The Availability of Phosphorus from Anoxic Hypolimnia to Epilimnetic Plankton

by

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Short Title:

The Availability of Phosphorus

from Anoxic Hypolimnia

For Mutti (G.N.)

Abstract

The availability of phosphorus from the anoxic hypolimnia of lakes to epilimnetic plankton was investigated by experimental studies on eight lakes in Ontario and Quebec. Availability was determined with a short-term bioassay based on the standardized retardation of planktonic uptake of phosphorus tracer in the presence of orthophosphate; availability was also estimated by SRP (soluble reactive phosphorus) analysis, since approximately 90% of SRP was available.

Iron concentrations were high in some hypolimnia, but should become diluted after mixing with surface water. When iron concentrations after mixing exceeded 0.20 mg/L, aeration lowered availability and SRP. Therefore, samples from anoxic hypolimnia were kept anoxic. The fate of hypolimnetic phosphorus at turnover was studied by construction of a budget for SRP, total phosphorus, particulate iron containing phosphorus and particulate biological phosphorus at fall turnover in Lake Magog. Despite high concentrations of hypolimnetic iron, only 30% of the upwelling hypolimnetic phosphorus combined with iron after complete mixing, 30% was incorporated into biomass and 38% stayed potentially available as SRP.

In two lakes, hypolimnetic iron was undetectable and hydrogen sulfide concentrations were high. H_2S interferred with the SRP analysis and poisoned plankton. After degassing,

routine SRP analysis was possible, and availability was close to 100%. Iron and H_2S interference in the SRP analysis were circumvented by maintaining anoxia or by degassing resp. A simpler method, the analysis of TRP (total reactive phosphorus) after aeration, was developed which analyses SRP quantitatively in anoxic waters.

Since the experimental studies suggest that 70-80% of hypolimnetic phosphorus is available, empirical models were developed to predict the effect of hypolimnetic phosphorus (i.e. internal phosphorus load) on the mass balance of phosphorus in lakes with anoxic hypolimnia. The first model, successfully predicted internal load; it was constructed from the deviations between observed phosphorus retention in anoxic lakes and the retention predicted by models for oxic lakes, and external load. Internal load may also be predicted from the average release rate (12 mg m^{-2} day^{-1}) of phosphorus from the surface of anoxic sediment, the duration of anoxia and the area of anoxic sediments. Empirical relationships built from data collected during this study and previously published data support the hypothesis that the major part of hypolimnetic phosphorus is available to epilimnetic plankton.

Résumé

La disponibilité au plancton épilimnétique du phosphore en provenance de l'hypolimnion anoxique fut examinée par des études expérimentales dans huit lacs du Québec et de l'Ontario. La disponibilité fut déterminée a l'aide de bioessais à court terme basés sur le taux de retardation standardisé de l'incorporation du P radioactif par le plancton en présence de l'orthophosphate. La disponibilité a également été estimée par l'analyse du PRS (Phosphore réactif soluble) puisque qu'approximativement 90% du PRS était disponible dans les eaux anoxiques.

Les concentrations de fer étaient élevées dans certains hypolimnions, mais devraient être diluées après le mélange avec les eaux de surface. L'aération diminue la disponibilité du phosphore lorsque les concentrations de fer excèdent 0.02 $mg.l^{-1}$ après le mélange des eaux. Conséquemment, les échantillons de l'hypolimnion anoxique étaient gardés anoxiques. L'utilisation du P hypolimnétique suite au mélange des eaux a été étudié par l'entremise d'un budget du PRS, TP, phosphore adsorbé sur les particules ferriques et des particules de phosphore biologique lors du brassage automnal dans le lac Magog. En dépit des fortes concentratins de fer hypolimnétique, seulement 30% du P hypolimnétique se combine avec le fer apres le brassage automnal; 30% sera incorporé dans la biomasse et ainsi 38% demeure partiellement disponible comme PRS.

Dans deux lacs, la concentration de fer hypolimnétique était inférieure à la limite de détection et les concentrations d'hydrogène sulfureux (H_2S) étaient élevées. Le H_2S a interféré avec les analyses du PRS et empoisonna le plancton. Après le dégazage, les analyses de routine du PRS étaient possibles et la disponibilite était près de 100%.

L'interférence par le fer et le H_2S dans l'analyse du PRS fut éliminée soit par le dégazage ou en maintenant l'anoxie. Une méthode simplifiée, l'analyse du PRT (phosphore reactif total) après aération a été développée, ce qui permet de determiner quantitativement le PRS dans les eaux anoxiques.

Puisque des études expérimentales suggèrent que 70-80% du P hypolimnétique est disponible, des modèles empiriques ont été développés dans le but de prédire l'effet du P hypolimnétique (i.e. la charge interne de P) sur le budget du P dans les lacs ayant un hypolimnion anoxique. Le premier modèle prédit avec succès la charge interne. Ce modèle a été construit à partir des déviations entre la rétention observée du phosphore dans les lacs anoxiques et la rétention prédite à partir des modèles pour les lacs oxiques, et la charge externe. La charge interne peut aussi être prédite à partir des taux moyens de décharge ($12\ mg.l^{-1}.day^{-1}$) de P de la surface des sédiments anoxiques, la durée de l'anoxie et l'aire des sédiments anoxiques. Les relations empiriques construites à partir des données amassées dans le cadre le mon projet et celles de la littérature supportent l'hypothèse que la majeure partie du phosphore hypolimnétique est disponible pour le plancton épilimnétique.

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Preface

The following statements are made to comply with the regulations of the Faculty of Graduate Studies and Research of McGill University.

This thesis has been prepared in the format of four separate papers, suitable for submission to learned journals, as permitted by Faculty regulations. Due to this, a certain amount of redundancy and stylistic idiosyncrasy is inevitable. Slightly abridged versions of Chapters three, four and six are in press in 'Water Research', 'Canadian Journal of Fisheries and Aquatic Sciences' and 'Limnology and Oceanography' respectively. Chapter five has been submitted. Much material from the first and the last chapter is to be published in the proceedings of the 'International Association of Theoretical and Applied Limnology'. The fourth chapter is co-authored by Dr. R.H. Peters, who supervised this study. The first person plural is accordingly used in this chapter. Tables and figures are numbered by two numbers combined with a dash: the first character references the chapter and the second the sequence in the chapter. Tables and figures belonging to the current chapter are referred to by their sequence number only.

This thesis constitutes a contribution to original knowledge in the following methodological developments and scientific findings:

Methodological developments:

- It is shown that iron and hydrogen sulfide interfere in the SRP (soluble reactive phosphorus) analysis of anoxic waters and an adequate SRP analysis in anoxic waters has been developed.
- A simple technique that can replace SRP analysis in anoxic waters (TRP - total reactive phosphorus) was developed.
- An analysis for freshly formed iron-phosphorus particles (PRP - particulate reactive phosphorus) evolved from these studies.
- A simplified technique for the analysis of ferrous iron is presented, which is suitable as a field technique.

Scientific findings:

- SRP can be used to estimate BAP (bioavailable phosphorus) in oxic and anoxic water, with the exception of recently aerated iron-rich waters.
- Most hypolimnetic phosphorus is available to epilimnetic plankton even when iron concentrations are high.
- The effect of iron concentration and dilution on the availability of phosphorus from anoxic hypolimnia has been quantified.
- Existing models that predict phosphorus retention and total phosphorus concentration by mass balance models do not apply to lakes with anoxic hypolimnia.
- A phosphorus mass balance model and two internal load models were developed for lakes with anoxic hypolimnia.
- A phosphorus retention model for oxic stratified lakes was developed.

Acknowledgements

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Chapter 1:

Introduction

Existing evidence suggests that phosphorus is the "limiting nutrient" that controls primary production in many lakes (Schindler 1975). This is reflected in the high correlations between phosphorus and phytoplankton biomass (Sakamoto 1966; Dillon and Rigler 1974b), and in the experimental demonstration that Canadian Shield Lakes are phosphorus limited: for lake trophy could be increased by artificial phosphorus fertilization, and eutrophication could be halted by stopping fertilization (Schindler 1974). Lake management, which is typically designed to reduce algal concentrations, is mainly concerned with reducing the amount of phosphorus coming into the lake (Loehr et al. 1980). Even in lakes where phosphorus is in surplus and nitrogen is limiting, attempts are made to reduce phosphorus so as to establish phosphorus limitation, because the low nitrogen to phosphorus ratios encountered in these lakes favor blooms of nuisance blue green algae (Smith 1983).

In lakes where external phosphorus input is the major phosphorus source, nutrient abatement has the desired effect: concentrations of algae are decreased and the trophic status improved. This has been well documented in Lake Washington (Edmondson 1970) where diversion of sewage effluents entering the lake began 1963 and was completed in 1968. During this period, phosphorus and chlorophyll concentrations decreased and secchi disk transparency increased, indicating a

successful reversal of eutrophication.

However, in lakes with an internal phosphorus source, nutrient reductions have not always resulted in complete recovery. Decaying macrophytes (Carpenter 1980), leaching from the soil in reservoirs (Ostrofsky 1978b) and phosphorus release from the sediment surface overlain by anoxic water (Holdren and Armstrong 1980) have been suggested to be significant internal phosphorus sources. Anoxic sediment surfaces are commonly found in the hypolimnion of shallow, stratified lakes. In this thesis, lakes in which the hypolimnion is partially anoxic for at least two weeks are termed "anoxic". The phosphorus released from anoxic sediments and accumulated in the anoxic hypolimnia of these lakes is the subject of this thesis.

"Anoxic" lakes recover more slowly after nutrient diversion than predicted from mass balance models (e.g. Vollenweider 1975). Such lakes include Lake Sammamish (Welch and Rock 1980), Stone Lake (Theis and Depinto 1976), Soera Bergundasjoen (Bengtsson 1978), East and West Twin Lakes (Cooke and Kennedy 1978), Lillesjoen (Ripl and Lindmark 1978) and Shagawa Lake (Larsen et al. 1981). In many of these cases, the delayed recovery has been attributed to loading from the anoxic sediment surface. This internal load can contribute up to 91% of the total phosphorus input (external and internal load) to the anoxic lake (Soera Bergundasjoen, Bengtsson 1978). For 23 stratified lakes with anoxic hypolimnia, internal load contributes 39%, on average, to the total

phosphorus load (Table 1). For such lakes, expensive restoration techniques may be required to improve water quality (for a general overview see: Dunst et al. 1974, and U.S. National Symposia on Lake Restoration, U.S.-EPA 1979 and 1981). These techniques include dredging (e.g. Bengtsson et al. 1975; Peterson 1982) or covering the sediments (reviewed by Cooke 1980), application of alum (e.g. Cooke and Kennedy 1978) and fly ash (e.g. Theis and McCabe 1978), nitrate oxidation of the sediment surface (Ripl and Lindmark 1978) and hypolimnetic aeration (e.g. Bernhardt 1975).

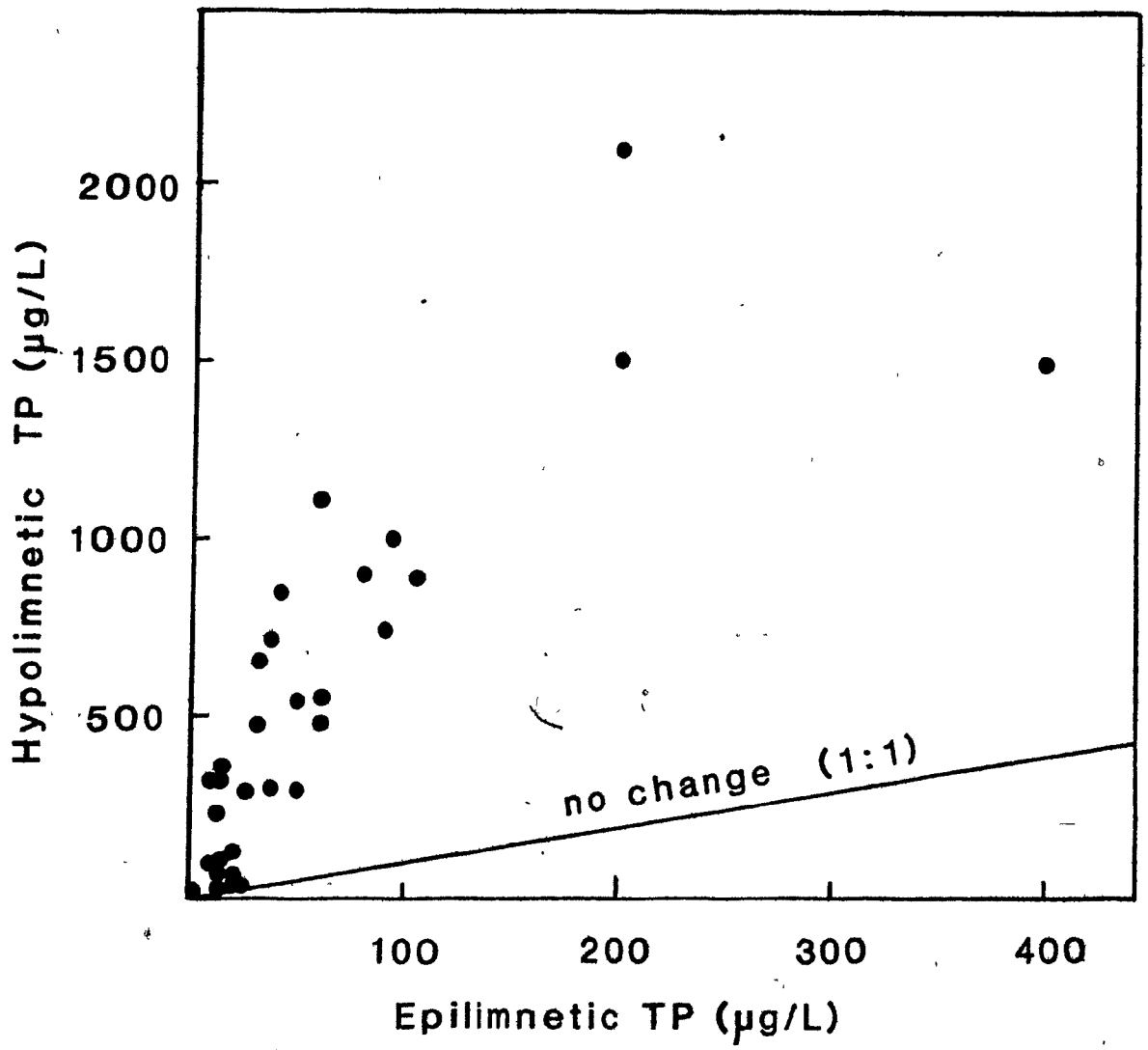
Despite this empirical evidence of enhanced eutrophication in anoxic lakes, the mechanisms of this eutrophication process are still controversial. There exist data which show that anoxic phosphorus release can be substantial and results in high hypolimnetic phosphorus concentrations: Mortimer (1941, 1942) discovered experimentally that phosphorus was released from the sediment of Esthwaite Water when it was overlain by oxygen free water. Einsele (1936) and Ohle (1937) observed high concentrations of phosphorus in the water overlying anoxic sediment surfaces in situ. To verify the generality of this phenomenon, data for anoxic lakes were collected from more recent literature. They demonstrate that hypolimnetic phosphorus concentrations are high compared to surface water concentrations (Fig. 1). If this phosphorus in the hypolimnion is available to the plankton, the anoxic lakes must be more productive than morphometrically comparable oxic lakes with similar external phosphorus inputs.

Table 1-1. Internal phosphorus load estimates (in situ) compared to external loads in mg m^{-2} yr^{-1}. %: 100 x int. load/ (ext.load + int. load).

Source: (1) Table 2c of Chapter 6; (2) Sonzogni 1974; (3) Imboden and Emerson 1978; (4) Allan et al. 1980.

Lake	Year	int. L	ext. L	%	Source
Bergundasjoen	74	4200	2110	67	(1)
	75	1860	410	82	(1)
	76	2400	240	91	(1)
Norrviken	71	400	420	49	(1)
Shagawa	71	291	739	28	(1)
	72	224	675	25	(1)
	73	332	231	59	(1)
	74	216	161	57	(1)
	75	293	110	73	(1)
West Twin	72	253	420	38	(1)
	73	336	180	65	(1)
	74	94	320	23	(1)
	76	53	280	16	(1)
East Twin	72	286	670	30	(1)
	73	314	470	40	(1)
	74	94	820	10	(1)
	76	74	470	14	(1)
Mendota	71	520	1580	25	(2)
Greifensee	76	2540	2670	49	(3)
Pasqua		1310	9410	12	(4)
Echo		1250	15540	7	(4)
Mission		1250	2576	33	(4)
Katepwa		1310	11840	10	(4)

Fig. 1-1. A comparison of hypolimnetic and epilimnetic total phosphorus concentration just before fall turnover for worldwide lakes.


2000
1500
1000
500
Hypolimnetic TP (µg/L)
no change (1:1)
100
200
300
400
Epilimnetic TP (µg/L)

However it is not generally accepted that this hypolimnetic phosphorus is or becomes available to epilimnetic plankton for the following reasons: 1) this phosphorus may never reach the phytoplankton in the trophogenic zone; 2) released phosphorus may be in a chemically unavailable form even within the hypolimnion; 3) ferrous iron, which is often released from the anoxic sediment surface with phosphorus, may form iron hydroxides that would adsorb and precipitate all the phosphorus derived from the hypolimnion when the lake finally destratifies. If these hypotheses hold, anoxic lakes should respond to nutrient abatement like oxic lakes. This is not generally found.

The hypothesis that hypolimnetic phosphorus never influences the phosphorus status of the surface water is inconsistent with other evidence from anoxic lakes. The surface concentration of phosphorus in such lakes reaches maximal values following turnover (Fig. 2) and these maxima correlate positively with the hypolimnetic phosphorus concentration before destratification (Fig. 3). These data suggest that hypolimnetic phosphorus is mixed into the surface water during turnover. Furthermore, the erosion of the thermocline during summer is sometimes accompanied by algal blooms (Kortmann et al. 1982; Stauffer and Lee 1974), suggesting that at least some hypolimnetic phosphorus may be used by algae well before turnover.

The remaining two hypotheses, which relate to the chemical form of phosphorus in the hypolimnion and after entrainment, need further evaluation. Accordingly, this thesis

Fig. 1-2. Total phosphorus concentrations before and after fall turnover in the surface water of worldwide lakes.

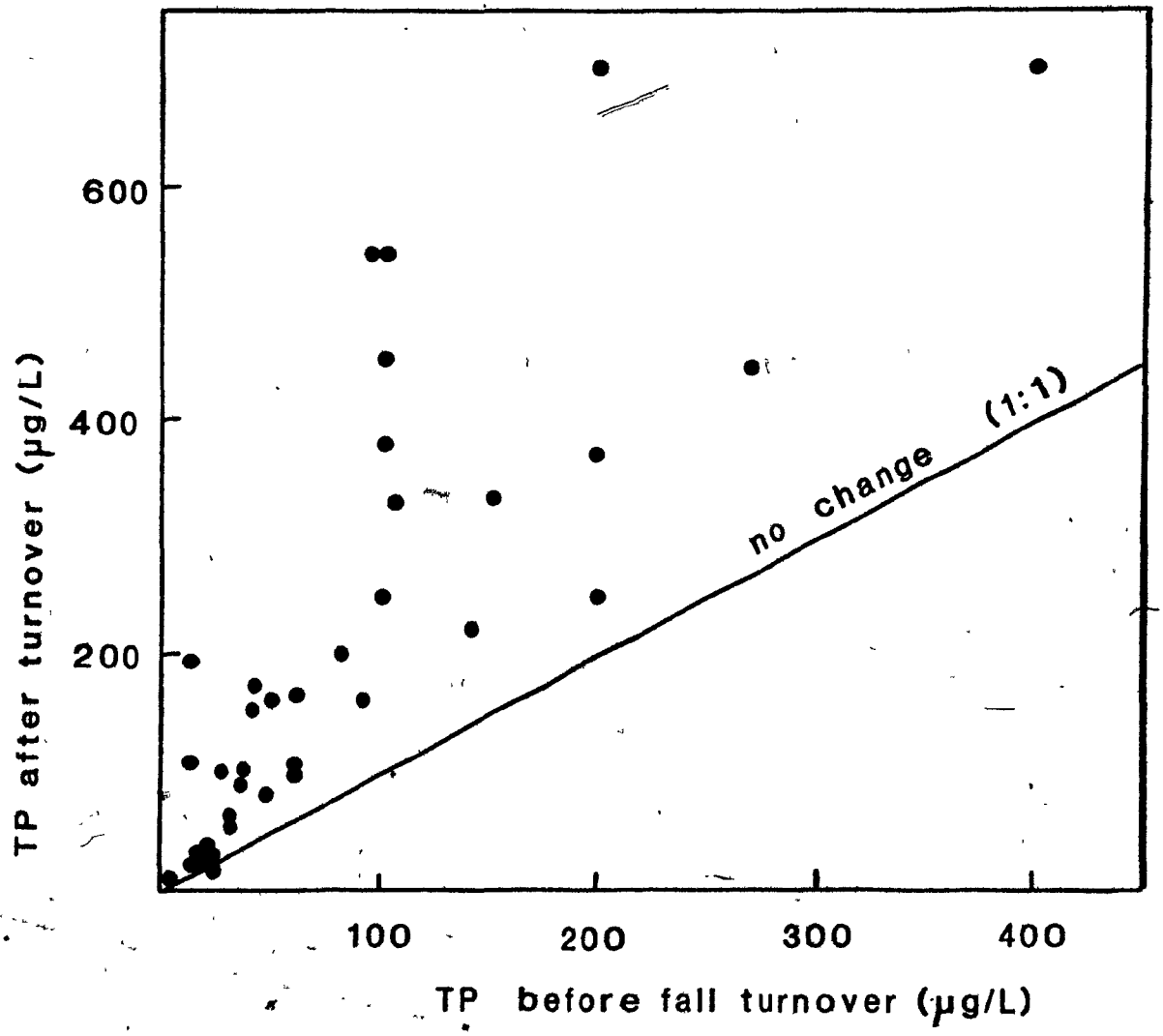
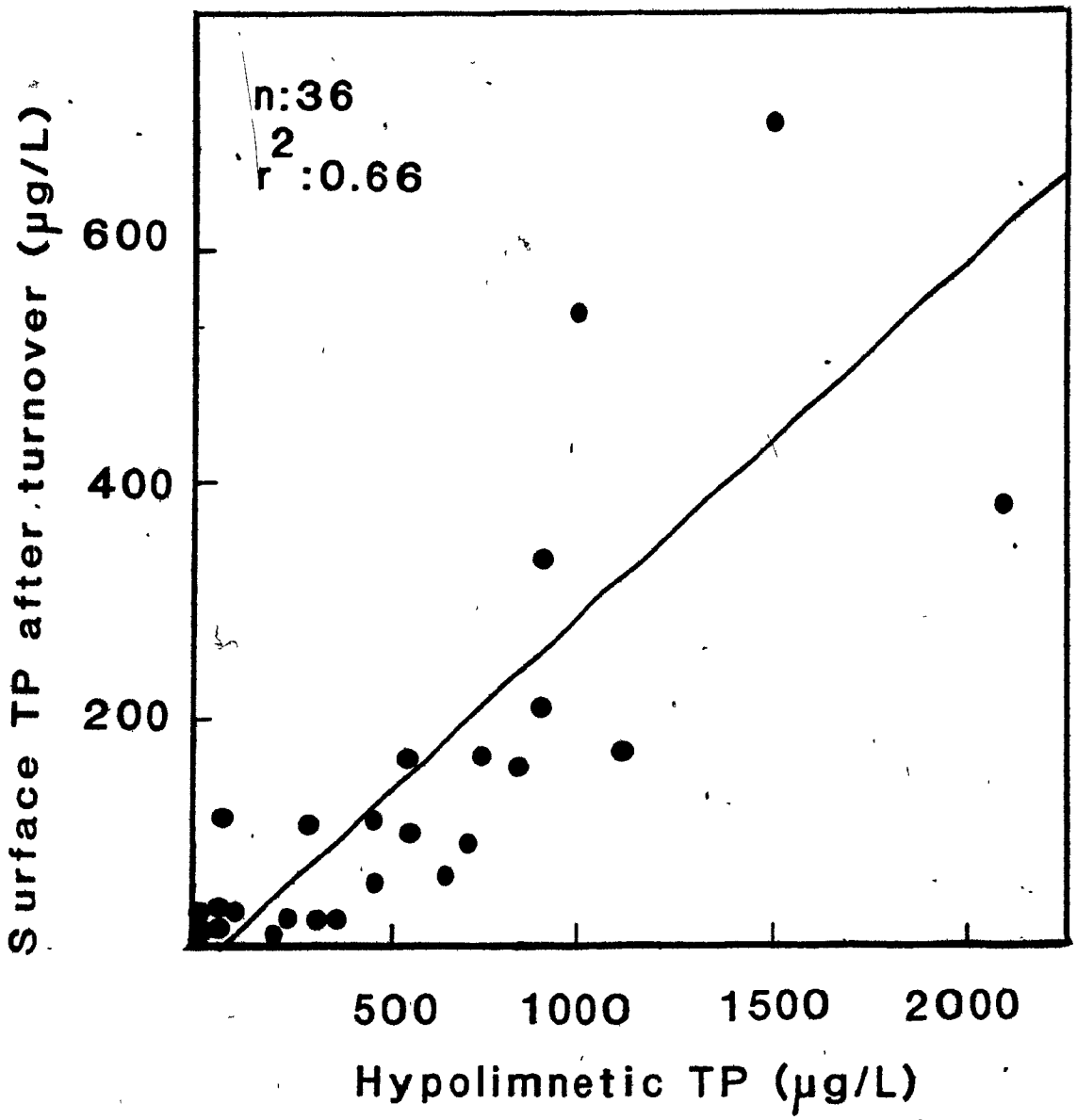

600
400
200
TP after turnover (µg/L)
no change (1:1)
100
200
300
400
TP before fall turnover (µg/L)

Fig. 1-3. Surface total phosphorus concentration after fall turnover in relation to hypolimnetic total phosphorus concentration before turnover; regression equation $f(x) = -18.92 + 0.30\ x$.


n:36
r 2 :0.66
600
400
200
Surface TP after turnover (µg/L)
500
1000
1500
2000
Hypolimnetic TP (µg/L)

seeks to test the following hypotheses in more detail: 1) Most of the hypolimnetic phosphorus in anoxic lakes is potentially available to the plankton as, within the hypolimnion, phosphorus is in a form which could be used if the plankton could reach it. 2) Even after mixing into aerated surface water, much of the hypolimnetic phosphorus remains available despite high iron concentrations. From these hypotheses a third more general hypothesis emerges, since, if hypolimnetic phosphorus accumulation can be substantial and can fertilize the lake, anoxic lakes should have different phosphorus mass balances than oxic lakes. The third hypothesis can be stated as 3) phosphorus models which concern anoxic lakes are different from those for oxic lakes, because of internal phosphorus load.

These hypotheses are tested with field and experimental studies on eight anoxic lakes in Quebec and Ontario and with published data. The study lakes have different geochemical characteristics and include hardwater and colored softwater lakes. The range of phosphorus concentrations among lakes is large which makes it possible to investigate lakes with different trophic states. This range of conditions makes the test of the first hypothesis more general. Also hypolimnetic iron concentrations differ from undetectable to substantial (6 mg/L) amounts which provides suitable conditions to test the second hypothesis regarding the influence of iron on the availability of hypolimnetic phosphorus. The third hypothesis is tested on published data for phosphorus retention and total

phosphorus concentration models.

The lakes used in my experimental studies are described in Chapter 2. That chapter also introduces the methods used to fractionate and analyse iron and phosphorus. More sophisticated methods are presented in Chapters 3 to 5.

The analysis of anoxic waters requires more precautions than recommended in standard procedures. SRP (soluble reactive phosphorus), which gives a maximum estimate of available phosphorus, can easily be underestimated by adsorption of soluble phosphorus onto iron hydroxides if anoxic iron-rich water was aerated accidentally. Even without detectable iron, hydrogen sulfide can interfere with the phosphorus analysis causing unstable and erroneous results. Therefore, SRP analysis was modified for use in anoxic waters high in iron or hydrogen sulfide. In addition, a standard analysis for ferrous iron was simplified to provide a quick method to detect high iron concentrations. These modifications are described in Chapter 3.

The availability of hypolimnetic phosphorus was measured directly in radiological bioassays. These assays are described in detail in Chapter 4. That chapter tests the hypothesis of the equivalence of biologically available phosphorus and SRP. Since hypolimnetic phosphorus is mostly SRP, this equivalence indicates that most phosphorus in the hypolimnion is available. Chapter 4 also compares biologically available phosphorus to SRP in oxic freshwater systems.

Chapter 5, 6 and 7 represent the results proper of this thesis. Chapter 5 quantifies the influence of iron

concentration with small scale experiments on hypolimnetic water and with a case study, which determines the distribution of phosphorus from the anoxic hypolimnion of Lake Magog, Quebec during fall turnover. This chapter shows that the internal phosphorus load in anoxic lakes can be substantial, even in the presence of iron (Hypothesis 2). Chapter 6 then develops models to predict both internal phosphorus load and average total phosphorus concentrations for anoxic lakes. These models are developed and tested with data from the literature. They show that phosphorus models for oxic lakes do not apply to anoxic lakes (Hypothesis 3). The concluding chapter (Chapter 7) synthesizes the results and conclusions obtained previously and evaluates further untested hypotheses on the subject. In particular, Chapter 7 tests Hypothesis 1, that phosphorus is in an available form while in the hypolimnion, for all the study lakes together.

Chapter 2:

Study Lakes and Basic Methods

Specific methods are presented in the methods sections of the chapters in which they are most relevant. This chapter gives some general characteristics of the studied lakes and outlines the most important analytical methods.

Lakes studied:

In order to investigate if water chemistry greatly influences the effect of phosphorus from anoxic hypolimnia on phytoplankton, waters with a wide range of iron, phosphorus, hydrogen sulfide, hardness, acidity and color were investigated. This range was achieved by sampling several lakes, which were spatially and chemically different. Frequent sampling of the same lake during summer stratification, when iron, phosphorus and reduced gases increased also provided heterogenity. Lake morphometry and hydrology are summarized in Table 1. Table 3-1 presents the location and some chemical characteristics of the study lakes. Maps indicating the sampling stations are given for each lake in Figs. 1 to 8.

Sampling:

Routine sampling of epilimnetic and hypolimnetic water is described in detail in Methods of Chapter 5. The anoxic water was sampled so as to avoid any oxygen contamination and the sample water kept in airtight BOD bottles until analysis.

Table 2-1 Morphometry and water residence time (q_s) of the study lakes.

Lake	Volume ($m^3 10^4$)	Area (ha)	z (m)	z_{max} (m)	q_s ($m\ yr^{-1}$)
Magog[a]	8,553	1,044	9.8	19	164
Fitch Bay[a]	2,807	280	10.0	17	n.a.
Jack (Williams Bay)[b]	700	100	8.8	22	1.1
St. George[c], West	22	4	5.3	15	2.4
East	30	5	5.9	16	2.4
Glen[d]	118	16	7.2	15	3.3*
Chub[d]	285	32	8.9	27	4.4*
Little Clear[d]	89	11	8.1	25	256.1*
Blue Chalk[d]	42	49	8.5	23	1.7*

n.a. not available; a: Lardner-Cornett (1981); b: Pick (1982); c: McQueen, Toronto (pers. comm.); d: Ministry of the Environment, Toronto, Ontario. *: average of the years 1976-1980.

Fig. 2 Maps of the study lakes. Sample sites are indicated by points, crosses or stars.

Fig. 2-1 Lake Magog

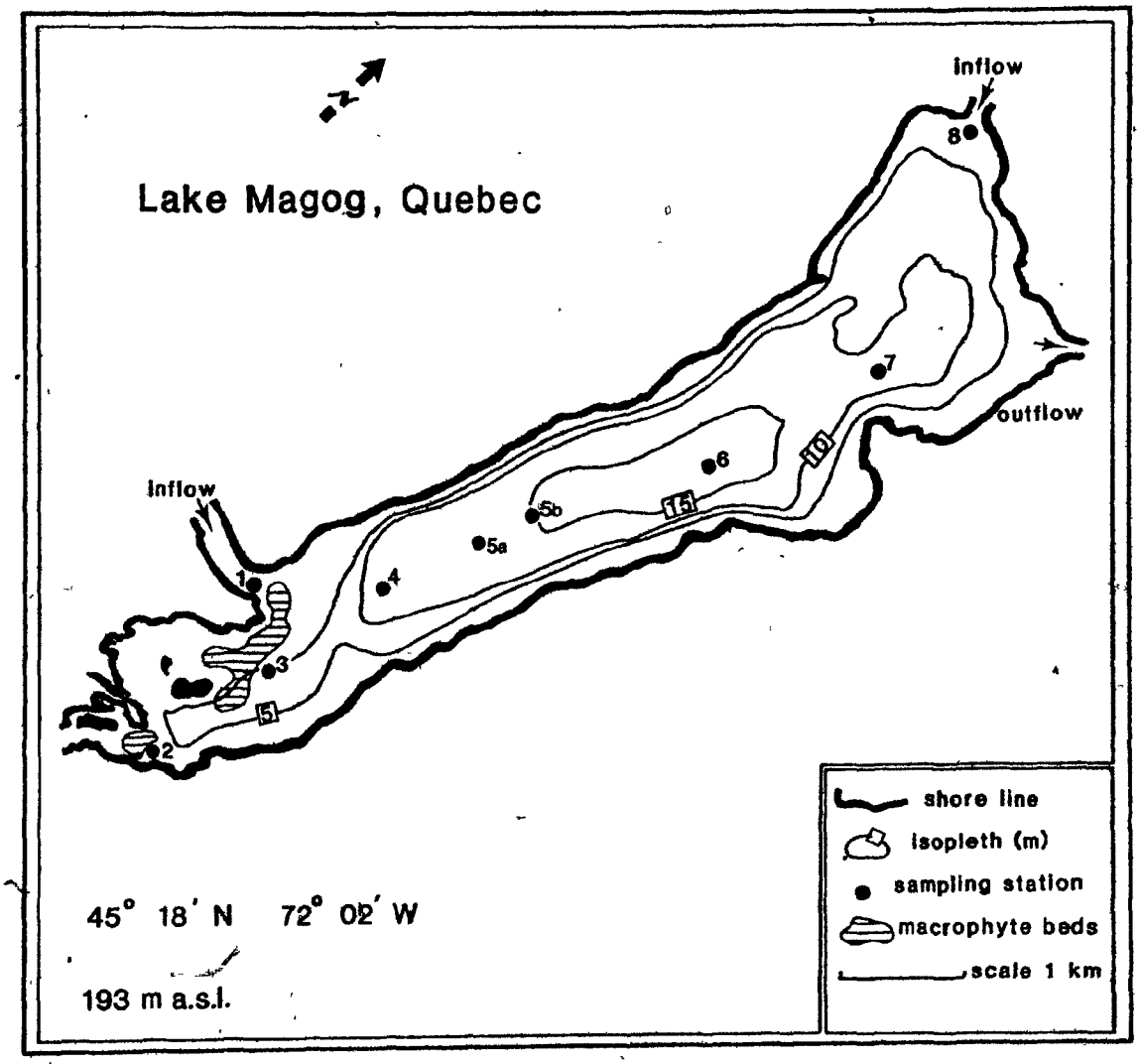

Lake Magog, Quebec
N
inflow
8
7
outflow
6
10
15
inflow
5b
5a
4
1
3
5
2
45° 18' N 72° 02' W
193 m a.s.l.
shore line
isopleth (m)
sampling station
macrophyte beds
scale 1 km

Fig. 2-2 Lake Memphremagog

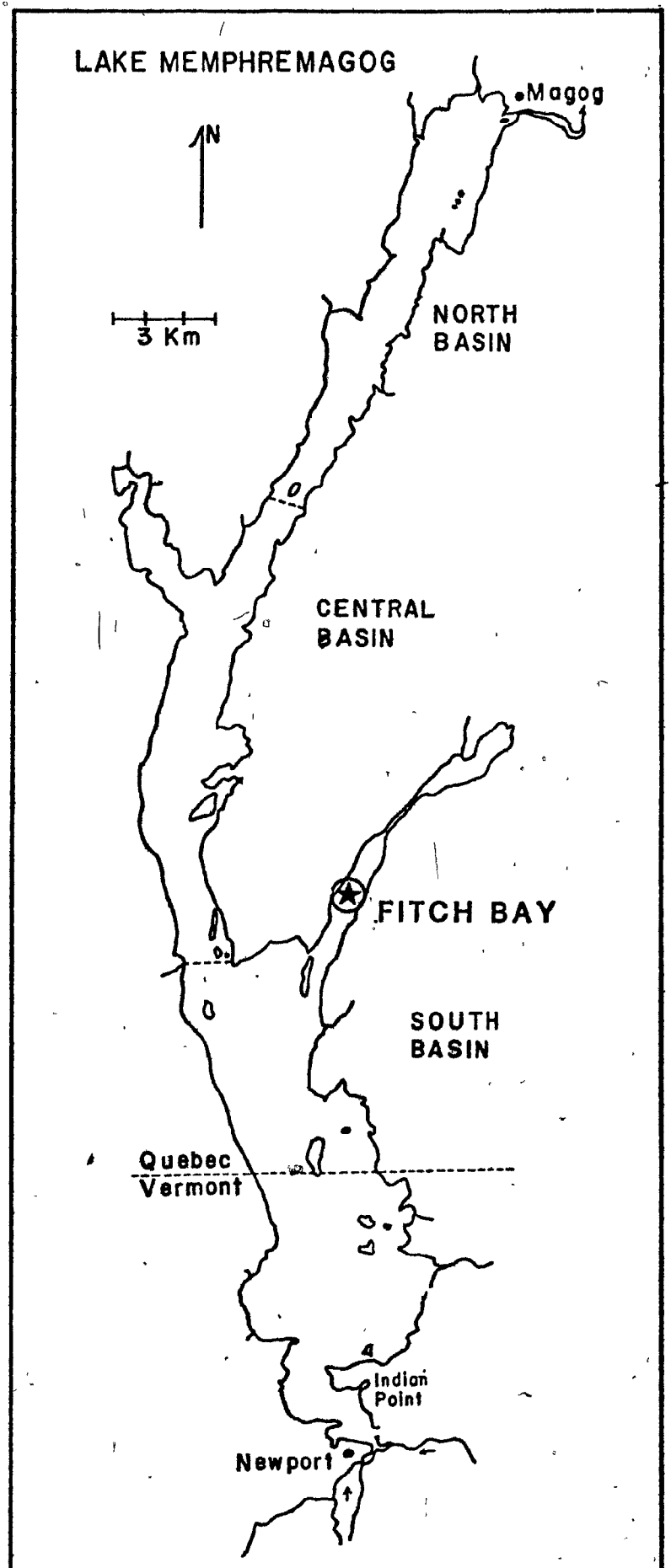

LAKE MEMPHREMAGOG
Magog
N
3 Km
NORTH BASIN
CENTRAL BASIN
FITCH BAY
SOUTH BASIN
Quebec
Vermont
Indian Point
Newport

Fig. 2-3 Jack Lake

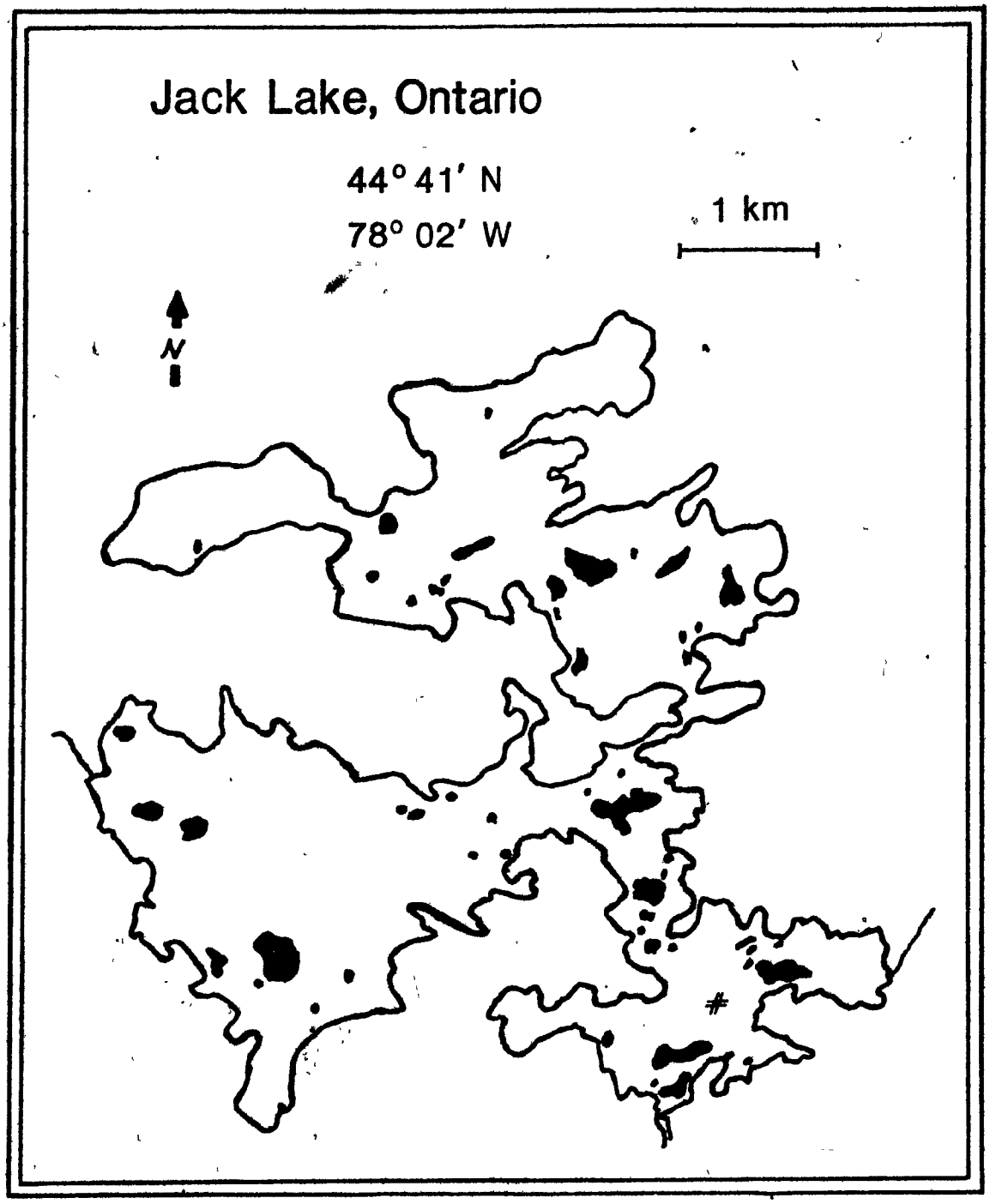

Jack Lake, Ontario
44° 41′ N
78° 02′ W
1 km
N

Fig. 2-4 Lake St.George (Mc Queen, pers. comm.)

Lake St.George

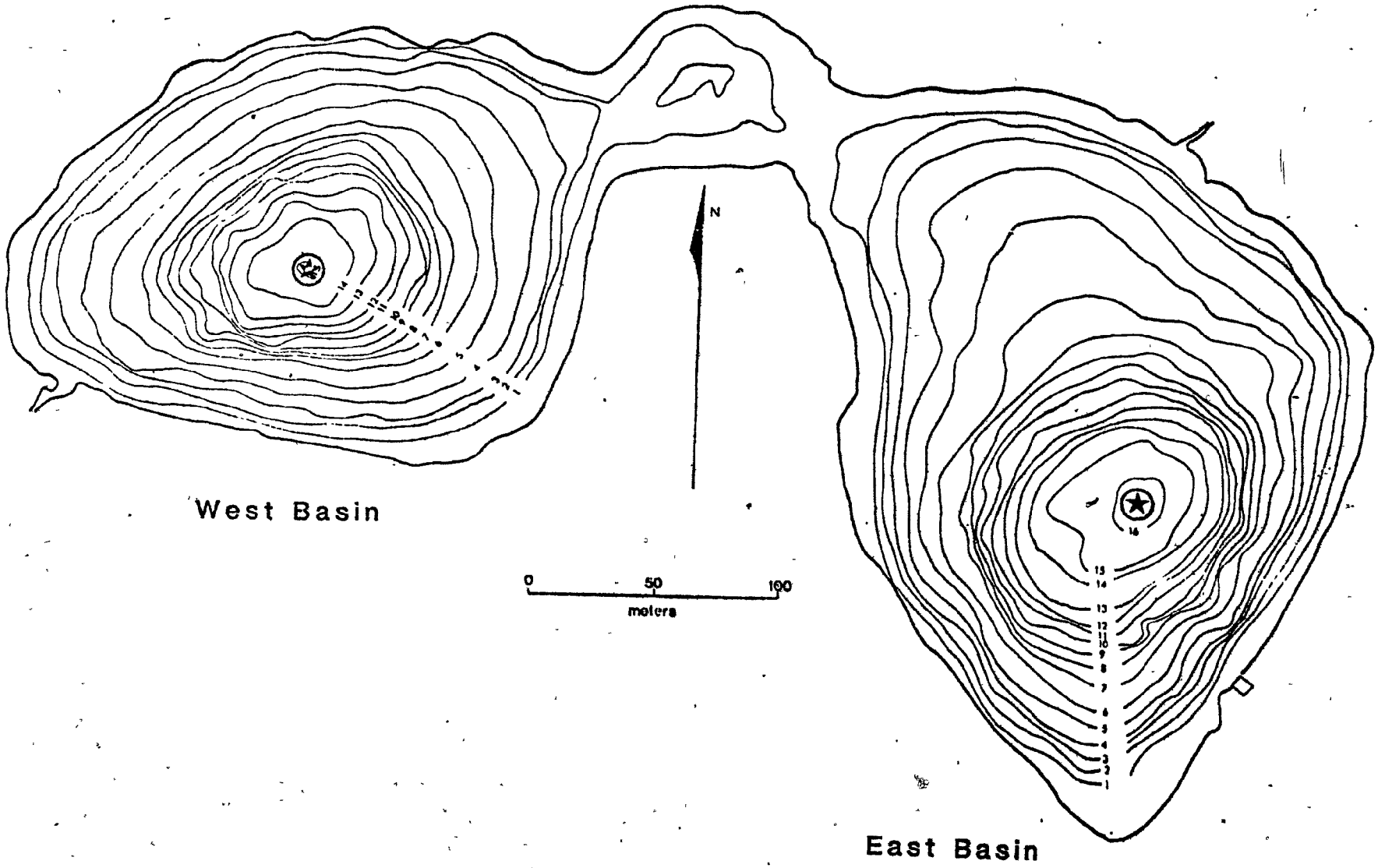


Fig. 2-5 Glen Lake (M.O.E., pers. comm.)

GLEN LAKE

HALIBURTON Co.

GUILFORD Tp.

Lat. 45°08′ Long. 78°30′

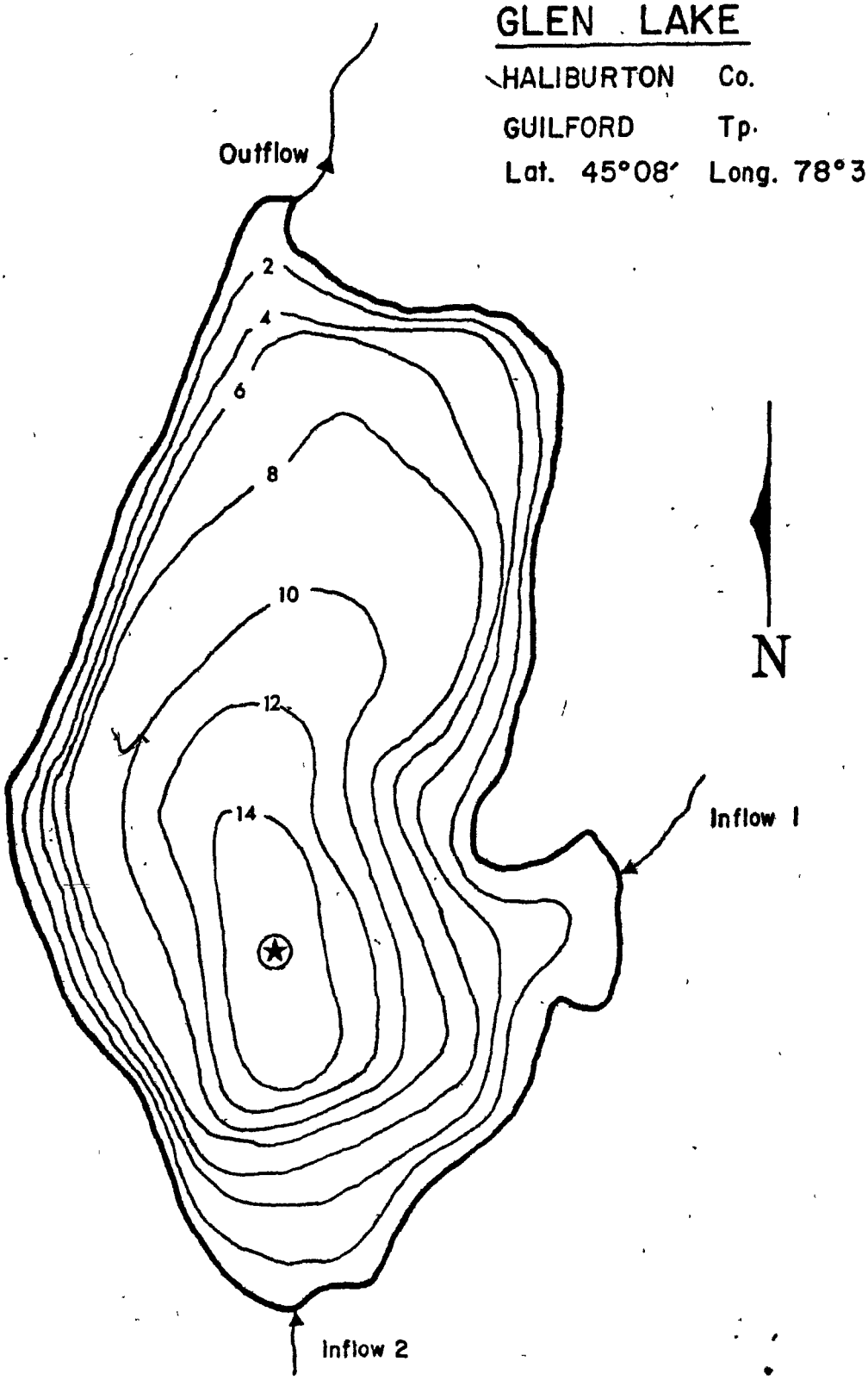


Fig. 2-6 Chub Lake (M.O.E., pers. comm.)

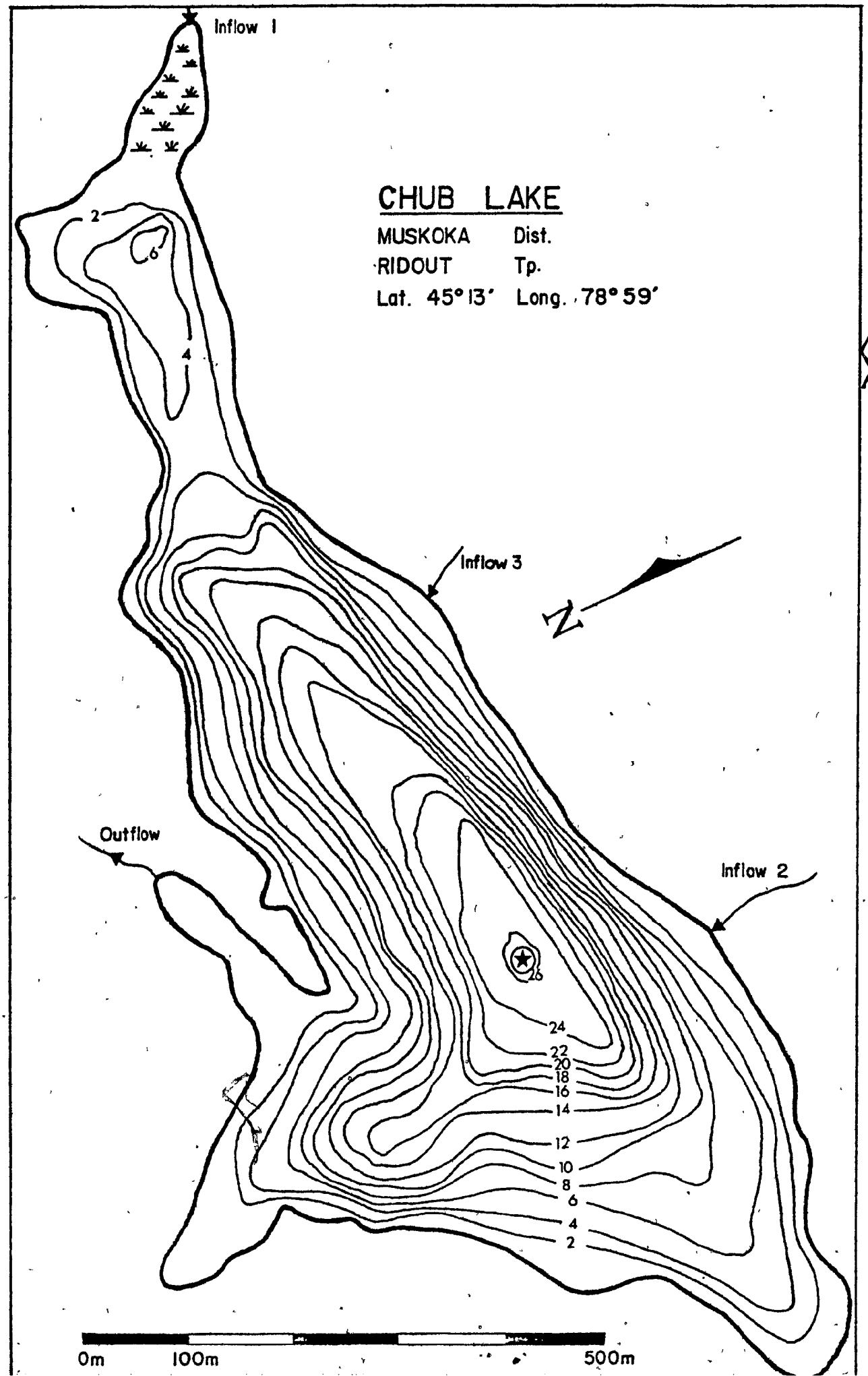

Inflow 1
CHUB LAKE
MUSKOKA Dist.
RIDOUT Tp.
Lat. 45° 13′ Long. 78° 59′
2
6
4
Inflow 3
N
Outflow
Inflow 2
26
24
22
20
18
16
14
12
10
8
6
4
2
0m
100m
500m

Fig. 2-7 Little Clear Lake (M.O.E., pers. comm.)

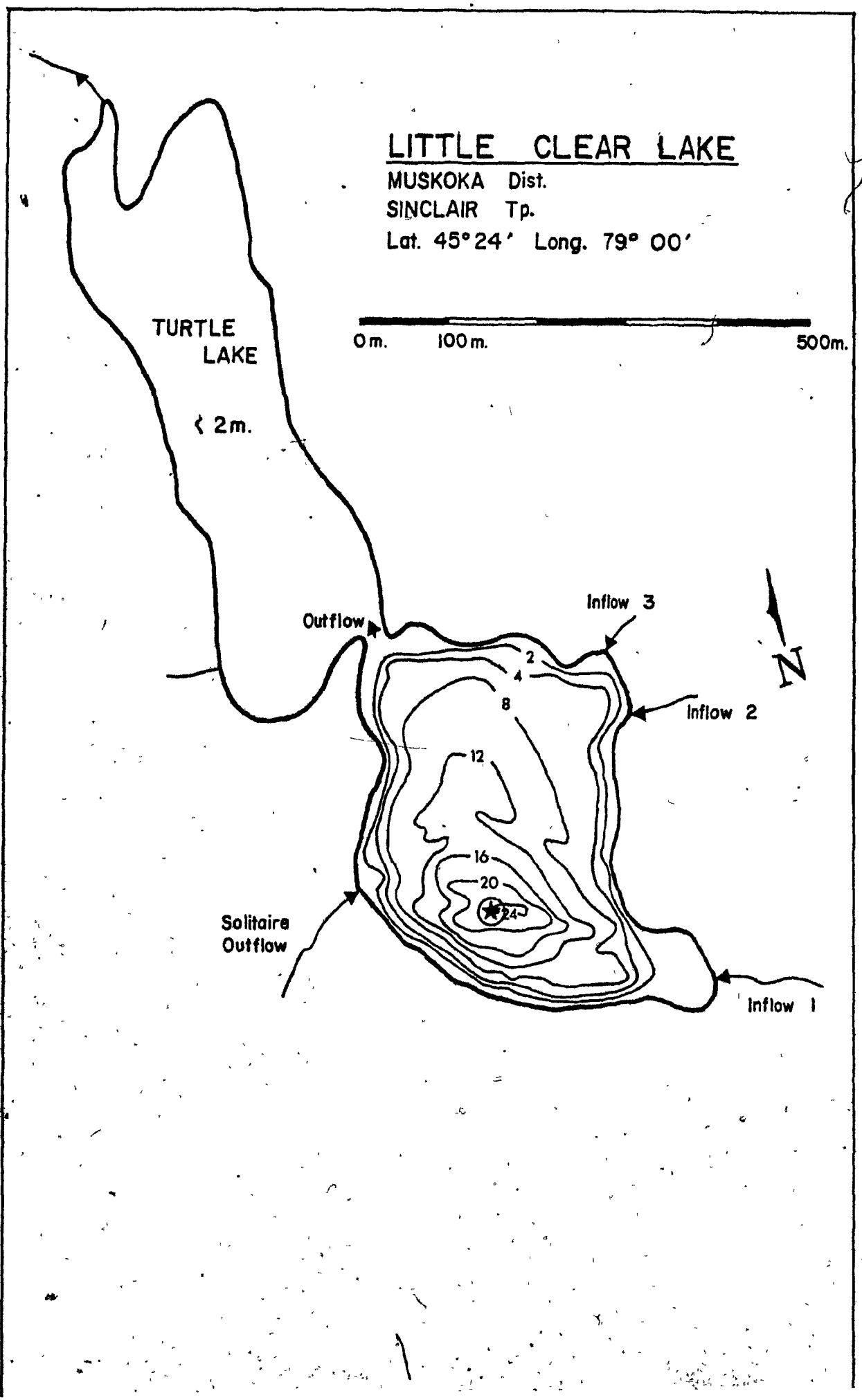
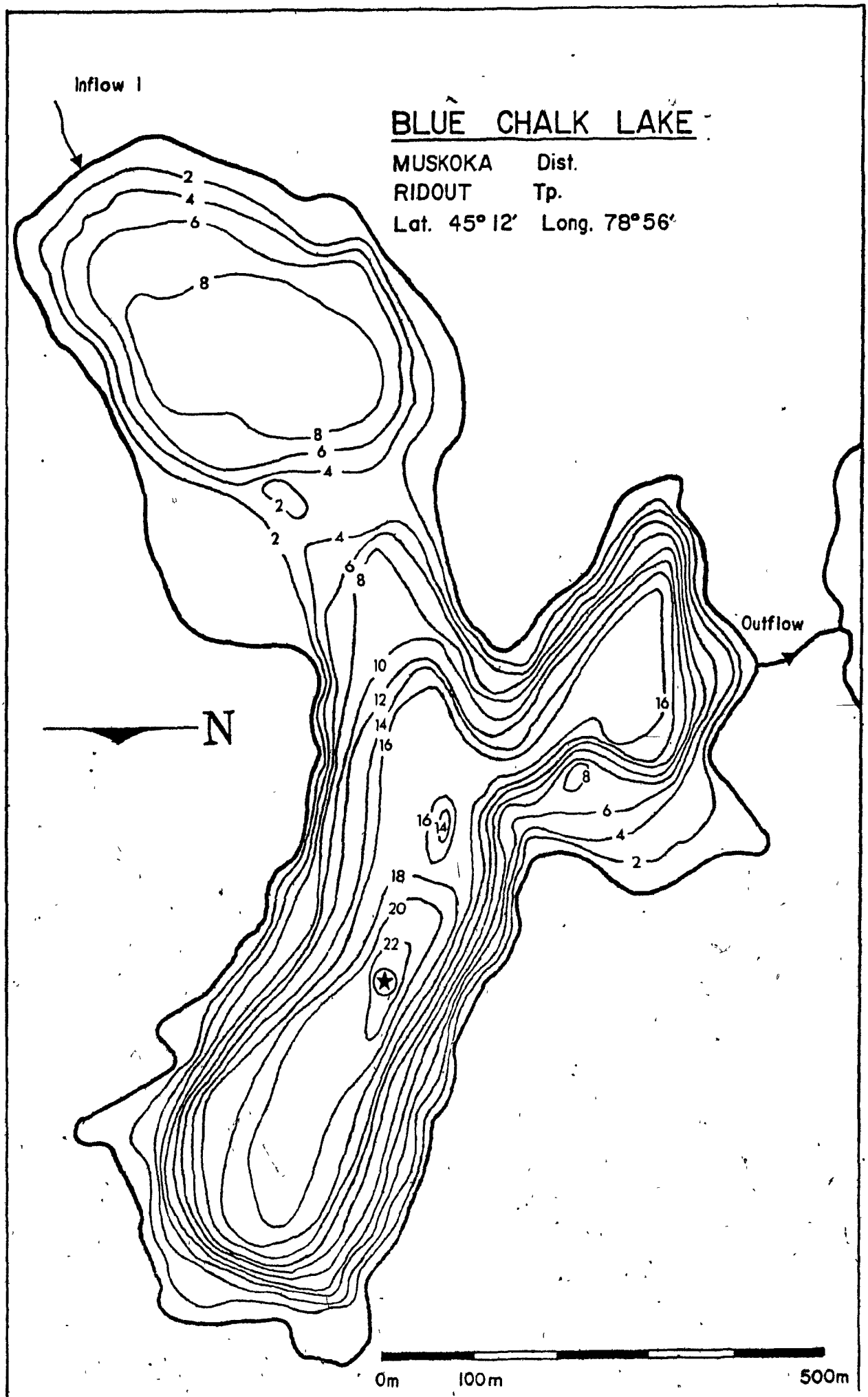

LITTLE CLEAR LAKE
MUSKOKA Dist.
SINCLAIR Tp.
Lat. 45° 24' Long. 79° 00'
0 m.
100 m.
500m.
TURTLE LAKE
< 2m.
Outflow
Inflow 3
Inflow 2
Inflow 1
Solitaire Outflow
N
2
4
8
12
16
20
24

Fig. 2-8 Blue Chalk Lake (M.O.E., pers. comm.)


Inflow 1
BLUE CHALK LAKE
MUSKOKA Dist.
RIDOUT Tp.
Lat. 45° 12' Long. 78° 56'
Outflow
N
0m
100m
500m

Analyses:

Phosphorus: Seven phosphorus fractions were analysed chemically and one biologically in order to assess potential availability of hypolimnetic phosphorus to plankton. All chemical analyses depend on the reaction of orthophosphate with an acid molybdate reagent to produce a colored molybdenum blue complex. The concentration of free phosphate is then measured colorometrically. Table 2 explains the abbreviations used throughout the text and indicates in which section the particular analysis is described in detail.

The procedure for total phosphorus (TP) analyses all phosphorus in the water and represents the maximum phosphorus concentration which could fertilize plankton. The relative importance of the other phosphorus fractions can be determined by comparison to TP.

Total soluble phosphorus (TSP) comprises all dissolved phosphorus (<0.45 μm). It serves to compute total particulate phosphorus from the difference (TP-TSP).

Total particulate phosphorus (TPP) consists mainly of living and dead plankton, but can also comprise chemical precipitates (e.g. iron-phosphate and phosphorus adsorbed to iron hydroxides) and other inorganic particles.

Total reactive phosphorus (TRP) comprises dissolved and undissolved phosphorus compounds which do not require chemical digestion (Table 2) to react with the molybdenum blue reagent.

Soluble reactive phosphorus (SRP) includes only the dissolved portion of TRP. SRP is often, but not always,

Table 2-2. Phosphorus fractions analysed in this thesis. "Treatment" indicates if the sample was autoclaved and digested with potassium persulfate (digested) or filtered through a 0.45 μ filter (filtered) or if the concentration is calculated from other fractions (=). The number indicates the chapter in which the procedure is described in more detail. Expressions in parentheses indicate the most likely chemical form.

Fraction	Chapter	Symbol	Treatment
Total phosphorus	5	TP	digested
Total soluble P	5	TSP	digested, filtered
Total particulate P	5	TPP	=TP-TSP
Total reactive P	3	TRP	corrected for turbidity
Soluble reactive P	3	SRP	filtered
Biological available P	4	BAP	bioassay (ortho-phosphate)
Particulate reactive P	5	PRP	=TRP-SRP (iron adsorbed P)
Biological PP	5	BPP	=TPP-PRP (plankton and seston)

bioavailable (Chapter 4). Bioavailable SRP is probably mostly orthophosphate. SRP was used to determine the maximum availability of hypolimnetic phosphorus.

The difference between TRP and SRP represents particulate reactive phosphorus (PRP), which will be shown to represent mostly iron particles in the studied lakes (Chapter 5).

Biological particulate phosphorus (BPP) can be calculated from the difference (TPP-PRP) in lakes which are poor in silt and suspended sediments, and should consist mainly of living and dead plankton. In lakes in which no ironbound phosphorus (PRP) exists, TP might closely resemble BPP.

Biological available phosphorus (BAP) is determined by a short-term bioassay based on uptake kinetics of $^{32}P\text{-}PO_4$. It therefore is probably the phosphorus fraction which most closely resembles orhophosphate, which is supposed to be an entirely available phosphorus fraction (Rigler 1973).

Iron: Iron can compete with the plankton for hypolimnetic phosphorus (Chapter 5) and therefore several fractions were often analysed: Total iron (TFe), Soluble iron (SFe) and ferrous iron (Fe^{2+}). The techniques are described in "Methods" of Chapter 3.

Chapter 3:

Iron and Hydrogen Sulfide Interference in the Analysis of SRP in Anoxic Waters

Abstract

Anoxic water from eight lakes containing various amounts of ferrous iron, hydrogen sulfide, calcium and total phosphorus was analysed for soluble reactive phosphorus (SRP). Hydrogen sulfide concentration higher than 1 mg/L and ferrous iron concentration above 0.20 mg/L produce interferences in the SRP analysis on many occasions (e.g. 80% underestimation of SRP). Interfering concentrations of these materials are shown to be present in anoxic water from a large number of lakes, groundwater springs and ocean basins.

The mechanisms of the interferences are discussed and methods described to prevent these analytical errors. Ferrous iron is not problematic if the sample is kept anoxic before and during filtration. On the other hand vigorous aeration is obligatory if hydrogen sulfide is present. Simple methods to test for both the possible interfering compounds are presented. It is shown for the water from the anoxic hypolimnia of eight lakes that a modified analysis of total (unfiltered) reactive phosphorus (TRP) yields on average only 2% higher phosphorus concentrations than SRP analysis. TRP hence can replace the complicated SRP analysis in anoxic waters.

Introduction

Soluble reactive phosphorus (SRP), is operationally defined as the phosphorus which passes a 0.45 μm filter and reacts with the molybdate blue reagent within a short period of time (Strickland and Parsons, 1968). It is commonly used to estimate orthophosphate (Chamberlain and Shapiro 1973), which is readily available to organisms, and biologically available phosphorus (Walton and Lee 1972; Young et al. 1982). However, it may sometimes overestimate orthophosphate as discussed in Chapter 4. Estimates of SRP are poor, however, if interfering substances are present. It is well known, for example, that arsenate (Sugawara and Kanamori, 1964; Chamberlain and Shapiro, 1977) causes an overestimate, as does silicate if the analysis is not carried out at appropriate pH (Stainton et al., 1977).

Anoxic waters, are frequently encountered in the hypolimnia of lakes, in ocean basins, in groundwater and in wastewater treatment pools. These waters often contain large amounts of total phosphorus (Livingstone, 1963; White et al., 1963), which could eventually stimulate biological production. The extent of this stimulation depends upon the amount of biologically available phosphorus, which makes the correct measurement of SRP in anoxic waters a useful predictive tool. Anoxic waters often contain large amounts of reduced substances, which are unstable under oxic conditions. Of these, ferrous iron and hydrogen sulfide interfere with the

standard SRP analyses and produce a substantial underestimate of SRP concentration as will be shown in this chapter.

Iron is highly soluble as the ferrous ion, provided that oxygen and hydrogen sulfide are absent (Davison, 1979). After oxidation iron forms ferric hydroxides that are much less soluble (Stumm and Morgan, 1970). These iron hydroxides form flocculants which can adsorb other substances including phosphate (Stumm and Morgan, 1970). The removal of phosphate by ferric iron compounds has been investigated in pure solutions (Bache, 1964; Warry and Kramer, 1976; Lijklema, 1980; Crosby et. al., 1981), in soils (e.g. Ryden et al.,1977; McLaughlin et al., 1981), in flooded soils (Khalid et al., 1977), in sea water (Berner, 1973) and is effectively applied in wastewater treatment (Thomas, 1965; Rupke, 1980). Early workers like Einsele (1936), Mortimer (1941, 1942) and others (Hutchinson, 1957) suggested that seasonal mixing of anoxic hypolimnetic bottom water with oxygenated surface water causes the sedimentation of iron-phosphate in lakes. Ohle (1937), Einsele (1938) and Tessenow (1974) did mixing and aeration experiments with hypolimnetic water containing iron and noted phosphorus precipitation. Although it is widely recognized that ferrous iron removes soluble phosphorus upon aeration, few limnologists acknowledge the possibility of underestimating SRP in anoxic waters. The problems of separating soluble phosphorus (e.g Bray et al., 1973) and soluble iron (Troup et al., 1974) from anoxic pore waters in marine sediments have been addressed. These studies demonstrate the

danger of underestimating soluble fractions if the filtration is not carried out in a completely oxygen free atmosphere. In sediment-water chemistry, scientists are aware that anoxic chemicals are changed by exposure to air, and in situ fractionations have recently been applied to avoid this problem (Hesslein, 1976). In situ filtration has also been employed for ultra fractionation in anoxic bog water (Koenings and Hooper, 1976).

Anoxic waters low in iron concentration can be rich in hydrogen sulfide. Interference by the sulfide ion for some analyses of anoxic waters is well known. For example, silver-sulfide precipitation onto the AgCl reference electrode makes the polarographic determination of pH and oxygen impossible (Skoog and West, 1976) unless a sulfide insensitive reference electrode such as calomel is used. Also interference in the analysis of nitrite (Melack et al., 1982), nitrate (Afghan et al. 1975), dissolved inorganic carbon (M.O.E. Laboratory, Toronto, pers. comm.) and orthophosphate in saltwater (De Jonge and Villerius, 1980) is known.

This chapter indicates the abundance of ferrous iron and hydrogen sulfide in anoxic waters, demonstrates their potential for interfering with SRP analysis and describes techniques to avoid such interferences. The equivalence of total (i.e. unfiltered) reactive phosphorus (TRP) to SRP is also shown. TRP is a simple method that is recommended as a replacement for the complicated analysis of SRP in anoxic water.

Materials and Methods

This study used anoxic hypolimnetic water from lakes in Quebec and Ontario, during summer stratification, in 1981 and 1982. As seen in Table 1, Lake Magog, Quebec, (Lardner-Cornett, 1981) and Fitch Bay from Lake Memphremagog, Quebec, (Lardner-Cornett, 1981) are iron-rich lakes. The Ontario lakes: Lake St. George (McQueen and Lean, 1983), Glen Lake (Ministry of the Environment, Ontario: M.O.E.) and Jack Lake (Pick, 1982) are hydrogen sulfide rich, hardwater lakes. Chub Lake, Little Clear and Blue Chalk (M.O.E.) are iron-rich, poorly buffered, softwater lakes situated on the Canadian shield. Chub Lake shows signs of acid stress (e.g inversed pH profile).

Samples were taken at different depths in the anoxic hypolimnion with a Van Dorn sampler and transferred with the overflow technique into airtight, glass BOD bottles. They were kept anoxic, cool and dark for up to 5 h until analysis.

Phosphorus analysis:

The chemical analysis of the phosphorus fractions is based on the molybdate blue reagent (Murphy and Riley, 1962) which contains 5 mg/L antimony after mixing to the sample.

SRP: For SRP analysis, the sample was filtered through a 0.45 µm cellulose acetate filter (Millipore), which was prerinsed with 250 mL distilled and 5 mL sample water, at a vacuum pressure of 34.5 kilopascals (5 psi). Comparisons with

Table 3-1. Geographical and chemical characteristics of the study lakes. The hypolimnetic concentrations represent maximum values. z_s: deepest sampling depth, 1-2 m above bottom at deepest spot. Ca: Calcium, TP: total phosphorus, TFe: total iron, H_2S: hydrogen sulfide, Color in Hazen Units (HU). 0: not detected, *: not determined.

Lakes	Lat.	Long.	Area	z_s	pH	pH	Ca	TP	TFe	H_2S	Color
					epi-	hypolimnetic					
			(ha)	(m)			(	mg/L		)	(HU)
Magog	45 18'N	72 03'W	1044	16	7-8	6.5	17	0.720	4.3	0	*
Fitch Bay	45 05'N	72 15'W	280	16	7-8	6.3	19	0.263	3.1	0	*
St.George	43 57'N	79 25'W	10	12	8.0	6.6	94	0.676	0.2	15	*
Jack	44 41'N	78 02'W	84	20	7.0	6.9	25	0.122	0.3	>1	13
Glen	45 08'N	78 30'W	16	12	7.4	6.9	36	0.162	0.1	>>1	27
Chub	45 13'N	78 59'W	32	23	5.7	6.2	3	0.086	6.4	0	165
Litlle Clear	45 24'N	79 00'W	11	18	6.9	6.5	4	0.060	7.2	0	48
Blue Chalk	45 12'N	78 56'W	49	21	7.0	6.4	3	0.037	3.8	0	32

polycarbonate filters (Nucleopore) revealed equal fractionation. Mixed reagents were added at once to 30 mL of the filtrate and the absorbance was read in a 10 cm cell after 10±1 min. The timing was kept short and constant to minimize hydrolysis of organic phosphates (Rigler, 1964), although no increase over time was detectable.

When high levels of iron were present (Table 1), the anaerobic sample was transferred in a 50 mL glass syringe from the BOD bottle to the filter manifold. The filter had been prerinsed with nitrogen bubbled water to expel any air, and the filtration was carried out under a permanent nitrogen atmosphere. This avoided any air contact before and during filtration. The handling time of the sample from the time of opening the anoxic bottle until adding the phosphorus reagents after filtration did not exceed 5 min.

When high levels of hydrogen sulfide were present (Table 1), the sample was aerated by an aquarium pump and, after 1 or 2 h of aeration, a standard SRP analysis (Murphy and Riley 1962) was carried out.

TRP: Total reactive phosphorus (TRP) represents the unfiltered fraction of phosphorus which reacts with molybdate reagent. The collection and handling of anaerobic samples for TRP analysis were identical to those for SRP procedure. If hydrogen sulfide interference was expected, aliquots for TRP were withdrawn from the aerated sample with the SRP sample. Otherwise, the TRP aliquots were taken directly from the BOD bottle after the anoxic SRP aliquot had been filtered. Phosphorus reagents were added to these aliquots, as in the

SRP analysis and the absorbance determined after 10 min. All TRP absorbances were corrected for turbidity using a turbidity blank. The turbidity blank was obtained by adding a "blank reagent" in which double distilled water replaced the ascorbic acid reductant normaly used in the molybdenum blue "phosphorus reagent" and reading after approximate 10 min at the same wave length. Acid antimony molybdate in both the phosphorus and blank reagents forms a complex with hydrogen sulfide which is visually recognized as a yellow color (see H_2S interference below and De Jonge and Vallerius, 1980). For this reason, the turbidity blank was also used to test if the aeration of hydrogen sulfide rich water had been sufficient.

Radioactive phosphorus precipitation experiments:

In order to investigate the effect of handling and aeration on orthophosphate in the samples, radioactively labelled phosphate was added to anoxic samples. Precipitation of this material indicates the extent to which oxygenation affects phosphate in the sample.

In the radioactive precipitation experiments about 0.1 mL carrier free ^{32}P as orthophosphate solution was added to the anoxic sample, and aliquots of 6 mL withdrawn and filtered through 0.45 µm millipore filters (25 mm in diameter) at intervals for up to 20 h. In some experiments, vigorous aeration was started after the first subsample. The activity of the filtrate was counted as Cerenkov radiation on the tritium channel of a liquid scintillation counter, corrected

for 5% filter absorbance and expressed as % of the activity in unfiltered aliquots.

Iron analysis:

Total and soluble iron were analysed with an atomic absorption flame spectrophotometer. For total iron, the sample was digested with potassium persulfate under pressure; colloidal flocculants were solubilized shortly before analysis by adding ascorbic acid to provide a 0.1% solution. I analyzed soluble iron in an aliquot from the filtrate for the appropriate SRP analysis. The aliquot was acidified with nitric acid to provide a 1% solution and stored in darkness until analysis (within eight weeks).

Ferrous iron analysis: A simplified analysis of ferrous iron is suggested here, based on the well known but more tedious method of analyzing ferrous iron with a solution of bathophenanthroline (4,7-diphenyl-1,10- phenanthroline) in ethanol as the complexing agent after acidification (to prevent oxidation) followed by extraction with hexanol (to decrease interference, Lee and Stumm, 1960).

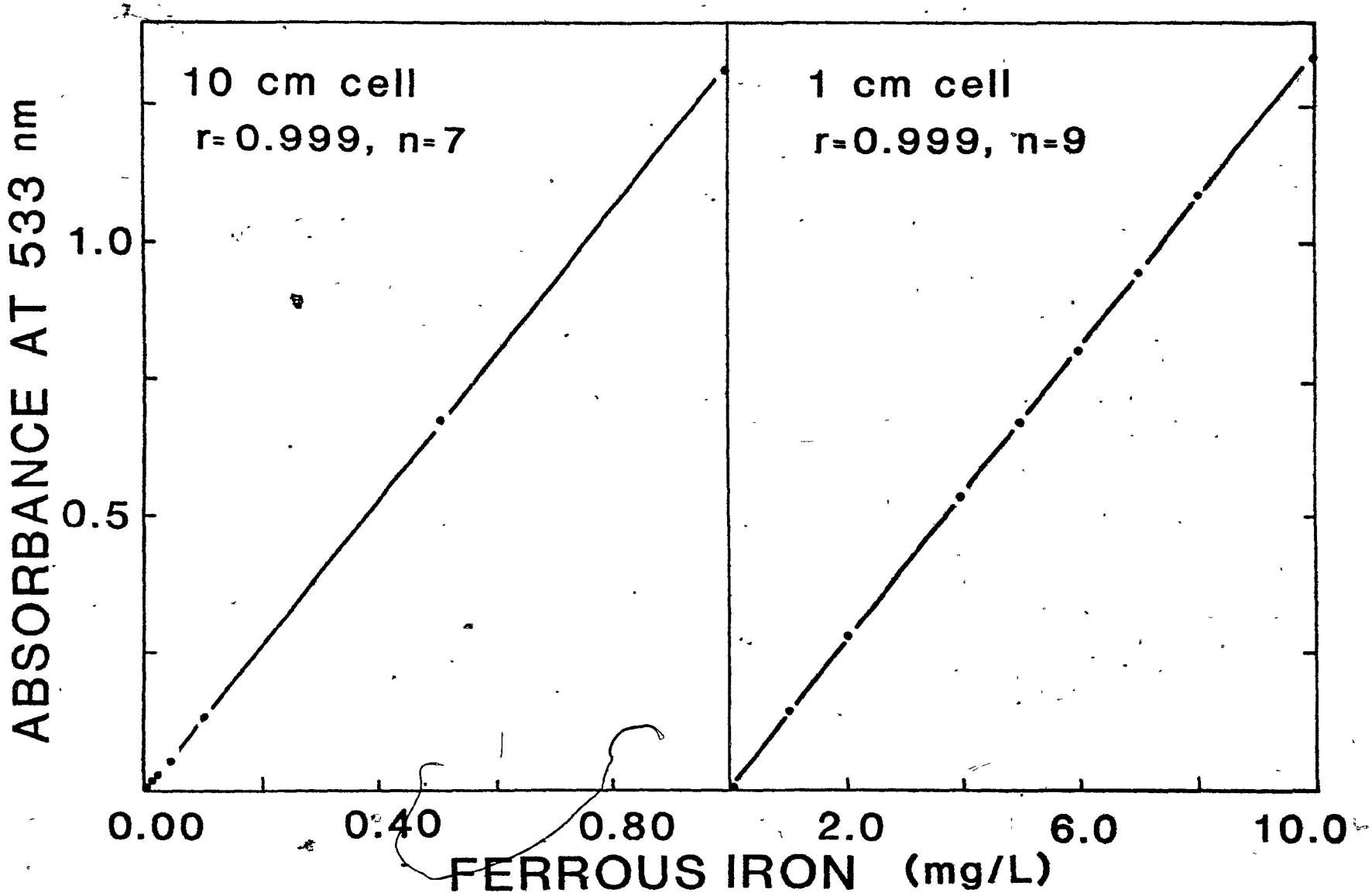
McMahon (1969) found acidification to be unnecessary. Furthermore it was noted that this may overestimate the ferrous fraction in natural water (McMahon 1967, Macalady et al., 1982). Consequently, acidification was deemed unnecessary. Since the concentration of interfering substances (the bivalent cations of cobalt, cadmium, copper, zinc, nickel, chromium and ruthenium; Lee and Stumm, 1960), are too low in most lake waters to interfere, I simplified the

procedure further by omitting the hexanol extraction. If however a quantitative estimate of low concentrations of ferrous iron is anticipated in waters where interfering metals are expected, e.g in industrial wastewater, this method should be compared to a method which includes extraction like that described by McMahon (1969). Unfortunately, bathophenanthroline is rather insoluble in water and tends to precipitate. To avoid this precipitation, the complexing agent was dissolved in enough ethanol so that the ethanol concentration of the final mixture was 40 - 50 %. I used a 0.005 M solution of bathophenanthroline, dissolving the crystals first in 98% ethanol and making it up with water to ca. 70% ethanol. This reagent solution was found stable for at least eight weeks (when kept well covered at 4° C). For the determination of ferrous iron, aliquots of 0.5 mL of blank, standard (Lee and Stumm, 1960) or anoxic sample were swiftly added (to avoid air contact) to 1 mL of 0.005 M bathophenanthroline solution and shaken for approximately 5 sec. The red color of the Fe-bathophenanthroline complex was stable after 5 min and remained so for at least 1 h in dim light. The sample was read within this period at a wavelength of 533 nm in a 1 cm cuvette. At low concentrations of ferrous iron, 10 mL aliquots were added to 20 mL of bathophenanthroline solution and read in a 10 cm cuvette. The analysis of ferrous iron in this way proved to be independent of pH over the tested range of 1.4 to 7.0 and linear over a range of 0 to 10 mg/L ferrous iron. The lowest concentration significantly different from zero was 0.050 mg/L for small

volumes read in a 1 cm cell. The sensitivity could be increased by 10 if larger volumes and a 10 cm cuvette were used. Calibration curves are shown in Fig. 1. The standard error of replicate analysis of 5.0 mg/L ferrous iron solution was 0.2% of the mean (n=5). In highly colored or turbid water, a color blank for each sample was obtained by replacing the bathophenanthroline-ethanol mixture by 70% ethanol. The interference of ferric iron with ferrous iron analysis is not crucial if the pH is higher than 6.5 (McMahon 1969). In this procedure, this interference was less than 1% of ferric iron present even when pH was as low as 1.5. If an estimate of the interference is required, the concentration of total iron can be determined by adding 10% hydroxylamine hydrochloride to the sample in proportion of 1:5 prior to bathophenanthroline. Hydroxylamine hydrochloride reduces all the ferric to ferrous iron (Lee and Stumm, 1960). The difference between this total and an estimate of ferrous iron represents ferric iron. Concentrations of ferric iron analysed in this way was linear over the range tested (0-5 mg/L).

If SRP analysis is anticipated, this technique easily determines if anoxic filtration and handling is advisable to avoid phosphate adsorption onto oxidized iron compounds. When ferrous iron is present, a bright red color developes almost instantaneously after adding the anoxic sample to the prepared bathophenanthroline-reagent; visual inspection alone is therefore sufficient to indicate if ferrous iron is abundant in the water sample. The method suggested here is probably as

Fig. 3-1 Calibration curves for the analysis of ferrous iron in 1 and 10 cm cuvettes. (Note the different scaling of the x-axis.) The standard error of the mean of replicate analysis is 0.2% (not shown).


10 cm cell
r=0.999, n=7
1 cm cell
r=0.999, n=9
ABSORBANCE AT 533 nm
1.0
0.5
0.00
0.40
0.80
2.0
6.0
10.0
FERROUS IRON (mg/L)

easy and simple as a method based on ferrozine (Stookey, 1970; Gibbs, 1979) but is not affected by hydrogen sulfide as ferrozine is (Attari and Jaselskis, 1972): ferrous iron analyzed with bathophenanthroline yields the same concentration as soluble iron analysis by atomic absorption spectrophotometry (0.20 mg/L) in lake water containing more than 8 mg/L hydrogen sulfide.

Hydrogen sulfide analysis:

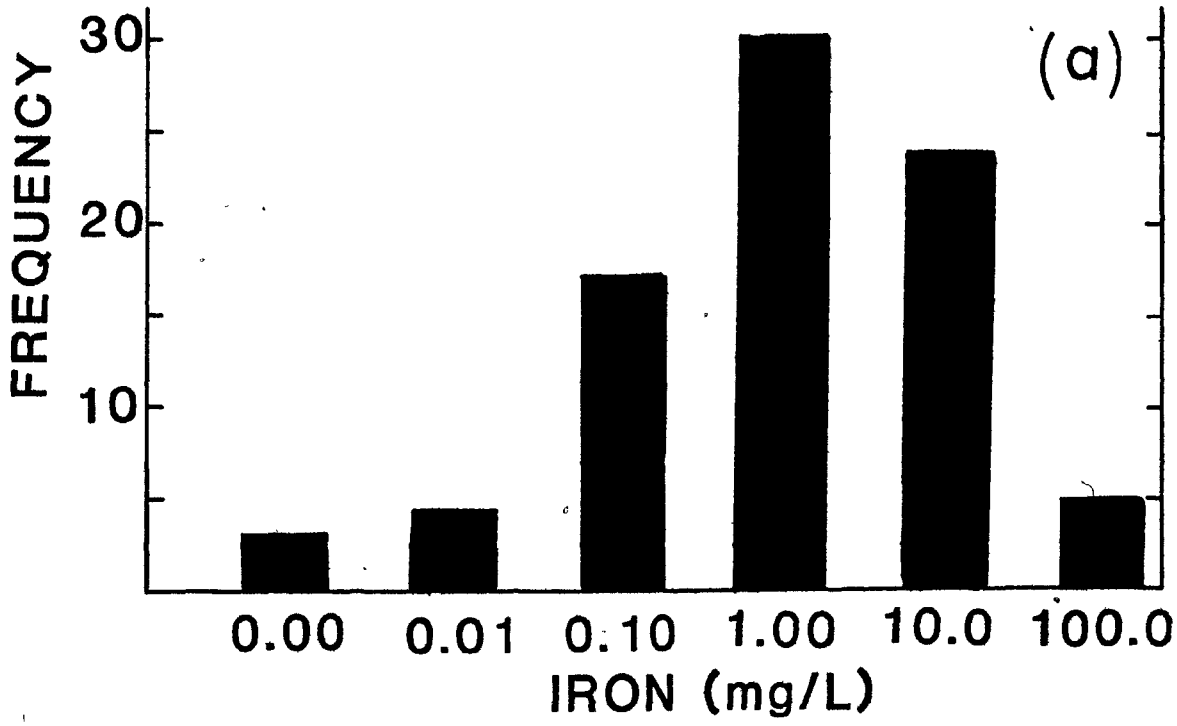
Hydrogen sulfide was analysed by the laboratory of the Ontario Ministry of the Environment in Toronto. For lake samples, a colorimetric method based on molybdate complexation of hydrogen sulfide after acidification of the sample was used. The hydrogen sulfide concentration for the laboratory tests was determined by a polarographic technique.

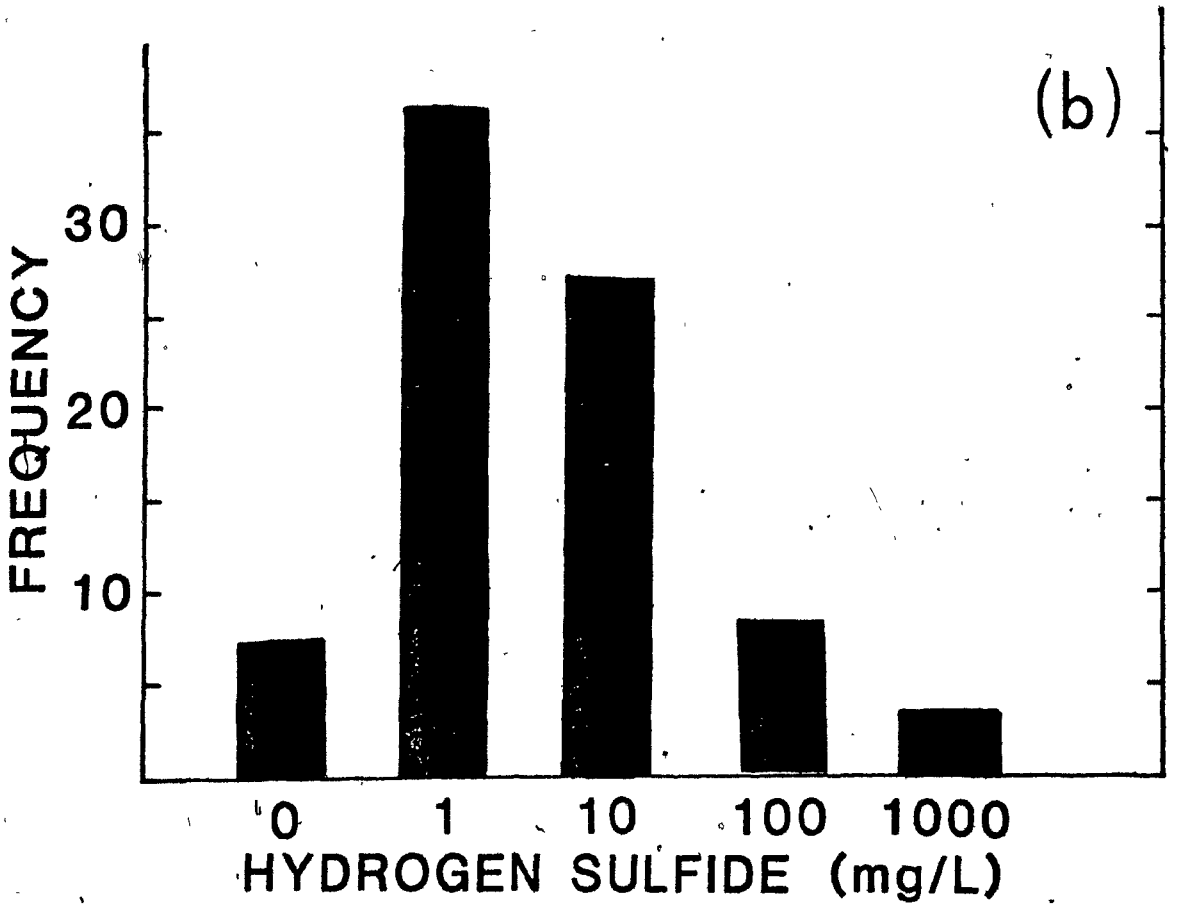
Results and Discussion

Iron and hydrogen sulfide in anoxic waters:

Before discussing the interference by iron and hydrogen sulfide with SRP analysis, I will provide evidence that these interfering substances occur quite frequently in natural waters. Fig. 2a and 2b show ferrous iron and hydrogen sulfide concentrations in anoxic waters, such as anoxic hypolimnia of stratified lakes, monimolimnia of meromictic lakes and anoxic ocean basins. The data were obtained from the English and German literature, from the Ministry of the Environment, Ontario (P. Dillon, pers. comm.) and from my studies on anoxic

Fig. 3-2 Frequency distributions of the maximum concentrations of iron (a) and hydrogen sulfide (b) in anoxic waters of hypolimnia, fresh and saline monimolimnia and ocean basins, collected from literature.


(a)
FREQUENCY
30
20
10
0.00
0.01
0.10
1.00
10.0
100.0
IRON (mg/L)

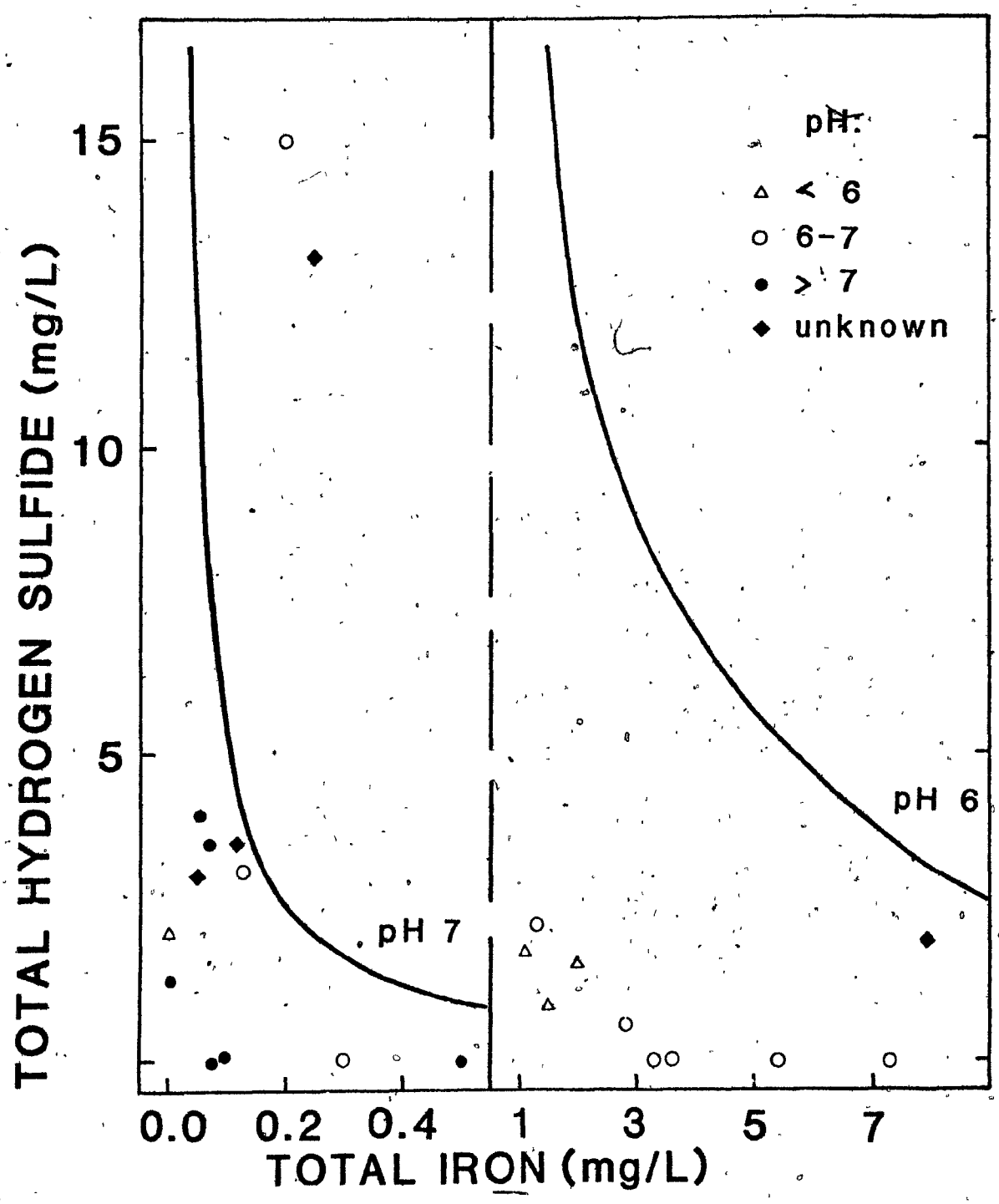

(b)
FREQUENCY
30
20
10
0
1
10
100
1000
HYDROGEN SULFIDE (mg/L)

hypolimnia of dimictic lakes in Quebec and Ontario. If available, the maximum concentration was recorded. All available data were included. From Fig. 2 it is concluded that both constituents can occur in appreciable amounts in anoxic waters.

Most of the recorded total iron in anoxic hypolimnia should be in the ferrous state (Stumm and Morgan, 1970). Solubility considerations suggest that ferrous iron and hydrogen sulfide cannot coexist in large amounts under the pH conditions usually encountered in natural waters, but precipitate as ferrous sulfide (Morel et al., 1974). Fig. 3 shows that the total iron and hydrogen sulfide concentration for several water bodies are inversely correlated as expected. They lie below the lines for iron sulfide precipitation which is demonstrated for pH 6 and 7. These lines, which represent the maximum concentrations for ferrous iron and total hydrogen sulfide at a given pH, are calculated from Berner's (1967) solubility constant for the precipitation of amorphous ferrous sulfide ($pK = -\log(Fe^{2+} * HS^{-}/H^{+}) = 2.9$), which is to be expected in natural waters (Davison and Heaney, 1978), and the first dissociation constant of hydrogen sulfide (Doyle 1968, $pK = -\log(HS^{-} * H^{+}/H_2S) = 7$). Both data and theory suggest that hydrogen sulfide and ferrous iron will not coexist at the pH usually encountered in natural waters. Consequently, a specific treatment for each source of interference in the analysis of SRP can be chosen.

Fig. 3 can be used to predict the maximum possible concentration of one interfering substance if pH value and

Fig. 3-3 Simultaneous hydrogen sulfide and total iron concentrations in anoxic hypolimnia of lakes. Theoretical lines of maximum concentrations of total H_2S and ferrous iron for pH 6 and 7 are also shown. It can be seen that both chemicals do not coexist in large amounts. (Note the different scalings of the x-axis.)


TOTAL HYDROGEN SULFIDE (mg/L)
15
10
5
0.0
0.2
0.4
1
3
5
7
TOTAL IRON (mg/L)
pH:
< 6
6-7
> 7
unknown
pH 7
pH 6

concentration of the other substance are known. In this way, it can be decided which of the substances is likely to be in high enough concentrations to interfere with SRP analysis. My results (see below) suggest that the critical concentrations are higher than 1 mg/L H_2S or higher than 0.20 mg/L Fe. An adequate procedure for the SRP analysis can than be chosen.

SRP analysis in the presence of ferrous iron:

To verify that air contact decreases SRP concentration, I vigorously aerated water samples from anoxic, iron-rich hypolimnia. Fig. 4 shows a representative example of such a precipitation experiment with anoxic hypolimnetic water from Lake Magog (total iron concentration = 3.25 mg/L). Chemical analysis for soluble reactive phosphorus and radioactive fractionation reveal a loss of soluble phosphorus at an average rate of 16%/h for the first 2 h. Slower phosphorus removal, 4%/h, was found in anoxic hypolimnetic water from Fitch Bay, Lake Memphremagog, which had an iron concentration of 0.40 mg/L. Without active aeration, air-exposure produced phosphorus precipitation, but at a slower rate for the same iron concentration. Water with iron concentrations less than 0.020 mg/L (e.g from the hydrogen sulfide rich lakes St. George and Glen, and high dilutions of iron rich waters with distilled water) did not show any precipitation. The correlation of the precipitation rate with iron concentration is significant for non acid-stressed lakes (Fig. 5). If the water was vigorously aerated (Fig. 5a) precipitation was

Fig. 3-4 Removal of soluble phosphorus during aeration in water from the anoxic hypolimnion of Lake Magog, 16 m, Aug. 11, 1981. The iron concentration is 3.15 mg/L. Circles represent soluble reactive phosphorus (SRP), triangles soluble radioactive phosphorus.

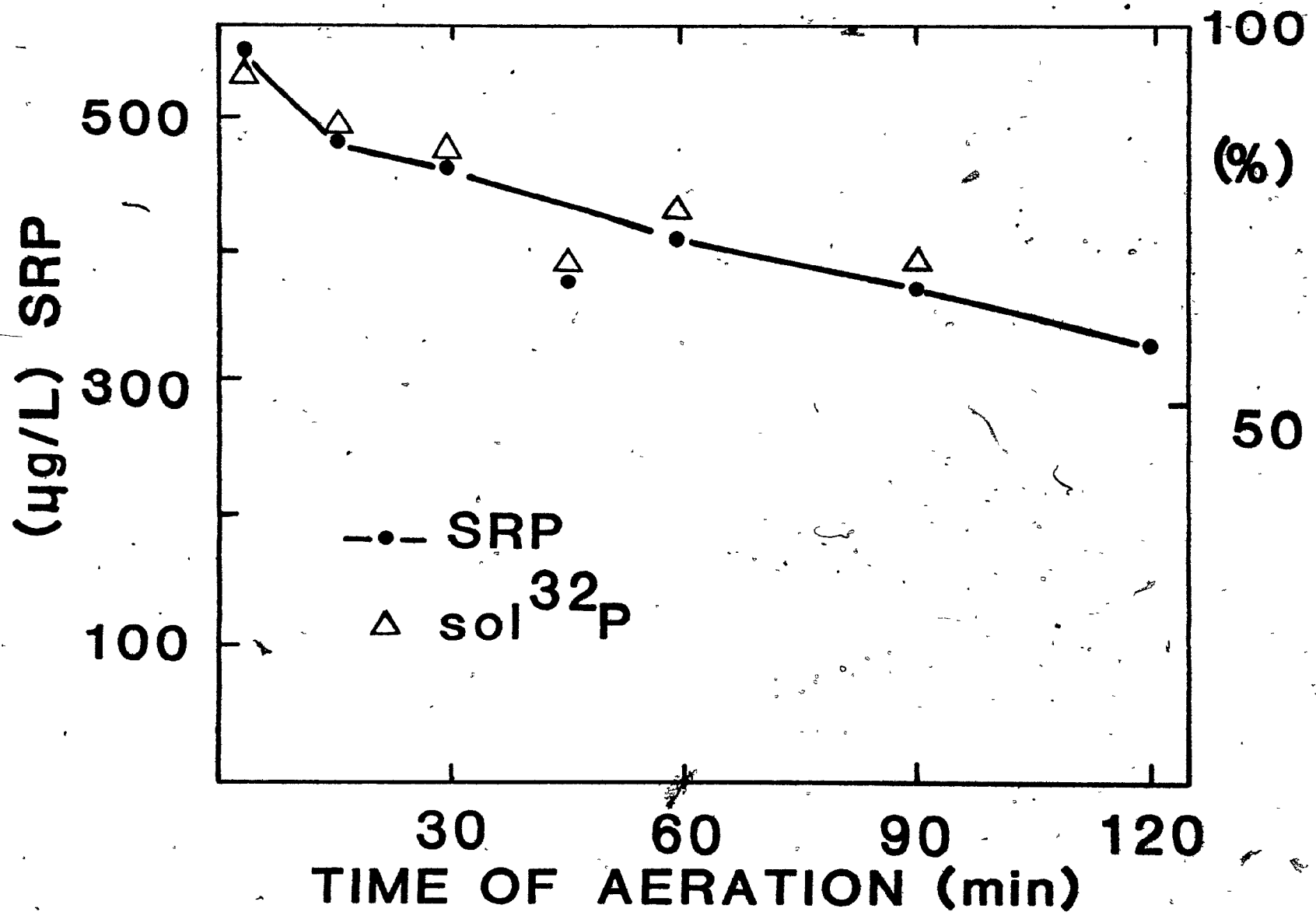
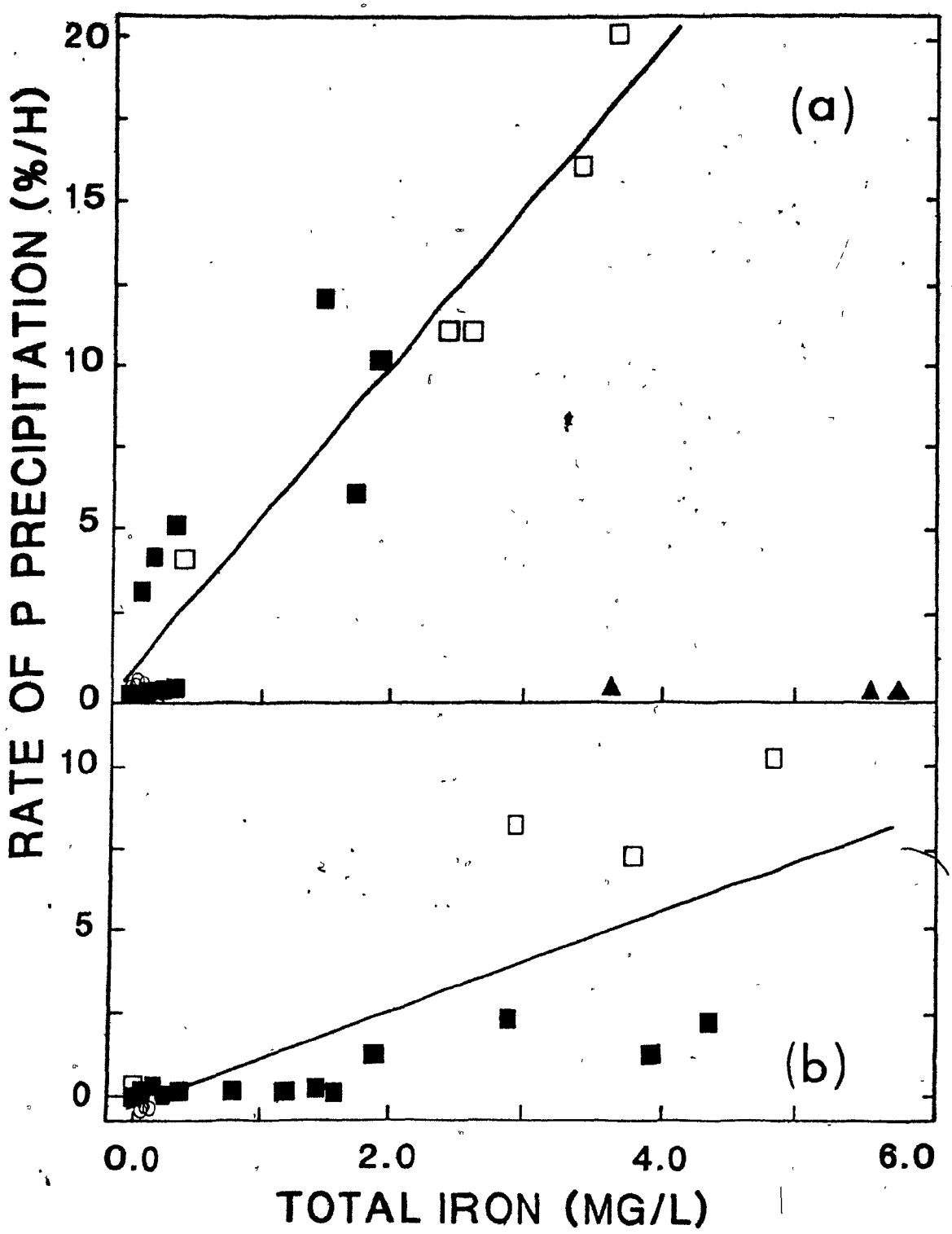

500
300
100
(μg/L) SRP
100
(%)
50
SRP
sol ^{32}P
30
60
90
120
TIME OF AERATION (min)

Fig. 3-5 The rate of phosphorus precipitation versus iron concentration for vigorously aerated (a), ($f(x)=0.53 + 4.98*x$, $r^2=0.90$, $n=20$) and diffusion aerated (b), ($f(x)=-0.42 + 1.39*x$, $r^2=0.55$, $n=24$) anoxic hypolimnetic water samples from eight lakes. Hardwater lakes with hydrogen sulfide (open circles), without hydrogen sulfide (open squares) and their dilutions (closed squares) and softwater lakes (triangles, not included in regression).


RATE OF P PRECIPITATION (%/H)
20
15
10
5
0
(a)
10
5
0
(b)
0.0
2.0
4.0
6.0
TOTAL IRON (MG/L)

detected for an iron concentration larger than 0.20 mg/L, but with simple exposure to air (Fig. 5b) precipitation was not observed below an iron concentration of 1.80 mg/L. The correlation in unaerated experiments with iron has more scatter which probably reflects higher variability in the rate of oxygen invasion.

Further support for the hypothesis that ferric iron removes phosphorus is given by following experiments. When acid ferrous iron solution is added to aerated water from the iron-poor lakes St. George, Jack and Glen neutralization oxidizes the iron almost quantitatively to ferric iron; this is evident from the loss of chemically determined, ferrous iron and the appearance of a yellowish brown color and turbidity which indicate iron hydroxides. At the same time, phosphate is almost instantaneously removed from solution, while the unfiltered reactive fraction (TRP) remains the same (Table 2). This means that SRP is affected by the aeration of water containing ferrous iron, but TRP is not.

Samples from anoxic waters of acidic, softwater lakes do not show this reaction. In such lakes, no precipitation of phosphorus onto the 0.45 μm filter was observed after 2 h, though ferrous iron concentrations were high (Fig. 5a). In water samples from these lakes, aeration results in a loss of ferrous iron and increases the brownish color of the water (Table 3), suggesting ferric oxide formation. However, free phosphate was removed by ferric hydroxide adsorption because a bioassay based on ^{32}P kinetics (Chapter 4) showed a decline in orthophosphate concentration (BAP in Table 3). But the

Table 3-2. Phosphorus precipitation induced in naturally iron-poor hypolimnetic water by the addition of a final ferrous iron concentration of 3.3 mg/L. These samples were degassed to expel hydrogen sulfide. The iron treatments alternatively received acidic ferrous iron solution, base and buffer. (Max. pH fluctuation for L. St.George: 6.1-8.7, for Jack L.: 5.6-8.5). The controls for Lake St.George and Jack Lake received the same amount of acid, base and buffer as the iron addition treatments. The control for Glen Lake represents concentrations of SRP and TRP obtained from undiluted samples and corrected for dilution. All phosphorus concentrations are in µg/L.

Lake	Control		Iron Addition	
	SRP	TRP	SRP	TRP
St.George	37	42	3	42
Glen	31	34	1	31
"	32	34	1	36
Jack	22	32	2	32

Table 3-3. Events in aerating softwater lakes high in iron for Chub Lake, and Blue Chalk Lake(*). Biologically available phosphorus (BAP) may largely be orthophosphate; soluble iron (SFe) is based on analysis of a subsample of the same filtrate used for the SRP analysis; color is expressed as Hazen Units.

Date	Aeration Time (h)	BAP (µg/L)	SRP (µg/L)	TRP (µg/L)	SFe (mg/L)	Fe^2 (mg/L)	Color (HU)
Aug.16	0	28	28	36	4.9	5.4	180
	0.5	3	31	38	4.8	0.4	300
Aug.18	0	-	27	31	4.7	-	160
	0.5	-	27	32	4.3	-	240
	24	-	12	24	1.7	-	-
Aug.31	0	-	33	35	4.7	-	-
	25	-	23	31	2.9	-	-
	47	-	20	28	2.6	-	-
Aug.6*	0	20	16	19	3.0	-	32
	0.5	2	-	-	-	-	-
	1.5	-	17	20	-	-	120

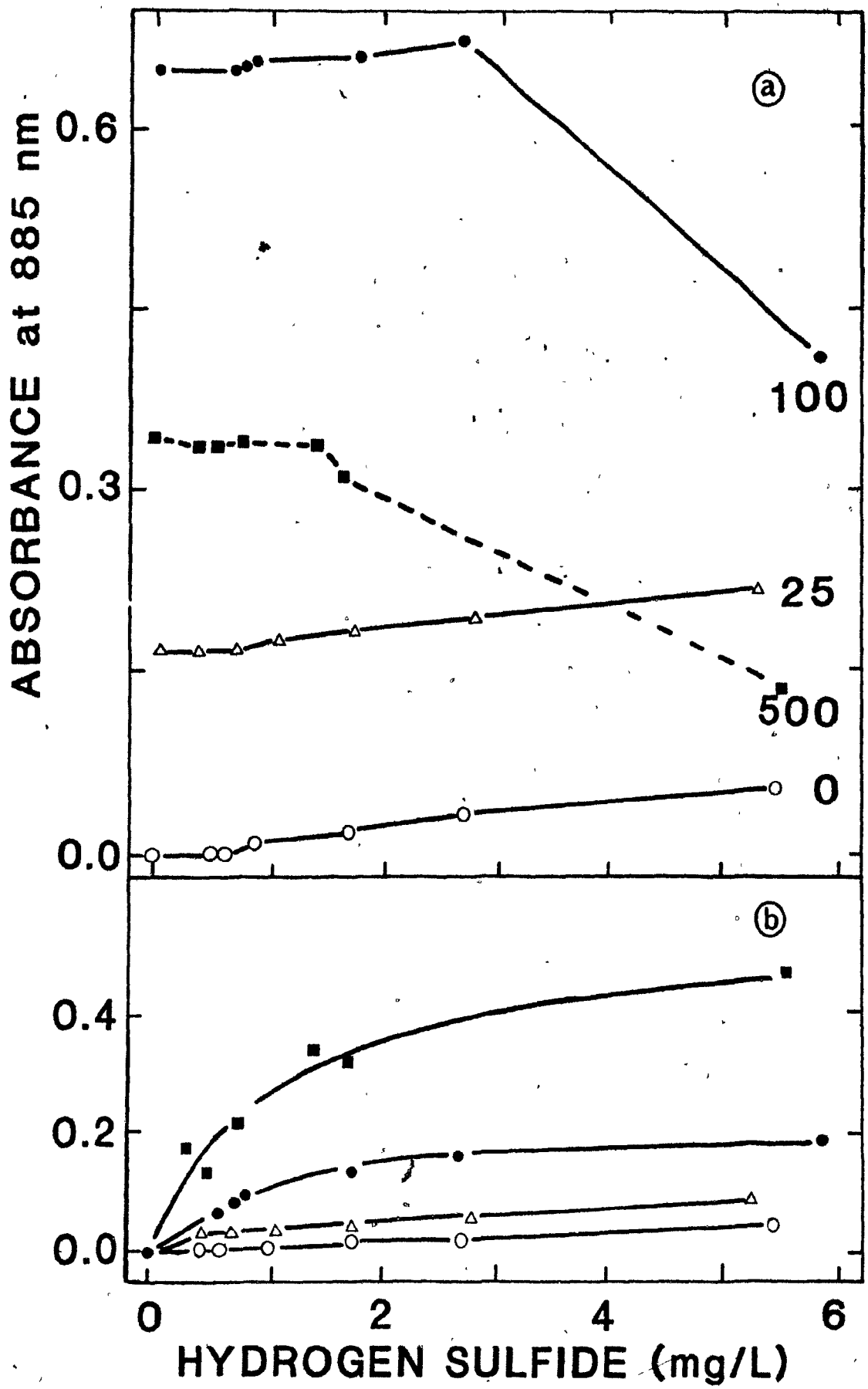
particle size of ferric phosphorus flocculants must be lower than 0.45 μm, since SRP and soluble iron remain unchanged for several hours after exposure to air. Apparently, ferric compounds remain finely divided in these waters in contrast to their behavior in well buffered, hardwater lakes. Furthermore, simultaneously adding ferrous iron and raising the pH did not decrease the soluble phosphorus and iron fractions, as this treatment did in naturally iron-poor lakes. Neither was the solubility decreased after 75% removal of the yellow acids by a macroreticular resin column (Mantoura and Riley, 1975) or artificially hardening the water with calcium carbonate, or phosphate addition. There exists, however, some indication that, over a longer time-span, the iron-phosphate flocculants become larger, since reduction in SRP and soluble iron (SFe) can be detected after 1 or 2 d (Table 3). A fraction of this decrease is probably due to biological uptake since TRP, which analyses iron bound phosphates and free phosphate, also decreases (Table 3). The kinetics are so slow, however, that this reduction is unlikely to affect the SRP analysis, if done on the day of sampling. It can be concluded therefore that in poorly buffered, soft waters, iron does not seem to interfere with the analysis of SRP and the application of procedures to maintain anoxia do not appear to be necessary.

SRP analysis in the presence of hydrogen sulfide:

This section first demonstrates the extent and specificity of hydrogen sulfide interference with the phosphorus molybdate blue analysis (Murphy and Riley, 1962) by laboratory experiments. Next, I will show that hydrogen sulfide leads to severe underestimation of SRP in hypolimnetic water of Lake St. George and experiments will be described leading to a procedure which allows a valid SRP determination nevertheless. Finally, a simple method to determine if hydrogen sulfide is likely to interfere will be presented.

In laboratory experiments, phosphate concentrations covering the range common in anoxic waters (0-500 µg/L) were spiked with hydrogen sulfide developed from a stock of sodium sulfide. The final concentration of hydrogen sulfide was in the lower range of natural occuring hydrogen sulfide; the concentration of hydrogen sulfide was determined simultaneously with phosphate. Fig. 6a shows that 1 mg H_2S or more led to an overestimate at low phosphorus concentrations (25 P µg/L and less) and an underestimate at higher phosphorus concentrations. The increased absorbance at 885 nm (which is the absorbance maximum for the phosphorus molybdenum-blue complex) for low phosphate concentrations is due to an increasing yellow color (absorbance maximum lower than 330 nm, as determined by an absorption spectrum). At higher phosphorus concentrations, sulfide and phosphate compete with each other, possibly for antimony (De Jonge and Villerius, 1980), and yield a color which becomes increasingly blue with time. (A

Fig. 3-6 The effect of hydrogen sulfide on molybdate blue analysis of standard phosphate solutions (0, 25, 100, 500 µg/L). a) The addition of phosphorus reagents, absorption of 10 cm cells, broken line: absorption of 1 cm cell. b) the addition of blank reagent measured in 10 cm cells.


ABSORBANCE at 885 nm
0.6
0.3
0.0
a
100
25
500
0
b
0.4
0.2
0.0
0
2
4
6
HYDROGEN SULFIDE (mg/L)

time course is presented below for a natural water sample in Fig. 7).

The development of yellow color (at 330 nm wavelength) is independent of phosphate and appears in both blank and phosphorus reagent (Table 4). The absorbance at 885 nm is dependent on phosphate even if ascorbic acid is eliminated from the mixed reagent (Fig. 6b and Table 4). This suggests that hydrogen sulfide acts as a weak reductant in the phosphate analysis when the stronger reductant, ascorbic acid, is not present. It leads to a gross overestimate of the turbidity blank in the TRP analysis. The phosphorus reagent which contains ascorbic acid forms phosphorus blue in addition to the sulfide yellow complexes, which both contribute to the absorbance at 885 nm.

Similar problems exist in natural water containing hydrogen sulfide. During attempted SRP and TRP analyses with the hypolimnetic water of three Ontario lakes sampled with a method which excludes oxygen, similar observations were made: the samples turn yellow instead of blue after addition of phosphorus reagents, the blue absorbance increases with time, and the turbidity blanks are increased. These samples smelled strongly of hydrogen sulfide. The increase of absorbance with time is especially conspicuous when both hydrogen sulfide and phosphate concentrations are high. A time course was recorded for Lake St. George with a total phosphorus concentration of 0.682 mg/L and ca. 15 mg/L hydrogen sulfide (Fig.7).

Since hydrogen sulfide interferes so drastically with the

Fig. 3-7 The increase of apparent SRP concentration with time after reagent addition to water from the anoxic hypolimnion of Lake St. George, 12m, June 4, 1982, containing ca. 15 mg/L hydrogen sulfide and 682 µg/L total phosphorus.

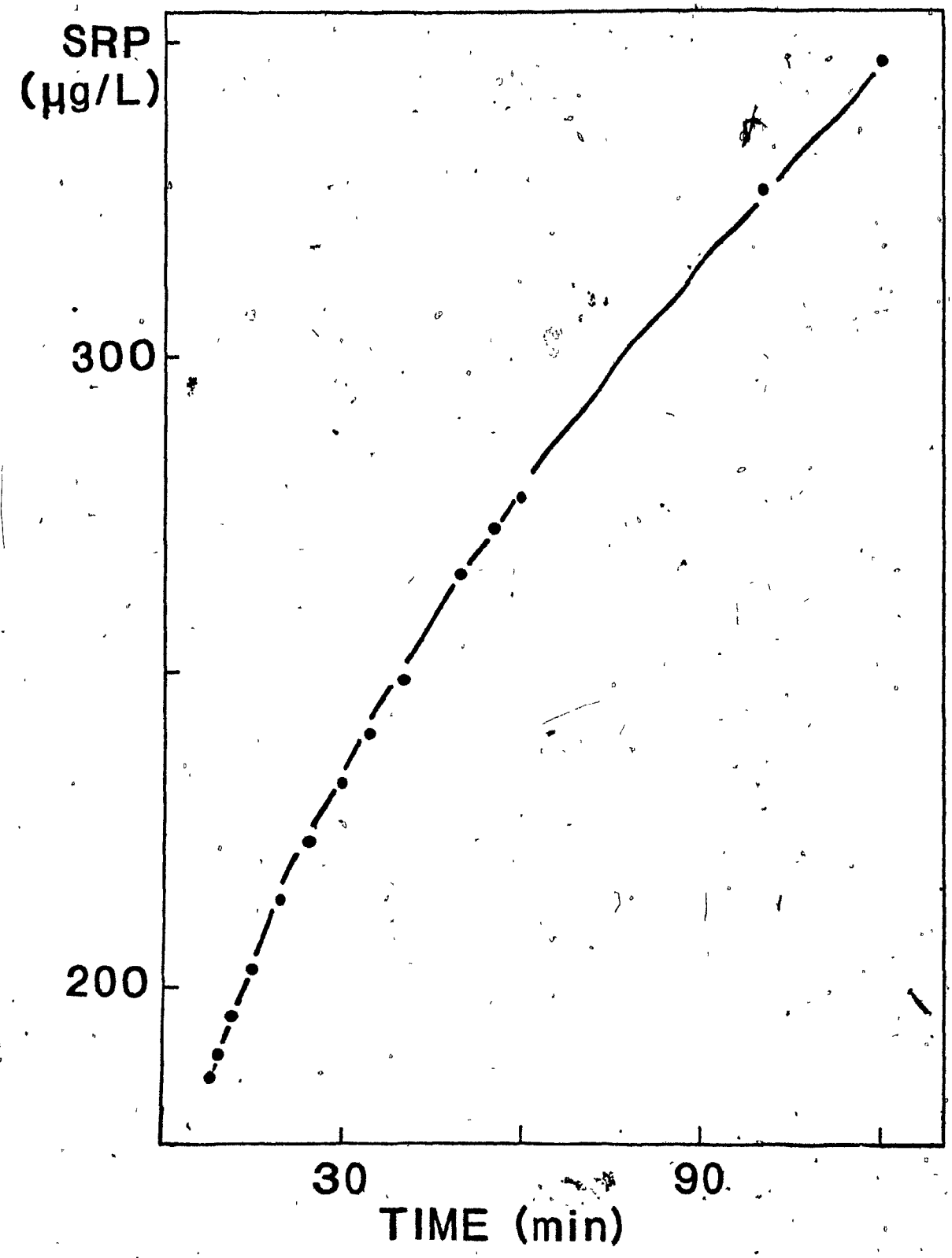

SRP
(µg/L)
300
200
30
90
TIME (min)

Table 3-4. The effect of reagents on the light extinction (E) in water containing 2 mg/L H_2S at 885 and 330 nm. Molybdate in the phosphorus and blank reagent (where the ascorbic acid in the phosphorus reagent is replaced by distilled water) reacts with hydrogen sulfide to yield a yellow complex.

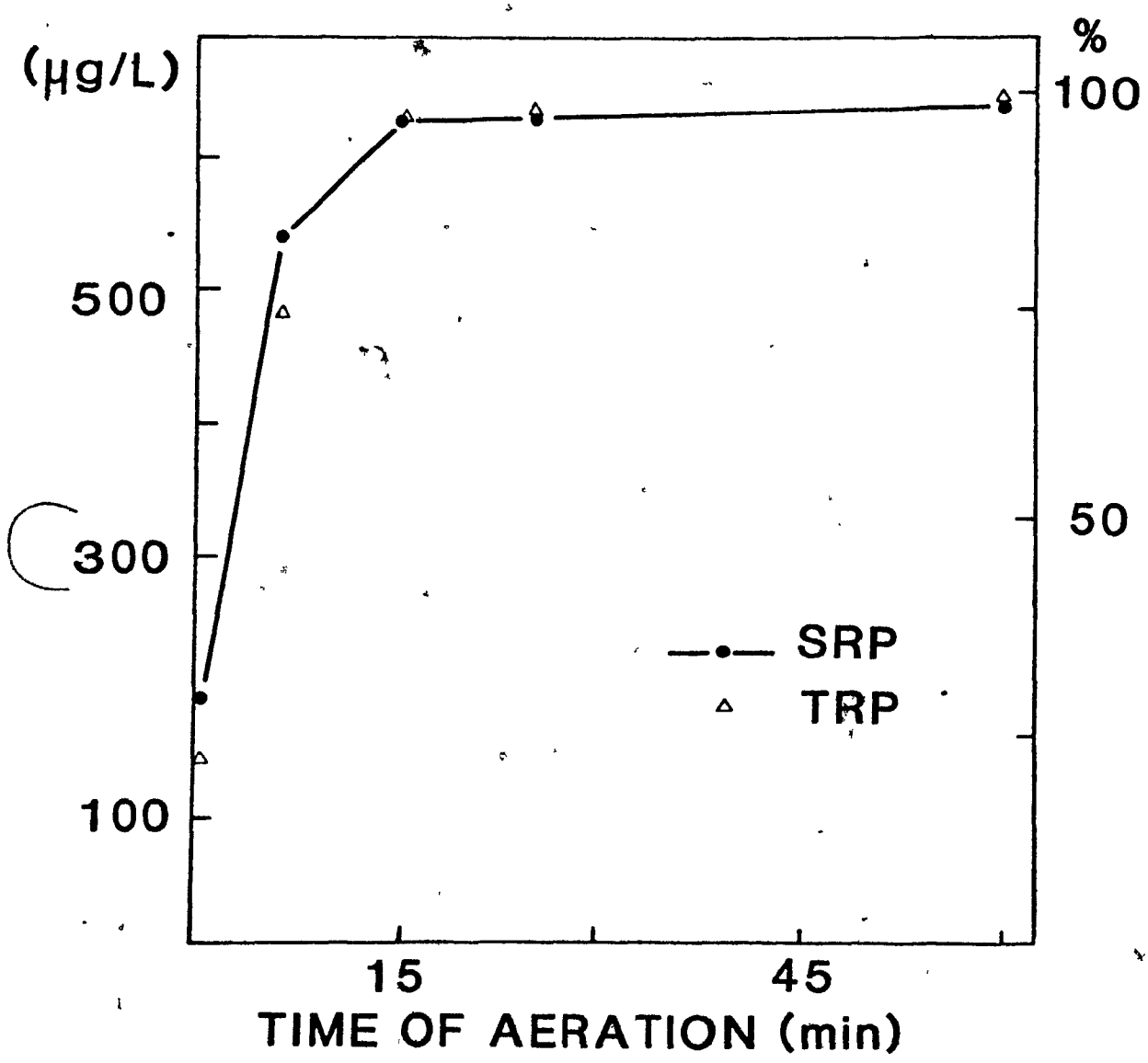
Phosphate (µg/L)	Reagent	E_{885}	E_{330}	Visual Color
0	blank	0.006	-	faint yellow
0	phosphorus	0.005	1.920	" "
50	blank	0.039	1.908	yellow
50	phosphorus	0.321	1.930	yellow/blue

analysis of SRP and TRP in pure and natural waters, ways to decrease this interference and tests of their effectiveness are required.

Hydrogen sulfide is very volatile at room temperature and bubbling with air can completely drive off the gas. Water from Lake St. George containing 15 mg/L hydrogen sulfide was aerated by an aquarium pump. After 30 min of vigorous aeration the turbidity blank no longer showed interference and SRP had increased to a constant value (Fig. 8). The length of time needed to drive off the gas depends on the concentration of hydrogen sulfide, temperature, sample volume and the extent of aeration. To determine simply and quickly if aeration has been sufficient, the blank reagent can be added. The samples will turn yellow in the presence of hydrogen sulfide and produce a high absorbance at 330 and 885 nm (Table 4, Fig. 6b).

In the section on iron interference (above), it is demonstrated that aeration can produce an underestimate of SRP due to phosphate adsorption onto ferric flocculants. In hydrogen sulfide rich water, soluble iron cannot coexist because of solubility constraints (Fig. 3). Hence, phosphate loss due to iron adsorption while aerating the sample is not expected. For experimental confirmation that aeration does not effect the fraction which is soluble reactive, SRP analysis was carried out with exclusion of oxygen. Instead of bubbling with air, the sample was kept airtight, bubbled with oxygen-free nitrogen and then filtered. This should reduce hydrogen sulfide interference but not induce ferric phosphate precipitation. In a different experiment, the sample was

Fig. 3-8 Removal of hydrogen sulfide interference in SRP (circles) and TRP (triangles) analysis by aerating anoxic water from Lake St. George, 12 m, June 24, 1982, containing ca 15 mg/L hydrogen sulfide and 719 µg/L total phosphorus.


(μg/L)
%
500
300
100
100
50
SRP
TRP
15
45
TIME OF AERATION (min)

filtered under anoxic conditions and the filtrate was then aerated. If ferric precipitates are formed on aeration before filtration, such samples should have low SRP concentrations. All these methods produced the same concentration of SRP for Lake St. George water as the aeration method. This is to be expected since the iron concentration was low, 0.02 mg/L. If hydrogen sulfide was not driven off, the SRP concentration would be underestimated by 80% (Fig. 8).

Direct evidence for precipitation of phosphorus is obtained by experiments involving radioactive tracer. In contrast to iron-rich lakes, the hydrogen sulfide-rich lakes (St. George, Glen and Jack) show little or no precipitation of ^{32}P after 5 h of aeration (Fig. 5a, open circles). This cannot reflect finely divided iron phosphorus complexes (as in soft water) because the iron concentration is very low and a radiological bioassay analyses all dissolved phosphorus as phosphate (Chapter 4).

The proposed method to deal with hydrogen sulfide interference is rather time consuming. On the other hand, it is essential to obtain valid estimates of the SRP concentration. A rapid method to determine if hydrogen sulfide will be a problem would therefore indicate when adjustments for hydrogen sulfide interference are necessary. As seen in laboratory experiments (Table 4 and Fig. 6b) and experiments with natural water, the turbidity blank is increased in the presence of hydrogen sulfide. This increase is due to the development of yellow color; the comparison of water with and without the

blank reagent gives a quick indication if hydrogen sulfide is present in interfering concentrations. A more quantitative estimate can be obtained by measuring the yellow color at its absorbance maximum of 330 nm or less.

A simple method to correct for hydrogen sulfide interference at concentrations lower than 6.4 mg/L in saltwater is suggested by De Jonge and Villerius (1980). They increase the antimony concentration to 12.2 mg/L Sb instead of 5 mg/L used in the procedure described above. However this method is not applicable to waters with hydrogen sulfide concentrations higher than 6.4 mg/L (Fig. 2b). Their suggested addition of sulfuric acid followed by nitrogen bubbling in cases of high hydrogen sulfide should be treated with caution because of the possible overestimation of orthophosphate due to acid hydrolysis. A combination of a mixed reagent enriched in antimony, a non acidic degassing of hydrogen sulfide-rich water and a test for interference using a turbidity blank (also enriched in antimony), is probably a better solution to hydrogen sulfide interference in the SRP analysis.

TRP as a substitute for SRP:

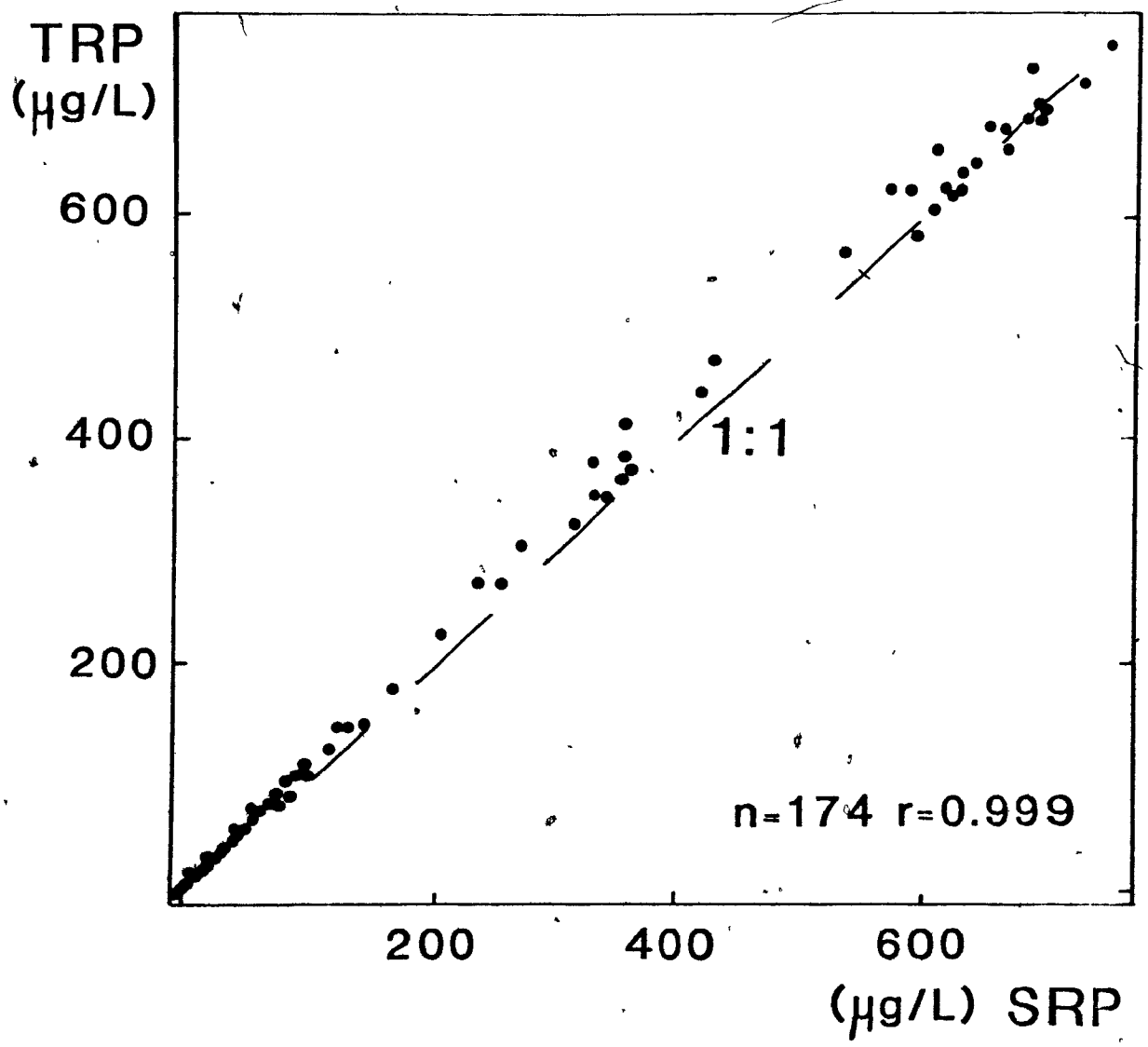
In anoxic waters, high concentrations of ferrous iron or hydrogen sulfide can lead to underestimation of the soluble reactive fraction of phosphorus. To obtain a valid determination of SRP, one must first establish which interference is likely to occur (iron or hydrogen sulfide). Then, one of the described techniques, anoxic filtration in the case of iron interference or aeration in the case of

hydrogen sulfide interference, can be applied. These two possible interferences render SRP analysis in anoxic waters very time consuming and exclude automatic analysis. A technique which appropriately describes SRP concentration in anoxic waters regardless of the interferences and which is simple enough for automated procedures would be of advantage. A modified TRP analysis will meet these requirements. In the example of water containing iron from Lake Magog water (Fig. 4), aeration diminishes SRP, but TRP stays the same (580 µg/L). That means TRP is unaffected by iron interference. Furthermore, its concentration is only slightly higher (2%) than SRP.

In the example of water from Lake St. George, containing hydrogen sulfide, TRP and SRP are equally affected by hydrogen sulfide (Fig. 8). However after sufficient aeration, TRP is only 1% higher than SRP and hydrogen sulfide interference is avoided.

The observation that TRP is only slightly higher than SRP in anoxic water containing iron and hydrogen sulfide was made on many occasions: SRP and TRP concentrations were compared in anoxic hypolimnetic water from eight lakes during summer stratification. SRP was estimated after appropriate treatment for interference and TRP was analysed after aeration when hydrogen sulfide was present; otherwise TRP was analysed untreated. The correlation of SRP with TRP concentration estimated in this way is highly significant ($r=0.999$, $n=174$, $SRP= -2.38 + 0.98*TRP$ or $TRP= 2.74 + 1.02*SRP$, Fig. 9).

Fig. 3-9 The correlation of SRP with TRP in anoxic hypolimnia from the eight lakes described in Table 1.


TRP
(µg/L)
600
400
200
1:1
n=174 r=0.999
200
400
600
(µg/L) SRP

Although Wilcoxon's matched pairs signed ranks test reveals that TRP concentration is significantly higher than SRP ($p<0.0001$), the overestimate is only small, on average 2%. This correlation holds only for strictly anoxic waters. For example, at the anoxic/ oxic interface in iron-rich lakes, iron hydroxides are abundant and absorb phosphate. SRP is only a small fraction of TRP at this interface.

Summary and Conclusion

Many anoxic waters are rich in ferrous iron or hydrogen sulfide. The correlation between iron concentration, the removal rate of soluble phosphorus and the induction of phosphorus precipitation by iron addition to waters which do not naturally precipitate phosphorus, all suggest that ferrous iron controls the amount of soluble phosphorus when the water is aerated. If no precautions are taken to avoid oxidation of ferrous iron, adsorption onto iron hydroxides or precipitation of ferric phosphate can occur; this lowers the apparent SRP concentration after the filtration step. This underestimation of SRP can be as high as 40% within 2 h of aeration, depending on iron concentration and oxygen tension. However in poorly buffered soft water, ferric iron phosphorus flocculants smaller than 0.45 µm are formed. Such waters show no interference in the standard oxic analysis of SRP, even though aeration of iron to the ferric state and loss of free orthophosphate occur.

Waters with low iron concentration can contain high

hydrogen sulfide levels. Hydrogen sulfide grossly interferes with the phosphorus analysis due to a reaction with the acid antimony molybdate reagent and can lead to a 80% underestimate of SRP. Sufficient aeration of hydrogen sulfide-rich samples is required to obtain a valid estimate of reactive phosphorus.

Rather than incur the danger of erroneous SRP estimates (if no precautions against the possible interferences are taken) or to cope with the inconvenience and time of carrying out a relatively complicated SRP analysis (if precautions are taken), I suggest sampling anoxic water without any precautions to maintain anoxia and aerating the aliquot for subsequent analysis of TRP. In this procedure it is essential that a blank reagent (described in method) for each sample is prepared to correct for the turbidity and color. This blank also indicates if the sample has been sufficiently aerated to reduce the interference of hydrogen sulfide. The necessary aeration time decreases with sample volume; once the aeration time is determined, the TRP procedure can easily be carried out by automated analysis.

Chapter 4:

Biological Availability of Soluble Reactive Phosphorus in Anoxic and Oxic Freshwaters.

Abstract

The availability of hypolimnetic phosphorus was assessed by a short-term bioassay, based on ^{32}P uptake kinetics. In the anoxic hypolimnia of eight lakes and in anoxic model systems (core tubes), at least 80% of soluble reactive phosphorus is biologically available. However, BAP is only a small fraction of SRP in iron rich, previously anoxic, waters after aeration and in lake water from the anoxic/ oxic interface. This result is supported by published data for oxic waters from epilimnia of lakes, rivers, sewage effluent and precipitation.

Introduction

Only a fraction of the phosphorus in lakes is readily available to microorganisms (Lee et al. 1980; Sonzogni et al. 1982). The major available fraction is free orthophosphate (PO_4) (Rigler 1973), but also PO_4 from oligophosphates and short-chain glycophosphates can be made available to plankton by phosphatases (Francko and Heath 1979; Petterson 1980). The determination of orthophosphate is most often based on the analysis of SRP (soluble reactive phosphorus) by molybdenum blue methology (Olsen 1967; Strickland and Parsons 1972).

SRP consists of orthophosphate (PO_4) but also of some acid-labile phosphorus compounds (Olsen 1967; Harwood et al. 1969). Several workers have found that SRP analysis overestimates PO_4 concentrations (Kuenzler and Ketchum 1962; Rigler 1966, 1968; Peters 1977, 1978, 1979; Tarapchak and Rubitschun 1981) though, in some cases, SRP and PO_4 were identical (White and Payne 1980). Since phosphorus compounds other than PO_4 might become available during a bioassay (Paerl and Downes 1978), SRP need not overestimate biologically available phosphorus (BAP), even if SRP overestimates PO_4 (Stainton 1980). Some reports show that SRP and BAP are indeed identical (Walton and Lee 1972; Chamberlain and Shapiro 1973).

In this paper, we investigate the equivalence of SRP and BAP. Our experimental work is largely confined to anoxic lake water from hypolimnia and cores containing phosphorus released from the sediment. The short-term radiological bioassays we used to measure BAP are specific for PO_4 and kinetically

similar substances. To cover a larger range of phosphorus concentrations, water bodies and techniques, we also compare published concentrations of SRP with BAP or PO_4.

Materials and Methods

Sample water: To estimate the bioavailability of phosphorus in anoxic hypolimnia, water was collected during summer stratification from two lakes in Quebec (weekly, 1981: Lake Magog and Fitch Bay of Lake Memphremagog) and six lakes in Ontario (weekly to monthly, 1982: Little Clear, Chub, Blue Chalk, Williams Bay of Jack Lake, Glen and St. George). Lakes and sampling techniques are described in Chapter 2 and 3. We also examined SRP and BAP released from anoxic lake sediments: Cores containing undisturbed sediment and hypolimnetic water from Fitch Bay were incubated under anoxic conditions in the dark, for 2 to 15 d. On several occasions, surface water from nitrogen-limited Lake Magog was also analyzed.

SRP analysis: SRP (like BAP) was analyzed within 5 h after sampling. In anoxic waters, ferrous iron and hydrogen sulfide interfere with SRP analysis (Chapter 3). Therefore, samples which were rich in iron were kept and filtered under anoxic conditions to avoid phosphorus adsorption to ferric iron, and subsequent underestimation of SRP; samples which were rich in hydrogen sulfide were bubbled with air to drive off H_2S (Chapter 3). Filtrates were analyzed for SRP by the molybdenum blue method following Stainton et al. (1977). The precision was less than 1% of the mean (standard error of four

repeated analyses at concentrations >10 µg P/L); the detection limit was 0.75 µg P/L. To determine if aeration affects the availability of SRP, about 100 mL of hypolimnetic water was aerated with an aquarium pump for 0.5-5 h before SRP and BAP analysis.

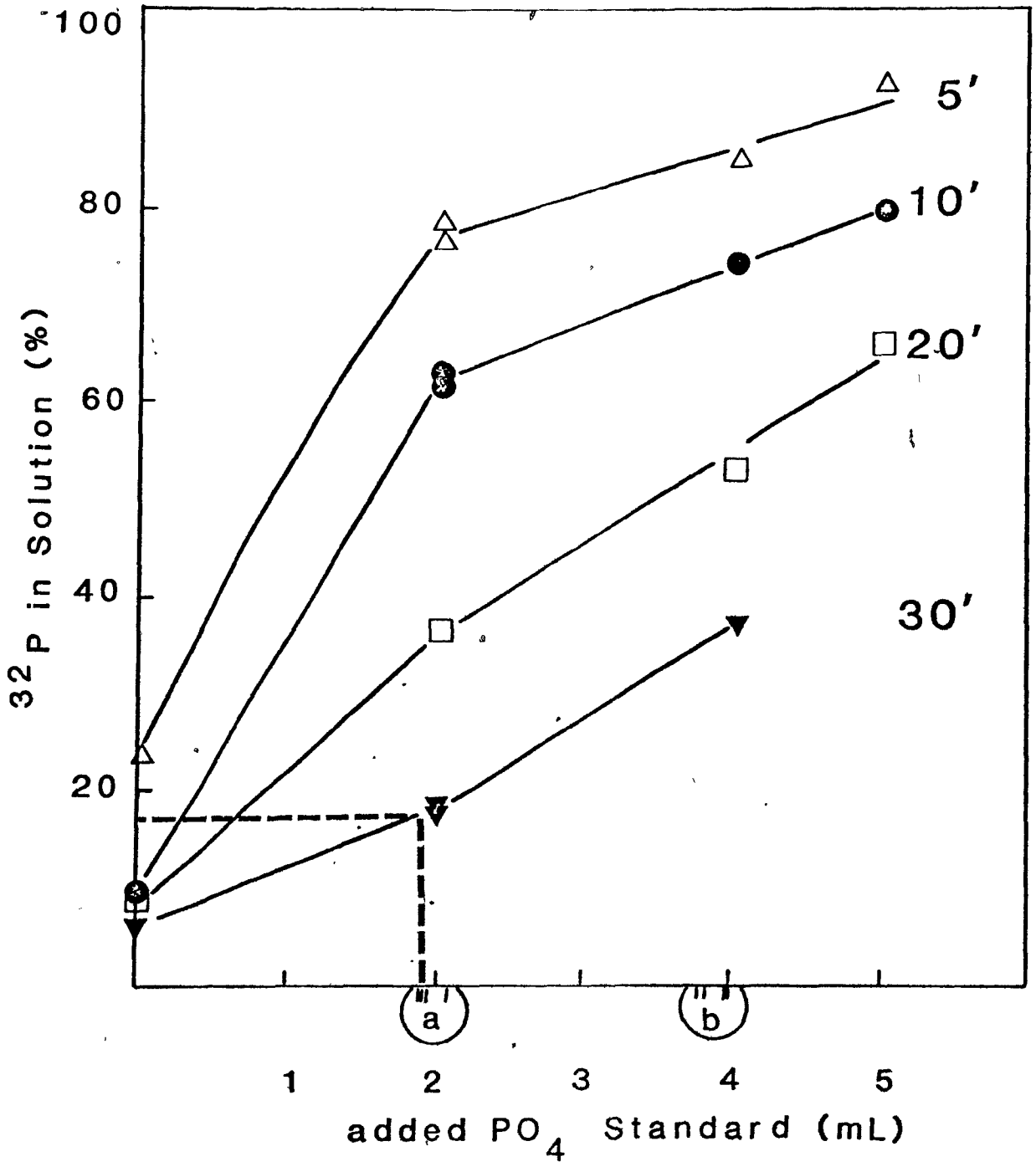
BAP analysis: Our analysis of BAP in the sample water (test-water) is based on the change in the amount of $^{32}P\text{-}PO_4$ uptake by plankton in phosphorus-limited lake water (assay-water) in response to additions of $^{31}P\text{-}PO_4$. This bioassay is essentially that described by Peters (1977, 1978, 1979), though it avoids filtration of the test-water and the dilution of assay-water with the filtrates. The assay is also similar to that described by Dillon and Reid (1981), except that the proportion of test-water added to the assay-water is smaller and the standard curves are based on the proportion of tracer taken up in a specific interval rather than on the rate constant of uptake. It is fundamentally different from Rigler's (1966) assay, because it compares uptake after addition of the test-water to uptake after the addition of a PO_4-standard; the estimation of BAP concentrations are therefore based on interpolations rather than extrapolations. In this assay, the fraction of $^{32}P\text{-}PO_4$ in solution at a given time correlates positively with the amount of $^{31}P\text{-}PO_4$. Carrier free $^{32}P\text{-}PO_4$ in 0.1 n HCl was obtained from the New England Nuclear Corporation and diluted to 0.001 n before experiments started. Standard curves were generated by adding known amounts of $^{31}P\text{-}PO_4$ and $^{32}P\text{-}PO_4$ to assay-water. Simultaneous

runs using additions of $^{32}P\text{-}PO_4$ plus test-water are then compared to the standard curves and the PO_4 concentration in the test-water determined by interpolation. Fig. 1 shows a typical result. This assay analyses only PO_4 and phosphorus compounds with similar uptake kinetics; it indicates the minimum phosphorus available (Peters 1981) and does not quantitatively detect phosphorus compounds with slower availability whose kinetics deviate from the PO_4 standard (Lean 1973; Paerl and Downes 1978).

Anoxic "test-water" was added unfiltered to avoid filtration artifacts upon aeration; epilimnetic test-water was filtered (Millipore 0.45 μm) before addition. The standard error of the BAP analysis was at most 10% of the mean, this is based on the average deviation of 10 replicate analyses at concentrations above 10 μg/L.

Orthophosphate standards were made from a stock solution of dehydrated K_2HPO_4, dissolved in double distilled water, diluted to approximate the SRP concentration of the test-water. Standard curves were produced by addition of several volumes (0, 1, 2 mL) of this solution to 100 mL of each assay-water. In all cases but one, the assay-water consisted of water from the epilimnion of the same lake from which the hypolimnetic water was taken. In nitrogen-limited Lake Magog, $^{32}P\text{-}PO_4$ uptake by microorganisms was too slow. Therefore, epilimnetic water from another lake, usually Fitch Bay, was used instead. The volume of test-water was diluted 10 to 1000 fold with the assay-water depending on the hypolimnetic SRP concentration. This dilution depressed the iron concentration

Fig. 4-1. A typical bioassay with Jack Lake epilimnetic water as assay water (5m, Aug. 26, 1982) calibrated with additions of 0, 2, 4, and 5 mL of 75 µg/L PO_4 standard solution. Subsampling times were 5, 10, 20 and 30 min. The addition of 2 (a) and 4 (b) mL of anoxic hypolimnetic water (20m) sampled at the same location, are comparable to additions of 1.95 and 3.9 mL of standard. This indicates that the test water concentration is 73 µg/L PO_4. Broken lines indicate how to arrive from the uptake value at 30 min (a), at the corresponding PO_4 concentration.

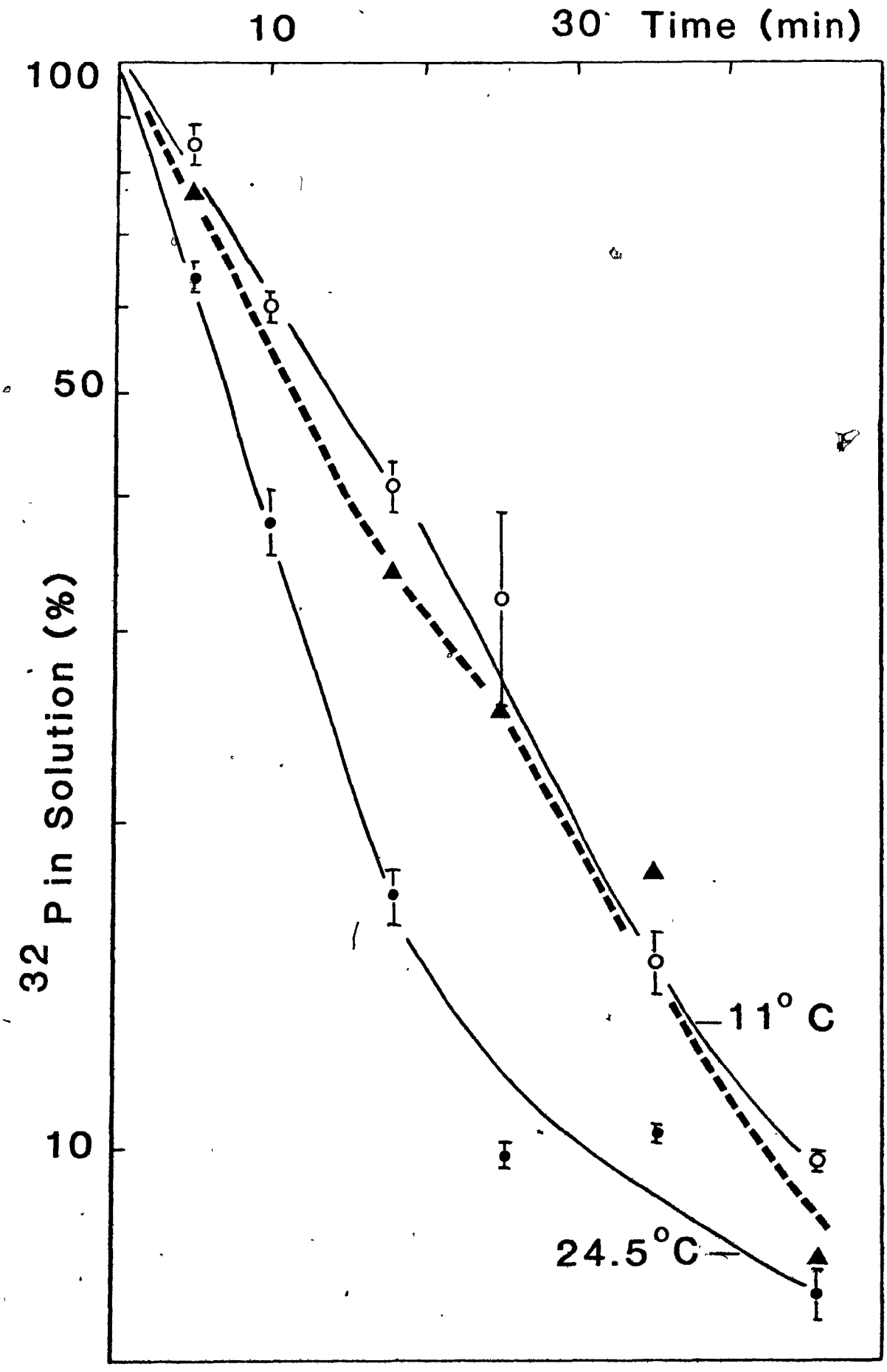

100
80
60
40
20
^{32}P in Solution (%)
5'
10'
20'
30'
a
b
1
2
3
4
5
added PO_4 Standard (mL)

in iron-containing hypolimnetic water below the threshold (0.20 mg/L Fe) for significant adsorption of phosphorus onto Fe particles (>0.45 μm) within the period of the bioassay (Chapter 3). To detect possible dilution effects, each determination involved at least two different volumes of test-water, though no significant deviations were ever detected. Because uptake rates are dramatically affected by temperature (Fig. 2) and possibly by light and time since collection, standards, blanks and two test-water samples were processed simulataneously. Stirring or shaking during the assay did not affect uptake and was not carried out routinely.

At zero time, 100 μL ^{32}P-PO_4 solution were added to the standard and test solutions. At each subsampling time, 6 mL subsamples were withdrawn and filtered (<35 kPa) simultaneously through 0.45 μm Millipore filters at 3-6 different times (usually 5, 10, 20, 30 min) within 1 h. The filter holders had been checked for filtering efficiency and reproducibility, and only those which had reproducible retention of 10 or 5% (for different manifolds) were selected. The sample was filtered directly into plastic minivials and the ^{32}P radioactivity measured by Cerenkov counting on the tritium channel of a liquid scintillation counter to 1% counting error. The counts of the filtrate, corrected for filter adsorption of some soluble tracer, were expressed as a percentage of the mean of two unfiltered 6 mL samples, taken before and after the assay.

Since Cerenkov counting is not often used in limnology, several possible sources of error had to be investigated.

Fig. 4-2. The importance of temperature control for all samples of a particular bioassay: The assay water (Fitch Bay, 5m, July 7, 1981) was enriched with phosphate standard to 0.25 µg/L by adding 1 mL of 25 µg/L PO_4 and ^{32}P uptake and recorded in triplicates at 24.5° C and 11° C after five h preconditioning at that temperature (solid lines). The uptake with 50% higher enrichment (1.5 mL of 25 µg/L PO_4 at 24.5° C is shown for comparison (triangles with broken line). The latter two uptake kinetics coincide meaning that decreased temperature can falsely pretend high phosphate concentrations.


10
30
Time (min)
100
50
10
32 P in Solution (%)
11° C
24.5°C

Plastic minivials appeared to be most efficient both from the point of view of counting efficiency (plastic is 40% more efficient than glass) and filtration volume needed (6 mL instead of 10-20 mL in large vials). Natural color could decrease the counting efficiency by 10% but this did not effect the results because the reference values were based on the same colored water. Since ^{32}P added to filtered and unfiltered lake water had the same activity, there seemed to be no self-adsorption of Cerenkov radiation by plankton.

To reduce the possibility of contamination, the assay vessels (250 mL Erlenmeyer flasks) were filled with a ca. 0.5% solution of a basic solvent ('Count Off', New England Nuclear) during storage. Before each bioassay, the vessels were rinsed three times with distilled water and once with the assay-water. Assay-water (100-200 mL) was placed in the vessels for at least 15 min (the late F.H. Rigler, McGill University, personal communication) so that available phosphorus could be reduced still further by the plankton. This water was discarded and exactly 100 mL of assay-water added and allowed to stay in the reaction vessel for at least 0.5 h before addition of tracer and carrier. Flasks and pipettes for subsampling were kept covered during the whole assay.

Hypolimnetic water might contain substances besides PO_4 which affect ^{32}P-PO_4 uptake kinetics. This was evaluated in the following ways:

a) The uptake kinetics after addition of the test-water were compared to uptake kinetics of the standard water. Deviation from the shape of the standard curves indicates

interference and no BAP concentration was calculated. These comparisons suggest that two points from Fitch Bay (n=9) and one from Little Clear Lake (n=8) were not reliable; these data were discarded. Since both lakes contain high iron concentrations, it is possible that the different kinetics reflect a phosphorus fraction which is available at a slower rate than PO_4 (Paerl and Downes 1978).

b) Another test for interfering and poisonous substances was achieved by additions of internal standards. A known concentration of $^{31}P\text{-}PO_4$ was added with the test-water for each lake at least once, but a deviation from the results without internal standards was detected on only one occasion: the hypolimnetic water of Glen Lake, where large amounts of hydrogen sulfide slowed uptake of tracer and thus produced an overestimate of BAP concentration. This problem was subsequently prevented by aerating the samples for at least 30 min before addition to the assay water.

c) Bacteria are primarily responsible for initial ^{32}P uptake (Hayes and Phillips 1958; Lean and White 1983). Therefore on two occasions, substances which are likely to support bacterial growth such as carbohydrates, nitrate, iron and calcium were added to the assay water at concentrations similar to those in hypolimnetic water; no deviation was found.

d) We determined whether differences in phosphorus limitation of the assay water or differences in the plankton community or water chemistry have any effect on the bioassay.

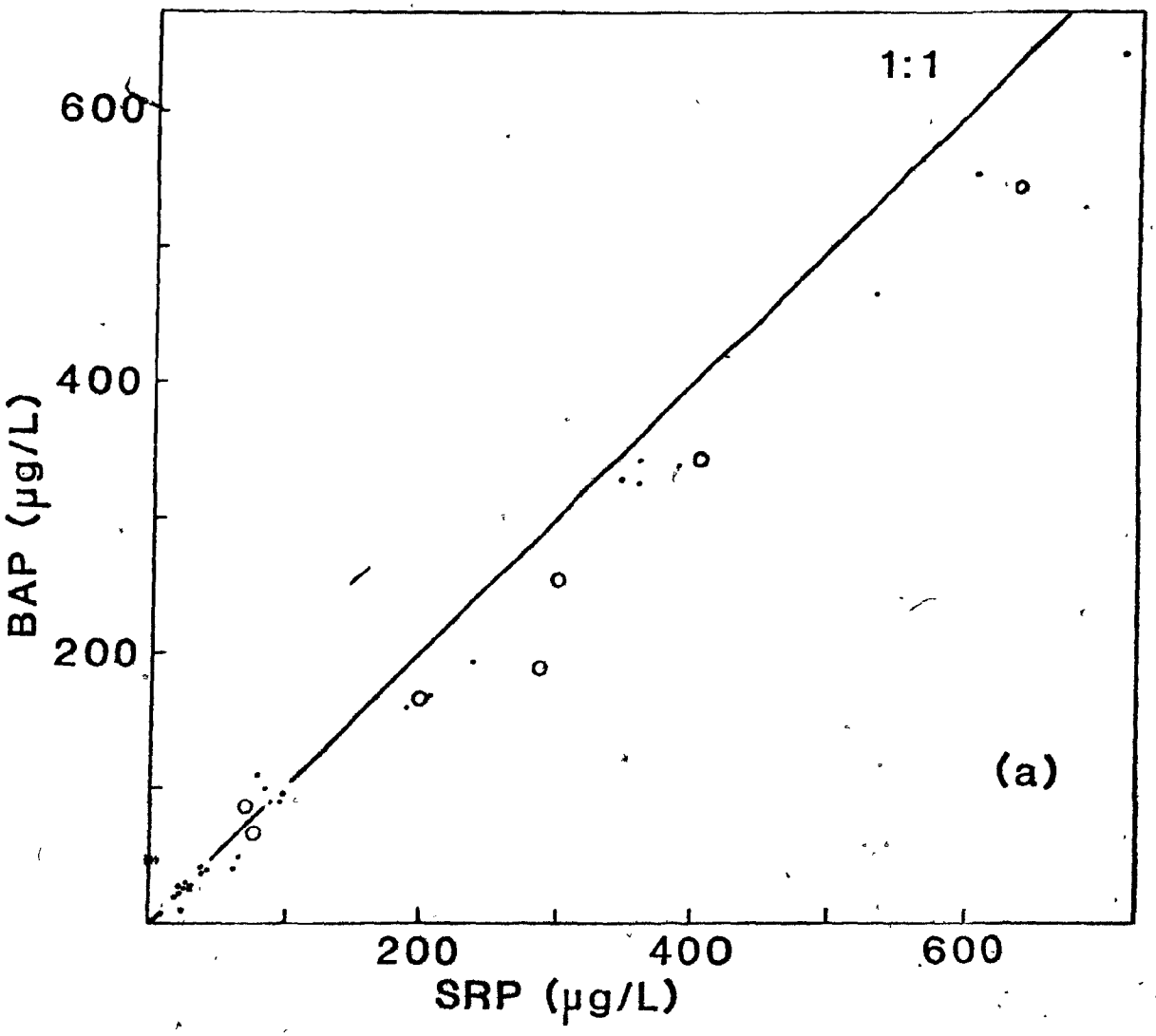
This was tested on several occasions by analyzing BAP in the same hypolimnetic water in separate bioassays with water from the epilimnia of two different lakes. Although the assay-waters differed in the amount of ^{32}P uptake by 60% within the first hour, no significant difference in the BAP concentration was found. This means that incubation and growing of cultures under standardized conditions can be circumvented by using phosphorus limited epilimnetic water as assay-water.

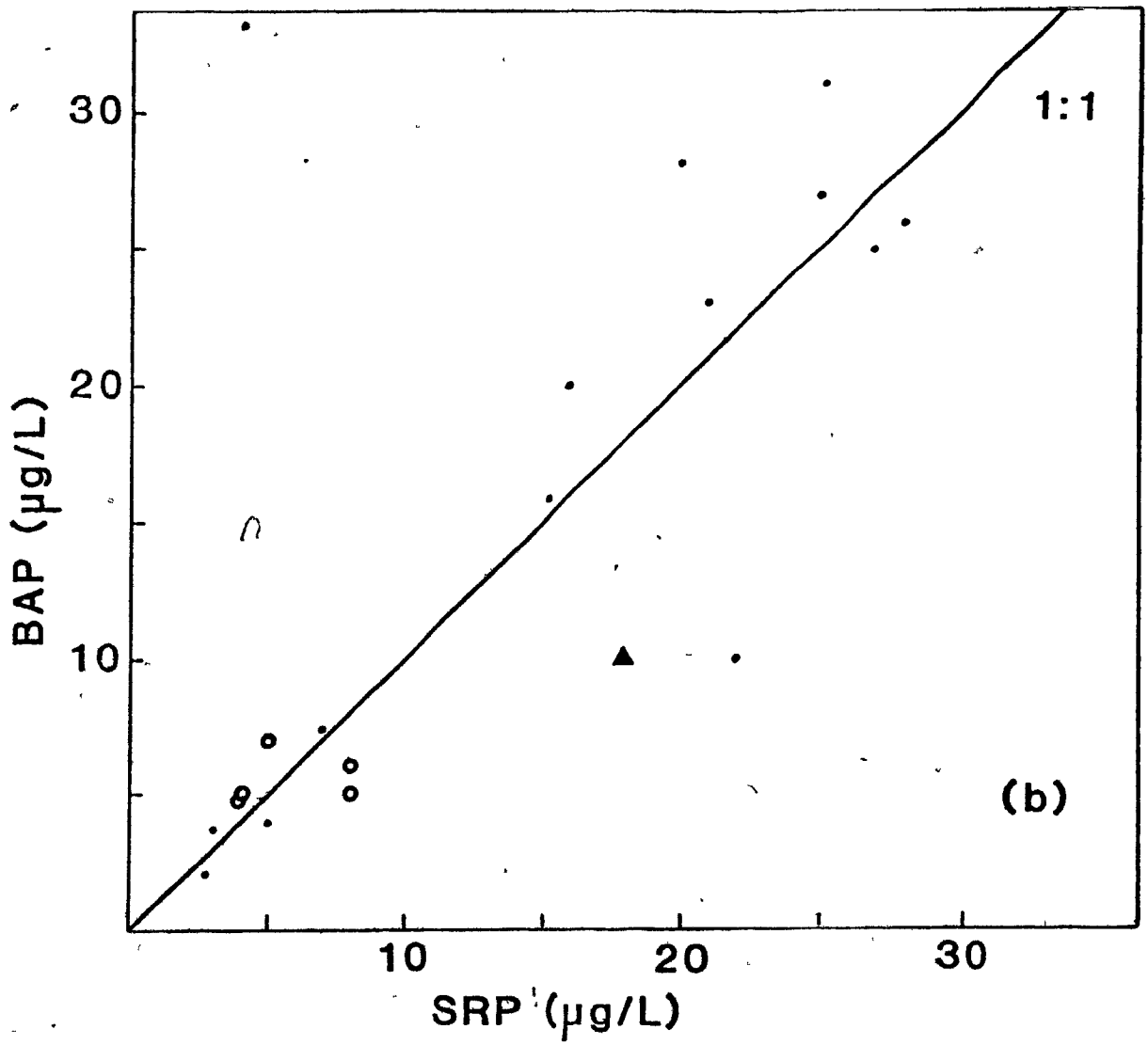
Results and Discussion

Short-term ^{32}P-Bioassays:

SRP concentrations for all anoxic lake samples (range of 2 to 531 µg SRP/L) are similar to (Wilcoxon matched pairs signed ranks test: $p>0.122$, $n=33$) and highly correlated with ($r^2=0.994$, $n=33$, Fig. 3a) BAP concentrations. The linear regression of BAP on SRP is BAP= 2.501+0.923 SRP ($SE_{slope}=0.0131$). This suggests that BAP exceeds SRP at concentrations below 30 µg SRP/L. Since BAP concentrations did not consistently exceed SRP at lower concentrations, linear regression over the whole range does not adequately describe the data. Therefore, the data set was divided into two subsets, consisting of values above and below 30 µg/L SRP, and reanalyzed. Again, the Wilcoxon test revealed no significant difference for SRP concentrations <30 µg/L ($n=13$, $p>0.422$), but the difference was significant for higher SRP concentrations ($n=20$, $p>0.032$). The regression line for the low concentration subset coincides with the 1:1 line (Fig. 3b,

Fig. 4-3. The correlation of SRP with BAP. The line of perfect agreement (1:1) is also shown. a) Water from anoxic hypolimnia of eight lakes (closed circles) and anoxic core tubes (open circles). b) Water from the same anoxic lakes with SRP concentrations less than 30 µg/L (closed circles), oxic epilimnia (open circles) and surface water during fall turnover (triangle) of Lake Magog.


1:1
600
400
200
BAP (µg/L)
200
400
600
SRP (µg/L)
(a)


30
20
10
BAP (µg/L)
1:1
(b)
10
20
30
SRP (µg/L)

BAP= 0.665+0.993 SRP, SE_{slope}=0.1558, r^2=0.787, n=13). For concentrations above 30 µg SRP/L, the regression equation (BAP= 3.441+0.921 SRP, SE_{slope}= 0.01977, r^2=0.992, n=20) indicates that SRP overestimates BAP concentration up to an average of 8% for the higher concentrations.

The tendency for SRP to overestimate BAP at high concentrations was also found in water from core tubes containing sediment and anoxic water (Fig. 3a). The highly significant regression for seven cores (r^2=0.98, BAP=0.305+0.841 SRP, n=7, range 71 to 636 µg/L SRP) shows that 84% of SRP, on the average, is available. The discrepancy between SRP and BAP at high SRP concentrations is unexplained, but it may represent a systematic experimental error. At such high concentrations, only 100 µL of test-water were pipetted into the assay-water and enough oxygen could have diffused into such a small volume to produce significant iron/phosphorus precipitation. This is suggested because the overestimate was pronounced in waters with high iron concentrations. In any case, the results show that at least 80% of SRP is biologically available.

In some anoxic hypolimnetic waters, oxidation of ferrous iron could interfere with SRP and BAP analyses, since ferric iron hydroxides can adsorb PO_4 (Stumm and Morgan 1970) rendering it insoluble and less available. Experiments were designed to determine the effect of aeration of the test-water on the close agreement between SRP and BAP. In hardwater lakes (Glen, St. George), SRP and BAP concentrations remained unchanged. In the other lakes, aeration decreased BAP (Little

Clear, Chub, Blue Chalk) or both SRP and BAP concentrations (Magog, Jack). Where BAP decreased but SRP stayed the same, subsequent SRP analysis drastically overestimated BAP concentration. Decrease of the BAP concentration depended on the total iron concentration in the hypolimnetic water (Table 1). In soft water lakes which were rich in organic acids (Little Clear, Chub and Blue Chalk), SRP and soluble iron remained unchanged, though BAP decreased and all the iron was converted to the ferric state (Chapter 3). This suggests that, in these lakes, the iron-phosphorus particles were initially smaller than 0.45 µm. In Lake Magog, an uncolored lake, the iron phosphorus particles were larger than 0.45 µm. As a result, SRP decreased after aeration and SRP overestimated BAP to a lesser extent (Table 1).

Although this discrepancy between SRP and BAP was induced artificially, iron-rich hypolimnetic water may be aerated naturally at the anoxic/ oxic boundary during the stratified period and at turnover. In Lake Magog, bioassays of hypolimnetic water from the oxic/ anoxic boundary and of surface water during destratification showed that less than 70% of SRP was BAP (Table 2). It appears that BAP concentration is lower than SRP in these cases, because of formation of colloids and particles containing iron and phosphorus. Such phosphorus might become available in the long run but this was not investigated.

Artificial formation of colloidal-iron phosphorus compounds was also observed by Koenings and Hooper (1976), who

Table 4-1. SRP and BAP concentrations in artifically aerated water samples from anoxic hypolimnia of seven lakes. The SRP concentration before aeration was similar to that after aeration, except for Jack Lake and Lake Magog. The difference between SRP and BAP after aeration depends on total iron concentration (TFe) and the concentrations of soluble iron before (SFe^{2+}) and after aeration (SF^{3+}).

Lake	Aeration (min)	SRP (µg/L)	BAP	BAP/SRP %	TFe (	SFe^{2+} mg/L	SFe^{3+})
Glen	35	39	40	102	<0.1	<0.1	<0.1
"	35	92	90	98	<0.1	<0.1	<0.1
St.George	35	343	329	96	<0.1	<0.1	<0.1
Jack[a]	150	59	60	102	0.4	0.2	0.2
Blue Chalk	92	16	2	13	3.4	3.0	3.0
Little Clear	35	25	1-2	6	5.2	4.9	4.9
Chub	35	31	3	9	5.5	4.9	4.8
Magog[b]	300	193	125	65	4.0	4.0	0.7
"	300	192	70	36	3.9	-	-

[a]SRP before aeration: 88 µg/L

[b]SRP before aeration: 672 µg/L

Table 4-2. SRP and BAP concentrations in naturally aerated, iron-rich water of Lake Magog (1981). The data were collected at the oxic/anoxic interface in the hypolimnion and in the epilimnion at fall turnover.

Date & Depth	O_2 (mg/L)	SRP (µg/L)	BAP (µg/L)	BAP/SRP %	Fe (mg/L)
9 VI, 16m	6	13	4	33	0.29
25 VI, 16m	6	89	50	56	0.71
3 VII, 16m	2	115	41	35	0.79
3 VII, 12m	4	25	9	37	0.30
8 VII, 16m	1	140	73	52	1.06
8 VII, 12m	2	14	9	69	0.27
Fall turnover	10	18	10[a]	53	0.22
" "	10	18	11	61	0.22

[a]filtered before analysis

found that aeration of anoxic bog water increased the colloidal phosphorus fraction from 0 to 33% (range of SRP: 266-605 µg/L). White and Payne (1980) found that "reactive high molecular weight phosphorus" (perhaps a colloidal iron-phosphorus component) accounted for up to 76% of the SRP concentration in three of five eutrophic anoxic hypolimnia of New Zealand lakes. This was not observed in the presumably oxic hypolimnia of mesotrophic or oligotrophic lakes and occurred only once in seven oxic epilimnia (at turnover, E. White, Dept. of Scientific and Industrial Research, Taupo, New Zealand, personal communication). This may indicate the artificial formation of phosphorus-iron colloids upon aeration of anoxic hypolimnetic water during analysis, since the two lakes with the highest deviation of PO_4 from SRP have substantial iron concentrations even in the epilimnia (1.6 and 0.4 mg/L Fe, White personal communication). On the other hand, Francko and Heath (1982) found that SRP increases with the reduction of iron by UV radiation, and that phosphorus in high molecular weight fractions containing ferric iron is not analyzed as SRP, though it passes a 0.45 µm filter. In such waters, SRP should not overestimate BAP in spite of the presence of iron hydroxides.

These results suggest that, in anoxic water, SRP is almost completely available in the short-term. In aerated, iron-rich waters, BAP may represent less than 10% of SRP. During stratification, SRP can be completely available in oxic surface waters: five tests of water from the epilimnion of

Lake Magog during summer stratification in the range of 4-8 µg/L show good agreement between SRP and BAP (Fig. 3b).

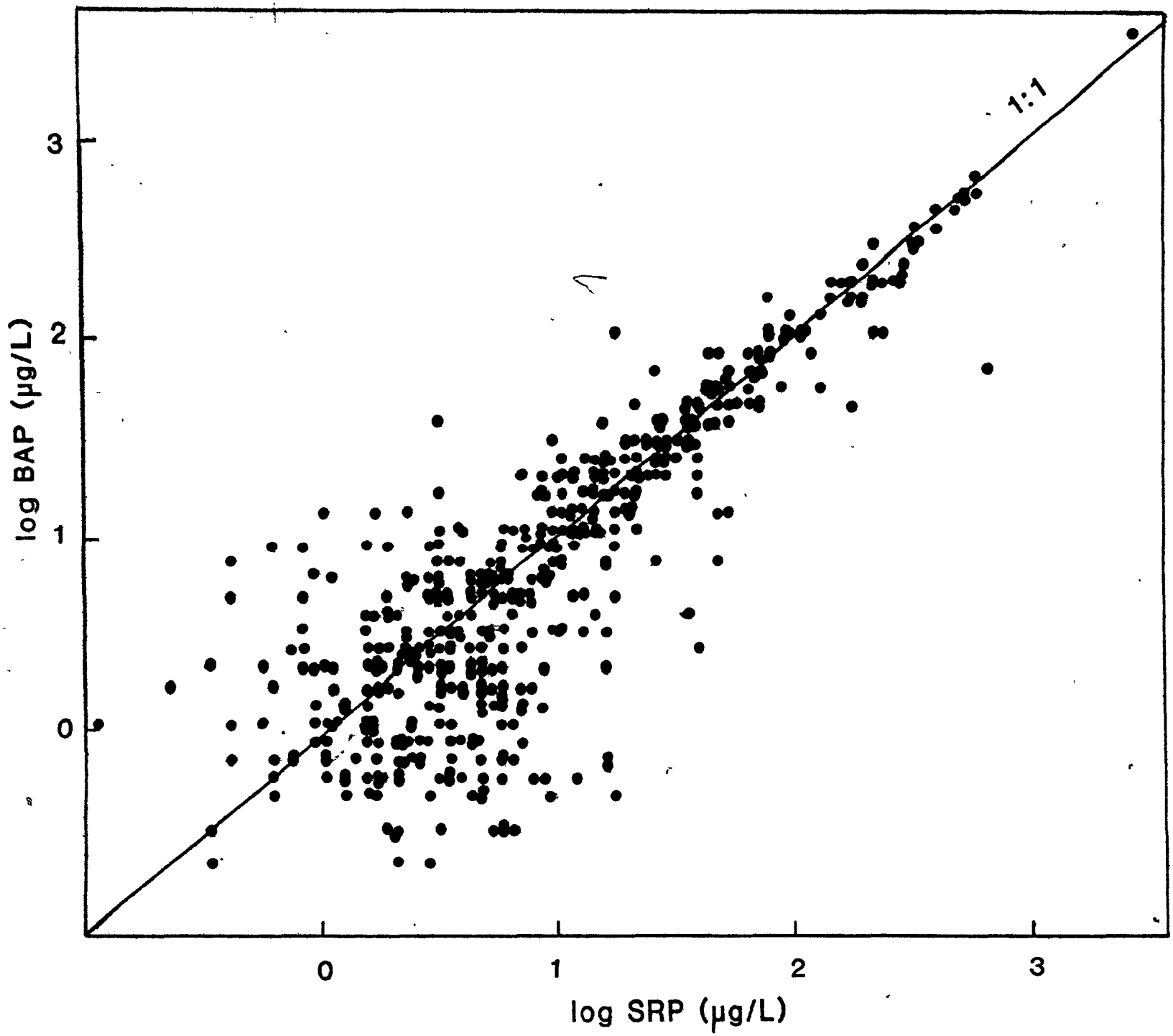
Literature Data:

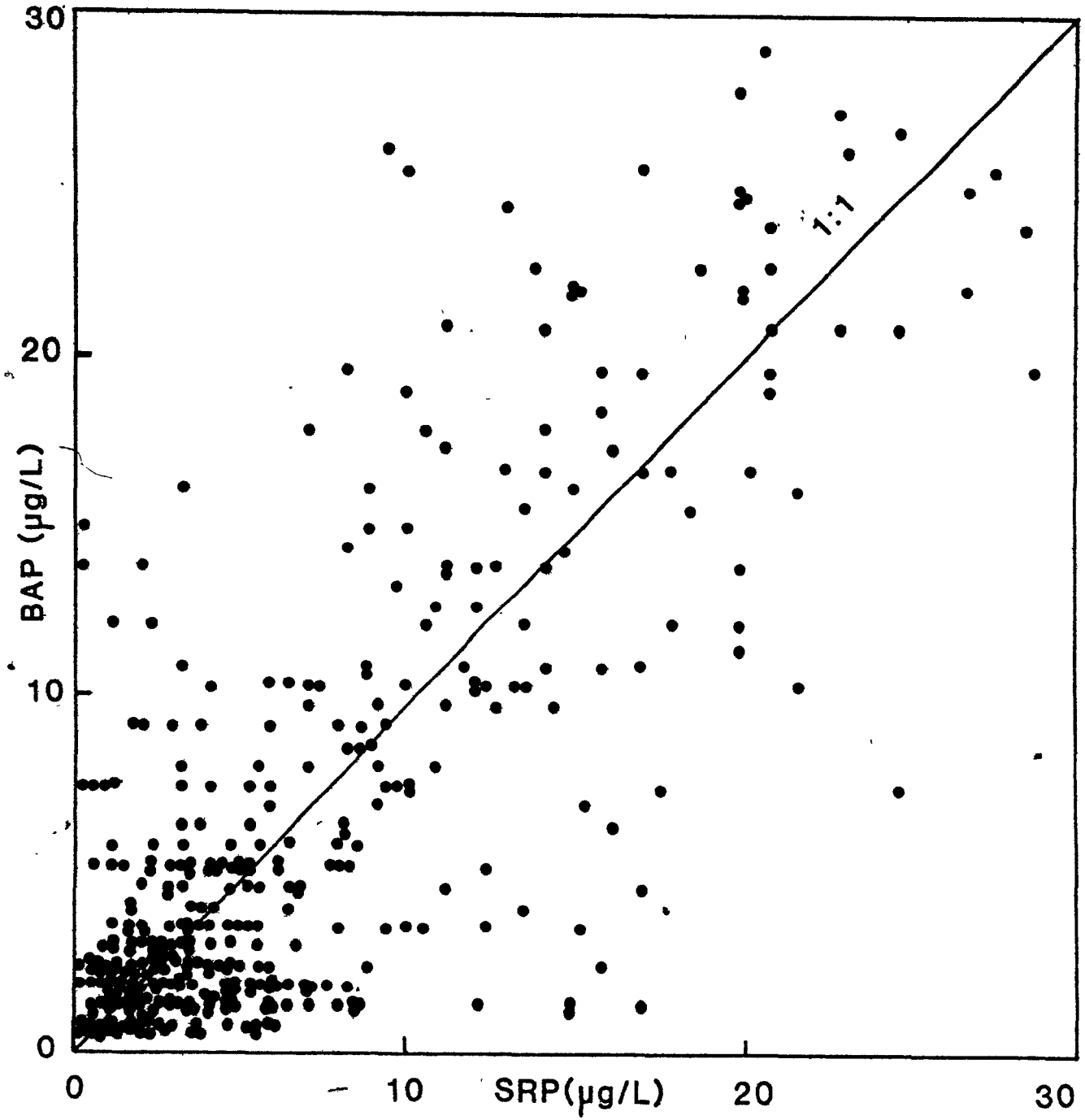
The literature survey includes 603 BAP and SRP data-pairs from phosphorus limited lakes, nitrogen limited lakes, sewage treatment effluents, atmospheric precipitation and streams. All the data from bioassays are called "BAP" in this paper, since bioassays may not identify chemically pure PO_4, even when they are thought to analyse largely PO_4 (Rigler 1966; Peters 1977, 1978, 1979; Tarapchak and Rubitschun 1981). Four classes of data were excluded from analysis. These are (1) some data of White and Payne (1980) which may be subject to iron hydroxide interference as described above; (2) BAP values based on Rigler's (1966) bioassay have been excluded because they are based on statistically questionable extrapolations. This deletion has no significant effect on the overall analysis since the number of data is small; (3) SRP analyzed with an extraction technique (Chamberlain and Shapiro 1973) was excluded to circumvent inhomogeneity in SRP analysis; (4) those data with reported arsenic interference were excluded. Regression analysis and mean differences (SRP-BAP) were used as a measure of the overall (positive or negative) deviation of BAP from SRP. Subsets of these data for low and high SRP concentrations, for different laboratories, BAP methods and types of water were investigated to determine whether these characteristics are important.

Overall correlations: The overall correlation of the SRP and BAP values is highly significant (r=0.97). The mean difference (SRP-BAP) is 2.18 µg/L which is significant by the Wilcoxon's matched pairs signed ranks test ($p<0.0001$). A parametric test is not appropriate because the data are very wide spread and not normally distributed. The linear regression equation is BAP=0.73 + 0.91 SRP (SE_{slope}=0.008, r^2= 0.96, n=601, range: 0-700 µg/L SRP). Two significantly influential outliers were excluded (Cook's [1977] criterion). The intercept is not significantly different from zero but the slope differs significantly from unity. The data are presented in a log/log plot in Fig. 4a. (53 data values of SRP or BAP were zero and had to be excluded from the logarithmic plot.) It can be concluded that there is a close agreement of SRP and BAP values and the difference, though significant, is only small.

It has been suggested that the amount of SRP concentration may influence the similarity of SRP and BAP (Chamberlain and Shapiro 1973). To investigate this, the data set was divided in two subgroups analogous to those formed earlier for the anoxic lake data set. The mean difference (SRP-BAP) for SRP concentrations < 30 µg/L (mean SRP= 6.2 µg/L) is 0.03 µg/L which, though small, is significant by a Wilcoxon test ($p<0.002$). The linear regression equation is BAP= -0.15 + 1.04 SRP (r^2=0.52, n=490) and the slope and intercept are not significantly different from unity and zero, respectively (Fig. 4b). For SRP values > 30 µg/L (mean SRP= 165 µg/L), the mean difference is 11.5, which is also

Fig. 4-4. The correlation of SRP with BAP with data from Table 3. "1:1" represents the line of perfect agreement. a) Log/log plot: log BAP= -0.11 + 0.97 * SRP, n=550, r^2= 0.70. b) Linear plot for SRP concentrations less than 30 µg/L: BAP= -0.15 + 1.04 * SRP, n=490, r^2= 0.52.


1:1
log BAP (µg/L)
log SRP (µg/L)
0
1
2
3
0
1
2
3


30
20
10
0
BAP (μg/L)
1:1
0
10
SRP(μg/L)
20
30

significant by a Wilcoxon test ($p<0.001$). The linear regression equation is BAP= 13.04 + 0.78 SRP (r^2= 0.80, n=112; one significant outlier is excluded). Both the mean differences and slopes indicate that, when SRP > 30 µg/L, the absolute amount of the overestimation increases. A similar result was obtained for the anoxic lakes presented above; hence it appears that SRP tends to overestimate BAP slightly (<10%) at higher SRP concentrations.

Data sources: Range and mean of SRP values and mean differences between SRP and BAP are presented separateley for each laboratory (Table 3). This analysis allows comparison of large and small data sets when a regression analysis would be misleading. The mean percentage difference with respect to mean SRP concentration (percentage difference: mean [SRP-BAP]/ mean [SRP]) corrects for the different phosphorus concentrations and indicates any bias (negative or positive) between SRP and BAP. Different sources show quite heterogeneous results: The percentage differences range from -23 to 87% indicating that SRP overestimates BAP in some cases and underestimates it in others; also, BAP is not always strongly correlated with SRP. To determine whether these differences are due to special water-types (for example, water rich in fresh iron hydroxides), or the result of the applied methods, the data were grouped by BAP method and water-types.

BAP methods: The variability in estimating BAP from SRP is quite large among different methods for BAP analysis (Table 4). BAP estimates from Rigler's (1966) tracer bioassay and

Table 4-3. Comparison between concentrations of SRP and BAP reported by different authors. Tabulated data include the range of SRP concentrations (µg/L), the number of data-pairs (n), the correlation coefficient for BAP and SRP (r), the mean concentration of SRP (x_1), the mean (x_2) and standard error (SE) of SRP-BAP, this mean expressed as a percentage of mean SRP ($100 \times x_2/x_1$) and characteristics of the bioassay type, organisms and duration of the assay. f: filtered, uf: unfiltered, AGP: Algal growth potential.

Source: 1- This paper; 2- Peters (1977, 1978, 1979); 3- Walton (1971). Algae counts given by the author were converted into BAP concentrations for Lake Mendota samples. Since Walton (1971) considers data for Lake Wingra unreliable these are not included. 4- Chamberlain & Shapiro (1969), SRP analyzed with Harvey's method for low arsenate concentrations only; 5- White and Payne (1980). Three values for anoxic hypolimnia were excluded, because of possible aeration artifacts (iron adsorption, see text). The phosphate extracted here was proven to be completely available to Chlorella (Paerl and Downes 1978). 6- Stewart and Alexander 1971; 7- Dillon and Reid (1981); 8- Dillon, Ontario Ministry of the Enbvironment, pers. comm.; 9- DePinto et al 1980; 10- Murphy et al. (1983); 11- Twinch and Breen (1982); 12- Rigler (1966); 13- Tarapchak and Rubitschun (1982); 14- Peters (1979).

Source	Range	n	r	SRP	SRP-BAP		%	Assay Type	Assay Organism	Period
				$\bar{x}_1$	$\bar{x}_2$	SE	$\bar{x}_2/\bar{x}_1$			
1	2 - 636	44	0.99	144.3	12.9	3.95	9	^{32}P-Uptake, uf	Lake Plankton	1 h
2	0.6- 54	181	0.73	7.2	3.2	0.51	44	^{32}P-Uptake, f	Lake Plankton	1 h
3	1- 181	25	0.99	45.4	0.2	0.85	0	AGP	Selenastrum	21 d
4	1- 30	5	0.98	13.5	1.9	0.92	14	SRP-Uptake	Microcystis	2 h
5	0- 592	16	0.99	46.1	1.0	0.75	2	Sephadex Fract.	Chlorella	96 h
6	2-3000	6	0.99	542.2	-123.3	115.52	-23	Acetylene Reduction	Anabaena	1-2 h
7	0- 90	49	0.87	12.1	-2.6	1.56	-21	^{32}P-Uptake, uf	Lake Plankton	15 min
8	0- 340	209	0.96	23.5	0.5	1.02	2	^{32}P-Uptake, uf	Lake Plankton	15 min
9	0- 500	22	0.95	1.2	-0.2	0.08	17	AGP	Scenedesmus	14-28 d
10	414- 549	2	-	481.5	0	0	0	Sephadex Fract.	none	-
11	0-1000	44	0.46	54.0	19.2	15.66	36	AGP	Selenastrum	14 d
12	0.3- 5	9	n.s.	1.78	1.3	0.49	74	Rigler-Bioassay	Lake Plankton	1-2 h
13	1- 8	21	n.a.	3.6	3.1	n.a.	87	Rigler-Bioassay	Lake Plankton	1-2 h
14	0- 11	13	n.s.	2.7	1.6	0.76	58	Rigler-Bioassay	Lake Plankton	1-2 h

Table 4-4. SRP and BAP mean differences sorted by method of BAP analysis. Synbols as in Table 3. Data from source (13) are not included since only ranges and means are available.

Method	n	r	SRP	SRP-BAP		%	Source
			$\bar{x}_1$	$\bar{x}_2$	SE		
^{32}P, uf	302	0.99	39.2	1.80	0.98	5	1,7,8
^{32}P, f	181	0.73	7.2	3.2	0.51	44	2
Sephadex frac.	18	1.00	94.5	0.87	0.67	1	5,10
AGP	91	0.53	38.9	9.32	7.60	24	3,9,11
Rigler assay	22	n.s.	2.3	1.46	0.49	64	12,(13),14
Acetylene Red.	6	0.99	542.2	-123.3	115.52	-23	6
unfiltered	320	0.99	42.3	1.75	0.93	4	1,5,7,8,10
filtered	283	0.97	28.9	2.45	3.51	8	2,3,4,6,9,11

from ^{32}P bioassays of filtered water were considerably less than SRP concentrations, while BAP estimates based on acetylene reduction were, on average, greater than SRP measurements. Sephadex fractionation and ^{32}P bioassays using unfiltered water usually gave concentrations of BAP which were close to those of SRP. Part of the discrepency between SRP and BAP measured with either ^{32}P bioassay may be associated with low SRP levels. At such levels, both SRP and BAP estimates are more variable (Fig. 4b), probably reflecting both greater analytical error and the more pronounced effects of contamination. Low SRP levels are not always poor estimators of BAP concentrations since Sephadex fractionation show only small differences between SRP and BAP (percentage difference = 3%) at low concentrations (mean [SRP]= 1.9, range 0.3-5.0 µg/L, n=11) and, overall, the mean percentage difference at SRP levels below 30 µg/L was only 1%. Further work may be required to determine if the large percentage differences reported using these ^{32}P bioassays represent pecularities of given lakes or methodological shortcomings.

To circumvent the problem of introducing unknown plankton into the bioassay vessel, many researchers filtered the water to be tested before the bioassay. Filtration before analysis does not reveal any difference in estimating BAP and might be unnecessary (Table 4). However, the percentage difference of ^{32}P uptake bioassay with filtered water was greater than with unfiltered water.

SRP methods: All the SRP methods used in these studies were based on the molybdenum blue method with stannous

chloride (Harvey 1948) or ascorbic acid (Strickland and Parsons 1972) as reductant. Although $Sn\ Cl_2$ has been reported to yield slightly higher values than the ascorbic acid method, they differ not more than by 20% (Stainton 1980, Tarapchak et al. 1982). Other factors can lead to deviation of apparent SRP concentrations: The presence of arsenate (Chamberlain and Shapiro 1969), calcium (Burnison 1983), high volume and high pressure filtration (Tarapchak et al. 1982 a) and extended exposure to acid and unclean conditions (Rigler 1964). These effects on the published SRP data reported here cannot be evaluated, but they probably contribute to the scatter in the data, particularly at low SRP concentrations.

Water types: Close agreement between BAP and SRP was found in most waters (Table 5), although SRP may overestimate BAP in groundwaters (Peters 1979) and in artificially enriched limnocorrals (Twinch and Breen 1982). These data are drawn from the work of single laboratories and may confound other differences in methods or sampling sites with effect of water type. It is also possible that aeration during sampling of groundwater induced phosphorus precipitation with iron and so reduced BAP levels since work with cores in the same area (Nürnberg unpublished) and general surveys (White et al. 1963) indicate that anoxic groundwater is often rich in ferrous iron. More evidence is required to evaluate the ability of SRP to measure BAP in artificially enriched enclosures. Underestimation of BAP by SRP in sewage effluents seems frequent, though the large standard error of the difference

Table 4-5. SRP and BAP mean differences sorted by the type of water. Symbols as in Table 3, ext.: extract. References 12 to 14 are not included.

Type	n	r	SRP	SRP-BAP		%	Source
			$\bar{x}_1$	$\bar{x}_2$	SE		
Hypolimnion	51	0.99	144.4	11.1	3.47	8	1,3,5
Epilimnion	98	0.99	12.1	0.4	0.51	3	1,2,3,4,5,6
Streams	283	0.96	18.0	1.6	0.73	9	1,2,6,8
Sewage	24	0.99	126.6	-29.1	29.17	-23	4,6,9
Sediment, Soil	4	0.99	284.5	-0.3	1.03	0	3,10
Bluegreen-ext.	2	-	33.0	5.5	-	17	3
Precipitation	100	0.95	15.6	0.1	1.37	1	2,7,8
Groundwater	6	n.s.	3.7	2.1	0.97	57	2
Limnocorrals	35	0.64	64.3	26.1	19.55	41	11

suggests that it may not be significant.

Although no experimental verification was done, the variation in predicting BAP from SRP in this data set seems to originate from the different methods used by different authors as well as from different natural water types. SRP analysis does not result in pronounced overestimate of BAP, especially at concentrations less than 30 ug/L SRP in lakes, streams, precipitation, soil amd sediment extractions. The study suggests that most available phosphorus analyzes as SRP during the period of the BAP assay. Therefore SRP analysis can be used to estimate bioavailable phosphorus over a range of three orders of magnitude in phosphorus concentration for oxic and anoxic freshwater of all types and presents a faster tool than bioassays. However, short-term BAP is substantially overestimated by SRP analysis in the presence of freshly formed iron hydroxides. In these cases the short-term bioassay described here can be applied.

Chapter 5:

Availability of Phosphorus Upwelling from Iron-rich Anoxic Hypolimnia

Abstract

It is hypothesized that the biological availability of phosphorus from anoxic, iron-rich hypolimnia after mixing with aerated surface water is high. Substantial accumulations of phosphorus are found in anoxic hypolimnetic water. This could affect the trophy of the lake surface water, if the phosphorus is biologically available after entrainment. Laboratory experiments revealed that the degree of availability depends upon hypolimnetic iron concentrations, dilution of the hypolimnetic water with surface water and the vigor of mixing. These results appear relevant to the internal phosphorus load of Lake Magog, Quebec. During stratification in that lake, slow thermocline erosion begins to fertilize the trophogenic zone with the upwelling phosphorus, as suggested by a decreased N:P ratio, decreased rates of phosphate uptake, increased soluble reactive (SRP) and total phosphorus concentrations. At fall turnover, rapid thermocline erosion results in significant increases in SRP, particulate reactive phosphorus, biological particulate phosphorus and total phosphorus. The fall mass balance of Lake Magog indicates, that, despite high iron concentrations in the hypolimnion, at most 30% of hypolimnetic phosphorus precipitated as an iron-phosphorus complex, while 30% was incorporated into plankton and 30% stayed as SRP. Bioassays showed that 55-85% of the surface SRP is bioavailable. Laboratory studies suggest that, in lakes without hypolimnetic iron and in iron-rich lakes where the hypolimnetic water is greatly diluted, at least 90% of hypolimnetic SRP is available to the plankton.

Introduction

High hypolimnetic phosphorus concentrations are common in lakes with anoxic bottom waters (Fig.1-1). In many cases, it has been demonstrated that phosphorus is released by the surficial sediment under reduced conditions (e.g. Mortimer 1971 and Chapter 6). This internal load contributes significantly to the phosphorus budget in lakes with anoxic hypolimnia. Phosphorus derived from the sediment stays in the tropholytic zone during most of the growing season, but can be gradually mixed into the epilimnion during thermocline erosion in late summer and at turnover. The effect of this hypolimnetic phosphorus on the epilimnetic phytoplankton is not clear: some argue that it is incorporated into plankton in the phosphorus-poor surface water (Stauffer and Lee 1974; Kortmann et al. 1982), while others suggest that it combines with iron and precipitates (Einsele 1936; Hutchinson 1957). This is an important distinction: If hypolimnetically derived phosphorus is available to the plankton it may indicate that anoxic bottom waters can significantly contribute to increasing lake trophy. Such lakes may prove resistant to lake restoration. On the other hand, if hypolimnetic phosphorus is not available to the plankton, such lakes should respond to standard pollution abatement.

The purpose of this chapter is to determine the variables which control the bioavailability of phosphorus originating in the anoxic hypolimnion when it is mixed into the aerated surface water. While phosphorus adsorption onto iron

hydroxides has been intensively studied by soil- and geochemists (reviewed by Förstner and Wittmann 1981), little work has been done with iron-rich water from natural hypolimnia. Einsele (1936) discovered that 80-90% of the phosphorus precipitated from solution when iron-rich water from the anoxic hypolimnion of Schleinsee was exposed to air for several weeks. Einsele (1938) and Tessenow (1974) found that dilution of precipitated iron phosphate compounds redissolves some of this phosphorus. Therefore, it appears possible that the availability of upwelling phosphorus depends on the degree of dilution of the anoxic water as well as on the concentration of iron and oxygen.

This study uses several approaches to address the effect of upwelling hypolimnetic phosphorus on the trophogenic zone. First, laboratory "beaker experiments" were used to quantify the potential effect of aeration, dilution and iron concentration on phosphorus availability in small scale experiments. The implications of these results for lakes were compared with observed changes in the mass of phosphorus in the hypolimnion and epilimnion during thermocline erosion and fall turnover in Lake Magog, Quebec. Finally, I examined the availability of soluble reactive phosphorus (SRP) and iron bound particulate phosphorus (PRP) to determine the potential effect of hypolimnetic phosphorus intrusions on the trophic status of the surface waters.

Materials and Methods

Lakes and sampling: Both laboratory and field experiments concentrate on Lake Magog, Quebec (Table 1). Some experiments were also made with water from the iron-rich hypolimnion of Fitch Bay, Lake Memphremagog, Quebec and with water from core tubes containing anoxic sediment and water from Fitch Bay.

The deepest station (#6 in Fig. 2-1) on Lake Magog was sampled weekly in the summer of 1981 and monthly in 1979 and 1980. Temperature and oxygen concentrations were measured at 1 m intervals. Water samples for chemical analysis were taken at several depths: 0-3, 0-5 or 0-8 m with a tube sampler for the epilimnion and every 2 m of the hypolimnion (usually 10, 12, 14, 16 m) with a 2 liter Van Dorn sampler. In order to characterize the lake's phosphorus budget during fall turnover in 1981, subsurface samples were collected at three shallower stations (#1 to 3 (Fig. 2-1) and integrated epilimnetic and discrete hypolimnetic samples were taken at stations #4 to 8. All samples from anoxic hypolimnia were collected and handled so as to avoid any contamination with oxygen. All the chemical data for each depth were obtained from the same Van Dorn sample.

For the mass balance of the different phosphorus fractions in fall 1981, phosphorus concentrations from stations 5, 6 and 7, bathymetric information (Lardner-Cornett 1981), and corrections for dilution and flushing (Quebec Ministere d'Environnement) were used to calculate the masses of phosphorus in the anoxic and oxic water layers for eleven

Table 5-1. Some characteristics of Lake Magog.

Surface area	(A)	: 10.8 km^2
Maximum depth	(z_{max})	: 19.1 m
Mean depth	(z)	: 9.8 m
Flushing rate	(ρ)	: 16.7 yr^{-1}
Water load	(q_s)	: 164 m yr^{-1}
Ext. TP load		: 5.0-6.0 g m^{-2} yr^{-1}
Spring TP (1980)		: 43 mg m^{-3}

from Janus and Vollenweider (1981)

Ext.: external; TP: total phosphorus

dates during fall turnover. From this information, potential increases of concentrations in the oxic layer were calculated and compared to observed changes. The 1 m transition zone from oxygenated to anoxic hypolimnetic water had the highest phosphorus gradient and was not included in the calculation since inexact sampling depths could introduce large errors.

Chemical analysis: Total phosphorus (TP) and total soluble phosphorus (TSP, <0.45 µm) were digested with potassium persulfate (Menzel and Corwin 1965) and colorimetrically analysed for orthophosphate with molybdenum blue and ascorbic acid (Murphy and Riley 1962). When the sample came from the anoxic hypolimnion, soluble reactive phosphorus (SRP) and total (i.e. unfiltered) reactive phosphorus (TRP, corrected for turbidity and color) were analysed under anoxic conditions, to prevent precipitation of phosphorus by iron (Chapter 3). The difference between SRP and TRP represents PRP (particulate reactive phosphorus, detection limit: 1.0 µg l^{-1}). Four sets of observations suggest that this fraction comprises mainly phosphorus bound to recently oxidized iron (iron hydroxides):

1) In iron-poor lakes (less than 0.2 mg l^{-1}, Chapter 3), aeration did not affect concentrations of soluble phosphorus (TSP or SRP) and the concentration of PRP stayed low. However PRP could be induced by adding ferrous iron in acidic solution and oxidizing it by simultaneous neutralization (Table 2). This treatment removed both phosphorus and the added (soluble) iron from solution.

Table 5-2. Induction of PRP (particulate reactive phoshorus) in naturally iron-free, anoxic, hypolimnetic water after aeration and after addition of 3.3 mg/l soluble iron. TFe: total iron, SFe: soluble iron, iron fractions in mg/l, phosphorus fractions in µg/l. Data from Table 3-2.

Lake	Aeration			Iron Addition		
	TFe	SRP	PRP	SFe	SRP	PRP
St. George	<0.1	37	5	-	3	39
Glen	<0.1	31	3	0.07	1	30
Glen	<0.1	32	2	0.07	1	35
Jack	0.4	22	10	-	2	30

2) In iron-rich water from the hypolimnion of Lake Magog and Fitch Bay, aeration increased PRP and decreased SRP by similar amounts (Table 3). Subsequent reduction by ascorbic acid solubilized phosphorus again (experiment of Sept. 3, Table 3).

Since both hypolimnetic iron and phosphorus increased during anoxic stratification, the following observations also indicate that PRP consists of ferric iron-phosphorus particles.

3) The concentration of PRP peaked at the anoxic/ oxic interface in iron-rich Lake Magog and increased during the anoxic period (Fig. 1).

4) The PRP concentration increased during fall turnover in the surface water of Lake Magog.

Biological particulate phosphorus (BPP) is computed as the difference between total particulate phosphorus (TPP=TP-TSP) and PRP (i.e. BPP=TPP-PRP). This seems to be appropriate, since Lake Magog water is very low in silt and phosphorus paraticles other than iron or organisms.

The analysis for total and soluble iron was done with an atomic absorption spectrophotometer.

Bioassays: A short-term bioassay (1/2 h) was used to determine the fraction of SRP which is directly bioavailable and represents orthophosphate. This bioassay is based on the slowing of ^{32}P uptake kinetics by the addition of phosphate and is described in detail in Chapter 4.

A different bioassay was used to determine the fraction of SRP and PRP which becomes available after 50 - 100 h. In

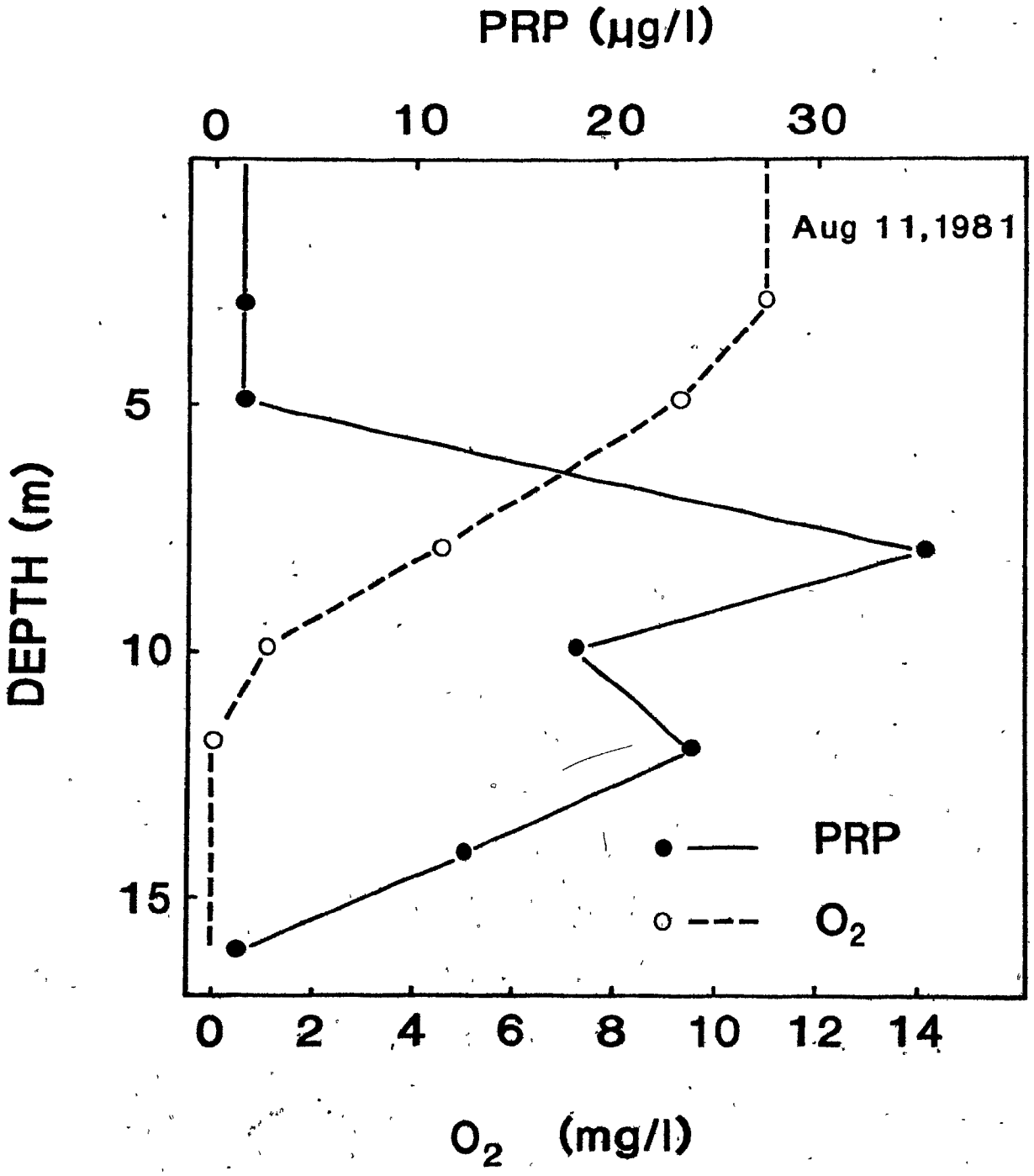
Table 5-3. PRP formation in naturally iron-rich, anoxic waters upon aeration. The soluble iron fraction in Lake Magog decreased to 0.7 mg/liter. Symbols and units as in Table 2.

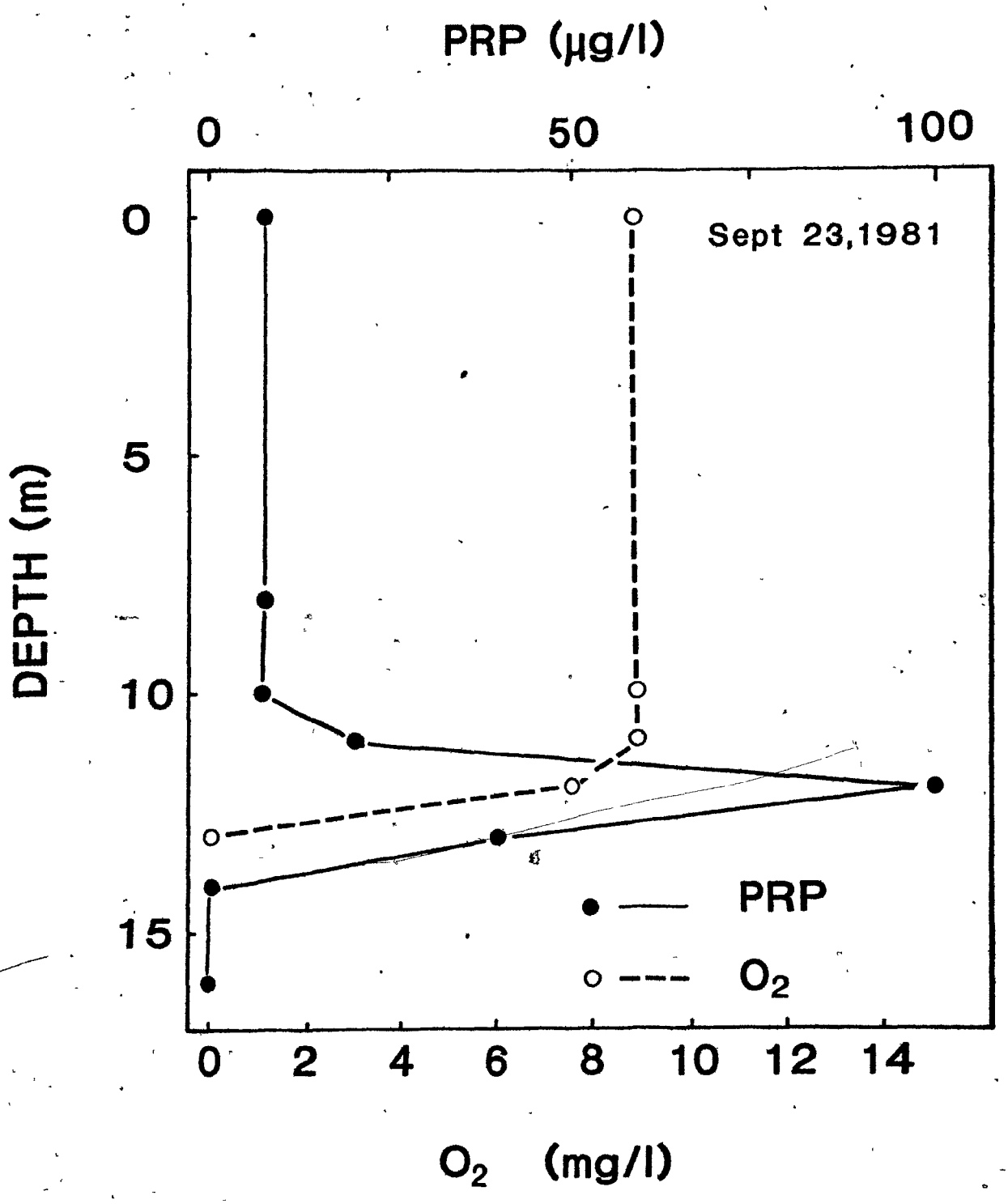
Water source	Control			Aeration		
	TFe	SRP	PRP	h	SRP	PRP
Magog, Aug.11	3.3	557	-19	2	313	225
Magog, Aug.25	4.0	646	41	5	193	468
Magog, Sept.3	4.0	696	36	5	192	540
Magog, Sept.3*					747	-14
Core tube, Aug.10	3.5	340	116	1.5	62	392
Core tube, Sept.1#	3.3	439	15	24	227	231
Core tube, Sept.1#	3.3	439	15	40	60	397

*after reduction by ascorbic acid

#aeration by diffusion only

Fig. 5-1. Two depth profiles showing the PRP (particulate reactive phosphorus) and oxygen concentration in Lake Magog 1981.


PRP (µg/l)
0
10
20
30
Aug 11,1981
5
10
15
DEPTH (m)
PRP
O2
0
2
4
6
8
10
12
14
O2 (mg/l)


PRP (µg/l)
0
50
100
Sept 23,1981
DEPTH (m)
0
5
10
15
PRP
O_2
0
2
4
6
8
10
12
14
O_2 (mg/l)

principle, this method is similar to the tracer uptake assay, for it involves monitoring the response of phosphorus limited "assay-water" to the additions of phosphorus in a standard or in an unknown sample of test water. But here the disappearance of SRP and PRP with time is recorded instead uptake of ^{32}P and compared to the disappearance of orthophosphate from a standard of similar concentration. The water to be tested was diluted four times with "assay-water" to approximate the dilution of hypolimnetic water at fall turnover (eight times in Lake Magog) more closely than did the tracer uptake experiments which involved a 100 fold dilution. For both assays, phosphorus-limited lake water from Lake La Truite, Quebec, served as assay water.

Dilution and aeration experiments: Hypolimnetic water from Lake Magog was aerated and diluted in order to simulate fall turnover. The rate of phosphorus precipitation was determined as the average rate of formation of particulate phosphorus during the first 5 h of an experiment. At zero time, 0.1 ml tracer (^{32}P) was added to 100 ml of anoxic hypolimnetic water or to a dilution of this water with aerated water. Vigorous aeration was applied immediately after tracer addition. The formation of iron-phosphorus particles greater than 0.45 µm was followed by sequential filtration of 6 ml subsamples through 25 mm "Millipore" cellulose filters. Six to ten such filtrations were performed at increasing intervals up to 8 h after tracer addition. The decrease of soluble ^{32}P was

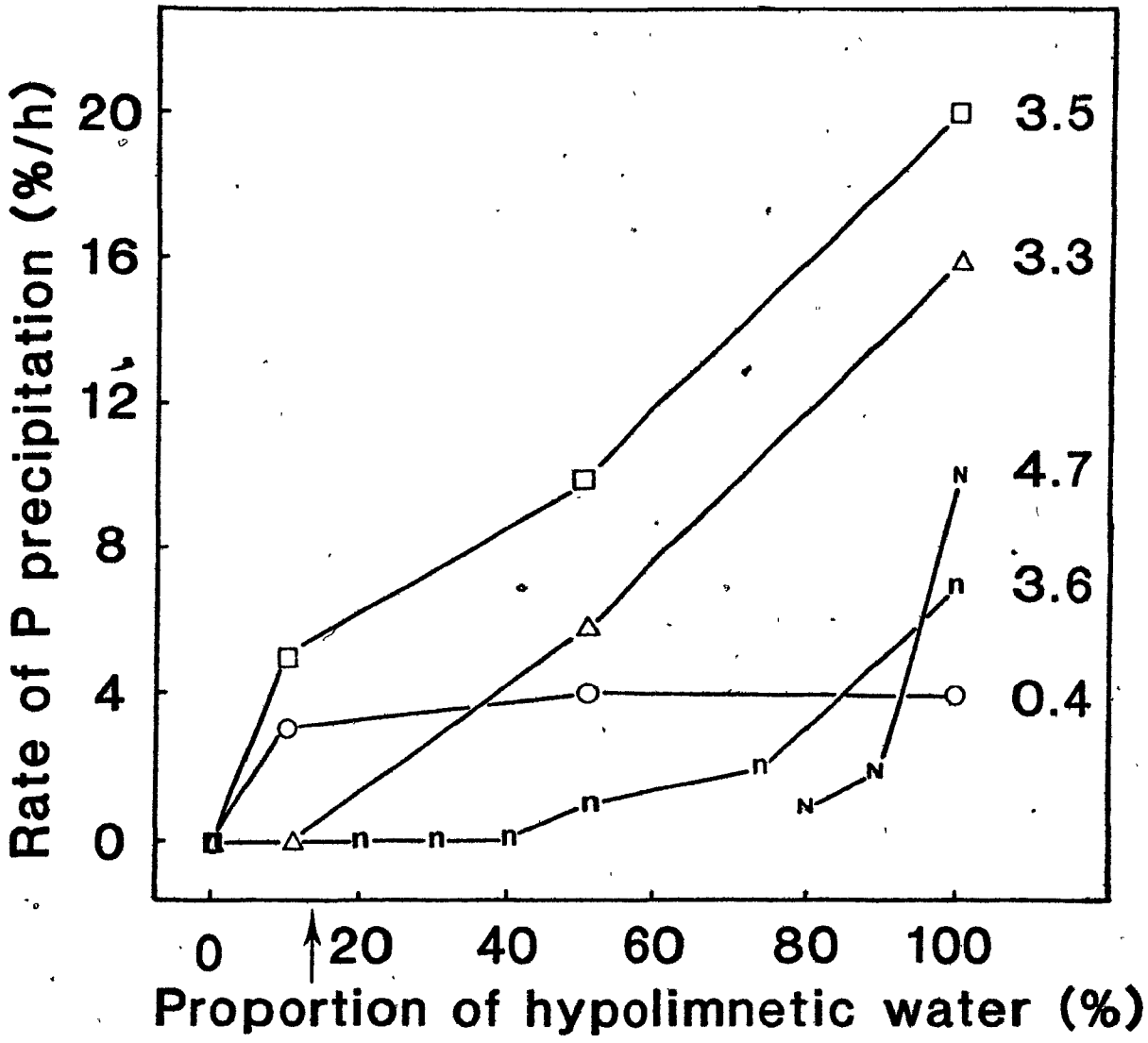
monitored by counting Cerenkov radiation in the filtrate. The counts were corrected for filter adsorption and expressed as a percentage of unfiltered (i.e. total) ^{32}P counts, measured in duplicate. Most of the dilutions used distilled, deionized water; the precipitation rates were comparable when filtered epilimnetic lake water was used instead.

Increasing dilution inhibited tracer precipitation. To determine if the precipitation could be reversed by subsequent dilution, concentrated and 50% diluted hypolimnetic water containing tracer was aerated as discribed above. After 5 h this water was diluted with different amounts of distilled water and the ^{32}P left in solution recorded eight times during a period of 27 h.

Results and Discussion

Simulation of fall turnover in beakers: Initial rates of phosphorus precipitation measured in these experiments decrease with dilution but are higher when vigorous aeration is applied (Fig. 2). In late summer the hypolimnion of Lake Magog comprises 17% of the lake's total volume. If turnover is instantaneous and complete an initial precipitation rate between 0 and 5% h^{-1} (depending upon the effectiveness of natural aeration) would be predicted from these simulation experiments. As mentioned in Methods, precipitation of phosphorus did not occur in hypolimnetic lake water where the final iron concentrations was less than 0.2 mg l^{-1}, but could be induced by addition of ferrous iron (Tab. 2). The maximum surface concentration of total iron observed in Lake Magog

Fig. 5-2. The effect of dilution with distilled water on the initial rate (5h) of phosphorus precipitation in water from Fitch Bay (open circles) and Lake Magog (all other symbols) under vigorous aeration (open symbols) and only aeration by diffusion (N,n symbols). Numbers represent iron concentrations (mg l^{-1}) of the undiluted sample. The arrow indicates the hypolimnetic dilution expected if turnover in Lake Magog is instantaneous and complete.


Rate of P precipitation (%/h)
20
16
12
8
4
0
3.5
3.3
4.7
3.6
0.4
N
n
0
20
40
60
80
100
Proportion of hypolimnetic water (%)

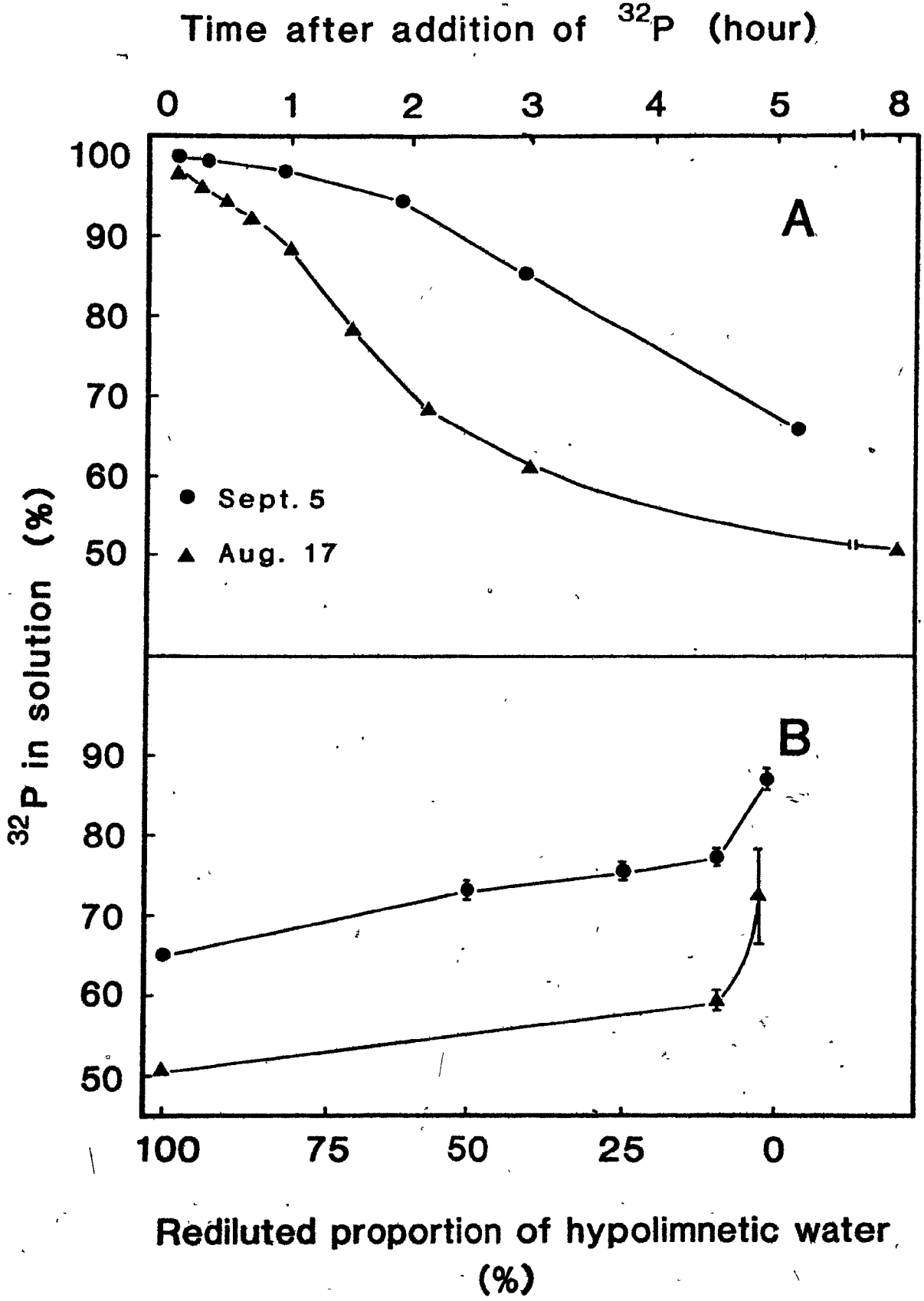
during fall turnover was 0.26 mg l^{-1} (Sept. 25. 1981). On the basis of the linear relation between precipitation rate and iron concentration (Chapter 3), this corresponds to a maximum initial precipitation rate of 1.8% of total phosphorus h^{-1}. One would therefore expect increased PRP concentration in the surface water of the lake during turnover.

Previously aerated and precipitated phosphorus was diluted with aerated water to determine if PRP dissolves upon dilution or if it is completely unavailable, once adsorbed to iron. Fig. 3 shows that recently precipitated phosphorus redissolves when diluted. The degree of resolubilization depends on the extent of dilution (Fig. 3 b). It is apparently instantaneous, for no increase in dissolved tracer was observed between 2 min and 27 h. These experiments predict that at least recently formed PRP, which had accumulated at the anoxic/ oxic boundary layer in Lake Magog (Fig. 1), partially redissolves when it is distributed into surface water upon thermocline erosion. As only PRP concentration from the anoxic/ oxic interface are high enough to be involved in Lake Magog (Fig. 1) this mechanism is here not very important.

My chemical experiments are comparable to Tessenow's (1974) studies on anoxic water from meromictic Ursee. In that case, aeration precipitated 86% of the soluble phosphorus within 3 h or 29%/h. After 20 h, only 1% of the initial SRP (3500 $\mu g, l^{-1}$) and only 0.5% of the initial dissolved iron (21.3 mg l^{-1}) remained. Though the initial concentrations of soluble phosphorus and iron were ten times those found in Lake

Fig. 5-3. A) Precipitation of radioactive orthophosphate added to anoxic hypolimnetic water from Lake Magog on aeration by either diffusion (Sept. 5) or vigorous aeration (Aug. 17). The lake water of Aug. 17 had been diluted with an equal volume of distilled water prior to the experiment.

B) Redissolution of these precipitates on dilution of these waters after 5 and 8 h aeration with distilled water.


Time after addition of ^{32}P (hour)
0
1
2
3
4
5
8
100
90
80
70
60
50
A
Sept. 5
Aug. 17
^{32}P in solution (%)
B
90
80
70
60
50
100
75
50
25
0
Rediluted proportion of hypolimnetic water (%)

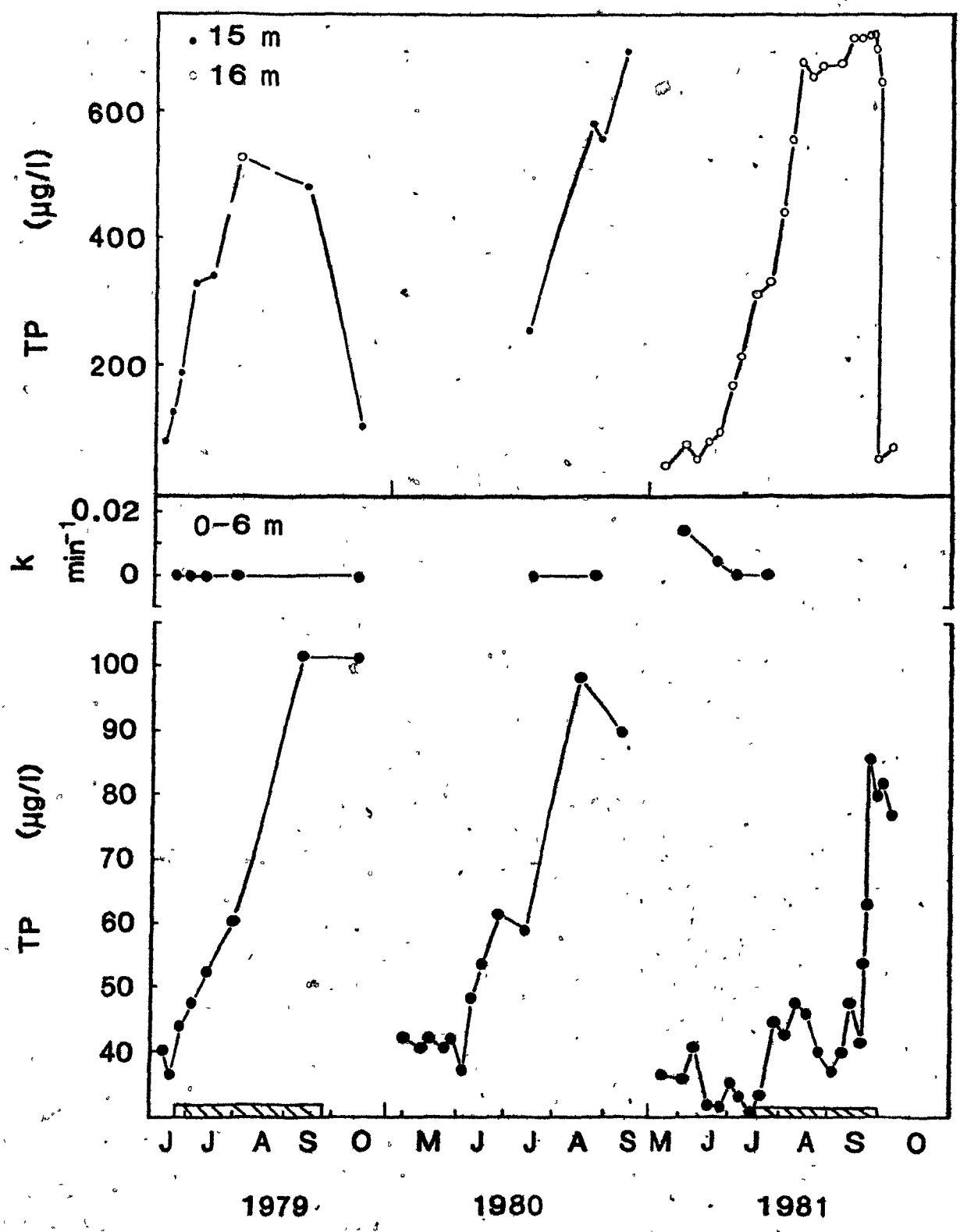
Magog, the precipitation rates are comparable (Fig. 2). Tessenow (1974) also found that the solubility of phosphorus increases with dilution. This trend is comparable to Einsele's (1938) and my results (Fig. 3 b).

These experiments yield a maximum estimate of precipitation rates since they are based on artificial aeration and since plankton had no opportunity to compete with the precipitation reaction for available phosphorus. Nürnberg and Peters (1984a: Chapter 7) found that at total phosphorus concentrations above 100 $\mu g\ l^{-1}$, SRP is at least 80% of hypolimnetic total phosphorus and that at dilutions of ten times or more 90% of SRP is biologically available (Chapter 4). From these results, I predict that at least 72% (0.9 * 80%) of hypolimnetic TP can be taken up by phosphorus deficient phytoplankton, when relatively small amounts of hypolimnetic water intrude into the epilimnion. If these intrusions happen frequently during stratification, phosphorus limitation ought to decline and the lake might become nitrogen limited.

Hypolimnetic phosphorus intrusion during summer stratification: Several observations suggest that the surface water in Lake Magog is fertilized by hypolimnetic phosphorus during summer stratification.

1) In three successive summers, both the surface and hypolimnetic concentrations of total phosphorus increased over the summer, long before complete turnover in the fall (Fig. 4). This provides only circumstantial evidence for internal phosphorus load to the surface water because one must assume

Fig. 5-4. Changes in total phosphorus (TP) concentration in the surface and hypolimnion and in ^{32}P uptake rate (rate constant k) of Lake Magog surface water. When k approaches zero, it is unlikely that the plankton are phosphorus limited. The period of hypolimnetic anoxia is indicated for the years 1979 and 1981.


• 15 m
○ 16 m
TP (µg/l)
600
400
200
k min⁻¹
0.02
0
0-6 m
TP (µg/l)
100
90
80
70
60
50
40
J J A S O M J J A S M J J A S O
1979
1980
1981

that the increase does not reflect an increasing external load over the summer.

2) Slow uptake of $^{32}P\text{-}PO_4$ (Fig. 4), increasing SRP concentration (from less than 1 in May 1981 to 2-6 $\mu g\ l^{-1}$ in midsummer), and decreasing N:P ratios (from 16 in July 1982 to 7-8 in September; J. Kalff personal communication) all indicate a reduction in the phosphorus deficiency of the surface water in late summer. Since the thermocline is eroding at this time, it can be hypothesized that this reduction reflects the intrusion of phosphorus rich hypolimnetic water.

3) The rate of phosphorus loading from the hypolimnion was calculated from the mean eddy diffusion coefficient for summer 1979 and 1980 (0.0965 $m^2\ d^{-1}$, Lardner-Cornett 1981) and the total phosphorus concentrations measured (1981) at the thermocline. As estimated from nine phosphorus and temperature profiles, the average vertical transport to the trophogenic zone is 4.1 mg $m^{-2}\ d^{-1}$ (SE: ± 0.63) and represents 32 % of the gross internal load estimated from phosphorus accumulated in the hypolimnion during the anoxic period (13.5 mg $m^{-2}\ d^{-1}$, Chapter 6). Because this vertical transport was calculated from eddy diffusion coefficients for different years and is very sensitive to the exact depth interval used, the value should be taken as an order of magnitude estimate. Since this hypolimnetic intrusion is diluted more than ten times, probably most is available and is either incorporated by plankton or accumulates as epilimnetic SRP.

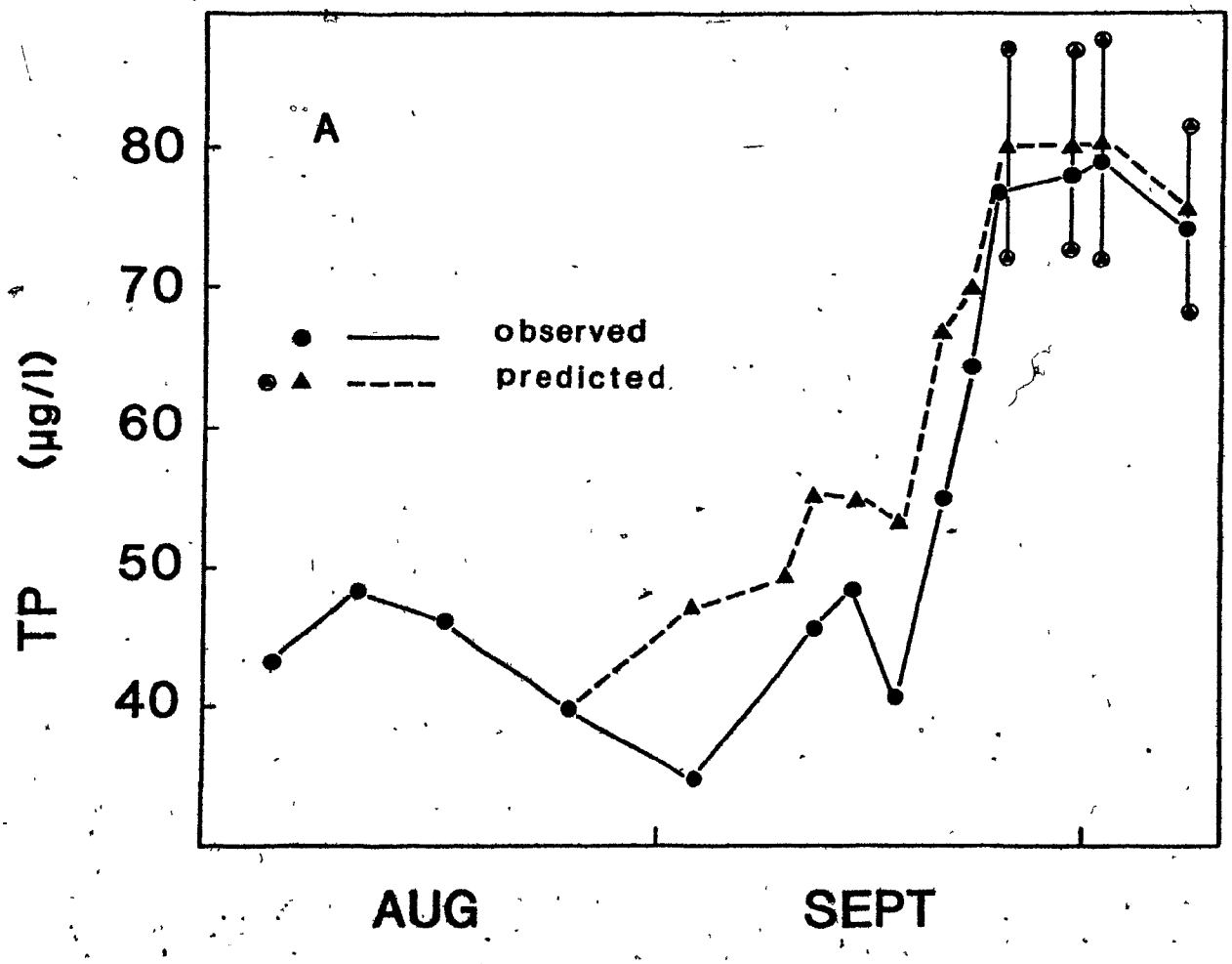
Some recent studies determined the eddy diffusivity of

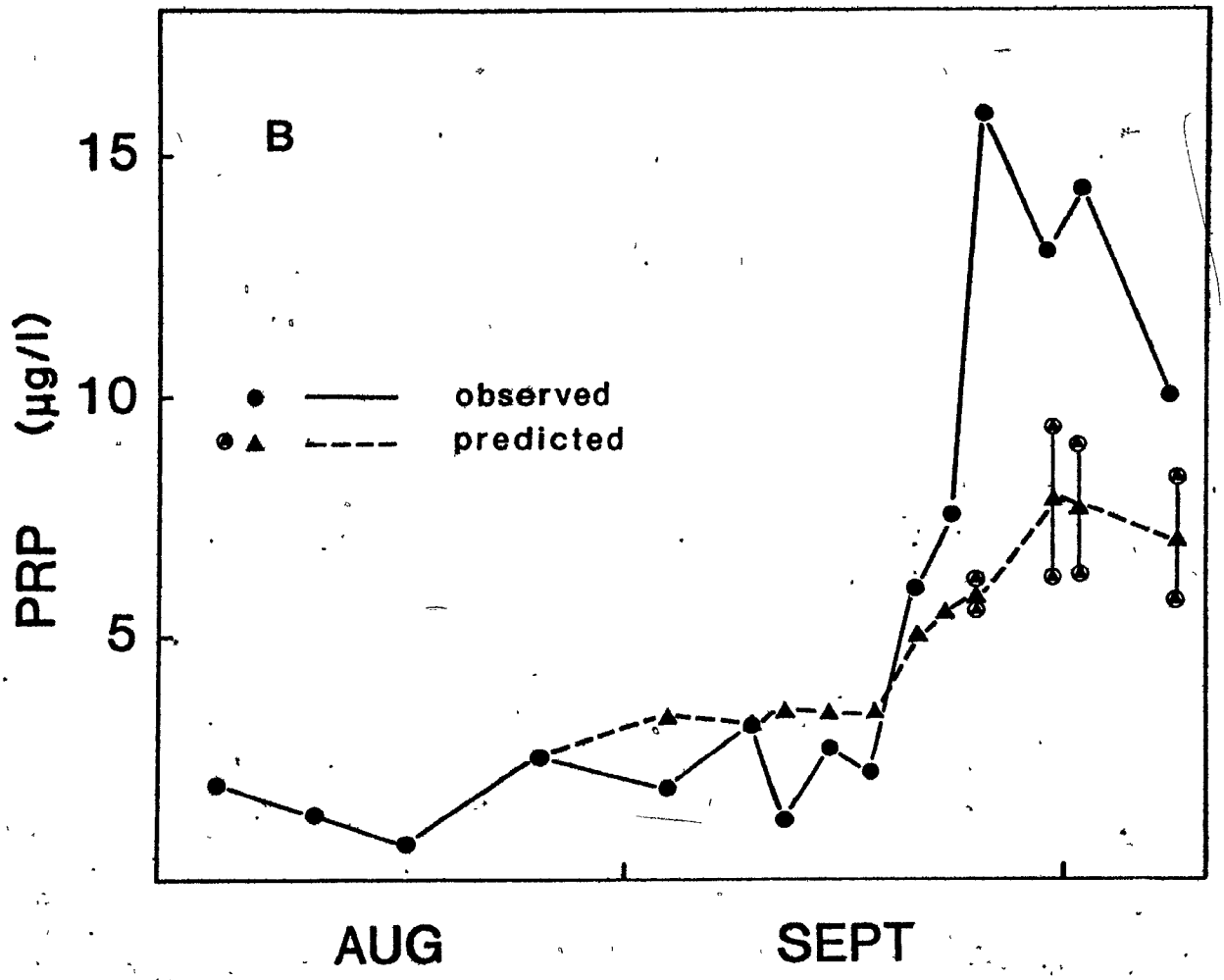
hypolimnetic water during summer stratification in different lakes. In Rotsee (Bloesch et al. 1977) and Greifensee (Imboden and Emerson 1978), eddy diffusivities of 33 and ca. 20 mg m^{-2} d^{-1} phosphorus respectively have been determined. The latter represents 50-100 % of the annual gross internal load (Imboden and Emerson 1978). This is more than in Lake Magog (ca. 4 mg m^{-2} d^{-1} and 30% of gross internal load) and suggests a less rigid stratification or higher phosphorus gradients in these lakes. In Dagowsee (Mothes 1980) and in shallow Alderfen Broad (Osborne and Phillips 1978), eddy diffusion provided 50% and 37% respectively of gross internal load to the surface waters.

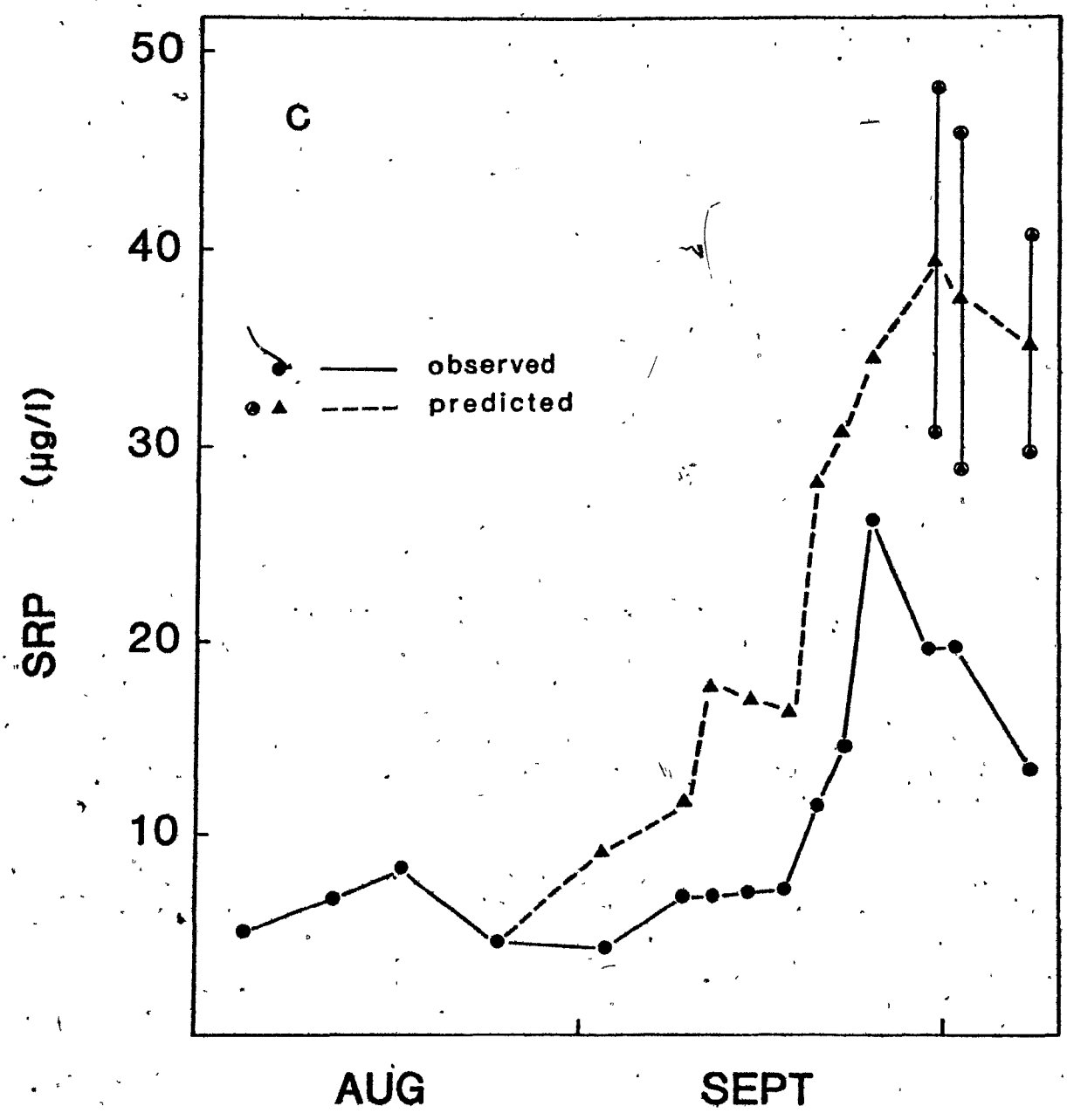
Upwelling phosphorus at fall turnover: A detailed budget of different phosphorus fractions was made in order to follow the fate of hypolimnetic phosphorus mixed into the surface water. The elongated shape of the lake permits comparison of numerous sample sites upstream and downstream of the deep hypolimnion and differences in the spatial concentration gradients present circumstantial evidence for hypolimnetic phosphorus loading as well.

At fall turnover, TP, SRP, and iron-bound particulate reactive phosphorus (PRP) increased significantly in the surface water (Fig. 5). Biologically bound particulate phosphorus also increased significantly. The phosphorus mass of each fraction lost from the hypolimnion during thermocline erosion was compared to this observed increase in the enlarged epilimnion for 11 overlapping intervals, each starting on Aug. 25. The values were corrected for flushing since the lake's flushing rate is high (16.7 yr^{-1}). If a large amount of

Fig. 5-5. Surface concentrations at fall turnover 1981. A: TP, B: PRP, C: SRP. Predicted values, calculated by assuming that all phosphorus in the eroded hypolimnion is conserved in the expanded epilimnion, are based on the mean (triangle) of profiles of station 5, 6 and 7. When these profiles differ significantly (circled triangle) the range for concentrations at the different stations is indicated by bars. Difference between observed and calculated values may indicate precipitaion or transformation of certain fractions.


A
80
70
60
50
40
TP (µg/l)
observed
predicted
AUG
SEPT


B
15
10
5
PRP (µg/l)
observed
predicted
AUG
SEPT


50
40
30
20
10
SRP (µg/l)
C
observed
predicted
AUG
SEPT

phosphorus precipitated to the sediment, the observed total phosphorus concentration in the epilimnion would be significantly lower than that calculated. Fig. 5a shows that, at the beginning of the 1981 fall turnover, the observed TP concentration tended to be lower than calculated suggesting phosphorus precipitation; at the end, however, there was no significant difference. The observed PRP concentration (15 $\mu g\ l^{-1}$, Fig. 5b) significantly exceeded that predicted by hypolimnetic erosion (ca. 8 $\mu g\ l^{-1}$) in the second half of fall turnover. The observed SRP concentration is lower than expected from a simple mass balance (Fig. 5c). These results suggest that some SRP was converted to PRP by adsorption onto or coprecipitation with iron. Some of this PRP could then have settled out from the surface water.

I calculated budgets for the whole turnover and the first half separately (Table 4) since calculated and observed concentrations seem to differ in these periods. It appears that 33-38% of the upwelling phosphorus remains as SRP, and 30-37% becomes incorporated into biomass (BPP). The remaining phosphorus (25-37%) combines with iron to form the PRP fraction if the whole period is considered (30%). Half the PRP formed in the first half of the period is lost from the open water, but this amount is insignificant over the whole turnover period. Only one third of the hypolimnetic total phosphorus combines with iron in Lake Magog; this implies that two thirds should be available. My beaker experiments showed that 72% of hypolimnetic total phosphorus could be

Table 5-4. The contribution of upwelling hypolimnetic phosphorus to the SRP pool, iron phosphorus particles (PRP) and planktonic phosphorus (BPP) during fall turnover. Predicted (pred) and observed (obs) increases in concentrations ($\mu g\ l^{-1}$) and proportions of expected increase in surface TP, if all hypolimnetic TP would have intruded into the surface water (%, in parantheses) are shown.

Period		TP		SRP		PRP		BPP	
Aug.25-	pred	30	(100)	26	(87)	3	(10)	1	(3)
Sept.23	obs	25	(83)	10	(33)	5	(17)	11	(37)
Aug.25-	pred	40	(100)	35	(88)	5	(12)	0	(0)
Oct.2	obs	39	(98)	15	(38)	12	(30)	12*	(30)

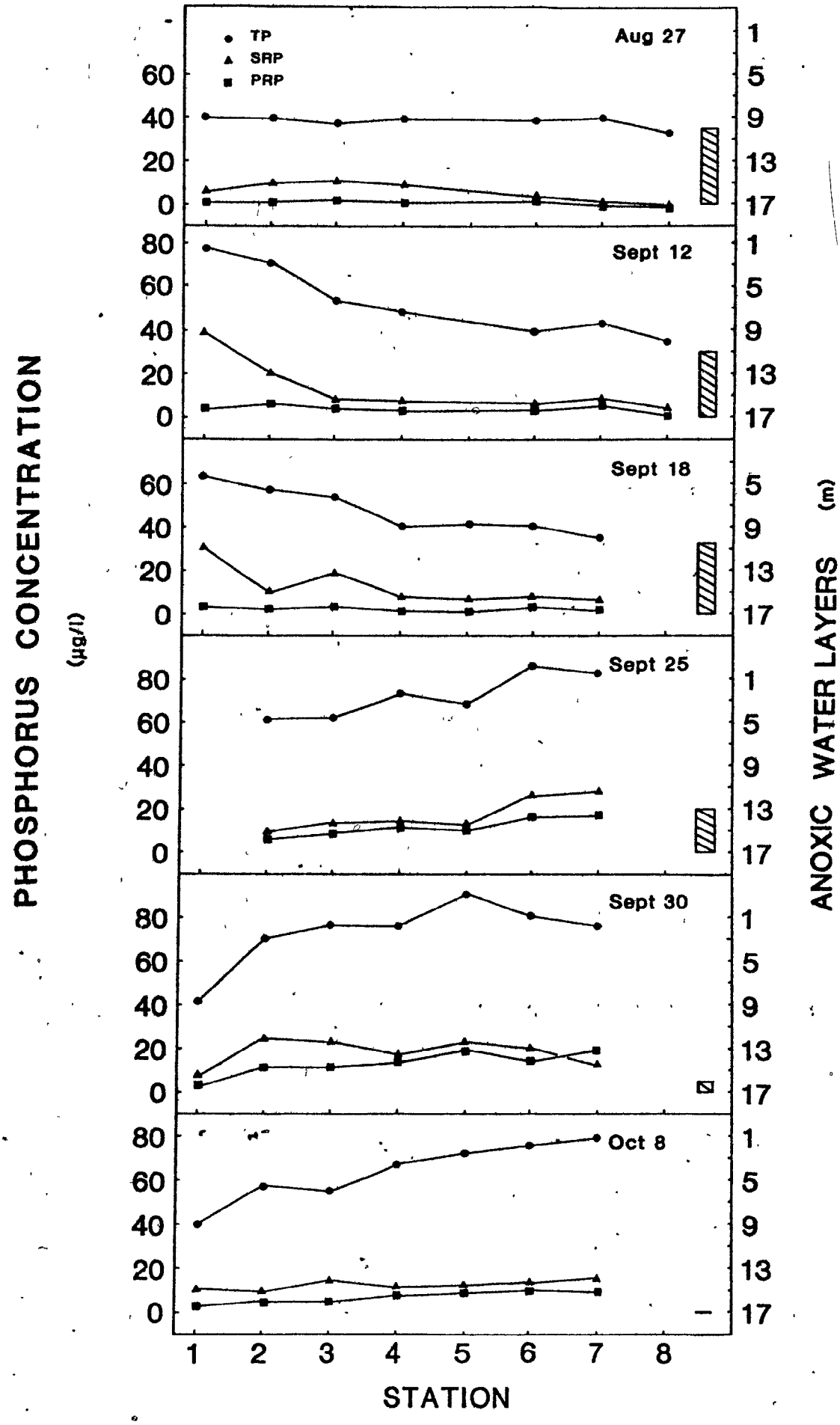
* determined by difference: BPP=TP-SRP-PRP

biologically available at large dilutions. This agreement suggests that in situ dilution is sufficient and iron concentration is low enough to prevent major precipitation.

The major external phosphorus input to Lake Magog is the Magog River at the south west corner of the lake. Before and at the start of fall turnover, the concentration of TP and SRP in the river were frequently higher than in the lake, though the PRP fraction was always similar or lower when measured (Fig. 6, Stn. 1, Aug.27, Sept. 12, Sept. 18). In the same period the TP and SRP concentrations decreased with distance from the inflow along the length axis of Lake Magog. Once rapid thermocline erosion had commenced (on Sept. 25), this concentration gradient reversed and the higher TP, SRP and also PRP concentrations appeared at the downstream stations (Fig. 6, Sept.25, Sept. 30, Oct. 8). SRP and PRP increased relative to TP at fall turnover. The proportion of SRP increased from 0.12 to 0.25 of TP and the PRP proportion increased from 0.10 to 0.17. The observed increase in PRP and SRP concentrations and the mass balance imply that the increase in surface phosphorus originated from upwelling hypolimnetic water.

Several in situ studies can be compared to these investigations: In Schleinsee, Einsele (1936, 1938) found that 25% of the SRP in the hypolimnion before turnover reached the surface water and remained there for one week. This lake had phosphorus and iron concentrations similar to those in the anoxic hypolimnion as Lake Magog. I found that, during fall

Fig. 5-6. Spatial distribution of surface TP, SRP and PRP concentrations (curves) and the depth of the anoxic hypolimnion (bar) during fall turnover 1981. Stations same as in map of Fig. 2-1.


PHOSPHORUS CONCENTRATION
(µg/l)
TP
SRP
PRP
Aug 27
Sept 12
Sept 18
Sept 25
Sept 30
Oct 8
ANOXIC WATER LAYERS (m)
STATION

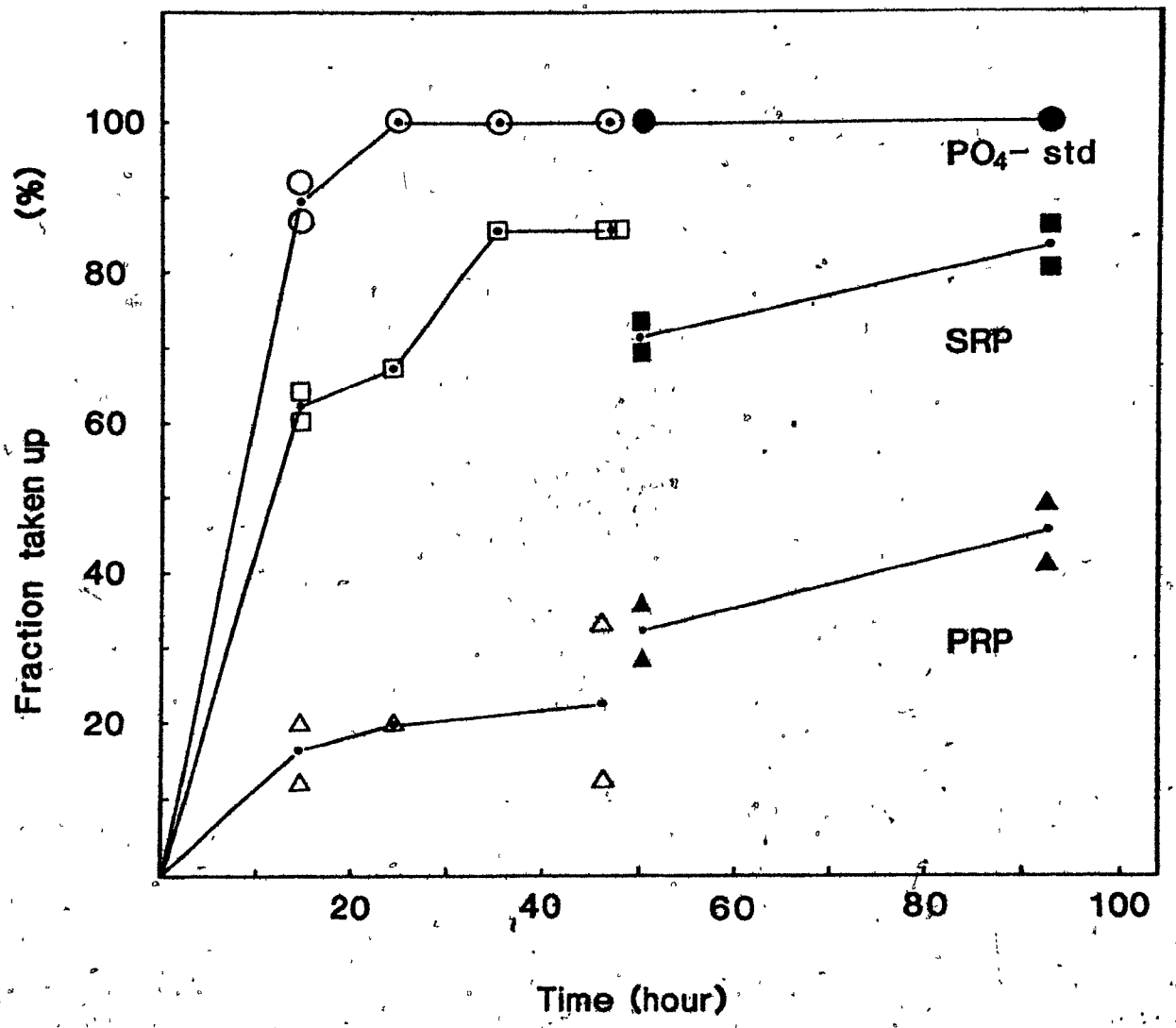
turnover 1981, an average of 40% of hypolimnetic SRP reached the surface water of Lake Magog and did not precipitate for at least the one week studied. The observed decrease of all the phosphorus fractions immediately after turnover (last date on Fig. 5), was caused by high flushing.

In Linsely Pond, Hutchinson (1941) detected high levels of "acid soluble seston phosphate" after the iron rich, anoxic hypolimnion mixed with the surface water. This fraction represents the difference between SRP and "unfiltered soluble phosphate" (i.e. TRP) and is similar to the PRP fraction represented here. Hutchinson suggested it was ferric phosphate which may eventually be used by phytoplankton.

Bioavailability of Lake Magog phosphorus during fall turnover: The concentration of biologically available phosphorus in the fall (10-11 $\mu g\ l^{-1}$) was significantly higher than the average concentration of SRP during the midsummer stratified period (approx. 5 $\mu g\ l^{-1}$). The short-term tracer bioassay of epilimnetic water sampled on Sept. 30 indicated that BAP (biological available phosphorus) represents 55% of SRP (18.2 $\mu g\ l^{-1}$ SRP) and 30% of TRP (35 $\mu g\ l^{-1}$ TRP) or 6% of PRP.

The longer term bioassay was carried out twice, independently (Fig. 7). Both SRP and PRP from the surface water of Lake Magog disappear less rapidly from solution than an orthophosphate standard. In the experiment of Sept. 30., net SRP and PRP uptake ceased within 50 h; by this time, SRP concentrations had declined to 15% and PRP to 80% of initial values. In the experiment of Sept. 25, a similar change in SRP

Fig. 5-7. Long-term bioassays based on uptake of SRP and PRP with surface water from Lake Magog on Sept. 30 (open symbols) and Sept. 25 (closed symbols).


100
80
60
40
20
Fraction taken up
(%)
20
40
60
80
100
Time (hour)
PO_4– std
SRP
PRP

was observed after 90 h but 10% more PRP was removed.

The long-term bioassays indicate that phosphorus limited algae take up more SRP and PRP than would be suggested by a short-term bioassay. The data are variable, but it appears that 55-85% of the SRP was available, even in the presence of recently aerated iron, while only 20-40 % of PRP was available after a longer incubation time. This also suggests that, in the aeration experiments described above, the labelled particulate fraction (precipitated phosphorus) is less and more slowly available, while the soluble fraction is largely available.

Some studies by other authors also indicate that upwelling hypolimnetic phosphorus can be available to phytoplankton. In iron-rich Lake Waramaug, Connecticut, Kortmann et al. (1982) related algal blooms to thermocline erosion: a fall bloom followed within ten days of the intrusion of enough hypolimnetic phosphorus, to provide 25% of the annual external load. In iron rich Frains Lake, Michigan, LaZerte (1980) observed a fall bloom of the diatom Asterionella formosa after the nutrient rich hypolimnion mixed with surface water. Stauffer and Lee (1974) recorded elevated chlorophyll concentrations in response to phosphorus from the iron-poor hypolimnion of Lake Madison, Wisconsin. In Lake Shagawa, continuous intrusion of phosphorus from the anoxic iron-rich hypolimnion prevented chlorophyll concentrations from declining though the external phosphorus load had been drastically reduced (Larsen et al. 1979).

Internal load and the effect on average TP concentration: Hypolimnetic phosphorus doubles the phosphorus concentration in the surface water of Lake Magog after complete destratification. But any phosphorus load to this lake, external as well as internal, will have only a modest effect on the annual average TP concentration because Lake Magog has a very high flushing rate (17 yr^{-1}) and high areal water load (152 m yr^{-1}) compared to other lakes (mean water load is less than 20 m yr^{-1}, Chapter 6). To calculate the effect of internal phosphorus load on the annual mean total phosphorus concentration of Lake Magog, internal load was assessed from the phosphorus mass in the hypolimnion just before major destratification began on Sept. 15. 1981 as 486 mg m^{-2} per summer. The effect of summer internal load (L_{int}) on the average TP concentration was calculated according to the modified Dillon and Rigler (1974) mass balance equation (Chapter 6):

$$TP = L_{ext}/q_s\ (1-R_{pred}) + L_{int}/q_s$$

where L_{ext} is external P load, in mg m^{-2} yr^{-1}; q_s is areal water load, in m yr^{-1}; R_{pred} is phosphorus retention predicted for oxic lakes (Chapter 6). The increase of TP, which was due to the internal load during summer was calculated as:

$$TP = L_{int}/\ q_s = 3.2\ ug\ l^{-1}\ summmer^{-1}$$

Lake Magog is anoxic and has high hypolimnetic phosphorus concentration in the winter period, too (Gauthier 1978). This suggests that the annual load of hypolimnetic phosphorus might be twice as large and increase mean TP concentration by 6.4 $\mu g\ l^{-1}$. Even this internal load (0.49 $g\ m^{-2} yr^{-1}$) is barely one tenth of external load (5-6 $g\ m^{-2}\ yr^{-1}$). In lakes with nutrient abatement, external load is usually less than 1 $g\ m^{-2}\ yr^{-1}$ and this internal load would then have a larger effect on the average and spring total phosphorus concentration.

Conclusion

The following results were obtained from dilution and aeration experiments: precipitation or adsorption of hypolimnetic phosphorus by oxygenated iron occurs, but is counteracted by dilution. When dilution is higher than 10 times e.g. during slow thermocline erosion in the summer, at most 4 %/h precipitates due to chemical adsorption (Fig. 2), but at least 72% of total phosphorus remains bioavailable. These experimental results are supported by the case study on Lake Magog. In Lake Magog, increasing fertilization during thermocline erosion was observed, for phosphorus uptake kinetics and N:P ratios decreased and the surface concentration of SRP increased. During the more rapid mixing at fall turnover, 68% of upwelling hypolimnetic total phosphorus was either incorporated into biomass or stayed potentially available as SRP.

Since the simulation experiments agree with the field

studies on anoxic Lake Magog, the results probably also apply to other iron-rich anoxic lakes. During thermocline erosion, the dilution of hypolimnetic into epilimnetic water can be very high in lakes. Even in rapid, complete, fall turnover, dilution must be similar to the ratio of epilimnetic to hypolimnetic volume. These ratios are often above 10:1 and so could allow fertilization of the trophogenic zone in lakes with phosphorus rich, anoxic hypolimnia, even when iron levels are high.

Chapter 6:

The Prediction of Internal Phosphorus Load in Lakes with Anoxic Hypolimnia

Abstract

Lakes with anoxic hypolimnia ("anoxic lakes") have significantly lower values for phosphorus retention than do lakes with aerobic hypolimnia ("oxic lakes"). This difference may reflect an increased internal phosphorus load from the anoxic hypolimnia.

This study develops two models to predict internal phosphorus load (L_{int}) in such lakes. The first model predicts internal load as the difference between the observed phosphorus retention in anoxic lakes and that predicted (R_{pred}) by a formula which adequately describes phosphorus retention in oxic lakes. The second model predicts internal load as the product of an average rate of phosphorus release from anoxic sediments, the surface area of the anoxic sediment and the period of anoxia. Predictions of the first model compare favourably with 17 observed values of internal load but further data are required to test the second model. These models suggest that mean total phosphorus concentration (TP) in anoxic lakes may be predicted in two ways. One can use whole lake phosphorus budget models which implicitly incorporate internal phosphorus load, because they employ a measurement of phosphorus retention. Alternatively, a term to account for the internal load can be added to current models based on external load (L_{ext}) and predicted retention (R_{pred}):

$$TP = L_{ext}/q_s \ (1-R_{pred}) + L_{int}/q_s$$

where q_s is areal water load (m yr^{-1}).

Introduction

Mass balance models have been widely used to predict the concentration of phosphorus, the major limiting nutrient, in lakes. In these models (e.g. Vollenweider 1969; Schindler and Nighswander 1970; Dillon and Rigler 1974) the mean total phosphorus concentration is calculated as the incoming phosphorus mass divided by the annual water load and diminished by a retention term which represents the proportion of incoming phosphorus apparently lost to the sediments.

Phosphorus retention can be determined from annual nutrient budgets - the mass of phosphorus entering and leaving the lake (Dillon and Rigler 1974) - or predicted from the lakes' morphometric and hydrological characteristics. These models predict that retention lies between 0.0 and 1.0 in all lakes (e.g. Dillon and Kirchner 1975; Larsen and Mercier 1976). Lakes having anoxic bottom water for a significant period show consistently low and sometimes negative retention (e.g. Bengtsson 1978; Larsen et al. 1981). Negative retention indicates phosphorus input from some source not considered in the mass balance.

Sonzogni (1974) and Sonzogni et al. (1976) used a "phosphorus residence time model" to predict phosphorus concentration after sewage diversion. Of six lakes, four showed higher phosphorus concentration than the model predicted. All the outliers had anoxic hypolimnia (Lake Mendota, Lake Sammamish, Shagawa Lake, Lake Waubesa). Subsequently Lorenzen et al. (1976) tried to predict

phosphorus concentration in anoxic Lake Sammamish by introducing an internal phosphorus loading term into this "phosphorus residence time model". This term must be estimated separately for each lake and requires elaborate measurements. For example, that model requires estimates of volume of the sediment which can release phosphorus, and the phosphorus concentration of the sediment. An equally complicated model, developed for anoxic White Lake, Michigan, involves more than seven estimated parameters (Lung et al. 1976). These models are far more complex than those used in oxic lakes and there seems to be a need for simple models of anoxic lakes.

In this chapter, I investigate the deviant behavior of phosphorus in lakes with markedly anoxic hypolimnia using published data for lakes which had or still have high external phosphorus inputs. I hypothesize that such anoxic lakes behave differently because their sediments release an internal load of phosphorus. The specific hypotheses examined here, are:

1. Models which describe phosphorus retention for oxic lakes overestimate retention in anoxic lakes.
2. The deviation of observed from predicted retention can be used to predict internal phosphorus load.
3. Phosphorus models can be built which apply to anoxic lakes. But these must either be based on measured retention or be corrected for internal load.

A method to compute internal phosphorus load from release rate estimates and known period and area of anoxia will also be presented.

The first hypothesis will be tested by comparison of

phosphorus retentions predicted by models which apply to oxic lakes with those measured in two classes of anoxic lakes: lakes believed to be in steady-state and lakes following nutrient diversion. To test the second hypothesis, internal loads are calculated from differences between the observed and predicted retentions and these estimates are compared to independent estimates of internal loads where such estimates are available. Finally, the performance of different phosphorus budget models is evaluated for anoxic lakes and a formula to predict total phosphorus in anoxic lakes is derived.

Data Base

To obtain data which ideally differ only in the variable to be investigated, the oxygen concentration of the hypolimnion, this survey was restricted to natural lakes that were definitely thermally stratified at least during summer and in which the hypolimnia could be clearly classed as oxic or anoxic. In this analysis, anoxic lakes are considered to be those that had an oxygen concentration of less than 0.5 mg l^{-1} in the hypolimnion for at least 2 weeks but for no longer than 7 months.

Approximately half of the data were compiled by Reckhow (1977); the other half was collected from the literature. Only data from North America and Europe were sufficiently complete for my purposes.

Three different data sets were established from these

data. The lakes' characteristics are listed in Tables 1 a, b, c; group averages and the geographical distribution of the lakes are given in Table 2. The first set consists of 54 different oxic lakes, the second includes 33 different anoxic lakes "in steady-state", meaning that no major disturbance of the lake's phosphorus status was reported; lakes with markedly increased rates of fertilization or which had been recently restored were not included. The third set consists of data for two to ten years from seven lakes (35 anoxic "lake-years") following sewage diversion. These lakes are not in steady-state, for both the concentration and retention of phosphorus changed rapidly. Although these lakes now have an external phosphorus load comparable to that of the oxic lakes (Table 2), they had previously been eutrophied by anthropogenic phophorus input. For 17 of these lake-years, internal load can be estimated from the measured increase in the mass of hypolimnetic phosphorus during anoxia. Because only seven lakes are considered, the 35 lake-years do not represent independent observations; this may compromise the statistical analysis because the lakes must be treated as independent to make analysis possible. The trends discussed below also appear in the mean values for the seven lakes, but statistical significance is reduced. Because the two anoxic groups differ substantially from oxic lakes in mean depth, water residence time and - for the anoxic set after nutrient diversion - water load (Table 2; see also Reckhow 1977), oxic lakes were divided into subgroups that have values more comparable to those of the anoxic sets. These standardized subsets permit comparison

Table 6-1. Lake characteristics of three lake groups as collected from literature and values of modeled internal load (L_{intN}, Eq.3, mg m^{-2} yr^{-1}). z: mean depth (m); tau: water detention time (yr^{-1}); q_s: anual water load (m yr^{-1}); R_{obs}: measured retention determined from mass balance studies (P_{in}-P_{out}) / P_{in}; R_N: predicted retention according to Eq. 2; L_{ext} and L_{int}: external and measured internal load (mg m^{-2} yr^{-1}); n.a.: data not available.

a) Oxic lakes b) Anoxic lakes c) Anoxic lake-years after sewage diversion.

z	tau	q_s	L_{ext}	R_{obs}	R_N	L_{intN}	Lake	Source
13.41	3.20	4.19	120.	0.58	0.68	12.	Long	Reckhow 1977
39.01	15.00	2.60	120.	0.60	0.73	15.	Canandaigua	"
54.50	8.60	6.34	550.	0.51	0.62	58.	Cajuga	"
22.56	7.80	2.89	100.	0.50	0.72	22.	Keuka	"
88.70	33.70	2.63	230.	0.74	0.73	-3.	Boneka	"
14.94	15.60	0.96	30.	0.67	0.79	4.	Higgins	"
49.00	8.60	5.70	160.	0.73	0.63	-16.	Aegerisee	"
14.00	2.20	6.36	300.	0.69	0.62	-22.	Turlersee	"
100.00	3.80	26.32	1110.	0.16	0.34	198.	Bodensee,-unter	"
50.00	4.90	10.20	1320.	0.75	0.53	-288.	Zuerichsee,-ober	"
46.00	17.50	2.63	770.	0.88	0.73	-118.	Sempachersee	"
89.00	7.90	11.27	680.	0.59	0.51	-53.	Ontario	"
84.00	31.00	2.71	100.	0.83	0.72	-11.	Michigan	"
59.00	48.00	1.23	70.	0.93	0.78	-11.	Huron	"
75.30	57.60	1.31	390.	0.90	0.78	-48.	Okanagan	"
26.50	1.11	23.87	2200.	0.34	0.36	40.	Skaha	"
32.90	3.30	9.97	460.	0.55	0.54	-6.	Washington	"
9.30	3.32	2.80	100.	0.84	0.72	-12.	Four Mile	"
18.00	2.99	6.02	158.	0.73	0.62	-17.	Bob	"
18.10	0.47	38.51	332.	0.37	0.27	-35.	12 Mile Boshkung	"
27.20	1.11	24.50	205.	0.53	0.35	-36.	Halls	"
9.80	0.05	196.00	1520.	0.06	0.07	15.	Beech	"
11.60	0.14	82.86	832.	0.32	0.15	-143.	Maple	"
10.40	1.20	8.67	140.	0.50	0.56	9.	Long	"
4.30	0.07	61.43	510.	0.19	0.19	-1.	Bay of Naples	"
30.80	5.40	5.70	80.	0.57	0.63	5.	Sebago	"
16.80	3.20	5.25	120.	0.63	0.65	2.	Charlevoix	"
12.80	0.52	24.62	230.	0.32	0.35	7.	Eagle N.	"

17.70	3.13	5.65	120.	0.72	0.63	-10.	Oblong	Reckhow 1977
58.00	71.30	0.81	320.	0.95	0.80	-49.	Kalamalka	"
177.00	4.00	44.25	3390.	0.64	0.24	-1353.	Lago Maggiore	OECD, Alpine 1980
12.50	7.90	1.58	40.	0.73	0.77	1.	Clear	Schindler 1970
10.70	4.70	2.28	62.	0.72	0.74	1.	Rawson	"
11.60	20.00	0.58	41.	0.92	0.81	-5.	Found	Dillon & Kirchner'75
5.70	1.06	5.38	89.	0.41	0.64	21.	Brewer	"
5.60	0.06	93.33	949.	0.16	0.13	-24.	Clarke	"
8.40	0.85	9.88	184.	0.47	0.54	13.	Costello	"
7.30	0.43	16.98	221.	0.28	0.43	33.	Kearney	"
3.80	0.95	4.00	89.	0.69	0.68	-1.	Little McCauley	"
3.70	0.12	30.83	600.	0.31	0.31	-2.	Mattawamkeag	Lorenzen 1979
16.40	3.03	5.41	80.	0.46	0.64	14.	Moose Head	"
14.30	2.78	5.14	90.	0.49	0.65	14.	Rangely	"
4.24	3.31	1.28	70.	0.74	0.78	3.	Crystal	"
14.94	15.58	0.96	30.	0.70	0.79	3.	Higgins	"
45.70	3.20	14.28	290.	0.47	0.46	-2.	Winnipesaukee	"
13.11	4.11	3.19	120.	0.77	0.71	-7.	McDonald	"
13.50	0.62	21.77	360.	0.34	0.38	13.	Flathead	"
1.50	0.18	8.33	110.	0.20	0.57	41.	Fallen Leaf	"
14.10	0.38	37.11	520.	0.01	0.27	136.	Moon	"
10.20	21.94	0.46	90.	0.67	0.81	13.	Bear	"
32.90	2.54	12.95	430.	0.56	0.48	-32.	White Fish	"
24.40	2.48	9.84	120.	0.99	0.54	-54.	Fremont	"
148.00	188.67	0.78	30.	0.93	0.80	-4.	Superior	Dillon 1975
303.00	714.29	0.42	42.	0.90	0.81	-4.	Tahoe	"

Table 6-1 b)

z	tau	q_s	L_{int}	R_{obs}	R_N	L_{intN}	Lake	Source
6.00	0.55	10.91	470.	0.30	0.52	103.	Sebasticook	Lorenzen 1979
9.91	1.50	6.61	1330.	0.56	0.61	66.	Nagawicka	"
6.92	1.40	4.94	340.	0.17	0.65	164.	Chautauqua	"
5.12	0.30	17.07	410.	0.10	0.43	134.	Lower St. Regis	"
7.92	0.41	19.32	1600.	0.53	0.40	-205.	Saratoga	"
9.10	2.90	3.14	100.	0.38	0.71	33.	Gull	"
8.50	4.20	2.02	220.	0.63	0.75	26.	Chemung	"
4.30	0.03	143.33	9230.	0.21	0.09	-1080.	Thornapple	"
4.60	0.05	92.00	8320.	0.20	0.14	-529.	Pigeon	"
6.10	0.07	87.14	4390.	0.11	0.34	143.	Westler	"
10.80	0.40	27.00	1530.	0.07	0.33	403.	Dallas	"
12.20	2.30	5.30	160.	0.56	0.64	13.	Oliver	"
15.20	0.70	21.71	1370.	0.67	0.38	-400.	Winnisquam	"
2.00	0.09	22.22	1590.	0.23	0.37	227.	Kent	"
17.70	1.75	10.11	310.	0.27	0.53	82.	Sammamish	"
2.40	0.33	7.27	500.	0.32	0.59	137.	Dunham Pond	Kortmann 1980
5.60	0.71	7.89	653.	0.49	0.58	58.	Shagawa'67	Larsen et al. 1981
10.60	1.30	8.15	850.	0.03	0.57	462.	Calhoun	Reckhow 1977
8.80	0.77	11.43	710.	0.01	0.51	355.	Harriett	"
4.80	0.30	16.00	9940.	0.02	0.44	4186.	Waubesa	"
4.60	0.35	13.14	6640.	0.11	0.48	2468.	Kogosa	"
6.10	1.60	3.81	350.	0.41	0.69	97.	Cedar	"
28.00	3.90	7.18	550.	0.47	0.60	69.	Hallwiler See	"
18.00	2.60	6.92	1360.	0.55	0.60	71.	Pfaeffiker See	"
34.00	4.50	7.56	1750.	0.31	0.59	485.	Baldegger See	"
17.70	1.38	12.83	2670.	0.08	0.49	1086.	Greifensee	OECD, Alpine 1980
9.00	0.34	26.47	2490.	-0.12	0.34	1139.	Rotsee	Bloesch 1977
1.00	0.33	3.03	730.	0.71	0.71	2.	Alderfen Broad	Osborne & Phillips '78

2.40	1.00	2.40	8810.	0.40	0.74	2954.	Bergundasjoen'73	Bengtsson 1975, 78
5.40	0.63	8.57	4050.	0.49	0.56	302.	Norrviken'61	Ahlgren 1979
22.70	4.10	5.54	1000.	0.90	0.64	-263.	Gjersjoen'72	OECD, Nordic 1980
12.30	16.60	0.74	600.	0.67	0.80	78.	Esrom'73	
2.00	0.25	8.00	7140.	0.10	0.58	3405.	Lillesjoen'69	Ripl & Lindmark '78

Table 6-1 c)

z	tau	q_s	L_{ext}	R_{obs}	R_N	L_{intN}	L_{int}	Lake	Source
2.40	1.00	2.40	2110.	-0.80	0.74	3239.	4200.	Bergundasjoen	Bengtsson 1975, 78
2.40	1.00	2.40	410.	-2.39	0.74	1281.	1860.	'75	"
2.40	1.00	2.40	240.	-6.54	0.74	1746.	2400.	'76	"
5.40	0.83	6.51	2100.	0.17	0.61	928.	n.a.	Norrviken'70	Ahlgren 1977, 79
5.40	1.62	3.33	420.	-0.95	0.70	694.	800.	'71	"
5.40	1.51	3.58	450.	0.18	0.70	232.	n.a.	'72	"
5.40	2.22	2.43	450.	0.44	0.73	132.	n.a.	'73	"
5.40	0.71	7.61	750.	0.17	0.59	312.	n.a.	'74	"
5.40	1.15	4.70	480.	0.08	0.66	279.	n.a.	'75	"
5.40	5.00	1.08	90.	0.0	0.79	71.	n.a.	'76	"
5.60	0.71	7.89	653.	0.49	0.58	58.	n.a.	Shagawa '67	Larsen et al. 81
5.60	0.71	7.89	744.	0.06	0.58	386.	n.a.	'68	"
5.60	0.71	7.89	733.	0.15	0.58	315.	n.a.	'69	"
5.60	0.71	7.89	797.	0.13	0.58	358.	n.a.	'70	"
5.60	0.71	7.89	739.	0.27	0.58	229.	291.	'71	"
5.60	0.71	7.89	675.	0.39	0.58	128.	224.	'72	"
5.60	0.71	7.89	231.	-0.43	0.58	233.	332.	'73	"
5.60	0.71	7.89	161.	-0.50	0.58	174.	216.	'74	"
5.60	0.71	7.89	110.	-0.36	0.58	104.	293.	'75	"
5.60	0.71	7.89	96.	-0.17	0.58	72.	n.a.	'76	"
4.34	1.27	3.42	420.	0.09	0.70	256.	253.	West Twin'72	Cooke et al. 77,78
4.34	1.56	2.78	180.	-0.48	0.72	216.	336.	'73	"
4.34	0.97	4.47	320.	-0.26	0.67	297.	96.	'74	"
4.34	0.99	4.38	460.	0.36	0.67	143.	n.a.	'75	"
4.34	1.60	2.71	280.	0.68	0.72	12.	53.	'76	"
5.03	0.68	7.40	670.	0.21	0.59	255.	286.	East Twin'72	"
5.03	0.70	7.19	470.	0.14	0.60	214.	314.	'73	"
5.03	0.54	9.31	820.	0.28	0.55	221.	94.	'74	"

5.03	0.45	11.18	810.	0.19	0.51	263.	n.a.		'75	Cooke et al. 77,78
5.03	0.55	9.15	470.	-0.06	0.55	288.	74.		'76	"
12.30	16.60	0.74	600.	0.67	0.80	78.	n.a.	Esrom	'73	Kamp Nielson 75,78
12.30	13.80	0.89	700.	0.57	0.79	157.	n.a.		'74	"
12.30	13.30	0.92	300.	0.33	0.79	139.	n.a.		'75	"
3.10	0.40	7.75	2100.	0.57	0.58	26.	n.a.	Tuusulanjaervi	OECD, Nordic 1980	
3.10	1.15	2.70	1800.	0.72	0.72	9.	n.a.		'75	"

Table 6-2. Mean and standard error for selected characteristics and geographical distribution of the three lake groups of Table 1. Symbols and units same as in Table 1.

	Oxic	Anoxic	
		Steady-state	Sewage Diversion
n	54	33	35
z	37.15 ± 6.98	9.75 ± 1.32	5.46 ± 0.40
tau	25.29 ± 13.56	1.75 ± 0.52	2.22 ± 0.67
q_s	16.82 ± 4.22	19.08 ± 5.26	5.44 ± 0.49
R_{obs}	0.57 ± 0.03	0.33 ± 0.04	-0.16 ± 0.21
L_{ext}	418 ± 84	2,490 ± 525	653 ± 93
Canada	21 (39%)	5 (15%)	0 (0%)
U.S.A.	27 (50%)	17 (52%)	20 (57%)
Europe	6 (11%)	11 (33%)	15 (43%)

among lakes that more closely approach the ideal in which oxic and anoxic lakes differ only in their hypolimnetic oxygen concentration.

Results and Discussion

Phosphorus retention models for oxic lakes- The first hypothesis addressed in this chapter compares retention measured in anoxic lakes with that predicted by models from the literature. This presumes that the models adequately describe retention in oxic lakes.

Three different types of retention models were tested (Table 3). The most common models are of the form

$$R=a/(b+q_s) \qquad (1)$$

where a and b are constants, and q_s is areal water load in m yr^{-1}. When a=b, this form reduces to $R=v/(v+q_s)$ where v is settling velocity (m yr^{-1}). Three values for v have been suggested by different authors: v=10 m yr^{-1} (Vollenweider 1975), v=13.2 m yr^{-1} (Dillon and Kirchner 1975) and v=16 m yr^{-1} (Chapra 1975). A model in which a and b differ was developed for lakes with water loads less than 10 m yr^{-1} by Ostrofsky (1978a). Another popular model is that of Larsen and Mercier (1976). This model, which was independently derived by Vollenweider (1976), assumes variable settling velocities in each lake depending on water residence time and mean depth. The third type of model (Kirchner and Dillon 1975) is obtained

Table 6-3. Six retention models tested in this study. q_s: areal water load ($m\ yr^{-1}$), tau: water residence time (yr).

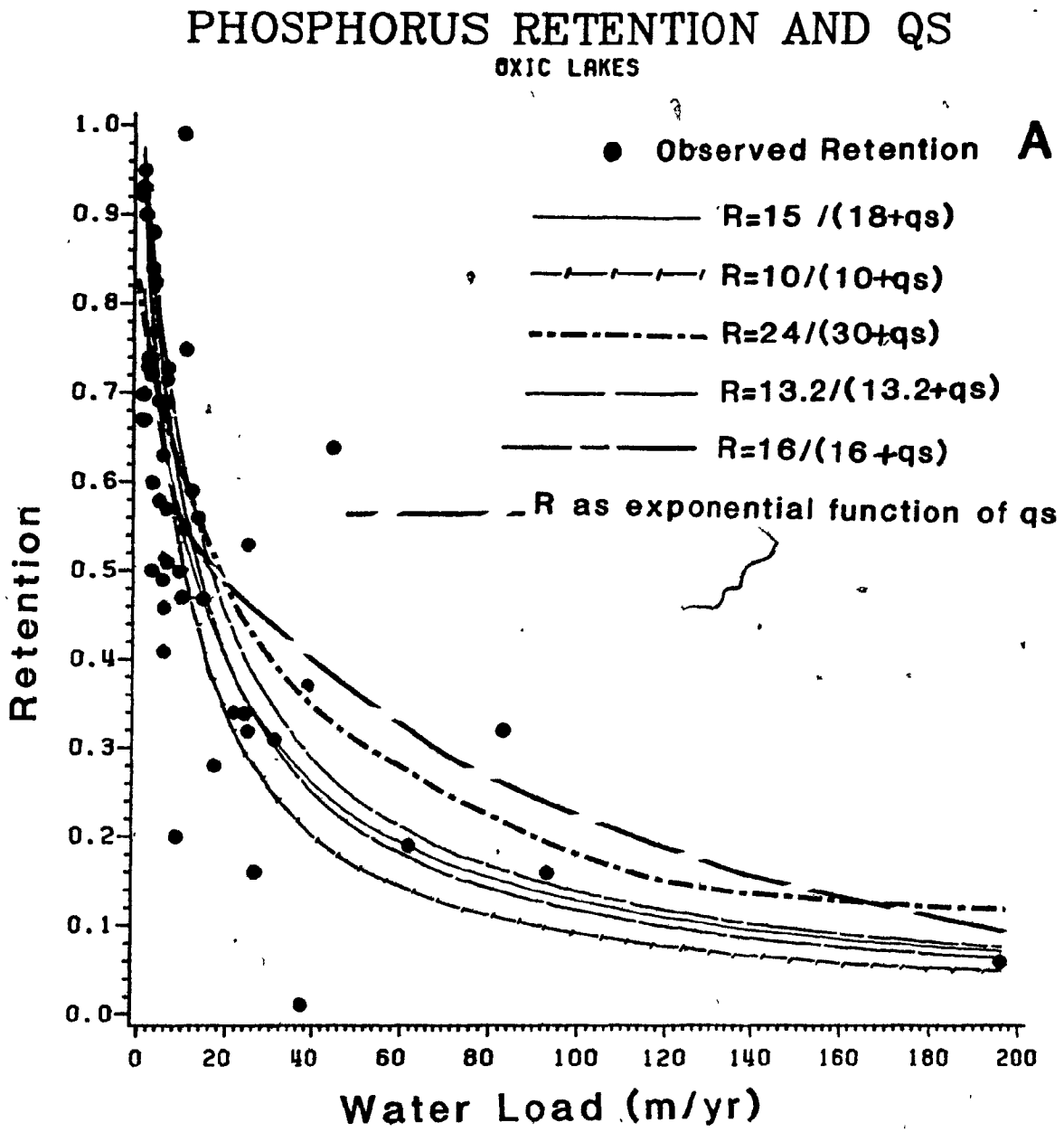
Formula	Reference
$R_V = 10/(10+q_s)$	Vollenweider 1975
$R_D = 13.2/(13.2+q_s)$	Dillon and Kirchner 1975
$R_C = 16/(16+q_s)$	Chapra 1975
$R_O = 24/(30+q_s)$	Ostrofsky 1978a
$R_K = 0.426\ \exp(-0.271 q_s) + 0.574\ \exp(-0.00949\ q_s)$	Kirchner and Dillon 1975
$R_L = 1/(1+1/\sqrt{tau})$	Larsen and Mercier 1976

by fitting measured retention as a double exponential function of areal water load (q_s). All tested retention models (Table 3) are based on the water load (q_s) or water residence time (tau), (Fig. 1a, b).

In general the available models tended to overestimate phosphorus retention in this set of oxic, stratified lakes. This is supported by statistical analysis of the differences between observed and predicted values (Table 4). Both parametric (matched-pairs t) and nonparametric (Wilcoxon signed ranks) tests indicate that the prediction of all models, except those of Vollenweider (1975) and Ostrofsky (1978a) differed significantly from observations. The other four models for oxic lakes (Chapra, Dillon-Kirchner, Kirchner-Dillon and Larsen-Mercier, Table 3) must be rejected, though they are frequently used to predict total phosphorus concentration in lakes. For example, Larsen and Mercier's model is used in the OECD Eutrophication Program. Differences between the performance of the various models likely do not reflect geographic or methodological idiosyncracies in the data because scrutiny of the residuals revealed no bias with respect to the data sources. Even the two retention models which seemed to describe the whole-lake data set are not successful when tested with the subgroups of oxic lakes formed to match the range of mean depth, water residence time and water load of the set of anoxic lakes.

These available retention models predict poorly, some because they were developed from a small number of lakes, many because the lakes were not necessarily oxic or stratified.

Fig. 6-1. Observed retention, as a function of the variables used to predict retention. Model $R=15/(18+q_s)$ has been developed from the oxic lakes data set. The other models are from literature (Table 3). A. Water load (q_s). B. Water residence time (tau).


PHOSPHORUS RETENTION AND QS
OXIC LAKES
A
Observed Retention
R=15 /(18+qs)
R=10/(10+qs)
R=24/(30+qs)
R=13.2/(13.2+qs)
R=16/(16+qs)
R as exponential function of qs
Retention
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
20
40
60
80
100
120
140
160
180
200
Water Load (m/yr)

PHOSPHORUS RETENTION AND TAU

OXIC LAKES

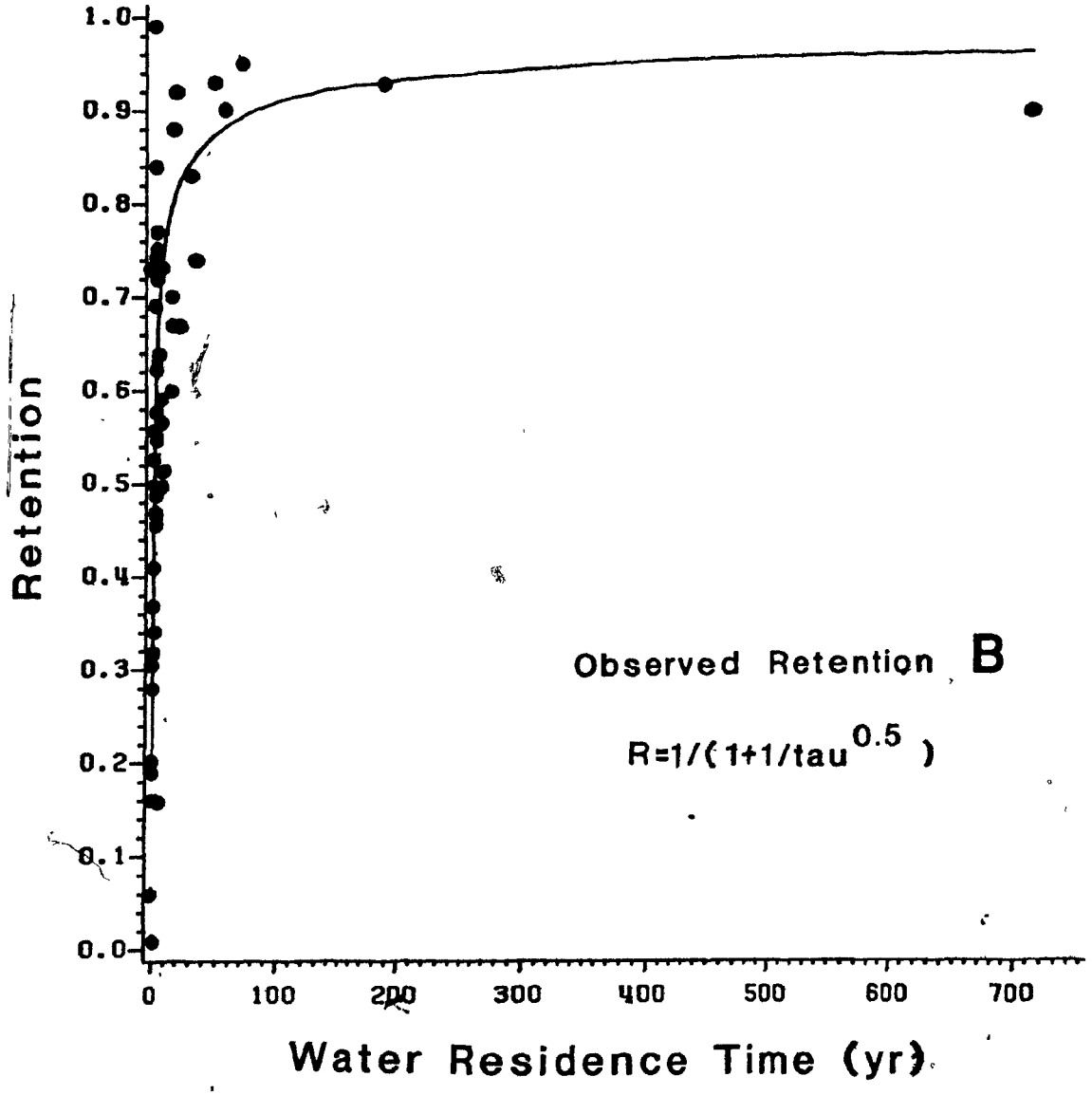


Table 6-4. Test of retention models (R) on oxic lakes. Mean retention and nonparametric probabilities (p) for testing the difference between observed and predicted retention. Symbols and units same as in Table 1 and Table 3. $R_N=15/18+q_s$.

R	All n=54		$z \leq 13$ n=18		tau ≤ 4 n=32		$q_s \leq 10$ n=36	
	mean	p	mean	p	mean	p	mean	p
R_{obs}	0.58	-	0.47	-	0.46	-	0.69	-
R_V	0.59	0.633	0.53	0.170	0.44	0.550	0.74	0.027*
R_D	0.63	0.010*	0.57	0.016*	0.50	0.191	0.79	0.000*
R_C	0.67	0.000*	0.60	0.002*	0.53	0.007*	0.82	0.000*
R_O	0.61	0.183	0.55	0.025*	0.52	0.017*	0.71	0.480
R_K	0.63	0.011*	0.58	0.001*	0.52	0.019*	0.74	0.044*
R_L	0.62	0.014*	0.48	0.411	0.50	0.076	0.71	0.278
R_N	0.57	0.760	0.51	0.145	0.46	0.708	0.69	0.875

* Model is rejected at the 95% significance level.

Also some of the models (Vollenweider 1975; Larsen and Mercier 1976; Ostrofsky 1978a) were developed for use in budget models to predict spring phosphorus concentration and have never been tested directly against observed retention. However it is crucial to use the best retention model possible in order to develop an internal load model.

Since none of the existing models seemed appropriate, a new model to describe retention in oxic stratified lakes was developed. The parameters a and b in Eq. 1 were optimized using the 54 oxic lakes and the DUD ("doesn't use derivatives") non-linear least square algorithm (Ralston and Jennrich 1978). The best fit yielded the model:

$$R_N=15/(18+q_s) \qquad (2)$$

This model applies over a large range of z, tau and q_s (Table 4). All other retention models tested in this study appear to be sensitive to these variables and should only be used in the range for which they have been verified (Table 4). Though other formulae could be developed, the model R_N described the data for all lakes and in all subgroups; this model was therefore selected to compare with retention in anoxic lakes. Nevertheless, comparisons were also made with other retention models, to remove the possibility of bias.

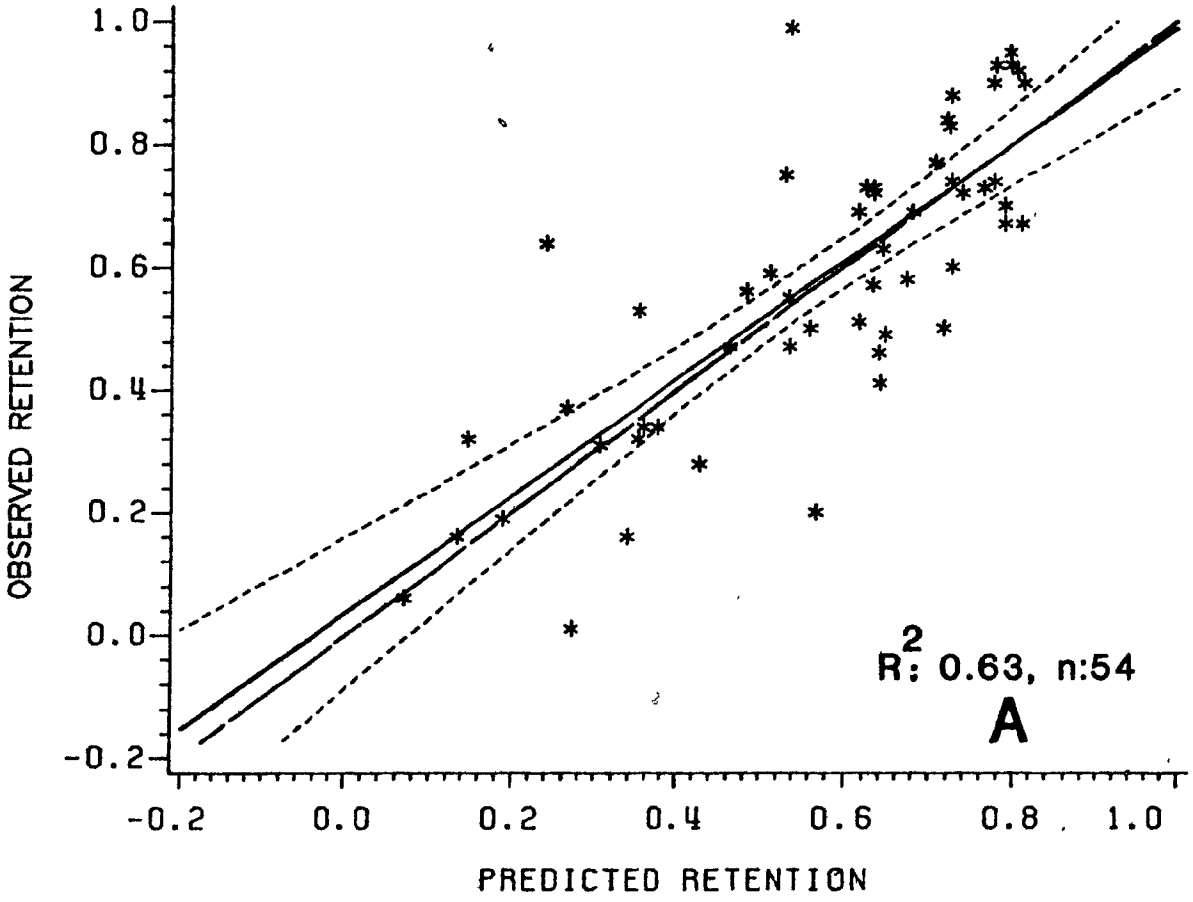
Phosphorus retention in anoxic lakes- Although the retention model $R=15/(18+q_s)$ describes retention in oxic stratified lakes (Fig. 2a), it substantially overestimates retention in both sets of anoxic lakes (Fig. 2 b,c). A similar

Fig. 6-2. Observed retention plotted against those predicted by the model $R=15/(18+q_s)$. The solid line represents regression line embraced by the 95% confidence band, the broken line represents perfect prediction (1:1 line). A. In oxic lakes, both lines coincide, since the model was parameterized using this data base. B. In anoxic lakes in steady state, the 1:1 line lies above the confidence band of the regression because here the retention is significantly overestimated by the model. C. In anoxic lakes after sewage diversion, the regression of observed versus predicted values is not significant; predicted retention is much less variable than observed retention.

RETENTION MODEL

OXIC LAKES

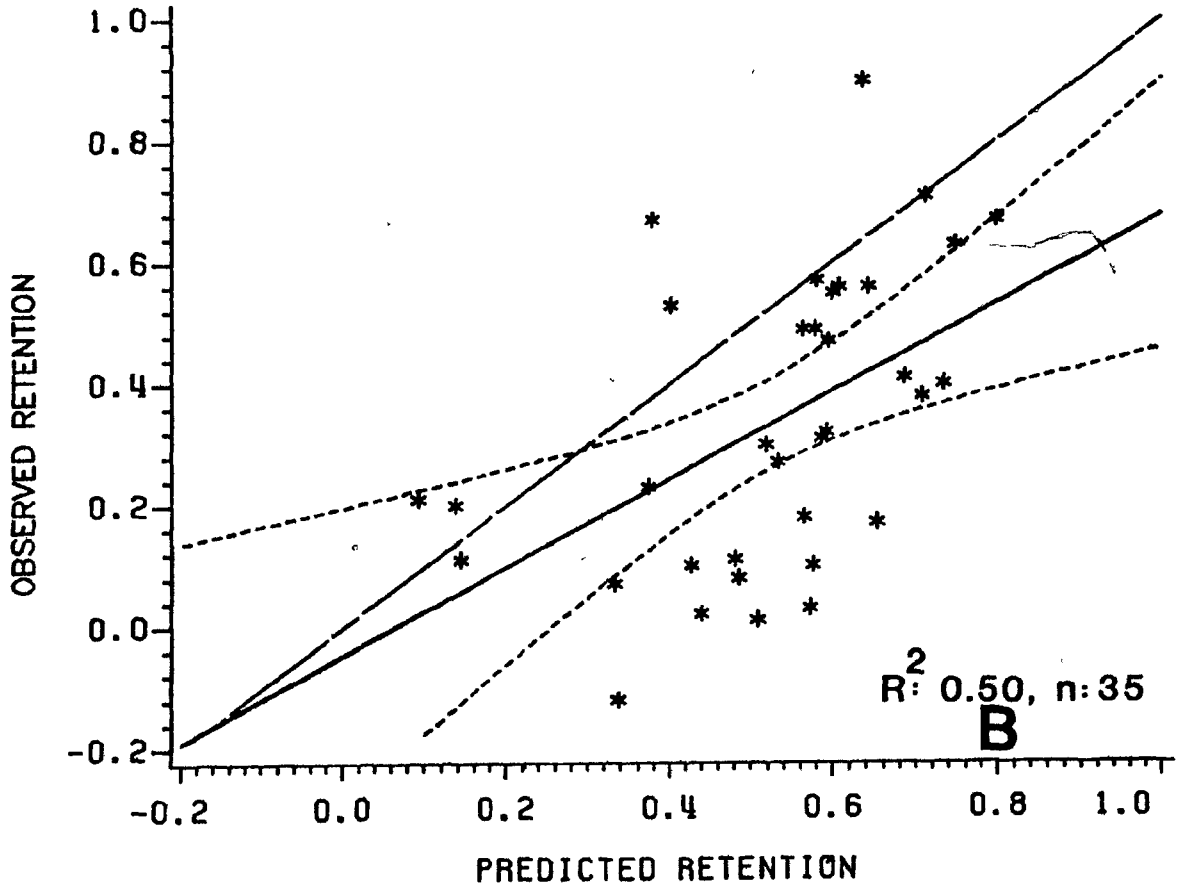
REGRESSION LINE AND 95% CONFIDENCE BAND



RETENTION MODEL

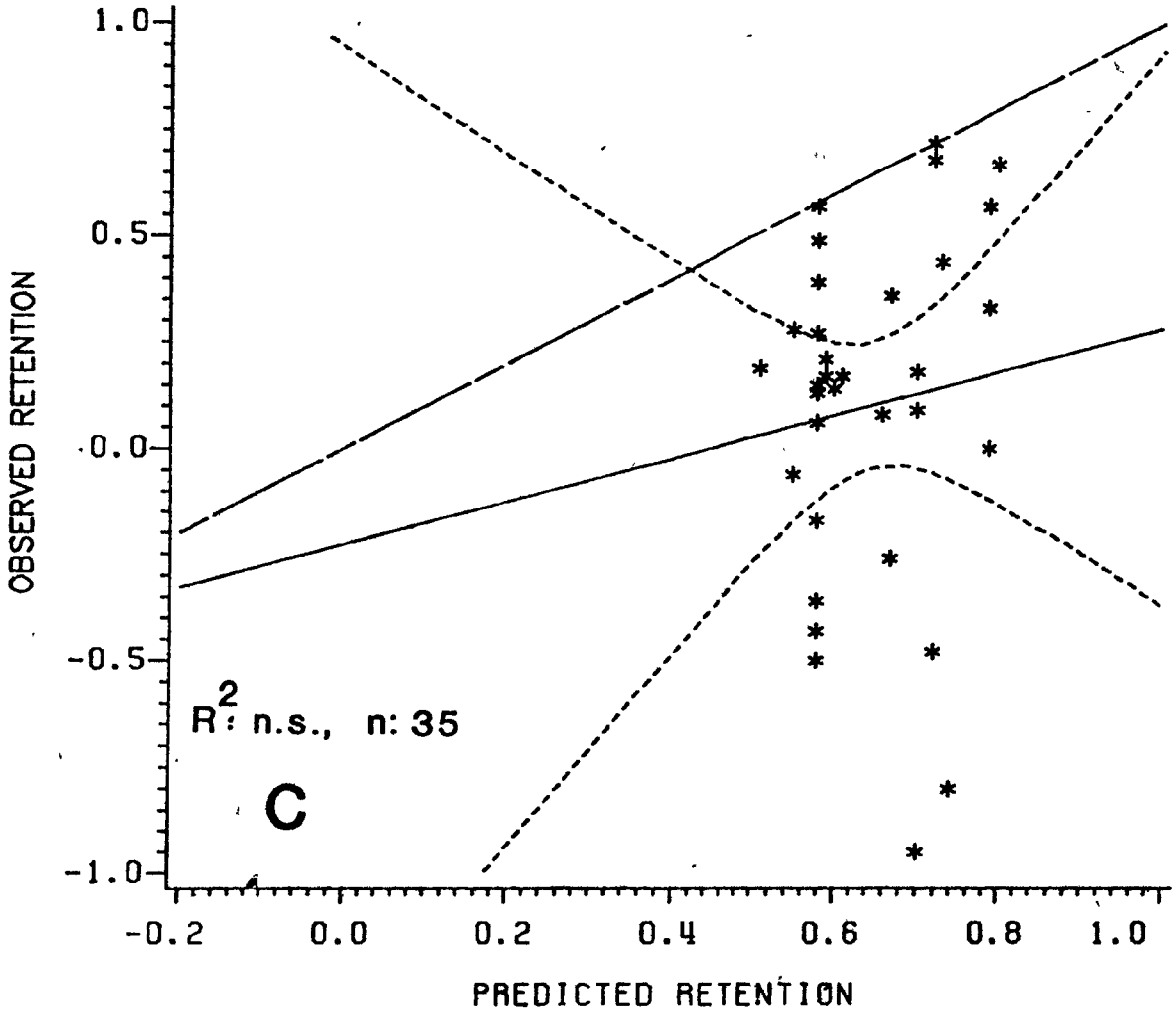
ANOXIC LAKES

REGRESSION LINE AND 95% CONFIDENCE BAND



RETENTION MODEL

ANOXIC LAKES AFTER SEWAGE DIVERSION
REGRESSION LINE AND 95% CONFIDENCE BAND



overestimate is obtained for each of the six other retention models (Wilcoxon signed ranks matched pairs test; $p < 0.0001$). The average (x) observed retention for anoxic lakes in steady state is 0.33 (SE= 0.04); for those after sewage diversion it is -0.16 (SE= 0.21). These values are significantly lower than those predicted by Eq. 2 (x= 0.52, SE= 0.03 and x= 0.65, SE= 0.01 respectively). Conceptually, reduced retention can be explained by either diminished sedimentation or by an unconsidered phosphorus source, but only the latter would permit negative retentions. Since the retention model applied over the whole range of mean depth, water residence time and water load encountered in the investigated anoxic lakes, there is little reason to suppose that they had different sedimentation characteristics. On the other hand, several studies show that the sediment provides an internal phosphorus source in lakes with anoxic hypolimnia (e.g. Welch and Rock 1980; Bengtsson 1978; Larsen et al. 1981; Ripl and Lindmark 1978).

Internal phosphorus load- If the failure of the model in anoxic lakes reflects an internal phosphorus source, then the deviation of observed from predicted retention can be used to predict internal phosphorus load. This is the second hypothesis mentioned in the introduction of this chapter. Internal phosphorus load can be estimated from residuals of the retention model as:

$$L_{int} = -L_{ext} \times (R_{obs} - R_{pred}) \qquad (3)$$

where L_{int} and L_{ext} are internal and external phosphorus load respectively, in mg m^{-2} yr^{-1}; R_{obs} is retention measured as 1- outflow P mass/ inflow P mass; R_{pred} is predicted retention; and (R_{obs} - R_{pred}) is the residual error of the retention model. This calculation assumes that the lower retention observed in anoxic lakes is entirely due to the internal phosphorus load.

The most direct test for the predictive power of a model compares observed and predicted values. Observed values of internal phosphorus load are available for 17 anoxic lake-years following sewage diversion from five lakes. These estimates are calculated from the increased mass of hypolimnetic phosphorus divided by the surface area of the lake. Such estimates might be biased since they assume that all hypolimnetic phosphorus is derived from the sediments and none from sedimenting plankton, and they do not consider sedimentation of hypolimnetic phosphorus; it is possible for example that a portion of the hypolimnetic phosphorus may precipitate on destratification. Internal load, estimated in this way, supports the internal load model (Eq.3, Fig.3). Both a parametric (matched-pairs t) and nonparametric (Wilcoxon signed ranks) test show no significant difference between predicted and observed values of internal load. Table 5 shows that five of the other retention models also predict internal phosphorus load. Only the Larsen-Mercier model predicted values significantly lower than observed.

Equation 3 can only be used to predict internal load if

Fig. 6-3. Comparison of the internal phosphorus load predicted by Eq. 3 (Lint) and from the difference of observed and predicted retention R_N with "observed" loads measured as the increase in hypolimnetic phosphorus during anoxia. Line represents perfect prediction.

TEST OF INTERNAL P LOADING MODEL

LINE REPRESENTS PERFECT PREDICTION

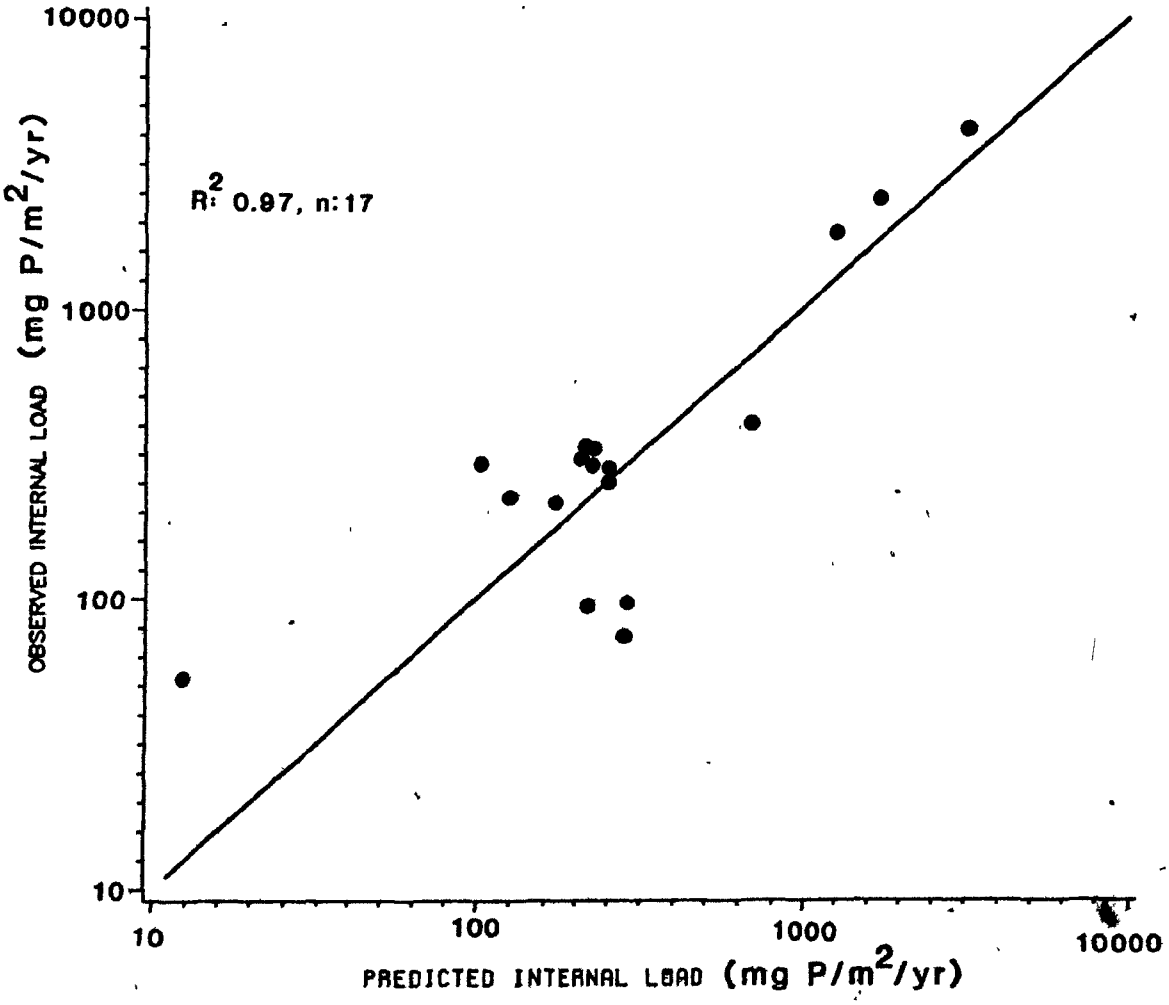


Table 6-5. Test of internal load models based on substituting different retention terms (Table 4) into Eq.3. Mean internal load (mg m^{-2} yr^{-1}) and nonparametric probabilities (p) for testing the difference between observed and predicted internal load; n=17.

Internal Load	mean	p
observed	689	-
L_{int} (R_N)	564	0.210
L_{int} (R_V)	574	0.149
L_{int} (R_D)	603	0.309
L_{int} (R_C)	620	0.492
L_{int} (R_O)	581	0.246
L_{int} (R_K)	576	0.210
L_{int} (R_L)	478	0.035*

* Model is rejected at the 95% significance level.

phosphorus retention is measured. Unfortunately, the accurate determination of annual phosphorus retention requires frequent sampling of phosphorus and water loads for at least one year. For those lakes where the observed retention is not available, but where the extent of hypolimnetic anoxia is known, internal phosphorus load may be predicted from estimates of phosphorus release rates. Internal phosphorus load in anoxic lakes represents phosphorus release from the sediment under reducing conditions (e.g. Mortimer 1941, 1942; Olsen 1964; Syers et al. 1973; Bengtsson 1975; Cooke et al. 1977; Larsen et al. 1981), thus

$$L_{int} = \text{anoxic area} \times \text{anoxic period} \times \text{P release rate/lake area} \quad (4)$$

where L_{int} is internal P load (mg m^{-2} yr^{-1}); anoxic area (m^2) is the sediment surface area that is in contact with anoxic water; anoxic period (d) is duration of anoxia; and P release rate is the rate at which phosphorus is released from the anoxic sediment surface (mg m^{-2} d^{-1}).

Area and period of anoxia can be determined by periodic sampling to describe the extent of anoxia during stratification. Area of anoxia can be approximated as the area below the oxic/anoxic boundary. There is some evidence that phosphorus release rates depend on an extended period of high phosphorus input (Bengtsson 1975; Ahlgren 1979), the concentration gradient of phosphorus across the mud-water interface (Kamp Nielsen 1974), and temperature (Banoub 1975).

However, a compilation of release rates, calculated as the increase in hypolimnetic phosphorus divided by anoxic sediment area and period of anoxia shows some homogenity (Table 6a). The mean and median of phosphorus release rates measured in core tubes containing anoxic sediment and water (Table 6b) do not differ significantly from these in situ estimates. This suggests that the in situ increase in hypolimnetic phosphorus reflects release from the sediments rather than the decay of sedimented plankton. Phosphorus release in oxic cores does not differ significantly from zero. I used the median of in situ phosphorus release rates from Table 6a (12 mg m^{-2} day^{-1}) to estimate internal phosphorus load for three different lakes (Table 7). Because these lakes were used (among others) to estimate release rate, the internal loads predicted by Eq. 4 (Table 7) are not independent of the observed values; more data from different lakes are needed to test this model.

High internal loads and low phosphorus retentions imply that the phosphorus cycle in anoxic lakes differs from that in oxic lakes. Since retention is often used to predict phosphorus concentrations in lakes, the applicability of existing total phosphorus models must be tested for anoxic lakes.

The prediction of phosphorus in lakes with anoxic hypolimnia- Testing phosphorus models in anoxic lakes is difficult because often only spring turnover phosphorus data are available (Dillon and Rigler 1974). But, in anoxic lakes, the total phosphorus concentration increases during summer

Table 6-6. Phosphorus release rate estimates (mg m^{-2} d^{-1}): a) in anoxic lakes, b) in anoxic and oxic core tubes. Negative release rates indicate adsorption of phosphorus by the sediment.

Lake	Release rate	Reference	
Shagawa	12.1	Larsen et al.	1981
Mendota	10.8	Sonzogni	1974
West Twin	6.5	Cooke et al.	1977
East Twin	6.0	Cooke et al.	1977
Erie	7.4	Burns and Ross	1972
White Lake	19	Holdren and Armstrong	1980
Barten Broad	9.6	Osborne and Phillips	1978
Alderfen Broad	20	Osborne and Phillips	1978
Baldeggersee	9.7	Vollenweider	1968
Rotsee	28	Vollenweider	1976
Norrviken	9.2	Ahlgren	1977
Bergundasjon	24.5	Bengtsson	1975
Esrom	11.5	Kamp Nielsen	1974
Bysjon	20	Enell	1982
Magog	13.5	Nürnberg	in prep.
mean ± SE	14 ± 1.8		
median	12		
n	15		

Table 6-6 b.

Lake	Release rate		Reference	
	Anoxic	Oxic		
White	34.3	-	Freedman and Canale	1977
Ursee	11	-	Holdren and Armstrong	1980
Furosoe	17.3	-4.5	Holdren and Armstrong	1980
Esrom	12.3	-1.4	Holdren and Armstrong	1980
St. Gribsoe	1.2	0.2	Holdren and Armstrong	1980
Grane Lángsoe	0.8	0.6	Holdren and Armstrong	1980
Bergundasjoen	34	-	Bengtsson	1975
Alderfen Broad	20	0	Phillips	1978
Mohegon	3	0	Fillos	1976
Glanningen	18	2	Ryding and Forsberg	1977
Ramsjoen	20	0.3	Ryding and Forsberg	1977
Ryssbysjoen	20	0.7	Ryding and Forsberg	1977
Charles East	31	-16	Theis and McCabe	1978
Stone	32	-	Theis and McCabe	1978
Trummen	1.5	0.3	Graneli	1979
Arungen	16	1.0	Graneli	1979
Vombsjoen	6	2.6	Graneli	1979
Byoesjoen	27	7	Enell	1982
Norrviken	10	5	Ahlgren	1972
Ontario	-	0.2	Bannerman et al.	1974
Memphremagog	10	-	Nürnberg	in prep.

Table 6-6 b cont.

mean	16	-0.1
SE	2.5	1.32
median	15	0.3
n	20	15

Table 6-7. Synopsis of measured internal load (obs) and predicted internal load (pred) according to different models for three lakes. RR: based on release rates, R: based on retention. Observed data for Lake Shagawa from Larsen et al. 1981, for the Twin Lakes from Cooke et al. 1977.

Lake	Year	Days*Area/ Lake Area ($d\ yr^{-1}$)	Internal Load ($mg\ m^{-2}\ yr^{-1}$) pred(RR)	pred(R)	obs
Shagawa	1971	33.0	396	229	291
	1972	33.0	396	128	224
	1973	32.5	390	233	332
	1974*	13.4	161	174	216
	1975	24.8	298	104	293
West	1972	44.8	538	256	253
Twin	1973	32.9	395	216	336
	1974**	26.1	313	297	96
East	1972	38.0	456	255	380
Twin	1973	38.0	456	214	314
	1974**	44.5	534	221	94

* Weak stratification,

** Alum addition to West Twin Lake: a lower release rate than normal can be expected.

stratification and this should be considered for mass balance models which predict average phosphorus concentrations. An adequate measure of average concentration in anoxic lakes requires frequent determination of phosphorus-depth profiles at several stations or estimates of phosphorus concentrations at fall turnover. A good prediction of phosphorus concentration based on areal water load (q_s) and external phosphorus load alone cannot be expected in anoxic lakes. Indeed, none was found when phosphorus concentration was predicted from external load and any of the phosphorus retention models in Table 3 and Eq. 2 (Wilcoxon non parametric matched pairs signed ranks test: $p < 0.001$, $n=33$). Measurements of both phosphorus release rates and internal load suggest that this failure is most likely due to an internal phosphorus source, the release of sediment phosphorus.

Two approaches may permit prediction of phosphorus concentration in anoxic lakes:

1. Retention can be measured and phosphorus concentration predicted from the phosphorus budget model (Dillon and Rigler 1974) according to the formula:

$$TP = L_{ext} \ (1-R_{obs})/q_s \qquad (5)$$

(Symbols same as Table 1).

This model should predict total phosphorus concentration in oxic and anoxic lakes, because changes in net sedimentation are accounted for by measured retention. This approach is successful in the anoxic lakes discussed here, for the

nonparmetric test showed no significant difference ($p = 0.898$, $n=33$).

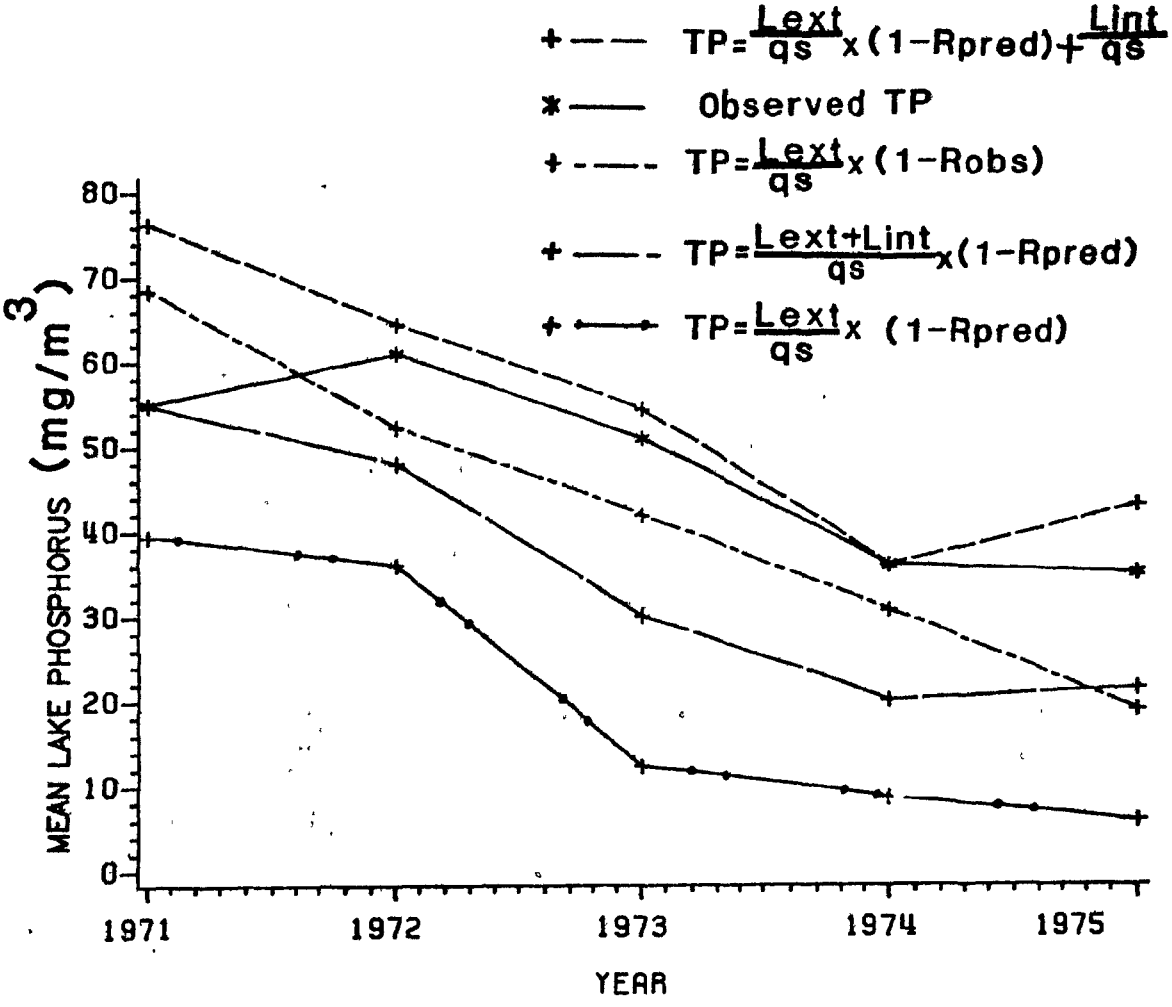
2. Internal load can be measured or predicted and corrected for q_s, and then combined with the retention-based budget model for external load according to the formula:

$$TP = L_{ext}/q_s\ (1-R_{pred}) + L_{int}/q_s \qquad (6)$$

(Symbols as in Table 1). If the internal load is predicted by the internal load model based on retention, the two approaches are identical, since replacing internal load in Eq. 6 by Eq. 3 yields the Dillon-Rigler model in Eq. 5.

Only a few data exist to test this model. Observed phosphorus (mean phosphorus concentration of the entire water column averaged over the year) and several predicted phosphorus concentrations are compared for Shagawa Lake (Fig. 4). The suggested model (Eq.6) describes the data best for 4 of 5 years. Equation 6 can also be combined with internal phosphorus load, measured as increased hypolimnetic phosphorus, for 14 lake-years following sewage diversion in five lakes. (For 3 lake-years, no total phosphorus concentrations are available.) A Wilcoxon signed ranks test showed total phosphorus concentration was predicted well ($p = 0.397$, $n=14$). If internal phosphorus load is ignored, the predictions underestimate phosphorus concentration ($p < 0.001$). Equation 6, the results from Lake Shagawa, and those for the lake-years after sewage diversion show that internal

Fig. 6-4. Prediction of mean total phosphorus concentration for five years in anoxic Lake Shagawa.


TP=Lext/qs x (1-Rpred)+Lint/qs
Observed TP
TP=Lext/qs x (1-Robs)
TP=Lext+Lint/qs x (1-Rpred)
TP=Lext/qs x (1-Rpred)
MEAN LAKE PHOSPHORUS (mg/m3)
0
10
20
30
40
50
60
70
80
1971
1972
1973
1974
1975
YEAR

loading is important for the prediction of phosphorus in anoxic lakes.

Equation 6 implies that both internal and external load are similarly affected by hydrology and morphometry expressed as areal water load (q_s). Since it is unlikely that the hypolimnion is flushed, the dependence of internal phosphorus load on q_s may imply that water load and flow through a lake occurs during unstratified periods. The retention of internally loaded phosphorus seems to be negligible. If a significant portion of internal load was retained by sedimentation, the internal load calculated from Eq. 3 would be less than that calculated from the increase in hypolimnetic phosphorus during stratification. However, Fig. 3 shows those two estimates agree well. Equation 6 therefore suggests that if external and internal loads are equal, the effect of internal load on the phosphorus concentration of the lake will be the larger, since it is not diminished by retention. This may indicate that phosphorus from the sediment does not precipitate out at turnover, as suggested by some authors (see Hutchinson 1957), but that the most remains in the water column.

The impact of internal phosphorus load on algal biomass will depend on temperature, light and the extent of phosphorus limitation (before hypolimnetic intrusion). Lakes with early thermocline erosion or frequent destratification sustain algae blooms (Stauffer and Lee 1974; Kortmann et al. 1982). Internal load would probably have less effect in northern lakes that

turn over in late fall when algal biomass is low (Schindler et al. 1980).

Conclusion

Models validated for oxic lakes do not necessarily apply to anoxic lakes because these models ignore internal phosphorus load. Predictions of internal phosphorus load from the residuals of a retention model or from anoxic release rate estimates agree with observed internal loads. Until better estimates exist, the proposed models of internal load are useful to predict the phosphorus concentration in anoxic lakes. For example the enigmatic delay in recovery of Lake Sammamish, compared to Lake Washington's rapid recovery, is readily explained by anoxia and internal phosphorus load. The models may help determine wether an expensive in-lake restoration technique is needed to reduce the phosphorus concentration of a lake to a desired level or wether a reduction in external load would be sufficient.

Models developed for oxic lakes may not be applicable to lakes with anoxic hypolimnia and to shallow lakes with short periods of anoxic stratification, such as the prairie pot-hole lakes (Schindler and Comita 1972; Barica 1974). This complication might apply to all lakes with an internal phosphorus source. For example, Ostrofsky (1978b) has found that aerobic phosphorus leaching in impoundments decreases phosphorus retention. Another type of phosphorus release from sediments is suggested for lakes with extensive macrophyte

cover (e.g. Lake Wingra, Carpenter 1980). Models for internal phosphorus load from these sources may also be developed from the residuals of the retention model for normal oxic lakes. Consideration of internal phosphorus load will, I hope, help reduce the error in predicting phosphorus retention and subsequently prove useful in managing total phosphorus concentration and its correlate, phytoplankton biomass, in lakes of all types.

The conclusions are derived from lakes that have a long history of anthropogenic pollution. Pristine lakes with natural anoxia due to morphometry and light regime may or may not have phosphorus release rates like those presented in Table 6 or low annual phosphorus retention.

Chapter 7:

Synthesis and Conclusions

This thesis examines the role of hypolimnetic phosphorus in anoxic lakes. In particular it investigates and supports three hypotheses: 1) Most of the hypolimnetic phosphorus in anoxic lakes is potentially available within the hypolimnion. 2) After mixing into aerated surface water much of hypolimnetic phosphorus remains available to epilimnetic plankton despite high iron concentrations. 3) Phosphorus models for anoxic lakes are different from those for oxic lakes because of internal phosphorus load. This chapter summatizes these hypotheses and considers several others dealing with the availability of hypolimnetic phosphorus:

(1) There is a significant accumulation of total phosphorus in anoxic hypolimnia.

(2) The phosphorus in hypolimnia is potentially available in the sense that it is in a form which phytoplankton can use.

(3) This phosphorus is "positionally available" because upwelling hypolimnetic phosphorus contacts the plankton in the trophogenic zone.

(4) The utilization and availability of this upwelling phosphorus is affected by the trophic status of the surface water and therefore differs in phosphorus deficient and sufficient waters.

(5) The availability of upwelling phosphorus is influenced by lake morphometry and hydrology.

(6) The chemistry of the lakes and their sediments influence the availability of hypolimnetic phosphorus.

(7) The timing of fall turnover can influence availability since at early turnover the growth conditions for algae are better and hence phosphorus utilization larger.

Finally experiments are suggested to test the unsupported hypotheses 6) and 7). This chapter closes with some notes on biological factors which could influence the phosphorus cycle in anoxic lakes.

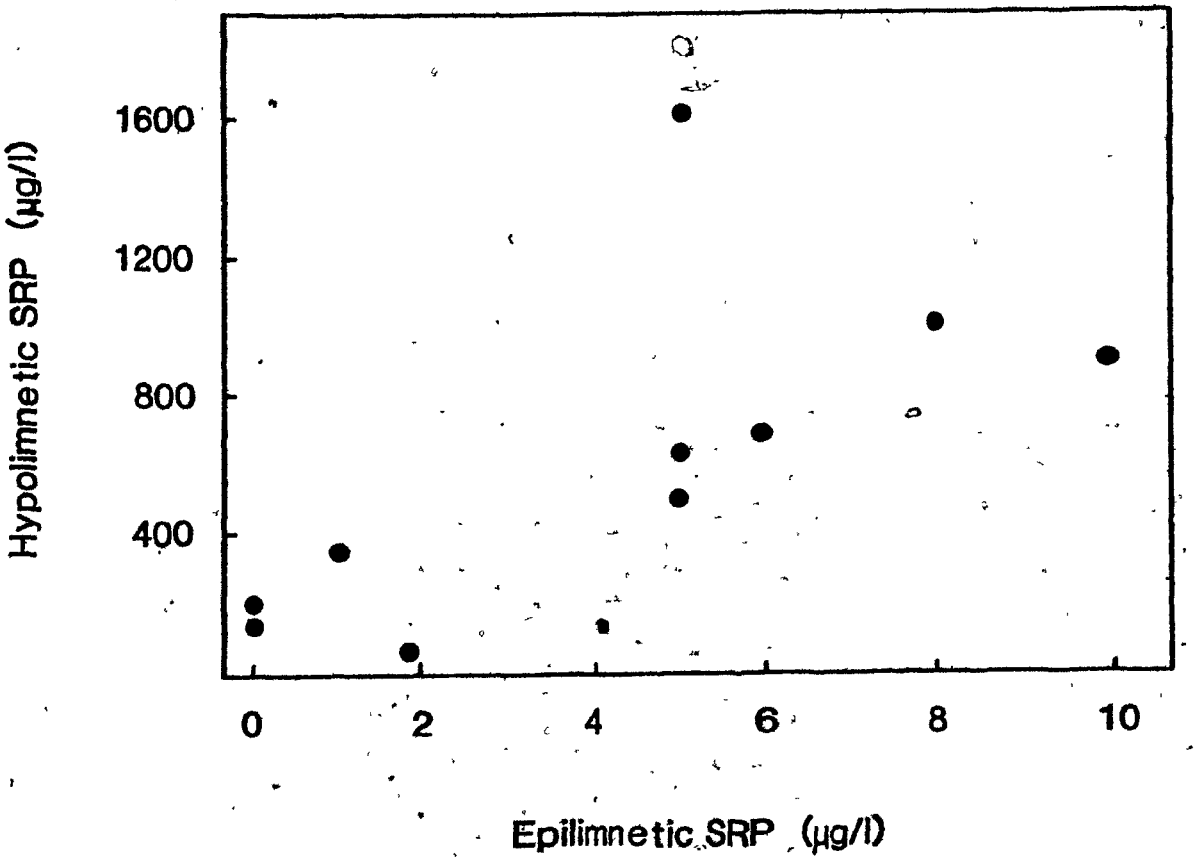
1) TP concentration in the anoxic hypolimnion:

Since Einsele (1936), it has been hypothesized that phosphorus is released by anoxic sediment surfaces and accumulates in the hypolimnion. A survey of the literature shows that anoxic sediments release phosphorus at a mean rate of 12 to 16 mg $m^{-2}d^{-1}$ (Table 6-6) producing steep phosphorus gradients in the anoxic hypolimnion (Fig. 1-1).

2) The bioavailability of phosphorus within the hypolimnion:

The proportion of total hypolimnetic phosphorus which is potentially available, provided it comes into contact with phosphorus deficient plankton, was determined in two ways. Measurements of SRP gives a maximum estimate, radiological bioassays provide a minimum. A survey of the literature shows that the hypolimnetic SRP concentration is substantial, approximately 100 times higher than the surface concentration during summer stratification (Fig. 1). The proportion of hypolimnetic TP which is SRP, increases with increasing TP

Fig. 7-1. A comparison of hypolimnetic and epilimnetic SRP concentrations just before fall turnover for worldwide lakes.


Hypolimnetic SRP (µg/l)
1600
1200
800
400
0
2
4
6
8
10
Epilimnetic SRP (µg/l)

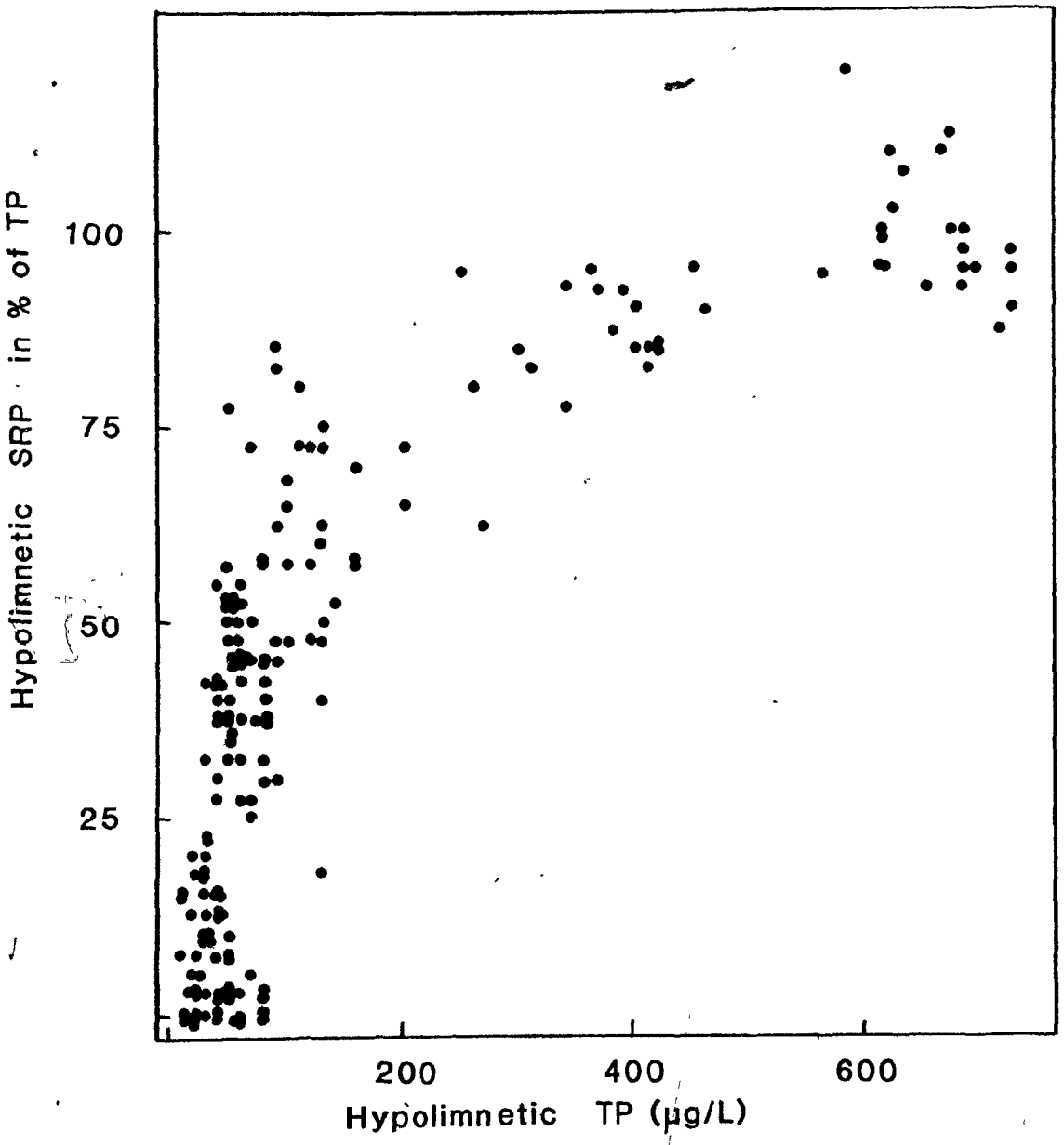
concentration in the study lakes (Fig. 2). At 100 to 200 ug/L total phosphorus - a concentration frequently encountered in anoxic hypolimnia - 80% is SRP. Hence the maximal availability is substantial.

The bioassay is based on additions of small amounts of anoxic water to epilimnetic water and simulates a thermocline erosion with nearly infinite dilution. At least 90% of SRP appears to be bioavailable (Fig. 4-3). This result suggests that, under optimal conditions (large dilution of hypolimnetic water, sufficient light and temperature), epilimnetic plankton can utilize approximately 70% (0.80 * 90%) of entrained hypolimnetic TP when concentrations in the hypolimnion exceed 100 ug/L TP. These experiments also show that epilimnetic plankton can outcompete chemical precipitation and adsorption by iron hydroxides when the dilution is high enough. For example, ca. 30% of the SRP derived from the hypolimnion of Lake Magog remains available at dilutions of ten times or more (Chapter 5).

3) The positional availability of hypolimnetic phosphorus:

In the bioassay, the hypolimnetic phosphorus is artificially mixed into epilimnetic water. Under natural conditions, hypolimnetic phosphorus can be "positionally available" to plankton at the oxic/ anoxic boundary (e.g. Konopka 1983), during thermocline erosion, or at spring and fall turnover. Total phosphorus concentration in the surface water of many anoxic lakes increases drastically after fall turnover and is correlated (r^2: 0.66) with the hypolimnetic

Fig. 7-2. The proportion (%) of total phosphorus which is soluble reactive in the hypolimnia of eight Canadian lakes.


Hypolimnetic SRP in % of TP
100
75
50
25
200
400
600
Hypolimnetic TP (µg/L)

phosphorus concentration before turnover (Fig. 1-2 and 1-3).

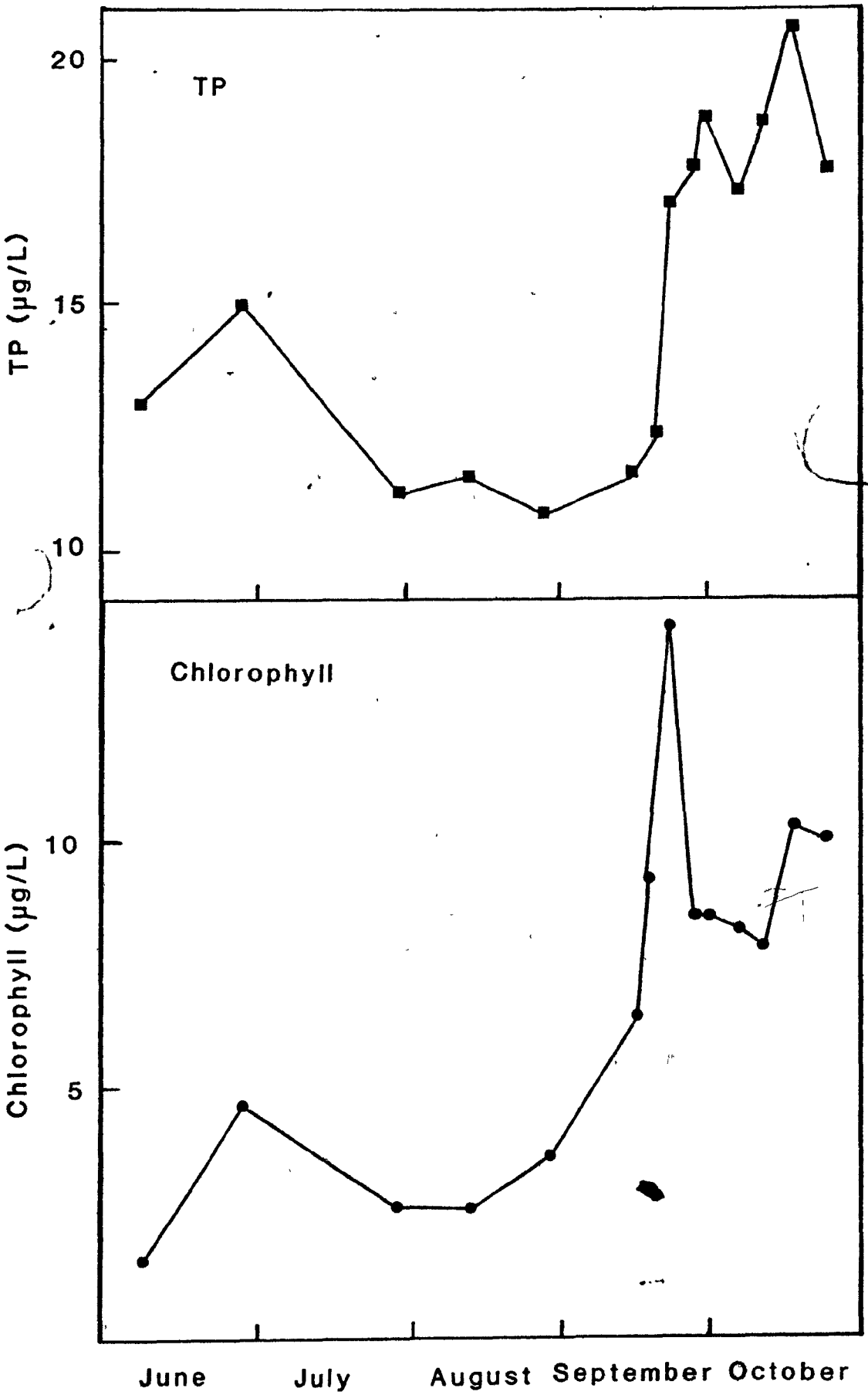
4) The effect of the nutrient status of the surface water on the availability of hypolimnetic phosphorus:

Upwelling hypolimnetic phosphorus is potentially highly available to organisms. The actual contribution of hypolimnetic phosphorus to eutrophication will depend on the capacity of the plankton to take up the hypolimnetic phosphorus after thermocline erosion and is more difficult to assess then potential availability.

In the case of phosphorus deficiency, algae will rapidly incorporate upwelling phosphorus and increase in biomass, provided light and temperature are sufficiently high. In this case, an algal bloom and increased chlorophyll concentrations can be expected. On the other hand, if phosphorus limitation is low, the effect of turnover on biomass within the lake should be less, but the potentially available phosphorus (e.g. SRP) would increase in the epilimnia of these lakes and subsequently fertilize downstream waters. My field studies indicate that hypolimnetic phosphorus enhances algal growth at fall turnover. Some data are also available in the literature to compare chlorophyll concentrations before and after turnover.

Phosphorus limited lakes: Fitch Bay of Lake Memphremagog is phosphorus limited at fall turnover, total phosphorus and chlorophyll concentrations increased significantly in 1981 (Fig. 3). Increased phosphorus concentrations after turnover correlate with elevated chlorophyll concentrations in several

Fig. 7-3. The change in TP (squares) and pheophytin corrected chlorophyll a (circles) in the 0-3 m water layer at fall turnover (Sept. 1980) in anoxic Fitch Bay, Lake Memphremagog.


TP
20
15
10
TP (µg/L)
Chlorophyll
10
5
Chlorophyll (µg/L)
June
July
August
September
October

other lakes as well (Fig. 4). Moreover, in most cases the chlorophyll increased more rapidly with phosphorus than would be predicted by the general relationship between mean summer chlorophyll and vernal TP concentrations in phosphorus limited lakes (Dillon and Rigler 1974). This suggests that the proportion of available phosphorus added at turnover exceeds that for spring phosphorus in normal (oxic) lakes.

Partial thermocline erosion can also fertilize epilimnetic phytoplankton during summer. This has been described for anoxic Lake Mendota (Stauffer and Lee 1974), Lake Waramaug (Kortmann et al. 1982), Budd and Sisseton Lake (Stefan and Hanson 1981), and was observed in Lake Magog, Quebec (Chapter 5).

Phosphorus sufficient lakes: In many anoxic lakes, the surface SRP concentration increases after fall turnover (Fig. 5) and is correlated with hypolimnetic SRP concentration before turnover (Fig. 6). For Lake Magog, which becomes nitrogen-limited in late summer, I constructed a mass balance to find out how much of the hypolimnetic phosphorus is taken up by plankton, how much forms iron/ phosphorus particles and how much stays in the form of SRP (Chapter 5). It was determined that 30% was taken up by plankton, 30% formed iron/ phosphorus particles, 38% remained as SRP and 2% was lost by precipitation or represents inaccuracy in the budget.

It has been reported several times that in hypertrophic, nitrogen limited systems, nuisance bluegreen algae collapsed after destratification despite fertilization with upwelling

Fig. 7-4. The relationship between chlorophyll a and total phosphorus before and after fall turnover for four lakes. The line represents Dillon and Rigler's (1974) regression (log Chlo= 1.45×log TP - 1.14).

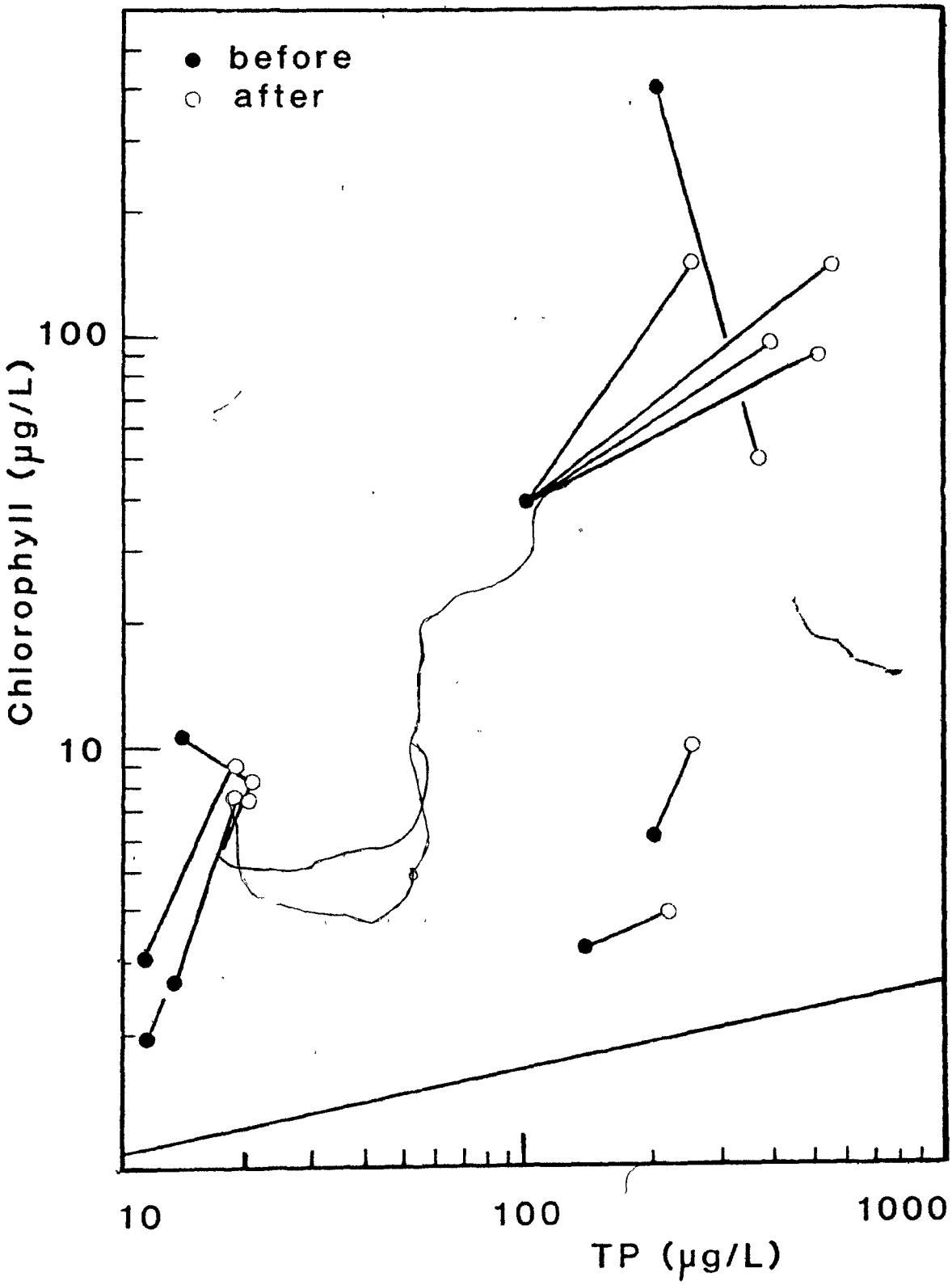

before
after
100
10
Chlorophyll (µg/L)
10
100
1000
TP (µg/L)

Fig. 7-5. Surface SRP concentration before and after fall turnover for lakes worldwide.

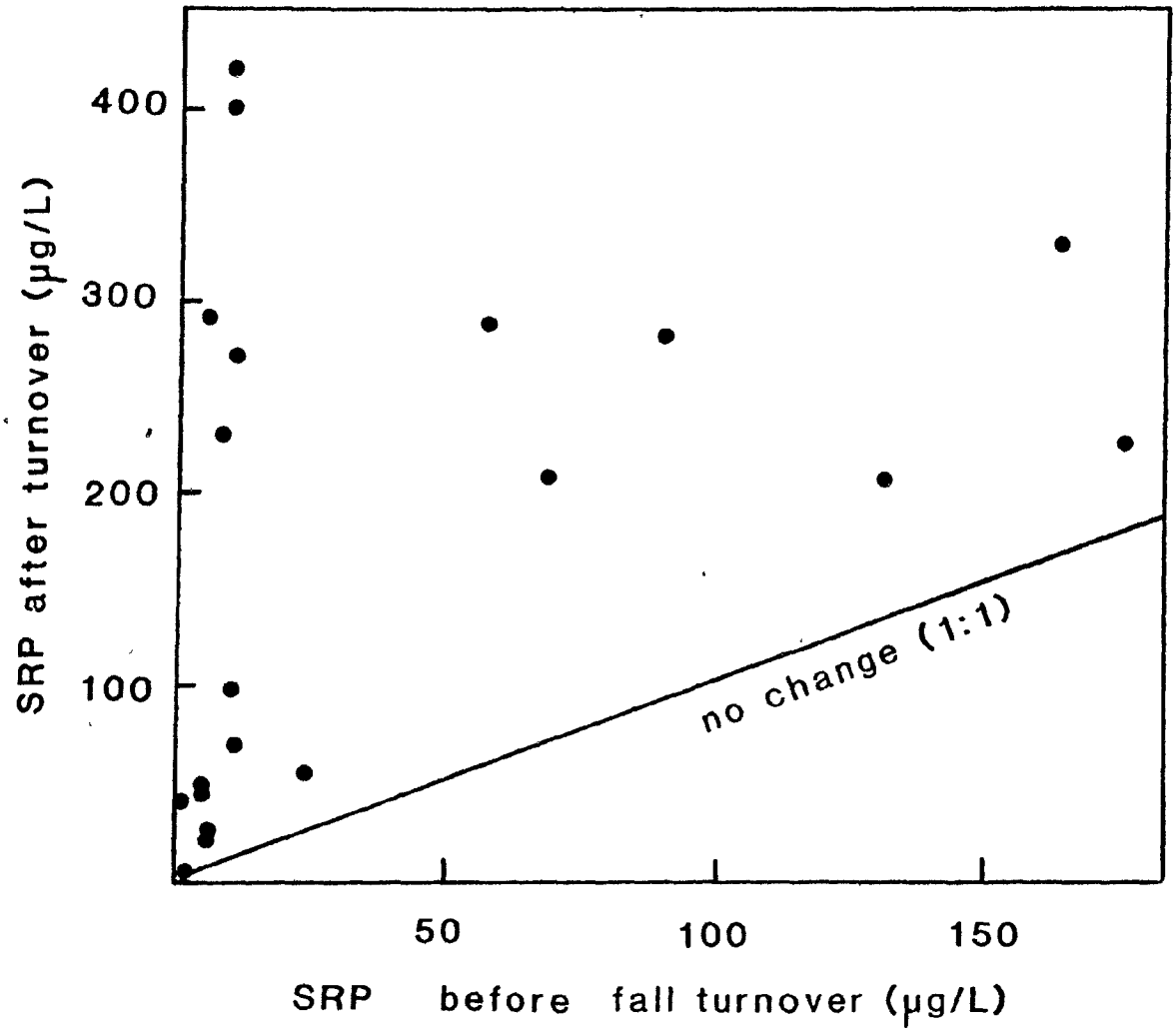
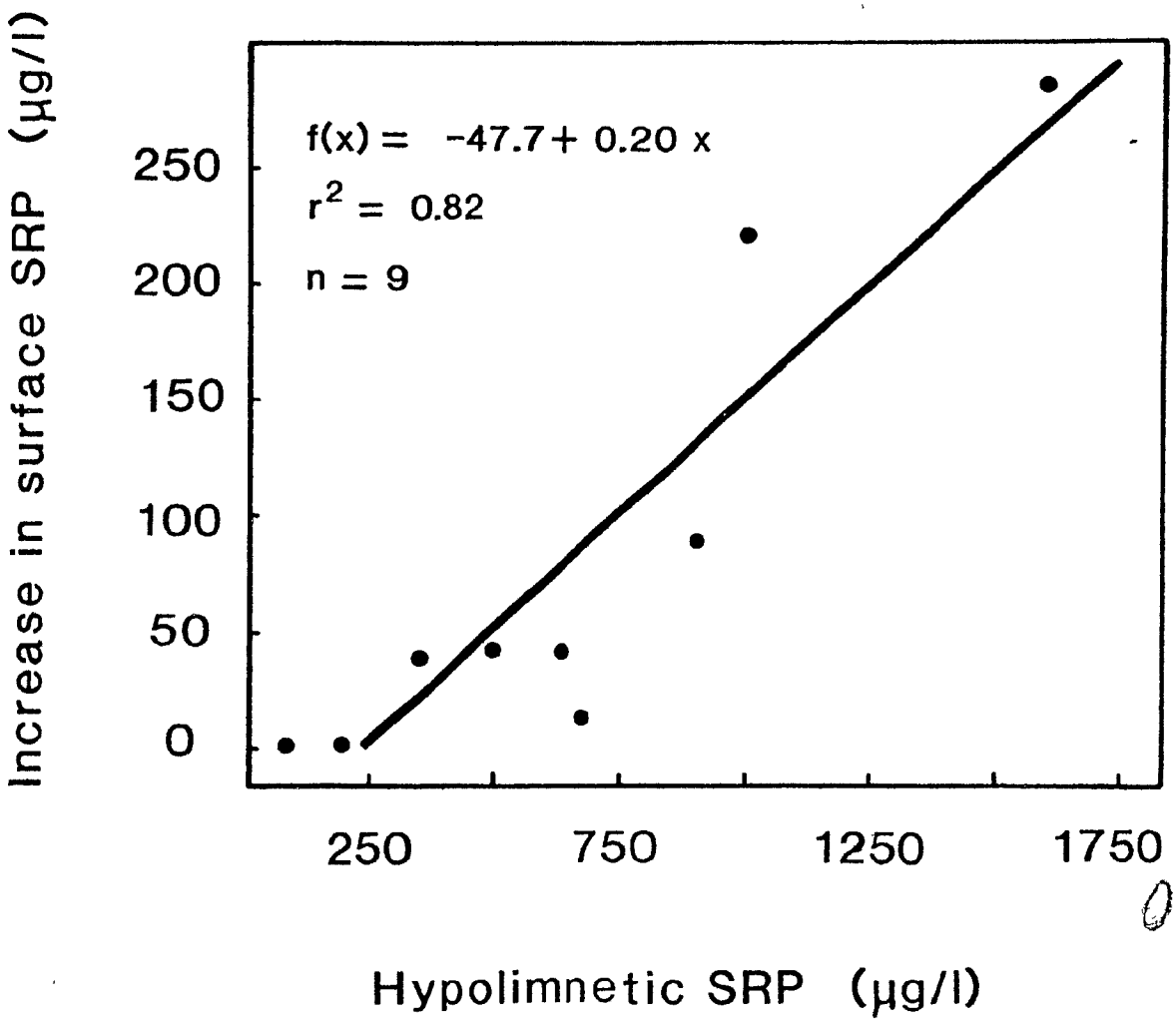

400
300
200
100
SRP after turnover (µg/L)
no change (1:1)
50
100
150
SRP before fall turnover (µg/L)

Fig. 7-6. The increase of surface SRP concentrations after fall turnover in relation to hypolimnetic SRP concentrations before turnover for worldwide lakes.


f(x) = -47.7 + 0.20 x
r² = 0.82
n = 9
Increase in surface SRP (µg/l)
250
200
150
100
50
0
250
750
1250
1750
Hypolimnetic SRP (µg/l)

phosphorus (Nichols et al. 1980; Robarts et al. 1982). In these systems most of the phosphorus was available SRP both before and after mixing. However the fertilizing effect of hypolimnetic phosphorus could have been overruled by physical processes.

5) The effect of lake morphometry and hydrology on availability:

Laboratory experiments showed (Chapter 5) that higher dilution of iron-rich hypolimnetic water increases the proportion of available hypolimnetic phosphorus. If a lake's morphometry and orientation relative to the prevailing wind allows gradual thermocline erosion starting early in the summer, the effect of internal phosphorus load can be high, since dilution would be large and algal growth conditions optimal (high light and temperature). This condition exists in Lake Waramaug (Kortmann et al. 1982), Lake Shagawa in the extraordinarily windy year 1974 (Larsen et al. 1979) and in Lake Magog, Quebec.

During complete fall or spring turnover the dilution of hypolimnetic iron could be reduced so that iron complexes might decrease the amount of available phosphorus. In addition, phytoplankton concentrations might not increase, despite any phosphorus enrichment, because they could be highly diluted by hypolimnetic water. The optimal volumetric proportions for enhanced algal growth considering the effect of this dilution alone can be predicted quantitatively by a model (Forsberg and Shapiro 1982). Applied to Fitch Bay 1981,

the model predicts increased phytoplankton biomass after fall turnover, because the epilimnion was large enough to cope with the dilution effect. An increase was observed (Fig. 3).

The higher the flushing rate, the more hypolimnetic phosphorus is likely to leave the lake. Such phosphorus is therefore not used by plankton after it is mixed into the whole lake. This is expressed quantitatively by the total phosphorus model developed for anoxic lakes in Chapter 6: Internal phosphorus load divided by the annual areal water load (q_s) represents the increase in average total phosphorus concentration which is due to internal phosphorus load. The agreement between the predicted and the observed changes show that such a correction is useful. Flushing seems to be particular important in Lake Magog (Chapter 5). I conclude that windfetch, ratio of epilimnetic and hypolimnetic volume and water load affect the utilization of hypolimnetic phosphorus.

6) The effect of lake geochemistry on the availability of hypolimnetic phosphorus:

In course of this study, I learned to distinguish between three lake-types with different geochemistry in their anaerobic hypolimnia (Table 3-1):

a) Lakes with iron-rich hypolimnia of intermediate hardness: Lake Magog and Fitch Bay of Lake Memphremagog

b) Lakes with iron-rich, colored, softwater hypolimnia: Little Clear, Chub and Blue Chalk on the Precambrian Shield.

c) Lakes with hydrogen sulfide rich, hardwater hypolimnia:

Glen Lake and Lake St. George.

This division is based on the behavior of hypolimnetic phosphorus after mixing into the surface water and affects the analysis of SRP (Chapter 3). Phosphorus in iron-rich lakes of intermediate hardness becomes adsorbed to ferric iron hydroxides and forms iron phosphorus particles which are retained by a 0.45 μm filter. In the second type, adsorption also takes place, but the resulting iron-phosphorus products pass a 0.45 μm filter and are colloidal (i.e. do not pass through dialysis tubing). In the third type, no soluble iron is present and no adsorption takes place.

Therefore, it can be generalized that in lakes with very low iron concentrations e.g. in hard water lakes with high hypolimnetic hydrogen sulfide concentrations, all the hypolimnetic SRP is available and remains so after intrusion into surface water. In lakes with detectable hypolimnetic iron concentrations, 90% of the hypolimnetic SRP is available, provided it is diluted at least ten fold at turnover. In the case of less dilution, a maximum phosphorus precipitation rate can be predicted from the ratio of hypolimnetic and epilimnetic volume or from the final iron concentration (Chapter 5).

Armstrong (1979) similarly distinguished anoxic lakes with high hypolimnetic iron concentration from those with no detectable iron. On theoretical grounds he suggested, that hypolimnetic phosphorus would be retained by an iron-rich lake (via precipitation), but would be flushed out in an iron-free, hardwater lake.

Phosphorus release rates might be related to sediment geochemistry. Armstrong (1979) suggested that the difference in these lake-types is probably a reflection of the sediment chemistry. I hypothesize that there are correlations between release rates of phosphorus or iron, and phosphorus or iron fractions in the sediments (e.g. oxalate, dithiocitrate or NaOH extractable fractions). Messer et al. (in press) correlated phosphorus release rates with NaOH extractable phosphorus in core tubes from sediments of several reservoirs. Even if dependent on sediment characteristics, the range of natural release rates is apparently narrow (Table 6-6).

7) The effect of timing of fall turnover on the availability:

The amount of upwelling hypolimnetic phosphorus which is incorporated in biomass likely depends on the growth conditions for the plankton. Since phosphorus, nitrogen and possibly other nutrients are supplied by the upwelling water, physical variables, like light and temperature, will then limit algal growth. It can be hypothesized that the earlier the fall turnover the more likely and the greater will be the phytoplankton response per increase of epilimnetic phosphorus, for a given latitude and altitude.

Suggested tests:

In this final section I want to propose some possible procedures to test the yet unverified hypotheses about sediment chemistry and timing of fall turnover. The following experimental studies could be conducted to test the influence of sediment chemistry on phosphorus release. This experiment is based upon the commonly accepted theory that phosphorus release is due to dissolved iron phosphorus compounds (Stumm and Leckie 1971; Syers et al. 1973) and that calcium-rich lakes do not accumulate phosphorus in the anoxic hypolimnia at the same rate (e.g. Lake Kinneret, Serruya 1978) as calcium-poor ones do. The release rate of phosphorus can be monitored in core tubes containing sediment and water, and then compared to different phosphorus fractions (in particular, extractions with NaOH, dithiocitrate and oxalate), iron fractions (extractions with dithiocitrate and oxalate) and calcium content in the same core. If this is done for a wide range in chemical composition, the hypothesis can be tested that the release rate of phosphorus from anoxic sediment surfaces is positively correlated to certain phosphorus and iron fractions, and negatively to calcium content.

The hypothesis that the increase of chlorophyll per increase in epilimnetic phosphorus is higher when fall turnover is earlier could be tested by regressing the ratio of increased chlorophyll to increased phosphorus, following turnover in phosphorus deficient lakes, against the date of fall turnover and latitude and altitude (to allow for geographical effects).

"Oxic" verses "anoxic" lakes:

This study suggests that anoxic lakes differ from oxic lakes because of internal phosphorus load. This is supported most clearly by the failure of models for oxic lakes to predict total phosphorus concentration and phosphorus retention in anoxic lakes (Chapter 6). However, the high trophy of anoxic lakes also reflects biological processes, not simply chemical phosphorus released from the sediments. Evidence for this has been collected by Shapiro (1979): anoxia can cause winterkill of fish (Schindler and Comita 1972) and reduces coldwater refugia for salmonids in the summer. This favours small planktivorous fish, like sunfish, smelt and alewife (Stewart et al. 1981), which prey upon large zooplankton, like Daphnia pulex and Mysis relicta (Janssen 1978; Janssen and Brandt 1980). Large zooplankton also lack a refugium because the hypolimnion is anoxic and hence rarely thrive in anoxic lakes. Consequently, smaller zooplankton tend to replace larger animals in anoxic lakes when planktivorous fish become abundant (Brooks and Dodson 1965; Wells 1970; Warshaw 1972). The smaller zooplankton (e.g. Bosmina, Ceriodaphnia, rotifers) prey upon smaller algae than larger ones (Schindler 1972), and consequently larger and colonial algae have an advantage in anoxic lakes. Such lakes could have higher phytoplankton biomass than oxic ones, at similar nutrient concentrations. This thesis does not address these biological interactions. Their effect on eutrophication of anoxic lakes has to be determined by further studies.

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Appendix A

Routinely measured characteristics of the study lakes. Julian day (Day), sampling depth (De, m), Temperature (T, ^{o}C), oxygen concentration (Ox, mg/L), standardized redox potential (EH, mv), pH; TP, SRP, TRP, TSP and BAP in µg/L; total iron (TFe), soluble iron (SFe), total manganese (TMn) and soluble manganese (SMn) in mg/L.

1.10 1.1 1. means missing value, data are not available.

Lake Magog, 1981

Day	De	T	Ox	EH	pH	TP	SRP	TRP	TSP	BAP	TFe	SFe	TMn	SMn
142.	2.	12.80	1.10	1.	1.10	37.68	0.75	1.10	1.10	1.10	1.10	1.10	1.10	1.10
142.	5.	11.00	1.10	1.	1.10	35.59	1.50	1.10	1.10	1.10	1.10	1.10	1.10	1.10
142.	8.	10.10	1.10	1.	1.10	31.94	1.65	1.10	1.10	1.10	1.10	1.10	1.10	1.10
142.	12.	9.70	1.10	1.	1.10	28.04	1.50	1.10	1.10	1.10	1.10	1.10	1.10	1.10
142.	16.	8.10	1.10	1.	1.10	47.56	13.17	1.10	1.10	1.10	1.10	1.10	1.10	1.10
154.	2.	17.40	1.10	1.	1.10	34.22	1.48	1.10	1.10	1.10	0.12	1.10	0.04	1.10
154.	5.	16.80	1.10	1.	1.10	38.28	1.43	1.10	1.10	1.10	0.10	1.10	0.03	1.10
154.	8.	11.90	1.10	1.	1.10	22.65	1.13	1.10	1.10	1.10	0.08	1.10	0.03	1.10
154.	12.	10.30	1.10	1.	1.10	29.33	1.83	1.10	1.10	1.10	1.10	1.10	1.10	1.10
154.	14.	10.00	1.10	1.	1.10	41.35	4.09	1.10	1.10	1.10	0.13	1.10	0.08	1.10
154.	16.	10.00	1.10	1.	1.10	78.87	14.00	1.10	1.10	1.10	1.10	1.10	1.10	1.10
160.	2.	17.60	9.00	1.	1.10	41.08	6.27	1.10	11.53	1.10	0.28	1.10	0.04	1.10
160.	5.	17.60	9.00	1.	1.10	41.20	6.19	1.10	11.30	1.10	0.19	1.10	0.05	1.10
160.	8.	14.20	8.10	1.	1.10	40.14	6.87	1.10	13.17	1.10	0.28	1.10	0.05	1.10
160.	12.	11.20	6.90	1.	1.10	39.44	6.27	1.10	10.70	1.10	0.21	1.10	0.11	1.10
160.	14.	10.90	6.50	1.	1.10	45.83	6.57	1.10	10.78	1.10	0.21	1.10	0.13	1.10
160.	16.	10.30	5.70	1.	1.10	62.93	13.14	1.10	18.19	4.38	0.29	1.10	0.25	1.10
168.	2.	19.80	1.10	1.	1.10	32.97	2.37	1.10	7.04	1.10	1.10	1.10	1.10	1.10
168.	5.	18.90	1.10	1.	1.10	28.93	1.60	1.10	6.89	1.10	1.10	1.10	1.10	1.10
168.	8.	13.60	1.10	1.	1.10	35.13	5.27	1.10	9.96	1.10	1.10	1.10	1.10	1.10
168.	12.	11.30	1.10	1.	1.10	42.39	12.39	1.10	16.32	1.10	1.10	1.10	1.10	1.10
168.	14.	10.50	1.10	1.	1.10	44.05	14.56	1.10	19.16	1.10	1.10	1.10	1.10	1.10
168.	16.	10.30	1.10	1.	1.10	88.20	36.87	1.10	41.62	1.10	1.10	1.10	1.10	1.10
176.	2.	20.00	13.00	1.	1.10	31.37	1.55	1.10	6.16	1.10	0.11	1.10	0.05	1.10
176.	5.	19.50	13.00	1.	1.10	33.00	1.86	1.10	5.79	1.10	0.10	1.10	0.05	1.10
176.	8.	19.50	13.00	1.	1.10	31.32	2.17	1.10	6.16	1.10	0.15	1.10	0.08	1.10
176.	12.	15.90	13.00	1.	1.10	57.63	13.98	1.10	16.94	1.10	0.26	1.10	0.22	1.10
176.	16.	12.50	5.50	1.	1.10	101.84	89.35	1.10	93.11	50.00	0.71	1.10	0.50	1.10
184.	2.	22.30	9.00	1.	1.10	41.06	14.24	1.10	21.44	1.10	0.06	1.10	0.04	1.10
184.	5.	20.50	15.00	1.	1.10	28.98	4.19	1.10	9.39	1.10	0.08	1.10	0.05	1.10
184.	8.	18.50	7.70	1.	1.10	54.25	2.69	1.10	6.86	1.10	0.19	1.10	0.14	1.10
184.	12.	12.00	3.60	1.	1.10	67.50	25.00	36.73	29.26	9.25	0.30	1.10	0.27	1.10
184.	14.	11.90	2.90	1.	1.10	110.75	66.77	85.30	71.08	1.10	0.53	1.10	0.36	1.10
184.	16.	10.50	2.10	1.	1.10	175.52	114.56	140.50	117.72	40.59	0.79	1.10	0.50	1.10
189.	2.	25.30	9.60	1.	1.10	32.52	6.95	1.10	12.37	1.10	0.10	1.10	0.04	1.10

Day	De	T	Ox	EH	pH	TP	SRP	TRP	TSP	BAP	TFe	SFe	TMn	SMn
189.	5.	24.50	9.80	1.	1.10	33.82	6.95	1.10	13.15	1.10	0.11	1.10	0.05	1.10
189.	8.	20.50	6.60	1.	1.10	47.40	7.40	1.10	14.65	1.10	0.11	1.10	0.05	1.10
189.	12.	13.00	1.90	1.	1.10	45.81	13.52	1.10	21.40	9.38	0.27	1.10	0.20	1.10
189.	14.	12.50	1.30	1.	1.10	179.23	123.26	1.10	140.59	1.10	0.86	1.10	0.51	1.10
189.	16.	12.00	1.00	1.	1.10	220.63	140.04	1.10	158.34	72.50	1.06	1.10	0.60	1.10
196.	2.	21.50	9.50	1.	1.10	28.25	6.04	6.40	11.74	1.10	0.11	1.10	0.03	1.10
196.	5.	22.00	8.60	1.	1.10	32.66	6.42	7.33	13.15	1.10	0.11	1.10	0.01	1.10
196.	8.	20.00	4.70	1.	1.10	64.73	32.80	39.54	39.71	1.10	0.24	1.10	0.12	1.10
196.	12.	12.50	0.90	1.	1.10	151.08	91.28	126.26	98.95	1.10	0.78	1.10	0.47	1.10
196.	14.	11.50	0.60	1.	1.10	237.12	138.43	211.16	147.97	1.10	1.20	1.10	0.58	1.10
196.	16.	11.00	0.60	1.	1.10	321.09	211.60	293.73	1.10	98.99	1.60	1.10	0.75	1.10
203.	2.	22.00	9.20	1.	1.10	34.97	3.98	4.76	11.74	4.50	0.15	1.10	0.03	1.10
203.	5.	22.50	9.30	1.	1.10	31.41	4.29	5.22	11.50	4.50	0.18	1.10	0.03	1.10
203.	8.	21.50	4.30	1.	1.10	86.06	52.92	66.33	59.43	1.10	0.36	1.10	0.17	1.10
203.	12.	13.50	0.70	1.	1.10	167.93	102.81	162.81	108.53	1.10	1.04	1.10	0.58	1.10
203.	14.	12.00	0.60	1.	1.10	241.11	118.05	238.67	124.87	1.10	1.40	1.10	0.63	1.10
203.	16.	11.50	0.60	1.	1.10	338.66	186.50	340.00	1.10	160.00	2.05	1.10	0.72	1.10
210.	16.	11.50	0.60	10.	6.80	483.87	416.54	1.10	1.10	1.10	2.43	1.10	0.76	1.10
211.	2.	20.40	9.60	1.	1.10	45.75	7.13	10.00	13.38	1.10	0.12	1.10	0.01	1.10
211.	5.	21.00	8.60	1.	1.10	44.08	7.50	9.56	13.69	1.10	0.13	1.10	0.0	1.10
211.	8.	21.50	8.90	1.	1.10	45.76	7.79	9.93	13.22	1.10	0.12	1.10	0.02	1.10
211.	12.	14.50	0.90	1.	1.10	184.04	1.10	142.65	1.10	1.10	0.90	1.10	0.62	1.10
211.	14.	13.00	0.70	1.	1.10	290.89	1.10	259.39	1.10	1.10	1.42	1.10	0.63	1.10
211.	16.	12.00	0.70	1.	1.10	446.70	356.10	414.51	366.33	343.00	2.27	1.10	0.75	1.10
216.	2.	22.20	10.40	1.	1.10	44.74	6.64	7.90	13.93	1.10	0.16	1.10	0.0	1.10
216.	5.	22.00	10.00	1.	1.10	40.43	5.21	6.95	12.29	6.99	0.17	1.10	0.0	1.10
216.	8.	21.00	5.60	1.	1.10	50.68	22.28	31.44	28.01	1.10	0.25	1.10	0.0	1.10
216.	12.	14.00	0.80	1.	1.10	251.03	235.61	271.50	1.10	192.50	1.27	1.10	0.67	1.10
216.	14.	12.50	0.70	1.	1.10	417.55	355.76	385.41	1.10	323.33	2.07	1.10	0.85	1.10
216.	16.	11.50	0.60	1.	1.10	557.74	531.29	565.62	1.10	468.00	2.82	1.10	0.73	1.10
223.	2.	21.50	11.00	1.	1.10	63.35	2.27	3.71	9.93	1.10	0.11	1.10	0.05	1.10
223.	5.	21.50	9.30	1.	1.10	33.13	6.82	8.11	11.15	1.10	0.13	1.10	0.03	1.10
223.	8.	20.50	4.50	1.	1.10	65.42	5.53	40.91	41.33	1.10	0.20	1.10	0.09	1.10
223.	10.	17.00	1.00	1.	1.10	126.55	78.36	96.27	89.51	109.00	0.33	1.10	0.69	1.10
223.	12.	14.50	0.60	1.	1.10	256.13	202.99	226.87	212.06	170.00	1.19	1.10	0.72	1.10

Day	De	T	Ox	EH	pH	TP	SRP	TRP	TSP	BAP	TFe	SFe	TMn	SMn
223.	14.	13.00	0.50	1.	1.10	401.06	361.19	373.88	364.63	1.10	2.07	1.10	0.73	1.10
223.	16.	11.50	0.50	1.	1.10	680.95	626.87	638.80	640.00	1.10	3.25	1.10	0.81	1.10
229.	2.	19.20	6.00	1.	1.10	45.53	8.33	9.79	13.55	5.17	0.09	1.10	0.05	1.10
229.	5.	20.00	5.40	1.	1.10	46.95	8.41	9.10	13.77	5.97	0.08	1.10	0.06	1.10
229.	8.	20.00	5.40	1.	1.10	43.65	8.72	9.17	13.62	1.10	0.10	1.10	0.07	1.10
229.	10.	19.50	0.0	1.	1.10	93.52	58.46	70.00	65.12	40.67	0.18	1.10	0.40	1.10
229.	12.	15.50	0.0	186.	6.00	299.62	253.85	272.31	248.95	1.10	1.42	1.10	0.76	1.10
229.	14.	14.00	0.0	62.	6.00	386.19	354.62	364.62	342.69	1.10	1.78	1.10	0.73	1.10
229.	16.	12.50	0.0	-53.	6.00	608.27	603.08	604.62	567.37	555.00	2.77	1.10	0.79	1.10
237.	2.	20.00	9.80	1.	1.10	44.25	3.52	6.01	8.96	1.10	0.04	1.10	0.0	1.10
237.	5.	20.00	9.60	1.	1.10	36.75	4.62	7.11	10.28	1.10	0.05	1.10	0.02	1.10
237.	8.	20.00	2.90	1.	1.10	40.48	11.14	14.15	16.01	1.10	0.06	1.10	0.05	1.10
237.	10.	18.50	0.0	192.	6.30	98.24	55.76	69.52	64.02	1.10	0.16	1.10	0.54	1.10
237.	12.	14.70	0.0	112.	6.00	343.73	268.65	304.13	273.19	1.10	1.55	1.10	0.83	1.10
237.	14.	14.00	0.0	-3.	6.30	459.76	417.81	441.71	422.05	1.10	2.43	1.10	0.75	1.10
237.	16.	12.50	0.0	22.	6.50	675.86	650.25	678.49	652.66	1.10	4.00	1.10	0.77	1.10
246.	2.	20.50	9.00	1.	1.10	36.75	4.44	5.52	10.18	1.10	0.05	1.10	0.01	1.10
246.	5.	20.50	9.50	1.	1.10	37.64	4.37	6.28	8.43	1.10	0.05	1.10	0.02	1.10
246.	8.	20.00	6.90	1.	1.10	41.96	12.03	15.71	17.07	1.10	0.08	1.10	0.03	1.10
246.	10.	18.00	1.70	1.	1.10	83.55	62.82	61.31	60.98	48.62	0.14	1.10	0.58	1.10
246.	12.	15.50	0.50	-39.	6.00	337.80	316.36	325.45	317.08	1.10	1.63	1.10	1.07	1.10
246.	14.	13.00	0.40	-44.	6.20	691.80	663.00	675.87	628.18	643.75	3.47	1.10	0.81	1.10
246.	16.	12.00	0.40	-39.	6.30	576.88	688.73	728.09	622.95	1.10	3.96	1.10	0.86	1.10
253.	2.	19.00	8.80	1.	1.10	39.82	6.20	9.77	1.10	1.10	0.03	0.0	0.01	0.0
253.	5.	19.50	8.10	1.	1.10	41.04	7.05	10.23	1.10	1.10	1.10	0.0	0.02	0.02
253.	8.	19.50	8.70	1.	1.10	45.13	7.75	12.25	1.10	1.10	0.11	1.10	0.02	1.10
253.	10.	19.50	7.90	350.	6.20	87.80	48.68	56.98	1.10	1.10	0.07	0.04	0.53	0.56
253.	11.	18.00	0.50	1.	1.10	128.18	94.50	107.62	1.10	1.10	0.10	0.20	1.14	1.14
253.	12.	15.00	0.40	1.	1.10	356.66	334.59	350.67	1.10	1.10	1.59	1.51	1.43	1.12
253.	14.	12.50	0.30	1.	1.10	611.82	614.05	623.24	1.10	1.10	3.10	3.07	0.86	0.86
253.	16.	11.50	0.20	-10.	6.10	722.83	694.45	684.49	1.10	1.10	3.98	3.87	0.81	0.81
258.	3.	18.50	10.40	1.	1.10	48.33	7.20	9.96	1.10	1.10	0.06	0.0	0.04	0.03
258.	8.	18.40	9.60	1.	1.10	44.00	8.75	12.51	1.10	1.10	0.03	0.01	0.09	0.03
258.	10.	17.50	5.00	270.	6.60	88.28	42.10	52.09	1.10	1.10	0.16	0.07	0.35	0.30
258.	12.	14.00	0.40	12.	6.60	450.12	426.92	470.00	1.10	1.10	2.19	2.05	1.00	1.00

Day	De	T	Ox	EH	pH	TP	SRP	TRP	TSP	BAP	TFe	SFe	TMn	SMn
258.	14.	12.50	0.30	-20.	6.50	670.26	666.15	658.46	1.10	1.10	3.42	3.37	0.91	0.90
258.	16.	11.50	0.30	-20.	6.50	718.68	698.46	692.31	1.10	1.10	4.27	3.88	0.87	0.87
261.	3.	18.00	11.40	1.	1.10	37.36	7.28	9.44	1.10	1.10	0.04	1.10	0.05	1.10
261.	5.	18.00	11.20	1.	1.10	46.30	6.73	9.99	1.10	1.10	0.07	1.10	0.07	1.10
261.	10.	18.00	9.70	1.	1.10	85.17	15.03	24.85	1.10	1.10	0.10	1.10	0.14	1.10
264.	2.	16.00	10.00	1.	1.10	53.66	1.10	1.10	1.10	1.10	0.09	1.10	0.08	1.10
264.	5.	16.50	10.00	1.	1.10	55.13	11.40	17.43	1.10	1.10	0.14	0.04	0.09	0.04
264.	10.	16.90	9.80	1.	1.10	54.07	12.47	17.33	1.10	1.10	0.10	1.10	0.08	1.10
264.	11.	16.90	9.30	431.	6.50	62.62	17.71	25.87	1.10	1.10	0.08	0.03	0.15	0.08
264.	12.	15.50	0.90	101.	6.30	378.93	331.59	378.74	1.10	1.10	1.68	2.00	1.12	1.17
264.	14.	12.50	0.40	41.	6.30	605.98	568.87	623.63	1.10	1.10	2.89	2.83	0.93	1.00
264.	16.	11.50	0.30	4.	6.30	658.00	725.99	715.65	1.10	1.10	4.21	4.08	0.87	0.85
266.	5.	15.50	8.80	1.	1.10	62.77	14.53	22.09	1.10	1.10	0.12	0.03	0.17	0.06
266.	10.	15.60	8.80	1.	1.10	63.34	15.44	22.09	1.10	1.10	0.12	0.07	0.13	0.04
266.	11.	15.60	8.80	1.	1.10	103.36	42.51	63.61	48.13	1.10	0.28	0.19	0.23	0.17
266.	12.	15.60	7.50	364.	6.30	270.87	134.71	235.63	1.10	1.10	1.09	0.45	0.71	0.62
266.	13.	12.50	0.30	-11.	6.30	610.53	584.46	622.22	1.10	1.10	3.18	2.17	1.03	0.75
266.	14.	12.00	0.0	-31.	6.20	627.95	682.62	683.38	1.10	1.10	3.80	3.57	0.98	0.92
266.	16.	11.00	0.0	-50.	6.30	669.52	749.83	749.07	1.10	1.10	4.75	4.79	0.99	0.88
268.	5.	14.50	9.00	1.	1.10	86.21	26.21	42.17	1.10	1.10	0.26	0.02	0.21	0.01
268.	10.	14.60	8.60	1.	1.10	84.06	27.86	44.35	1.10	1.10	0.24	0.11	0.17	0.04
268.	12.	14.50	7.60	481.	6.40	160.82	88.10	128.16	1.10	1.10	0.66	0.39	0.22	0.17
268.	13.	13.60	2.00	408.	6.30	337.33	148.49	185.75	1.10	1.10	1.53	0.67	0.54	0.50
268.	14.	12.80	0.60	182.	6.40	563.48	291.88	542.49	1.10	1.10	2.73	1.47	0.76	0.73
268.	16.	11.20	0.30	54.	6.40	622.64	691.38	695.81	1.10	1.10	3.91	3.54	0.89	0.82
273.	5.	12.80	10.20	1.	1.10	80.18	19.63	32.69	1.10	11.20	0.22	0.06	0.10	0.03
273.	10.	13.00	10.20	1.	1.10	78.62	20.15	35.37	1.10	1.10	0.20	0.03	0.10	0.02
273.	12.	13.10	10.20	1.	1.10	78.92	19.48	33.13	1.10	1.10	0.31	0.03	0.11	0.02
273.	14.	13.20	10.20	353.	6.60	76.21	20.30	33.88	1.10	1.10	0.24	0.08	0.08	0.05
273.	15.	12.40	9.40	350.	6.60	90.73	20.00	34.93	1.10	1.10	1.10	0.08	1.10	0.03
273.	16.	11.80	1.00	53.	6.40	647.53	605.88	657.48	1.10	1.10	3.36	2.87	1.02	1.00
275.	2.	12.90	9.70	1.	1.10	82.47	18.91	32.70	1.10	1.10	0.20	0.13	0.11	0.03
275.	5.	12.50	9.20	1.	1.10	81.74	19.60	34.00	1.10	1.10	0.22	0.14	0.10	0.05
275.	5.	12.80	9.70	1.	1.10	84.56	19.60	33.77	1.10	1.10	0.20	0.15	0.11	0.04
275.	10.	12.50	9.20	1.	1.10	79.32	17.23	31.70	1.10	1.10	0.18	0.15	0.10	0.05
275.	12.	12.50	9.30	1.	1.10	76.02	15.70	30.17	1.10	1.10	0.18	0.14	0.11	0.04

Day	De	T	Ox	EH	pH	TP	SRP	TRP	TSP	BAP	TFe	SFe	TMn	SMn
275.	14.	12.00	9.70	1.	1.10	70.94	12.63	24.35	1.10	1.10	0.17	0.11	0.08	0.02
275.	16.	11.50	9.90	424.	6.80	61.80	14.86	22.97	1.10	1.10	0.17	1.10	0.09	1.10
281.	5.	11.40	10.60	1.	1.10	77.44	13.63	23.75	1.10	1.10	0.21	0.10	0.06	0.04
281.	10.	11.40	11.20	1.	1.10	75.99	14.64	24.53	1.10	1.10	0.22	0.11	0.04	0.04
281.	12.	11.40	11.20	1.	1.10	75.58	14.02	23.83	1.10	1.10	0.20	0.10	0.07	0.02
281.	14.	11.40	11.20	1.	1.10	75.89	13.32	23.83	1.10	1.10	0.17	0.10	0.02	0.03
281.	16.	11.40	11.20	1.	1.10	77.86	14.25	24.92	1.10	1.10	0.18	0.12	0.04	0.05

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Day	De	T	Ox	EH	pH	TP	SRP	TRP	TSP	TFe	SFe	TMn	SMn
124.	2.	8.00	9.00	480.	1.10	11.97	1.10	1.10	1.10	1.10	1.10	1.10	1.10
124.	5.	6.70	9.00	480.	1.10	15.20	1.10	1.10	1.10	1.10	1.10	1.10	1.10
124.	10.	10.00	7.90	480.	1.10	15.39	1.10	1.10	1.10	1.10	1.10	1.10	1.10
124.	14.	5.00	7.90	480.	1.10	13.77	1.10	1.10	1.10	1.10	1.10	1.10	1.10
132.	2.	1.10	9.00	480.	1.10	19.70	1.10	1.10	1.10	1.10	1.10	1.10	1.10
132.	5.	1.10	9.00	480.	1.10	21.15	1.10	1.10	1.10	1.10	1.10	1.10	1.10
132.	10.	1.10	7.90	480.	1.10	12.73	1.10	1.10	1.10	1.10	1.10	1.10	1.10
132.	14.	1.10	7.90	480.	1.10	15.81	1.10	1.10	1.10	1.10	1.10	1.10	1.10
140.	2.	1.10	9.00	480.	1.10	16.38	1.10	1.10	1.10	1.10	1.10	1.10	1.10
140.	5.	1.10	9.10	480.	1.10	15.05	1.10	1.10	1.10	1.10	1.10	1.10	1.10
140.	10.	1.10	7.90	480.	1.10	12.01	1.10	1.10	1.10	1.10	1.10	1.10	1.10
140.	14.	1.10	7.80	480.	1.10	12.20	1.10	1.10	1.10	1.10	1.10	1.10	1.10
146.	2.	13.50	9.00	480.	1.10	12.72	1.10	1.10	1.10	1.10	1.10	1.10	1.10
146.	5.	12.20	9.00	480.	1.10	11.18	1.10	1.10	1.10	1.10	1.10	1.10	1.10
146.	10.	9.90	7.90	480.	1.10	11.23	1.10	1.10	1.10	1.10	1.10	1.10	1.10
146.	14.	8.00	7.00	480.	1.10	15.87	1.10	1.10	1.10	1.10	1.10	1.10	1.10
152.	2.	17.00	9.00	480.	1.10	10.30	1.10	1.10	1.10	1.10	1.10	1.10	1.10
152.	5.	13.80	9.00	480.	1.10	15.60	1.10	1.10	1.10	1.10	1.10	1.10	1.10
152.	10.	9.20	7.90	480.	1.10	12.46	1.10	1.10	1.10	1.10	1.10	1.10	1.10
152.	14.	7.80	7.00	480.	1.10	14.33	1.10	1.10	1.10	1.10	1.10	1.10	1.10
159.	3.	17.00	8.50	480.	1.10	11.45	0.0	1.10	1.10	0.03	1.10	0.0	1.10
159.	10.	9.80	7.90	480.	1.10	10.55	0.0	1.10	1.10	0.03	1.10	0.0	1.10
159.	12.	9.10	7.70	480.	1.10	11.60	0.0	1.10	1.10	0.04	1.10	0.04	1.10
159.	15.	8.30	6.80	1.	1.10	15.08	0.63	1.10	1.10	0.09	1.10	0.10	1.10
167.	3.	19.90	9.00	480.	1.10	25.15	0.0	1.10	3.82	1.10	1.10	1.10	1.10
167.	10.	13.20	7.80	480.	1.10	11.95	0.0	1.10	2.75	1.10	1.10	1.10	1.10
167.	12.	11.80	7.80	480.	1.10	8.62	0.0	1.10	2.77	1.10	1.10	1.10	1.10
167.	15.	10.90	6.20	1.	1.10	12.02	1.50	1.10	3.67	1.10	1.10	1.10	1.10
175.	3.	18.90	9.00	480.	1.10	15.02	0.0	1.10	2.49	0.05	1.10	0.03	1.10
175.	10.	15.20	7.70	480.	1.10	14.08	0.0	1.10	2.27	0.04	1.10	0.04	1.10
175.	12.	10.10	7.00	480.	1.10	11.25	0.0	1.10	2.27	0.04	1.10	0.05	1.10
175.	15.	8.10	5.60	1.	1.10	15.51	3.75	1.10	5.87	0.12	1.10	0.27	1.10
181.	3.	21.00	9.00	480.	1.10	12.92	0.0	1.10	2.79	1.10	1.10	1.10	1.10
181.	10.	17.50	7.60	480.	1.10	13.62	0.0	1.00	2.96	0.04	1.10	0.03	1.10
181.	12.	11.50	6.70	1.	1.10	14.11	1.54	3.60	4.02	0.10	1.10	0.11	1.10
181.	15.	9.00	4.90	1.	1.10	18.96	3.09	7.60	5.71	0.13	1.10	0.35	1.10

Day	De	T	Ox	EH	pH	TP	SRP	TRP	TSP	TFe	SFe	TMn	SMn
187.	3.	23.00	9.00	480.	1.10	11.10	0.0	1.10	2.47	0.0	1.10	0.04	1.10
187.	10.	12.50	7.80	480.	1.10	10.34	0.0	1.10	2.15	0.04	1.10	0.05	1.10
187.	12.	10.50	6.50	1.	1.10	12.90	0.0	1.10	2.23	0.05	1.10	0.05	1.10
187.	15.	8.50	2.90	1.	1.10	20.11	2.66	1.10	5.85	0.26	1.10	0.56	1.10
194.	3.	22.40	9.00	480.	1.10	24.23	0.0	1.10	1.52	0.05	1.10	0.0	1.10
194.	10.	18.00	6.70	1.	1.10	11.47	0.0	1.10	1.30	0.09	1.10	0.02	1.10
194.	12.	1.10	6.00	1.	1.10	13.43	1.17	1.10	2.38	0.19	1.10	0.40	1.10
194.	15.	1.10	2.20	1.	1.10	34.57	6.37	1.10	7.73	0.67	1.10	0.76	1.10
197.	15.	9.60	2.40	1.	6.80	1.10	5.02	1.10	1.10	1.10	1.10	1.10	1.10
201.	3.	1.10	1.10	1.	1.10	16.69	0.16	0.44	2.99	0.07	1.10	0.01	1.10
201.	10.	1.10	1.10	1.	1.10	14.41	0.47	0.59	3.85	0.08	1.10	0.01	1.10
201.	12.	1.10	1.10	1.	1.10	10.23	0.71	0.59	3.07	0.08	1.10	0.14	1.10
201.	15.	1.10	1.10	1.	1.10	33.33	7.60	18.53	10.90	0.81	1.10	0.92	1.10
209.	3.	23.00	9.00	480.	1.10	7.50	0.0	0.88	2.79	0.0	1.10	0.05	1.10
209.	10.	19.50	5.60	1.	1.10	10.76	0.0	0.59	3.02	0.02	1.10	0.09	1.10
209.	12.	13.00	4.50	1.	1.10	6.09	0.0	0.88	2.57	0.01	1.10	0.23	1.10
209.	15.	8.50	1.00	390.	6.80	24.25	4.70	9.63	7.79	0.41	1.10	0.80	1.10
212.	15.	1.10	1.00	1.	1.10	79.46	15.27	1.10	1.10	1.43	1.10	1.16	1.10
217.	3.	23.00	9.40	480.	1.10	10.11	0.0	0.47	2.26	0.05	1.10	0.0	1.10
217.	10.	19.30	5.00	1.	1.10	8.45	0.0	0.47	2.19	0.04	1.10	0.0	1.10
217.	12.	15.00	3.50	1.	1.10	12.48	0.47	1.40	2.49	0.07	1.10	0.17	1.10
217.	15.	10.00	1.20	300.	6.60	113.93	22.40	96.74	22.63	1.05	1.10	1.28	1.10
219.	15.	1.10	1.10	1.	1.10	30.20	5.27	15.50	1.10	1.10	1.10	1.10	1.10
224.	3.	21.70	9.50	480.	1.10	12.35	0.0	0.0	3.37	0.02	1.10	0.03	1.10
224.	10.	20.20	5.30	1.	1.10	10.72	0.0	1.10	2.55	0.04	1.10	0.06	1.10
224.	12.	15.00	3.40	1.	1.10	12.20	0.0	0.76	2.84	0.03	1.10	0.21	1.10
224.	14.	10.70	1.40	423.	1.10	26.52	5.34	15.59	9.88	0.38	1.10	0.84	1.10
231.	3.	20.50	8.90	480.	1.10	10.67	0.0	0.76	1.12	0.05	1.10	0.03	1.10
231.	10.	20.00	7.90	480.	1.10	13.41	0.0	1.06	2.11	0.12	1.10	0.06	1.10
231.	12.	13.30	2.10	1.	1.10	7.48	0.38	0.68	1.12	0.05	1.10	0.16	1.10
231.	15.	9.50	0.70	1.	1.10	34.97	7.13	19.27	5.71	0.48	1.10	1.18	1.10
231.	15.	1.10	1.10	1.	1.10	28.39	5.31	17.45	4.95	1.10	1.10	1.10	1.10

Day	De	T	Ox	EH	pH	TP	SRP	TRP	TSP	TFe	SFe	TMn	SMn
238.	3.	20.50	9.50	480.	1.10	11.40	0.40	0.52	2.86	0.0	1.10	0.02	1.10
238.	10.	18.50	4.90	1.	1.10	13.22	0.30	0.30	2.32	0.01	1.10	0.09	1.10
238.	12.	13.00	1.70	1.	1.10	9.61	0.44	0.30	2.16	0.05	1.10	0.09	1.10
238.	15.	8.50	0.40	192.	6.30	138.24	90.34	124.19	1.10	1.10	1.31	1.10	2.12
238.	15.	8.50	0.40	232.	6.30	87.79	47.57	74.04	54.47	0.14	1.10	0.40	1.10
238.	15.	8.50	0.40	352.	6.20	50.44	15.41	33.92	19.29	1.10	1.10	1.10	1.10
239.	15.	1.10	0.40	162.	6.20	1.10	100.60	1.10	1.10	1.10	1.10	1.10	1.10
245.	2.	21.00	9.20	480.	1.10	14.07	0.0	0.0	2.79	0.01	1.10	0.0	1.10
245.	10.	20.00	8.20	480.	1.10	11.91	0.0	0.45	2.65	0.03	1.10	0.0	1.10
245.	12.	13.50	0.70	1.	1.10	10.93	0.0	0.61	3.24	0.02	1.10	0.11	1.10
245.	15.	9.00	0.50	137.	6.10	158.53	114.61	135.81	115.29	1.17	1.10	2.03	1.10
247.	15.	1.10	0.40	1.	1.10	1.10	102.27	114.16	1.10	1.65	1.10	2.44	1.10
245.	15.	9.00	0.50	112.	6.20	1.10	91.29	114.31	94.41	1.10	1.10	1.10	1.10
245.	15.	9.00	0.50	137.	6.30	114.27	71.61	97.20	77.35	1.10	1.10	1.10	1.10
254.	3.	19.00	9.00	480.	1.10	14.40	0.0	0.0	1.37	0.0	0.0	0.0	0.03
254.	10.	19.00	8.00	480.	1.10	12.25	0.0	0.0	1.74	0.0	0.0	0.02	0.02
254.	12.	12.50	0.50	1.	1.10	16.95	1.16	2.16	5.21	0.0	0.0	0.0	0.01
254.	13.	11.50	0.50	1.	1.10	20.32	3.31	11.47	6.89	0.22	0.04	0.66	0.77
254.	15.	9.00	0.20	160.	6.20	110.34	82.45	96.69	1.10	1.45	1.10	2.30	1.10
254.	15.	9.00	0.20	30.	1.10	207.25	166.20	186.76	176.42	1.10	2.27	1.10	2.50
260.	3.	17.60	8.30	480.	1.10	14.66	0.0	1.09	2.32	0.0	0.04	0.03	0.01
260.	10.	18.00	8.00	480.	1.10	12.60	0.0	1.16	2.32	0.0	0.01	0.04	0.0
260.	12.	13.00	0.40	381.	6.10	18.48	1.71	7.91	1.10	0.18	0.01	0.61	0.59
260.	13.	10.20	0.30	376.	6.10	30.09	3.41	17.84	1.10	0.36	0.06	1.03	0.96
260.	14.	9.00	0.30	261.	6.20	46.45	14.59	31.50	1.10	0.51	0.23	1.65	1.64
260.	15.	8.50	0.20	1.	6.30	134.10	96.04	107.06	1.10	1.50	1.10	2.41	1.10
260.	15.	8.50	0.20	1.	6.30	166.90	132.97	149.73	1.10	1.10	1.95	1.10	2.52
267.	3.	15.00	9.40	1.	1.10	9.94	0.0	0.77	2.50	0.0	0.01	0.08	0.01
267.	10.	15.20	9.40	1.	1.10	11.58	0.0	0.77	2.50	0.0	0.0	0.07	0.02
267.	12.	15.00	9.10	261.	6.60	13.22	1.38	1.99	1.10	1.10	0.02	1.10	0.06
267.	13.	13.50	2.50	291.	6.50	14.10	1.99	4.13	1.10	1.10	0.02	1.10	0.33
267.	14.	10.50	0.70	241.	6.40	44.34	15.60	27.83	1.10	0.33	0.15	1.60	1.55
267.	15.	8.00	0.40	-39.	6.30	241.42	195.81	211.31	1.10	2.78	2.55	2.75	2.57
267.	16.	8.00	0.40	-39.	6.30	262.63	225.02	238.62	1.10	3.07	2.96	2.76	2.78

Day	De	T	Ox	EH	pH	TP	SRP	TRP	TSP	TFe	SFe	TMn	SMn
272.	3.	14.30	9.60	1.	1.10	1.10	0.0	0.61	2.68	0.0	0.0	0.06	0.02
272.	10.	14.50	9.70	1.	1.10	11.62	0.0	0.99	2.68	0.0	0.02	0.06	0.02
272.	12.	14.50	9.80	442.	6.40	15.44	0.61	1.97	1.10	0.0	0.01	0.07	0.03
272.	13.	14.10	8.90	442.	6.40	18.70	2.28	5.16	1.10	0.03	0.05	0.32	0.24
272.	14.	10.60	1.50	223.	6.30	57.48	37.33	46.74	1.10	0.50	0.45	2.16	2.06
272.	15.	9.60	0.70	103.	6.30	83.65	61.91	70.11	1.10	0.83	0.72	2.39	2.23
282.	3.	11.00	10.00	1.	1.10	23.08	1.16	4.32	5.08	0.13	0.01	0.12	0.03
282.	10.	11.00	10.10	1.	1.10	19.72	1.00	3.78	5.08	0.08	0.0	0.10	0.03
282.	12.	11.10	10.10	1.	1.10	20.28	1.08	3.16	4.06	0.07	0.01	0.12	0.03
282.	15.	10.50	7.00	439.	6.60	20.59	1.47	3.32	3.77	0.07	0.01	0.16	0.03

Jack Lake, Williamsbay, 1982

Day	De	T	Ox	EH	pH	TP	SRP	TRP	TSP	TFe	SFe	TMn	Fe^{2+}
237.	5.	20.00	9.00	336.	1.10	8.16	0.0	0.0	0.58	0.19	0.03	0.02	0.0
237.	10.	6.00	1.20	352.	1.10	26.33	1.10	1.32	2.92	0.19	0.06	0.16	0.0
237.	12.	5.00	0.0	315.	1.10	23.32	1.32	0.88	2.77	0.18	0.03	0.30	0.03
237.	14.	4.00	0.0	69.	1.10	18.21	3.80	2.92	4.66	0.17	0.03	0.37	0.08
237.	16.	4.00	0.0	10.	1.10	25.47	10.67	9.94	13.70	0.22	0.05	0.43	0.12
237.	18.	4.00	0.0	0.	1.10	50.28	39.04	37.87	43.15	0.31	0.19	0.65	0.17
237.	20.	4.00	0.0	2.	1.10	87.27	73.68	71.20	78.57	0.33	1.10	0.78	0.36
237.	20.	4.00	0.0	0.	1.10	91.15	74.56	72.08	79.74	0.37	0.19	0.76	1.10
237.	20.	4.00	0.0	1.	1.10	1.10	83.92	79.53	88.77	1.10	1.10	1.10	1.10
265.	5.	16.10	8.10	1.	1.10	8.97	0.44	0.0	1.10	0.0	0.20	0.02	1.10
265.	10.	9.20	0.50	406.	6.95	26.73	3.77	3.91	1.10	0.0	0.0	0.21	0.02
265.	12.	7.00	0.0	332.	6.99	24.18	1.40	0.30	1.10	0.05	0.0	0.40	0.06
265.	14.	6.20	0.0	-45.	6.97	22.59	1.74	1.74	1.10	0.10	0.04	0.43	0.12
265.	16.	6.00	0.0	-51.	6.97	36.11	19.71	22.46	1.10	0.14	0.15	0.48	0.21
265.	18.	5.60	0.0	-52.	6.94	66.71	48.12	52.61	1.10	0.21	0.20	0.60	0.29
265.	20.	5.00	0.0	-42.	6.75	113.62	81.44	95.65	1.10	0.38	0.30	0.72	1.10
265.	20.	5.00	0.0	-54.	6.92	121.81	88.41	100.29	1.10	0.30	0.23	0.70	0.39
265.	20.	5.00	0.0	-50.	6.90	114.44	90.44	97.10	1.10	0.28	1.10	0.72	1.10

Lake St. George, West Basin, 1982

Day	De	T	Ox	EH	pH	TP	SRP	TRP	TFe	TMn
154.	6.	5.00	0.30	1.	1.10	72.78	1.10	1.10	1.10	1.10
154.	12.	4.00	0.0	-118.	1.10	612.98	1.10	1.10	1.10	1.10
155.	3.	17.00	9.00	1.	1.10	22.10	1.10	1.10	1.10	1.10
155.	6.	4.50	0.0	353.	1.10	75.25	0.0	4.02	0.04	0.24
155.	8.	4.50	0.0	-88.	1.10	65.23	3.95	8.12	0.37	0.71
155.	10.	4.00	0.0	-113.	1.10	400.71	1.10	1.10	0.47	0.53
155.	10.	4.00	0.0	-68.	1.10	184.06	1.10	1.10	0.18	0.36
155.	12.	4.00	0.0	-188.	1.10	681.81	1.10	1.10	0.49	0.50
155.	3.	17.00	9.00	1.	1.10	25.54	1.10	1.10	0.0	0.01
155.	6.	4.50	0.0	42.	1.10	71.96	1.10	1.10	0.07	0.17
155.	10.	4.00	0.0	-168.	1.10	349.74	1.10	1.10	0.25	0.55
174.	3.	18.00	10.00	1.	1.10	23.13	1.10	1.10	0.06	0.01
174.	6.	5.50	0.60	-308.	1.10	42.47	1.10	1.10	0.04	0.15
174.	10.	4.00	0.0	-438.	1.10	474.25	1.10	1.10	0.22	0.49
174.	12.	4.00	0.0	-458.	1.10	709.85	1.10	661.57	1.10	1.10
175.	12.	4.00	0.0	-138.	1.10	1.10	635.00	1.10	1.10	1.10
175.	12.	4.00	0.0	-138.	1.10	1.10	625.71	623.00	1.10	1.10
175.	12.	4.00	0.0	-138.	1.10	1.10	591.00	581.00	1.10	1.10
175.	12.	4.00	0.0	-138.	1.10	710.60	619.00	617.00	1.10	1.10
175.	12.	4.00	0.0	-138.	1.10	718.00	639.00	646.00	1.10	1.10
180.	2.	18.50	11.50	382.	8.26	26.23	1.30	1.10	0.03	0.02
180.	6.	6.30	0.90	384.	7.24	82.91	1.36	1.10	0.0	0.22
180.	8.	4.00	0.30	-98.	7.18	80.34	1.66	2.71	0.09	0.93
180.	10.	4.00	0.30	-128.	6.90	365.97	341.54	1.10	0.30	0.55
180.	12.	4.00	0.30	-128.	6.80	623.49	636.16	1.10	0.24	0.52
180.	12.	4.00	0.30	-133.	6.80	621.93	1.10	1.10	0.20	0.52
186.	2.	21.00	12.20	262.	7.98	24.49	0.61	0.30	0.05	0.03
186.	6.	6.00	0.50	292.	7.00	41.75	0.15	2.44	0.05	0.10
186.	8.	4.00	0.30	-108.	6.77	58.32	1.10	1.10	0.15	0.82
186.	10.	4.00	0.0	-218.	6.62	307.30	256.92	1.10	0.22	0.58
186.	10.	4.00	0.0	-188.	6.60	419.15	352.31	1.10	0.17	0.56
186.	12.	4.00	0.0	-368.	6.60	676.86	656.92	1.10	0.20	0.53
186.	12.	4.00	0.0	-428.	6.54	676.37	672.31	1.10	0.22	0.55
214.	2.	23.50	7.50	362.	7.40	21.85	0.0	0.0	0.10	0.0
214.	6.	12.00	0.0	362.	6.30	83.38	0.0	4.07	0.10	0.42
214.	8.	9.00	0.0	-153.	6.50	128.45	95.83	100.75	0.20	0.81
214.	10.	7.50	0.0	-78.	6.50	397.14	338.81	350.75	0.20	0.51
214.	12.	7.10	0.0	-218.	6.60	414.76	343.28	347.76	0.20	0.59
214.	12.	7.10	0.0	-210.	6.60	408.57	343.28	349.25	0.30	0.51
214.	12.	7.10	0.0	-218.	6.60	1.10	344.78	347.76	1.10	1.10
269.	2.	15.60	7.50	1.	1.10	22.01	0.64	0.30	0.0	0.01
269.	6.	11.00	0.0	227.	6.98	133.61	22.88	23.72	0.0	0.93
269.	8.	9.20	0.0	-38.	6.96	134.78	54.89	59.73	0.09	0.71
269.	10.	8.80	0.0	-78.	6.96	128.94	63.79	71.15	0.10	0.75
269.	12.	8.50	0.0	-119.	6.89	163.18	112.40	123.02	0.10	0.76
269.	12.	8.50	0.0	-110.	6.90	269.53	165.87	174.52	0.10	0.77
269.	12.	8.50	0.0	-118.	6.90	1.10	121.15	142.79	1.10	1.10

Lake St. George, East Basin, 1982

Day	De	T	Ox	EH	pH	TP	SRP	TRP	TFe	TMn
174.	6.	1.10	0.40	242.	1.10	64.77	1.10	1.10	0.07	0.03
174.	12.	1.10	0.0	-48.	1.10	102.76	1.10	1.10	0.08	0.41
180.	2.	18.50	12.50	1.	8.50	81.91	1.36	1.10	0.03	0.03
180.	6.	7.20	0.40	102.	7.30	61.11	1.81	1.10	0.07	0.03
180.	8.	5.20	0.30	102.	7.24	50.49	1.51	1.10	0.05	0.17
180.	10.	4.80	0.0	82.	7.22	46.06	3.77	1.10	0.01	0.30
180.	12.	4.80	0.0	82.	7.20	119.60	55.72	1.10	0.01	0.46
180.	12.	4.80	0.0	82.	7.20	128.81	60.99	1.10	0.01	0.47
186.	2.	20.50	14.00	132.	8.14	48.88	1.22	0.61	0.04	0.03
186.	6.	6.90	0.30	142.	7.13	49.88	1.52	1.68	0.04	0.06
186.	8.	5.10	0.0	72.	6.98	46.89	1.68	1.37	0.0	0.20
186.	10.	4.90	0.0	-347.	6.97	41.06	2.90	2.44	0.05	0.34
186.	12.	4.90	0.0	-148.	6.92	99.05	48.02	1.10	0.10	0.45
214.	2.	22.50	7.50	282.	8.20	27.03	1.51	2.41	0.10	0.0
214.	6.	12.50	0.0	-208.	7.00	45.65	1.06	0.0	0.0	0.20
214.	8.	10.50	0.0	-208.	7.00	41.06	1.51	0.0	0.10	0.21
214.	10.	9.00	0.0	-58.	7.00	57.11	18.55	18.70	0.0	0.28
214.	12.	8.20	0.0	-218.	7.00	123.80	72.70	77.22	0.10	0.39
214.	12.	8.20	0.0	1.	7.00	133.04	81.15	95.32	0.10	0.35
214.	12.	8.20	0.0	1.	7.00	1.10	83.11	85.52	1.10	1.10
269.	2.	16.00	8.20	1.	1.10	21.15	0.45	0.59	0.0	0.0
269.	6.	10.40	0.40	-42.	7.21	1.10	1.78	0.89	0.0	0.26
269.	8.	7.00	0.20	-11.	7.13	40.22	0.45	0.0	1.10	1.10
269.	10.	6.40	0.20	1.	7.13	38.89	0.59	0.0	1.10	0.39
269.	12.	6.00	0.20	-73.	7.10	103.80	68.77	75.15	0.05	0.37
269.	12.	6.00	0.20	-73.	7.10	99.80	66.11	74.11	0.05	0.46

Glen Lake, 1982

Day	De	T	Ox	EH	pH	TP	SRP	TRP	TFe	TMn
194.	3.	20.00	9.00	1.	8.97	7.07	0.0	0.0	0.0	0.0
194.	7.	7.00	3.80	400.	7.31	14.07	0.0	0.0	0.0	0.0
194.	8.	6.10	0.50	202.	1.10	14.88	0.0	0.0	0.0	0.12
194.	10.	5.50	0.0	-28.	6.99	55.30	0.0	0.74	0.0	0.35
194.	12.	5.50	0.0	-288.	6.95	80.51	30.16	34.47	0.10	0.34
194.	12.	5.50	0.0	-253.	1.10	83.77	36.40	36.65	0.10	0.34
202.	10.	5.50	0.0	112.	1.10	64.77	0.0	0.0	0.10	0.40
202.	12.	5.00	0.0	-208.	1.10	83.63	30.63	31.31	0.20	0.33
216.	3.	20.50	9.00	1.	8.56	1.10	1.10	1.10	1.10	0.0
216.	7.	11.00	11.00	372.	7.69	15.40	0.0	0.0	0.10	0.0
216.	8.	8.40	1.10	307.	7.00	1.10	0.0	0.0	0.10	0.10
216.	10.	6.20	0.0	257.	6.94	59.00	0.0	0.0	0.10	0.45
216.	12.	6.20	0.0	-148.	6.49	89.40	39.39	38.06	0.10	0.34
216.	12.	6.20	0.0	-140.	1.10	1.10	41.19	41.34	0.10	1.10
216.	12.	6.20	0.0	-140.	1.10	1.10	38.06	39.10	0.10	1.10
249.	8.	11.50	4.50	364.	1.10	13.84	0.30	0.0	0.06	0.12
249.	9.	9.50	0.0	355.	1.10	15.76	0.45	0.0	0.02	0.21
249.	12.	7.00	0.0	-114.	1.10	157.66	92.00	98.34	0.14	0.44
249.	12.	7.00	0.0	-110.	1.10	201.35	129.69	142.19	1.10	1.10
249.	12.	7.00	0.0	-115.	1.10	198.20	142.19	145.31	1.10	1.10
258.	3.	17.50	8.90	1.	1.10	6.54	0.60	0.30	0.02	0.01
258.	7.	13.50	8.70	412.	7.04	14.87	0.75	0.30	0.01	0.07
258.	8.	12.00	1.10	402.	7.12	13.04	0.50	0.0	0.01	0.04
258.	9.	10.50	1.10	403.	6.97	14.87	0.50	0.30	0.01	0.16
258.	10.	8.50	1.10	340.	6.92	30.29	0.0	0.50	0.01	0.42
258.	12.	6.00	0.0	-111.	6.86	161.84	93.26	101.05	0.04	0.41
258.	12.	6.00	0.0	-111.	6.86	136.40	72.90	78.14	0.05	0.40
307.	3.	9.70	9.00	1.	1.10	8.47	0.76	0.50	0.03	0.04
307.	7.	9.50	1.10	344.	7.49	8.05	0.0	0.0	0.0	0.04
307.	8.	9.50	1.10	338.	7.49	10.07	0.91	0.0	0.01	0.05
307.	9.	9.40	1.10	341.	7.36	13.93	0.61	0.0	0.0	0.07
307.	10.	7.50	1.10	343.	7.18	13.95	0.61	0.0	0.02	0.16
307.	11.	6.60	1.10	330.	6.91	48.43	1.06	0.0	0.0	0.63
307.	12.	6.50	0.0	-88.	6.83	47.55	1.21	0.0	0.16	0.67

Chub Lake, 1982

Day	De	T	Ox	EH	pH	TP	SRP	TRP	TSP	TFe	SFe	TMn	Fe^{2+}	HU
228.	3.	19.00	8.00	1.	5.96	4.60	0.0	0.0	1.07	0.0	0.0	0.0	1.10	40.00
228.	23.	6.20	0.0	88.	5.70	117.18	39.36	52.78	59.05	6.90	5.80	0.16	1.10	178.00
228.	23.	6.20	0.0	88.	5.70	90.03	27.88	35.79	1.10	5.50	4.90	0.15	1.10	178.00
228.	23.	6.20	0.0	88.	5.70	80.93	26.84	31.16	1.10	4.90	4.70	0.14	1.10	178.00
230.	3.	19.00	8.00	1.	5.97	5.62	0.0	0.0	2.45	0.0	0.0	0.0	1.10	31.00
230.	10.	5.00	6.00	465.	5.20	8.08	0.75	1.20	4.60	0.20	0.10	0.03	0.05	44.00
230.	15.	4.50	3.00	475.	5.22	13.65	1.96	3.91	7.82	0.40	1.10	0.03	0.05	56.00
230.	17.	4.50	1.20	475.	5.29	15.50	3.61	7.37	8.13	0.70	0.30	0.04	0.02	76.00
230.	19.	4.50	0.50	477.	5.43	30.76	3.46	11.58	9.05	1.30	0.30	0.06	0.03	112.00
230.	21.	4.50	0.0	341.	5.93	46.11	3.46	10.98	11.35	2.90	2.00	0.12	1.79	141.00
230.	23.	4.50	0.0	61.	6.03	68.85	17.30	23.32	38.34	4.20	4.30	0.17	1.10	155.00
230.	23.	4.50	0.0	61.	6.03	71.67	19.86	25.73	1.10	1.10	1.10	1.10	1.10	155.00
243.	21.	4.10	0.0	288.	1.10	46.27	5.16	14.01	14.43	3.60	2.87	0.14	1.10	1.10
243.	23.	4.10	0.0	80.	1.10	79.18	35.10	39.09	1.10	5.57	5.32	0.18	1.10	1.10
243.	23.	4.10	0.0	80.	1.10	62.19	23.16	25.37	1.10	4.41	3.82	0.17	1.10	1.10
243.	23.	4.10	0.0	80.	1.10	74.18	32.89	34.96	1.10	5.23	4.69	0.21	1.10	1.10
243.	23.	4.10	0.0	80.	1.10	1.10	34.66	34.66	1.10	1.10	4.82	1.10	1.10	1.10
243.	23.	4.10	0.0	80.	1.10	1.10	33.63	35.84	52.52	1.10	4.99	1.10	1.10	1.10
256.	3.	18.00	8.20	1.	1.10	6.89	0.0	0.0	1.10	0.04	0.10	0.01	1.10	27.00
256.	10.	5.40	5.70	456.	5.23	7.03	0.74	1.34	1.10	0.19	0.10	0.05	0.06	44.00
256.	15.	4.30	1.10	446.	5.35	12.05	3.00	4.00	1.10	0.44	0.31	0.06	0.10	61.00
256.	17.	4.30	1.10	444.	5.35	21.23	5.34	8.01	1.10	1.11	0.61	0.08	0.17	91.00
256.	19.	4.30	0.0	316.	5.75	37.44	5.04	8.31	1.10	2.85	1.73	0.13	1.78	131.00
256.	21.	4.30	0.0	123.	6.03	53.18	18.99	22.55	1.10	4.25	3.16	0.17	4.02	133.00
256.	23.	4.30	0.0	60.	6.19	78.45	35.31	37.83	1.10	6.00	4.25	0.19	5.79	165.00
256.	23.	4.30	0.0	60.	6.19	86.38	41.54	43.62	58.56	6.38	5.01	0.19	1.10	165.00
256.	23.	4.30	0.0	60.	6.19	85.26	1.10	1.10	1.10	6.12	1.10	0.19	1.10	165.00
263.	23.	4.20	0.0	196.	5.95	53.05	17.60	21.24	1.10	1.10	3.20	1.10	1.10	1.10
263.	23.	4.20	0.0	175.	5.95	1.10	17.31	19.93	1.10	1.10	3.44	1.10	1.10	1.10
263.	23.	4.20	0.0	180.	5.95	50.46	17.31	25.90	1.10	1.10	3.58	1.10	3.50	1.10
266.	23.	4.20	0.0	38.	6.09	73.73	26.97	31.63	1.10	1.10	4.50	1.10	4.74	1.10
266.	23.	4.20	0.0	38.	6.08	77.58	31.20	35.13	1.10	1.10	5.00	1.10	1.10	1.10
271.	22.	4.20	0.0	81.	6.00	81.66	23.87	29.15	1.10	1.10	4.12	1.10	4.31	1.10

Day	De	T	Ox	EH	pH	TP	SRP	TRP	TSP	TFe	SFe	TMn	Fe^{2+}	HU
309.	3.	7.20	8.00	1.	1.10	9.09	0.0	0.0	1.10	0.14	0.06	0.04	1.10	1.10
309.	10.	6.00	8.00	428.	5.23	8.40	0.76	1.53	1.10	0.37	0.18	0.07	0.02	1.10
309.	15.	4.40	1.10	432.	5.28	17.68	4.28	5.20	1.10	0.88	0.56	0.09	0.05	1.10
309.	17.	4.40	1.10	380.	5.51	28.59	3.36	5.20	1.10	1.82	1.03	0.14	0.55	1.10
309.	19.	4.20	0.0	132.	5.94	35.36	10.24	9.94	1.10	3.36	3.23	0.16	3.22	1.10
309.	21.	4.10	0.0	73.	6.05	51.52	19.88	20.34	1.10	4.28	4.26	0.16	4.14	1.10
309.	23.	4.10	0.0	58.	6.10	64.02	28.59	28.59	1.10	4.76	4.89	0.17	4.80	1.10
309.	23.	4.10	0.0	60.	6.08	67.14	34.10	32.72	1.10	4.89	5.20	0.16	1.10	1.10
314.	3.	6.20	9.50	1.	5.68	9.44	0.0	0.0	1.10	0.22	0.09	0.05	1.10	1.10
314.	10.	6.20	9.40	437.	5.67	9.49	0.0	0.0	1.10	0.24	0.08	0.04	1.10	1.10
314.	15.	4.50	0.80	451.	5.41	16.83	2.97	2.38	1.10	0.85	0.52	0.10	1.10	1.10
314.	17.	4.50	0.10	387.	5.51	28.28	2.53	1.04	1.10	1.84	1.04	0.13	1.10	1.10
314.	19.	4.10	0.0	192.	5.98	37.33	11.45	14.12	1.10	3.40	3.36	0.16	1.10	1.10
314.	21.	4.10	0.0	103.	6.08	49.17	18.43	19.48	1.10	4.22	4.11	0.16	1.10	1.10
314.	23.	4.10	0.0	81.	6.14	58.22	24.98	26.46	1.10	4.57	4.54	0.17	1.10	1.10
319.	3.	5.30	8.00	1.	1.10	9.64	1.62	0.0	1.10	0.32	0.21	0.06	1.10	1.10
319.	23.	4.10	0.0	1.	1.10	54.55	25.57	23.75	1.10	4.00	4.38	0.21	4.24	1.10
319.	23.	4.10	0.0	74.	6.06	59.39	26.25	25.81	1.10	4.05	4.39	0.17	4.32	1.10
321.	3.	4.60	9.20	1.	1.10	10.52	0.44	0.52	1.10	0.34	0.23	0.06	1.10	1.10
321.	5.	4.60	9.10	421.	5.57	10.13	0.30	0.89	1.10	0.33	0.24	0.05	0.03	50.00
321.	7.	4.60	9.00	420.	5.60	10.13	0.52	1.26	1.10	0.30	0.19	0.05	0.01	48.00
321.	10.	4.60	9.10	437.	5.57	9.32	0.52	1.11	1.10	0.31	0.22	0.06	1.10	48.00
321.	13.	4.60	8.60	450.	5.54	10.56	1.48	1.48	4.40	0.46	0.26	0.05	0.01	48.00
321.	15.	4.50	8.50	447.	5.89	10.71	1.04	1.48	4.84	0.46	0.25	0.05	0.04	48.00
321.	17.	4.40	6.60	455.	5.59	13.79	1.63	1.93	5.58	0.78	0.47	0.07	0.0	76.00
321.	19.	4.20	0.50	471.	5.46	27.62	2.96	6.00	10.57	1.78	0.80	0.11	0.0	114.00
321.	21.	4.10	0.0	104.	5.99	47.40	17.19	19.19	1.10	3.64	3.54	0.15	2.57	118.00
321.	23.	4.10	0.0	66.	6.05	57.33	25.35	26.58	41.54	4.25	4.35	0.17	3.04	110.00
321.	23.	4.10	0.0	66.	6.05	55.72	24.60	26.24	39.63	4.19	4.28	0.17	1.10	1.10
323.	3.	4.50	9.50	1.	1.10	10.51	0.31	0.70	3.87	0.41	0.26	0.06	1.10	1.10
323.	7.	4.50	9.50	450.	5.57	10.53	0.31	0.61	4.17	0.38	0.23	0.05	1.10	1.10
323.	21.	4.00	0.0	117.	6.04	48.75	19.17	20.40	34.07	3.68	1.10	0.15	1.10	1.10
323.	23.	4.00	0.0	69.	6.09	56.91	25.00	26.84	41.06	4.21	1.10	0.15	1.10	1.10

Day	De	T	Ox	EH	pH	TP	SRP	TRP	TSP	TFe	SFe	TMn	Fe^{2+}	HU
330.	3.	3.60	9.20	1.	1.10	11.80	0.67	1.48	1.10	0.42	0.27	0.06	0.0	1.10
330.	5.	3.60	9.20	437.	5.58	11.80	0.89	1.19	4.65	0.40	0.26	0.05	0.0	51.00
330.	7.	3.60	9.10	449.	5.66	11.45	1.03	1.48	4.35	0.42	0.28	0.06	0.0	51.00
330.	10.	3.60	9.50	455.	5.63	11.90	1.19	1.56	4.35	0.41	0.27	0.06	0.0	49.00
330.	13.	3.60	9.40	463.	5.63	11.60	0.59	1.56	4.35	0.39	0.28	0.05	0.0	49.00
330.	15.	3.60	9.40	474.	5.63	11.90	0.59	1.19	4.65	0.43	0.23	0.05	0.0	49.00
330.	17.	3.60	9.20	470.	5.65	11.95	0.74	1.19	4.80	0.38	0.25	0.05	0.0	50.00
330.	19.	3.60	9.10	472.	5.61	11.05	0.74	1.19	4.35	0.41	0.27	0.05	0.0	50.00
330.	21.	3.60	9.70	475.	5.63	11.30	1.19	0.74	4.65	0.42	0.26	0.06	0.0	52.00
330.	23.	3.60	9.50	478.	5.60	12.20	0.74	1.11	4.80	0.39	0.24	0.06	0.0	52.00

Little Clear Lake, 1982

Day	De	T	Ox	EH	pH	TP	SRP	TRP	TSP	TFe	SFe	TMn	Fe^{2+}
196.	2.	22.00.	8.60	1.	6.81	6.22	0.0	0.0	1.10	0.0	0.0	0.0	0.0
196.	10.	5.50	1.90	397.	1.10	9.09	0.0	0.76	1.10	0.10	0.10	0.08	0.0
196.	11.	5.50	0.50	372.	6.00	18.52	0.0	1.98	1.10	0.10	0.10	0.14	1.10
196.	13.	4.60	0.0	292.	6.19	17.35	0.0	1.52	1.10	0.90	0.50	0.29	1.10
196.	15.	4.60	0.0	182.	6.42	19.39	0.0	1.68	1.10	2.00	1.70	0.33	1.10
196.	17.	4.50	0.0	-18.	1.10	40.33	16.16	18.45	1.10	5.10	4.70	0.56	1.10
196.	19.	4.50	0.0	-38.	6.64	76.97	44.82	48.17	1.10	7.40	6.80	0.56	1.10
196.	19.	4.50	0.0	-48.	1.10	78.13	44.82	47.71	1.10	7.40	6.80	0.43	1.10
208.	5.	14.00	13.40	1.	1.10	8.38	0.0	0.76	1.10	0.20	0.0	0.0	1.10
208.	15.	4.60	0.0	12.	1.10	26.16	4.42	4.24	1.10	3.10	2.80	0.40	1.10
208.	17.	4.60	0.0	-28.	1.10	38.71	14.71	15.30	1.10	4.90	4.70	0.44	1.10
208.	18.	4.60	0.0	-23.	1.10	1.10	21.08	22.56	1.10	5.20	4.90	0.56	1.10
208.	18.	4.60	0.0	-23.	1.10	1.10	26.68	27.56	1.10	1.10	5.30	1.10	1.10
208.	18.	4.60	0.0	-18.	1.10	43.36	18.05	17.87	1.10	1.10	4.70	1.10	1.10
210.	5.	1.10	1.10	1.	1.10	9.51	0.70	0.0	1.10	0.10	1.10	0.01	1.10
210.	18.	4.60	0.0	-20.	1.10	1.10	24.47	1.10	1.10	1.10	5.30	1.10	1.10
210.	18.	4.60	0.0	-20.	1.10	1.10	27.78	1.10	1.10	5.80	5.50	1.10	1.10
210.	18.	4.60	0.0	-20.	1.10	1.10	28.53	1.10	1.10	1.10	5.60	1.10	1.10
210.	18.	4.60	0.0	-20.	1.10	48.14	24.77	23.57	1.10	5.80	1.10	0.44	1.10
210.	18.	4.60	0.0	-20.	1.10	53.37	27.78	27.48	1.10	1.10	1.10	1.10	1.10
222.	5.	1.10	12.80	1.	7.18	8.66	0.0	0.0	1.34	0.10	0.0	0.0	0.0
222.	15.	4.60	0.0	383.	6.46	23.13	2.75	2.94	4.63	3.50	3.30	0.42	0.0
222.	17.	4.60	0.0	20.	6.53	38.76	16.03	15.00	20.30	5.90	4.70	0.47	1.10
222.	18.	4.60	0.0	8.	1.10	57.61	27.65	27.21	21.19	6.80	5.70	0.48	1.10
222.	18.	4.60	0.0	8.	1.10	47.61	25.29	23.80	27.91	6.10	5.50	0.47	1.10
222.	18.	4.60	0.0	8.	1.10	53.68	27.50	25.00	32.84	6.90	6.70	1.10	1.10
244.	15.	4.60	0.0	68.	1.10	26.95	0.59	0.73	4.76	3.62	3.09	0.57	1.10
244.	16.	4.60	0.0	21.	1.10	30.76	6.16	5.72	1.10	4.98	4.15	0.54	1.10
244.	16.	4.60	0.0	21.	1.10	27.73	2.64	2.64	1.10	4.30	3.64	0.58	1.10
244.	16.	4.60	0.0	21.	1.10	30.44	6.74	7.04	1.10	4.99	3.99	0.51	1.10
246.	16.	4.60	0.0	76.	1.10	32.63	10.54	9.79	1.10	4.98	4.59	0.48	5.09
246.	17.	4.60	0.0	13.	1.10	42.39	21.39	26.66	1.10	5.39	5.59	0.38	6.05
246.	18.	4.60	0.0	6.	1.10	55.37	30.42	30.42	1.10	5.84	1.10	0.45	6.68
246.	18.	4.60	0.0	6.	1.10	49.44	26.05	25.60	34.17	5.87	1.10	0.51	1.10
246.	18.	4.60	0.0	6.	1.10	51.07	29.52	27.41	1.10	1.10	1.10	1.10	1.10

Day	De	T	Ox	EH	pH	TP	SRP	TRP	TSP	TFe	SFe	TMn	Fe^{2+}
259.	3.	16.20	8.70	1.	6.82	4.88	0.30	0.60	1.10	0.04	0.0	0.01	1.10
259.	10.	6.50	1.00	386.	6.04	7.35	1.04	1.34	1.10	0.14	0.08	0.07	0.01
259.	12.	5.00	0.50	294.	6.06	22.98	0.74	1.49	1.10	0.92	0.53	0.41	0.38
259.	14.	5.00	0.0	222.	6.26	24.95	0.45	0.89	1.10	2.98	2.38	0.47	2.63
259.	16.	5.00	0.0	29.	6.42	36.75	10.27	9.52	1.10	5.30	4.62	0.51	5.05
259.	18.	5.00	0.0	-2.	6.48	58.56	30.21	29.32	1.10	7.25	5.44	0.56	6.39
259.	18.	5.00	0.0	-2.	6.48	59.74	29.76	28.72	36.16	7.25	5.37	0.53	1.10
259.	18.	5.00	0.0	-2.	6.48	59.43	1.10	1.10	1.10	1.10	1.10	0.50	6.19
306.	3.	8.50	8.00	1.	1.10	4.98	0.0	0.0	1.10	0.08	0.03	0.03	1.10
306.	8.	8.50	8.00	396.	6.44	5.47	0.0	0.91	1.10	0.15	0.0	0.04	0.01
306.	10.	7.00	1.10	416.	6.13	13.15	0.0	0.91	1.10	0.26	0.06	0.19	0.04
306.	12.	6.00	1.10	294.	6.16	19.31	0.0	0.91	1.10	0.87	0.72	0.45	0.77
306.	14.	5.20	0.0	179.	6.37	32.17	0.0	3.48	1.10	3.95	3.84	0.53	3.98
306.	16.	5.00	0.0	74.	6.46	31.82	7.27	9.85	1.10	5.34	5.28	0.54	5.37
306.	18.	5.00	0.0	36.	6.49	39.56	15.00	16.67	1.10	6.04	5.90	0.55	6.02
306.	19.	5.00	0.0	45.	6.49	42.36	18.03	19.85	1.10	6.03	1.10	0.55	6.17

Appendix B

Data for calculation of the fall turnover budget in Lake Magog 1981 (Chapter 5). The eroded hypolimnetic water layer (m, column 2) was obtained from oxygen profiles. This eroded volume (10^3 m^3, column 3) and aerated surface volume (10^3 m^3, column 4) were calculated with morphometric information form Lardner-Cornett (1981) and column 2. The volume of aerated surface water (column 4) was corrected for flushing by daily low data from a downstream dam at Rock Forest (Quebec, Ministere d'Environnement), (column 5). From these data and the phosphorus concentrations of the eroded hypolimnetic layer (Appendix A), changes in the surface concentrations of TP, SRP and PRP (µg/L, column 6, 7, 8) were calculated. These changes can than be compared to observed changes calculated from the surface concentrations (Appendix A).

Date	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Aug. 4 - 11	11 - 11	0	67,510	77,110	00	00	00
Aug.11 - 17	11 - 10	0	62,910	70,250	00	00	00
Aug.17 - 26	10 - 10	0	67,510	97,762	00	00	00
Aug.26 - Sept.4	10 - 11	3,650	62,910	86,314	6.75	4.61	0.81
Sept. 4 - 11	11 - 11.5	1,585	67,510	75,090	3.73	3.23	00
Sept.10 - 12	11.5 - 12	1,585	71'520	76,695	7.38	6.90	0.35
Sept.12 - 15	12 - 11	0	71,520	75,924	00	00	00
Sept.15 - 21	11 - 12	3,170	71,520	75,924	15.03	13.81	1.69
Sept.21 - 23	12 - 12.5	1,287	71,170	78,106	4.88	3.79	0.76
Sept.23 - 25	12.5 - 14	825	78,337	87,625	21.74	21.58	0.98
Sept.25 - 30	14 - 15.5	1,057	78,337	96,072	11.62	7.57	4.00
Sept.30 - Oct.2	15.5 - 17	845	84,213	89,596	6.22	5.72	0.49
Oct. 2 - 8	17 -17	0	85,530	94,966	-7.90	-1.70	-1.40

Appendix C

Dataset for SRP and BAP comparisons in Chapter 4. The variables are listed in two columns per page of SRP and BAP (µg/L), data source and water type. Data sources are the same as in Table 3 of Chapter 4, water type is water from:
1 - hypolimnia; 2 - epilimnia; 3 - streams; 4 - sewage effluents; 5 - sediment and soil extracts; 6 - bluegreen algae extracts; 7 - atmospheric precipitation; 8 - groundwater; 9 - artificially enriched water from limnocorrals.

356.0	343.0	1.	1.
236.0	196.0	1.	1.
356.0	323.0	1.	1.
531.0	468.0	1.	1.
78.0	109.0	1.	1.
203.0	170.0	1.	1.
59.0	41.0	1.	1.
603.0	555.0	1.	1.
63.0	49.0	1.	1.
663.0	644.0	1.	1.
3.0	4.0	1.	1.
3.0	2.0	1.	1.
15.0	16.0	1.	1.
22.0	10.0	1.	1.
5.0	4.0	1.	1.
7.0	8.0	1.	1.
83.0	99.0	1.	1.
96.0	95.0	1.	1.
73.0	63.0	1.	1.
636.0	548.0	1.	1.
297.0	255.0	1.	1.
197.0	160.0	1.	1.
71.0	88.0	1.	1.
402.0	345.0	1.	1.
283.0	190.0	1.	1.
82.0	88.0	3.	1.
53.0	63.0	3.	1.
181.0	178.0	3.	1.
5.0	5.0	5.	1.
2.3	2.3	5.	1.
2.1	2.1	5.	1.
14.0	14.0	5.	1.
9.2	9.2	5.	1.
2.3	2.3	5.	1.
95.6	95.0	5.	1.
592.0	580.0	5.	1.
4.0	5.0	1.	2.
4.0	5.0	1.	2.
5.0	7.0	1.	2.
8.0	5.0	1.	2.
8.0	6.0	1.	2.
2.2	2.7	2.	2.
3.0	1.6	2.	2.
3.6	0.5	2.	2.
1.6	0.5	2.	2.
1.6	0.1	2.	2.
1.6	0.8	2.	2.
1.0	0.6	2.	2.
1.7	0.1	2.	2.
3.3	1.0	2.	2.
1.4	2.0	2.	2.
3.3	1.8	2.	2.
3.0	0.0	2.	2.
5.8	1.0	2.	2.
1.4	1.6	2.	2.
2.0	0.3	2.	2.
0.4	0.5	2.	2.
1.8	1.6	2.	2.
0.8	2.8	2.	2.
2.0	0.2	2.	2.
3.0	1.3	2.	2.
7.6	4.6	2.	2.
4.8	4.9	2.	2.
4.4	0.5	2.	2.
8.2	19.6	2.	2.
2.0	0.9	2.	2.
1.8	0.1	2.	2.
1.0	0.7	2.	2.
2.0	0.6	2.	2.
3.0	7.2	2.	2.
0.7	0.7	2.	2.
9.6	7.1	2.	2.
6.8	1.3	2.	2.
2.0	0.9	2.	2.
1.8	0.1	2.	2.
0.6	0.4	2.	2.
2.0	0.8	2.	2.
2.0	1.4	2.	2.
1.7	0.1	2.	2.
3.9	4.9	2.	2.
4.0	1.9	2.	2.
3.4	1.7	2.	2.
3.0	1.7	2.	2.
2.0	0.3	2.	2.
5.6	0.7	2.	2.
5.6	0.5	2.	2.
4.0	0.9	2.	2.
3.4	0.5	2.	2.
7.8	2.9	2.	2.
5.0	1.2	2.	2.
6.8	1.3	2.	2.
3.0	0.1	2.	2.
2.8	0.9	2.	2.
66.0	65.0	3.	2.
70.0	67.0	3.	2.
21.0	20.0	3.	2.
53.0	55.0	3.	2.
48.0	52.0	3.	2.
45.0	44.0	3.	2.
49.0	52.0	3.	2.
43.0	43.0	3.	2.
34.0	34.0	3.	2.
46.0	34.0	3.	2.
52.0	52.0	3.	2.
40.0	39.0	3.	2.
1.0	1.0	3.	2.
1.0	1.0	3.	2.
1.0	1.0	3.	2.
5.0	5.0	3.	2.
1.0	2.0	3.	2.
30.0	30.0	4.	2.
1.3	0.6	4.	2.
1.0	0.5	4.	2.
1.2	1.2	5.	2.
2.5	2.5	5.	2.
1.4	1.1	5.	2.
6.3	4.0	5.	2.
1.5	1.1	5.	2.
0.3	0.3	5.	2.
0.7	0.7	5.	2.

14.0	18.0	6.	2.
8.0	6.0	6.	2.
3.0	2.0	6.	2.
210.0	250.0	6.	2.
5.7	1.3	2.	3.
5.7	8.9	2.	3.
11.2	13.6	2.	3.
4.4	0.4	2.	3.
10.4	3.0	2.	3.
3.0	0.1	2.	3.
1.2	0.5	2.	3.
8.8	15.2	2.	3.
3.8	3.0	2.	3.
3.4	0.7	2.	3.
1.8	3.3	2.	3.
2.1	0.1	2.	3.
0.6	1.6	2.	3.
3.0	2.9	2.	3.
2.0	0.6	2.	3.
8.4	0.5	2.	3.
2.4	0.9	2.	3.
1.8	0.5	2.	3.
12.0	0.5	2.	3.
2.0	0.5	2.	3.
1.6	0.6	2.	3.
1.5	0.1	2.	3.
4.5	2.1	2.	3.
4.3	2.0	2.	3.
8.4	5.5.	2.	3.
2.2	5.0	2.	3.
7.8	9.0	2.	3.
5.8	1.3	2.	3.
2.0	0.5	2.	3.
2.4	0.7	2.	3.
1.2	0.4	2.	3.
3.4	3.2	2.	3.
3.0	1.0	2.	3.
1.7	0.5	2.	3.
3.2	2.0	2.	3.
2.4	0.1	2.	3.
1.5	1.0	2.	3.
1.6	1.9	2.	3.
2.8	0.1	2.	3.
1.2	0.1	2.	3.
6.0	5.0	2.	3.
2.6	0.4	2.	3.
3.0	0.3	2.	3.
1.8	0.3	2.	3.
8.6	1.8	2.	3.
1.8	3.3	2.	3.
3.0	0.1	2.	3.
17.7	7.5	2.	3.
1.5	2.4	2.	3.
9.0	6.4	2.	3.
39.6	2.5	2.	3.
37.5	3.3	2.	3.
5.5	0.3	2.	3.
4.6	1.5	2.	3.
8.2	1.3	2.	3.
20.8	29.5	2.	3.
3.4	4.8	2.	3.
5.4	3.0	2.	3.
28.9	24.1	2.	3.
8.9	9.5	2.	3.
17.2	4.2	2.	3.
9.9	2.9	2.	3.
3.4	3.7	2.	3.
6.4	1.1	2.	3.
4.5	0.7	2.	3.
3.6	0.9	2.	3.
4.0	0.9	2.	3.
4.2	0.9	2.	3.
5.2	0.3	2.	3.
4.0	0.4	2.	3.
7.8	5.6	2.	3.
7.4	1.4	2.	3.
5.4	0.3	2.	3.
4.5	1.3	2.	3.
2.2	1.0	2.	3.
12.4	2.9	2.	3.
7.0	1.5	2.	3.
15.0	0.7	2.	3.
1.7	0.5	2.	3.
4.4	1.3	2.	3.
2.6	2.1	2.	3.
4.6	0.1	2.	3.
1.8	9.0	2.	3.
46.4	56.4	2.	3.
6.2	3.4	2.	3.
7.8	0.5	2.	3.
2.8	1.3	2.	3.
12.4	4.8	2.	3.
6.4	5.2	2.	3.
4.8	2.1	2.	3.
2.2	0.8	2.	3.
6.8	10.2	2.	3.
41.9	40.1	2.	3.
5.4	1.8	2.	3.
1.4	1.0	2.	3.
1.6	1.5	2.	3.
3.3	0.8	2.	3.
1.9	0.1	2.	3.
17.2	10.8	2.	3.
15.3	2.9	2.	3.
11.7	11.1	2.	3.
15.8	1.9	2.	3.
15.0	0.6	2.	3.
5.6	0.7	2.	3.
7.0	0.9	2.	3.
6.6	2.5	2.	3.
6.2	0.6	2.	3.
4.6	2.1	2.	3.
9.0	7.6	2.	3.
4.6	2.5	2.	3.
18.0	17.0	6.	3.
20.5	17.0	4.	3.
14.5	9.9	4.	4.
3000.0	3700.0	6.	4.
2.6	2.4	9.	4.
0.1	0.1	9.	4.

2.4	2.1	9.	4.
0.1	0.3	9.	4.
1.6	1.8	9.	4.
0.9	1.0	9.	4.
1.4	1.3	9.	4.
1.6	1.6	9.	4.
1.0	1.0	9.	4.
0.1	0.2	9.	4.
4.8	5.1	9.	4.
2.1	2.3	9.	4.
0.9	0.9	9.	4.
1.5	3.1	9.	4.
1.1	1.6	9.	4.
0.4	0.6	9.	4.
1.1	1.7	9.	4.
0.0	0.1	9.	4.
0.0	0.0	9.	4.
0.9	1.2	9.	4.
0.0	0.1	9.	4.
0.0	0.1	9.	4.
102.0	100.0	3.	5.
73.0	76.0	3.	5.
414.0	414.0	10.	5.
549.0	549.0	10.	5.
12.0	10.0	3.	6.
54.0	45.0	3.	6.
0.1	0.0	8.	7.
0.9	0.0	8.	7.
1.1	5.0	8.	7.
0.1	0.0	8.	7.
2.1	2.4	8.	7.
0.5	0.0	8.	7.
1.4	1.0	8.	7.
0.1	0.0	8.	7.
0.1	0.0	8.	7.
0.8	2.3	8.	7.
5.5	4.0	8.	7.
0.8	0.0	8.	7.
38.0	39.5	8.	7.
2.6	4.1	8.	7.
1.1	1.7	8.	7.
35.0	39.1	8.	7.
1.6	2.5	8.	7.
1.0	0.0	8.	7.
1.9	0.0	8.	7.
0.6	0.7	8.	7.
170.0	215.8	8.	7.
0.5	0.0	8.	7.
1.1	2.0	8.	7.
0.1	0.0	8.	7.
0.4	4.8	8.	7.
0.5	0.0	8.	7.
0.1	0.0	8.	7.
0.1	0.0	8.	7.
42.0	47.6	8.	7.
0.8	4.8	8.	7.
1.0	0.0	8.	7.
2.1	0.0	8.	7.
0.5	0.0	8.	7.
1.0	0.0	8.	7.
0.1	0.0	8.	7.
0.1	0.0	8.	7.
315.0	239.4	8.	7.
0.5	0.0	8.	7.
2.9	2.4	7.	7.
5.3	1.4	7.	7.
1.5	0.5	7.	7.
1.7	0.4	7.	7.
86.0	53.0	7.	7.
27.4	34.0	7.	7.
10.5	17.9	7.	7.
13.5	3.5	7.	7.
6.6	4.3	7.	7.
5.7	10.0	7.	7.
1.2	0.0	7.	7.
2.8	2.9	7.	7.
1.0	0.0	7.	7.
20.0	32.5	7.	7.
1.5	0.8	7.	7.
8.6	10.8	7.	7.
11.0	17.5	7.	7.
2.6	9.0	7.	7.
1.0	0.8	7.	7.
0.5	1.0	7.	7.
2.2	1.1	7.	7.
9.3	7.5	7.	7.
3.5	2.0	7.	7.
4.6	3.0	7.	7.
3.4	2.5	7.	7.
5.2	1.5	7.	7.
2.1	5.2	7.	7.
4.6	5.0	7.	7.
1.5	8.8	7.	7.
2.8	2.3	7.	7.
2.9	8.0	7.	7.
44.0	40.5	7.	7.
3.2	2.3	7.	7.
25.0	65.5	7.	7.
1.2	1.2	7.	7.
2.5	0.6	7.	7.
37.0	48.5	7.	7.
0.8	0.0	7.	7.
45.0	56.0	7.	7.
0.7	2.4	7.	7.
0.9	0.0	7.	7.
0.6	0.5	7.	7.
6.6	4.5	7.	7.
1.2	0.5	7.	7.
22.0	43.0	7.	7.
8.8	11.0	7.	7.
78.0	79.0	7.	7.
15.0	22.5	7.	7.
45.5	89.5	7.	7.
9.7	13.5	2.	7.
9.4	3.1	2.	7.
35.2	38.8	2.	7.
6.0	0.3	2.	7.
54.4	60.0	2.	7.
30.4	31.6	2.	7.
14.0	17.0	2.	7.

8.4	0.4	2.	7.	11.1	13.8	8.	3.
8.4	0.4	2.	7.	0.4	7.3	8.	3.
14.8	14.4	2.	7.	38.5	18.7	8.	3.
52.2	12.2	2.	7.	41.0	16.5	8.	3.
46.5	13.6	2.	7.	19.0	22.8	8.	3.
46.9	6.1	2.	7.	13.0	24.5	8.	3.
2.8	0.2	2.	8.	0.6	7.5	8.	3.
3.2	2.0	2.	8.	13.5	12.2	8.	3.
4.4	0.4	2.	8.	29.0	19.8	8.	3.
3.0	5.2	2.	8.	28.5	38.4	8.	3.
3.2	0.5	2.	8.	7.8	4.7	8.	3.
5.8	1.6	2.	8.	0.9	0.0	8.	3.
3.6	0.0	8.	3.	2.0	0.0	8.	3.
2.2	0.0	8.	3.	3.6	0.0	8.	3.
0.3	1.9	8.	3.	3.3	4.6	8.	3.
0.9	0.1	8.	3.	2.3	2.7	8.	3.
0.4	0.0	8.	3.	1.5	0.0	8.	3.
1.3	0.0	8.	3.	0.2	1.7	8.	3.
0.1	1.0	8.	3.	2.4	2.0	8.	3.
0.5	2.0	8.	3.	0.9	5.6	8.	3.
0.9	2.0	8.	3.	1.6	3.4	8.	3.
3.0	0.0	8.	3.	0.3	0.2	8.	3.
0.8	7.5	8.	3.	1.8	0.0	8.	3.
1.1	1.6	8.	3.	1.4	0.0	8.	3.
0.6	0.0	8.	3.	1.0	0.0	8.	3.
1.1	1.0	8.	3.	1.9	0.8	8.	3.
10.9	7.7	8.	3.	0.9	0.0	8.	3.
4.4	4.0	8.	3.	3.1	0.5	8.	3.
8.4	8.4	8.	3.	5.4	7.6	8.	3.
8.3	8.8	8.	3.	3.8	7.1	8.	3.
4.9	2.9	8.	3.	5.3	5.5	8.	3.
1.9	2.0	8.	3.	3.8	1.7	8.	3.
2.2	0.6	8.	3.	2.3	0.1	8.	3.
8.6	8.4	8.	3.	4.0	2.5	8.	3.
0.8	0.0	8.	3.	3.6	2.8	8.	3.
1.4	3.3	8.	3.	1.5	3.9	8.	3.
0.8	1.9	8.	3.	1.8	2.3	8.	3.
1.0	11.9	8.	3.	2.3	2.6	8.	3.
0.5	0.0	8.	3.	3.9	3.5	8.	3.
36.0	27.0	8.	3.	3.8	10.1	8.	3.
13.3	10.2	8.	3.	1.9	3.3	8.	3.
32.0	25.6	8.	3.	0.3	2.0	8.	3.
36.0	29.0	8.	3.	1.8	4.4	8.	3.
14.0	10.6	8.	3.	3.6	0.0	8.	3.
2.6	5.1	8.	3.	0.4	1.1	8.	3.
12.0	12.4	8.	3.	9.9	7.2	8.	3.
33.5	28.7	8.	3.	20.0	11.6	8.	3.
6.8	18.0	8.	3.	20.0	11.9	8.	3.
9.9	7.0	8.	3.	16.1	6.2	8.	3.
1.1	1.6	8.	3.	15.4	6.9	8.	3.
7.2	10.3	8.	3.	4.4	1.5	8.	3.
1.5	0.4	8.	3.	3.7	1.5	8.	3.
10.9	12.6	8.	3.	3.7	3.6	8.	3.
37.0	29.1	8.	3.	11.0	4.2	8.	3.
38.0	23.0	8.	3.	25.0	7.0	8.	3.
21.0	21.2	8.	3.	13.5	10.3	8.	3.
39.0	44.1	8.	3.	0.1	2.0	8.	3.
5.2	5.9	8.	3.	6.1	4.7	8.	3.
8.6	16.5	8.	3.	6.8	9.8	8.	3.
12.0	10.4	8.	3.	0.8	2.7	8.	3.

88.0	79.0	8.	3.
108.0	112.9	8.	3.
108.0	112.9	8.	3.
3.1	4.8	8.	3.
18.5	15.5	8.	3.
45.0	50.1	8.	3.
51.0	48.8	8.	3.
14.0	21.1	8.	3.
15.0	22.0	8.	3.
8.1	8.3	8.	3.
9.2	26.6	8.	3.
3.4	3.2	8.	3.
240.0	207.9	8.	3.
64.0	77.1	8.	3.
13.7	22.7	8.	3.
47.5	81.5	8.	3.
150.5	152.7	8.	3.
255.0	209.5	8.	3.
185.0	166.0	8.	3.
156.0	213.0	8.	3.
225.0	287.5	8.	3.
340.0	273.8	8.	3.
310.0	198.1	8.	3.
18.0	11.9	8.	3.
12.2	10.5	8.	3.
12.6	13.8	8.	3.
5.4	2.5	8.	3.
17.0	0.4	8.	3.
20.0	25.5	8.	3.
5.6	6.7	8.	3.
3.5	6.1	8.	3.
2.1	5.1	8.	3.
5.6	0.0	8.	3.
13.0	16.7	8.	3.
5.2	3.2	8.	3.
1.6	2.0	8.	3.
1.5	1.0	8.	3.
110.0	96.6	8.	3.
133.0	132.6	8.	3.
12.5	9.5	8.	3.
11.0	9.9	8.	3.
2.7	4.3	8.	3.
13.5	15.4	8.	3.
41.0	45.6	8.	3.
52.0	71.9	8.	3.
8.1	14.6	8.	3.
1.7	14.0	8.	3.
10.4	12.0	8.	3.
23.0	27.7	8.	3.
23.5	26.4	8.	3.
3.7	9.3	8.	3.
4.1	4.8	8.	3.
26.0	36.1	8.	3.
5.6	7.1	8.	3.
16.1	17.3	8.	3.
44.0	59.5	8.	3.
6.3	10.4	8.	3.
2.1	11.9	8.	3.
16.0	18.5	8.	3.
97.0	130.0	8.	3.
21.0	23.0	1.	1.
21.0	19.0	11.	2.
17.0	26.0	11.	2.
10.0	15.0	11.	2.
22.0	16.0	11.	2.
20.0	22.0	11.	2.
25.0	21.0	11.	2.
0.1	14.0	11.	2.
12.0	14.0	11.	2.
0.1	7.0	11.	2.
21.0	24.0	11.	9.
15.0	35.0	11.	9.
10.0	10.0	11.	9.
17.0	17.0	11.	9.
20.0	25.0	11.	9.
25.0	35.0	11.	9.
3.0	16.0	11.	9.
3.0	6.0	11.	9.
0.1	26.0	11.	9.
27.0	22.0	11.	9.
20.0	25.0	11.	9.
40.0	40.0	11.	9.
70.0	45.0	11.	9.
78.0	143.0	11.	9.
52.0	35.0	11.	9.
3.0	37.0	11.	9.
3.0	11.0	11.	9.
0.1	15.0	11.	9.
17.0	20.0	11.	9.
10.0	26.0	11.	9.
16.0	11.0	11.	9.
20.0	14.0	11.	9.
20.0	22.0	11.	9.
23.0	21.0	11.	9.
77.0	67.0	11.	9.
132.0	52.0	11.	9.
10.0	19.0	11.	9.
17.0	106.0	11.	9.
700.0	62.0	11.	9.
248.0	112.0	11.	9.
75.0	45.0	11.	9.
15.0	22.0	11.	9.
220.0	107.0	11.	9.
178.0	47.0	11.	9.
64.0	57.0	11.	9.
1.9	1.9	5.	1.
1.0	1.0	3.	2.
27.0	25.0	1.	1.
25.0	27.0	1.	1.
28.0	26.0	1.	1.
25.0	31.0	1.	1.
16.0	20.0	1.	1.
20.0	28.0	1.	1.
35.0	38.0	1.	1.
35.0	43.0	1.	1.
88.0	90.0	1.	1.
39.0	40.0	1.	1.
92.0	90.0	1.	1.
343.0	329.0	1.	1.
187.0	160.0	1.	1.

127.0	85.1	8.	3.
11.0	21.0	8.	3.
4.4	5.6	8.	3.

Appendix D

Total phosphorus, SRP and chlorophyll (Chloroph.) concentration before (bef) and after (aft) fall turnover and maximum concentrations of TP and SRP in the hypolimnion (hypo) during summer stratification.

Source: 1 - Phillips (1977); 2 - Mothes (1981); 3 - Stauffer (1974); 4 - Stewart and Markello (1974); 5 - LaZerte (1978); 6 - Ryding (1980); 7 - Kortmann (1980); 8 - Serruja (1978); 9 - Sonzogni (1974); 10 - Fricker (1980); 11 - Kothandaraman and Evans (1978); 12 - Imboden and Emerson (1978); 13 - Mitchell and Burns (1981); 14 - I. Ahlgren (1967) and G. Ahlgren (1970); 15 - Bloesch et al. (1977); 16 - Emery et al. (1973); 17 - Burns and Ross (1972); 18 - this thesis.

Lake	Year	Total Phosphorus			SRP			Chloroph.		Source
		bef	aft	hypo	bef	aft	hypo	bef	att	
Alderfen Broad	72	100	380	-	10	270	-	40	95	(1)
	73	100	250	-	10	67	-	40	115	(1)
	74	100	450	-	10	400	-	40	90	(1)
	75	100	540	-	10	420	-	40	110	(1)
Dagow See	71	200	700	1500	-	-	-	-	-	(2)
	74	400	700	1500	-	-	-	-	-	(2)
Delavan	-	60	164	1114	-	-	-	-	-	(3)
Java	69	30	55	475	-	-	-	-	-	(4)
Lime	69	20	18	125	-	-	-	-	-	(4)
Frains	76	30	60	655	-	-	-	-	-	(5)
Devils	72	11	12	225	-	-	-	-	-	(3)
Fish	72	14	-	66	-	-	-	-	-	(3)
Gjersjoen	72	23	25	-	-	-	-	-	-	(6)
	73	16	20	-	-	-	-	-	-	(6)
	74	16	17	-	-	-	-	-	-	(6)

Dunham Pond	-	2	7	13	-	-	-	-	-	(7)
Kinneret	69	12	14	60	-	-	-	-	-	(8)
	70	22	12	30	-	-	-	-	-	(8)
	71	14	13	32	-	-	-	-	-	(8)
	72	14	20	30	-	-	-	-	-	(8)
	73	20	30	65	-	-	-	-	-	(8)
	74	20	27	32	-	-	-	-	-	(8)
Mendota	71	40	150	850	-	-	-	-	-	(9)
	72	50	160	550	-	-	-	-	-	(9)
	73	90	160	750	-	-	-	-	-	(9)
Nehmitzsee	71	35	100	300	-	-	-	-	-	(2)
	72	25	100	300	-	-	-	-	-	(2)
	73	35	100	300	-	-	-	-	-	(2)
	74	35	100	300	-	-	-	-	-	(2)
Baldeggersee	74	268	445	-	163	330	-	-	-	(10)
Esrom	74	139	222	-	131	208	-	3	4	(6)
	75	200	250	-	175	225	-	6	10	(6)
Catherine	75	80	200	900	10	10	900	-	-	(11)
Ceder	75	50	-	300	0	-	140	-	-	(11)

Greifensee	75	152	333	-	90	281	-	-	-	(10)
	76	106	329	900	57	287	-	-	-	(10)
Hallwilersee	73	41	171	-	68	209	-	-	-	(12)
Lac Leman	76	48	79	-	23	55	-	-	-	(12)
Hayes	70	-	-	-	5	48	500	7	30	(13)
	71	-	-	-	1	40	350	-	-	(13)
Johnson	70	-	-	-	5	46	630	5	15	(13)
Norrviken	61	200	370	2100	5	290	1600	140	49	(14)
Rotsee	69	94	542	1000	8	228	1000	-	-	(15)
Sammamish	64	12	110	80	-	-	-	-	-	(16)
	65	12	190	-	-	-	-	-	-	(16)
	70	15	27	100	-	-	-	-	-	(16)
Zürichsee	76	19	35	-	6	25	-	-	-	(10)
Erie	70	14	12	99	2	4	62	-	-	(17)
Fitch Bay 0-5 m	79	14	21	370	-	-	-	10.4	8.2	(18)
0-3 m	80	12	19	322	-	-	-	3.0	8.9	(18)
5 m	80	14	20	322	-	2	331	2.7	7.5	(18)
8 m	80	12	20	322	-	-	-	1.9	7.1	(18)
0-5 m	81	13	21	241	0	1	196	-	-	(18)

Magog	79	60	105	480	-	-	-	-	-	(18)
	80	60	95	564	-	-	-	-	-	(18)
	81	35	85	720	6	20	680	-	-	(18)