Evaluation of iron-phosphate as a source of internal lake phosphorus loadings

Ellen L. Petticrew*, Joselito M. Arocena

*Faculty of Natural Resources and Environmental Studies, University of Northern British Columbia, 3333 University Way,
Prince George, BC V2N 429, Canada*

Abstract

Biological, physical and chemical characteristics of the water column of a shallow ($z_{max} = 9.2$ m), small (surface area 3.8 km^2) residential and recreational lake near Prince George, British Columbia, indicated that the system was being loaded internally with phosphorus (P) from the sediments. The abundance of P released from the fine glaciolacustrine, and organic rich sediments was resulting in excess algal and weed growth. It was postulated that iron–phosphate reduction at redox potentials below approximately 200 mV and/or bacterially mediated orthophosphate (PO_4–P) releases could be occurring. The development of an appropriate nutrient management strategy required that the process associated with the sediment P release be determined. The MINTEQA2 geochemical model was used to predict the release of orthophosphate (PO_4–P) into the interstitial water with the assumption that P is present alternately as strengite, variscite and hydroxyapatite. The predicted release of PO_4–P from these P containing minerals was compared to the concentration of PO_4–P and total phosphorus (TP) in the overlying hypolimnion. In order to improve the accuracy of the model prediction, the proportion of the sediment present as iron-bound phosphate was estimated. A significant correlation between the observed hypolimnetic TP and interstitial PO_4–P concentrations as predicted from iron-bound P dissolution ($r^2 = 0.59$) was found. Total phosphorus release rates to the hypolimnion were also found to be strongly correlated to the iron-bound P component of the sediment ($r^2 = 0.88$). Multivariate regression analyses showed significant relationships between hypolimnetic PO_4–P and sediment iron-bound P, Eh, and interstitial Fe ($r^2 = 0.76$). These results provided sufficient evidence to conclude that PO_4–P in the system is predominantly bound to Fe-containing minerals and therefore could be managed using treatment techniques that address iron-bound phosphates. © 2001 Elsevier Science B.V. All rights reserved.

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* Corresponding author. Tel.: +1-250-960-6645; fax: +1-250-960-5538.
E-mail address: ellen@unbc.ca (E.L. Petticrew).

1. Introduction

In August of 1993, a major fish kill on Tabor Lake resulted in the creation of a task force to evaluate potential approaches to lake management and restoration. Tabor Lake was known to be eutrophic with extensive weedbeds and noxious algal blooms. In 1994, volunteer workers sampled the open water column weekly for temperature, oxygen, chlorophyll *a*, and total phosphorus. A full lake survey of the phosphorus content of the bottom sediments also was undertaken. The sediments exhibited high levels of total phosphorus (mean = 1318, S.E. = 99 μg $g_{dry\ wt.}^{-1}$) and high organic matter content ($> 30\%$) (Petticrew, unpublished data). In 1995 a phosphorus budget was determined (Simmons, 1997) and both sediments and weeds were identified as problematic in the context of internal loadings. Simmons (1997) suggested that the focus on management should take two approaches, which included regulating weed biomass and managing sediment P release and/or hypolimnetic P concentrations. Weed biomass control by harvesting had been initiated in 1994 but no approach to deal with the internal loading from the sediment had been decided upon.

Data from the deep portion of the lake indicated a strong inverse correlation between hypolimnetic phosphorus and oxygen concentrations. The process of iron-phosphate dissolution with the reduction of Eh (Kamp-Nielsen, 1974; Enell and Lofgren, 1988; Nürnberg, 1988) was assumed to be of importance, but the role of organic matter was also considered a potential source of available P. Ostrofsky et al. (1989) reviewed the literature and noted that sediment organic P was a significant factor in anoxic release of P in some systems (Bates and Neafus, 1980; Bostrum, 1984). Montigny and Prairie (1993) found that sediment bacterial cell lysis following anoxia and/or sterilization was a direct source of orthophosphate to the overlying water column. As Tabor Lake sediments were in excess of 30% organic matter, we were interested in evaluating the relative significance of the mineral and organic sources of phosphorus.

In the summer of 1996, data were collected from the sediment, interstitial and bottom waters to allow the use of the MINTEQA2 geochemical assessment model (Allison et al., 1991). The objective was to determine if iron-bound phosphates were the predominant sediment component associated with the release of phosphorus to the hypolimnion during periods of anoxia. This information would allow the evaluation of potential approaches to managing Tabor Lake, as a variety of methods for inactivating iron-bound phosphate have been documented (Cooke et al., 1993). While some of these involve the direct treatment of the sediments (alum and calcium carbonate additions), other approaches treat the oxygen concentrations of the hypolimnetic waters. If iron-bound phosphate or other mineral-P forms were not found to be associated with the anoxic release, bacterially-mediated processes would be considered the alternate source and regulation of hypolimnetic oxygen levels in the lake would be recommended as the management approach.

2. Study site and methods

Tabor Lake is a small residential and recreational lake located 10 km east of Prince George, British Columbia, Canada. The lake has a maximum depth of 9.2 m and a mean depth of 5.4 m. The watershed size is approximately 25 km^2 with a mix of residential and forested land uses. Seasonal means, from samples taken between 1974 and 1992, of spring TP, summer TP and chlorophyll *a* are 0.025, 0.025 and 10.5 respectively (Carmichael, unpublished data). In the spring of 1996 a weir was installed at the lake outlet to allow regulation of the water level. This combined with weed harvesting were the initial approaches to lake management.

Weekly sampling of the water column at the deepest portion of the lake was undertaken from late May to early October of 1996. Water temperature and oxygen measurements were taken from the surface to a depth of 8.5 m at 0.5 m intervals using a calibrated YSI Model 57 meter (accuracy $\pm$ 0.1 mg l^{-1}). Samples of total phosphorus (TP) and orthophosphate (PO$_4$–P) were collected from the epilimnion (0.5 m) and hypolimnion (7.5 m)

approximately 3−4 days following the date of sediment sampling. Water samples with duplicates and blanks were submitted to a federal government laboratory, Pacific Environmental Science Centre (PESC), for total and orthophosphate analysis using the molybdenum blue method (Eaton et al., 1995). Sediment was collected using an Eckman dredge. Water in the dredge was carefully decanted and measurements of pH and Eh were taken using a standardized Omega PHH-82 meter (accuracy ± 0.015 pH, ± 1 mV Eh). These measurements were obtained over a 9-week period from 25 July to 25 September. Duplicate subsamples of sediment were taken from the dredge using a 6.4-cm diameter core tube. The core was then subdivided into 0−3.9 cm and 4−8 cm sections and bagged. The sediment was returned to the university laboratory (UNBC) and centrifuged at 4°C to separate the interstitial water from the sediments. Both materials were sent to the PESC laboratory for analysis of anions and metals using inductively coupled plasma spectroscopy. Calcium, iron and aluminum were measured in both the water and sediment while total phosphorus was analysed only on the sediment. Separate sediment subsamples were analysed at UNBC for water and organic matter content by drying at 110°C and ashing at 550°C, respectively.

We used MINTEQA2 (Allison et al., 1991) to predict the release of orthophosphate from the bottom sediments (4−8 cm) to the interstitial water. This prediction required input values of Eh, pH, temperature, elemental composition of the interstitial solution and total P (mg $g_{wet\ wt.}^{-1}$) in the sediments. We had planned to evaluate the role of variscite ($AlPO_4 \cdot 2H_2O$) in contributing to interstitial phosphorus but the levels of interstitial Al were at or below detection limit over the 9 week study period. To evaluate the role of iron and calcium we assumed that the phosphate content in the sediment is alternately in the form of strengite ($FePO_4 \cdot 2H_2O$) or hydroxyapatite [$Ca_5(PO_4)_3OH$]. A further assumption included an equilibrium condition between the interstitial solution and the sediment at 1.0 atm pressure. The range of sampled water depths (7.5−9.0 m), combined with the sensitivity of this parameter in the MINTEQA2 model, allowed for this assumption.

A further refinement of the model included a prediction of PO_4−P released as a function of the amount of bicarbonate-dithionite-P (BD-P) in our samples. This component of the sediment better represents iron-bound sediment (Nürnberg, 1988). The amount of BD-P was estimated from the empirical relationship presented by Nürnberg (1988). Sediment from seven lakes that exhibited hypolimnetic anoxia and covered a wide trophic range was used to develop her relationship. The equation used for the BD-P estimates was BD-P $= -0.31 + 0.298$ TP ($r^2 = 0.90$, $P < 0.0001$, $n = 76$) (Nürnberg, 1988).

MINTEQA2 predictions of interstitial orthophosphate were compared to observed phosphate concentrations in the overlying water to evaluate the role of the various sediment components in altering hypolimnetic phosphorus concentrations. Daily hypolimnetic release rates of phosphorus from the sediment were calculated using differences in both the weekly hypolimnetic PO_4−P and TP loads. The concentration of the P forms combined with the volume of lakewater below the point of phosphorus sampling, approximately 1.5 m above the sediments, were used to calculate the load.

3. Results

Hypolimnetic conditions for the period of 30 May−6 October, 1996 are shown in Fig. 1. Note the inverse relationship between dissolved oxygen and both total and PO_4−P concentrations. Six of the seasons sampling dates exhibit oxygen concentrations below 1.0 mg l^{-1} at a depth approximately 0.5 m above the bottom sediments. Large increases in P are associated with these events implying anoxia at the sediment−water interface. Note the re-oxygenation of the hypolimnetic waters on 18 July and 22 August. This relatively shallow, poorly stratified lake is often noted to mix fully throughout the summer. While this provides oxygen to the bottom water it also mixes the large hypolimnetic P load into the surface waters, which reduces P concentrations in the hypolimnion and encourages epilimnetic algal growth.

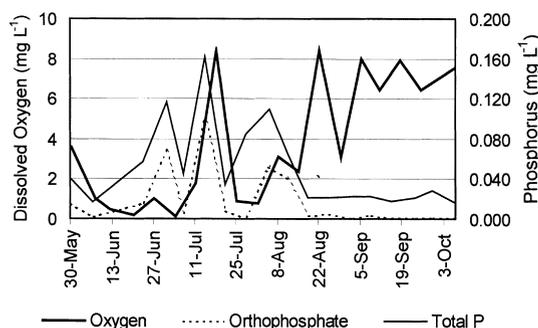Predicted and measured hypolimnetic and sedi-

Fig. 1. Hypolimnetic conditions for the 1996 sampling period. Oxygen is measured at a depth of 8.5 m while total-P and orthophosphate are measured at a depth of 7.5 m.

ment parameters for the 9-week period are presented in Table 1. When all of the sediment P was assumed to be in the form of strengite, MINTEQA2 predictions of interstitial PO_4–P (P_{int}) were between 22 and 106 mg l^{-1}. To improve the accuracy of the predictions we ran the

model using the estimated amounts of iron-associated P or BD-P. For these data the predicted P_{int} varied between 0.07 and 14.2 mg l^{-1}, and on all dates except 18 September, sediment conditions, especially Eh, favoured dissolution of strengite. The high Eh (141 mV) measured on 18 September resulted in very low predicted P_{int} (0.07 mg l^{-1}) as strengite was predominantly precipitated from the interstitial water. The regression of the nine predicted P_{int} values from dates exhibiting P-dissolution against hypolimnetic TP (TP_h) results in a significant linear relationship ($r^2 = 0.59$, $P = 0.016$) (Fig. 2).

Of the nine calculated TP release rates, three were negative indicating losses of TP from the hypolimnion (Table 1). When the remaining six were plotted against the amount of sediment BD-P a significant linear relationship was observed ($r^2 = 0.88$, $P = 0.005$) (Fig. 3). The line of best fit had a slope similar to one determined

Table 1
Selected parameters measured in the water column and sediment of Tabor Lake[a]

Water column parameters					Sediment parameters					Model predictions
Date	Total P mg l^{-1}	Ortho-P mg l^{-1}	Total P release rate mg m^{-2} day^{-1}	Temp °C	Total P mg g^{-1}_{wet}	BD-P mg g^{-1}_{wet}	OM (%)	Eh (mV)	pH	Interstitial PO_4-P mg l^{-1}
960721	0.034	0.008								
960725				18	0.208	0.028	34.33	−159	7.04	14.2
960728	0.084	0.001	2.06							
960801				16	0.105	0.024	34.64	−173	6.95	12.4
960805	0.11	0.052	−4.64							
960808				17	0.116	0.023	34.85	−96	7.02	11.8
960811	0.066	0.04	−3.97							
960815				17	0.117	0.019	34.65	49	6.76	9.46
960818	0.022	0.004	0.00							
960822				17	0.132	0.021	35.01	−9	6.97	10.6
960825	0.022	0.005	0.08							
960829				16	0.113	0.021	34.77	−98	6.95	10.8
960902	0.023	0.0005[b]	0.00							
960905				16	0.084	0.019	34.01	−90	6.52	9.44
960909	0.023	0.004	−0.45							
960911				15	0.141	0.022	33.82	−33	7.04	11.1
960915	0.018	0.0005[b]	0.24							
960918				14	0.162	0.022	33.81	141	7.09	0.07
960923	0.021	0.0005[b]	0.84							
960925				12	0.143	0.023	33.08	39	7.25	11.5

[a] Predictions from the MINTEQA2 model using the estimated BD-P sediment component are also shown.
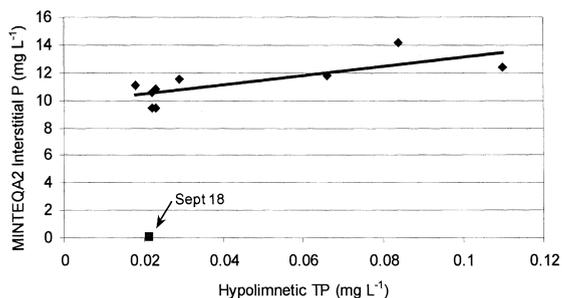[b] Below detection limit.

Fig. 2. The regression of nine P_{int} values predicted from the MINTEQA2 model using the BD-$P_{(4-8\ wet)}$ sediment component and hypolimnetic TP concentration. Note that the 18 September datum point represents conditions that are not conducive to strengite dissolution therefore it behaves as an outlier in this data set. The equation for the regression line is $P_{int} = 33.44\ TP_h + 9.78$, $r^2 = 0.59$, $P = 0.016$.

by Nürnberg (1988) for the BD-P fraction of wet sediments from 5 to 10 cm depth in 14 anoxic lake cores.

A multiple regression approach was used to evaluate the relationships between sediment characteristics and hypolimnetic $PO_4−P$ and TP. No significant relationships are found with orthophosphate concentrations, but several variables are correlated ($P < 0.05$) with TP_h. BD-P ($r^2 = 0.53$) and Eh ($r^2 = 0.50$) are each significant while together they explain 72% of the variance in hypolimnetic TP concentrations. Improvement to 76% explained variance ($P = 0.01$) is achieved with the addition of interstitial Fe concentrations
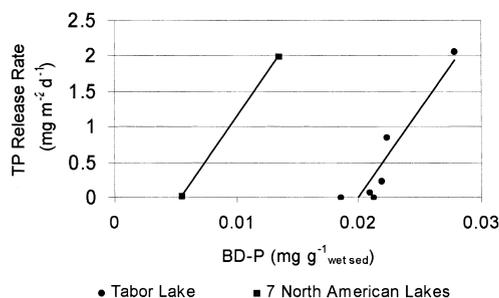

Fig. 3. The relationship between the BD-P sediment component and the TP release rates (RR). The significant linear relationship found for Tabor Lake data is TPRR = 247BD-P−4.9, $r^2 = 0.88$, $P = 0.005$, $n = 6$. The relationship for similar variables (BD-P wet, 5−10 cm) presented by Nürnberg (1988) has a similar slope but a different intercept with the equation being TPRR = 248BD-P−1.4, $r^2 = 0.90$, $P < 0.0001$, $n = 14$).

(Fe_{int}) ($P = 0.03$). In a stepwise regression the addition of organic matter does not improve the statistical relationship.

4. Discussion

The use of the MINTEQA2 model allows an evaluation of the role of the dominant mineral forms of phosphate in contributing to interstitial $PO_4−P$. The concentrations predicted by assuming that all of the measured sediment phosphorus is present as strengite or hydroxyapatite are not significantly correlated to either of the forms of phosphorus measured in the hypolimnion. Hydroxyapatite dissolution associated with the measured conditions does not produce marked changes in P_{int} levels, indicating that calcium-bound P was not playing a significant role. Hydroxyapatite dissolution is more a function of low pH rather than Eh (Lindsay et al., 1989) and during the study period the pH of the interstitial water did not drop below pH 6.8, which would prevent the dissolution of hydroxyapatite. However the measured pH and Eh values of the interstitial water are conducive to the dissolution of strengite ($FePO_4 \cdot 2H_2O$) on all but one of the dates of measurement.

When the amount of total P in the lower portion of the sediment (4−8 cm) was used to estimate the proportion of bicarbonate-dithionite P in wet sediment, using Nürnberg's equation (1988), it provided a more realistic measure of Fe-associated P for predicting the magnitude of P_{int} release. The values of the MINTEQA2 predictions of P_{int} estimated from BD-P concentrations are near the top of the range of interstitial concentrations presented in a review paper by Enell and Lofgren (1988). Bear in mind that we were not attempting to calibrate the model for predictive purposes but rather were using it to identify the source of P release in Tabor Lake sediment. While we cannot test MINTEQA2's predictions directly against interstitial P concentrations as they were not measured, we can test the relationship between the predicted changes in P_{int} and the changing concentrations of P forms in the overlying water.

The significant linear relationship observed between hypolimnetic TP and the model predictions is found only after removing the outlier (18 September) which represents conditions (high Eh) not conducive to strengite dissolution. The low P_{int} value predicted for 18 September is associated with a recent re-oxygenation of the bottom waters and an increase in sediment Eh (-33 to 141 mV). Increases of oxygen in the bottom waters were noted on other dates as well (Fig. 1), but the degree of change in the Eh of the lower (4−8 cm) sediments was not as extreme, therefore reducing conditions were maintained. An evaluation of the daily wind speed records along with the oxygen and thermal profiles of the water column indicates that the lake had been mixed on 16 September, 2 days previous to sediment sampling. The model was rerun with the 18 September sediment conditions but with Eh values of 100, 50 and 0 mV to evaluate the effect of the changing redox conditions. Predicted P_{int} values were 1.41, 3.89 and 11.13 mg l^{-1}, respectively. Tabor Lake sediment P is clearly sensitive to changes in Eh. The fact that the structural data from the water column show the re-establishment of anoxic conditions above the sediment−water interface by 23 September and that TP in the hypolimnion increased to 0.021 mg l^{-1} indicates that the sediment Eh must have lowered. In Fig. 2 the measured 23 September TP_h of 0.021 mg l^{-1} would be associated with a P_{int} of approximately 10 mg l^{-1} which could have been released if the actual Eh conditions between 18 and 23 September had fallen between 0 and 50 mV, as is suggested by the structural profiles.

Measured positive release rates are presented in Fig. 3 along with the results of Nürnberg (1988) who found a significant linear relationship between BD-P and TP release rate ($r^2 = 0.90$, $n = 14$). The slopes of the two lines are nearly identical while their intercepts are quite different. The similar slopes suggest the process of anoxic driven release of iron phosphates is occurring in both data sets, while the different intercept likely reflects an overestimate of the actual amount of BD-P in Tabor Lake sediments. The relatively high P_{int} values predicted by the MINTEQA2 model also indicate the BD-P values may initially

be slightly large. The BD-P estimates may also be elevated as the laboratory separation of interstitial water was not undertaken in an anaerobic environment, potentially introducing some error. It is interesting to note that in this data set none of the predicted or measured parameters are correlated with the hypolimnetic PO_4−P. All the significant relationships occur with hypolimnetic TP. This also could be a function of the handling of the water samples, in that they were filtered in an oxic environment. Three of the PO_4−P values are below the detection limit (Table 1), possibly indicating that the soluble iron and phosphorus had precipitated and was therefore measured as TP.

We noted that the BD−P fraction explained 53% of the variance in hypolimnetic TP while only 8% was explained by the proportion of sediment organic matter. A statistically significant proportion of the variance (72%, $P = 0.01$) was explained by Eh and BD-P together, which is logical as a reduction in Eh is known to regulate P release from iron-associated sediment (Ostrofsky et al., 1989). Montigny and Prairie (1993) point out that a drop in Eh could also trigger releases from the organic portion of the sediment. Therefore we tested to see if the addition of the OM% in the equation would improve it, however our measure of sediment organic content improved the explained variance by only 1%. Alternately, the inclusion of Fe_{int} increased the explained variance to 76% ($P = 0.03$), implying that iron dissociation regulated by low Eh plays the dominant role in this system. These relationships are developed from a small data set ($n = 10$) and so should not be used in a general predictive manner; rather they provide us with an opportunity to evaluate the processes which appear to be operating in this lake over this 9 week period.

5. Conclusions

Empirical data from several summers of sampling on Tabor Lake indicated that hypolimnetic anoxia was strongly associated with dissolved phosphorus release from the sediments. An evaluation of a 9-week period in 1996 indicated sig-

nificant relationships between iron-associated P in the sediment but not with the organic matter content of the sediment. While the specific role of the bacterial contribution to hypolimnetic water cannot be discerned in our data set, we concluded that remediation approaches that address the iron-bound phosphate would be most suitable for managing the internal P loading of Tabor Lake.

Acknowledgements

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