

## COMPARISONS OF SOLUBLE REACTIVE PHOSPHORUS AND ORTHOPHOSPHORUS CONCENTRATIONS AT AN OFFSHORE STATION IN SOUTHERN LAKE MICHIGAN

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**ABSTRACT.** Soluble reactive phosphorus (SRP), measured by Harvey's method and the Chamberlain-Shapiro extraction technique from May to October 1976 in the epilimnion at an offshore station in southeastern Lake Michigan, was higher and more variable than previously published measurements, suggesting that phosphorus loaded into the nearshore zone is being transported into offshore water. Pronounced vertical variations in SRP occurred periodically in the water column and near the sediments, but accumulation in the hypolimnion over the period did not occur. Both molybdenum blue methods overestimated maximum possible  $PO_4$ -P concentrations (MPPC) (as measured by Rigler's radiobioassay method) in water from 4 m by up to two orders of magnitude, but MPPC concentrations averaged 22.5% and 25.6% of the mean value measured by Harvey's method and by the extraction technique, respectively. Comparisons with radioassay estimates from other lakes suggest that MPPC concentrations may be lower in eutrophic than in mesotrophic or oligotrophic lakes.

### INTRODUCTION

Surveillance programs on the water quality of Lake Michigan usually include measurements of "orthophosphorus" because of its role in cultural eutrophication (Torrey 1976). Radiotracer techniques, however, have shown that molybdenum blue methods can overestimate orthophosphorus ( $PO_4$ -P) concentrations, i.e., truly dissolved phosphate-phosphorus, by an order of magnitude or more in lakes where tests have been made (Rigler 1966). For this reason, analytical  $PO_4$ -P determinations in samples of filtered lake water are termed soluble reactive phosphorus (SRP) (Strickland and Parsons 1965).

SRP values in Lake Michigan often are near the detection limit (ca. 1.0  $\mu g$  P/L) of conventional methods in offshore water and range from 10-60  $\mu g$  P/L in nearshore water in the vicinity of polluted tributaries (Torrey 1976). Even though SRP has been measured frequently, very few data on the degree to which concentrations are depleted by

phytoplankton growth or the magnitude of seasonal and vertical variations in a water column are available, and comparative studies using different methods have not been undertaken even though SRP values can be method specific (Jones 1966). In addition, there is no information on the degree of discrepancy between SRP and  $PO_4$ -P concentrations in the lake. These issues are important because (1) monitoring programs by the Environmental Protection Agency (Region V, Chicago, IL) and Environment Canada use different methods and, therefore, may draw different inferences on long-term eutrophication trends in the Great Lakes system, (2) the effects on concentrations of different phosphorus fractions in Lake Michigan due to a reduction of phosphate in detergents by states bordering the lake currently are being evaluated (R. J. Bowden, personal communication), and (3) knowledge of  $PO_4$ -P concentrations is required to model phosphorus cycling in lakes (Rigler 1973).

The objectives of this work were to compare temporal and vertical variations in SRP measured by two molybdenum blue methods and to determine to what extent  $PO_4$ -P concentrations at an

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offshore station in southern Lake Michigan are overestimated by analytical methods. Harvey's method (Harvey 1948) was selected because it has been used widely in the Great Lakes and is recommended by Environment Canada (1974). The Chamberlain-Shapiro (1969) extraction method was chosen because it has a lower detection limit and is less subject to interferences than most methods (Shapiro, Chamberlain, and Barrett 1970). True  $\text{PO}_4\text{-P}$  concentrations cannot be measured by analytical procedures; therefore, maximum possible  $\text{PO}_4\text{-P}$  concentrations (MPPC) were estimated by Rigler's (1966) radiobiassay method.

## METHODS

### Collection and Filtration of Samples

Water was collected in 5-L niskin bottles equipped with reversible thermometers at an offshore station ( $43^\circ 05' 12''\text{N}$ ,  $86^\circ 25' 45''\text{W}$ ) located in 90 m of water 15 km west of Grand Haven, Michigan, at weekly intervals from 14 May to 20 October 1976. One of two sampling arrays was used: 0, 2, 4, 6, 8, 10, 15, and 20 (or 25 m) and 0, 1.5, 3, 6, 9, 12, 18, and 25 (or 30 m). Samples were filtered at a vacuum of 300 mm Hg through previously rinsed (ca. 75 mL distilled deionized water) 0.45- $\mu\text{m}$  Millipore filters (47-mm diameter) into 1-L linear polyethylene (LPE) bottles. Tests on several lots of filters showed that an average of  $7.2 \pm 0.2 \mu\text{g P}$  of contaminant  $\text{PO}_4\text{-P}$  was released from filters when 25 mL of distilled water was filtered and analyzed, but rinsing filters with a second, separate 25-mL aliquot showed that molybdate reactive P had been removed by the first rinse. Containers were placed in the dark at  $4^\circ\text{C}$ , transported to the laboratory in portable ice chests, and analyzed within 1-2 days.

All glassware and sample bottles used in SRP and  $\text{PO}_4\text{-P}$  analysis were washed in hot water and Liquinox (Alconox, Inc., N.Y.), a phosphate-free detergent, soaked at least 12 hr in concentrated  $\text{HNO}_3$ , and rinsed six times in distilled water before use.

### Harvey's Method

Filtrates were analyzed in duplicate or triplicate by Harvey's method as modified by Rigler (1964). Fifty-mL subsamples received 2 mL of 2.5% ammonium molybdate (w/v) in 10 N  $\text{H}_2\text{SO}_4$  and 15-20 s later 0.3 mL of 0.8%  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  (w/v) in 0.24 N HCl. Optical density was measured in a cuvette with a 5.0-cm light path at 650 nm in a

Fisher Electrophotometer II or a Bausch and Lomb Model 88 spectrophotometer  $9 \pm 0.25$  min after the reductant was added. External standards were prepared in distilled, deionized water and internal standards were prepared in filtered lake water by serial dilution using known concentrations of a stock solution of  $\text{KH}_2\text{PO}_4$ . Distilled and filtered lake water reagent blanks were run with each set of samples. Small traces of organic color in filtrates were eliminated by running color blanks (the addition of all reagents except ammonium molybdate). Comparisons of the slopes of standard curves (corrected optical density vs.  $\text{PO}_4\text{-P}$  concentration) showed the presence of a 20-25% salt effect. *Standards prepared in distilled water, therefore, underestimate SRP.* All values reported here are based on internal standards. The detection limit was ca.  $1.0 \mu\text{g P/L}$ ; "within-run" precision (standard error of the mean) based on triplicate determinations in lake-water samples at concentrations between 1.3 and  $12.5 \mu\text{g P/L}$  was  $\leq 0.1 \mu\text{g P/L}$ . Silica ( $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ ) at 10 mg Si/L did not interfere. Ten  $\mu\text{g As/L}$  ( $\text{NaHAsO}_4 \cdot 7\text{H}_2\text{O}$ ) was detected as  $5 \mu\text{g P/L}$ .

### Extraction Method

Filtrates from selected depths were analyzed in duplicate or triplicate by the Chamberlain-Shapiro (1969) extraction method. One-hundred mL subsamples received 25 mL of reagent grade isobutanol, 5 mL of 1% aqueous ammonium molybdate, and 5 mL of 3.3 N HCl. Extracts received 2 mL of absolute ethanol containing 140 mg  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ /mL, and optical density was measured  $9 \pm 0.25$  min later in a cuvette with a 2.3-cm light path at 650 nm. Color blanks and distilled water and filtered lake water reagent blanks were run with external and internal standards.  $\text{PO}_4\text{-P}$  standards prepared above were split and used in extraction analysis. The detection limit was ca.  $0.3 \mu\text{g P/L}$ ; precision (standard error of the mean) based on "within run" triplicate determinations in lake-water samples at concentrations between 0.4 and  $12.5 \mu\text{g P/L}$  was  $\leq 0.1 \mu\text{g P/L}$ . Arsenate at 100  $\mu\text{g As/L}$ , silica at 10 mg Si/L, and organic color did not interfere. A salt effect did not occur because phosphomolybdate was extracted into the organic solvent before reduction.

### Rigler's Radiobiassay Method

Water from 4 m was poured into 250-mL Pyrex reagent bottles, and the bottles were placed in a

deck-top incubator maintained at *in situ* temperature.  $\text{KH}_2\text{PO}_4$  was added at concentrations ranging from 0.01 to 2.5  $\mu\text{g P/L}$ , followed within 3 s by the addition of 1–5  $\mu\text{Ci}$  of carrier-free orthophosphoric acid obtained from New England Nuclear (NEN), Boston, Massachusetts. Ten-mL subsamples were removed immediately and at intervals over 2–3 hr and filtered through 0.45- $\mu\text{m}$  Millipore filters (25-mm diameter) at a vacuum of 200 mm Hg. Filters were counted in Aquasol (NEN) in a Beckman, Model LS-150, liquid scintillation counter. MPPC were obtained by graphical analysis (Rigler 1966), and replicate analyses showed that estimates varied by  $<\pm 5\%$ . Water used in these tests also was filtered and analyzed by both molybdenum blue methods.

#### Container and Storage Effects

Periodic tests during July–October 1976 and in August 1977 were performed to determine the effects of short-term storage on SRP concentrations. Water collected from 4 m was filtered and stored in the dark at 4°C in Pyrex glass reagent bottles (G), conventional polyethylene (CP), and LPE containers. SRP was measured immediately after filtration and over time on subsamples from each container. SRP in LPE and G bottles remained within  $\pm 15\%$  of the initial concentration for the first four days. Filtrates stored in CPE containers were 30–60% lower than initial measurements after one day. Samples collected over surface-to-bottom profiles in August, September, and October 1976 and in August 1977 were filtered into LPE and G bottles. SRP was measured immediately, and the bottles were stored in the dark with periodic subsampling over a period of 7 days. SRP levels differed by  $\leq \pm 15\%$  from the initial concentration during the first 4 days. Short-term storage of filtrates in G and LPE bottles apparently did not affect SRP measurements significantly. Mean SRP estimates differing by  $< \pm 15\%$ , therefore, cannot be considered dissimilar.

## RESULTS

#### Harvey's Method

Average SRP concentrations in the epilimnion, based on analysis of five to seven samples on each date by Harvey's method, ranged from 2.0  $\mu\text{g P/L}$  on 7 September to 10.3  $\mu\text{g P/L}$  on 4 October, with an overall mean of 4.9  $\mu\text{g P/L}$ . Although average

epilimnetic concentrations were often similar on consecutive weeks, variations of 50–100% or more between sampling dates were common in late summer and early fall (Figure 1A).

Variations over surface-to-bottom profiles on 7 July, 10 August, 7 September, and 18 October 1976 often were relatively small over large portions of the column (Figure 2). Significant variations were represented by a marked increase from 30 to 80 m on 7 July, by a sharp increase from 60 to 80 m on 7 September, and by relatively low concentrations in near-surface water and at 40 m on 18 October.

#### Extraction Method

Average SRP concentrations in the epilimnion, based on analysis of three or four samples on each date by the extraction technique, ranged from 1.2  $\mu\text{g P/L}$  on 2 August to 7.7  $\mu\text{g P/L}$  on 4 October, with an overall mean of 3.4  $\mu\text{g P/L}$  (Figure 1B). Mean SRP values varied irregularly over the period, but higher levels often were detected from mid-September to late October. Weekly variations in SRP in the epilimnion generally ranged from 10 to 50%, and relative trends in vertical variations over surface-to-bottom profiles usually paralleled those based on Harvey's method (Figure 1A).

#### Rigler's Radioassay Method

MPPC ranged over two orders of magnitude, with a mean of nearly 0.5  $\mu\text{g P/L}$ , and were never greater than 1.0  $\mu\text{g P/L}$  (Figure 1C). There was no apparent temporal pattern, but values were consistently higher and less variable from early August through October than from May through July.

#### Comparison of SRP and $\text{PO}_4\text{-P}$ Measurements

##### *Euphotic Zone and Epilimnion*

Since the number of samples analyzed by Harvey's method exceeded the number of samples analyzed by the extraction method each week, rigorous comparisons only could be made for those subsamples where SRP had been measured by both methods. Differences between average values in the euphotic zone (determined from *in situ* primary production profiles) for each date, computed as a ratio of mean SRP measured by Harvey's method to mean SRP measured by extraction (or *vice versa* depending upon which method gave the highest average value), showed a large spread in values (Figure 3). The ratio of mean Harvey to mean extraction ranged from 6.7 and 3.8 on 2 August and

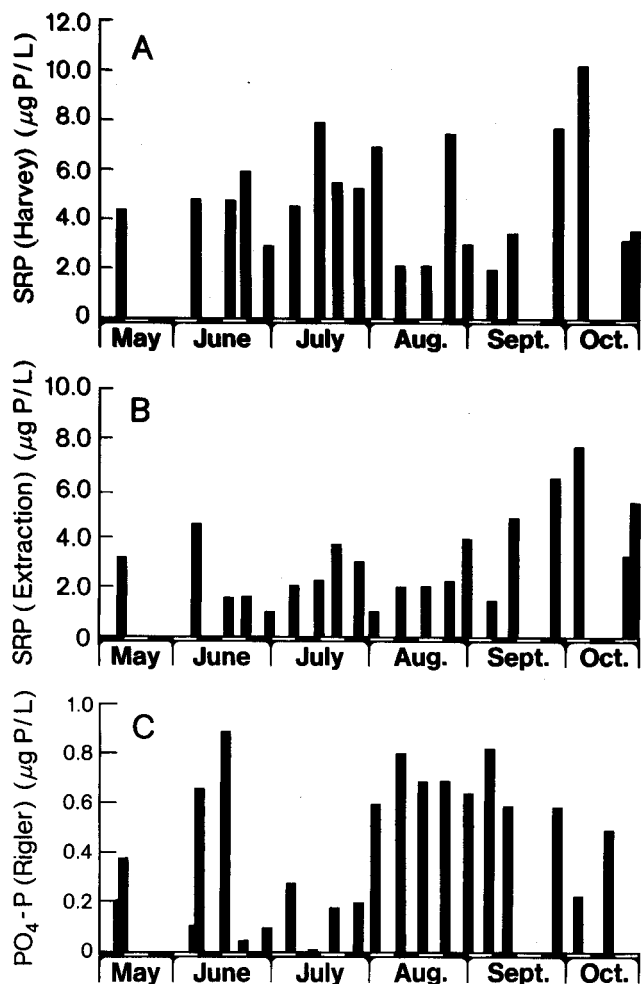


FIG. 1. Variations in mean dissolved P concentrations based on (A) Harvey's method, (B) the Chamberlain-Shapiro extraction method, and (C) maximum possible  $\text{PO}_4\text{-P}$  concentrations measured by Rigler's radiobioassay method, from 14 May to 20 October 1976 in the epilimnion at an offshore station in southern Lake Michigan. Each mean value is based on five to seven measurements made above the thermocline.

21 June, respectively, to mean extraction to mean Harvey ratios of 1.6 on 9 September and 20 October. In some individual subsamples, SRP determined by extraction was at least twice as high as measurements made by Harvey's method. Mean concentrations measured by Harvey's method were over twice as high as average values determined by extraction in six dates, between twice as high or equal to extraction values on nine dates, and less than extraction values on five dates.

SRP measured by the two molybdenum blue methods on all samples collected in the epilimnion,

in the euphotic zone, and at the surface, 6 m, and at the lowest depth in the water column (between 15 and 30 m) were tested with a paired t-test (Snedecor and Cochran 1967). Harvey's method gave statistically higher SRP concentrations than the extraction method in samples from the epilimnion ( $P < 0.05$ ) and the euphotic zone ( $P < 0.01$ ) and for surface and 6-m samples ( $P < 0.1$ ), but measurements on samples from 15 to 30 m (usually in the hypolimnion) were statistically similar ( $P > 0.10$ ) (Table 1). MPPC measured by Rigler's method in water from 4 m ranged between 1 and 42% ( $\bar{x}=22.5\%$ ) of Harvey's method and between 3 and 100% ( $\bar{x}=25.6\%$ ) of values measured by extraction (Table 2).

**Vertical profiles.** Measurements over surface-to-bottom profiles (Figure 2) showed that Harvey's method generally yielded higher values early in the season, but extraction values often were higher in late summer and fall (Table 3). The mean column value on 7 July based on Harvey's method was statistically higher than the mean obtained by extraction ( $P < 0.01$ ). On 10 August, extraction values were higher than those obtained by Harvey's method from 25–40 m and near the bottom, but mean column values were statistically equivalent ( $P > 0.1$ ). Mean column values on 7 September were equivalent at  $P < 0.1$ , but Harvey's method gave a statistically higher mean when paired samples were tested ( $P < 0.05$ ). On 18 October, vertical variations were relatively pronounced, but average column values were statistically equivalent ( $P > 0.1$ ).

## DISCUSSION

SRP concentrations measured by Harvey's method and the extraction technique generally are higher than previous measurements on epilimnetic water in offshore regions in southern and central Lake Michigan (Torrey 1976). For example, Schelske and Callender (1970) reported  $\leq 0.5$  to  $3.1 \mu\text{g P/L}$  using Stephens' (1963) extraction method for surface samples collected in July 1969 at seven offshore stations in southeastern Lake Michigan; Rousar (1973) measured  $\leq 1.0$  to  $4.0 \mu\text{g P/L}$  (mean =  $1.1 \mu\text{g P/L}$ ) with the method of Ambühl and Schmid (1965) in samples from a depth of 4.0 m between April 1970 and April 1971 from a station 32 km southwest of Ludington, Michigan; and Huh *et al.* (1972) reported  $< 1.0$  to  $4.0 \mu\text{g P/L}$  (mean =  $2.0 \mu\text{g P/L}$ ) using Harvey's method in surface

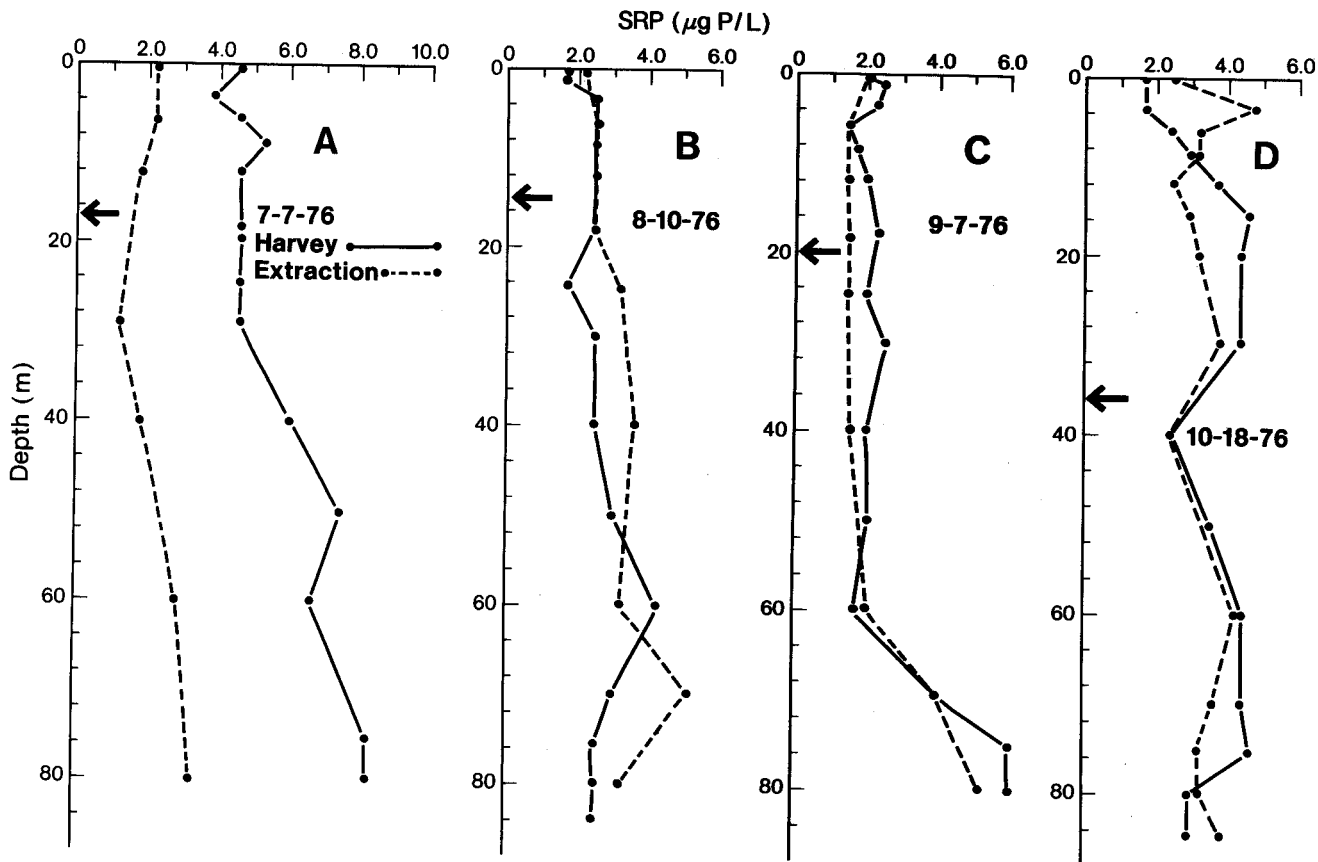


FIG. 2. Comparison of SRP concentrations as measured by Harvey's method and the Chamberlain-Shapiro extraction technique for surface-to-bottom profiles on (A) 7 July, (B) 10 August, (C) 7 September, and (D) 18 October at an offshore station in southern Lake Michigan in 1976. The depth of the thermocline on each date is indicated with an arrow.

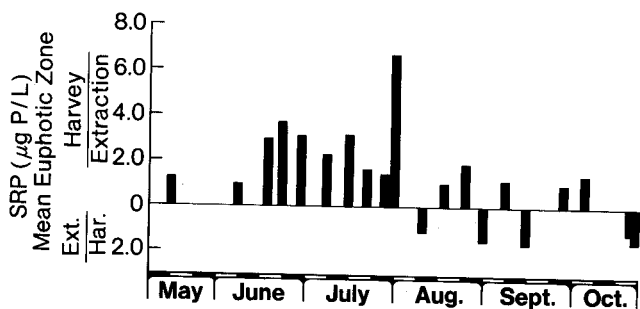


FIG. 3. Variations in the ratio of mean SRP concentrations based on Harvey's method and the Chamberlain-Shapiro extraction technique from 14 May to 20 October 1976 in the euphotic zone at an offshore station in southern Lake Michigan. Ratios were computed as mean Harvey to mean extraction (upper histogram) or as mean extraction to mean Harvey (lower histogram) depending upon which method gave the highest average SRP concentration.

samples collected from January 1970 to April 1971 at a station 9.6 km east of Zion, Michigan, in southwestern Lake Michigan.

Measurements by Harvey's method would have been at least 20% lower if external standards had been used. The seasonal mean for the epilimnion would then have been ca. 4.0 µg P/L. Although many authors cited in Torrey (1976) do not state how standards were prepared, our estimates, even if based on external standards, are higher than previously published values. Three factors could account for this: (1) short-term storage of filtrates or inconsistencies in analytical procedures might cause overestimation of SRP; (2) the methods used in this study may have higher hydrolytic potentials than methods used by other investigators; or (3) SRP concentrations in 1976 could have been higher than in previous years.

We were unable to detect a positive bias in procedures: the accuracy of the P standard was

**TABLE 1.** Comparison of SRP concentrations measured by Harvey's method and the Chamberlain-Shapiro extraction technique for samples taken from the surface, 6 m, the lowest depth (15-30 m) sampled in the euphotic zone, and all paired measurements on samples collected in the epilimnion and the euphotic zone between 14 May and 20 October 1976 at an offshore station in southern Lake Michigan. Data sets were treated with a paired t-test (Snedecor and Cochran 1967).

	Number samples	Range (µg P/L)	Mean (µg P/L)	S.D.	Paired t-statistic
<b>Surface samples</b>					
Extraction	18	0.6-7.3	3.3	1.72	
Harvey	18	1.5-8.0	4.2	2.12	t = 2.24*
<b>6-Meter samples</b>					
Extraction	18	1.0-8.3	3.6	2.24	
Harvey	18	1.5-10	5.6	4.71	t = 2.30*
<b>15-30-Meter samples</b>					
Extraction	18	0.7-7.7	3.5	1.90	
Harvey	18	2.2-8.5	4.8	2.00	t = 1.68
<b>Epilimnion</b>					
Extraction	87	0.6-8.3	3.5	1.78	
Harvey	87	1.2-8.5	4.2	1.97	t = 2.62**
<b>Euphotic zone (0-30m)</b>					
Extraction	97	0.6-8.3	3.5	1.88	
Harvey	97	1.5-11.4	4.2	2.01	t = 3.89***

Significance at P ≤ 0.10\*, ≤ 0.05\*\*, ≤ 0.01\*\*\*

**TABLE 2.** Comparison of SRP concentrations as measured by Harvey's method and the Chamberlain-Shapiro extraction method and maximum possible PO<sub>4</sub>-P concentrations (Rigler's radiobioassay method) on water collected on 21 dates from a depth of 4 m between 14 May and 18 October 1976 at an offshore station in southern Lake Michigan.

Method	Range (µg P/L)	Mean (µg P/L)	S.D.
Harvey	1.2-7.8	3.6	1.84
Extraction	0.9-7.7	3.0	1.84
Radioassay	0.01-0.89	0.48	0.30

verified by comparing it with standards obtained from The Water Quality Assurance Branch, U.S. Environmental Protection Agency, Cincinnati, Ohio, and from an independent laboratory; no evidence of nonspecific reduction of phosphomolybdate was detected; P contamination in filters was removed before filtration; and silica and organic color did not interfere. Although As interferes in Harvey's method, total As levels at the station were ≤ 0.5 µg As/L (Eadie *et al.* 1979). Sorption of PO<sub>4</sub>-P may have occurred, but this would lead to a

**TABLE 3.** A comparison of SRP concentrations measured by Harvey's method and the Chamberlain-Shapiro extraction technique for four vertical profiles at an offshore station in southeastern Lake Michigan in 1976. The two sets of measurements for each profile were treated with a paired t-test if the number of observations was equal. Profiles with unequal numbers of samples were treated with a t-test based on the assumption of unequal variances and the August and September profiles also were tested with a paired t-test omitting unpaired samples (Snedecor and Cochran 1967).

	Number samples	Range (µg P/L)	Mean (µg P/L)	S.D.	t-statistic
<b>7 July</b>					
Extraction	7	1.2-3.2	2.2	0.67	unpaired
Harvey	14	3.8-8.2	5.6 <sup>1</sup>	1.47	7.11***
<b>10 August</b>					
Extraction	9	2.2-5.1	3.1 <sup>2</sup>	0.88	unpaired
Harvey	16	1.7-4.2	2.5	0.59	1.64
<b>7 September</b>					
Extraction	9	1.5-5.2	2.3	1.35	unpaired
Harvey	15	1.5-6.0	2.7 <sup>3</sup>	1.45	1.82
<b>18 October</b>					
Extraction	14	2.5-4.8	3.4	0.62	paired
Harvey	14	1.7-4.6	3.4	1.06	0.04

\*\*\*significance at P ≤ 0.01

<sup>1</sup>paired t-test significant at P < 0.10; n = 7

<sup>2</sup>paired t-test significant at P < 0.10; n = 9

<sup>3</sup>paired t-test significant at P < 0.05; n = 9

decrease, not an increase, in SRP. Moreover, elevations in SRP also could be caused by enzyme-mediated hydrolysis of organic organic compounds in filtrates. Alkaline phosphatase or other enzymes dissolved in lake water or released from ruptured algae could lead to increases in SRP (Berman 1970). Although phytoplankton was P-limited during summer 1976 (Tarapchak, unpublished), alkaline phosphatase probably had little effect since phytoplankton biomass was low (< 1.5 mg/L fresh weight), and increases in SRP did not occur in containers.

Harvey's method causes more hydrolysis than other methods and, therefore, gives higher SRP values. Although comparative tests on solutions of P-containing organic and condensed inorganic compounds verified that Harvey's method has a higher hydrolytic potential than either the extraction method or the Murphy and Riley (1962) ascorbic acid method (Tarapchak, unpublished data), SRP values measured by the extraction technique at times exceeded those made by Harvey's method (Figures 1, 3). This suggests that SRP

values detected in this study were, in fact, higher than concentrations detected in previous years.

The station is located 15 km west of the Grand River. The discharge of total P from three rivers, the St. Joseph River (160 m<sup>3</sup>/s and 956 MT P/yr), the Kalamazoo River (72 m<sup>3</sup>/s and 0.294 MT P/yr), and the Grand River (125 m<sup>3</sup>/s and 989 MT P/yr), contributes at least 30% of the tributary input of total P to Lake Michigan (Lee 1974). [The Grand River discharged an average of 800 MT of P in 1975 and 1976 (Eadie *et al.* 1979).] Although the mass transport of P from nearshore into offshore water is not known, higher SRP levels detected at this station suggest that significant amounts of P are being transported into offshore water in this region of the lake.

Davis (1977, personal communication) has shown that high concentrations of particulate and dissolved materials in river water are carried out in surface water or along the thermocline to distances of 10–15 km from shore in this region. If this mixing pattern persists throughout the year, it could account for higher SRP levels detected at the station. Increases in SRP in the fall (Figure 1) also may be caused by increased loadings from the nearshore zone caused by stormy weather and higher discharge rates from rivers after heavy rains during fall. Transport of P from the nearshore zone also is plausible since 1976 was a wet year and water outflow from the Grand River greatly exceeded the 44-year mean flow average (Chambers and Eadie 1980).

SRP increases detected near the sediments (Figure 2) might be attributed to bioturbation or to the excretion of molybdate reactive P by benthic organisms. Chambers and Eadie (1980, 1981), however, showed that a "nepheloid layer" (Baker and Feely 1978) in bottom water at the station occurs during thermal stratification. During stormy weather, particulate material in nearshore sediments is resuspended and carried lakeward near the bottom. This phenomenon or local resuspension could account for the pronounced increase in SRP observed on 7 September near the sediments (Figure 2C) when stormy weather prevailed, and for its absence on 10 August (Figure 2B) when the weather was relatively calm prior to sampling. Further studies on the formation and persistence of the "nepheloid layer" and on sedimentation and decomposition rates of particulate materials originating in the epilimnion are required to interpret SRP gradients in the hypolimnion and near the sediments.

Relative differences between SRP concentrations measured by the two molybdenum blue methods varied during the period (Figure 1) and with depth (Figure 2), suggesting that the chemical composition of the SRP pool changed during the period and varied with depth in the water column. During late summer and fall, the extraction technique often gave higher values than did Harvey's method (Figure 1). We have shown elsewhere that acid hydrolysis rates of the SRP pool can be enhanced by ammonium molybdate and that the acid-molybdate regime of the extraction method at times yields higher hydrolysis rates and final SRP concentrations than Harvey's method (Tarapchak, Bigelow, and Rubitschun 1981). Our results and those of other investigators also show that a significant fraction of SRP detected in filtrates is derived from hydrolysis of organic molecules or is released from colloidal material < 0.45  $\mu\text{m}$  in filtrates (Tarapchak *et al.* 1981, unpublished data; Lean 1976; Downes and Paerl 1978; Rigler 1973; Stainton 1980). This accounts for the difference between SRP and MPPC (Figure 1), and suggests that the acid-molybdate regime of the extraction technique may be more effective at times in releasing PO<sub>4</sub>-P from bound sources than Harvey's method.

Rigler's (1966) original demonstration that molybdenum blue methods overestimate MPPC concentrations by one to two orders of magnitude is frequently quoted, but few attempts have been made to compare temporal variations in SRP and MPPC in different types of lakes. Data from this station show that SRP values can overestimate MPPC by up to two orders of magnitude (Figure 1), but most values were  $\geq 0.2 \mu\text{g P/L}$ , and the mean concentration was 22.5% of the average SRP value based on Harvey's method (Table 2). The relatively small average difference between MPPC and SRP is brought about by consistently high MPPC during mid-summer to early fall. This suggests that true PO<sub>4</sub>-P concentrations during the P-limited period in Lake Michigan may be much higher than previously suspected. PO<sub>4</sub>-P concentrations in the epilimnion of the lake are maintained at relatively high levels because of rapid biotic recycling of PO<sub>4</sub>-P and because large silica-limited diatoms (the dominant phytoplankton in the lake) impose a low P demand. (Tarapchak, unpublished data). In contrast, MPPC in Lake 227, an artificially enriched lake in the Experimental Lakes Region, Ontario, Canada, are as low as  $0.59 \times 10^{-4} \mu\text{g P/L}$  and range from one to several orders

of magnitude below our estimates (Levine 1975, Levine and Schindler 1980). Collectively, these data suggest that true  $\text{PO}_4\text{-P}$  concentrations may be lower in the epilimnion of eutrophic lakes than in mesotrophic lakes because of higher biological utilization rates and less efficient recycling mechanisms. This hypothesis may be difficult to test, however, because  $\text{PO}_4\text{-P}$  concentrations also will be affected by inorganic complexing with iron or other inorganic-organic complexes in lake water (Stumm and Morgan 1970, Golterman 1973).

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