Phosphorus retention in a mesotrophic lake under transient loading conditions: Insights from a sediment phosphorus binding form study

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ABSTRACT

Phosphorus retention in sediments has been estimated for three basins in Lake Simcoe, a mesotrophic lake in Ontario, Canada. Total phosphorous (TP) fractionation was used to examine the concentration of phosphorus (P) binding forms in the sediments of Cook's Bay, Kempenfelt Bay, and the Main Basin. The extended sequential extractions allowed us to differentiate between organic-, inorganic-, carbonate-bounded and redox-sensitive phosphorus. Our results showed different mechanisms of P release in each of the three investigated basins, which may be linked to their distinct loading histories, present land-uses and morphology of the sampling sites. In the deep Main Basin, where moderate changes in P loading have been induced by deforestation, sediments are not an important long-term source of diagenetically mobile P, as almost 75% of P is released within a short time scale. P release is predominantly generated by a continuous epilimnetic P flux, rather than a large inventory of temporary P stored in the sediments. Diagenesis in the upper sediment layers is fast enough to prevent a large accumulation of temporary P. In the much deeper glacially formed Kempenfelt Bay with a highly urbanized catchment, P release from the sediments is dominated by the redox-sensitive P fraction, representing up to 40% and 57% of long- and short-term sediment P release, respectively. In the shallow and agriculturally-impacted Cook's Bay, the main P binding form that can be mobilized through diagenesis is carbonate-bound P. This fraction contributes 40.1% and 37.6% to the long- and short-term P sediment release, respectively. Although different mechanisms of P release have been revealed for the three basins in Lake Simcoe, the vertical profiles indicate that the sediments throughout the system are still able to bind deposited P.

1. Introduction

Lake Simcoe is the largest lake in Southern Ontario, after the Great Lakes, with a surface area of 772 km² and is situated 50 km north of the city of Toronto (MOE, 2010). The lake has been subjected to anthropogenic disturbances for several decades and the integrity of its ecosystem has been challenged (Winter et al., 2007; Young et al., 2011). This problem

became particularly severe in the 1970s, when excessive algal and macrophyte growth were stimulated by increased phosphorus (P) loading. Moreover, the insufficient hypolimnetic oxygen levels were causally linked with a failure of cold-water fish recruitment (Evans, 2007; Johnson and Nicholls, 1989). In Lake Simcoe, hypoxic conditions are occasionally manifested at the end of summer stratification (Eimers et al., 2005). Importantly, the projected rise in global temperature is likely to prolong the duration of summer stratification, thereby accentuating the problem of hypolimnetic hypoxia in Lake Simcoe. In fact, Stainsby et al. (2011) provided evidence that stratification occurs 20 days earlier in the spring and terminates 15 days later in the fall compared to thirty years ago (Stainsby et al., 2011). The likelihood of an increase in the severity of hypoxic conditions is troublesome, as it can potentially trigger the release of P from the sediments to the overlying waters (Christophoridis and Fytianos, 2006).

Efforts to reduce P inputs into the lake have resulted in water quality improvements, decline of TP and chlorophyll-*a* concentrations, and a gradual shift to conditions that typically prevail in mesotrophic lakes (Winter et al., 2002). However, despite the additional reductions of total P loading over the last two decades (1990: 156.5 t P/year, 2006: 71.5 t P/year), the ambient TP concentrations have not declined accordingly (Young et al., 2010). While the lake's water quality, hydrology, and external non-point and point P loading have been extensively monitored in the area (Palmer et al., 2011), we still have very limited understanding of the fate of P in the lake sediments, and especially the nature of the mechanisms of P accumulation or burial in the diverse basins of this large system.

In addition to acting as a habitat for many life forms, such as micro- and benthic organisms, sediments play a fundamental role in determining the concentration of many nutrients and pollutants in the water. For example, lake sediments play a critical role in determining the fate and vertical transport of phosphorus, thereby modulating the magnitude of internal P loading. Phosphorus is present in many chemical forms in the sediments and each form contributes differently to the internal loading depending on the prevailing conditions (Christophoridis and Fytianos, 2006). P mobilization in sediments has been extensively investigated in many eutrophic lakes, but there are only a few studies on P retention in mesotrophic systems, and thus the mechanisms are currently not fully understood. In general, P release is dependent on the ability of the sediments to retain P, the conditions of the overlying water, and the biological characteristics of the lake (Abdel-Satar and Sayed, 2010). The main driving factors are temperature, redox conditions, pH, dissolved oxygen, and the concentrations of other inorganic species, such as nitrate and sulfate in the sediments and water column (Ribeiro et al., 2008). P can be released through a wide array of physical, chemical, and biological processes, including ligand exchange mechanisms, mineralization, and release of living cells (Christophoridis and Fytianos, 2006). The prediction of internal P loading requires rigorous quantification of the different P forms present in the sediments.

Phosphorus-binding forms play an important role in predicting how a system will react under changing loading conditions. P exists in inorganic and organic forms.

Inorganic forms of P are typically adsorbed to sediment metallic oxides, like Al- or Fe-hydrooxides. Organic forms can be found in microorganisms, detritus, humic compounds, poly-phosphates and phospholipids (Ribeiro et al., 2008). A substantial amount of P is generally stored for relatively long time periods, as refractory material of organic matter in the sediments. In particular, together with P bound to $CaCO_3$ and apatite, humic material acts as a P sink that contributes to the repository pool (Bostrom, 1984).

The reduction of external P loading has not always rendered a prompt recovery from eutrophication (Ahlgren et al., 2005; Carey and Rydin, 2011). Such delayed responses typically stem from the positive feedback between eutrophication-driven anoxia and internal P release (Gachter and Muller, 2003; Schindler, 2006). The importance of diagenetic processes in the estimation of sediment P release in eutrophic lakes has long been recognized, although an empirical relationship between TP in sediments and internal P loading to the water column is still missing (Nürnberg, 1988; Carey and Rydin, 2011; Golterman, 1999). On the other hand, the internal loading in oligotrophic lakes is typically limited and the sediments are capable of greater P burial (Nürnberg, 1988). Mesotrophic lakes represent a transition zone between oligo- and eutrophic lakes, and as such investigations on P diagenesis processes in conjunction with their loading and land-use history, can improve our fundamental understanding of the relative importance and effective control of internal loading (see Lewis et al., 2007).

Recent studies on the reconstruction of primary productivity in Lake Simcoe, based on the total P sediment records and isotopic ratios of carbon and nitrogen, suggested that autochthonous primary productivity has increased over the last four decades and more organic P has been buried in lake sediments (Hiriart-Baer et al., 2011). This is a somewhat counterintuitive trend, given that the monitoring results show that P loading in Lake Simcoe has generally decreased. Furthermore, a recently published modeling study estimated the net epilimnetic TP loss rates in Cook's Bay and Kempenfelt Bay to be at the level of 300 mg P/m^2/yr and 150 mg P/m^2/yr, respectively (Gudimov et al., 2012), whereas sediment dating data suggest accumulation rates to be twice as high, 250—750 mg P/m^2/yr (Hiriart-Baer et al., 2011). It is still unclear what the reasons are for these discrepancies. The sediment core investigations are a useful tool to understand the role of the sediments in the P budgets of lakes (Dillon and Molot, 1996; Hupfer and Lewandowski, 2005).

In this study, our main objective is to quantify the potentially mobile P pool stored in the sediments of three basins in Lake Simcoe. By studying the variability of P binding forms in space and time, our study aims to understand the mechanisms of internal P release under a wide range of loading conditions, diverse spatial settings, ranging from flat, macrophyte-dominated to deep glacier-formed basins, and different periods of the year. For this purpose, we selected three different basins of Lake Simcoe with different loading histories: Cook's Bay, Kempenfelt Bay and Main Basin (Hiriart-Baer et al., 2011; Landre et al., 2011). The catchment area of the shallow Cook's Bay is characterized by both agricultural and urban land uses, and has been subjected to river channelization and wetland draining since the beginning of the 19th century. In the

deep Kempenfelt Bay, the land-use and P loading history reflect the urbanization activities associated with the City of Barrie's population growth after the 1950s (Hiriart-Baer et al., 2011). The catchment of the Main Basin experienced gradual defor-estation, which has been the main driver of the P loading variability.

The concentrations of five phosphorus-binding forms were measured in sediment cores down to 28 cm depth in three different basins at two distinctly different periods of the year, before the stratification onset and toward the end of thermal stratification. We investigated redox conditions (pH and oxygen profiles) at the sediment−water interface with high (0.5 mm) vertical resolution. The concentrations of dissolved substances in the pore water were also measured and subse-quently used to calculate the diffusive fluxes of phosphorus during turnover, ice cover, and summer stratification. Finally, we calculated P retention in Lake Simcoe based on the sedi-ment P depth profiles and external loading estimates, and compared our findings with those provided by a whole-lake mass balance model (Gudimov et al., 2012).

2. Methods

2.1. Site description

Lake Simcoe is the largest lake in Southern Ontario after the Great Lakes. Lake Simcoe has a surface area of 722 km^2 with a watershed area of 2899 km^2, a maximum and mean depth of 14.2 m and 41.5 m respectively. The lake is divided into three major regions: the deep-water Kempenfelt Bay near the city of Barrie (area 22 km^2), the shallow Cook' Bay (area 24 km^2) near the Holland Marsh, and the "Main" Basin. Some 400,000 people currently reside in the Lake Simcoe watershed, while millions are attracted to the lake for swimming, boating, fishing in summer and winter, and other recreational activities. There are also six drinking water treatment plants that are supplied water from the Lake Simcoe.

In this dimictic lake, our three sampling sites were in Cook's Bay (C9), Kempenfelt Bay (K42) and Main Basin (K45) (Fig. 1). The large Main Basin has a mean depth of 14 m, a maximum depth of 33 m and an area of 643 km^2, while the narrow and deep Kempenfelt Bay on the west side of the lake has a mean depth of 20 m and an area of 34 km^2. The shallow Cook's Bay at the southern end of the lake has a mean depth of 13 m and an area of 44 km^2 (Palmer et al., 2011). The lake drains out of its northern end through a single outflow at Atherley Narrows and has a flushing time of approximately 10.5 years (Table 1). Due to the limestone bedrock underlying its catchment, Lake Simcoe is a hard-water lake with a mean calcium concentration of 41 mg/L, mean alkalinity of 116 mg/L and a pH of 8.3 (Table 1). Cook's Bay (C9) has a transparency of 6.4 m, while the corresponding values in Kempenfelt Bay (K42) and the Main Basin (K45) are 7 m and 7.1 m, respectively (Young et al., 2010). Finally, the lake's sedimentation rate is about 2 mm/year (Hiriart-Baer et al., 2011).

Agriculture is the dominant land use, comprising 43% of the total watershed area. Agricultural land is concentrated along the Holland River system that feeds Cook's Bay at the southern limit of the lake, including a 49 km^2 cultivated marsh
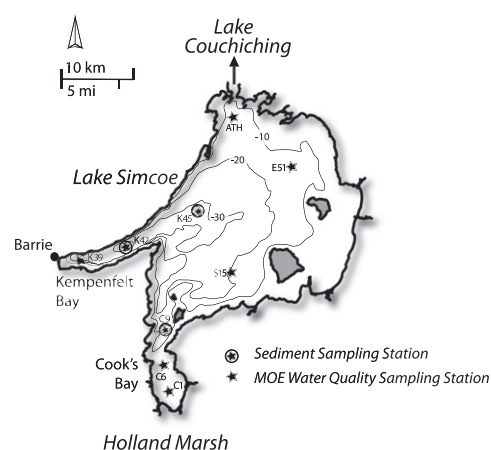
Fig. 1 − Sampling locations for the three basins in Lake Simcoe. Solid circles represent sites where the sediment cores were collected and water column was sampled for this study; empty circles represent sites where water samples were collected for the monitoring program of the Ontario Ministry of Environment (Young et al., 2010).

or "polder." The water level within the polder is maintained through a series of pumping stations and canals, which discharge the excess water into Cook's Bay. In the early 1980s, the Secchi depth values in Cook's Bay averaged between 1 and 2 m, while the phytoplankton abundance was high. Phos-phorus levels in Cook's Bay are still relatively higher than other sites (Table 1, 2000−2003, range 14.4−22.7 μg/L), as a result of elevated P inputs (generally >100 μg/L) from the highly agricultural Holland Marsh, which enter Cook's Bay via the Holland River (Winter et al., 2002). Cook's Bay has also experienced a fairly rapid proliferation of macrophytes, stemming from the gradual improvements in the water clarity.

Total P levels were historically high in Kempenfelt Bay, near the city of Barrie, which in 2001 was the fastest growing city in Canada, increasing in population by 25% between 1996 and 2001 (Eimers et al., 2005). In the past, the deep Kempenfelt Bay has experienced periods of low hypolimnetic oxygen at the end-of the summer stratification (Eimers et al., 2005). Quite recently though, the TP levels in Kempenfelt Bay were similar to those in the Main Basin (Table 1). The overall TP trend in the Main Basin has not demonstrated a statistically significant change over the past three decades, although the decline in TP occurred primarily in the 1980s.

Lake Simcoe in its current state is considered mesotrophic (Table 1) and the major sources of phosphorus include the non-point loading from tributaries and atmospheric deposi-tion, the vegetable polders (e.g., Holland Marsh), the waste-water treatment plants, and the septic systems. Tributaries represent the load of phosphorus from agricultural areas as well as the urban runoff that typically carries phosphorus from lawn fertilizers, pet waste, and detergents (Gudimov et al., 2012). Between 2004 and 2007, the total phosphorus loading into the lake was 74 ± 3 tones/year (MOE, 2009), rep-resenting a significant reduction from over 100 tones/year during the 1980s and early 1990s (Evans, 2007).

Table 1 – Physical, chemical and biological properties of the study sites (Evans et al., 1994; Young et al., 2010), mean values over ice-free period with standard deviations (stdev) for 2004–2007.

Property	Lake Simcoe	Main Basin	Kempenfelt Bay	Cook's Bay
Surface area, m^2	722	643	34	45
Mean depth, m	14.2	14	20	13
Maximum depth, m	42	33	42	15
Flushing time, year	10.05			
Volume $\times 10^9$ m^3	11.408	10.113	0.936	0.358
Mean annual outflow, $m^3\,s^{-1}$	32.3			
Total phosphorus load, MT/year		42 (2)	10 (1)	20 (3)
Total phosphorus load, volume weighted, $mg/m^2/yr$		4 (0.2)	13 (1)	61 (8)
Total phosphorus, mg/L (1980–1993)		16.4 (11.9)	15.3 (7.5)	17.1 (7.6)
Total phosphorus, mg/L		13.8 (5.8)	14.7 (3.7)	14.8 (4.0)
Soluble reactive phosphorus, mg/L		0.8 (0.7)	0.7 (0.5)	1.3 (4.2)
Total nitrogen, mg/L		0.45 (0.05)	0.47 (0.09)	0.45 (0.05)
Alkalinity, mg/L		116 (3)	116 (3)	115 (3)
Chlorophyll-*a*, mg/L		2.5 (1.5)	2.8 (1.6)	2.5 (1.6)
Secchi depth, m		7.1 (1.8)	7.0 (2.0)	6.4 (1.4)

2.2. Sediment sampling

Samples were collected using a core sampler Uwitec in a 60 cm long sampling tube. Cores were obtained in March 2011 and September 2011 from three locations (C9, K42 and K45). Water depth profiles of dissolved oxygen, temperature, pH and conductivity were collected using a seabird sensor at each sampling site before the sediment sampling occurred. The cores were sealed on site, to prevent any atmospheric exchanges, and were then transferred to the lab in a thermo-isolated custom built box, where they were preserved at 4 °C. The time period between the collection of the samples and the measurements in laboratory was less than 2 h; microsensor measurements were carried out immediately upon arrival to the laboratory. One to three cores were used for microsensor analysis for O_2 and pH.

Two cores were used for pore water analysis, and two to three cores were used for the fractionation of phosphorus, and the analysis of porosity, dry weight and total organic matter. Additionally, one core was sectioned for image analysis and two cores were frozen for future analysis. The core sections were chosen for fractionation based on visual analysis of the exposed sediment cores that were cut longitudinally (Fig. 2).

Two to three sediment cores were sectioned in 1–2 cm thick slices. In most cases, the 0–1 cm, 1–2 cm, 2–4 cm, 4–6 cm and 6–10 cm horizons were pooled. For deep core analysis, the horizons 10–15, 15–20 cm were also collected. The above mentioned layers taken from the cores were added in a beaker and were then mixed. Samples from each layer, from the two to three cores, were combined and centrifuged (11,000 rpm $\times$ 10 min), decanted, and filtered (0.45 μm) for pore water analysis. For each layer at least two samples were prepared for the pore water analysis and analyzed in replicates. The average values of these measurements are presented; the standard deviations are less than 5%. The P binding forms were analyzed in duplicates of approximately 1 g fresh sediment with the sequential extraction scheme proposed by Psenner and Pucsko (1988). The filtrate was used for P analysis and analysis of Fe, Mn, Ca and Si by ICP optical emission spectroscopy (ICP-OES) (Perkin Elmer Optima

7300DV). The detection limits are 0.02 mg/L for Fe, 0.004 mg/L for Mn, 0.0002 mg/L for Ca and 0.04 mg/L for Si.

2.2.1. Oxygen and pH measurements at the sediment–water interfaces
Vertical distributions of dissolved oxygen in sediment pore waters were determined in cores (i.d. ∼5 cm) that were kept at

Fig. 2 – Sediment core image from Kempenfelt Bay, March 2011.

4 °C and were thermostated following their recovery. Oxygen concentrations were measured using a Unisense (Clark-type) microelectrode positioned with a micromanipulator (Revsbech, 1989). The electrode was calibrated in air-saturated and nitrogen-purged water at the temperature of measurement. Sub-cores after oxygen profiling were capped with stoppers and incubated under 4 °C in a dark environment. To avoid contamination with atmospheric oxygen, electrical tape was wrapped around the tube ends. Oxygen profiles were measured several times in at least two cores at the laboratory. The pH profiles were measured by pH needle electrodes (Unisense). The pH electrode was calibrated with three points, and the measurements were performed in the same cores where oxygen profiles were measured. Oxygen and pH profiles were measured several times in at least two cores at the laboratory. Depth profiles for oxygen and pH presented in this study are the values averaged from three to four profiles, while the standard deviations were less than 10%.

2.3. Water content, P binding forms, total organic carbon

The cores were sectioned under N_2 atmosphere in the lab. Sub-samples of the obtained sections were dried at 105 °C for 60 h, and were weighted again. The sediment water content was calculated based on the weight lost, which was then used to estimate the porosity. Lost of Ignition (LOI) was estimated based on the weight lost by drying at 550 °C for 2 h. The total carbon was estimated as LOI/2.5 (%) (Heiri et al., 2001). For each measurement two samples were prepared and measured in replicates, the data presented in this study are averaged values for these measurements, while the standard deviations were less than 7%.

For each layer two separate samples of fresh sediments were fractionated, and all measurements were performed in duplicates. The average of four data points for one fraction of one horizon is presented in this study. The standard deviations were less than 5% for P fractionation as well as the dissolved and total P measurements. Additionally, the deviations between total P as a sum of total P in all fractions and total P directly measured in the same horizon were less than 7% in all samples presented in this study. For the calculation of sedimentation rates, we used the recently published results on sediment dating (Hiriart-Baer et al., 2011).

The phosphorus fractionation method used in this study was the Psenner Scheme (Psenner and Pucsko, 1988) as modified by Rydin (2000). The P forms separated in this sequential fractionation include loosely adsorbed (labile) P (extracted with NH_4Cl, NH_4Cl-TP), redox-sensitive bound P (extracted with bicarbonate dithionite, BD-TP), P bound to hydrated oxides of aluminum (extracted with NaOH, NaOH-SRP), organic bound P (extracted with NaOH-NRP), carbonate-bound P (apatite-P) (extracted with HCl, HCl-TP) and refractory P (Refract-P) (Psenner and Pucsko, 1988). Two replicates were obtained for each layer, using approximately 1 g of fresh sediment. After each step, the samples were centrifuged at 8000 rpm for 10 min, filtered through a 0.45 μm filter, and then analyzed with a spectrophotometer for Soluble Reactive Phosphorus (SRP) and with an Inductive Coupled Plasma (ICP) for metals. Additionally, total phosphorus

(organic and inorganic) analysis was performed on the unfiltered supernatant of each fraction. This unfiltered sample was diluted with deionized water, and after addition of $K_2(SO_4)_2$, each sample was autoclaved and P concentration was analyzed photometrically. The organic bound P (NRP) concentration was subsequently determined by subtracting SRP from TP.

2.4. Calculations of diffusive P flux

Diffusive P fluxes J_{sed} across the sediment interface were calculated using Fick's first law of diffusion (Schulz and Zabel, 2000)

$$J_{sed} = \phi^* D_{sed} * \frac{\partial C}{\partial Z},$$

where φ is porosity, C is concentration, Z is the sediment depth and D_{sed} is a diffusion coefficient in the pore water volume of sediment, which can be calculated on the basis of the porosity and the diffusion coefficient in free solutions of sea-water (Boudreau, 1997):

$$D_{sed} = \frac{D^{sw}}{1 - \ln(\phi^2)}$$

3. Results

In March 2011, Lake Simcoe was covered with ice during our sampling. Temperature profiles for all three stations showed that the water column was inversely stratified (Fig. 3a). Oxygen concentrations in the bottom layers were 12, 7, and 7.5 mg/L in Cook's Bay, Kempenfelt Bay and the Main Basin, respectively. Lake Simcoe was still stratified at the middle of September, while the pH values were between 7.04 and 7.12 at the bottom of the lake (Fig. 3b and d). Oxygen concentrations in the bottom layers were 5.58, 5.91 and 6.47 mg/L in Cook's Bay, the Main Basin and Kempenfelt Bay, respectively (Fig. 3c). The pH values in Cook's Bay were 7.04 at the bottom, while the pH was higher in the other two basins with values of 7.12 and 7.11 in Kempenfelt Bay and the Main Basin, respectively (Fig. 3d).

All O_2 profiles at the sediment–water interface were characterized by a steep gradient (Fig. 4). At the sediment surface, oxygen concentration was highest in March at the Main Basin (5 mg/L) and the lowest in Kempenfelt Bay (3 mg/L). In September, oxygen concentration reached the level of 2 mg/L in Kempenfelt Basin. At the sediment–water interface in March, pH varied from 7.6 to 7.3 in Cook's Bay and Kempenfelt Bay, while the respective pH values in Main Basin were varying between 7.2 and 7.0. These pH values were 0.2–0.6 units higher than those measured in the bottom water, possibly due to the carbonate dissolution in the sediments, which may also modulate the Ca^{2+} and HCO_3^- fluxes into overlying waters.

3.1. Phosphorus binding forms

The P binding forms in the three basins in March and September 2011 are shown in Fig. 5. The dominant binding form of phosphorus in the Main Basin was carbonate-bound
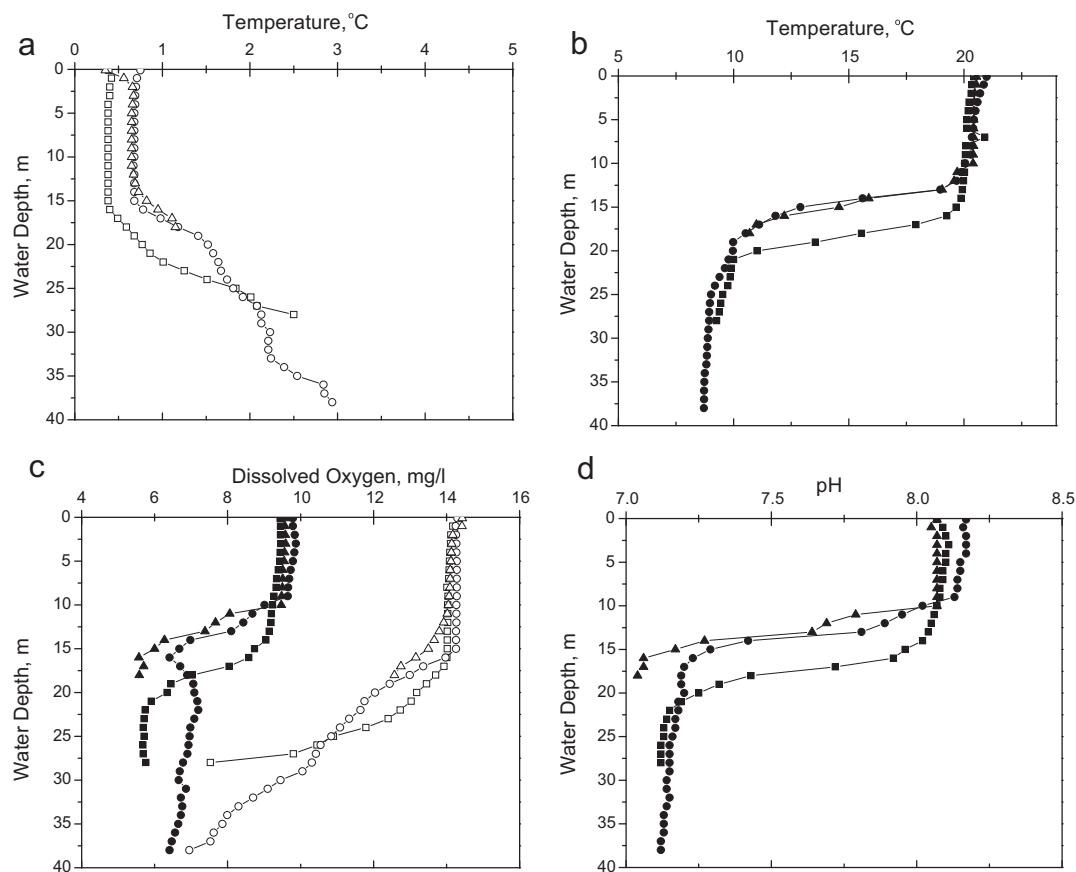
Fig. 3 – Water depth profiles of temperature (a, b), oxygen (c) and pH (d) for three study sites on March and September 2011. Squares indicate Main Basin, circles indicate Kempenfelt Bay and triangles indicate Cook's Bay. Open symbols indicate March sampling and closed symbols represent September sampling.

(HCl-TP), which contributed 35–50% to the total P content in the sediment (Fig. 5a and b). The redox-sensitive form (BD-P) was the second most abundant form (20% of total P), especially in the top sediment layer. This fraction decreased dramatically toward the deeper sediment. The NaOH-fraction contributed significantly to P content in the sediment surface. The dominant part of this fraction was organic-bound, NaOH-NRP fraction, approximately representing 20% of the total phosphorus. Both refractory (Refract-P) and easily adsorptive phosphorus (NH$_4$Cl-TP) did not change with the sediment depth, contributing about 7% to the total phosphorus pool.

The surficial sediment TP in Kempenfelt Bay is higher (TP$_{Surface}$ = 1.9 ± 0.2 mg P/g DW) than in the Main Basin (TP$_{Surface}$ = 1.2 ± 0.1 mg P/g DW). The P binding forms are also distributed differently in Kempenfelt Bay (Fig. 5c and d), in that a significant part of phosphorus (42%) was bound as a redox-sensitive component (BD-TP), which was the highest amount among all the stations sampled in Lake Simcoe. HCl-fraction was about 20% of the total phosphorus throughout the sediment depths studied. The redox-sensitive fraction declined from 42% of the total P at the sediment surface to around 3% in 20 cm depth, while organic-bounded P (NaOH-NRP) declined from 20% to 2%, and refractory phosphorus from 6.7% to 1.8 %.

At station C9, Cook's Bay, the P content was the lowest among the investigated stations (Fig. 5e and f). Interestingly, the carbonate-bounded (HCl-TP) fraction was the predominant one, accounting for up to 48% of the total phosphorus. The second important fraction was the organic-bounded P (NaOH-NRP). Approximately 50% of the P content in the deeper sediment was decreased due to the depletion of the BD-TP fraction and about 40% was associated with a decrease of the NaOH-NRP form. The other fractions did not demonstrate notable changes over depth.

3.2.   Dissolved substances in the sediment pore water

The pore water concentration profiles of phosphorus, calcium and silica at the three studied sites are shown in Fig. 6. The concentration ranges for all three substances did not differ among the three sites and demonstrated similar trends, in that they increased from the surface to the deeper sediment layers. Fe concentrations were close to the detection limit of 0.02 mg/L in all three basins. The phosphorus concentration gradients were steeper in September than those in March; therefore, the corresponding diffusive phosphorus fluxes were higher in all sites (Bostrom, 1984, Table 2).
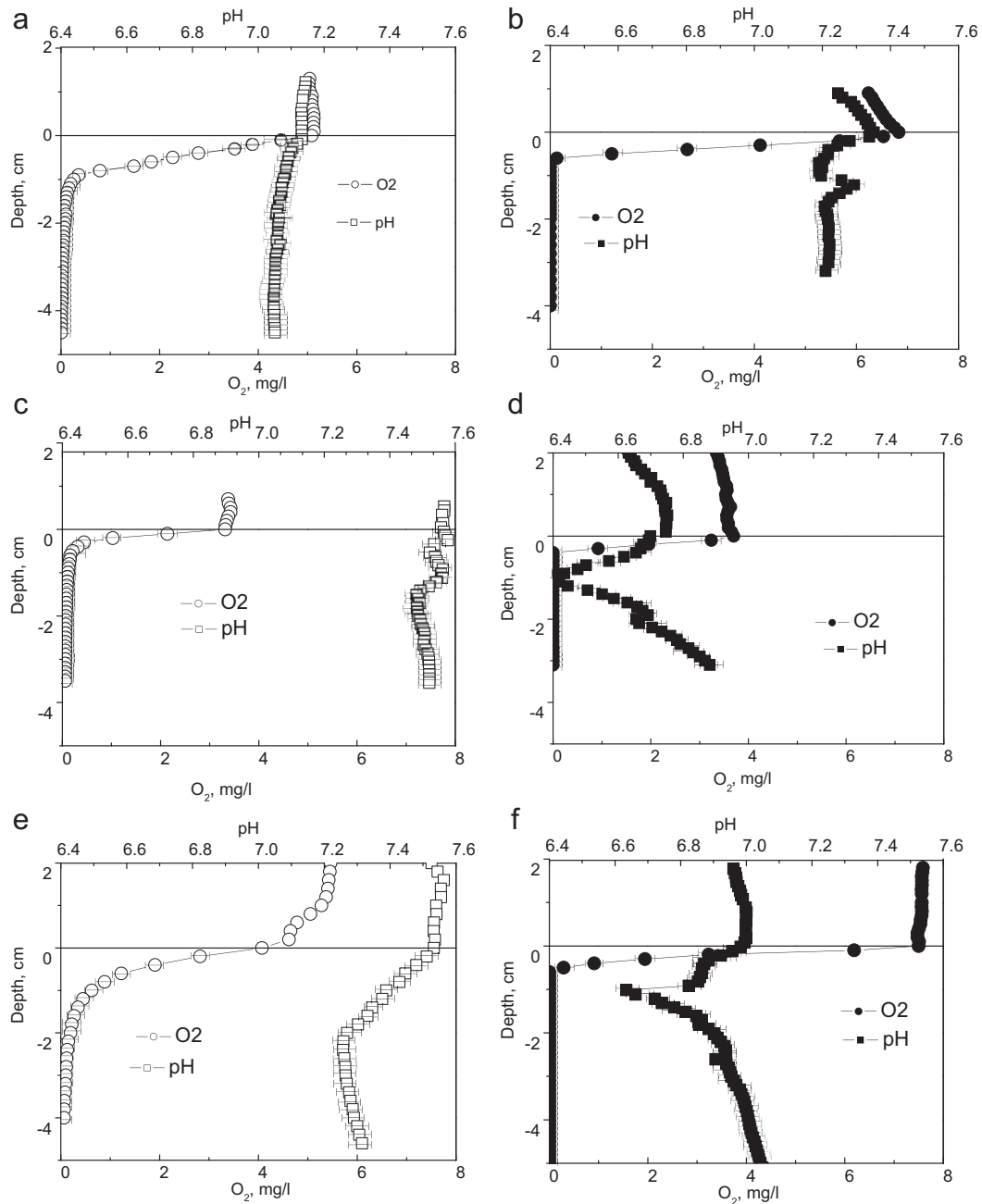
Fig. 4 – Oxygen and pH profiles at the sediment–water interface for three study sites: Main Basin (a, b), Kempenfelt Bay (c, d), and Cook's Bay (e, f) for March (open symbols/left panel) and September (closed symbols/right panel).

3.3.   *Organic carbon and total phosphorus*

Depth profiles of the organic carbon and total phosphorus content in the sediments are shown in Fig. 7. In all three basins, the highest concentrations of organic carbon were observed in the surface sediments and values in Kempenfelt Bay and Main Basin were comparable, lying close to values 7–8%, while the organic carbon content in Cook's Bay was lower, 5–6%. Organic carbon in Kempenfelt Bay and Main Basin decreased steadily from ca. 8% to ca. 5%, remaining stable at the bottom of the core. Cook's Bay showed variations throughout the core, decreasing

from the top to the first 8 cm, circa 1990–2011 based on the results of Hiriart-Baer et al. (2011), then increasing and decreasing again at the bottom of the core (circa 1930–1950).

Sediment total P was very similar in March and September for all basins, with the highest P measured in Kempenfelt Bay, and lower values in the Main Basin and the lowest ones in Cook's Bay (Fig. 7). P increased toward the surface of the sediment in all of the Lake Simcoe cores. An increase of total P was pronounced in the top 8–10 cm of the sediment cores, which corresponded to 1970 in Main Basin, 1950 in Kempenfelt Bay, and 1990 in Cook's Bay (Fig. 7).
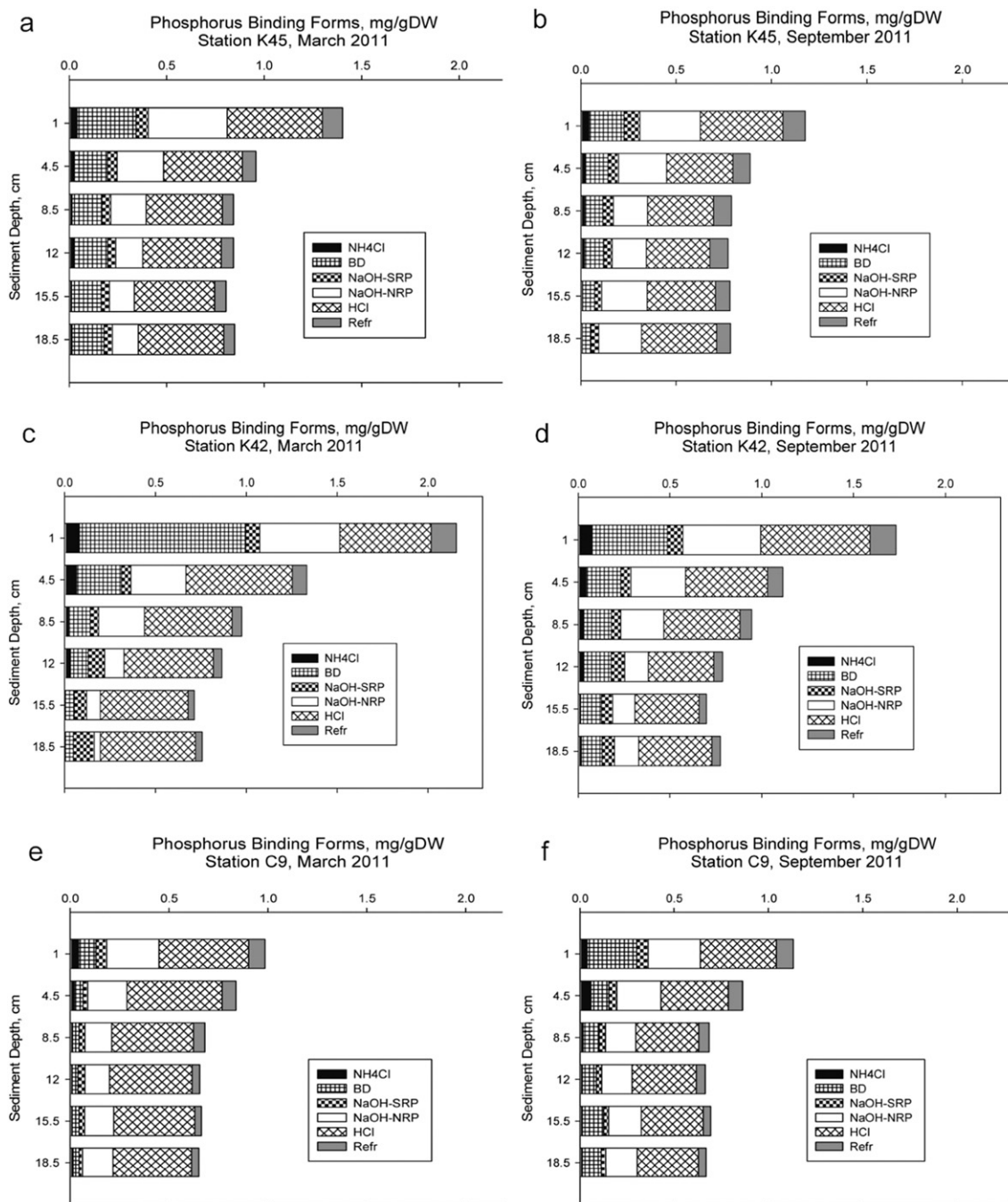
Fig. 5 – Depth profiles of phosphorus binding forms in Lake Simcoe sediments from the Main Basin (a, b), Kempenfelt Bay (c, d), and Cook's Bay (e, f) for March (left panel) and September (right panel).

4.   Discussion

4.1.   Mechanisms of P release from sediments

We used historical information for sediment accumulation (Hiriart-Baer et al., 2011) and detailed data collected from water quality monitoring to estimate phosphorus mobile pool and phosphorus retention in the three basins of Lake Simcoe (Winter et al., 2007). Our calculations are also based on the depth profiles of P binding forms, while also accounting for their transformation over depth (Hupfer and Lewandowski, 2005; Eckert et al., 2003). The fast P release rate has been estimated by comparing the P-fraction content in the two uppermost layers, while the slow P release rate has been calculated as a difference between P at the surface and deep sediment layers (Hupfer and Lewandowski, 2005). In doing so, we were able to compare the processes in both short (fast release) and long time (slow release) scales and linked them to the history of P loading and historical sediment investigations in Lake Simcoe.
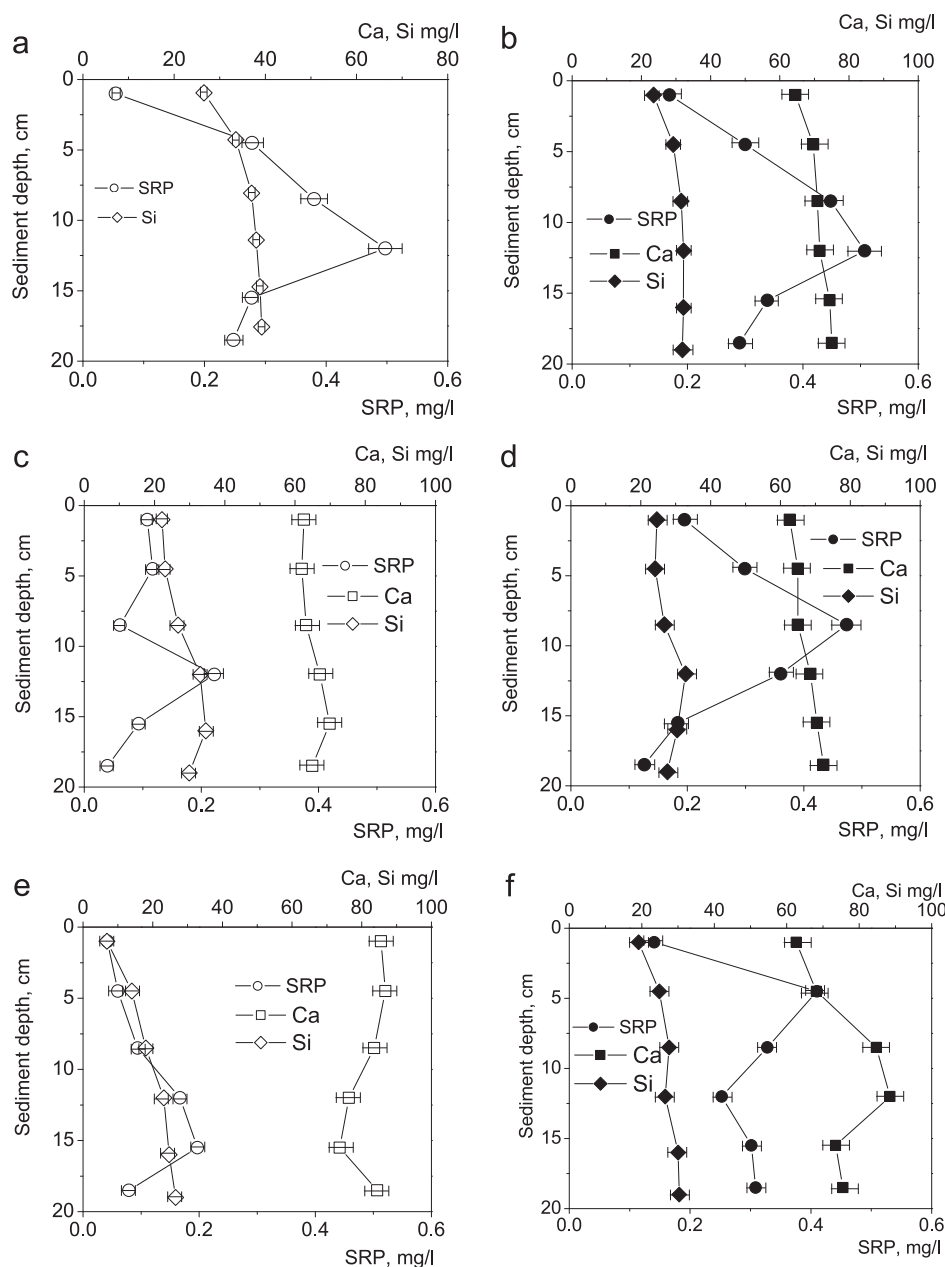
Fig. 6 – Depth profiles of dissolved phosphorus, calcium and silica concentration in sediment pore water from the Main Basin, without Ca-measurements (a, b), Kempenfelt Bay (c, d), and Cook's Bay (e, f) in March (left panel) and September 2011 (right panel).
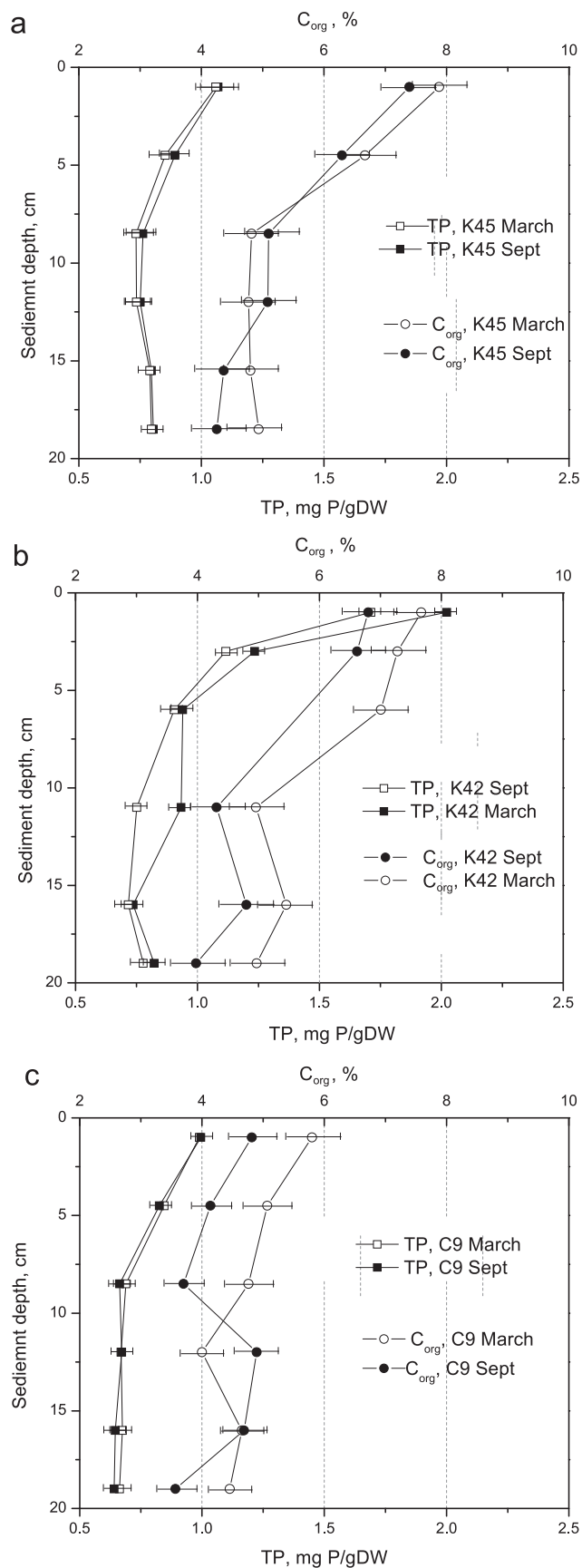
4.1.1. Main Basin

In the Main Basin, the decrease of BD-TP (21%) has been caused by reductive dissolution of redox-sensitive-bound P (Fig. 8). However, we found that Fe^{2+} in pore water were close to the detection limits in all sampling dates, so we assume that the formation of iron-sulfide in the sediment may prevent the release of Fe^{2+}, leading to decoupling of the Fe and P cycle (Roden and Edmonds, 1997, Fig. 2, black layers in sediment). An additional argument may be the lack of surface Fe enrichment that can be attributed to the lower redox potential required for Fe reduction than for Mn reduction (Landre et al., 2011). In contrast, manganese was enriched in the pore water at the sediment surface, characterized by

a relatively strong correlation between manganese in BD fraction and BD-TP. Beside BD-P, the NaOH-NRP (30%) and HCl-TP (30%) fractions decreased during the diagenesis in Lake Simcoe (Fig. 5). As shown in a number of studies (e.g., see

Table 2 – Diffusive phosphorus flux (mg/m²/d) from sediment.

Study site	March 2011	September 2011
Cook's Bay	0.033	0.31
Kempenfelt Bay	0.034	0.10
Main Basin	0.12	0.11

Fig. 7 — Organic carbon (circles) and total phosphorus (squares) in sediments of the Main Basin (a), Kempenfelt

review by Hupfer and Lewandowski, 2005), NaOH-NRP is a good measure for organic P and poly-phosphate and its decrease is typically the result of microbial degradation. The organic fraction is usually the predominant P form of the sedimenting material (Guede and Gries, 1998). Together with HCl-P fraction, organic P is the main source for fast diagenesis. The HCl-P fraction decreased in first centimeters, most probably because the pH dropped below 7. This fraction is redox insensitive and represents an immobilized P pool. The most important source of this fraction is the erosion process associated with the land-use changes in the carbonate-rich Lake Simcoe watershed during the last decades, especially deforestation in the catchment of the Main Basin (MOE). The accumulation of this fraction in surface sediments may be explained by the high pH values (>7.3) in the Main Basin sediments as well as the overall pH increase at the sediment–water interface compared to deep-water layers.

Our findings are in agreement with the recent findings by Hiriart-Baer et al. (2011), who reported a larger portion of terrestrial plant- and/or macrophyte-derived organic matter inputs and increased burial of autochthonous organic matter in the Main Basin relative to the Kempenfelt Bay. Furthermore, isotopic investigations on $\delta^{13}C$ and carbon to nitrogen ratio in the sediments showed that there is a general increasing trend in autochthonous primary productivity in recent years (Hiriart-Baer et al., 2011). Because total P loading has been decreasing since 1990, the hypothesis proposed to explain the increase in primary production may be the increase in the bio-available fraction of total P in loading.

A small difference in total release rates between fast (0.006 mg/cm²/yr) and slow processes (0.0044 mg/cm²/yr) indicates that almost 75% of P releases in a short time scale, and the sediments are not an important long-term source of diagenetically mobile P. P release is generated by a continuous flux of settling P from the epilimnion, and not by a large inventory of P stored in the sediments. Diagenesis in the upper sediment layers is fast enough that prevents any P accumulation trend.

4.1.2. Kempenfelt Bay
In contrast to the Main Basin, the BD-P fraction in Kempenfelt Bay contributes up to 40% and 57% of P release in long- and short-term scales, respectively. The other two significant fractions that contributed to P release are NaOH-NRP and HCl-TP. The proportions of these binding-forms in total P release correspondingly are 25% and 17.5% in a long-term time scale and 17.4 and 9% in a short time scale. The high amount of BD-TP fraction distinguishes the Kempenfelt Bay sediments from the Main Basin and Cook's Bay. The BD-TP fraction was the largest fraction with ca. 0.7 mg P/g DW in March 2011. Kempenfelt Bay, which is a remnant of glacial scouring (Hiriart-Baer et al., 2011), experienced the largest anthropogenic P loading along with prolonged periods of low hypolimnetic dissolved oxygen levels (Palmer et al., 2011; Young et al., 2010). It has been demonstrated that the sedimentation rates are

Bay (b) and Cook's Bay (c). Open symbols indicate March sampling and closed symbols represent September sampling.
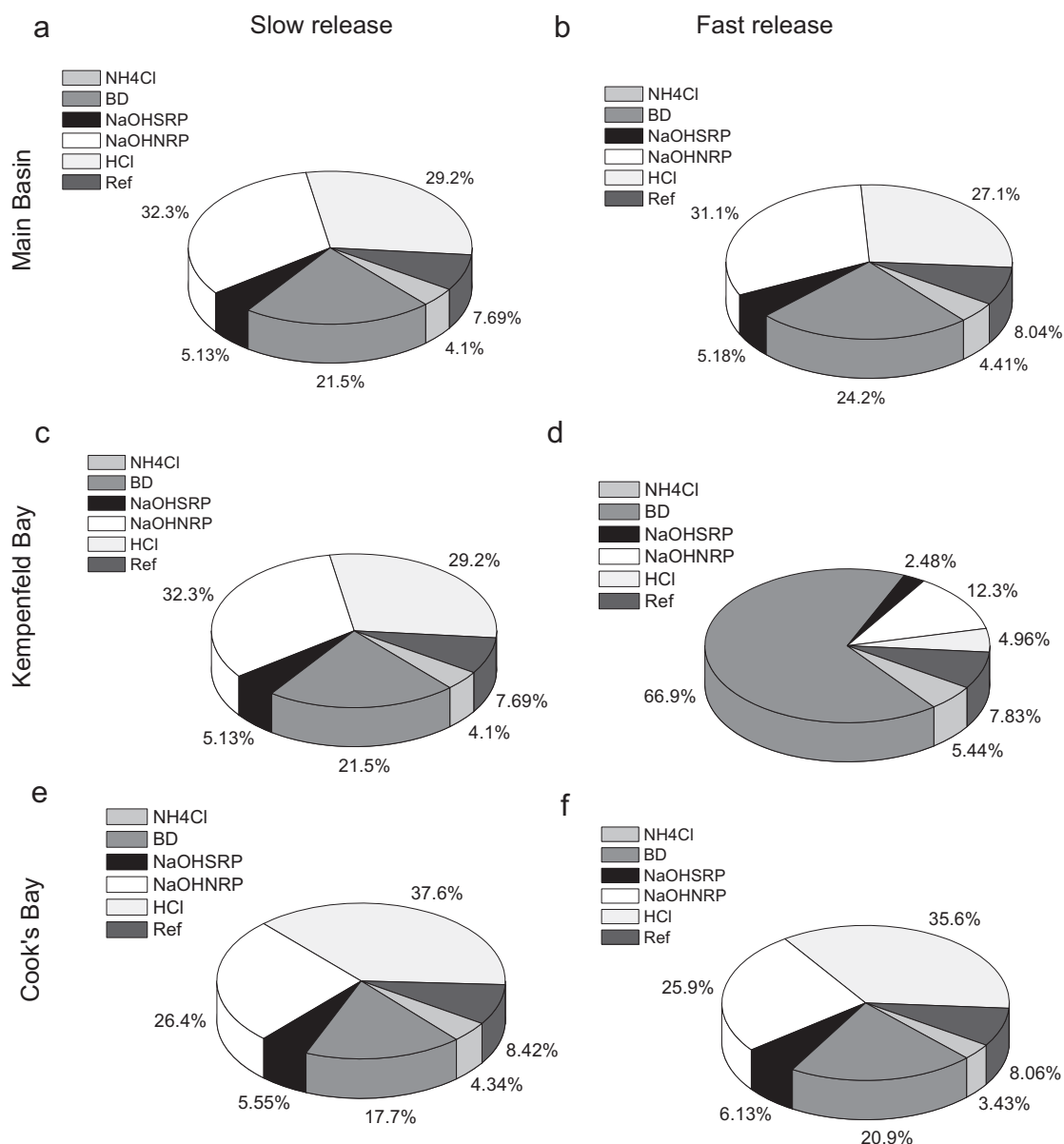
Fig. 8 – Phosphorus release from sediment: dynamics of phosphorus binding forms responsible for the slow and rapid phosphorus release in Main Basin (a, b), Kempenfelt Bay (c, d) and Cook's Bay (e, f).

recently increasing in Kempenfelt Bay, after being at their lowest values in the 1990s (Hiriart-Baer et al., 2011). Also during the 1980s, anoxic conditions were regularly manifested in late summer in the deepest part of Kempenfelt Bay due to the change in land-use or accelerated urbanization, but conditions gradually improved in the following decades (Landre et al., 2011). These events and morphology of Kempenfelt Bay may have led to the depletion of the redox-sensitive fraction, BD-TP, in the deeper sediment and the accumulation of BD-TP at the surface sediments. These findings are also conceptually on par with the occurrence of Mn-enriched layers at the surface sediments (Hiriart-Baer et al., 2011). The pH values lower than 7 in the sediment cores collected during the summer stratification are a possible reason for the decrease of HCl-fraction with the sediment depth (Fig. 4). A difference in total release rates between fast

(0.007 mg/cm^2/yr) and slow processes (0.012 mg/cm^2/yr) indicates that 58% of P releases occur within a short time scale, but a substantial fraction (42%) of diagenetically mobile P sediments represents a long-term P source in the system.

4.1.3. Cook's Bay

The TP content in the sediments of Cook's Bay is the lowest among the three studied basins in Lake Simcoe, and the limited P accumulation could be attributed to the higher sedimentation rates that may dilute P concentration as well as the substantial amount of P flushed out from Cook's Bay in the form of decaying macrophytes biomass. The TP profiles collected in March and September 2011 are qualitatively similar to the TP depth profiles recently documented along the transect section in Cook's Bay (Hiriart-Baer et al., 2011). The main P binding form that has been mobilized through

diagenesis is HCl-TP fraction, which is also the dominant fraction of TP in Cook's Bay. This fraction contributes 40.1% and 37.6% to the P release from the sediments in a long- and short-time time scale. This pattern may also be reflected in the reduced P retention values for this site (see Discussion in Section 4.3). The dominance of this fraction is caused most probably by the accelerated erosion in the catchment of Cook's Bay. Furthermore, the low TP content provides evidence that the high sedimentation rates and natural watershed sources lead to a "dilution" of P in the sediment dry matter. Hiriart-Baer et al. calculated that the TP loads into Cook's Bay are two-fold higher than in Kempenfelt Bay and about half of the inflows into the Main Basin (Hiriart-Baer et al., 2011). Sedimentation rates in Cook's Bay increased steadily over time and have doubled their actual values (Landre et al., 2011).

4.1.4. Lake Simcoe

In all basins of Lake Simcoe, organic P (NaOH-NRP) represents a substantial part ($\approx 28\%$) of P released from the sediments. Prior to 1995, phytoplankton biomass predominantly contributed to the organic P fraction (Eimers et al., 2005) but macrophytes proliferated ever since and now cover significant fractions of the nearshore zones, e.g., 65% of Cook's Bay surface area. Macrophytes most probably support the periphyton or biofilm that contributed to the NaOH-NRP fraction which is an indicator of microbial activities in the sediments (Borovec et al., 2009; Jaschinski et al., 2011). Redox-sensitive BD-TP does not play a significant role in P-release, contributing 13.6% and 15.6% over long- and short-time scales.

Lake Simcoe is a mesotrophic lake and does not release appreciable dissolved P from its bottom sediments (Table 2). The analysis of P binding forms offers insights into the mechanisms of P release in the three Lake Simcoe basins. Depending on which fraction is responsible for the P release, we may interpret the process as "biotic", e.g., changes in NaOH-NRP fraction or "abiotic", e.g., changes in HCl-TP fraction. Cycling of P at the sediment–water interface was generally believed to be a redox-driven process. Biologically-mediated storage and release of P is controlled by microbial mineralization, P incorporation into macrophyte biomass, and redox-dependent processes. The contributions of biotic versus abiotic processes will vary between eutrophic and oligotrophic systems and may be a function of sediment chemistry (Wilson et al., 2010). Importantly, the distinction between biotic and abiotic processes is sometimes difficult, as microbial activity may lead to redox or pH changes.

NaOH-SRP is mainly Al-oxides bound P while organic and biogenic P compounds (e.g., poly-P, pyrophosphates, monoesters, and diesters) make up the NaOH-NRP fraction (Ahlgren et al., 2005). The NaOH-SRP fraction reflects P burial in the sediments and was negligible in all sites and sampling dates. Permanent sorption and burial occur in sediments that have excess of $Al(OH)_3$ relative to reducible Fe hydroxide, which releases P with the onset of anoxia. Recently, Kopacek et al. (2005) developed a concept that the ratio of Al–NaOH/Fe-BD has a threshold value of 25, and lake sediments with this ratio higher than 25 do not release significant P concentrations during the development of hypolimnetic anoxia (Kopacek et al., 2005). In Lake Simcoe, NaOH-SRP is small relative to NaOH-NRP (the organic and biogenic P). However, the

Al–NaOH–P concentrations are 2.87, 2.24 and 1.99 mg/g DW in Kempenfelt Bay, Cook's Bay and the Main Basin, (Lewis Molot, personal communication), and therefore the ratio Al–NaOH–P/Fe-BD-P lies between 11 and 2. Thus, the Lake Simcoe sediments tend to have a low permanent sorption and burial linked to Al. It is possible though that the high portion of HCl-TP in lake sediments supports permanent sorption (on carbonates) and burial (Gonsiorczyk et al., 1998). This mechanism is most likely the explanation of the high P retention in Lake Simcoe sediments.

NaOH-NRP concentration has been shown to be linked to the microbial activity in the sediments (Goedkoop and Pettersson, 2000). Ahlgren et al. (2005) showed that NaOH-NRP and TP in the Swedish mesotrophic Lake Erken decreased with increasing sediment depth, reflecting the biogenic P mineralization and subsequent release into the water column over time (Ahlgren et al., 2005). We observed this trend in both Cook's Bay and the Main Basin and this leads us to infer that microbial biological processes contribute to P release in these two studied sites. On the other hand, the redox-sensitive fraction of P was a significant part of mobile P pool in Kempenfelt Bay indicating that the biogeochemical processes occurring in Kempenfelt are different from those in other Bays. In all three studied sites, HCl-TP or carbonate-P contributes around 30% to P release, suggesting that carbonate dissolution in sediments is a process that governs P release in all Lake Simcoe basins.

4.2. P mobilization in Lake Simcoe

For mesotrophic lakes, like Lake Simcoe, with ambient TP between 10 and 30 μg/L, it is important to estimate how they react to the change of exogenous loading and their vulnerability toward eutrophication, as the prevailing conditions (prolongation of thermal stratification, and hypolimnetic oxygen depletion) will be accentuated due to global climate change. A great deal of research has been performed regarding the P internal loading and retention in eutrophic and oligotrophic lakes (Hupfer and Lewandowski, 2005), but the processes in mesotrophic lakes remain still unclear.

In this study, the interpretation of the P sediment depth profiles and the associated P binding forms took into consideration both rapid and slow diagenesis processes as well as the deposition history, such as the changes in exogenous loading or land-use patterns. Generally, the amount of P that exceeds the constant P content of the deep layers can be classified as a potentially mobile pool. The sharp P decline with increasing depth indicates that most depositional P mobilization occurs within the upper sediment layers. In other words, to determine the share of P that will be released from lake sediments into the water column over time, it is essential to compare the sediment surface TP with a reference concentration, i.e., the TP concentration at which phosphorus diagenesis processes have stabilized (Carey and Rydin, 2011). The depth of the "stabilization point" depends on the sedimentation rates, which in turn are determined by the external and internal sediment loading, re-suspension, and sediment characteristics (Carey and Rydin, 2011). Recently, it has been shown that the slope of TP concentrations over the sediment depth reflects the trophic state of the lake: the increase of P at the sediment surface indicates a eutrophic lake and

a constant TP profile or even an increase with the depth is typical for oligotrophic lakes. In the case of mesotrophic lakes, such as Lake Simcoe, we deal with a transition between positive (eutrophic) and negative (oligotrophic) slopes.

A review by Carey and Rydin (2011) compiled the slopes of the linear function of sediment phosphorus with the depth in 94 lakes, suggesting a TP_{Water} threshold of approximately 15.3–20.7 µg/L (Carey and Rydin, 2011). At this water column TP concentration, the sediment P profiles fundamentally change from an increase of P with depth to a monotonic decrease. Therefore, the transition between lakes with sediments that tend to permanently bury P (i.e., oligotrophic) and lakes with sediments that release P to the water column (i.e., eutrophic) falls exactly within the suggested water column TP range for mesotrophic conditions: 10–30 µg/L.

The regression models for all our data profiles are shown in Table 3. We present the slopes of the linear function of sediment total phosphorus with depth, best sediment total phosphorus model fit, model equation, and model R^2 for each Basin and sampling time. The mean values for $ln(TP_{Water}, µg/L)$ for Kempenfelt Bay, Cook's Bay and the Main Basin are 2.69, 2.69 and 2.62 (Young et al., 2010). Following the Carey and Rydin's (Carey and Rydin, 2011) threshold of $ln(TP_{Water}) = 2.73 \pm 1.40$, where a transition between positive and negative slopes occurs (or between eutrophic and oligotrophic lakes), we can infer that all three basins are representative of mesotrophic conditions. However, the TP depth profiles showed the best fit to an exponential model, which is typical for eutrophic lakes. Also slopes of the linear function of TP with sediment depths are negative for Kempenfelt (−0.093 and −0.066), for Main Basin (−0.045 and −0.030) and for Cook's Bay (−0.023 and −0.024) (Table 3). These values are similar to those for oligotrophic Lake Stechlin (−0.091) with total phosphorus concentrations of $TP_{Water} = 18$ µg/L or Lake Muskoka (−0.085), $TP_{Water} = 17$ µg/L, but also near to values for the mesotrophic Lake Erken (−0.020), $TP_{Water} = 25$ µg/L or Lake Washington with a slope −0.035 and $TP_{Water} = 35$ µg/L. It has also been demonstrated that the thresholds in sediment P release may correlate with thresholds in sediment P burial processes (Carey and Rydin, 2011). Profiles of increasing P with depth in oligotrophic lakes might be an indicator of their relative tolerance to nutrient enrichment, especially in comparison with mesotrophic lakes, which have a limited capability to absorb additional P loads.

Our analysis is on par with these findings and the patterns of TP sediment profiles suggest release of phosphorus into the water column, although the time scales and the amount of P released are different at the three sites studied; i.e., longer and intensive P release in Kempenfelt Bay and shorter time along with quantitatively lower P release in the Main Basin and Cook's Bay. Overall, our results indicate that the Lake Simcoe sediments are still able to bind deposited P.

4.3. P retention in Lake Simcoe

From a management point of view, the primary interest is to estimate how P loading into the different basins will impact P sediment retention and consequently the Lake Simcoe water quality. P accumulation in relation to the P loading in each basin can provide insights into the local net P sedimentation (or retention) rates. From sediment depth profiles of P content and data on mass sedimentation rates (Hiriart-Baer et al., 2011; Johnson and Nicholls, 1989), we estimated the recent (1990–present), past (1860–1990) and pre-settlement (<1860) P accumulation rates in the three basins. Combining these data with available estimates on P loading and outflows from each basin P retention was calculated (Gudimov et al., 2012; Young et al., 2010). Cook's Bay received 0.144 mg/m²/yr during the period 1999–2007. Cook's Bay sediments accumulated with an annual rate of 0.052 mg/cm²/yr, which is representative of the period 0–10 years before present and 0–2 cm in sediment cores. Therefore, 0.092 mg/cm²/yr were transported to the Main Basin and the level of retention for Cook's Bay was 36%. This is a slight decrease compared to the retention value of 48% in the late 1980s (Johnson and Nicholls, 1989), and it may be partly associated with the colonization of the embayment by dreissenids and/or the recent proliferation of macrophytes. Notably, our P output estimate is very similar to the TP net loss rate of 0.106 mg/cm²/yr derived from water quality modeling (Gudimov et al., 2012). In contrast, the retention for Kempenfelt Bay increased to 70% compared to 25% in the 1980s (Johnson and Nicholls, 1989). The main explanation for the higher retention value in Kempenfelt Bay may be the lower external P loading since the 1990s (Winter et al., 2007), fewer events of severe oxygen depletion over profundal sediments since 1990s (Johnson and Nicholls, 1989), and higher end-of-summer dissolved oxygen levels in 2000–2003 (3.8–4.6 mg/L) than the long-term average (3.3 mg/L) at the 39 m water depth (Eimers et al., 2005). During the last two decades, point sources in urbanized area of Kempenfelt Bay have been successfully removed, and this change combined with the morphology of the basin may have led to an increase of P retention.

The Main Basin retained 92% of P compared to 54% in the 1980s (Johnson and Nicholls, 1989) and exported to the outlet basin with a rate of 0.003 mg/cm²/yr. Our P retention estimations are similar to a retention value for the whole lake, 88%, calculated independently from an inventory of inputs and outputs (Young et al., 2010) and are also in agreement with recent calculation based on water quality modeling (Gudimov et al., 2012).

To recap, our findings suggest substantial spatial heterogeneity in respect to P retention in large lakes. While in the two deep basins, Kempenfelt Bay and Main Basin, the P retention increased compared to the 1980s, it decreased in the shallow Cook's Bay. The increase of P retention in Kempenfelt and Main Basins caused mainly by their deep morphology and land-use

Table 3 – The linear slope of the function of sediment total phosphorus with depth (slope), intercept, and model R^2 for Kempenfelt Bay, Cook's Bay and Main Basin. Ln(TP_{Water}) values are 2.688 for Kempenfelt Bay, 2.625 for Cook's Bay and 2.695 for Main Basin.

Basin	Datum	Slope	Intercept	R^2
Kempenfelt Bay	March	−0.093	1.99	0.66
	September	−0.066	1.62	0.65
Main Basin	March	−0.044	1.40	0.60
	September	−0.030	1.17	0.62
Cook's Bay	March	−0.022	0.98	0.76
	September	−0.024	0.98	0.76

changes. On the other hand, despite the recent decline of P loading in Cook's Bay catchment, its intensive agricultural land-use in the past, its morphology with flat bottom, the colonization of the embayment by dreissenids and/or the recent proliferation of macrophytes, may lead to decrease of P retention. Therefore, P retention in Lake Simcoe evolved differently in three main basins, depending on the morphology, history, and land-use practices in their catchments.

5. Conclusions

The dynamics of P sediment depend on the lake trophic status and other biogeochemical conditions. In this study, we focused on the processes that regulate P sediment retention and release into the water column of a mesotrophic lake.

- P binding forms need to be explicitly considered, if we strive to achieve robust forecasts of P release from the sediments.
- P immobilization in the sediments of three basins in Lake Simcoe is driven by different diagenesis processes, linked to their distinct loading histories, present land-uses and morphology and as a result any variations in external P loading are not expected to bring spatially-uniform changes.
- Redox sensitive P was responsible for ca. 50% of P release in Kempenfelt Bay, carbonate-P dominates P release in Cook's Bay, and organic P is the main driver of P immobilization in the Main Basin. In all sites, carbonate-P and organic P each contribute approximately 20–30% to internal loading.
- Our study complements the work done in eutrophic and oligotrophic lakes. It is likely that in all lakes, regardless of their trophic status, organic P is mineralized in the sediments and their sorption capacity controls the extent to which dissolved P is released into the water.
- The determination of the concentrations of different P fractions and metals, and the O_2 and pH values at the sediment–water interface, offer insights into the sediment characteristics that modulate internal loading as well as into the possible mechanisms of P release.
- The techniques used in this study are potentially applicable to any lake with an available sediment record. Studies of these attributes help defining historical trophic conditions and evaluating potential impacts related to nutrient loading from anthropogenic disturbances.

Acknowledgments

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.watres.2012.12.006.

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