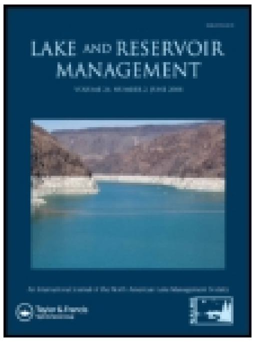

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A Simplified Assessment of Factors Controlling Phosphorus Loading from Oxygenated Sediments in a Very Shallow Eutrophic Lake

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Abstract

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Factors controlling the release of bioavailable soluble reactive phosphorus (SRP) from sediments in very shallow lakes are not fully understood. Our approach involved relatively simple measurements of four factors affecting the calculation of internal phosphorus load: the number of sampling sites, sediment freezing, incubation temperature and oxic state in Cootes Paradise Marsh, now a very shallow (Z = 70 cm) eutrophic degraded urban lake in Ontario, Canada. Our results indicate that all of these factors need to be considered when attempting to estimate the internal phosphorus load of a shallow system. The total internal load of phosphorus in Cootes Paradise Marsh was 34% of the total loading (both internal and external), with diffusion from the sediment accounting for 23% of all phosphorus inputs. Large carp are now excluded from the lake and were estimated by difference to have contributed 23% to summer internal loading.

Key Words: eutrophication, phosphorus, internal loading, wetlands

Control of cultural eutrophication usually focuses on reducing external inputs of phosphorus. However, numerous researchers have found that internal loading from phosphorus-rich sediments can delay restoration measures by sustaining primary production even after most external phosphorus loadings have been reduced (Jacoby *et al.* 1982; Lijklema 1993). For example, no improvements were observed in Lake Søbygaard, Denmark or Barton Broad, England for 8 to 12 years after a 80 to 90% reduction in external loading (Phillips *et al.* 1994; Søndergaard *et al.* 1993). Similarly Shagawa Lake, Minnesota, continued to be highly productive particularly during July and August despite an 80% reduction in external phosphorus supplies (Larsen *et al.* 1981). In contrast, Lake Sammamish, Washington saw improved water quality after a decrease in total phosphorus (TP) loading by one-third through wastewater diversion; however, improvements were not seen during the first 6 years after diversion (Welch *et al.* 1986).

In highly eutrophic, anoxic systems, sediment can release phosphorus at levels comparable to external sources (from 30 to 100%) and is the controlling factor in maintaining elevated concentrations of phosphorus in the water column (Jacoby *et al.* 1982; Nürnberg 1988; Auer *et al.* 1993). Increases in internal loading in shallow eutrophic lakes are usually prominent in the summer months when external loading is low and anoxia occurs (Riley & Prepas 1984), as evidenced by increases in TP concentrations in the water column during these months.

Although they are not well studied, coastal marshes of the Laurentian Great Lakes exhibit many of the same limnological responses to cultural eutrophication as shallow lakes in other parts of the world (Chow-Fraser 1999). They tend to be algal-dominated, lack submersed aquatic macrophytes, and are very turbid (up to 276 NTU) from wind resuspension and bioturbation (Chow-Fraser *et al.* 1998; Lougheed *et al.* 1998). Cootes Paradise Marsh, a very shallow eutrophic lake located in the city of Hamilton, Ontario, Canada (Fig. 1) is an example of such an ecosystem that was degraded after more than sixty years of nutrient and sediment enrichment from a local sewage treatment plant. As part of an overall

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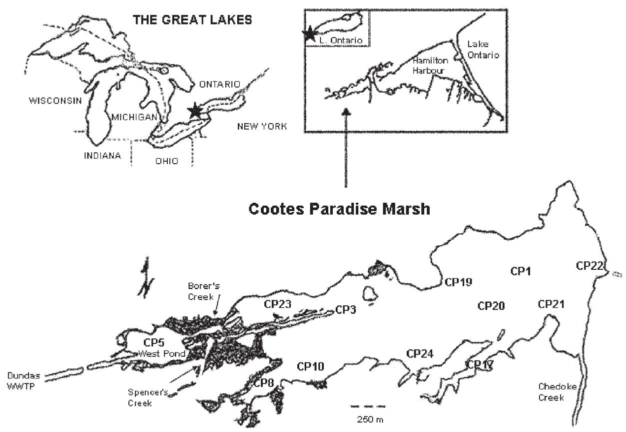

Figure 1.-Map of Cootes Paradise Marsh. Approximate locations of samplings stations are indicated in bold. Shaded regions represent areas of the wetland that remain vegetated.

Table 1.-Mean total phosphorus (TP) and chlorophyll *a* (CHL*a*) concentrations at 7 sites in Cootes Paradise Marsh over mid-May to mid-September during 1993 and 1994 (Lougheed & Chow-Fraser 1997).

Site	TP ($\mu g\ L^{-1}$)	CHL*a* ($\mu g\ L^{-1}$)
CP1	144	39
CP3	97	18
CP5	315	146
CP8	216	27
CP10	149	57
CP12 (CP19 this study)	157	51
CP13 (CP17 this study)	187	51

marsh restoration program, a nutrient mass balance study was conducted by Prescott & Tsanis (1997) to determine the relative contributions of all phosphorus sources. They found that during the summer months, internal phosphorus sources, which they identified to be wind-induced sediment resuspension and bioturbation by a fish population dominated by common carp, accounted for 57% of the total phosphorus load. They had not considered the possible contribution of phosphorus diffusion into the water column resulting from biological or chemical activities at the water-sediment interface, a process that is known to contribute significant amounts of phosphorus to eutrophic shallow waters.

There are two methods commonly used to directly quantify internal loading: 1) measuring seasonal accumulation of phosphorus in anoxic hypolimnia and 2) conducting in vitro phosphorus release experiments with sediment cores. Because many systems are very shallow and do not stratify, such as Cootes Paradise Marsh (mean depth of 0.7m, Chow-Fraser 1999), the first method is not appropriate. We sought to develop an efficient method using a few key environmental parameters and assumptions from which we could measure potential P release. The literature on lakes indicates that the most important environmental parameters are oxidation-reduction status, degree of mixing, resuspension and/or bioturbation activities, amount of bacterial activity, ambient temperature, sediment composition, and concentration gradients in pore water (Premazzi & Provini 1985). We considered those parameters that we could readily manipulate and measure in the laboratory, oxidation-reduction status, freezing and ambient water temperature. To monitor changes in microbial community structure, and presumably bacterial activity, we also performed in vitro experiments with sediments collected monthly over the summer season (June to August inclusive), which allowed us to compare our results with previous evaluations of P loadings in the marsh. In this work, we demonstrate the importance of phosphorus loading to the overall budget in Cootes Paradise Marsh.

Description of Study Site

Cootes Paradise Marsh is approximately 250 ha and lies within an 850 ha wildlife sanctuary located at the western end of Hamilton Harbour. Prior to the early 1900s, Cootes Paradise Marsh was almost completely vegetated with emergent vegetation (Painter *et al.* 1989), but by the early part of the twentieth century, only 80% of the marsh was vegetated. Over the century, the macrophyte community continued to decline to the extent that by 1993, only 10% of the marsh was covered with emergent vegetation (Chow-Fraser *et al.* 1998). The cause of the decline has been partly attributed to eutrophication resulting from historic nutrient loadings of the Dundas Wastewater Treatment Plant (WWTP) and more recent loadings from agricultural and urban runoff (Remedial Action Plan for Hamilton Harbour Stage 2 Report 1992). A remedial action plan under the Great Lakes Water Quality Agreement was formulated in 1992 to improve water quality in both Hamilton Harbour and Cootes Paradise Marsh to enhance sediment quality and fish and wildlife habitat. Cootes Paradise Marsh was included in the plan because it was considered a substantial source of suspended sediment and phosphorus to the Harbour and is the largest residual spawning and nursery habitat for the warm-water fish community of Hamilton Harbour (Remedial Action Plan for Hamilton Harbour Stage 2 Report 1992).

West Pond (CP5, Fig. 1) is a sewage lagoon in the marsh, located just east of the Dundas WWTP outfall. Because of its proximity to the WWTP outfall, this area has elevated nutrient concentrations (Chow-Fraser 1999) compared with other long-term monitoring sites such as CP8 (Table 1). Assuming that the highest phosphorus release rates were associated with the most eutrophic sediments, we studied West Pond sediment to determine the maximum potential internal loading. By collecting sediment from West Pond, where there was no vegetation, we eliminated confounding effects of macrophyte uptake and/or secretion of nutrients (Carpenter 1981). Since West Pond currently has only a fringe of emergent vegetation, it is more characteristic of a shallow lake than a typical wetland and results from this study may be directly compared with data from published studies of shallow lakes.

Remediation Efforts

The Dundas WWTP was constructed in 1919 to provide primary treatment to the town's sewage before releasing the effluent into West Pond. Prior to its construction, raw sewage was discharged directly into the marsh and although the facility now provides tertiary treatment (sand filters to improve phosphorus and suspended solids removal), historically it was the primary contributor of nutrients responsible for the eutrophication of Cootes Paradise Marsh (Remedial Action Plan for Hamilton Harbour Stage 1 Report 1992; Chow-Fraser *et al.* 1998).

Carp (*Cyprinus carpio*) were first recorded in the marsh in 1911 (Homes & Whillans 1984). The effects of carp on vegetation have been well documented: feeding and spawning activities uproot submergent macrophyte beds and increase turbidity levels (Lougheed *et al.* 1998). The Cootes Paradise Fishway was subsequently installed at the outlet to reduce carp disturbance to the marsh. The Fishway prevents the access of large carp (>30 cm) and facilitates access and departure of other species. Despite restoration efforts and tremendous declines in external loading from the WWTP (45 $kg \cdot d^{-1}$ in the 1970s to levels below 4 $kg \cdot d^{-1}$ in recent years), phosphorus concentrations remain high (Chow-Fraser *et al.* 1998).

Materials and Methods

Long-term water quality monitoring of Cootes Paradise Marsh has shown that certain locations within the marsh are more eutrophic than others (Table 1). Based on this knowledge, we selected 11 sites (Fig.1) to determine if large differences in sediment P release rates exist. In lieu of cores, sediment samples were collected in June 1999 with an Ekman Grab to retrieve the top 5 cm of sediment. Although this method increases the sediment-water interface as compared to cores, we do not feel this will produce substantially higher flux rates. The long axis of Cootes Paradise Marsh is oriented in the direction of prevailing winds and hence, the marsh is quite vulnerable to wind-induced resuspension (Chow-Fraser 1999). Excess water was drained and samples were stored in Freezer Ziploc™ bags and frozen for 2 months prior to experimentation. Phosphorus release experiments were conducted in the manner of Chow-Fraser *et al.* (1996). Wet sediment was spread over the bottom of acid-washed glass jars in triplicate and deionized water was added to each jar. Jars designated for "aerobic" treatment were covered with foil that received several puncture holes with a pencil tip to allow a greater rate of air exchange. All jars were incubated in dark growth chambers for up to 8 days at 25°C. Three jars from each treatment were removed from their respective growth chamber daily. Water samples were extracted from each jar using a pipette to limit disturbance at the sediment-water interface. Samples were analyzed for soluble reactive phosphorus (SRP) and total phosphorus (TP) using the molybdate blue method (Murphy & Riley 1962) to measure inorganic P in the extracts. The slope of the best-fit line relating phosphorus release ($mgP \cdot m^{-2}$) to time (d) was used to estimate release rate ($mgP \cdot m^{-2} \cdot d^{-1}$).

Since the above sediments had been frozen prior to experimentation, we collected parallel sediment samples from CP5 in June 2000 to assess the effect of freezing. One set was used immediately to determine phosphorus-release rates, while the other was frozen for up to 4 months prior to experimentation. Release rates were determined as indicated above.

We conducted release rate experiments over a range of temperatures (10, 15, 20, 25°C as well as the maximum reported temperature in the field) using CP5 sediment to determine the effect of temperature on phosphorus release rates.

In release experiments, simulated oxic and anoxic conditions were created with CP5 sediment using methods described by Boström & Pettersson (1982) through the addition of nitrate (5 mg N l^{-1}) and acetate (10 mg C l^{-1}), respectively. Nitrate produces a redox potential slightly less than that of O_2 and prevents release of phosphorus, while acetate stimulates microbial activity, increasing oxygen consumption and thus lowering the redox potential to a point where iron-phosphate complexes dissolve. We compared the results for all treatments (control, addition of nitrate, addition of acetate) to assess the relative effect of oxic state on release rate measurements. The use of acetate to simulate anaerobic conditions dramatically increased P release rates, while the use of nitrate did not appear to have any effect compared to the control. An ANCOVA indicated that release rates under the influence of nitrate did not differ significantly from the control ($p=0.4903$) and therefore, the results suggest that the addition of nitrate is not necessary to maintain aerobic conditions. Jars designated for "anaerobic" treatment were tightly covered with foil to limit gas exchange. In addition, we measured diel dissolved oxygen (DO) concentrations at the sediment-water interface at CP5 in July 2000 to determine whether conditions approach anoxia in the field.

Table 2.-Literature data on ranges of P release rates ($mgP \cdot m^{-2} \cdot d^{-1}$), determined from laboratory incubations.

Study	Sediment Condition	TP	SRP
This study	Oxic (fresh and frozen)		0.96-28.3
Premazzi & Provini (1985)	Oxic	1.80-3.99	
Nurnberg (1988)	Anoxic	0.04-9.22	0.09-6.51
Auer *et al.* (1993)	Anoxic		13.33
Pant & Reddy (2003)	Oxic		4-25
Pitkänen *et al.* (2001)	Oxic		0.013
Krivstov *et al.* (2001)	Oxic	7-11	
Andersen & Ring (1999)	Oxic	0.82-2.48	
Andersen & Ring (1999)	Anoxic	4.85-9.78	

Results

There was a significant linear relationship between SRP and TP release rates (SRP release rate = 0.742*TP release rate - 0.349, $r^2 = 0.90$). Since there was a high correlation between SRP and biologically available P (Nürnberg & Peters 1984), it can be assumed that most of the P released from Cootes Paradise Marsh sediment is biologically available (Nürnberg 1988). The slope of the relationship (0.74) indicates that the proportion of SRP changed predictably with magnitude of P release. Even though the SRP:TP ratio was not constant, the relationship was predictable, and since determination of TP release rates requires an additional digestion step, we decided to focus the remainder of the investigation on SRP release rates.

A significant difference among previously frozen sediment samples from the eleven sites within Cootes Paradise Marsh in June 1999 was observed with respect to SRP release rates (Table 1; P<0.0001). The "oxic" rates reported in this study ranged from 0.96 to 28.3 $mgP \cdot m^{-2} \cdot d^{-1}$ which are within the range of published data, although values for 3 sites (CP5, CP8 and CP17) were substantially greater than that of the highest reported for lakes (see Table 2). These results indicate that phosphorus release rates are highly variable throughout Cootes Paradise Marsh and reveal that one cannot assume a homogeneous sediment when attempting to estimate the internal load in a morphologically diverse wetland.

We determined that freezing samples produced mean release rates five times higher (17.18 $mg \cdot m^{-2} \cdot d^{-1}$) than those obtained from CP5 oxic fresh sediments (3.21$mg \cdot m^{-2} \cdot d^{-1}$). We hypothesize that freezing may have resulted in cell lysis with subsequent release of phosphorus to the overlying water. Alternatively, freezing may have altered sediment geochemistry.

Increasing incubation temperature produced elevated phosphorus release rates in freshly collected sediment (Fig. 2),

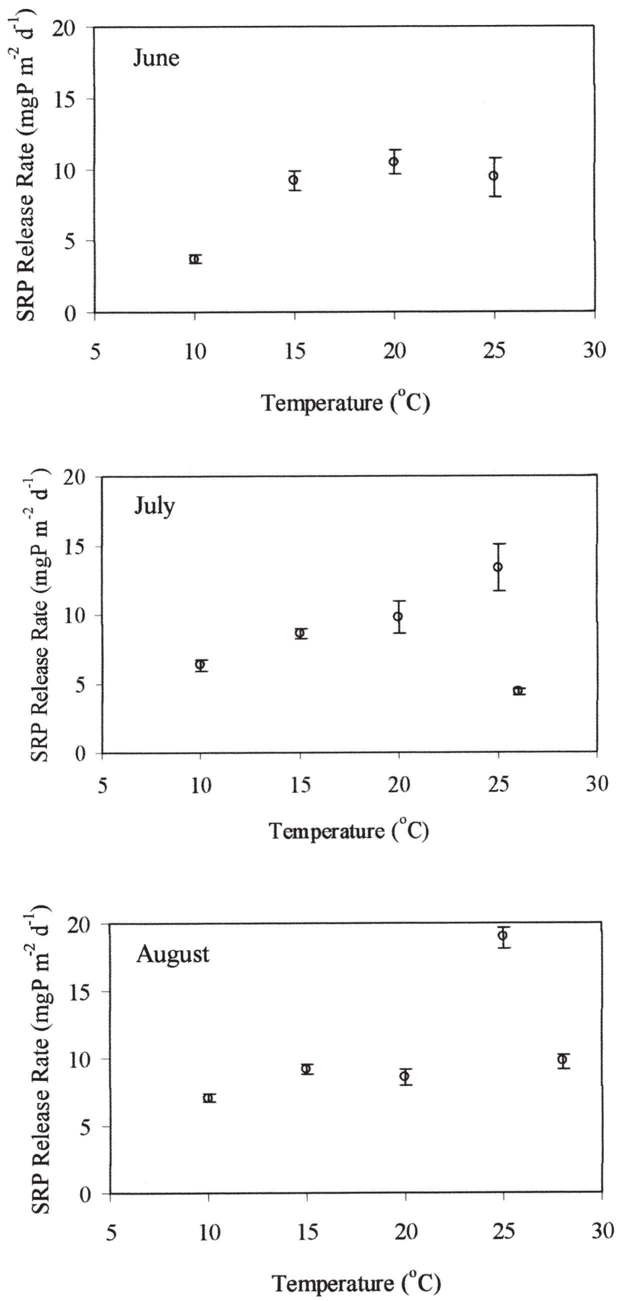

Figure 2.-Relationship between temperature and SRP release rate from freshly collected CP5 sediment under anaerobic conditions in June, July and August.

though rates did not double for every 10°C increase, as expected. Instead, Q_{10} values ranged from 1.03 to 2.81 (Table 3) and no pattern was evident, although values for July were less variable than those of June and August. Release rates dropped dramatically at temperatures greater than 25°C. Figure 2 also shows the importance of time of sampling. For example, sediments collected in June had a much lower

Table 3.-Q_{10} values of anaerobic SRP release rates ($mgP{\cdot}m^{-2}{\cdot}d^{-1}$) from freshly collected CP5 sediment sampled in 2000.

Month	Temperature Range (°C)	Q_{10}
June	10 to 20	2.81
	15 to 25	1.03
July	10 to 20	1.54
	15 to 25	1.55
August	10 to 20	1.21
	15 to 25	2.06

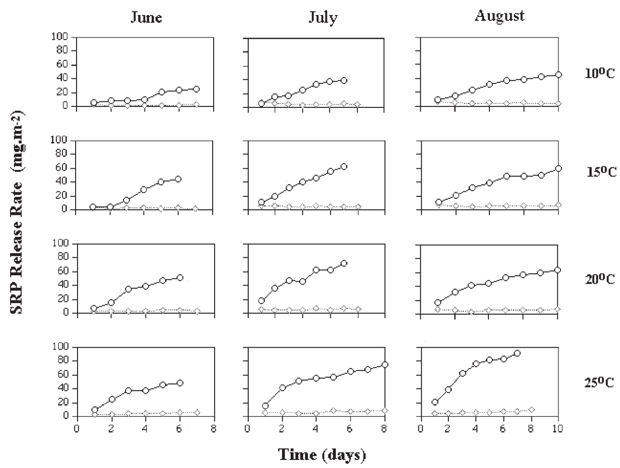

Figure 3.-Soluble reactive phosphorus (SRP) release rates from freshly collected CP5 sediment under simulated anaerobic (open circles) and aerobic conditions (diamonds). Vertical bars are standard errors.

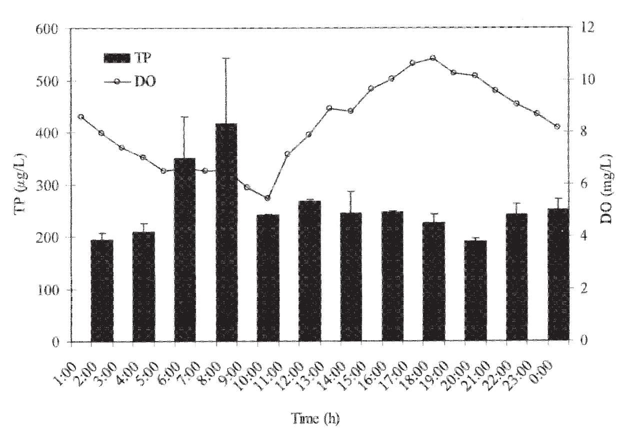

Figure 4.-Diel changes in total phosphorus (TP) and dissolved oxygen (DO) concentrations (approximately 10 cm above the substrate) in West Pond (CP5). Measurements were taken 17/07/00.

release rate (3.71 $mg{\cdot}m^{-2}{\cdot}d^{-1}$) at 10°C compared to both July (6.33 $mg{\cdot}m^{-2}{\cdot}d^{-1}$) and August (7.07 $mg{\cdot}m^{-2}{\cdot}d^{-1}$).

Generally, phosphorus concentrations in overlying water increased linearly with time for "anaerobic" treatments (Fig. 3). By comparison, rates associated with the "aerobic" treatments were more variable and difficult to summarize. In many cases, concentrations either did not change or actually declined with time. Regardless, phosphorus release rates were substantially greater in "anaerobic" treatments. The effect of low DO concentrations on P-release was reflected in our field data. An *in situ* diurnal DO profile taken about 10 cm above the sediment at CP5 showed a minimum of 6 mg/L at 10:00 a.m. (Fig. 4), and this was associated with higher TP concentrations from 6:00 to 8:00 a.m., providing further evidence of the influence of oxygen depletion on phosphorus release from sediments.

Using fresh sediment release rates determined at only 2 sites (CP5 and CP1) under oxic and anoxic conditions and at both maximum and minimum in situ monthly temperatures along with 'marsh' area, we estimated the internal load in Cootes Paradise due to net mineralization and/or diffusion to be 8.8 $kg{\cdot}d^{-1}$ (Table 4). As previously indicated, Prescott & Tsanis (1997) estimated an internal load in Cootes Paradise Marsh of 23.7 $kg{\cdot}d^{-1}$ (assuming 57% of 41.6 $kg{\cdot}d^{-1}$, their values), which could be apportioned among carp bioturbation, wind resuspension and mineralization (Table 4); however, this estimate was made prior to the construction of the Cootes Paradise Fishway, which has effectively excluded 90% of the carp from the marsh since 1997. Using exclosure experiments, Lougheed *et al.* (1998) demonstrated that exclusion of carp reduced water turbidity and nutrients up to 45%. Using this information, we calculated that internal loading from wind resuspension alone should be 4.2 $kg{\cdot}d^{-1}$, assuming that loading from mineralization and diffusion remains the same irrespective of the presence/absence of carp. Assuming that contributions from carp bioturbation are negligible, this analysis indicates that internal loading through wind resuspension, remineralization and diffusion still accounts for 34% of the total P-load in Cootes Paradise Marsh.

Discussion

Our results have shown that the number of sites, site selection, sampling date, sample storage, incubation temperature and oxic state are all important considerations when conducting sediment phosphorus release experiments. The number of sites selected for such a study will influence results; too few could potentially yield misleading results, while too many may be redundant. For example, 11 sites were used in this study and the results indicated that 8 sites would have been sufficient (the release rates of CP1, CP20 and CP21 did not differ significantly). However, at the outset we speculated that there may have been differences based on water flow

Table 4.-A comparison of seasonal (June-August) phosphorus loading in Cootes Paradise Marsh following carp exclusion.

Source	Load (kgd^{-1})	% of All Sources
External Loading[1]		
Dunday WWTP	3.2	8.2
Spencer Creek	3.7	9.5
CSO	3.0	7.7
Urban Runoff	15.9	41.0
Total of External	**25.8**	**66.4**
Internal Loading (after carp exclusion)[2]		
Wind resuspension	4.2	10.8
Net mineralization/Diffusion	8.8	22.7
Total of Internal	**13.0**	**33.5**
Internal Loading (prior to carp exclusion)[3]		
Bioturbation/diffusion/ mineralization	23.7	57
Total of all sources	**38.8**	**100**

[1]XCG Consultants (1997)

[2]Internal loading was assumed to be 57% of the total external load prior to exclusion of carp (Prescott & Tsanis 1997). The contribution from carp was assumed to be 45% of the external load (Lougheed *et al.* 1998) which therefore generated an estimated 13.0 $kg{\cdot}d^{-1}$ once large carp were excluded by a barrier. Using our estimates of SRP release rates and marsh area, we predict that 8.8 $kg{\cdot}d^{-1}$ was due to net mineralization and diffusion with the remaining 4.2 $kg{\cdot}d^{-1}$ attributed to wind resuspension.

[3]Prescott & Tsanis (1997)

patterns. Therefore, site selection should be based on any number of characteristics including the purpose of the study, sediment type, known chemical characteristics of the sediment, the presence or absence of macrophytes, water flow patterns or water quality.

The SRP release rates from fresh sediment are substantially lower than from frozen sediment. Freezing of the sediment inactivates bacteria that would normally produce spores and eliminates their influence on internal loading through phosphorus sequestering. In this case, release may be a function of chemical processes (diffusion, adsorption/desorption) alone and could potentially under- or overestimate internal loading. deMontigny & Prairie (1993) observed an increase in phosphorus release from sediment that had been sterilized (*i.e.*, no viable microbial community). Our results support this finding: freezing, which presumably kills the microbial flora, can result in higher phosphorus release rates than when fresh samples (with presumably viable bacteria) are used. We conclude that benthic bacteria may be a relatively large phosphorus sink, attributable to P release through cell lysis or altered sediment geochemistry and thus, only fresh sediment with minimal storage time should be used to conduct phosphorus release experiments.

Increases in temperature accounted for a substantial proportion of the variability in sediment P release. Temperature is often overlooked as an environmental parameter to be included in predictive models. Jensen and Andersen (1992) examined SRP release in aerobic sediments and discovered that the effects of lake water temperature was more pronounced than that of nitrate and pH, accounting for greater than 70% of the seasonal variation in gross internal loading. Temperature has an indirect effect on P release by increasing microbial activity and hence, oxygen consumption. It also increases organic matter mineralization and liberates inorganic phosphates (Boström & Pettersson 1982), although sediment bacteria do not necessarily release P when they mineralize settled organic matter (Gächter & Meyer 1993).

Interestingly, we discovered that anaerobic release rates at temperatures above 25°C did not increase linearly (in fact, they were significantly lower than those at 25°C, Figure 2) in the in vitro experiments. These observations may either reflect autolysis of cells and corresponding decline in phosphorus release or enhanced microbial growth and increased demand of phosphorus. It is also possible that lower release rates were observed due to microbial community succession. We were not too concerned about this phenomenon in our internal load calculations because average daily temperatures did not rise beyond 26°C in Cootes Paradise Marsh during this study. Decreasing anaerobic release rates may be significant for P release in aquatic systems that reach high temperatures. Regardless of the causes, it is typically assumed that increases in temperature (as are predicted to occur with global warming) will result in increased phosphorus release from sediment. This finding suggests that, depending on the magnitude of temperature increase with global warming climate change, internal loading may in fact subside in Cootes Paradise Marsh at least for a period of time. Our results also indicate that one should not make the assumption that reaction rates double for every 10°C rise in temperature.

Choosing an incubation temperature is somewhat difficult. The seasonal average should be chosen to incubate the sediment samples to provide a general release rate. Ideally, it is preferable to keep and incubate sediment samples at the same temperature as in the field (*i.e.*, sample over a range of field temperatures) to minimize disruption to the microbial community and provide the most accurate results.

The extent and duration of anoxia is also very important in developing predictions since the amount of phosphorus released depends on these factors (Nürnberg 1988), although release can still be substantial in well aerated waters (Premazzi & Provini 1985). In shallow systems (*i.e.*, Cootes Paradise Marsh) without emerging vegetation, wind and bioturbation processes dominate P releases (Marsden 1989).

In these systems, epipelic algae are thought to mediate exchange across the sediment/water interface through changes in redox conditions (Carlton & Wetzel 1988). Our work does not explicitly reveal anoxia at the sediment-water interface, but our observations do suggest that conditions approaching anoxia may occur in Cootes Paradise Marsh. Further work is required to confirm the duration and magnitude of the anoxia. Therefore, when conducting phosphorus release experiments one needs to account for anoxic conditions at sites even in shallow, non-stratifying systems.

Through direct measurements of release rates from sediments using the aforementioned guidelines, we have verified that mineralization can easily contribute as much 22.6% of the total phosphorus load calculated in Prescott and Tsanis' (1997) mass-balance study. It would have been extremely useful to the restoration program if we could have determined the extent to which sediments would continue to release phosphorus, but that would have required mass balancing of phosphate as well as all potential adsorbents and absorbents (Lijklema 1993). Shallow systems, such as Cootes Paradise Marsh, are very dynamic, heavily influenced by meteorological conditions that are unpredictable and therefore difficult to incorporate into a scientific study. Difficulty in forecasting wind velocities, direction and ambient water temperatures will likely emerge as the main obstacle to proper assessment of the long-term release of phosphorus from the sediments of this and other degraded coastal wetlands of the Great Lakes.

The internal phosphorus budget reported in this study is only a portion of the total internal load as it only takes into account mineralization and diffusion of the surface sediment and does not consider resuspension due to wind or bioturbation from deeper layers or horizontal transport of contaminated sediments. Since release experiments in this investigation were conducted with only the top 5 cm of sediment, future studies should be carried out to verify the extent to which our results have been biased by the sampling protocol.

In this work, we have demonstrated the significance of phosphorus loading to the overall budget in Cootes Paradise Marsh and have attempted to develop some guidelines helpful to researchers attempting to estimate internal P loads. We hope that our findings will direct future research to establish more generally applicable predictive models for shallow lake/wetland environments.

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