

Canadian Technical Report of
Fisheries and Aquatic Sciences 1881

1993

**COMPARISON OF TWO METHODS COMMONLY USED
AT THE EXPERIMENTAL LAKES AREA FOR COLLECTING
CHEMISTRY SAMPLES FROM VERTICALLY STRATIFIED LAKES**

by

P. Campbell

Central and Arctic Region
Department of Fisheries and Oceans
Winnipeg, Manitoba R3T 2N6

This is the 50th Technical Report
from the Central and Arctic Region, Winnipeg

(c) Minister of Supply and Services Canada 1993

Cat. No. Fs 97-6/1881E

ISSN 0706-6457

Correct citation for this publication is:

Campbell, P. 1993. Comparison of two methods commonly used at the Experimental Lakes Area for collecting chemistry samples from vertically stratified lakes. Can. Tech. Rep. Fish. Aquat. Sci. 1881: iv + 21 p.

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT/RÉSUMÉ	iv
INTRODUCTION	1
METHODS	1
RESULTS AND DISCUSSION	1
Vertical definition	2
Comparisons of constituent masses	2
Error biases	4
CONCLUSIONS AND RECOMMENDATIONS	4
ACKNOWLEDGMENTS	5
REFERENCES	5

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1 One-meter interval depth profiles of temperature, total phosphorus, soluble reactive silicon and chlorophyll <i>a</i> , Lake 442, June 6, 1990	6

LIST OF TABLES

<u>Table</u>	<u>Page</u>
1 Morphometrically-determined aliquot formula used during 1990 for collecting the integrated, composite chemistry sample from Lake 442	7
2 Fluorometrically-determined concentrations of chlorophyll <i>a</i> , Lake 442 - 1990	8
3 Total dissolved phosphorus (TDP) and total phosphorus concentrations, Lake 442 - 1990	9
4 Soluble reactive silicon concentrations, Lake 442 - 1990	10
5 Dissolved sodium concentrations, Lake 442 - 1990	11
6 Masses of chlorophyll <i>a</i> calculated for selected depth-zones of Lake 442	12

Table

<u>Table</u>	<u>Page</u>
7 Masses of total phosphorus calculated for selected depth-zones of Lake 442	13
8 Masses of soluble reactive silicon calculated for selected depth-zones of Lake 442	14
9 Masses of dissolved sodium calculated for selected depth-zones of Lake 442	15
10 Frequency that constituent masses derived from the 5-sample profile and the 2-sample composite differed from the 1-meter interval profile by i) >10% and ii) >25%	16
11 Estimates of analytical uncertainties for chemical determinations, based on comparisons of discrete samples collected independently from depths of 1 meter and 1.5 meters	17
12 Frequency and direction of deviation (+ or -) of constituent masses a) calculated from the 5-sample profile, and b) calculated from the 2-sample composite relative to masses derived from the 1-meter interval profile	18
13 Frequency at which differences in constituent masses computed from the 5-sample profile and 2-sample composite exceeded 10% relative to masses derived from the 1-meter interval profile	19

LIST OF APPENDICES

<u>Appendix</u>	<u>Page</u>
1 Procedures used to compute constituent masses from the 1-meter interval profile, the simulated 5-sample profile, and the 2-sample composite	20

ABSTRACT

Campbell, P. 1993. Comparison of two methods commonly used at the Experimental Lakes Area for collecting chemistry samples from vertically stratified lakes. Can. Tech. Rep. Fish. Aquat. Sci. 1881: iv + 21 p.

Two different sampling procedures are commonly used in the Experimental Lakes Area (ELA) for chemical characterization of the water columns of vertically stratified lakes. These two procedures, a 5-sample profile and a 2-sample composite, were assessed by comparing them with 1-meter interval profiles. Both sampling methods were found to provide only rather crude definition of specific water column features; the 2-sample composite is particularly deficient in this regard. On the other hand, the 2-sample composite is superior to the 5-sample profile for collecting complete samples, representative of the entire water column. For the 2-sample composite, a critical limiting factor is analytical precision in the laboratory; that is, the accurate quantification of the water column of a stratified lake by analyzing only two samples requires corresponding chemical analyses of high reliability and precision. A 3-sample variation of the 2-sample composite procedure assessed here is proposed for future consideration.

Key words: Sampling (chemical); lakes; thermal stratification; Experimental Lakes Area.

RÉSUMÉ

Campbell, P. 1993. Comparison of two methods commonly used at the Experimental Lakes Area for collecting chemistry samples from vertically stratified lakes. Can. Tech. Rep. Fish. Aquat. Sci. 1881: iv + 21 p.

On utilise couramment, dans la Région des Lacs Expérimentaux (RLE), deux méthodes différentes de prélèvement pour caractériser l'eau des lacs stratifiés verticalement. On a évalué ces deux méthodes, l'une permettant de déterminer le profil à partir de cinq échantillons et l'autre utilisant un composite de deux échantillons, en les comparant à des profils obtenus par prélèvements à intervalles de 1 mètre. Les deux méthodes de prélèvement ne définissaient que grossièrement, a-t-on constaté, les caractéristiques spécifiques de la colonne d'eau; la méthode du composite de deux

échantillons donnait des résultats particulièrement décevants à cet égard, mais elle était néanmoins supérieure à la méthode de détermination du profil à l'aide de cinq échantillons pour ce qui est du prélèvement d'échantillons complets représentatifs de la colonne d'eau dans son ensemble. Dans le cas de la méthode du composite de deux échantillons, la précision analytique au laboratoire est un facteur limitatif très important, c'est-à-dire que la caractérisation avec précision de la colonne d'eau d'un lac stratifié, par l'analyse de seulement deux échantillons, doit faire appel à des méthodes d'analyse chimique très fiables et très précises. Comme variante de la méthode du composite de deux échantillons dont on décrit l'évaluation dans le présent document, on propose une méthode à trois échantillons qui pourra être étudiée ultérieurement.

Mots-clés: Prélèvement (chimique); lacs; stratification thermique; Région des Lacs Expérimentaux.

INTRODUCTION

Lakes used at the Experimental Lakes Area (ELA) for experimental studies or as natural references are, generally, small (10-50 ha) but deep (10-35 m). As a result, these systems exhibit marked thermal stratification during most of the open-water season. Often, significant vertical gradients in chemical constituents (particularly, major nutrients) as well as biological components (e.g. phytoplankton, zooplankton, fish) are also evident and are coupled, in part at least, to the vertical stratification in temperature. Lake 442 serves to illustrate the strong, and sometimes rather complex, stratification evident in ELA lakes, even relatively early in the summer (Fig. 1). Vertical profiles shown in Fig. 1 are from measurements made at depth intervals of 1 meter. For most parameters of interest, sampling ELA lakes at 1 meter depth intervals reveals the water column at a level of detail and accuracy that would normally meet or exceed our requirements.

In recent years, from 20 to 30 lakes (not to mention streams, etc.) have been studied simultaneously at ELA; they are sampled anywhere from four to 20+ times per year; and, on the order of 30 to 40 physical and chemical parameters are usually monitored. Given the preceding, and if water columns 10-30 m deep were sampled and analyzed at 1 m intervals, the analytical load quickly escalates to a point where labour and materials' costs become prohibitive. As a result, then, and despite the known vertical complexity and concomitant potential for jeopardizing accuracy, chemistry sampling schemes adopted at ELA generally involved some "compromise".

Typically, chemical characterization of stratified ELA lakes has been from profiles consisting of individual samples collected at five points in the water column. When the Lake Variation and Climate Change Study (Campbell 1993) was initiated at ELA (7 lakes and 17 streams, sampled biweekly), resources were very limited. So, a 2-sample scheme to characterize the entire water column was devised. One is an "integrated" sample, collected at 1 m intervals starting 1/2 m above the bottom and ending in the surface mixed layer. This sample is composited in the field; relative aliquot volumes are based on lake morphometry. The second sample, collected at a depth of 1 m, is taken to be representative of the surface, mixed layer. In this report, the typical 5-

sample profile method and the 2-sample composite method are assessed and compared.

METHODS

For purposes of this study, samples were collected from Lake 442 at 4-week intervals, commencing on June 6 and ending on October 24, 1990. Collections were made at the central station located at the point of maximum depth (see McCullough and Campbell 1993 for bathymetric map of Lake 442). Field methods and protocols followed were as described by Cruikshank et al. (1993). Water samples were collected by pumping at 1 m intervals, starting 0.5 m above the bottom and ending 0.5 m below the surface. Two sets of samples were collected in order to a) construct a 1-meter interval profile of the water column, and b) to produce the 2-sample composite collected routinely by the Lake Variation and Climate Change Program. So, samples collected at the same time at each depth included 1) a discrete 500 mL sample, and 2) a morphometrically pre-determined aliquot, measured and dispensed by graduate cylinder into the 2 L composite bottle (see Table 1 for the exact aliquot formula used). As part of the 2-sample composite method, a second 2 L bottle was filled from a depth of 1 m.

All water samples were collected by the same operator in the morning, generally between 9:00 a.m. and 10:00 a.m. They were placed in coolers within minutes of collection and delivered to the Winnipeg Analytical Unit the same day. The samples were refrigerated overnight, processed the next day and analyzed using methods described by Stainton et al. (1977).

Computational procedures employed in calculating constituent water-column masses from the 1-meter interval profile, the 5-sample profile, and the 2-sample composite are outlined in Appendix 1.

RESULTS AND DISCUSSION

In this report, the emphasis will be on parameters intimately connected with the biology of the lake, i.e. those most likely to exhibit strong, vertical stratification gradients. Total phosphorus (total dissolved phosphorus plus suspended,

particulate phosphorus), soluble reactive silicon, and chlorophyll a results will be assessed. One conservative element, dissolved sodium, will also be considered. The raw data are reported in Tables 2, 3, 4, and 5. A typical ELA profile has been simulated by selecting 5 samples from the 1 meter-interval profile. Depth intervals chosen for this simulation were as advised by G. Linsey (Freshwater Institute, pers. comm.). In Tables 2, 3, 4 and 5, depths used to simulate the 5-sample profile have been highlighted in bold face, i.e. 0.5, 3.5, 7.5, 12.5, and 17.5 m.

Assessments and comparisons of the 5-sample profile and 2-sample composite method which follow are strongly predicated on having accepted the 1-meter interval profile as defining the water column in detail and at a level of accuracy which allows it to be used as a benchmark or "standard". It is, of course, recognized that fully integrated, volume-weighted samples covering the entire water-column would provide the best possible benchmark. But, we did not have the capability of collecting such samples.

VERTICAL DEFINITION

It is obvious that the 2-sample composite method has only very limited potential for defining vertical differences in the water column. The only vertical definition that this procedure can provide is the gross differentiation of the surface, mixed layer (epilimnion) from the rest of the lake (metalimnion and hypolimnion). The 5-sample profile is certainly superior in this regard because, in summer, it can be used to roughly describe, separately, each of the three main thermal zones, i.e. the epilimnion (both the top and bottom), metalimnion (one point, only), and the hypolimnion (top and bottom). However, when linearly interpolating over 3-5 meter intervals, major water column features can still be missed (for example, see chlorophyll a, July 4, 5-7 m or 13-16 m, Table 2); or, they may be over-accentuated (for example, see chlorophyll a, August 1, 10-15 m, Table 2). Linearly-interpolating relatively long distances between sampling points can result in integrations that lead to serious inaccuracies in constituent masses derived for the whole or for parts of the lake.

COMPARISONS OF CONSTITUENT MASSES

The relative accuracies of constituent masses derived from the 5-sample profile method and the 2-sample composite method have been assessed by comparing each of these procedures with the 1 m interval profile benchmark (Tables 6, 7, 8, and 9). Due to restrictions imposed by the 2-sample composite method, direct comparisons can be made for three depth zones, only, i.e. the surface-mixed layer, the metalimnion plus hypolimnion, and the whole lake. To facilitate the comparative analyses which follow, the surface-mixed layer has been fixed at a constant depth of 4 meters, fully recognizing that during fall mixing in September and October the epilimnion deepens considerably. Specific strata used for comparing the 2-sample composite method with the 5-sample profile, each of the six sampling times were 0-4 m, 4-18 m, and 0-18 m.

Chlorophyll a

Seven of 18 times, differences between masses derived from the 5-sample profile and the 1-m interval profile were greater than 10%; on four of these occasions, the differences exceeded 25% (Table 6). However, more than 1/2 of the masses of chlorophyll a derived from the 5-sample profile were within 5% of masses derived from the 1-meter interval profile. Sixteen of the 18 chlorophyll a masses computed from the 2-sample composite were within 10% of those derived from the 1-meter interval profile. Differences never exceeded 25%. Approximately 2/3 of the composite samples produced chlorophyll a masses which were within 5% of those from the 1-meter interval profiles. Whole-lake chlorophyll a masses computed from the 2-sample composite never deviated by more than 10% from those derived from the 1-meter interval profile. These data suggest that masses of chlorophyll a computed from the 2-sample composite method are more reliable than ones derived from the 5-sample profile.

TP

Total phosphorus masses obtained from the 2-sample composite method deviated by more than 10% from those calculated from the 1-meter interval profile, 13 times of 18 (Table 7). That is, the likelihood of significant error in phosphorus masses derived from the composite samples appears to be quite high. In fact, 1/3 of the composite-derived masses differed from the 1-meter interval profile

masses by more than 25%. For the 5-sample profile, 1/3 of the TP masses differed by more than 10% from those derived from the 1-meter interval profiles; 2 of 18 differed by more than 25%. So, the probability for large errors in TP masses derived from the 5-sample profile is also rather high. From the phosphorus data, the conclusion is that the 5-sample profile is superior to the 2-sample composite sampling procedure; but, the accuracy of TP masses derived by either method may be so poor as to be of only limited use.

SRSi

Four of 18 SRSi masses derived from the 2-sample composite differed from the 1-meter interval profile by more than 10%; however, these differences never exceeded 25% (Table 8). Results were similar for the 5-sample profile. Differences were in excess of 10%, 3 times of 18; none deviated from the 1-meter interval profile by more than 25% (however, also see 4-10 m, September 26, and 10-18 m, October 24). For both the 2-sample composite and the 5-sample profile, approximately 60-70% of silicon masses calculated were within 5% of those from the 1-meter interval profile. Using SRSi, it is difficult to conclude that either of the methods being assessed is better than the other in terms of potential for producing accurate water column constituent masses.

Na

Masses from the 2-sample composite and the 5-sample profile were always within 10% of those from the 1-meter interval profile (Table 9). Differences exceeded 5% on one occasion, only; on June 6, masses computed from the 2-sample composite were 6-7% higher than those from the 1-meter interval profile. The overall conclusion, then, is as was expected for a conservative element which exhibits little in the way of vertical stratification. That is, the 2-sample composite and the 5-sample profile are comparable and, the level of accuracy of Na masses computed from either is relatively high.

Discussion

For three of the four parameters tested, the 2-sample composite method was as good as (or, in the case of chlorophyll *a*, probably superior to) the 5-sample profile method for computing constituent lake masses (Table 10). Since the vertical stratification exhibited by chlorophyll *a* and SRSi is

as complex and marked as for TP (Fig. 1), the composite procedure's apparent failure, in terms of its ability to accurately account for phosphorus, is not likely a function of the inadequacy of the sampling method but, rather, of the higher analytical uncertainty for phosphorus determinations (particularly TDP) relative to that for analyses of the other three parameters assessed. TDP in Lake 442 is sometimes at, or even below, the limits of detection of the method routinely employed by our Analytical Chemistry Unit (Table 3). Estimations of "analytical error", derived by comparing discrete samples collected from 1.0 m and 1.5 m (Table 11), indeed, show a much higher analytical or laboratory-oriented uncertainty for phosphorus than the other parameters, particularly during the first half of the study when concentrations of TDP were lowest. For epilimnetic waters, the "analytical error" for chlorophyll *a*, SRSi, and Na is <10%, whereas that for TDP or TP is frequently >50%.

Taken collectively, a large number of independent determinations such as on the 18 samples constituting each 1-meter interval profile, tends to counteract the high uncertainty inherent in a single phosphorus analysis. Five determinations, collectively, as per the simulated profile, tends also to counteract the high analytical uncertainty associated with a single determination, but not as well as 18. However, two determinations, only, are too few to even out the analytical error. And, as a result, phosphorus masses derived from the 2-sample composite procedure often differ greatly from those derived from the 1-meter interval profile.

The largest differences in phosphorus masses between the composite and the 1-meter interval profile also coincided with times when the laboratory TDP analyses were done on different days, i.e. when the analyses on the 2 L composite samples were run on a day different from those on the 500 mL samples comprising the detailed profile (e.g. samples collected on June 6). For the June 6 sampling, run-related differences also apparently had an important impact even on our conservative parameter, Na. That is, for Na, the one time that large discrepancies between the 2-sample composite and 1-meter interval profile occurred (recall Table 9), they were not likely a function of sampling procedures but rather mainly analytical (laboratory-generated) differences (Table 11).

All comparisons between the 5-sample profile and the 1-meter interval profile presented here are

"best-case" scenarios; unlike the composite samples which were collected independently, the samples used to simulate the 5-sample profiles were sub-sets of those making up the 1-meter interval profiles.

In the preceding assessment of the 2-sample composite and the 5-sample profile, it was implied that "errors" in constituent masses exceeding 10% would likely be unacceptable. The selection of 10% is, of course, rather arbitrary, depending on a variety of factors, including how the computed masses are to be applied, the hydrological characteristics of the system, and the nature of the particular parameter being considered. In an attempt to provide some perspective, let's consider phosphorus, a key nutrient in Lake 442, a lake of size, flushing rate, etc. typical of ones used at the ELA for experimental manipulations. A 10% change in the whole-lake mass of phosphorus obtained accidentally and applied over one sampling interval (normally two weeks) would be roughly equivalent to one-half the total input of P from all external sources during the entire open-water season. This example illustrates that, especially for low order lakes such as those typically used for whole ecosystem experiments, and particularly for constituents in low supply, even a small sampling or analytical error can potentially have very serious implications for interpreting mass balance studies.

ERROR BIASES

It is interesting to note that characterization of the water column using fewer samples, either by "incomplete" profiles or composites, tended to result more frequently in overestimates than underestimates in comparison to a 1-meter interval profile, i.e. the direction of "error" does not seem to be random. This tendency towards more frequent overestimation appears to be true for most, if not all, parameters considered here and for both the 5-sample profile and the 2-sample composite methods (Table 12). That tendency remains evident even if the analysis is restricted to only larger differences (say differences greater than 10%). From the same data used to construct Table 12, 67% of the chlorophyll *a* deviations exceeding 10% were positive; 85% were positive for TP; and, for silicon, 100% were positive. At this time, it is not understood why there is a positive bias in the errors in masses derived from the 5-sample profile and the 2-sample composite.

Not unexpectedly, it was found that the smallest errors in constituent masses computed from the "abbreviated" sampling schemes was for the depth zone exhibiting the least variation and weakest stratification gradients. Table 13 shows that, for the surface-mixed layer (0-4 m), there were fewer large differences than for deeper parts of the lake between masses derived from either the 5-sample profile or 2-sample composite (exception = TP) and those from the 1-meter interval profile. Also as expected, the incidence of large errors was much lower for the conservative parameter, Na, than for the others with strong biological associations (Table 13). Sodium exhibited practically no vertical stratification (Table 5), whereas there were often very marked vertical gradients in chlorophyll *a*, TP, and SRSi (Fig. 1).

CONCLUSIONS AND RECOMMENDATIONS

A small, deep, vertically stratified lake can be described at only a rather low level of resolution using either the 5-sample profile or 2-sample composite methods assessed here. The 5-sample profile does allow the three main thermal zones, the epilimnion, metalimnion, and hypolimnion, to be characterized separately. However, important details can be missed. Even main features of the water column are sometimes grossly over-accentuated or under-accentuated; this can result in large errors in constituent mass calculations. The 2-sample composite provides even less vertical definition; only two strata can be differentiated from one another, i.e. the epilimnion from the metalimnion plus hypolimnion. However, the composite method, largely as a function of the morphometrically integrated sample, provides a more complete and, therefore, a more accurate representation of the composition of the whole water column. But, high degrees of precision in the laboratory are essential, if quantitatively correct lake masses are to be produced from only two samples. That is, there will be a high degree of uncertainty for lake masses derived from a 2-sample composite if the analytical precision is poor. As well, of course, for volumetrically-derived integrated samples, care must be taken to ensure aliquot volumes are measured accurately (although not done here, composite sampling replicability should be assessed).

A 3-sample variation of the 2-sample composite method is proposed for future

consideration. This procedure would entail collection of two morphometrically-derived integrated samples, plus a third sample from the surface mixed layer as shown below.

- Sample I: from a depth of 1 m
- Sample II: integrated, lake surface to bottom of photic zone.
- Sample III: integrated, bottom of photic zone to bottom of lake.

The 3-sample composite would provide vertical definition of the water column in at least as much detail as the 5-sample profile, but with 40% less analytical effort. And, because two of the samples integrate the entire water column, vertical coverage would be very complete and morphometrically correct, thereby eliminating the possibility for over- or under-accentuation of water column features, a serious problem inherent to the 5-sample profile. Strata that could be described separately in our deep transparent lakes using this 3-sample composite approach would include the epilimnion (I), the photic zone (II), the "metalimnion" (II-I), the "hypolimnion" (III), and the whole lake (II + III).

ACKNOWLEDGMENTS

I am grateful to personnel of the Winnipeg Analytical Unit for analyzing the large number of extra samples generated by this study; most of the analyses were performed by Ron Schade, Jack Boughen, Brian Hauser and Gerry Regehr. The manuscript was typed by Donna Laroque. Graphics were by A. Blouw and assistants. Critical reviews by Susan Kasian, Bob Hecky, and Dana Cruikshank were appreciated.

REFERENCES

- CAMPBELL, P. 1993. Lake variation and climate change study: ELA lakes, 1986-1990. I. Study rationale and lake selection criteria. Can. Tech. Rep. Fish. Aquat. Sci. 1897: iv + 5 p.
- CRUIKSHANK, D.R., P. CAMPBELL, S.E.M. KASIAN, E.U. SCHINDLER, and G.K. McCULLOUGH. 1993. Lake variation and climate change study: ELA lakes, 1986-1990. III. Field observations, hydrological, light, and temperature measurements. Can. Data Rep. Fish. Aquat. Sci. (in prep.).
- McCULLOUGH, G.K., and P. CAMPBELL. 1993. Lake variation and climate change study: ELA lakes, 1986-1990. II. Watershed geography and lake morphology. Can. Tech. Rep. Fish. Aquat. Sci. 1898: iv + 28 p.
- STANTON, M.P., M.J. CAPEL, and F.A.J. ARMSTRONG. 1977. The chemical analysis of fresh water. 2nd ed. Can. Fish. Mar. Serv. Misc. Spec. Publ. 25: 166 p.

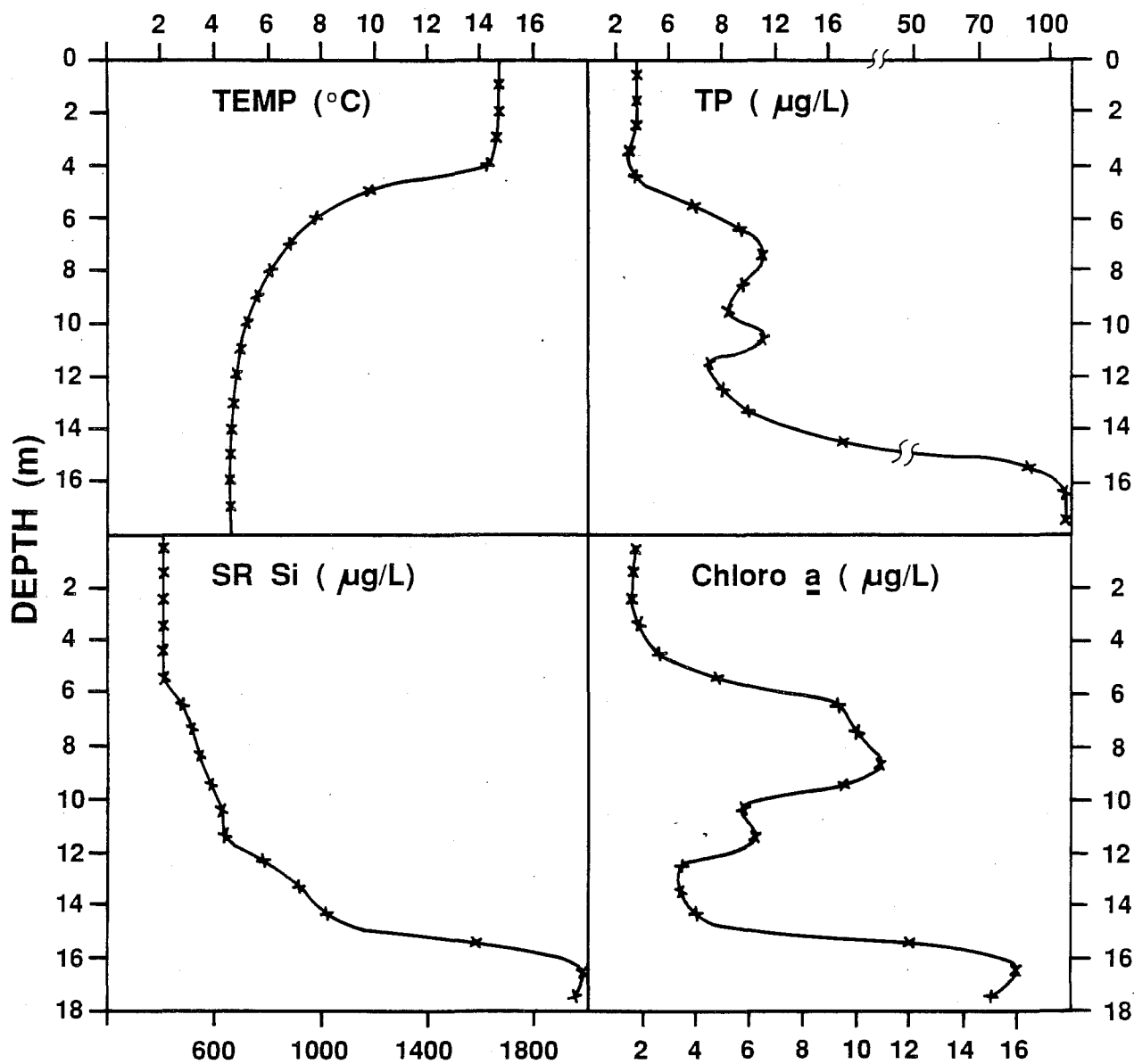


Figure 1. One-meter interval depth profiles of temperature (Temp), total phosphorus (TP), soluble reactive silicon (SR Si) and chlorophyll *a* (Chloro *a*), Lake 442, June 6, 1990.

Table 1. Morphometrically-determined aliquot formula used during 1990 for collecting the integrated, composite chemistry sample from Lake 442.

Depth (m)	Volumes of 1-meter interval strata (m ³)	Sample aliquot volume (mL)
0.5	156,376	-
1.5	146,579	-
2.5	140,030	-
3.5	134,074	260
4.5	128,396	250
5.5	121,813	236
6.5	114,341	222
7.5	106,520	208
8.5	97,483	190
9.5	87,167	170
10.5	74,024	144
11.5	57,016	110
12.5	40,953	80
13.5	29,701	58
14.5	19,165	38
15.5	10,760	20
16.5	6,311	12
17.5	1,220	3
	<hr/> 1,471,929	<hr/> 2,001

Table 2. Fluorometrically-determined concentrations of chlorophyll *a* ($\mu\text{g}\cdot\text{L}^{-1}$).
Lake 442 - 1990.

Depth (m)	June 6	July 4	Aug. 1	Aug. 29	Sept. 26	Oct. 24
a) Discrete 500 mL samples, constituting 1-meter interval profiles						
0.5	1.76	1.72	1.58	1.35	2.00	2.90
1.5	1.69	1.70	1.63	1.34	1.88	2.80
2.5	1.65	1.59	1.67	1.38	2.00	2.80
3.5	1.86	1.83	1.85	1.32	2.10	2.80
4.5	2.60	2.40	2.10	1.81	2.30	2.80
5.5	4.80	6.10	2.00	3.00	2.50	2.80
6.5	9.40	4.10	2.60	5.50	2.50	2.80
7.5	10.00	2.80	3.20	4.70	2.80	2.80
8.5	11.00	2.60	4.50	4.50	2.90	2.80
9.5	9.60	2.70	4.00	3.50	5.20	2.80
10.5	5.80	2.30	2.60	3.20	5.70	2.70
11.5	6.30	2.50	2.20	10.00	10.00	2.60
12.5	3.50	2.90	19.00	14.00	9.30	4.80
13.5	3.50	10.00	12.00	14.00	9.30	5.30
14.5	3.90	8.70	8.40	9.50	8.90	4.90
15.5	12.00	9.00	7.30	9.00	8.70	5.10
16.5	16.00	8.70	7.00	9.00	7.80	5.40
17.5	15.00	9.20	6.80	8.60	8.30	7.10
b) 2-liter samples, constituting 2-sample composites						
1.0	1.65	1.61	1.79	1.32	1.67	2.80
Integrated, 3.5-17.5	6.30	3.50	3.70	5.00	4.40	3.10

Table 3. Total dissolved phosphorus (TDP) and total phosphorus (TP) concentrations ($\mu\text{g}\cdot\text{L}^{-1}$).
Lake 442 - 1990.

Depth (m)	June 6		July 4		Aug. 1		Aug. 29		Sept. 26		Oct. 24	
	TDP	TP	TDP	TP	TDP	TP	TDP	TP	TDP	TP	TDP	TP
a) Discrete 500 mL samples, constituting 1-meter interval profiles												
0.5	<1	3.5	1	4	3	5	5	7	4	6	4	9
1.5	<1	3.5	3	6	4	6	6	8	5	8	4	9
2.5	<1	3.5	2	4	4	7	5	7	4	7	3	8
3.5	1	3	2	5	5	7	5	7	4	7	3	8
4.5	<1	3.5	2	5	6	10	5	7	3	6	4	9
5.5	1	7	2	6	5	8	6	9	4	7	3	8
6.5	<1	9.5	2	8	7	11	6	10	5	8	3	9
7.5	1	11	2	9	5	10	6	10	5	9	3	8
8.5	<1	9.5	2	7	5	12	6	10	5	9	3	8
9.5	<1	8.5	2	9	5	10	7	11	6	11	4	9
10.5	4	11	3	10	<1	6.5	6	11	6	20	3	8
11.5	<1	7.5	3	14	1	7	6	31	6	27	4	10
12.5	1	8	2	15	1	39	7	37	6	42	5	33
13.5	1	10	4	34	1	42	9	51	6	57	6	37
14.5	2	17	3	49	3	52	9	58	6	59	6	35
15.5	4	88	4	62	3	52	8	59	7	53	8	37
16.5	5	110	5	66	3	52	9	60	10	56	17	52
17.5	5	111	5	65	5	57	9	62	9	55	39	88
b) 2-litre samples, constituting 2-sample composites												
	TDP	TP	TDP	TP	TDP	TP	TDP	TP	TDP	TP	TDP	TP
1.0	3	6	2	4	<1	3.5	5	8	5	8	5	10
Integrated, 3.5-17.5	4	18	3	16	1	12	6	17	5	15	4	12

TDP <1 $\mu\text{g}/\text{L}$ was taken to be 0.5 $\mu\text{g}/\text{L}$ for purposes of computing TP.

Table 4. Soluble reactive silicon (SRSi) concentrations ($\mu\text{g}\cdot\text{L}^{-1}$). Lake 442 - 1990.

Depth (m)	June 6	July 4	Aug. 1	Aug. 29	Sept. 26	Oct. 24
a) Discrete 500 mL samples, constituting 1-meter interval profiles						
0.5	416	525	415	376	277	335
1.5	415	525	416	378	276	336
2.5	419	525	415	380	278	336
3.5	420	522	438	383	278	335
4.5	420	368	332	380	278	334
5.5	420	360	336	255	276	334
6.5	484	420	368	252	271	335
7.5	514	470	490	327	231	334
8.5	546	511	477	427	358	337
9.5	590	590	586	374	623	338
10.5	638	670	756	690	816	351
11.5	630	767	885	964	893	407
12.5	795	898	1130	987	1250	1150
13.5	929	1000	1340	1250	1400	1450
14.5	1010	1270	1480	1420	1390	1530
15.5	1580	1410	1540	1450	1460	1660
16.5	1990	1410	1540	1490	1510	1890
17.5	1950	1410	1590	1530	1530	2360
b) 2-liter samples, constituting 2-sample composites						
1.0	415	527	454	453	280	338
Integrated, 3.5-17.5	605	554	590	567	523	458

Table 5. Dissolved sodium (Na) concentrations ($\mu\text{g}\cdot\text{L}^{-1}$). Lake 442 - 1990.

Depth (m)	June 6	July 4	Aug. 1	Aug. 29	Sept. 26	Oct. 24
a) Discrete 500 mL samples, constituting 1-meter interval profiles						
0.5	900	930	910	960	1000	970
1.5	890	930	920	980	990	980
2.5	890	910	920	970	1000	990
3.5	900	920	930	990	990	1000
4.5	900	910	920	970	1010	990
5.5	880	920	910	940	980	990
6.5	900	930	940	950	990	990
7.5	890	920	900	960	960	990
8.5	890	920	920	940	970	980
9.5	900	910	900	950	960	990
10.5	900	920	920	940	980	980
11.5	900	910	920	960	980	990
12.5	890	910	930	930	1010	980
13.5	900	910	960	970	990	990
14.5	880	910	970	960	1020	970
15.5	930	910	960	990	990	980
16.5	910	910	960	970	1010	990
17.5	950	940	970	1000	1020	1010
b) 2-liter samples, constituting 2-sample composites						
1.0	960	930	930	970	1010	990
Integrated, 3.5-17.5	950	920	930	940	1020	1020

Table 6. Masses of chlorophyll a calculated for selected depth-zones* of Lake 442: a) from the 1-meter interval profile (g); b) % differences between masses derived from the 5-sample profile and those from the 1-meter interval profile; and c) % differences between masses derived from the 2-sample composite method and those of the 1-meter interval profile.

	1990						
	June 6	July 4	Aug. 1	Aug. 29	Sept. 26	Oct. 24	\bar{x}
<u>0-4 m</u>							
a) 1-meter interval profile, n=4	1,003	986.2	967.9	777.7	1,150	1,631	
b) 5-sample profile, n=2	+ 4.0	+ 3.7	+ 1.8	- 0.9	+ 2.7	+ 0.9	+ 2.0
c) 2-sample composite, n=1	- 5.1	- 5.8	+ 6.7	- 2.1	<u>-16.2</u>	- 1.0	- 3.9
<u>4-10 m</u>							
a) 1-meter interval profile, n=6	4,968	2,307	1,939	2,471	1,920	1,836	
b) 5-sample profile, n=2	<u>+11.0</u>	<u>-25.8</u>	- 0.7	+ 7.2	- 9.1	0.0	- 2.9
<u>10-18 m</u>							
a) 1-meter interval profile, n=8	1,359	1,058	1,744	2,142	1,973	893.6	
b) 5-sample profile, n=2	<u>-22.9</u>	<u>-23.6</u>	<u>+147.7</u>	<u>+51.7</u>	<u>+11.8</u>	<u>+33.2</u>	+33.0
<u>4-18 m</u>							
a) 1-meter interval profile, n=14	6,327	3,365	3,683	4,614	3,893	2,730	
b) 5-sample profile, n=4	+ 3.7	<u>-25.1</u>	<u>+69.6</u>	<u>+27.8</u>	+ 1.5	<u>+10.9</u>	+14.7
c) 2-sample composite, n=2	- 1.0	+ 0.6	- 3.2	+ 7.7	<u>+10.6</u>	+ 3.1	+ 3.0
<u>0-18 m</u>							
a) 1-meter interval profile, n=18	7,330	4,351	4,651	5,391	5,043	4,361	
b) 5-sample profile, n=5	+ 3.7	<u>-18.6</u>	<u>+55.5</u>	<u>+23.7</u>	+ 1.8	+ 7.1	+12.2
c) 2-sample composite, n=2	- 1.6	- 0.9	- 1.1	+ 6.3	+ 4.5	+ 1.6	+ 1.5

* In mid summer, 0-4 m generally defines the epilimnion; the depth of the photic zone is usually 10 m.

n = number of discrete chemical analyses contributing to computed mass.

Table 7. Masses of total phosphorus (TP) calculated for selected depth-zones* of Lake 442: a) from the 1-meter interval profile (g); b) % differences between masses derived from the 5-sample profile and those from the 1-meter interval profile; and c) % differences between masses derived from the 2-sample composite method and those of the 1-meter interval profile.

	1990						
	June 6	July 4	Aug. 1	Aug. 29	Sept. 26	Oct. 24	\bar{x}
<u>0-4 m</u>							
a) 1-meter interval profile, n=4	1,953	2,735	3,580	4,186	4,030	4,919	
b) 5-sample profile, n=2	- 3.6	- 5.6	- 4.1	- 3.5	- 7.2	0.0	- 4.0
c) 2-sample composite, n=1	<u>+77.3</u>	<u>-15.6</u>	<u>-43.6</u>	<u>+10.3</u>	<u>+14.6</u>	<u>+17.3</u>	+10.1
<u>4-10 m</u>							
a) 1-meter interval profile, n=6	5,227	4,713	6,623	6,137	5,333	5,576	
b) 5-sample profile, n=2	<u>+18.3</u>	<u>+14.3</u>	- 6.8	+ 0.6	+ 5.9	- 5.9	+ 4.4
<u>10-18 m</u>							
a) 1-meter interval profile, n=8	3,969	5,265	5,679	7,812	8,554	5,117	
b) 5-sample profile, n=2	- 4.3	<u>-14.5</u>	<u>+70.0</u>	<u>+19.1</u>	<u>+20.2</u>	<u>+73.9</u>	+27.4
<u>4-18 m</u>							
a) 1-meter interval profile, n=14	9,196	9,978	12,302	13,950	13,887	10,693	
b) 5-sample profile, n=4	+ 8.6	- 0.9	<u>+28.7</u>	<u>+11.0</u>	<u>+14.7</u>	<u>+32.2</u>	+15.7
c) 2-sample composite, n=2	<u>+92.7</u>	<u>+59.6</u>	- 3.4	<u>+17.7</u>	+ 3.4	+ 2.9	+28.8
<u>0-18 m</u>							
a) 1-meter interval profile, n=18	11,149	12,713	15,882	18,136	17,917	15,612	
b) 5-sample profile, n=5	+ 6.4	- 1.9	<u>+21.2</u>	+ 7.6	+ 9.7	<u>+22.1</u>	+10.9
c) 2-sample composite, n=2	<u>+90.0</u>	<u>+43.4</u>	<u>-12.5</u>	<u>+16.0</u>	+ 5.9	+ 7.5	+25.1

* In mid summer, 0-4 m generally defines the epilimnion; the depth of the photic zone is usually 10 m.
n = number of discrete chemical analyses contributing to computed mass.

Table 8. Masses of soluble reactive silicon (SRSi) calculated for selected depth-zones* of Lake 442: a) from the 1-meter interval profile (kg); b) % differences between masses derived from the 5-sample profile and those from the 1-meter interval profile; and c) % differences between masses derived from the 2-sample composite method and those of the 1-meter interval profile.

	1990						
	June 6	July 4	Aug. 1	Aug. 29	Sept. 26	Oct. 24	\bar{x}
<u>0-4 m</u>							
a) 1-meter interval profile, n=4	240.9	302.6	242.7	218.8	160.0	193.6	
b) 5-sample profile, n=2	+ 0.1	- 0.1	+ 1.3	+ 0.3	0.0	0.0	+ 0.3
c) 2-sample composite, n=1	- 0.6	+ 0.5	+ 7.9	<u>+19.5</u>	+ 1.0	+ 0.7	+ 4.8
<u>4-10 m</u>							
a) 1-meter interval profile, n=6	319.8	290.4	275.4	217.7	214.1	219.8	
b) 5-sample profile, n=2	+ 1.6	+ 8.4	<u>+14.2</u>	+ 1.8	<u>-26.4</u>	- 0.3	- 0.1
<u>10-18 m</u>							
a) 1-meter interval profile, n=8	194.6	209.9	249.1	237.7	257.8	201.3	
b) 5-sample profile, n=2	+ 8.6	+ 6.8	<u>+11.9</u>	+ 3.4	<u>+17.9</u>	<u>+47.6</u>	+16.0
<u>4-18 m</u>							
a) 1-meter interval profile, n=14	514.4	500.4	524.5	455.4	471.9	421.1	
b) 5-sample profile, n=4	+ 4.2	+ 7.7	<u>+13.1</u>	+ 2.7	- 2.2	<u>+22.6</u>	+ 8.0
c) 2-sample composite, n=2	<u>+10.2</u>	- 0.2	+ 4.1	<u>+14.8</u>	+ 6.1	+ 1.1	+ 6.0
<u>0-18 m</u>							
a) 1-meter interval profile, n=18	755.3	802.9	767.2	674.2	631.9	614.7	
b) 5-sample profile, n=5	+ 2.9	+ 4.8	+ 9.4	+ 1.9	- 1.6	<u>+15.5</u>	+ 5.5
c) 2-sample composite, n=2	+ 6.8	0.0	+ 5.3	<u>+16.3</u>	+ 4.8	+ 1.0	+ 5.7

* In mid summer, 0-4 m generally defines the epilimnion; the depth of the photic zone is usually 10 m.
n = number of discrete chemical analyses contributing to computed mass.

Table 9. Masses of dissolved sodium (Na) calculated for selected depth-zones* of Lake 442: a) from the 1-meter interval profile (kg); b) % differences between masses derived from the 5-sample profile and those from the 1-meter interval profile; and c) % differences between masses derived from the 2-sample composite method and those of the 1-meter interval profile.

	1990						
	June 6	July 4	Aug. 1	Aug. 29	Sept. 26	Oct. 24	\bar{x}
<u>0-4 m</u>							
a) 1-meter interval profile, n=4	516.5	532.5	530.7	562.3	574.3	568.0	
b) 5-sample profile, n=2	+ 0.6	+ 0.3	0.0	0.0	0.0	0.0	+ 0.2
c) 2-sample composite, n=1	+ 7.3	+ 0.8	+ 1.1	- 0.5	+ 1.5	+ 0.5	+ 1.8
<u>4-10 m</u>							
a) 1-meter interval profile, n=6	585.7	602.3	600.5	624.4	642.8	648.2	
b) 5-sample profile, n=2	- 0.1	+ 0.2	- 1.1	+ 1.4	- 1.5	+ 0.3	- 0.1
<u>10-18 m</u>							
a) 1-meter interval profile, n=8	214.9	218.4	223.3	227.6	237.0	235.1	
b) 5-sample profile, n=2	- 0.4	- 0.1	- 0.1	- 1.7	+ 2.0	- 0.1	- 0.1
<u>4-18 m</u>							
a) 1-meter interval profile, n=14	800.6	820.7	823.8	852.0	879.8	883.3	
b) 5-sample profile, n=4	- 0.2	+ 0.1	- 0.8	+ 0.6	- 0.5	+ 0.2	- 0.1
c) 2-sample composite, n=2	+ 6.0	+ 0.2	+ 1.0	- 1.7	+ 3.9	+ 3.8	+ 2.2
<u>0-18 m</u>							
a) 1-meter interval profile, n=18	1,317	1,353	1,354	1,414	1,454	1,451	
b) 5-sample profile, n=5	+ 0.1	+ 0.2	- 0.5	+ 0.3	- 0.3	+ 0.1	0.0
c) 2-sample composite, n=2	+ 6.5	+ 0.4	+ 1.1	- 1.2	+ 3.0	+ 2.5	+ 2.1

* In mid summer, 0-4 m generally defines the epilimnion; the depth of the photic zone is usually 10 m.

n = number of discrete chemical analyses contributing to computed mass.

Table 10. Frequency (% of the time) that constituent masses derived from the 2-sample composite method and the 5-sample profile differed from those derived from the 1-meter interval profile by i) >10% and ii) >25%. These frequencies are based on the masses calculated for the 0-4 m and 4-18 m depth zones (n=12).

		>10%	>25%
Chlorophyll <u>a</u>	5-sample profile	33	25
	2 sample composite	17	0
TP	5-sample profile	33	17
	2-sample composite	75	33
SRSi	5-sample profile	17	0
	2-sample composite	25	0
Na	5-sample profile	0	0
	2-sample composite	0	0

Table 11. Estimates of analytical uncertainties for chemical determinations, based on comparisons of discrete samples collected independently from depths of 1 meter (C = composite method) and 1.5 meters (P = profile method). Since both samples were taken in close proximity and from the surface-mixed layer, they should theoretically be the same; nevertheless, because they were collected from different depths, comparisons presented here should probably be considered as "worst case" scenarios.

	June 6	July 4	Aug. 1	Aug. 29	Sept. 26	Oct. 24	\bar{x}
a) <u>Chlorophyll a</u>							
C, 1.0 m ($\mu\text{g/L}$)	1.65	1.61	1.79	1.32	1.67	2.8	
P, 1.5 m ($\mu\text{g/L}$)	1.69	1.70	1.63	1.34	1.88	2.8	
$\frac{P_{1.5} - C_{1.0}}{C_{1.0}} \times 100 (\%)$	+ 2.4	+ 5.6	- 8.9	+ 1.5	+ 12.6	0.0	+ 2.2
b) <u>TDP</u>							
C, 1.0 m ($\mu\text{g/L}$)	3	2	0.5	5	5	5	
P, 1.5 m ($\mu\text{g/L}$)	0.5	3	4	6	5	4	
$\frac{P_{1.5} - C_{1.0}}{C_{1.0}} \times 100 (\%)$	<u>-83.3</u>	<u>+50.0</u>	<u>+700</u>	<u>+20.0</u>	0.0	20.0	+111
c) <u>IP</u>							
C, 1.0 m ($\mu\text{g/L}$)	6	4	3.5	8	8	10	
P, 1.5 m ($\mu\text{g/L}$)	3.5	6	6	8	8	9	
$\frac{P_{1.5} - C_{1.0}}{C_{1.0}} \times 100 (\%)$	<u>-41.7</u>	<u>+50.0</u>	<u>+71.4</u>	0.0	0.0	<u>-10.0</u>	+11.6
d) <u>SRSi</u>							
C, 1.0 m ($\mu\text{g/L}$)	415	527	454	378	280	338	
P, 1.5 m ($\mu\text{g/L}$)	415	525	416	378	276	336	
$\frac{P_{1.5} - C_{1.0}}{C_{1.0}} \times 100 (\%)$	0.0	-0.4	-8.4	0.0	-1.4	-0.6	- 1.8
e) <u>Na</u>							
C, 1.0 m ($\mu\text{g/L}$)	960	930	930	970	1010	990	
P, 1.5 m ($\mu\text{g/L}$)	890	930	920	980	990	980	
$\frac{P_{1.5} - C_{1.0}}{C_{1.0}} \times 100 (\%)$	-7.3	0.0	-1.1	+1.0	-2.0	-1.0	- 1.7

Table 12. Frequency and direction of deviation (+ or -) of constituent masses a) calculated from the 5-sample profile, and b) calculated from the 2-sample composite, relative to masses derived from the 1-meter interval profile, for depth zones 0-4 and 4-18 m, combined.

	No. of times/12			
	a) 5-sample profile		b) 2-sample composite	
	+	-	+	-
Chlorophyll <u>a</u>	10	2	5	7
TP	5	6	9	3
SRSi	8	2	10	2
Na	5	3	10	2
Σ	28	13	34	14

Table 13. Frequency at which differences in constituent masses computed from the 5-sample profile (P) and 2-sample composite (C) exceeded 10% relative to masses derived from the 1-meter interval profile.

	No. of times/6						
	0-4 m		4-10 m	4-18 m		10-18 m	Σ
	C	P	P	C	P	P	
Chlorophyll <u>a</u>	1	0	2	1	4	6	14
TP	6	0	2	3	4	5	20
SRSi	1	0	2	2	2	3	10
Na	0	0	0	0	0	0	0
Σ	$\overline{8}$	$\overline{0}$	$\overline{6}$	$\overline{6}$	$\overline{10}$	$\overline{14}$	

APPENDIX 1

PROCEDURES USED TO COMPUTE CONSTITUENT MASSES FROM THE 1-METER INTERVAL PROFILE, THE SIMULATED 5-SAMPLE PROFILE, AND THE 2-SAMPLE COMPOSITE

Definitions

In the formulae that follow:

$M_{i,j}$ = mass (mg) between the depths i and j

C_i = concentration ($\mu\text{g}\cdot\text{L}^{-1}$) at depth i

$V_{i,j}$ = volume (m^3) between the depths i and j

i, j, k = depth (m).

Constituent masses were computed at 1-meter intervals for both the 1-meter interval profile and the simulated 5-sample profile.

a) 1-meter interval profile:

For any 1-meter interval slice, the corresponding constituent concentration was applied directly:

$$M_{i,i+1} = V_{i,i+1} * C_{i+0.5} \quad \text{for } i = 0 \text{ to } 17$$

b) 5-sample profile

Constituent concentrations from 5 depths, only, were applied to volumes at 1-meter intervals according to the scheme shown below:

$$M_{i,i+1} = V_{i,i+1} * C_{0.5} \quad \text{for } i = 0 \text{ to } 1$$

$$M_{i,i+1} = V_{i,i+1} * C_{3.5} \quad \text{for } i = 2 \text{ to } 4$$

$$M_{i,i+1} = V_{i,i+1} * C_{7.5} \quad \text{for } i = 5 \text{ to } 9$$

$$M_{i,i+1} = V_{i,i+1} * C_{12.5} \quad \text{for } i = 10 \text{ to } 14$$

$$M_{i,i+1} = V_{i,i+1} * C_{17.5} \quad \text{for } i = 15 \text{ to } 17$$

For either the 1-meter interval profile or the 5-sample profile, masses for depth intervals larger than 1 meter were calculated by summing the appropriate 1-meter interval masses:

$$M_{j,k} = \sum_{i=j}^{k-1} M_{i,i+1}$$

c) 2-sample composite

Masses for the depth interval 0 to 3 m were computed by multiplying the volume by the constituent concentration measured at 1.0 m (the assumption here is that a sample collected from a depth of 1 meter is representative of the epilimnion):

$$M_{0,3} = \sum_{i=0}^2 V_{i,i+1} * C_{1.0}$$

The constituent concentration determined for the integrated sample was applied to the depth interval 3 to 18 m to compute the mass in that stratum:

$$M_{3,18} = V_{3,18} * C_{3.5,17.5}$$

The mass for the whole lake was obtained by summation:

$$M_{0,18} = M_{0,3} + M_{3,18}$$

The mass for the depth interval 0 to 4 m was computed by multiplying the volume by the constituent concentration measured at 1.0 m:

$$M_{0,4} = \sum_{i=0}^3 V_{i,i+1} * C_{1.0}$$

And, the mass for the 4 to 18 m stratum was calculated by subtraction:

$$M_{4,18} = M_{0,18} - M_{0,4}.$$