

## Modeling the Interplay between Phosphorus Dynamics and Sediment Diagenesis in a Eutrophic Lake

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**Abstract:** In this study, we investigated phosphorus cycling in the Bay of Quinte, an embayment of Lake Ontario, Canada. Despite the large decline in external P loading to the Bay of Quinte during the last decades, it still experiences harmful cyanobacterial algal blooms, which may be connected to nutrient loading from sediments. Nevertheless, the dynamics of nutrient loading from sediments remains mostly unknown. Thus, we applied a non-steady-state diagenesis reaction-transport model to evaluate the impact of organic matter loading on oxygen demand and to conduct specific modeling scenarios to investigate the impact of organic matter loading on the seasonal dynamics of phosphorus release, and burial efficiency in three different basins of the bay: Belleville, Napanee, and Hay Bay. Our modeling framework integrates physical and biogeochemical processes at the sediment-water interface and incorporates dynamic boundary conditions, such as oxygen, soluble reactive phosphorus concentrations, and organic matter sedimentation at the sediment-water interface. Our scenarios suggested that phosphorus release and burial efficiency can profoundly respond to shifts in sedimentation conditions. At all three studied stations, phosphorus burial efficiency did not change significantly after the scenario year 2034, when we reduced the flux of organic matter by 20%. Meanwhile, phosphorus release at stations Belleville and Napanee was significantly reduced in 2034 compared with the present condition. The 20% reduction in the flux of organic matter at station Hay Bay may not be large enough to remarkably reduce phosphorus release.

**Keywords:** Eutrophic lakes, phosphorus release; phosphorus burial efficiency, sediments; diagenetic modelling.

### 富營養化湖泊中磷動力學與沈積物成岩作用的相互作用

**摘要:** 在这项研究中, 我们调查了加拿大安大略湖的一个昆特湾的磷循环。尽管在过去的几十年中, 昆特湾的外部 P 含量大幅下降, 但它仍然遭受有害的蓝藻藻华, 这可能与沉积物中的养分含量有关。然而, 沉积物中养分负载的动力学仍然未知。因此, 我们应用了非稳态成岩反应-运输模型来评估有机物负荷对氧气需求的影响, 并进行特定的建模方案来研究有机物负荷对磷释放和埋藏的季节性动态的影响。海湾三个不同盆地 ( 贝尔维尔, 纳帕尼和干草湾 ) 的能量效率。我们的建模框架整合了沉积物-水界面处的物理和生物地球化学过程, 并结合了动态边界条件, 例如氧气, 可溶性活性磷浓度和沉积物-水界面处的有机物沉降。我们的情景表明磷的释放和埋藏效率可以对沉积条件的变化产生深刻的响应。在所有三个研究站中, 当情景 2034 年将有机物通量降低 20% 时, 磷掩埋效率没有显著变化。同时, 与目前状况相比, 到 2034 年, 在贝尔维尔和纳帕尼站的磷释放量显著减少。干草湾站有机物通量减少 20% 可能不足以明显减少磷的释放。

**關鍵詞:** 富營養化湖泊磷釋放磷埋藏效率, 沉積物; 成岩模型乘。

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## 1. Introduction

Phosphorus (P) is a main 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 algal production, bottom-water hypoxia, and water quality deterioration [1]. The amount of P in the water column is determined by the balance of nutrient input loading and output from surface water, and sediment nutrient release and burial in sediments. Internal P loading (P release) depends on the ability of sediments to retain P, the conditions of the overlying water, and early diagenesis of P in sediments [2]. P retention depends on burial in deeper sediment layers [3].

Fluxes at the sediment–water interface (SWI), which are estimated by in-situ measurements or laboratory experimentation, are rarely and not easily obtained [4]. Diagenetic modeling is a powerful tool to calculate fluxes across the SWI as well as concentrations and reaction rates at temporal and spatial resolutions, which can be linked to water quality management [5].

Specifically, our objectives are to (i) estimate the seasonal dynamics of P release, (ii) delineate the spatiotemporal trends of P sediment burial efficiency, (iii) quantify the contribution of sediments to oxygen demand, and (iv) investigate the impact of organic matter loading on the seasonal dynamics of P release, and retention in three basins of the Bay of Quinte.

## 2. Methods and Model Application

### 2.1. Study Site

The Z-shaped Bay of Quinte is located at the northeastern shore of Lake Ontario, Canada, and surrounded by a 18,604 km<sup>2</sup> watershed. The bay is about 100 km long and has an area of 254 km<sup>2</sup> and volume of 2.67 km<sup>3</sup> (Fig. 1). The Bay of Quinte has a long history of eutrophication problems, such as extensive harmful algal blooms and hypolimnetic oxygen depletion [6]. Water pollution control in the Bay of Quinte began in the 1970s, with the strategy mainly including control of external load [7]. For instance, the point-source P loads were reduced to < 80 kg d<sup>-1</sup> in 1978 and have been steadily decreasing since. The latest recommended cap is 15 kg d<sup>-1</sup> [8]. While point-source P loads continue to decline, total P concentration has been reduced but is not necessarily following the same trend, since total P is influenced by many non-point factors, including tributary loadings and sediment release or internal loading [9]. The Bay of Quinte receives substantial internal subsidies, although the actual mechanisms of internal P loading and P retention in the sediments have not been thoroughly investigated [10].

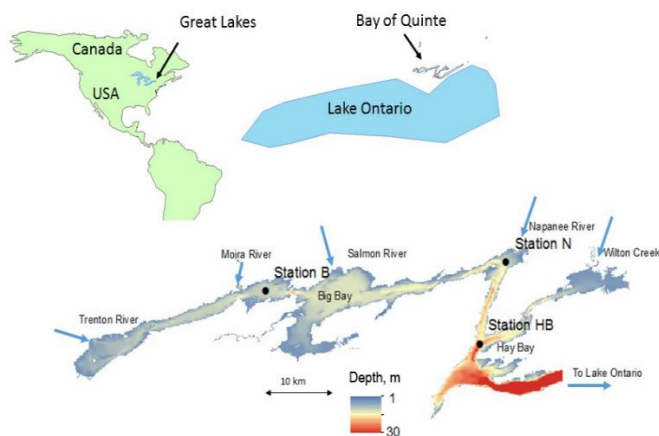


Fig. 1 Study site: (i) Location of Great Lakes in North America; (ii) Location of the Bay of Quinte in Lake Ontario; (iii) Map of the Bay of Quinte and three sampling locations (B, N and HB)

The Bay of Quinte consists of three morphologically distinct segments: the upper, middle, and lower bay. The upper area is shallow, with a mean depth of 5 m, and has historically experienced the most adverse eutrophic conditions [11]. The bay deepens rapidly in the middle and lower segments to a maximum depth of 35 m at its confluence with Lake Ontario. This work focuses on three different locations with distinct differences in morphology, loading history, and land-use practices in the surrounding catchments: Belleville (B; 44°9'13.20"N, 77°20'44.00"W) and Napanee (N; 44°10'49.00"N, 77°2'22.80"W) in the upper bay, and Hay Bay (HB; 44°5'36.00"N, 77°4'18.00"W) in the middle bay (Fig. 1c). The water depths for stations B, N, and HB are 5.3, 5.6, and 15.3 m, respectively.

### 2.2. Field Data

Sediment and pore-water datasets collected from the Bay of Quinte from stations B, N, and HB in 2013 and 2014 were used to calibrate and validate the sediment diagenesis model. Sediments were collected using an Uwitec sampler with Plexiglas core tubes measuring 5.5 cm in diameter and 70 cm in length. Microsensor measurements were conducted immediately upon the samples' arrival at the laboratory for dissolved oxygen (DO), temperature, and pH at the sediment surface with high vertical resolution time (0.5 mm). The three cores (B, N, and HB) were used for pore-water analysis and P fractionation analysis. The sediment sections were analyzed for porosity, dry weight, and total-organic-matter and P fractions. Peepers were applied to collect pore-water samples and subsequently determine their vertical profiles for metal content, alkalinity, and soluble reactive P (SRP). Sedimentation rates were estimated from the <sup>210</sup>Pb and <sup>226</sup>Ra profiles [12].

### 2.3. Modeling Approach

We used a 1-D non-steady state transport reactive model for sediment diagenesis of solid and dissolved substances, as implemented in the computer program

Aquasim, version 2.1e. The Aquasim model is an open-source software program designed for simulation and data analysis of aquatic systems. The model is able to perform simulations, sensitivity analyses and parameter estimations automatically [13]. The sediment depth profile of 31 cm was discretized through a vertical grid of 310 layers. The conceptual diagram of the sediment diagenesis model comprises primary and secondary redox reactions, mineral precipitation dissolution reactions, acid dissociation reactions and P binding form reactions. The species considered in the model, mathematical descriptions of the different diagenetic reactions, and values assigned to the associated rates were presented in [12]. For calibration and validation, the sedimentation flux of organic matter, and DO and SRP concentrations at the SWI over the last 10 years were set as the boundary conditions to account for seasonal variations in sedimentation rates and lake stratification [12].

#### 2.4. Model Scenarios

After calibration and validation of the data in 2013 and 2014, for the results presented in [12], some scenarios were estimated. In order to support Bay of Quinte water quality management strategy for a future 20% reduction of agriculture-based P loads, we modeled sediment response to reduction 20% of total sedimentation flux ( $X_{flux}$ ) corresponding to 20% reduction of organic and inorganic P. This was done by conducting specific modeling scenarios (i) to evaluate how far in the future the new sediment based equilibrium would be established, (ii) to investigate the impact of organic matter loading on seasonal dynamics of P release, and burial efficiency in three basins of the Bay. In this section, our scenarios reduce 20% of total sedimentation flux ( $X_{flux}$ ) for scenarios of the decade years (2024, 2034, 2044, and 2054).

##### 2.4.1. Boundary Conditions

The boundary conditions of total sedimentation flux ( $X_{flux}$ ) were projected to the years 2024, 2034, 2044, and 2054. Our scenarios considered varying  $X_{flux}$  (-20%) relative to 2014 conditions. All other boundary conditions remained the same from the calibration year 2014. The seasonal boundary conditions of organic matter flux ( $X_{OM}$ ) under this scenario are presented in Fig. 2.

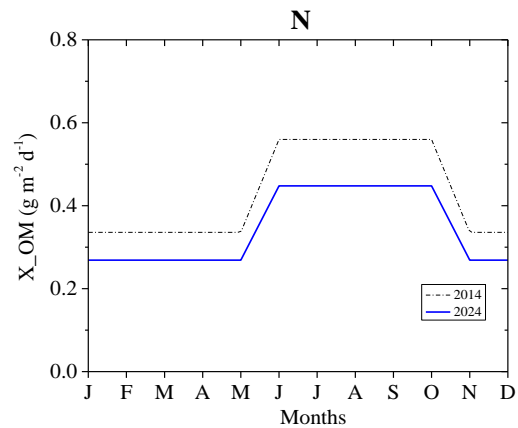


Fig. 2 The seasonal sedimentation flux of organic matter ( $X_{OM}$ ) over a one-year period for the site N in 2014 and 2024

### 3. Results and Discussion

The figures below present the model results after decreasing 20% P flux (20% of organic and 20% of inorganic P) for the different scenario years (2024, 2034, 2044, and 2054), in comparison with the present condition in 2014 (no P flux change).

#### 3.1. Dissolve Oxygen Profiles in Different Years

We examined the sediment depth profiles of DO concentration at three stations (B, N, and HB) under the different scenario years (2024, 2034, 2044, and 2054) (Fig. 3). Our analysis suggests that oxygen penetration depth in the sediments can profoundly respond to shifts in sedimentation flux. When the total sedimentation flux was reduced by 20%, the oxygen penetration depth in the sediments increased (Fig. 3). A strong increase of oxygen penetration depth was observed at station B, increasing from 0.02 m in 2014 to 0.2m in 2054 (Fig. 3a). At station N, the oxygen penetration depth increased from 0.03m in 2014 to 0.15m in 2054 (Fig. 3b). At station HB, the oxygen penetration depth increased slightly, from 0.005m in 2014 to 0.02m in 2054 (Fig. 3c).

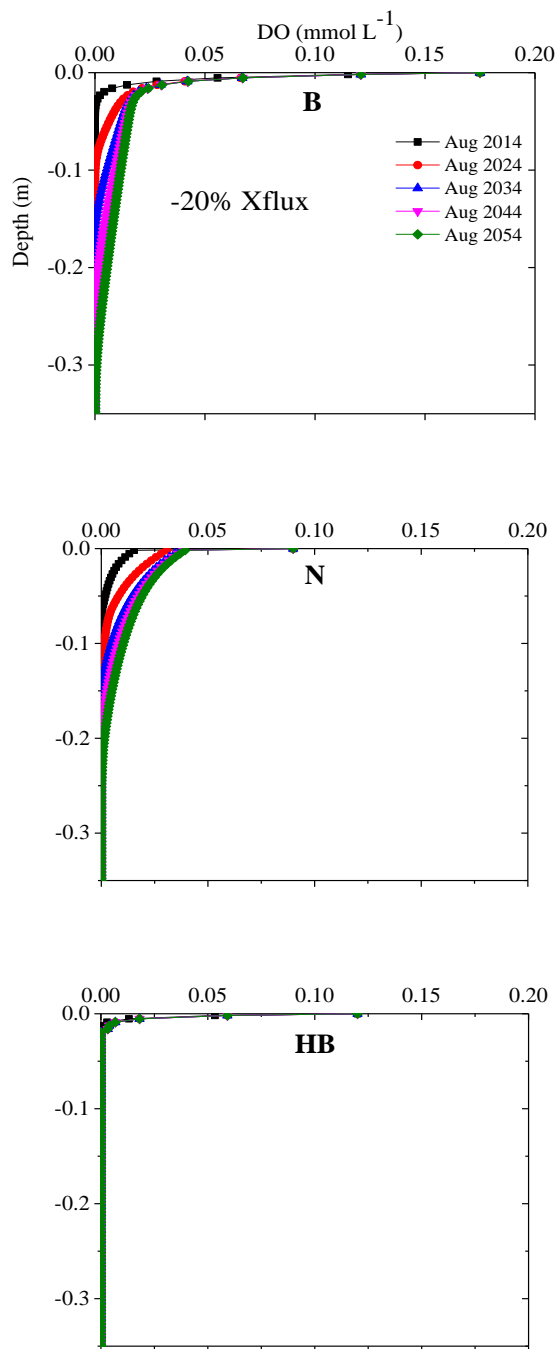
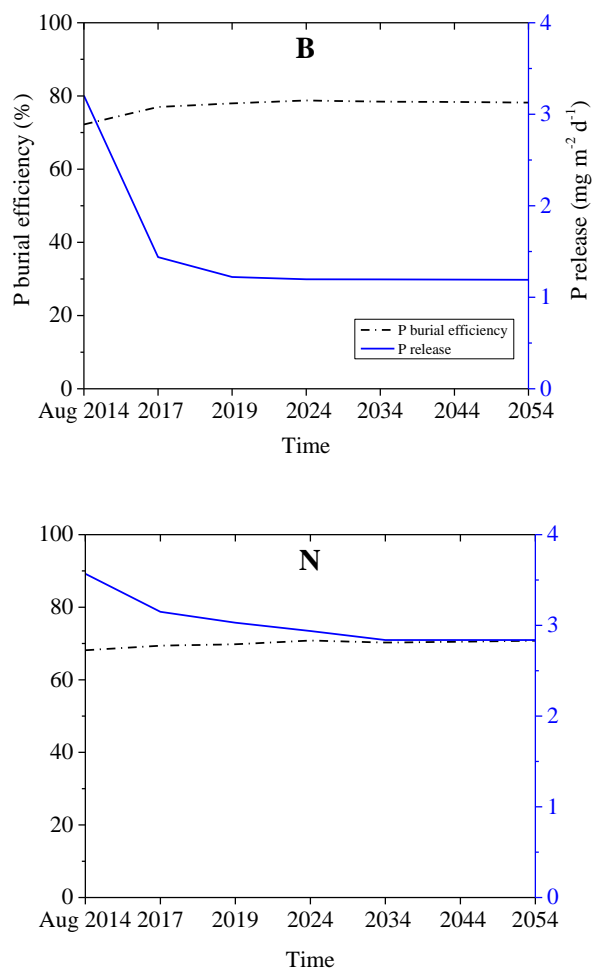


Fig. 3 Simulated vertical profiles DO at three stations

### 3.2. P Release and Burial Efficiency in Different Years

The results indicate a spatial and temporal variability of SRP concentration in the bay (not shown in figure). At station B, after reducing total sedimentation flux by 20%, P release decreased remarkably, from  $3.2 \text{ mg m}^{-2} \text{ d}^{-1}$  in 2014 to  $1.2 \text{ mg m}^{-2} \text{ d}^{-1}$  in 2024 (Fig. 4a). The P release was similar (about  $1.2 \text{ mg m}^{-2} \text{ d}^{-1}$ ) in later years (2034, 2044, and 2054) (Fig. 4a). At station N, the P release decreased from  $3.6 \text{ mg m}^{-2} \text{ d}^{-1}$  in 2014 to  $2.9$  and  $2.8 \text{ mg m}^{-2} \text{ d}^{-1}$  in 2024 and 2034, respectively, and appeared to be almost constant after the year 2034 (Fig. 4b). For station HB, after

reduction of total sedimentation flux, the P release had a slight decrease, from  $1.6 \text{ mg m}^{-2} \text{ d}^{-1}$  in 2014 to  $1.52 \text{ mg m}^{-2} \text{ d}^{-1}$  in 2024 and  $1.48 \text{ mg m}^{-2} \text{ d}^{-1}$  after the year 2034 (Fig. 4c). P burial efficiency at the three stations (B, N, and HB) was calculated based on the fluxes of P burial and settling (Doan et al., 2018). At station B, P burial efficiency increased from 72% in 2014 to 78% in 2034 and 78.2% in 2054 (Fig. 4a). The levels of P burial efficiency at station N increased slightly from 68% in 2014 to 70% in 2034 and remained almost constant in the later years (2044, 2054) (Fig. 4b). At station HB, levels increased from 71% in 2014 to 73% in 2034 and 74% in 2054 (Fig. 4c).



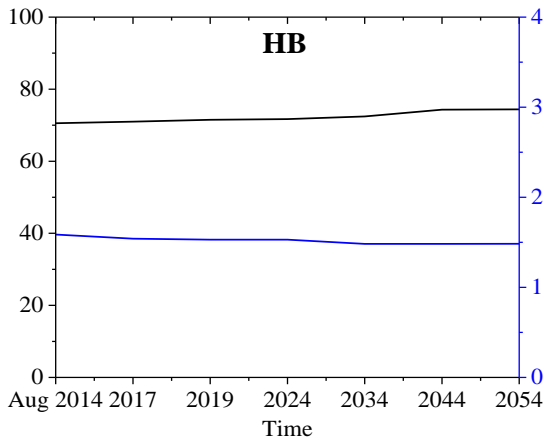


Fig. 4 Temporal trends of P release and burial efficiency at three stations after reducing 20%  $X_{flux}$

### 3.3. Seasonal Dynamics of P Release and Burial Efficiency

The dissolved SRP depth profiles are characterized by seasonal variations. Figure 5 shows dynamic P release at the baseline level (2014) and in the scenario year (2034).

On a seasonal timescale, P release is also dynamic. At all three stations, P release decreased during each season, reducing by 20%  $X_{flux}$  compared to its baseline level (no change  $X_{flux}$ ) (Fig. 5).

For example, at station B, the average P release decreased from 3.2 to 1.2  $mg\ m^{-2}\ d^{-1}$  in summer (June–October) and from 1.9 to 0.7  $mg\ m^{-2}\ d^{-1}$  in winter (November–May), representing about 30% reduction after reducing by 20%  $X_{flux}$  (Fig. 5a). At station N, the P release decreased about 18% after reducing by 20%  $X_{flux}$  but was still high (2.8  $mg\ m^{-2}\ d^{-1}$  in summer and 1.8  $mg\ m^{-2}\ d^{-1}$  in winter 2034) (Fig. 5b). At station HB, P release decreased from 1.4 to 1.3  $mg\ m^{-2}\ d^{-1}$  in summer and from 1.15 to 1.05  $mg\ m^{-2}\ d^{-1}$  in winter, representing 8% reduction (Fig. 5c).

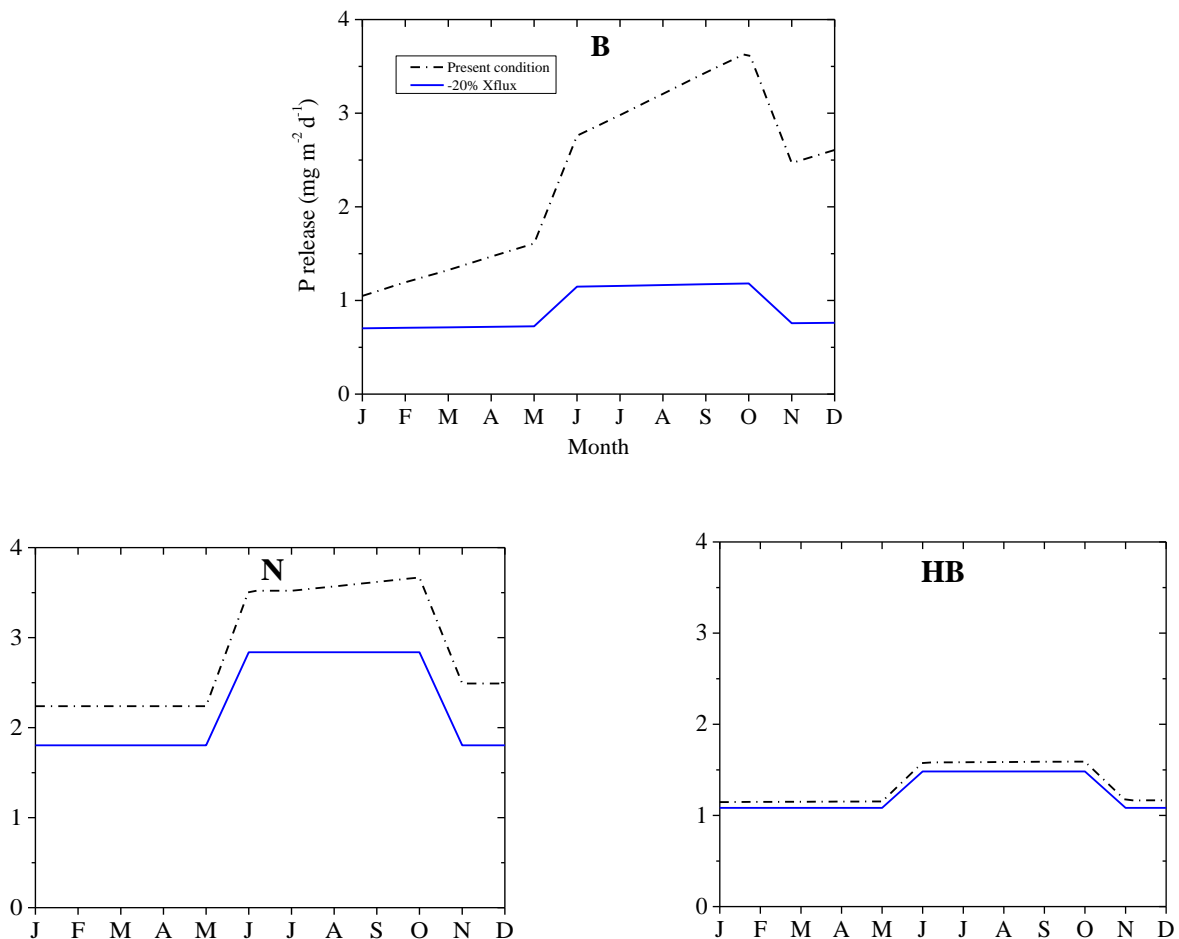


Fig 5. Seasonal dynamics of P release at three stations in the present condition 2014 and the scenario year 2034

## 4. Conclusion

We used a reaction-transport diagenesis model to conduct specific modelling scenarios for a 20% reduction in agriculture, based on total loads in the Bay of Quinte. Our scenarios suggested that P release and

burial efficiency can respond greatly to shifts in sedimentation conditions. At all three studied stations, P release and burial efficiency did not change significantly after the scenario year of 2034 when we reduced  $X_{flux}$  by 20%. Station B showed an especially

large reduction in P release in 2034 after reducing 20%  $X_{flux}$  compared to the baseline level (i.e. reducing from 3.4 to 1.1 mg m<sup>-2</sup> d<sup>-1</sup>). However, for station HB, the reduction of 20% flux in organic matter may not be large enough to reduce P release significantly.

Our results predict an increase in the oxygen penetration depth and organic matter depletion in the upper sediment layer, following the establishment of conditions for lower organic sedimentation flux. The spatial oxygen penetration depth is heterogeneous in different basins, suggesting a response mechanism in the sediment that affects the oxygen concentration near the bottom of the bay. This study showed that P release from sediments can react greatly to shifts in sedimentation conditions. The developed model can be applied to other eutrophic lakes.

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