

**A COMPARISON OF  
PHOSPHORUS RETENTION  
IN LAKES  
DETERMINED FROM MASS BALANCE  
AND  
SEDIMENT CORE CALCULATIONS**

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DETERMINED FROM MASS BALANCE  
AND SEDIMENT CORE CALCULATIONS**

Report Prepared By:

P.J. Dillon

Ontario Ministry of the Environment

Water Resources Branch

P.O. Box 39, Dorset, Ontario P0A 1E0

and

H.E. Evans

RODA Environmental Research Limited

P.O. Box 447, Lakefield, Ontario K0L 2H0

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## ABSTRACT

Phosphorus retention ( $TP_{acc}$ ) was determined in 7 lakes in Ontario, Canada from mass balances and from the direct measurement of phosphorus accumulation in the sediments. Phosphorus retentions determined using the mass balance technique ranged between  $20 \pm 3.9$  and  $94 \pm 23$  mg/m<sup>2</sup>/yr and were slightly lower than those calculated by multiplying sediment total phosphorus (TP) concentrations by sediment accumulation rates ( $49 \pm 14$  to  $135 \pm 48$  mg/m<sup>2</sup>/yr). The lower  $TP_{acc}$  values measured using the mass balance approach may result from the underestimation of external TP inputs. Alternatively, it is suggested that in the more acidic lakes, a decrease in TP concentrations in the lakewaters and/or a decrease in TP export from the catchment may have resulted in a decrease in  $TP_{acc}$  through time. Thus, relatively higher  $TP_{acc}$  values calculated using the sediment approach (since  $TP_{acc}$  values calculated from the sediment data are averaged over a greater number of years than those calculated from the mass balance data).

Provided several cores are collected from the lake, the direct measurement of sediment TP and sediment accumulation rates for estimating  $TP_{acc}$  may be a suitable alternative to mass balances, especially in situations where it is not possible to measure all inputs of TP to the lake.

Short title: phosphorus retention in lakes

Keywords: phosphorus, retention, sedimentation, mass balance, cores

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## INTRODUCTION

Information concerning the retention of total phosphorus (TP) in the sediments of lakes is of prime importance in predicting phosphorus concentrations in the water column (Vollenweider 1969; Dillon and Rigler 1974; Lam *et al.* 1982), in determining areal hypolimnetic oxygen deficits, AHOD (Cornett and Rigler 1979; Cornett 1989), and in discerning changes in the biological behaviour of lakes (Fraser 1980). Furthermore, since mass-balance calculations of phosphorus retention can be used to predict *in situ* the rate of return or release rate of phosphorus from the sediments to the water column (Bostrom *et al.* 1982; Larsen *et al.* 1981; Nurnberg 1984; Garber and Hartman 1985; and Van der Molen 1991), a knowledge of the net amount of TP retained by lake sediments is potentially useful for establishing the success of lake recovery programmes following reductions in external phosphorus loadings (Fraser 1980; Osborne 1981; Larsen *et al.* 1981; Levine and Schindler 1989; Van Liere *et al.* 1990; Chapra and Canale 1991; Rossi and Premazzi 1991).

The methods for estimating net phosphorus retention ( $TP_{acc}$ , in  $mg/m^2/yr$ ) are varied. While gross phosphorus retention can be measured from sediment traps, the theoretical and methodological problems associated with sediment traps (Kirchner 1975; Hargrave and Burns 1979; Bloesch and Burns 1980; Rosa *et al.* 1991) as a result of resuspension, mineralization, and over/undertrapping of the settling material means that great care must be taken in the employment and selection of traps and in the interpretation of the data derived from them. Furthermore, sediment traps provide only short-term (usually only a few weeks) estimates of  $TP_{acc}$  which may be inadequate for many studies.

A second method for estimating  $TP_{acc}$  is by mass balance calculations whereby phosphorus retention is simply the difference between the total input and the total output of phosphorus to the lake. The fraction retained or retention coefficient ( $R_p$ ) is thus the net proportion of the total phosphorus input that is not lost by outflow. Mass balance estimates of  $TP_{acc}$  have been calculated for many lakes in Ontario, Canada

including Blue Chalk Lake (Dillon *et al.* 1990), Bob Lake (Dillon 1974; Cross and Rigler 1983), Lake Simcoe (Johnson and Nicholls 1989), Lake St. Clair (Lang *et al.* 1988) and Lake Ontario (Fraser 1980), as well as for lakes in other parts of Canada, the USA and Europe such as Nakamum and Halfmoon Lakes, Alberta (Riley and Prepas 1984), Mirror Lake, New Hampshire (Caraco *et al.* 1988), Toolik Lake, Alaska (Whalen and Cornwell 1985), Edinboro Lake, Pennsylvania (Garber and Hartman 1985), Shagawa Lake, Minnesota (Malueg *et al.* 1975; Larsen *et al.* 1981), Ijsselmeer, the Netherlands (de Kloet 1978) and Lakes Stugsjon, Hymenjaure and Magnusjaure, Sweden (Janson 1978).

Mass balance estimates of  $TP_{acc}$  are probably the most accurate of the phosphorus retention methods. However, the measurements involved are both time consuming and expensive, requiring data collection for at least one year. Empirical models relating the phosphorus retention coefficient,  $R_p$ , and the mean depth of the lake, the areal water load, or the water renewal time (Kirchner and Dillon 1975; Vollenweider 1975, Larsen and Mercier 1976; Ostrofsky 1978) have been reported. However, the confidence intervals for the prediction of  $R_p$  are quite broad.

The last alternative for estimating  $TP_{acc}$  involves the direct measurement of the total phosphorus concentration (in mg/g) in the sediments, which together with calculations of the bulk sediment accumulation rate (in  $g/m^2/yr$ ) yields an estimate of net phosphorus retention (in  $mg/m^2/yr$ ). Unlike the mass balance approach, a measure of  $R_p$  is not obtained unless the total input of phosphorus is known. However, this method has an advantage over mass balance calculations in that sediment cores can be collected one or two times during the year, thus eliminating the need for extensive monitoring programmes. In the past, the direct measurement of  $TP_{acc}$  from sediment cores has been inhibited by our inability to obtain accurate estimates of sediment accumulation. However, the development and refinement of techniques such as  $^{210}Pb$  for dating recent (i.e., during the past 100 years) lake sediments (Koide *et al.* 1973; Robbins 1978; Krishnaswami and Lal 1978) have resulted in an increase in the number of studies which have used sediment cores to estimate  $TP_{acc}$  in lakes (Evans and Rigler

1980, 1983; Cross and Rigler 1983; Whalen and Cornwell 1985; Armengol *et al.* 1986; Moeller and Wetzel 1988; Johnson and Nicholls 1989), reservoirs or man-made lakes (Moss 1980; Armengol *et al.* 1986) and in the Baltic Sea (Jonsson *et al.* 1990). A potential disadvantage of this technique is that only a long-term average estimate of  $TP_{acc}$  is produced.

In light of the comparative simplicity of the sediment core method relative to mass balance calculations, we tested whether these two independent measurements of  $TP_{acc}$  are analogous. While comparisons between sediment trap estimates of  $TP_{acc}$  and mass balance estimates of  $TP_{acc}$  are relatively common (e.g., Charlton 1983; Dillon *et al.* 1990), in only a few studies have comparisons been made between mass balance calculations of  $TP_{acc}$  and sediment core estimates of  $TP_{acc}$  (Evans and Rigler 1980, 1983; Osborne 1981; Cross and Rigler 1983; Whalen and Cornwell 1985) and all of these investigations have been limited to single lake comparisons and/or mass balance data collected in only a single year. The purpose of this study is to compare  $TP_{acc}$  determined from mass balance calculations (using long-term data) with the accumulation of phosphorus estimated from  $^{210}Pb$  measurements of sediment accumulation and the analysis of phosphorus concentrations in the surface sediments of several lakes.

## STUDY AREA

The 7 study lakes are located in south-central Ontario, Canada, about 200 km north of Toronto and 250 km southeast of Sudbury. All are situated on the Canadian Precambrian Shield, an area underlain by metamorphic, plutonic and volcanic silicate rocks that have been substantially altered by glacial processes. The unconsolidated surficial material in the lakes' watersheds consists of subglacially deposited tills with pockets of peat (organic matter) in poorly drained areas (often adjacent to the lakes themselves) and small accumulations of sand and gravel deposited by glacial meltwaters.

The soil profiles are weakly developed.

The locations and morphometric features of the study lakes are given in Table 1 and are described in detail in Rustad *et al.* (1986), Dillon *et al.* (1986, 1987, 1990) and Molot and Dillon (1991). All are small (21 to 57 ha), with mean depths ranging between 3.3 m (Heney Lake) and 14.2 m (Red Chalk Lake) and maximum depths ranging between 5.8 m (Heney Lake) and 38 m (Red Chalk Lake). Six of the lakes are dimictic with the shallowest, Heney Lake, being only weakly stratified or not stratified at all. All are headwater lakes with the exception of Red Chalk Lake which is downstream of Blue Chalk Lake. Red Chalk Lake consists of two discrete basins connected by a narrow, shallow (<2 m deep) channel.

There are no population centres or industrial activities in any of the lakes' watersheds as the area is primarily recreational. However, seasonal cottages occupy the shorelines of several of the lakes.

## METHODS

### Retention Measured Using Sediment Cores

#### a) Core collection and treatment

Sediment samples were collected in 1978, 1979 and 1980 as part of other investigations (Dillon and Evans 1982; Evans *et al.* 1983, 1986). Between 36 cores (Crosson Lake) and 94 cores (Red Chalk Lake) were collected from the accumulating areas of each lake. In the epilimnetic sediments (water depth generally less than 10 m), cores often could not be obtained because the substrate was composed of bedrock, coarse gravel or boulders. These areas were defined as "uncoreable" and were mapped in each lake. It was assumed that phosphorus and Pb ( $^{210}\text{Pb}$ ) did not accumulate to any significant extent in these uncoreable areas.

All the cores were collected with a K-B gravity corer (Brinkhurst *et al.* 1969) using clear Plexiglass core tubes having an inner diameter of 4.8 cm. In six of the lakes, 5 sites were selected from widely differing lake depths (8 sites were

selected in Red Chalk Lake). At each of these sites, either two or three cores were collected and then sectioned into 1 cm slices to a depth of 20 cm using an extruder and collar (Cross 1977). Then the two or three replicate slices were combined to provide adequate material so that TP, stable Pb and  $^{210}\text{Pb}$  sediment measurements could be made. The remaining cores (31 to 89) were not divided into 1 cm sections; rather the entire upper 20 cm of the core was taken for the analysis of stable Pb and other elements.

All sediment samples were dried at 100-105°C for a minimum of 24 hours, ground with a mortar and pestle, and then subsampled for chemical analyses.

b) Analysis of sediment phosphorus concentration

Total phosphorus was measured (OMOE 1983) by oxidizing the sample overnight in a mixture of 2 g of  $\text{K}_2\text{S}_2\text{O}_8$  in 7 mL of concentrated  $\text{H}_2\text{SO}_4$ . The acidic digestate was neutralized to the methyl-red endpoint with 6.3 N NaOH and treated to remove heavy metal interference (where necessary). Ammonium molybdate and stannous chloride were added and the absorbance at 660 nm was determined spectrophotometrically.

c)  $^{210}\text{Pb}$  analyses and dating

The  $^{210}\text{Pb}$  methodology and the calculation of sediment accumulation rates in these lakes have been described elsewhere (Evans 1980; Evans and Rigler 1980; Evans *et al.* 1986). Briefly, total  $^{210}\text{Pb}$  ( $^{210}\text{Pb}_{\text{tot}}$ ) was measured by assaying a subsample of the dried sediment for  $^{210}\text{Po}$ , its alpha-emitting granddaughter. Analyses were performed in the laboratory of the late Dr. F.H. Rigler (McGill University, Montreal Canada).

Bulk sediment accumulation rates (SAR) were determined using the constant initial concentration (CIC) method (Robbins 1978). Excess, or unsupported  $^{210}\text{Pb}$  was calculated by subtracting the radium-supported  $^{210}\text{Pb}$  ( $^{210}\text{Pb}_{\text{sup}}$ ) activity from

the total  $^{210}\text{Pb}$  activity in each section. Background or  $^{210}\text{Pb}_{\text{sup}}$  concentrations were estimated from the  $^{210}\text{Pb}_{\text{tot}}$  in the deepest few sections of each core. Where background concentrations were not apparently reached,  $^{210}\text{Pb}_{\text{sup}}$  was taken from the lowest background value observed in the other cores collected from the same lake.

d) Measurement of stable Pb concentrations and whole-lake anthropogenic Pb burdens

A subsample of the dried sediment material was digested for 16 hours at 70°C in a 2:1 mixture of HCl:HNO<sub>3</sub> (Bronson 1975). HCl was added and the sample was analyzed for Pb using a Varian M1250 atomic absorption spectrophotometer equipped with deuterium background correction. All analyses were performed in duplicate.

In the 5 (8 in Red Chalk Lake) sectioned cores collected from each lake, the Pb profiles were used to estimate background Pb concentrations. The anthropogenic Pb content (in mg/m<sup>2</sup>) of these sectioned cores was then calculated by integrating the background-corrected concentration versus depth profile (where depth is expressed as cumulative dry mass per unit area; Robbins 1978). In the unsectioned cores, the entire mass of the 20 cm slice was multiplied by the background-corrected Pb concentration for the whole slice to obtain anthropogenic Pb burden.

Whole-lake anthropogenic Pb burdens (Pb burden<sub>(WL)</sub>) were calculated as outlined in Dillon and Evans (1982). Each lake was divided into 1 to 4 m depth zones (depending on the maximum depth of the lake) and the average anthropogenic Pb burden for each depth zone was determined. This number was pro-rated by the proportion of the lake which that depth zone occupies, corrected for uncoreable area and summed, resulting in a value which should represent the accumulation of anthropogenic Pb averaged on a whole-lake basis (in mg/m<sup>2</sup>).

e) Calculation of sediment TP retention

The calculation of  $TP_{acc}$  (in  $mg/m^2/yr$ ) using sediment cores requires an estimate of the average whole-lake sediment TP concentration ( $mg/g$ ) and the average whole-lake SAR ( $g/m^2/yr$ ). Because of the phenomenon of sediment focusing (Lehman 1975; Kamp-Nielson and Hargrave 1978; Kimmel 1978; and Davis and Ford 1982), both these values are difficult to obtain unless many core profiles have been analyzed. Since only 5 or 8 sectioned cores were obtained from each lake, we employed an approach first suggested by Evans (1980) and utilized later by Dillon and Evans (1982) and Evans *et al.* (1983). The average surface concentration (i.e., 0-3 cm) of TP measured at each of the 5 or 8 sites in each lake was multiplied by the recent SAR and the result was then multiplied by the ratio of the mean whole-lake anthropogenic Pb burden/anthropogenic Pb burden accumulated at each site (i.e.,  $Pb\ burden_{(WL)} / Pb\ burden_{(site)}$ ) such that:

$$[TP] \cdot SAR \cdot Pb\ burden_{(WL)} / Pb\ burden_{(site)} \quad (1)$$

where [TP] is the average concentration of total phosphorus in the surface (0-3 cm) sections of the core (in  $mg/g\ dw$ ), SAR is the sediment accumulation rate ( $g/m^2/yr$ ),  $Pb\ burden_{(WL)}$  is the anthropogenic whole-lake Pb burden ( $mg/m^2$ ) and  $Pb\ burden_{(site)}$  is the anthropogenic Pb burden measured in each of the sectioned cores ( $mg/m^2$ ). The 5 or 8 independent estimates of phosphorus retention were then averaged to give a single value for  $TP_{acc}$  ( $mg/m^2/yr$ ) for each lake.

### Mass Balance Calculations

a) Hydrologic budgets

The hydrologic methods have been described by Scheider *et al.* (1983) and Locke and Scott (1986). Hydrologic and mass budgets reported here cover 12 years (1977-1989) for Blue Chalk, Chub and Red Chalk Lakes, 10 years (1979-1989) for Plastic Lake, 9 years (1980-1989) for Crosson and Heney Lakes

and 3 years (1977-1980) for Jerry Lake. The hydrologic year is the period from June 1 to May 31.

b) Stream sampling

Samples for total TP were collected in Nalgene bottles and filtered through 80  $\mu\text{m}$  Nitex mesh into pre-rinsed 50 mL culture tubes. Samples were obtained bi-weekly during the winter, more than once per week during the period of spring melt and weekly during the remainder of the year.

c) Precipitation sampling

Methods are described in detail in Scheider *et al.* (1981) and Dillon *et al.* (1988). In 1977-1978, polyethylene funnels (30 cm opening) fastened to 250 L plastic containers were used to collect "bulk" deposition. Funnels were fitted with 500  $\mu\text{m}$  Nitex mesh to prevent contamination by insects. Beginning in May 1978, bulk deposition was collected with 0.25  $\text{m}^2$  square collectors having Teflon-coated, stainless steel funnels leading into 18 L glass bottles (summer) or 43 cm diameter x 63 cm high polyethylene containers (winter). The funnels were fitted with fibreglass window screening to prevent insect contamination.

Beginning in November 1978, snow samples were obtained with the 0.25  $\text{m}^2$  Teflon funnel collector modified for winter use with a wider throat opening. In May 1981, 18 L polyethylene carboys replaced the 18 L glass bottles for summer collection.

The "bulk" precipitation collectors were open at all times and thus collected both wet and dry deposition of phosphorus. Since samples were removed from the collectors only when there was sufficient volume for chemical analyses, collection periods ranged from 1 (spring) to 40 (winter) days, with most samples being collected weekly. All samples were filtered through 76  $\mu\text{m}$  (1977-1982) or 102  $\mu\text{m}$  (1982-1989) Nitex mesh to remove coarse particulate material.

d) Analysis of TP in precipitation and streamwater

Total phosphorus was measured in all precipitation and streamwater samples using an automated ascorbic acid reduction, ammonium molybdate colourimetry technique (OMOE 1983). Prior to March 22, 1979, the automated stannous chloride, molybdate reduction technique described above for phosphorus in sediment samples was used also on the precipitation and stream water samples.

e) Phosphorus mass balance calculations

The methods for calculating the inputs of phosphorus to the lakes from precipitation and from the watersheds as well as the outflow of phosphorus from the lakes are described in Scheider *et al.* (1979). Briefly, the daily deposition of phosphorus from precipitation for each bulk collector was calculated by first multiplying the TP concentration in the sample by the cumulative precipitation depth for the sampling period and then dividing by the number of days in the period. Phosphorus loads for the gauged inflow streams and the outflows, were calculated by multiplying the concentration of TP in the inflows or outflow (measured during the midpoint of a time period) by the total discharge over that time period. Inputs of TP to the lake from ungauged portions of the watersheds were estimated by pro-rating the gross export (i.e., output per unit basin area) data obtained from the hydrologically gauged areas of the basins. In the case of Heney Lake, with no major inflowing streams, the hydrologic data from the 5 major inflows to a nearby lake (Dickie Lake) were used.

As there is some shoreline development on 5 of the lakes (Red Chalk and Jerry Lakes have essentially no development), anthropogenic inputs of TP from sewage disposal systems (i.e.,  $J_A$  in kg/yr) were calculated using the equation from Dillon *et al.* (1986):

$$J_A = 0.80 \cdot \text{usage} \cdot (1-f_h) \quad (2)$$

where 0.80 is the input of TP in kg/capita/yr. The quantification of dwelling usage (in capita yr/yr) and  $f_h$  (the fraction of the dwellings on the lake on holding tanks) was determined from surveys conducted by the Ontario Ministry of Housing from 1976-1978 (Dillon *et al.* 1986). It was assumed that both usage and  $f_h$  have remained constant since then.

f) Calculation of TP retention by mass balance

The annual  $TP_{acc}$  (mg/m<sup>2</sup>/yr) for each lake was calculated as the difference between the total inputs of TP to the lake (i.e., from precipitation + runoff + anthropogenic) and the export of phosphorus from the lake, all divided by the lake area. Standard deviations in the  $TP_{acc}$  estimates were obtained by averaging the 3 to 12 years of data for each lake.

## RESULTS

### TP retention calculated from sediment cores

Typical sediment phosphorus profiles for 2 of the lakes are shown in Figures 1 and 2 while the average surface (0-3 cm) concentrations of TP, the SARs and the anthropogenic Pb burdens measured in each of the 5 or 8 cores (Pb burden<sub>(site)</sub>) collected from each lake are given in Table 2. The whole-lake anthropogenic Pb burdens (Pb burden<sub>(WL)</sub>) determined for each lake are reported in Table 1.

Average sediment surface phosphorus concentrations (Table 2) generally range between 1 and 2.5 mg/g dw (dry weight) with concentrations as high as 3.2 and 3.3 mg/g dw being found in single cores from Jerry and Red Chalk Lakes, respectively. There is some trend towards increasing TP concentration with increasing lake depth, but this trend is statistically significant ( $p < 0.05$ ) in only Crosson and Jerry Lakes. The high SAR observed in the cores from the epilimnetic sites in these two lakes is a result

of the high weight of the sediments which are composed almost exclusively of dense, coarse-textured inorganic material (as opposed to fine-textured organic material).

The phosphorus retention ( $TP_{acc}$  in  $mg/m^2/yr$ ) for each lake, calculated as outlined in equation (1), is shown in Table 2. There is considerable variability in the estimated average  $TP_{acc}$  values for each lake, with the coefficients of variation (c.v.) ranging between 25% in Crosson Lake and 85% in Jerry Lake. However, the  $TP_{acc}$  calculated from the epilimnetic core (at 4.8 m) in Jerry Lake is more than 3 standard deviations greater than the mean of the other 4 cores. If this core is excluded from the average for the lake, then the c.v. in the average  $TP_{acc}$  for Jerry Lake is reduced to 36%. Similarly, if one core from Red Chalk Lake, collected from a depth of 18.6 m, is excluded from the average for the lake, then the c.v. in the average  $TP_{acc}$  value is reduced from 62% to 33%. Thus, the overall range in c.v. values for all the lakes is only 25-49% (average =  $37 \pm 8.4\%$ ,  $n = 7$ ) and the average  $TP_{acc}$  values range between  $49 \pm 14 mg/m^2/yr$  in Blue Chalk Lake and  $148 \pm 37 mg/m^2/yr$  in Crosson Lake.

#### TP retention calculated from mass balance data

A summary of the total inputs (in  $mg/yr$ ) of TP (from precipitation, runoff and human activities) to each lake, the output (in  $mg/yr$ ) of TP from each lake and the net retention of TP ( $mg/m^2/yr$ ) by each lake (inputs - output)/ $A_0$ ) is given in Table 3.  $TP_{acc}$  values measured from these mass balance calculations range between  $20 \pm 3.9 mg/m^2/yr$  (Plastic Lake) and  $94 \pm 23 mg/m^2/yr$  (Jerry Lake). The variability in the retention estimates are slightly lower than those encountered with the sediment TP retention method with c.v. values ranging between 18 and 30% (average =  $24 \pm 6\%$ ,  $n = 7$ ).

## **DISCUSSION**

In 5 of the study lakes, there is reasonable agreement between the sediment method (Table 2) and the mass balance method (Table 3) for calculating  $TP_{acc}$ . In all the lakes

except Crosson and Plastic, the  $TP_{acc}$  values calculated using the sediment retention technique are within the standard deviation of the  $TP_{acc}$  values estimated from mass balance calculations.

Few attempts been made to compare TP retention in lakes using both sediment cores and mass balance calculations. Evans and Rigler (1980) examined  $TP_{acc}$  in Bob Lake, Ontario and found that their estimates obtained from sediment cores (i.e., 143-170  $mg/m^2/yr$ ) were reasonably close to the mass balance calculations obtained by Dillon (1974) of 115  $mg/m^2/yr$  and Cross (1977) of 140  $mg/m^2/yr$  (this value was later revised to 133.5  $mg/m^2/yr$  by Cross and Rigler, 1983). Evans and Rigler (1980) point out that Cross' mass balance calculation of  $TP_{acc}$  is probably more accurate because she included inputs of TP from small temporary streams, although the difference between the mass balances measured by Cross and by Dillon are within the year-to-year variability observed in our study lakes.

In other comparisons of  $TP_{acc}$  using sediment cores and mass balance calculations, Evans and Rigler (1983) found that using sediment cores, TP retention in Costello Lake, Ontario was 93.5  $mg/m^2/yr$  which compared favourably to the mass balance estimate obtained by Scheider (1974) of 86.5  $mg/m^2/yr$ . Whalen and Cornwell (1985) reported that TP retention in Toolik Lake, Alaska was 43  $mg/m^2/yr$  based on mass balance calculations and 52-56  $mg/m^2/yr$  based on sediment cores.

Osborne (1981) reported mass balance estimates of  $TP_{acc}$  for Barton Broad, a man-made lake in the U.K., of 2.81  $g/m^2/yr$  (1974-75) and 1.53  $g/m^2/yr$  (1975-76) which were lower than the  $TP_{acc}$  value of 3.5  $g/m^2/yr$  determined by Moss (1980) using dated sediment cores. Similarly, Avnimelech and Lacher (1979) found that the mass balance estimates for  $TP_{acc}$  in a 3000  $m^2$  fish pond in Israel (10 and 7.7  $g/m^2/yr$  in 1973-74 and 1974-75, respectively) were lower than the sediment core estimates (i.e., 39 and 16  $g/m^2/yr$  in 1973-74 and 1974-75, respectively).

Although the agreement between the two methods was good in our study lakes, the mass balance approach yielded a lower estimate of  $TP_{acc}$  than the sediment core approach did (see Table 2). This was true in all of the above mentioned studies, as well as our own. There are several mechanisms which might account for this discrepancy. These can be categorized as being either sampling and analytical errors or conceptual errors. Sampling errors are self-explanatory and include human errors in coring, in discharge measurements and in other measurement techniques. Likewise, analytical inaccuracies include the errors associated with the chemical analyses of the samples for TP, Pb and  $^{210}Pb$ .

For the sediment core method, analytical errors in the  $^{210}Pb$  methodology can be quite high (Schleske *et al.* 1988; Gubala *et al.* 1990) while for the mass balance method, errors in hydrologic measurements including precipitation and discharge estimates can be high (LaBaugh and Winter, 1984; Lang *et al.* 1988). However, while the source of the errors (i.e., sampling or analytical) in the two techniques may differ, this should not necessarily result in systematic differences between the two approaches, but rather will yield a lack of precision in the  $TP_{acc}$  values obtained for each technique. Thus, it is unlikely that sampling and/or analytical problems have caused inconsistencies between the two approaches.

On the other hand, conceptual discrepancies can possibly lead to an incongruity in the results obtained using the two techniques. For example, disparity between the sediment approach and the mass balance approach might result from the fact that different time periods are being averaged to obtain the  $TP_{acc}$  value. For the mass balance approach, this time period is (in our study) 3 to 12 years, whereas for the sediment approach, this time period averages  $13 \pm 5$  years ( $n = 5$  cores) for Chub Lake to  $37 \pm 17$  years ( $n = 5$  cores) for Plastic Lake based on  $^{210}Pb$  dates for the upper 3 cm of sediment. Provided the lakes have remained in steady state for the duration of both studies, this averaging of different time frames should not be a problem. However, if a change in  $TP_{acc}$  has occurred during the period of time not encompassed by the mass balance measurements (i.e.,  $>12$  years), then a discrepancy between the two approaches might result.

It is possible that a change in  $TP_{acc}$  through time may have occurred in both Plastic and Crosson Lakes, the most acidic of the study lakes (whole-lake ice-free mean pH =  $5.74 \pm 0.06$  and  $5.59 \pm 0.05$  from 1979-1989 for Plastic and Crosson Lakes, respectively). From 1979 to 1989, TP concentrations in these lakewaters have decreased by about 30% in Plastic Lake and about 12% in Crosson Lake (Dillon, unpub. studies).

This decline in TP concentrations may be a consequence of acidification of a catchment resulting in lower yield or export of TP. A possible consequence of catchment and/or lakewater acidification is that the net TP flux to the sediments may have decreased. For example, Evans and Hakanson (in press) found that bulk sedimentation (as measured by sediment traps) in 29 Swedish lakes was positively related to pH.

The net result of a decline in actual retention or a decrease in TP export from the catchment through time is that higher  $TP_{acc}$  values would be observed using the sediment retention approach (since more "higher retention" years are included in the  $TP_{acc}$  value) relative to the mass balance approach. This might explain why the mass balance approach yielded significantly lower  $TP_{acc}$  values than the sediment approach in both Plastic and Crosson Lakes.

A second explanation for lower  $TP_{acc}$  values using the mass balance approach is due to the omission of external inputs of TP and is potentially a major problem with the mass balance technique (Cross and Rigler 1983; Caraco *et al.* 1988). For example, groundwater inputs of TP not included in the mass balance measurements would result in an underestimate of  $TP_{acc}$  (Shaw *et al.* 1990). In our study lakes, the paucity of surficial material in the watersheds of the lakes and the impervious nature of the bedrock make it unlikely that groundwater is an important component of the water and phosphorus budgets as is also the case in other Canadian Shield lakes (Schindler *et al.* 1976).

Likewise, an underestimate of the known measured inputs of TP to the lakes or an overestimate of the measured output of TP from the lakes would result in an underestimate of  $TP_{acc}$ . However, it is difficult to imagine hydrologic or chemical

budgets that could be, on the one hand, overestimated with respect to output and, on the other hand, underestimated with respect to inputs.

Alternatively, precipitation inputs may have been underestimated by our collection technique. Recently, Cole *et al.* (1990) found that during summer stratification, particle fallout (i.e., 0.7  $\mu\text{m}$  - 1 mm and  $>1$  mm) consisting mainly of terrestrial insects, insect parts and plant fragments, represented a significant input of TP to Mirror Lake, New Hampshire. Their particle collectors which included both precipitation and particle fallout collected about 65 times as much TP as rainfall alone and was 50 to 60% larger than the fluvial input of TP. Since our bulk precipitation collectors included only those particles  $<72$   $\mu\text{m}$  (1977-1982) or  $<102$   $\mu\text{m}$  (1982-1989) in size, an underestimate of TP from large particle fallout might account for the smaller  $\text{TP}_{\text{acc}}$  value obtained using the mass balance approach.

On the other hand, a potential problem with the sediment  $\text{TP}_{\text{acc}}$  approach results from the possibility of post-depositional migration of TP in the sediments. Carignan and Flett (1981) found that sediment cores collected from Lake Memphremagog, Quebec, showed a pronounced peak in total TP concentration within the " $^{210}\text{Pb}$  mixed zone", suggesting that TP was migrating upwards and accumulating in the surface sediments. Similarly, Whalen and Cornwell (1985; citing earlier work) gave evidence that post-depositional migration may have increased the surface concentration of TP in Toolik Lake, Alaska. Therefore, Whalen and Cornwell (1985) normalized their sediment core estimates of  $\text{TP}_{\text{acc}}$  in Toolik Lake (i.e., 52 and 56  $\text{mg}/\text{m}^2/\text{yr}$ ) to Al concentrations in the sediments. The lower value of 52  $\text{mg}/\text{m}^2/\text{yr}$  was derived from weighting the mean SAR in five depth intervals with the proportion of the lake encompassed by each depth interval (similar to the method used in this study) while the higher estimate of 56  $\text{mg}/\text{m}^2/\text{yr}$  involved multiplying the whole-lake Al retention by the average P:Al ratio for the lake.

Post-depositional movement also can affect the accuracy of the  $^{210}\text{Pb}$  dating technique. Recently, Gubala *et al.* (1990) reported that post-depositional diagenesis of Fe about the sediment-water interface and through the sediment resulted in a small error in the SARs calculated for Big Moose Lake, New York, using the CIC model.

While the TP profiles in our study lakes vary with depth in the core (see Figures 1 and 2), the range in concentrations recorded by Carignan and Flett (1981) was much greater, differing by as much as 100% (i.e., from about 1.5 to 3 mg/g) within the  $^{210}\text{Pb}$  mixed zone. Furthermore, where changes in TP concentration are evident, most of the cores from our study lakes exhibit a gradual decrease in TP concentration towards the surface and not an increase as was found by Carignan and Flett. Some of our study lakes exhibit hypolimnetic anoxia during a portion of the summer stratification period, this decrease might be a result of post-depositional migration and subsequent release of TP into the water column (i.e., internal loading of TP) during periods of anoxia.

In conclusion, phosphorus retention calculated from the direct measurement of TP in sediment cores may be a suitable alternative to the more tedious and expensive mass balance approach for determining  $\text{TP}_{\text{acc}}$ , provided that accurate SARs can be obtained and that several cores are collected from the lake. Furthermore, in situations where it is difficult to measure all inputs of TP to the lake (for example from groundwater sources or human activities), the sediment  $\text{TP}_{\text{acc}}$  approach may be in fact the preferred technique.

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**Table 1.** Locations, morphometric characteristics and anthropogenic whole-lake Pb burdens (Pb burden<sub>(WL)</sub>) for each of the study lakes.  $A_o$  = lake area,  $\bar{z}$  = mean depth,  $z_{max}$  = maximum depth.

Lake	Latitude	Longitude	$A_o$ (ha)	$\bar{z}$ (m)	$z_{max}$ (m)	Pb burden <sub>(WL)</sub> (mg/rn <sup>2</sup> )
Blue Chalk	45°12'N	78°56'W	52.4	8.5	23	539
Chub	45°13'N	78°59'W	34.4	8.9	27	647
Crosson	45°05'N	79°02'W	56.7	9.2	25	692
Heney	45°08'N	79°06'W	21.4	3.3	5.8	724
Jerry	45°23'N	79°06'W	50.1	12.4	35	733
Plastic	45°10'N	78°48'W	32.1	7.9	16	763
Red Chalk	45°11'N	78°56'W	57.1	14.2	38	661

**Table 2.** Average surface (0-3 cm) concentrations of total phosphorus ([TP]), sediment accumulation rates (SAR), anthropogenic Pb burdens at each site (Pb burden<sub>(Site)</sub>, and TP retention (TP<sub>acc</sub>) at each site calculated according to equation (1).

Lake	Lake Depth (m)	[TP] (mg/g)	SAR (g/m <sup>2</sup> /yr)	Pb burden <sub>(Site)</sub> (mg/m <sup>2</sup> )	TP <sub>acc</sub> (mg/m <sup>2</sup> /yr)
Blue Chalk	8.4	1.2	64.7	1038	40.3
	12.0	1.2	28.5	254	72.6
	15.3	1.5	82.8	1402	47.8
	19.9	1.4	96.1	1630	44.5
	23.0	1.6	50.1	1100	39.3
Mean (s.d.)					48.9 (13.7)
Chub	6.9	1.6	98.0	529	191.7
	13.1	1.5	137.5	1085	123.0
	18.4	1.7	77.8	1409	60.7
	19.9	1.7	89.9	1383	71.5
	23.5	2.5	198.5	2012	159.6
Mean (s.d.)					121.3 (56.1)
Crosson	4.6	0.98	314.7	1257	169.8
	7.6	1.4	96.7	520	180.2
	11.4	1.4	91.7	920	96.6
	12.9	1.6	126.9	973	144.4
	23.3	1.9	-	2122	-
Mean (s.d.)					147.7 (37.3)
Heney	3.9	1.4	67.3	1061	62.9
	4.0	1.3	73.8	1184	58.7
	4.3	1.3	105.6	851	114.1
	4.5	1.4	117.1	1084	105.6
	5.5	1.5	111.1	738	163.4
Mean (s.d.)					100.9 (42.8)

**Table 2.** (continued)

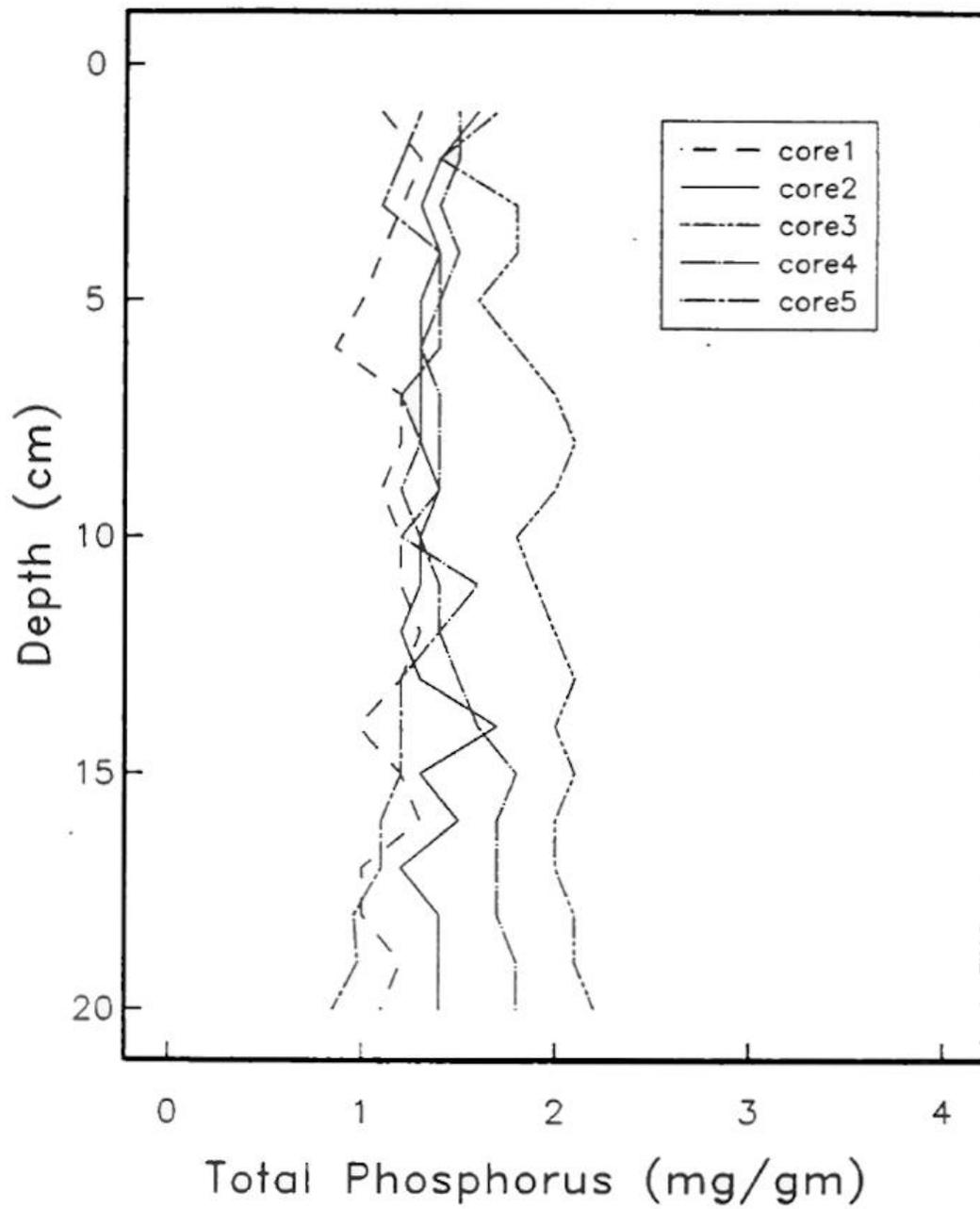
Lake	Lake Depth (m)	[TP] (mg/g)	SAR (g/m <sup>2</sup> /yr)	Pb burden <sub>(Site)</sub> (mg/m <sup>2</sup> )	TP <sub>acc</sub> (mg/m <sup>2</sup> /yr)
Jerry	4.8	0.99	464.8	637	529.6*
	11.0	1.3	90.9	1034	85.7
	17.3	1.8	117.5	965	158.0
	20.2	1.7	108.9	1262	105.6
	32.2	3.2	173.1	2139	191.6
Mean (s.d.)				(n=4)	135.2 (48.4)
Plastic	9.8	2.5	58.8	931	120.5
	10.1	1.9	55.8	1128	71.7
	11.9	1.4	45.6	951	51.2
	15.8	1.6	54.8	925	72.3
	17.5	2.1	85.0	1289	105.7
Mean (s.d.)					84.3 (28.1)
Red Chalk (East Basin)	4.9	0.92	125.0	601	126.6
	10.3	1.2	116.6	1001	92.4
	15.8	1.4	134.7	1555	80.1
(Main Basin)	9.5	1.2	59.4	971	48.5
	14.5	1.3	39.5	447	75.9
	18.6	2.9	56.8	457	238.5*
	28.0	3.3	66.4	1906	76.0
	34.0	1.7	62.8	1326	53.2
Mean (s.d.)				(n=7)	79.0 (26.0)

\* omitted (see text for explanation)

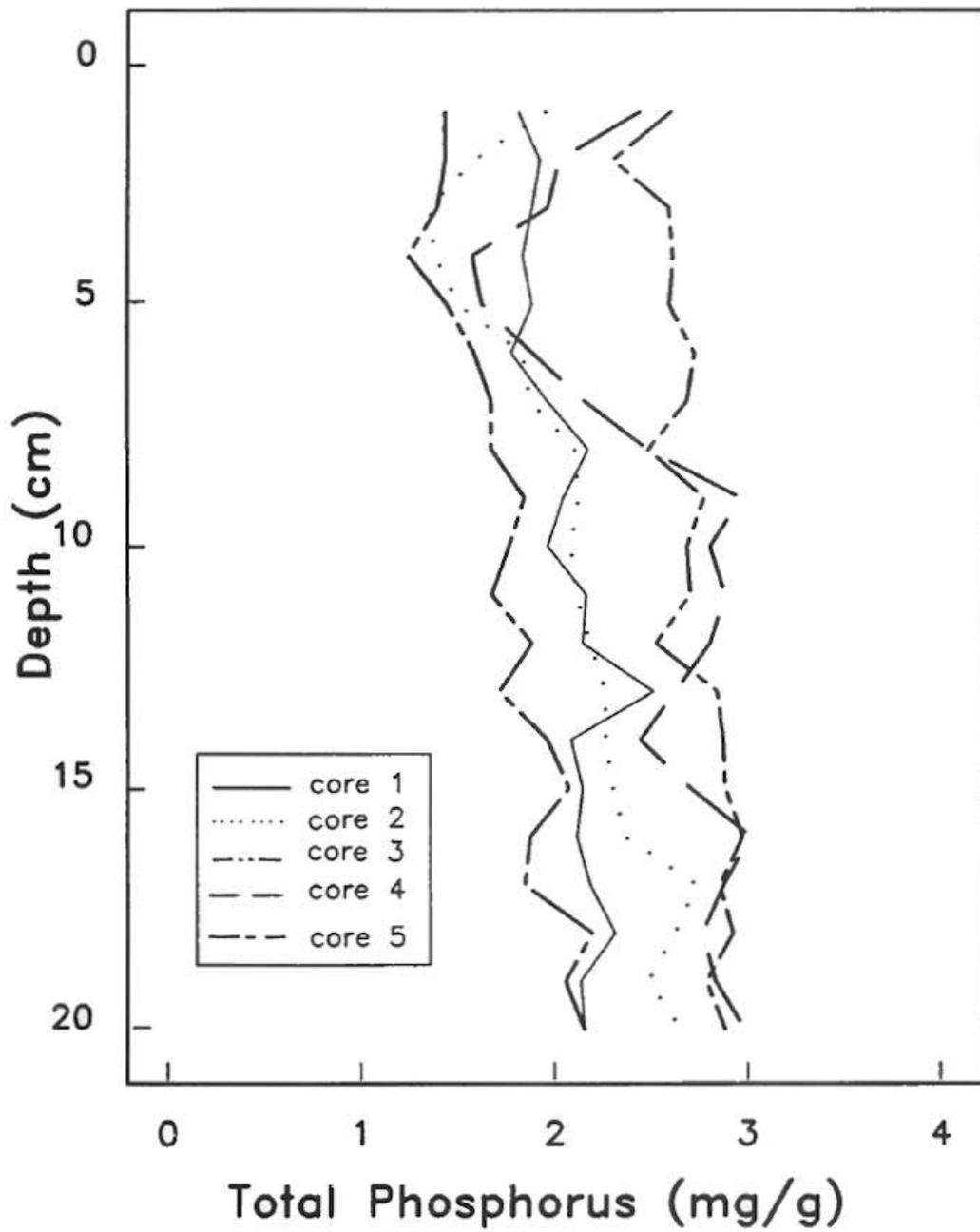
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**Table 3.** Total inputs of TP to each lake, output of TP from each lake and the net retention ( $TP_{acc}$ ) of TP by each lake.

Lake	Hydrologic Years	Total Input	Total Output	Input-Output	$TP_{acc}$
		----- (10 <sup>7</sup> mg/yr) -----			(mg/m <sup>2</sup> /yr)
Blue Chalk	1977-89	2.28 ±0.46	0.46 ±0.12	1.83 ±0.45	35 ±8.6
Chub	1977-89	3.16 ±0.71	1.39 ±0.35	1.77 ±0.53	51 ±15
Crosson	1980-89	5.61 ±0.68	3.24 ±0.76	2.37 ±0.42	42 ±7.4
Heney	1980-89	2.11 ±0.53	0.30 ±0.07	1.81 ±0.50	85 ±23
Jerry	1977-80	8.77 ±1.24	4.03 ±1.10	4.74 ±1.15	94 ±23
Plastic	1979-89	1.06 ±0.14	0.41 ±0.16	0.65 ±0.13	20 ±3.9
Red Chalk	1977-89	4.20 ±0.96	1.76 ±0.42	2.44 ±0.65	43 ±11



**Fig. 1.** Total phosphorus concentration in 5 sediment cores collected from Blue Chalk Lake.



**Fig. 2.** Total phosphorus concentration in 5 sediment cores collected from Plastic Lake.