MODELLING OF SEDIMENT DIAGENESIS AND ITS LINKAGE WITH THE WATER COLUMN. THE CASE STUDY OF BAY OF QUINTE, CANADA

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Abstract - In this study, the Aquasim model has been applied and developed to simulate the processes occurring in the sediments of the eutrophic system at Quinte Bay, Canada. The findings reveal that phosphorus (P) retention varies both spatially and temporally across the three basins of the Bay. These variations are influenced by factors such as sedimentation history, the chemical form of P, topography, and historical land use. According to the model, recent data indicates a decline in accumulated P at two shallow sediment sites (B and N), potentially leading to increased P release from these sediments. In contrast, the deeper sediment site (HB) continues to show high and stable P accumulation, resulting in consistently low and relatively unchanged P release. This explains why P levels in the Bay remain high, contributing to the growth of algae. The study also highlights the importance of adequately reducing external P loading. Internal P loads only play a supportive role in achieving the desired ecological conditions of the Bay.

Key words - P released from sediments; P retention; Sediment model; Aquasim.

1. Introduction

Phosphorus (P) serves as a primary limiting nutrient in many lakes and reservoirs. However, increased P levels from human activities such as urban growth, mining, industrial processes, agricultural runoff, and internal recycling can significantly impact these water bodies. This heightened P loading often triggers excessive algae growth, causes hypoxic conditions in deeper waters, and ultimately degrades overall water quality [1].

The concentration of P in the water column depends on the balance between external input loads, losses through surface water, and the processes of release and burial within sediments. Internal loading, or the release of reactive phosphorus from sediments, is a significant concern due to its potential to greatly elevate the levels of bioavailable phosphorus in a lake [2, 3]. Thus, investigation of P mechanisms in the sediments is indispensable to understand P budgets of lakes [4, 5].

Study on sediment modeling has not been extensively studied in Vietnam and faces many challenges. Sediment modeling research is still underdeveloped in Vietnam and encounters several challenges. A primary challenge in numerical modeling is striking a balance between the complexity of the model and the availability of data. The aim is to optimize model performance while minimizing the risk of adding excessive uncertainty [6]. To implement sediment diagenesis models, a detailed dataset of vertical profiles for both dissolved and solid components is essential [7].

The distinct sediment and pore-water datasets available for the Bay of Quinte [8, 9] provide a valuable opportunity to model the dynamics of P and better understand its role in controlling the release of P from sediments. Specifically, our objectives are (i) to assess the temporal and spatial trends of P release and retention in sediments, and (ii) to simulate P fluxes in three basins of Quinte Bay when sediment flux is reduced by 20% in the future.

2. Methods and Model Application

2.1. Study site

The Bay of Quinte lies along the northeastern shore of Lake Ontario in Canada, bordered by a watershed that spans 18,604 km². Extending approximately 100 km in length, the Bay covers an area of about 254 km² and contains a water volume of 2.67 km³ (see Figure 1).

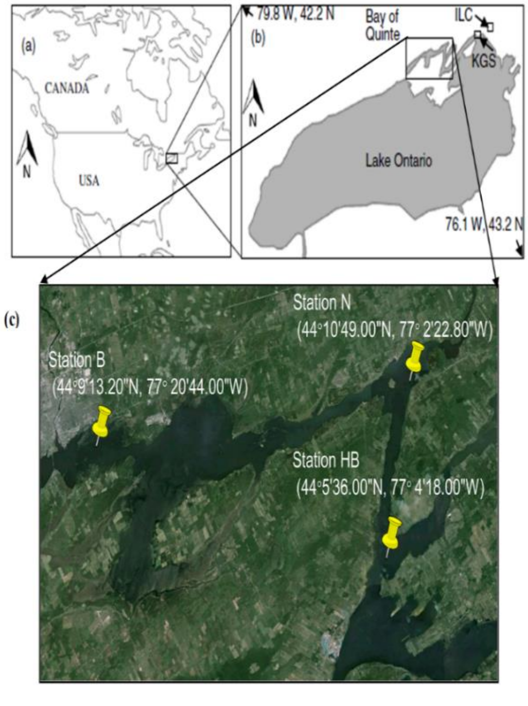

Figure 1. *Map of the Bay of Quinte highlighting three sampling sites: B, N, and HB*

In this study, we focus on three distinct locations with varying nutrient loading histories: Belleville (B) and Napanee (N) in the upper Bay, and Hay Bay (HB) in the middle Bay (Figure 1c). The average water depths at the three stations are: B, N and HB are 5.3 m, 5.6 m and 15.3 m, respectively [10].

2.2. Field data

The calibration of the sediment diagenesis model was carried out using sediment and pore-water data collected in 2013 and 2014. All data from the stations B, N, and HB have been measured and analyzed in detail in previously published papers [11, 12].

2.2.1. State variables

The model simulated both dissolved components and solid components.

2.2.2. Model equations

The Aquasim non-steady state reaction-transport diagenetic model used the following two differential equations that were presented in detail in [6].

$$\frac{\partial(\varphi S_i)}{\partial t} = \frac{\partial}{\partial z}\left(D_B \frac{\partial(\varphi S_i)}{\partial z} + + \varphi D_{S_i} \frac{\partial(S_i)}{\partial z}\right) + r_{S_i} - \alpha_{bioirrig} * \emptyset * (S_i - S_i^{SWI})$$

$$\frac{\partial X_i}{\partial t} = -\frac{\partial(\upsilon_{s\,\epsilon\,d} X_i)}{\partial z} + \frac{\partial}{\partial z}\left(D_{B,X_i} \frac{\partial(X_i)}{\partial z}\right) + r_{X_i}$$

2.2.3. Model processes

A conceptual diagram illustrating the processes incorporated into our diagenetic reaction transport model. The model encompasses a range of geochemical reactions (Figure 2). The different reactions in Aquasim sediment model have been described in detail in our previous study [13].

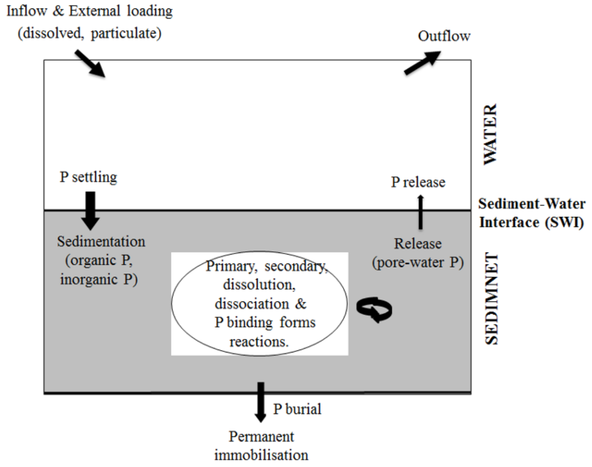

Figure 2. *Conceptual diagram of the diagenetic model*

2.3. P release and retention

2.3.1. P release

The concentration profiles of soluble reactive phosphorus (SRP) in porewater can be utilized to estimate P release from sediments into the overlying water by applying Fick's diffusion law [14].

$$P_{release} = D_{sw} \frac{\varphi}{\theta^2} \frac{\partial C}{\partial z}$$

Where $F_{release}$ is the release of phosphorus (mg m^{-2} d^{-1}); *z* is the depth coordinate within sediments (m); C is the concentration of substances at the SWI (mg m^{-3}); φ is the sediment porosity (dimensionless); $\theta = 1 - \ln(\varphi^2)$ is the sediment tortuosity; D_0 = f (T, φ) is the solute diffusion coefficient (m^2 d^{-1}); T is the sediment temperature (°C) [15].

2.3.2. P retention

The retention percentage of P is the ratio between fluxes of P burial (F_{burial}) and settling ($F_{settling}$)

$$P_{retention}\ (\%) = 100\ F_{burial} / F_{settling}$$

The burial flux of dissolved and particulate P (F_{burial}) [17, 18] is:

$$F_{burial}\ (mg\ m^{-2}\ d^{-1}) = Sed_{acc}.\ P_{d\text{-}sed}$$

The P settling flux ($F_{settling}$) [16] is calculated by:

$$F_{settling}\ (mg\ m^{-2}\ d^{-1}) = Sed_{acc}.\ P_{t\text{-}sed}$$

Where Sed_{acc} (g m^{-2} d^{-1}) is the sediment accumulation rate calculated from the excess ^{210}Pb, ^{226}Ra profiles measured through the sediment cores in the Bay of Quinte.

3. Results and Discussion

After successfully calibrating and validating the model with measured data from 2013 and 2014, the results were detailed in our previous study [8]. In this study, the authors evaluate and propose scenarios from both the past and the future.

3.1. Inter-annual variability of P fluxes in 70 past years

3.1.1. Inter-annual variability of soluble reactive phosphorus (SRP)

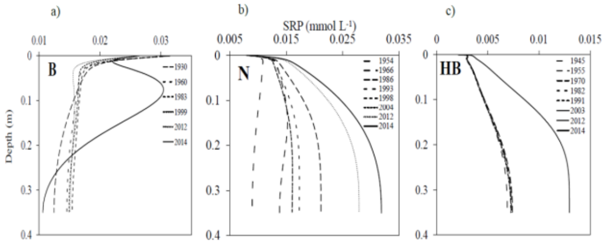

Figure 3. *Inter-annual variability of SRP at three stations*

Pore-water SRP concentrations are influenced by many of the model parameters: phosphate concentration gradient, oxygen concentration, organic matter flux, iron oxide presence, organic matter reactivity. The results from our reaction-transport diagenetic model reveal spatial and temporal variability in SRP concentrations in the Bay of Quinte over the past years (Figure 3). The modelled SRP profiles offer a reasonable representation of phosphate concentration gradients at the sediment-water interface (SWI) and enable an estimation of the variability in internal phosphorus loading. The station N provided highest phosphate concentration gradient at the SWI and highest P release (Figure 3b). The sediment P release links to redox condition at the SWI that are controlled by DO concentration at the SWI. When the SWI is oxic, strong adsorption of dissolved phosphate to solid iron oxyhydroxides prevents phosphate diffusion into water columns from sediments, limiting sediment P release. In contrast, when the SWI is anoxic iron oxyhydroxides reductively dissolve and phosphate is released into water columns, increasing sediment P release [4].

3.1.2. Inter-annual variability of P release and P retention

From previous studies in the Bay of Quinte at three stations (B, N, and HB), point-source P loads were cut to

< 80 kg d^{-1} in 1978 and have been steadily reduced since. The current recommended cap is 15 kg d^{-1} (Minns and Moore, 2004). In 2014, P loadings into the Bay were estimated to be 5.3 kg d^{-1} during the May to October period.

The amount of P release (kg d^{-1}) at the three stations (B, N and HB) in the past years was showed in Figure 4. High amount of P release (ranged between 44 to 71 kg d^{-1}) was observed at the station B (Figure 4a) and lowest amount of P release was observed at the HB station (from 7 to 10 kg d^{-1}; Figure 4c) in the past years. At the station N, the amount P released was between 10 and 25 kg d^{-1} over the period 1954 to 2014 (Figure 4b).

Figure 5 shows the temporal trends of P retention at the three stations (B, N and HB). The P retention levels at both stations (B and N) showed an increasing trend before 1999, similar to the early stages of eutrophication in the 1950s. These levels rose sharply following the reduction of external phosphorus loading in 1978.

Our model results demonstrated decreasing trends of P retention at these two stations after 2012, as well after the arrival of zebra mussels in the system (Figure 5a, b). Notably, for the station N, the lowest P retention with 19% was observed in 1954, and it considerably increased to 63% in 1986. The highest P retention around 68% was observed in 2012 and it appeared to be decreasing later on. There are about 63% of P currently was retained in the sediments at the station N (Figure 5b). Similarly, for the station B, the lowest P retention was estimated at 31% in 1930. It significantly increased after the reduction of external P loading. The P retention increased from 50% in 1983 to 80% in 1999, as a consequence of the point source P loading reduction initiated in late 1970s (Figure 5a). In contrast, the P retention at the HB station was quite high, ranging from 84% to 91% (Figure 5c). This implies a high retention efficiency of P in the area.

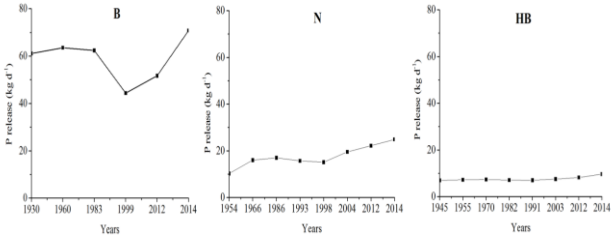

Figure 4. *Long-term trends of P release at three stations*

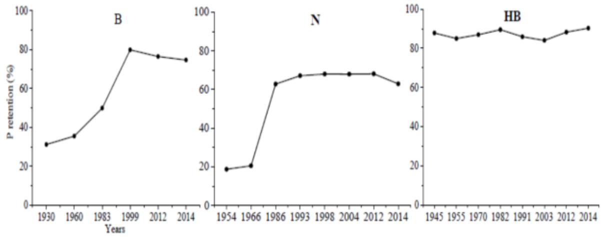

Figure 5. *Long-term trends of P retention at three stations in the past years*

Based on the model results of long-term total P in sediments and SRP in pore-water, P settling, burial and release for annual averages in the past years at each station were estimated. Our model results demonstrate strong dynamics of P settling fluxes at the two stations B and N (Figure 6a, b). High P settling was observed at the station N (2.7 - 5.6 mg P m^{-2} d^{-1}; Figure 6b). A peak of P settling, exceeding 5 mg m^{-2} d^{-1}, was shown in 1986 at the station N (Figure 6b). Lower values of P settling were observed at the station B (1.0 - 3.6 mg m^{-2} d^{-1}; Figure 6a). At the station HB, the P settling fluxes did not change significantly in all the past years (2.4 - 2.9 mg m^{-2} d^{-1}; Figure 6c).

The trend in P burial flux varies from site to site in the Bay. The strong dynamics of P burial were observed at the stations B and N, varying from 0.3 to 2.7 mg m^{-2} d^{-1} and from 0.8 to 3.5 mg m^{-2} d^{-1}, respectively (Figure 6a, b). Interestingly, low P burial was presented in the deep sediment layers of the two stations B and N earlier the 1970s (0.3 - 0.8 mg m^{-2} d^{-1}; Figure 6a, b). At the station HB, the P burial flux did not change significantly (2.0 - 2.6 mg m^{-2} d^{-1}; Figure 6c).

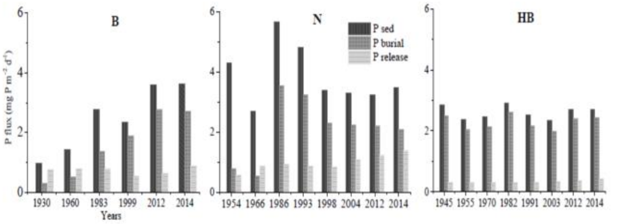

Figure 6. *Year-to-year variability of P settling, burial, and release in the three stations*

The P loadings over time can be generalized through mass balance analysis (Figure 7).

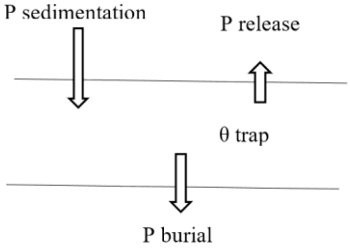

Figure 7. *Mass balance considerations and the recycling of P*

Our calculation pointed out that in a steady state at three stations, the sediment P release is linked to the permanent P burial flux so that

P release = P settling - P burial

Exceptionally for the station N, the P settling flux was much higher than the sum of P burial and P release before the point-source P loading reduction in 1978 (Figure 9b).

3.2. Linking sediment diagenesis model results with water column data over the period 2002-2009

3.2.1. Internal P fluxes and water column data in past years

We have enough data including external P loading and water column data over the period 2002-2009 [19]. Therefore, we can link and discuss our sediment model results with water column data in more detail over this period. The figures below (Figure 8-11) present the water column data and our sediment diagenesis model results over the period 2002-2009. The external P loading data and total P concentration in the water column of the Bay during the period 2002-2009 were applied from [19]. The P release and retention were estimated by our sediment diagenesis model.

From 2002 to 2009, the average external P loading was 5.6, 25.1, and 23.5 mg m^{-2} d^{-1} at the B, N, and HB stations, respectively (Figure 8). Among the five rivers (Trent River, Moira River, Salmon River, Napanee River, and Wilton Creek), the Napanee River had the highest total P concentration, contributing the greatest external P flux of 25.1 mg m^{-2} d^{-1} at station N (Figure 8b). The lowest external P flux of 5.6 mg m^{-2} d^{-1} at station HB mainly came from Wilson Creek (Figure 8c).

The internal P loadings (P release) at three stations over 2002-2009 are showed in Figure 9. The P release demonstrated small increasing trends at B and N over this period (Figure 9a, b), but appears to be decreasing slightly in HB basin (Figure 9c). Highest P release (0.95 – 1.05 mg m^{-2} d^{-1}; Figure 9. b) was observed at the station N and lowest P release (0.2 -0.35 mg m^{-2} d^{-1}; Figure 9c) was observed at the station HB. The P release at station B was between 0.65 and 0.75 mg m^{-2} d^{-1} (Figure 9a). In 2007, higher P release was observed at the stations B and N, but lower P release was observed at the station HB (Figure 9).

In contrast with P release, P retention demonstrated small increasing trends at B and N over time, but appears to be decreasing in HB basin (Figure 10). At the station B, the P retention was between 79.3 and 81.7% (Figure 10a). Highest P retention (84.1 – 94.8 %) was observed at the station HB (Figure 10c) and lowest P retention (67.5 – 68.2 %) was observed at the station N (Figure 10b).

High total P concentrations in the water column were observed at all three stations of the Bay although there has been considerable variability (Figure 11). At all three stations, high total P was observed in 2005 (Figure 11). For instance, the highest total P reached 36.8 µg l^{-1} in 2005 at the station N (Figure 11b). At the station HB, the maximum total P concentration (35.5 µg l^{-1}) was observed in 2005 (Figure 11c). Whilst at the station B, the total P concentration reached 41.6 µg l^{-1} in 2005 (Figure 11a). In 2007, high total P was observed at B and N stations but low total P was observed at HB station (Figure 11).

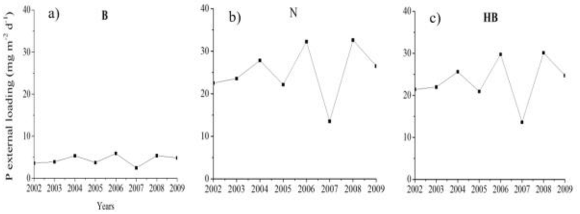

Figure 8. *External P loading at three stations over the period 2002-2009*

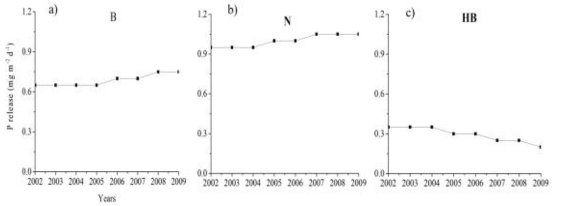

Figure 9. *Internal P loading (P release) at three stations over the period 2002-2009*

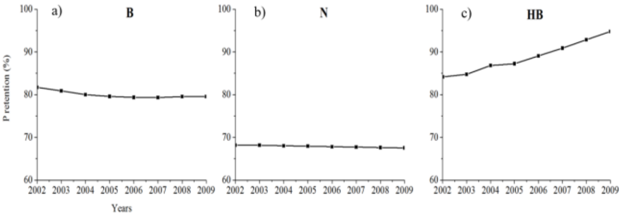

Figure 10. *P retention at three stations over the period 2002-2009*

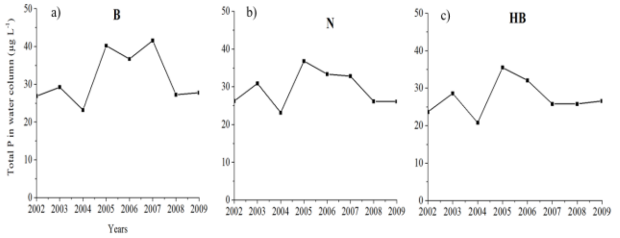

Figure 11. *Total P in the water column at three stations*

The fluxes represent the mass of P associated with various compartments (water column, sediments), averaged over the study period from 2002 to 2009. The spatial variability of the different external and internal P flux rates is shown in Table 1.

Table 1. *Average flow rate P at three stations during the period 2002-2009*

Station / P flux components (mg m^{-2} d^{-1})	B	N	HB
Inflow & External loading	5.6	25.1	23.5
Outflow	5.1	24.5	23.2
Release	0.7	1.0	0.3
Sedimentation	2.9	3.3	2.4
Burial	2.3	2.3	2.1

Our model calculation pointed out that long-term mass balance of P in the Bay of Quinte sediments was equilibrium at a steady state (P release = P settling - P burial).

3.3. Model scenarios

To support the water quality management strategy for Quinte Bay aimed at reducing P from agricultural sources by 20% in the future, we ran model scenarios by reducing sediment flux (X_{flux}) by 20%, corresponding to a 20% reduction in both organic and inorganic P. The objectives are to: (i) assess the time required to establish a new sediment equilibrium in the future, and (ii) investigate the impact of organic loading on changes in P release and retention processes in the three basins of the Bay. In this section, the authors reduce sediment flux by 20% for five scenarios in 2034 and compare them with the current condition in 2014 (keeping sediment flux constant).

3.3.1. Soluble reactive phosphorus profiles at three stations in different years

After reducing 20% total sedimentation flux, the concentrations of SRP were decreased (Figure 12). A large reduction of SRP concentration was observed at the station B (Figure 12a), while a smaller reduction of SRP concentration was observed at the stations N and HB (Figure 12b, c).

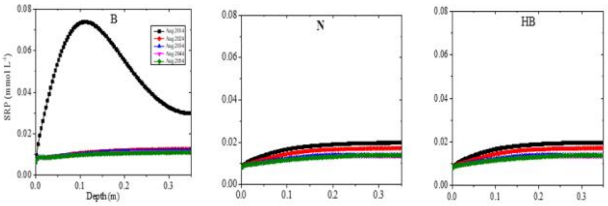

Figure 12. *Simulated vertical profiles of SRP at three stations in the different scenario years after reducing 20% Xflux*

3.3.2. The mass balance of P for the current condition in 2014 and the scenario year 2034

Spatial variability of the various internal P fluxes and P burial efficiency at three stations is presented in Table 2. The average P flux components (P settling, burial, and release) represent the mass of P associated with the sediment compartment in the present condition 2014 and the scenario year 2034 (20% total sedimentation flux was reduced). The internal P fluxes at each station consist of the variability of P in the sediment pool, driven by P inputs via settling from the water column (P settling), P outputs via sediment release to the water column (P release) and losses to deeper sediment layers through burial (P burial) (Table 2).

Table 2. *Spatial variability of the various internal P fluxes for the present condition 2014 and the scenario year 2034*

Station	B		N		HB	
P flux components (mg m^{-2} d^{-1})	Year 2014	2034 (-20% X_{flux})	Year 2014	Year 2034	Year 2014	Year 2034
P settling	3.83	2.77	3.43	2.51	4.01	3.53
P burial	2.77	2.12	2.34	1.77	2.83	2.46
P release	2.31	0.91	2.84	2.23	1.33	1.25
P burial efficiency (%)	72	78	68	70	70.5	72.4

For station B:

After reducing 20% flux of total sedimentation, the P fluxes at station B were reduced significantly. For instance, the P settling was reduced from 3.83 mg m^{-2} d^{-1} in the present condition (2014) to 2.77 mg m^{-2} d^{-1} in the scenario year (2034). The P buried into the deep sediments were responsible for 2.77 mg m^{-2} d^{-1} in the present condition and 2.12 mg m^{-2} d^{-1} in the scenario year. Similarly, after reducing 20% total flux of sedimentation, the P release from sediments was reduced considerably, from 2.31 to 0.91 mg m^{-2} d^{-1}.

Our analysis suggests that at the station B, in the present condition 2014, the P burial and P release were much higher than the P settling flux. After reducing 20% total flux, the new sediment P release is almost linked to the P settling and the permanent P burial fluxes so that P release ~ P settling - P burial. It means that the new sediment-based equilibrium may be established in 2034 after reducing 20% flux of total sedimentation at station B.

For station N:

After reducing 20% flux of total sedimentation, the P settling, burial and release fluxes at station N were reduced. For example, the P settling flux was 3.43 mg m^{-2} d^{-1} in the present condition (2014) and 2.51 mg m^{-2} d^{-1} in the scenario year (2034). The P burial fluxes were 2.34 mg m^{-2} d^{-1} in the present condition and 1.77 mg m^{-2} d^{-1} in the scenario year. The P release from sediments was reduced, from 2.84 to 2.23 mg m^{-2} d^{-1} after reducing 20% total flux of sedimentation. Our analysis suggests that at the station N, in the present condition 2014, the P burial and P release were higher than the P settling flux. After reducing 20% total flux, the P burial and P release were still higher than the P settling flux, thus the new sediment has still not established an equilibrium.

For station HB:

The P settling, burial and release fluxes at station HB were reduced slightly after reducing 20% flux of total sedimentation. In two cases (the present condition and 20% reduction of total flux), the P release is linked to the P settling and the P burial fluxes so that P release = P settling - P burial. This could be drawn that the sediments in the station HB are close to an equilibrium state.

Our model calculation pointed out that long-term mass balance of P in the Bay of Quinte sediments was equilibrium at a steady state (P release = P settling - P burial). We hope augers well for a self-cleansing of the Bay in the future. Exceptionally for the station N, the P settling flux was much higher than the sum of P burial and P release before the point-source P loading reduction in 1978. This may be P was accumulated at the station N before 1978.

Our results showed that the fluxes of P settling and burial are higher and the P release is lower than those reported in previous studies [19]. This is because, after adjusting for the excessively high sedimentation rates used in earlier models [19], our results align with the conclusion of Kim et al, which suggests that the sediments in the Bay of Quinte do not consistently act as a net source of P.

4. Conclusion

Our result indicated the spatio-temporal heterogeneity with respect to the P retention in the studied three basins of the Bay. P retention demonstrated decreasing trends at the two stations B and N over time, this may increase P release and maximize the likehood of refueling primary production in the water column. Meanwhile, the P retention appears to be increasing at the station HB leading to decrease P release into the overlying water.

P release and P retention were somewhat inversely correlated, indicating the dynamics of P binding forms influence on P retention and release in the sediments and seem to be connected with the eutrophication in the Bay. Specifically, the station N exhibited the lowest P retention with the amount of 63% of P retained in 2014, and greatest P release from sediments (1.3 mg P m^{-2} d^{-1} in 2014). Highest P retention (91% in 2014) and lowest P release (0.4 mg P m^{-2} d^{-1} in 2014) were observed at the station HB due to high erosion and agriculture activities in the watershed.

In summary, our results at the Bay of Quinte confirm the importance of a sufficient reduction of external loadings. The internal loadings were at best supportive for reaching the target trophic lake condition.

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