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Phosphorus retention and internal loading in the Bay of Quinte, Lake Ontario, using diagenetic modelling

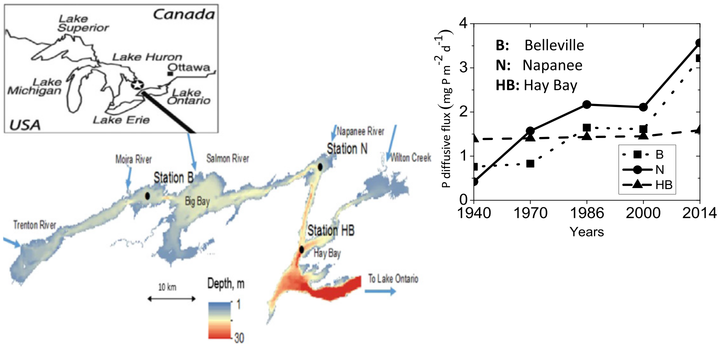
Phuong T.K. Doan [a,d,*], Sue B. Watson [b], Stefan Markovic [a], Anqi Liang [a], Jay Guo [b], Shan Mugalingam [c], Jonathan Stokes [a], Andrew Morley [e], Weitao Zhang [f], George B. Arhonditsis [a], Maria Dittrich [a]

[a] *University of Toronto Scarborough, 1265 Military Trail, Toronto, ON M1C 1A4, Canada*
[b] *Environment and Climate Change Canada, Watershed Hydrology and Ecology Research Division, Water Science and Technology, 867 Lakeshore Road, Burlington, ON L7S 1A1, Canada*
[c] *Lower Trent Conservation Authority, 714 Murray Street, Trenton, ON K8V 5P4, Canada*
[d] *The University of Danang-University of Science and Technology, 54 Nguyen Luong Bang, Danang, Viet Nam*
[e] *Ontario Ministry of the Environment and Climate Change, Eastern Region, 1259 Gardiners Road, Unit 3, P.O. Box 22032, Kingston, ON K7M 8S5, Canada*
[f] *AEML Associates LTD, Canada*

HIGHLIGHTS

- Internal P flux contributes significantly to P budget in the Bay of Quinte.
- Dynamics of sediment P transformations were studied using diagenetic modelling.
- Summer sediment P diffusive fluxes varied between 1.5 and 3.6 mg P m^{-2} d^{-1}.
- Diagenesis of redox sensitive and organic P forms drives substantial P diffusive flux.
- Sediment P retention was dominated by apatite formation and varied between 71 and 75%.

GRAPHICAL ABSTRACT



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ABSTRACT

Internal phosphorus (P) loading significantly contributes to hysteresis in ecosystem response to nutrient remediation, but the dynamics of sediment P transformations are often poorly characterized. Here, we applied a reaction-transport diagenetic model to investigate sediment P dynamics in the Bay of Quinte, a polymictic, spatially complex embayment of Lake Ontario, (Canada). We quantified spatial and temporal variability of sediment P binding forms and estimated P diffusive fluxes and sediment P retention in different parts of the bay. Our model supports the notion that diagenetic recycling of redox sensitive and organic bound P forms drive sediment P release. In the recent years, summer sediment P diffusive fluxes varied in the range of 3.2–3.6 mg P m^{-2} d^{-1} in the upper bay compared to 1.5 mg P m^{-2} d^{-1} in the middle-lower bay. Meanwhile sediment P retention ranged between 71% and 75% in the upper and middle-lower bay, respectively. The reconstruction of temporal trends of internal P loading in the past century, suggests that against the backdrop of reduced external P inputs, sediment P exerts growing control over the lake nutrient budget. Higher sediment P diffusive fluxes since mid-20th century with particular increase in the past 20 years in the shallower upper basins, emphasize limited sediment P retention potential and suggest prolonged ecosystem recovery, highlighting the importance of ongoing P control measures.

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* Corresponding author at: Department of Physical and Environmental Sciences, University of Toronto Scarborough, 1265 Military Trail, ON M1C 1A4, Canada.
E-mail address: kimphuongdhbk@gmail.com. (P.T.K. Doan).

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1. Introduction

Phosphorus (P) is a major limiting nutrient in lakes and reservoirs. In many of these environments, however, accelerated P loading due to urbanization, industrial activities, agricultural fertilization, and internal nutrient recycling may lead to excessive primary productivity, algal blooms, bottom water hypoxia, and deteriorated water quality (Smith et al., 1999; Qiu et al., 2014). The amount of P in the water column is determined by the balance of inputs and outputs from catchment drainage, atmospheric loading, and groundwater, and also the release from and burial in the sediments. The release of P from sediments (or internal loading) is of great concern because it can contribute significantly to the total in-lake bioavailable P pool and can have a profound impact on the trophic state and water quality (Nürnberg, 2009; McCulloch et al., 2013; Matisoff et al., 2016).

The investigation of P release and the immobilization mechanisms in sediments is indispensable for understanding P budgets of lakes (Dillon and Molot, 1996; Hupfer and Lewandowski, 2005; Dittrich et al., 2013). Internal P loading depends on the ability of sediments to retain P, the conditions of overlying water, and early P diagenesis in sediments (Abdel-Satar and Sayed, 2010; Dittrich et al., 2013). P retention due to burial in deeper sediment layers is also a factor regulating algal productivity in the water column (Boers et al., 1998; Katsev et al., 2006).

Total P in natural waters consists of a variety of inorganic and organic forms, and knowledge of their abundance, distribution, chemical speciation, and environmental behavior is important to understanding P release from sediments to the water column (Karl and Björkman, 2001). Inorganic forms are typically adsorbed to sediment metallic oxides, such as Al- or Fe-(oxy)hydroxides. Organic forms can be found in microorganisms, detritus, humic compounds, poly-phosphates, and phospholipids (Ribeiro et al., 2008). Different P forms have distinct environmental behavior and varying bioavailability to aquatic organisms (Karl and Björkman, 2001). Detailed chemical speciation of P and its causal association with algal blooms, however, remains poorly characterized and quantified (Lin et al., 2016).

In situ measurements or laboratory experiments to estimate fluxes at the sediment-water interface (*SWI*), or both, are sparse and difficult to obtain. Furthermore, most field measurements can only represent snapshots of highly dynamic processes (Luff and Moll, 2004). In this regard, diagenetic modelling is a powerful tool to provide insights into the nature of sediment diagenesis processes at the *SWI*, and to generate hypotheses about the sediment-water column coupling (Boudreau, 1999; Canavan et al., 2007; Lewis et al., 2007; McCulloch et al., 2013). This family of models has the capacity to provide the foundation for both retrospective and prospective studies in the dynamics of P in sediments (Dittrich et al., 2013; Torres et al., 2015; Gudimov et al., 2016). For instance, diagenetic models are used to outline retention and mobilization of sediment P under different loading regimes, examine sediment response to planned nutrient control strategies and help identify causes of temporal discrepancy between nutrient control measures and sediment P release on decadal time scales (e.g., Katsev et al., 2006; Katsev and Dittrich, 2013; McCulloch et al., 2013). While diagenetic modelling enables the calculation of fluxes across the *SWI*, as well as concentrations and reaction rates at a high-temporal and -spatial resolution, it is rarely applied in water quality management studies (Smits and van Beek, 2013; Paraska et al., 2014).

In the present study, we adopted McCulloch et al. (2013) model to characterize diagenetic processes in the sediments of an eutrophic system, the Bay of Quinte, Ontario, Canada. The embayment has a long history of eutrophication problems, such as extensive harmful algal blooms, and heavy metals pollutants in the sediments and has been classified as an “Area of Concern” under the U.S.-Canada Great Lakes Water Quality Agreement since 1986 (Minns et al., 2011). Recent modelling analysis suggested that the Bay of Quinte receives substantial internal subsidies (Kim et al., 2013; Arhonditsis et al., 2016). The actual internal P loading and P retention in the sediments, however, have still not been unequivocally investigated.

One of the major challenges in numerical modelling is to effectively balance between model complexity and data availability to maximize the model performance and minimize the underlying uncertainty (Grayson and Blöschl, 2000; Arhonditsis et al., 2007; Doan et al., 2015).

Sediment diagenesis models require a comprehensive dataset of vertical profiles of dissolved and solid components (Dittrich et al., 2009). In this study we combine our field data and diagenetic modelling with the aim to advance the quantitative understanding of sediment P dynamics and the impact of diagenetic processes on water quality in ecosystem undergoing prolonged drastic reduction of external nutrient loading. The main objectives of this study are (*i*) to evaluate the long-term dynamics of P binding forms in the sediments, (*ii*) to estimate the seasonal dynamics of sediment P diffusive fluxes, and (*iii*) to delineate the spatio-temporal trends of P sediment retention.

2. Methods

2.1. Study site

The *Z*-shaped Bay of Quinte is located at the northeastern shore of Lake Ontario, Canada, and is surrounded by an 18,604 km^2 watershed. The bay is approximately 100 km long, covers an area of about 254 km^2, and has a volume of 2.67 km^3 (Fig. 1). The Bay of Quinte supports a variety of human uses, such as a resource for drinking water, as well as swimming, boating, and both commercial and recreational fishing. Historically, minimally treated wastewater from municipal sewage treatment plants, mines, and industries is discharged directly into the system or into the tributaries that feed the bay. Extensive remedial efforts and advances in wastewater treatment since the 1970s have curtailed the external point-source P inputs by more than 90% (Minns et al., 1986, 2011). These efforts have resulted in decreased ambient total P concentrations and reduced phytoplankton biomass volume by approximately 50% (Nicholls et al., 1986; Shimoda et al., 2016).

The Bay of Quinte consists of three morphologically distinct segments: the upper, middle and lower bay. Historically, the shallow upper area (mean depth of 5 m) has experienced the most severe eutrophic conditions (Johnson and Owen, 1971; Minns et al., 1986). The bay deepens abruptly in the middle and lower segments to a maximum depth of 35 m at its outflow to Lake Ontario (Fig. 1). Our model describes the geochemistry of sediments at three different sites, based on their trophic status and degree of impairment. The Belleville site (B, 44°9′15″N, 77°20′45.00″E) is located offshore from the city of Belleville about 2 km from the Moira River mouth and represents conditions in the upper bay. The Napanee site (N, 44°10′49.00″N, 77°2′25″E) is located offshore from the town of Deseronto proximal to the mouth of the Napanee River, representing a transitional zone between the upper and middle bay. The Hay Bay site (HB, 44°6′25.00″N, 77°1′51″E) is located south of Ram Island in Hay Bay and represents conditions in the middle bay. The depths at stations B, N, and HB are 4.6 m, 5.0 m, and 15.0 m, respectively. Upper bay stations (B and N) are well mixed throughout summer, while HB is ephemerally stratified, as a result of intrusion of cold lake Ontario bottom waters with typical temperature difference between surface and bottom waters of 5–8 °C (e.g., Oveisy et al., 2015). Of the three basins, HB has the longest water retention time (154 days), while those at B and N are 90 and 110 days, respectively (Oveisy et al., 2015).

2.2. Field data

Sediment and pore-water datasets collected at stations B, N, and HB from the 2013 summer season (August) and 2014 winter season (February) were used to calibrate and validate the sediment diagenesis model, respectively. In brief, 6–7 cores were collected using Uwitec corer with polycarbonate liners 5.5 cm in diameter and 70 cm in length,