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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, Lake Michigan, 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 $CaCO_3$-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.

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., 2013; 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., 2012). 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_2 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,

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especially the role of 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 $CaCO_3$-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 and from organic to inorganic species 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 (25th–26th) 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

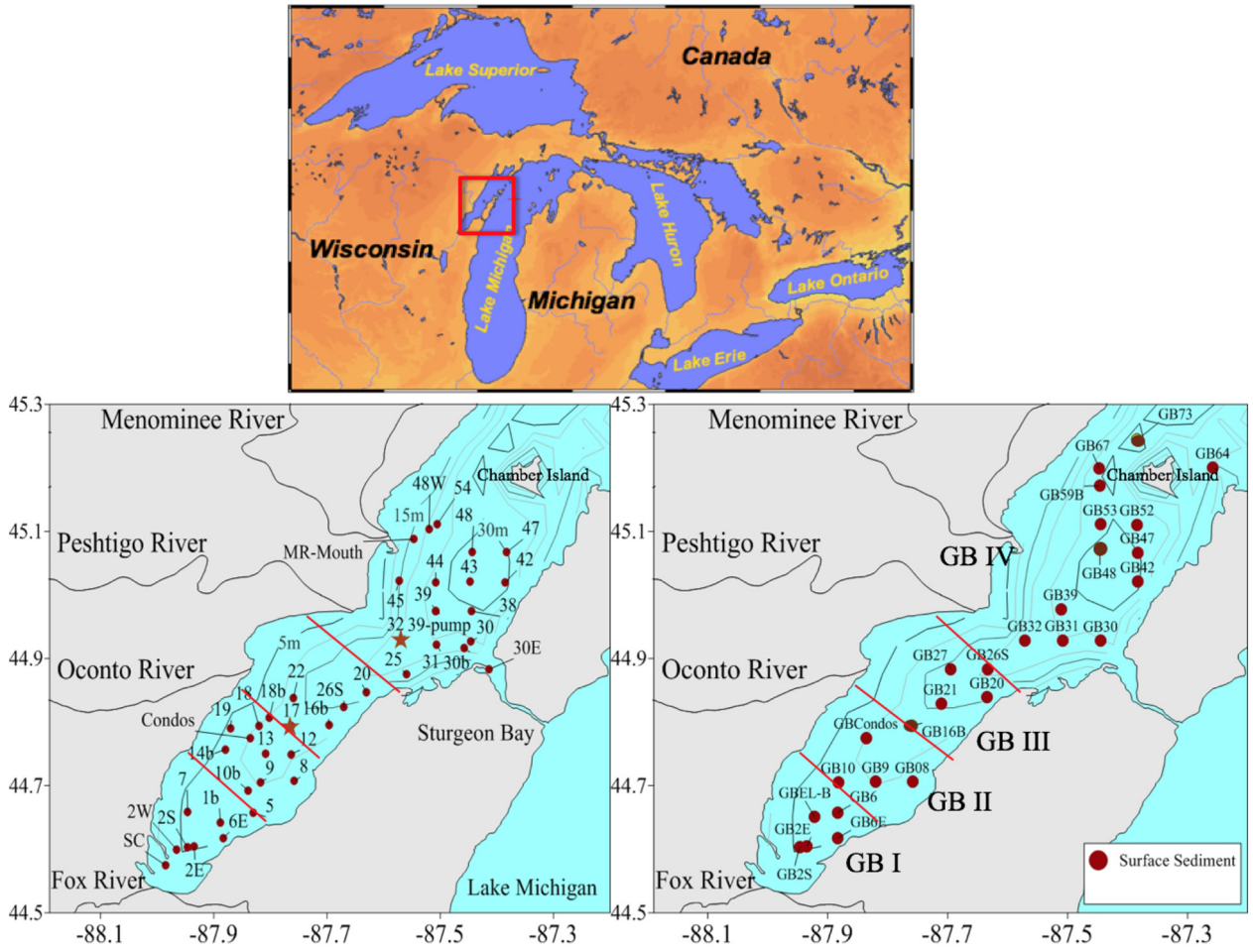

Fig. 1. A map showing the sampling locations for suspended particulate matter (left panel) and surface sediment (right panel) in Green Bay, Lake Michigan, during summer 2014. Stations 17 and 32 (star symbols) were the two vertical profile sampling stations. Contour lines are depth contours or bathymetry 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).

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