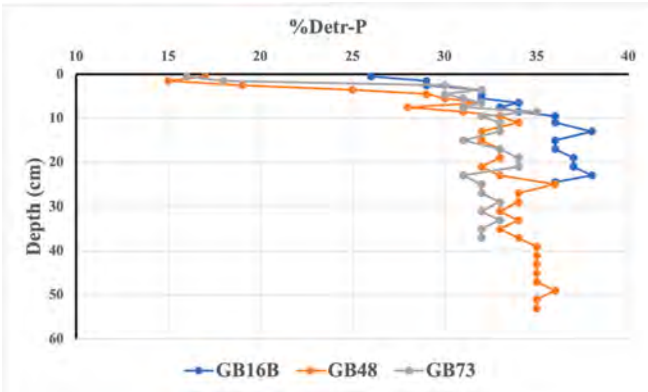

Fig. 5. Vertical distributions of detrital apatite P (Detr-P) as a percentage of the total P pool (%-Detr-P) in Green Bay, showing a recent decrease in Detr-P in the upper sediment cores at all three stations.

(TOP) in sediments have been demonstrated to be useful indicators of depositional conditions in aquatic environments (Algeo and Ingall, 2007; Slomp and Van Cappellen, 2007; Mort et al., 2010). For example, both TOC/$P_{reactive}$ and TOC/TOP ratios were elevated in sediments deposited under anoxic bottom waters (Ingall et al., 2005). Given the potential of Ex-P, Fe-P and CFA-P to release dissolved P within the upper sediment, TOC/TOP may serve as a compelling proxy for tracking changes in sources, cycling and deposition in the study area. As shown in Fig. 4, significantly higher TOC/TOP ratios at both GB48 and GB73 were observed in sediments deposited after 1963 (i.e., 11 cm at GB48 and 5.5 cm at GB73), suggesting that this sediment later contained more degraded organic matter with higher TOC/TOP ratios and less terrestrial particulate organic P. In addition, state regulation on nutrient loadings, especially phosphate, since the 1960s and the persistent P-limitation in Lake Michigan and open Green Bay may result in higher organic C/P ratios observed in the water column (Lin et al., 2016; Yang et al., 2021) and sediment in Green Bay (Lin et al., 2018), even though the more frequent hypoxia events and reducing conditions in Green Bay (Klump et al., 2018) should facilitate the recycling of P in the water column (Lin et al., 2018) during the past half century compared to the period before 1963.

Overall, changes in detrital apatite, potentially bioavailable P, and the organic C/P ratios allow one to reconstruct the sediment deposition history related to changes in management and anthropogenic activities, such as the implementation of agricultural conservation practices, reductions in industrial and municipal point sources, and remedial dredging, in Green Bay and its watersheds. Nevertheless, unlike detrital apatite which is hardly affected by post-diagenetic processes (Jaisi and Blake, 2010), the internal transformation between active P species (e.g., Ex-P, Fe-P, and CFA-P) and the more refractory Org-P in Green Bay might still occur during post-diagenesis in sediment (Cha et al., 2005; Joshi et al., 2015), which could consequently interfere with the historical signal recorded by the organic C/P ratios.

4. Conclusions

Our results identified readily exchangeable P (Ex-P), redox-sensitive P (Fe-P), and biogenic apatite and $CaCO_3$-associated P (CFA-P) species in Green Bay sediment as potentially bioavailable sedimentary P with active exchange with the overlying water column. Nevertheless, Green Bay sediments were dominated by inert detrital apatite (Detr-P) and Org-P, with their relative abundance increasing from the upper sediment layer to deeper sediment columns, suggesting they serve as the main sink of P in Green Bay. Based on these observations, our study provided the first attempt to estimate the potential regeneration effluxes of P in Green Bay based on the potentially bioavailable P fractions (i.e., Ex-P + Fe-P + CFA-P) in the TP pool. We observed an increase in the potential regeneration of sediment P from 2.8 mmol-P/m^2/yr (87 mg-P/m^2/yr) and 3.3 mmol-P/m^2/yr (101 mg-P/m^2/yr) in the southern and central bay to 5.6 mmol-P/m^2/yr (173 mg-P/m^2/yr) in the northern bay. This corresponds with decreasing P burial efficiency along the trophic gradient, suggesting a more efficient exchange of sedimentary BAP with the prevalent oligotrophic water column in Green Bay. Higher potential P regeneration effluxes, as an internal P loading, are especially important in northern Green Bay, where it may act as the predominant P loading to the water column since majority of terrestrial external P loading is mostly consumed and deposited in the southern bay.

Our measurements covering different sedimentary P species provide improved estimates of the potential regeneration of P from sediment in Green Bay. Our findings emphasize the importance of investigating the chemical speciation of sedimentary P, allowing a better understanding of P biogeochemical cycling and the deposition history of P species and their linkages to changes in anthropogenic activities, nutrient management, and climate and environmental changes in the basin. Further studies covering more areas of Green Bay are needed to elucidate the interplay among nutrient loading, chemical speciation, hypoxia extent, and internal P cycling in Green Bay.

CRediT authorship contribution statement

Peng Lin: Writing – original draft, Data curation, Conceptualization. **J. Val Klump:** Writing – review & editing, Data curation, Conceptualization. **Laodong Guo:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare no competing interests.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2024.174957.

References

Algeo, T.J., Ingall, E., 2007. Sedimentary Corg: P ratios, paleocean ventilation, and Phanerozoic atmospheric pO_2. Palaeogeogr. Palaeoclimatol. Palaeoecol. 256 (3–4), 130–155.
Bala Krishna Prasad, M., Ramanathan, A.L., 2010. Characterization of phosphorus fractions in the sediments of a tropical intertidal mangrove ecosystem. Wetl. Ecol. Manag. 18, 165–175.
Bartlett, S.L., Brunner, S.L., Klump, J.V., Houghton, E.M., Miller, T.R., 2018. Spatial analysis of toxic or otherwise bioactive cyanobacterial peptides in Green Bay, Lake Michigan. J. Great Lakes Res. 44, 924–933.
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., Zhao, P., 2011. Acidification of subsurface coastal waters enhanced by eutrophication. Nat. Geosci. 4 (11), 766–770.

Cha, H.J., Lee, C.B., Kim, B.S., Choi, M.S., Ruttenberg, K.C., 2005. Early diagenetic redistribution and burial of phosphorus in the sediments of the southwestern East Sea (Japan Sea). Mar. Geol. 216 (3), 127–143.

Coelho, J.P., Flindt, M.R., Jensen, H.S., Lillebø, 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 (4), 583–590.

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 (24), 5315–5320.

Dadey, K.A., Janecek, T., Klaus, A., 1992. 37. Dry-bulk density: its use and determination. In: Proceedings of the Ocean Drilling Program, Scientific Results, 126, pp. 551–554.

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. Glob. Biogeochem. Cycles 26 (2).

Doan, P.T., Watson, S.B., Markovic, S., Liang, A., Guo, J., Mugalingam, S., Stokes, J., Morley, A., Zhang, W., Arhonditsis, G.B., Dittrich, M., 2018. Phosphorus retention and internal loading in the Bay of Quinte, Lake Ontario, using diagenetic modelling. Stoten 636, 39–51.

Dolan, D.M., Chapra, S.C., 2012. Great Lakes total phosphorus revisited: 1. Loading analysis and update (1994–2008). J. Great Lakes Res. 38 (4), 730–740.

Dove, A., Chapra, S.C., 2015. Long-term trends of nutrients and trophic response variables for the G reat L akes. Limnol. Oceanogr. 60 (2), 696–721.

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.

Environmental, U.S., 2012. Total Maximum Daily Load and Watershed Management Plan for Total Phosphorus and Total Suspended Solids in the Lower Fox River Basin and Lower Green Bay.

Fang, T.H., Chen, J.L., Huh, C.A., 2007. Sedimentary phosphorus species and sedimentation flux in the East China Sea. Cont. Shelf Res. 27 (10−11), 1465–1476.

Filippelli, G.M., 2010. Phosphorus and the gust of fresh air. Nature 467 (7319), 1052–1053.

Finlay, J.C., Small, G.E., Sterner, R.W., 2013. Human influences on nitrogen removal in lakes. Science 342 (6155), 247–250.

Gao, L., Zhou, Z., Reyes, A.V., Guo, L., 2018. Yields and characterization of dissolved organic matter from different aged soils in northern Alaska. J. Geophys. Res. Biogeo. 123 (7), 2035–2052.

Guo, L., Semiletov, I., Gustafsson, Ö., Ingri, J., Andersson, P., Dudarev, O., White, D., 2004. Characterization of Siberian Arctic coastal sediments: implications for terrestrial organic carbon export. Glob. Biogeochem. Cycles 18 (1), GB1036. https://doi.org/10.1029/2003GB002087.

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. 41 (4), 1024–1036.

Hansen, H.P., Koroleff, F., 1999. Determination of nutrients. In: Grasshoff, K., Kremling, K., Ehrhardt, M. (Eds.), Methods of Seawater Analysis, third edition. Wiley-VCH Verlag GmbH, Weinheim Germany. https://doi.org/10.1002/9783527613984.ch10.

Harris, H.J., Wenger, R.B., Sager, P.E., Klump, J.V., 2018. The Green Bay saga: environmental change, scientific investigation, and watershed management. J. Great Lakes Res. 44 (5), 829–836. https://doi.org/10.1016/j.jglr.2018.08.001.

Ingall, E., Jahnke, R., 1997. Influence of water-column anoxia on the elemental fractionation of carbon and phosphorus during sediment diagenesis. Mar. Geol. 139, 219–229.

Ingall, E., Kolowith, L., Lyons, T., Hurtgen, M., 2005. Sediment carbon, nitrogen and phosphorus cycling in an anoxic fjord, Effingham Inlet, British Columbia. Am. J. Sci. 305 (3), 240–258.

Jaisi, D.P., Blake, R.E., 2010. Tracing sources and cycling of phosphorus in Peru Margin sediments using oxygen isotopes in authigenic and detrital phosphates. Geochim. Cosmochim. Acta 74 (11), 3199–3212.

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.

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, 10–26.

Klump, J.V., Fitzgerald, S.A., Waplesa, 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., Brunner, S.L., Grunert, B.K., Kaster, J.L., Weckerly, K., Houghton, E.M., Kennedy, J.A., Valenta, T.J., 2018. Evidence of persistent, recurring summertime hypoxia in Green Bay, Lake Michigan. J. Great Lakes Res. 44 (5), 841–850.

Larson, J.H., James, W.F., Fitzpatrick, F.A., Frost, P.C., Evans, M.A., Reneau, P.C., Xenopoulos, M.A., 2020. Phosphorus, nitrogen and dissolved organic carbon fluxes from sediments in freshwater rivermouths entering Green Bay (Lake Michigan; USA). Biogeochemistry 147, 179–197.

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. https://doi.org/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. https://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., Klump, J.V., Guo, L., 2018. Variations in chemical speciation and reactivity of phosphorus between suspended-particles and surface-sediment in seasonal hypoxia-influenced Green Bay. J. Great Lakes Res. 44 (5), 864–874.

Lin, H., Bartlett, S.L., Guo, L., 2023. Distinct variations in fluorescent DOM components along a trophic gradient in the lower Fox River-Green Bay as characterized using one-sample PARAFAC approach. Stoten 902, 165891.

Liu, J., Krom, M.D., Ran, X., Zang, J., Liu, J., Yao, Q., Yu, Z., 2020. Sedimentary phosphorus cycling and budget in the seasonally hypoxic coastal area of Changjiang Estuary. Stoten 73, 136389.

Matisoff, G., Kaltenberg, E.M., Steely, R.L., Hummel, S.K., Seo, J., Gibbons, K.J., Bridgeman, T.B., Seo, Y., Behbahani, M., James, W.F., Johnson, L.T., 2016. Internal loading of phosphorus in western Lake Erie. J. Great Lakes Res. 42 (4), 775–788.

Mort, H.P., Slomp, C.P., Gustafsson, B.G., Andersen, T.J., 2010. Phosphorus recycling and burial in Baltic Sea sediments with contrasting redox conditions. Geochim. Cosmochim. Acta 74 (4), 1350–1362.

Nürnberg, G.K., LaZerte, B.D., 2016. More than 20 years of estimated internal phosphorus loading in polymictic, eutrophic Lake Winnipeg, Manitoba. J. Great Lakes Res. 42 (1), 18–27.

Nürnberg, G.K., LaZerte, B.D., Loh, P.S., Molot, L.A., 2013a. Quantification of internal phosphorus load in large, partially polymictic and mesotrophic Lake Simcoe, Ontario. J. Great Lakes Res. 39 (2), 271–279.

Nürnberg, G.K., Molot, L.A., O'Connor, E., Jarjanazi, H., Winter, J.G., Young, J.D., 2013b. Evidence for internal phosphorus loading, hypoxia and effects on phytoplankton in partially polymictic Lake Simcoe, Ontario. J. Great Lakes Res. 39, 259–270.

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. Can. J. Fish. Aquat. Sci. 74 (12), 2005–2029.

Parsons, C.T., Rezanezhad, F., O'Connell, D.W., Van Cappellen, P., 2017. Sediment phosphorus speciation and mobility under dynamic redox conditions. Biogeosciences 14 (14), 3585–3602.

Qin, B., Zhu, G., Zhang, L., Luo, L., Gao, G., Gu, B., 2006. Estimation of internal nutrient release in large shallow Lake Taihu, China. Sci. China Series D 49, 38–50.

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., Díaz, R.J., Justić, D., 2009. Global change and eutrophication of coastal waters. ICES J. Mar. Sci. 66 (7), 1528–1537.

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.

Robertson, D.M., Siebers, B.J., Diebel, M.W., Somor, A.J., 2018. Water-quality Response to Changes in Phosphorus Loading of the Winnebago Pool Lakes, Wisconsin, With Special Emphasis on the Effects of Internal Loading in a Chain of Shallow Lakes (No. 2018–5099). US Geological Survey.

Robertson, D.M., Diebel, M.W., Bartlett, S.L., Fermanich, K.J., 2023. Changes in phosphorus and suspended solids loading in the Fox River, northeastern Wisconsin, 1989–2021. In: U.S. Geological Survey Scientific Investigations Report 2023–5112. https://doi.org/10.3133/sir20235112 (29 pp.).

Ruttenberg, K.C., 1992. Development of a sequential extraction method for different forms of phosphorus in marine sediments. Limnol. Oceanogr. 37, 1460–1482.

Santschi, P.H., 1995. Seasonality in nutrient concentrations in Galveston Bay. Mar. Environ. Res. 40, 337–362.

Scavia, D., Allan, J.D., Arend, K.K., Bartell, S., Beletsky, D., Bosch, N.S., Brandt, S.B., Briland, R.D., Daloğlu, I., DePinto, J.V., Dolan, D.M., 2014. Assessing and addressing the re-eutrophication of Lake Erie: central basin hypoxia. J. Great Lakes Res. 40 (2), 226–246.

Scavia, D., DePinto, J.V., Bertani, I., 2016. A multi-model approach to evaluating target phosphorus loads for Lake Erie. J. Great Lakes Res. 42 (6), 1139–1150.

Schenau, S.J., De Lange, G.J., 2001. Phosphorus regeneration vs. burial in sediments of the Arabian Sea. Mar. Chem. 75 (3), 201–217.

Slomp, C.P., Van Cappellen, P., 2007. The global marine phosphorus cycle: sensitivity to oceanic circulation. Biogeosciences 4 (2), 155–171.

Slomp, C.P., Mort, H.P., Jilbert, 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.

Sterner, R.W., Reinl, K.L., Lafrancois, B.M., Brovold, S., Miller, T.R., 2020. A first assessment of cyanobacterial blooms in oligotrophic Lake Superior. Limnol. Oceanogr. 65 (12), 2984–2998.

Tellier, J.M., Kalejs, N.I., Leonhardt, B.S., Cannon, D., Höök, T.O., Collingsworth, P.D., 2022. Widespread prevalence of hypoxia and the classification of hypoxic conditions in the Laurentian Great Lakes. J. Great Lakes Res. 48 (1), 13–23.

Valenta, T.J., 2013. Oxygen depletion in Green Bay (MS Thesis). Univ. Wisconsin-Green Bay.

Wang, Y.P., Law, R.M., Pak, B., 2010. A global model of carbon, nitrogen and phosphorus cycles for the terrestrial biosphere. Biogeosciences 7 (7), 2261–2282.

Xu, H., McCarthy, M.J., Paerl, H.W., Brookes, J.D., Zhu, G., Hall, N.S., Qin, B., Zhang, Y., Zhu, M., Hampel, J.J., Newell, S.E., 2021. Contributions of external nutrient loading and internal cycling to cyanobacterial bloom dynamics in Lake Taihu, China: implications for nutrient management. Limnol. Oceanogr. 66 (4), 1492–1509.

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.

Yang, B., Zhou, J.B., Lu, D.L., Dan, S.F., Zhang, D., Lan, W.L., Kang, Z.J., Ning, Z.M., Cui, D.Y., 2019. Phosphorus chemical speciation and seasonal variations in surface sediments of the Maowei Sea, northern Beibu Gulf. Mar. Pollut. Bull. 141, 61–69.

Yang, B., Lin, H., Bartlett, S.L., Houghton, E.M., Robertson, D.M., Guo, L., 2021. Partitioning and transformation of organic and inorganic phosphorus among dissolved, colloidal and particulate phases in a hypereutrophic freshwater estuary. Water Res. 196, 117025.

Zhang, J.Z., Fischer, C.J., Ortner, P.B., 2004. Potential availability of sedimentary phosphorus to sediment resuspension in Florida Bay. Glob. Biogeochem. Cycles 18 (4).

Zhang, J.Z., Guo, L., Fischer, C.J., 2010a. 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.

Zhang, J., Gilbert, D., Gooday, A., Levin, L., Naqvi, S.W.A., Middelburg, J.J., Scranton, M., Ekau, W., Pena, A., Dewitte, B., Oguz, T., Monteiro, P.M.S., Urban, E., Rabalais, N.N., Ittekkot, V., Kemp, W.M., Ulloa, O., Elmgren, R., Escobar-Briones, E., Van der Plas, A.K., 2010b. Natural and human-induced hypoxia and consequences for coastal areas: synthesis and future development. Biogeosciences 7, 1443–1467.

Zhou, Y., Obenour, D.R., Scavia, D., Johengen, T.H., Michalak, A.M., 2013. Spatial and temporal trends in Lake Erie hypoxia, 1987–2007. Environ. Sci. Technol. 47 (2), 899–905.

Zorn, M.E., Waples, J.T., Valenta, T.J., Kennedy, J., Klump, J.V., 2018. In situ, high-resolution time series of dissolved phosphate in Green Bay, Lake Michigan. J. Great Lakes Res. 44 (5), 875–882.