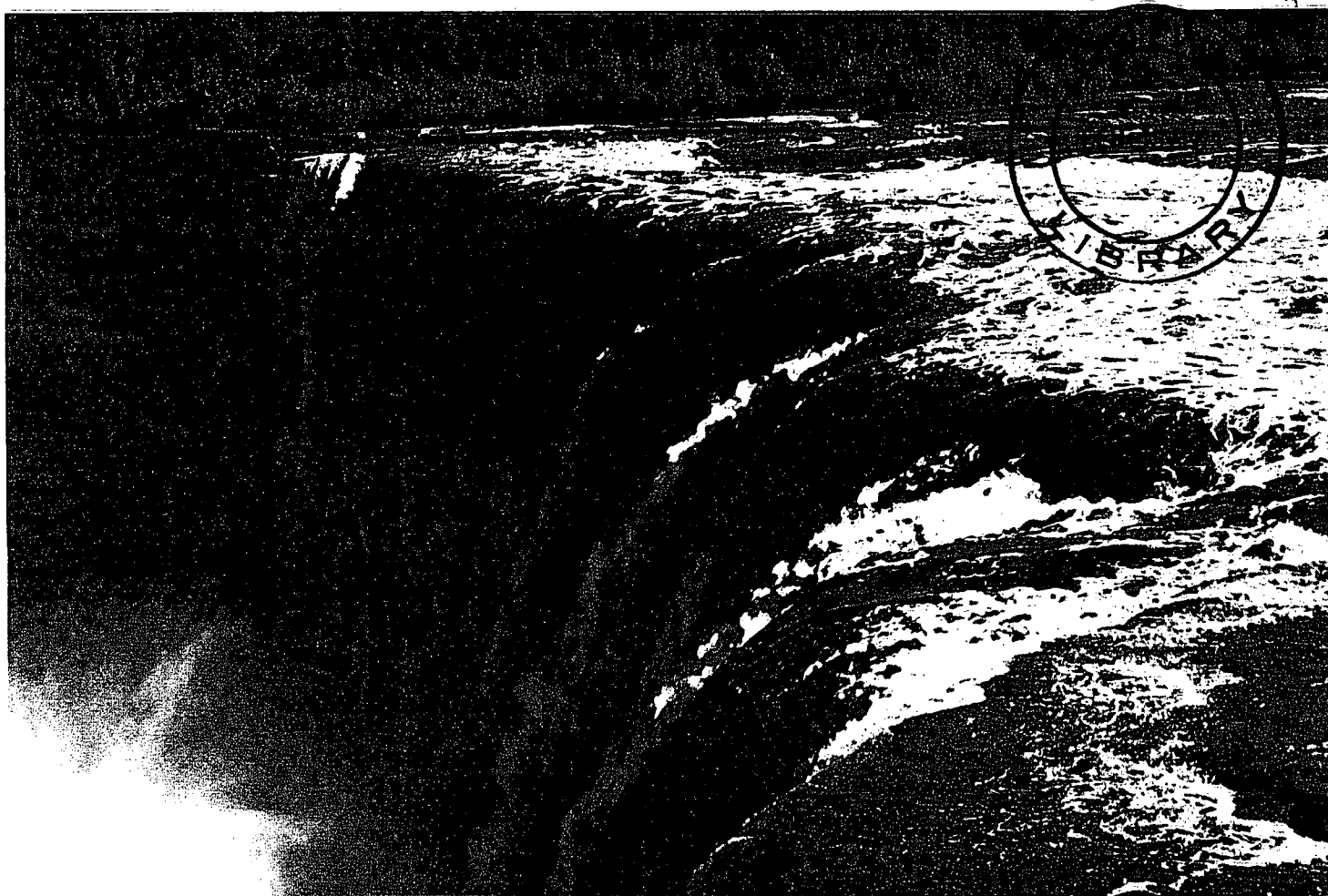


Limitations of Single Water Samples
in Representing Mean Water Quality

III. Spatial and Temporal Variation in Dissolved
Calcium Levels in the Great Lakes
A. C. H. B. C.

Report No. 107, published in 1975



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**Fisheries
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Limitations of Single Water Samples in Representing Mean Water Quality

II. Spatial and Temporal Variation in Nutrient Concentrations in the Okanagan River at Oliver, B.C.

P. Kleiber, P.H. Whitfield and W.E. Erlebach

TECHNICAL BULLETIN NO. 107
(Résumé en français)

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Contents

	Page
ABSTRACT	y
RÉSUMÉ	v
INTRODUCTION	1
STUDY AREA	1
METHODS	1
Sampling sites	1
Parameters examined	1
Sampling techniques	1
Statistical analysis	4
RESULTS AND DISCUSSION	4
Seasonal mean values of concentration	4
Total phosphate	4
Nitrate plus nitrite	6
Total organic carbon	6
Components of variance	6
Replicate variance, σ_r^2	6
Temporal variance, σ_t^2	6
Spatial variance, σ_s^2	13
Confidence limits	13
Confidence limits of seasonal means	14
Confidence limits of single samples	14
Optimal sampling design	15
SUMMARY	15
ACKNOWLEDGMENTS	16
REFERENCES	16
APPENDIX A. DESIGN OF OPTIMAL SAMPLING PROGRAM FOR DETECTING TRENDS IN WATER QUALITY PARAMETERS	17
APPENDIX B. RESULTS OF CHEMICAL ANALYSES	23

Tables

1. Sampling schedule	4
2. Analysis of variance for determination of spatial, temporal and replicate components of variance	4
3. F values for differences among stations	6
4. Components of variance	6
5. Results of run tests above and below the median	13
6. Confidence limits of single samples	14
7. Optimum sampling design for detecting trends at a single station (VDS No. 3) in March and June	15

Illustrations

	Page
Figure 1. Sampling stations on Okanagan River near Oliver	2
Figure 2a. Automatic (ISCO) sampler positioned on the shore at monitoring station VDS No. 3 at Okanagan River	3
Figure 2b. Automatic (ISCO) sampler intake hose being held approximately 3 m into the stream and 0.3 m from the bottom by an iron rod arrangement	3
Figure 3. Inland Waters Directorate replicate sampler with Teflon displacement probes in raised position allowing access to cups holding sample bottles	3
Figure 4. The geometric means of the total phosphate concentrations at the four stations on the Okanagan River at Oliver, for each of the four seasons from the fall of 1974 to the summer of 1975	5
Figure 5. The geometric means of the nitrate plus nitrite concentrations at the four stations on the Okanagan River at Oliver, for each of the four seasons from the fall of 1974 to the summer of 1975	7
Figure 6. The geometric means of the concentrations of total organic carbon at the four stations on the Okanagan River at Oliver, for three seasons from the winter of 1974 to the summer of 1975	8
Figure 7. Sequential samples for total phosphate and nitrate plus nitrite during September 1974	9
Figure 8. Sequential samples for total phosphate and nitrate plus nitrite during December 1974	10
Figure 9. Sequential samples for total phosphate and nitrate plus nitrite during March 1975	11
Figure 10. Sequential samples for total phosphate and nitrate plus nitrite during June 1975	12

Abstract

The Water Quality Branch, Pacific and Yukon Region, is investigating the spatial and temporal variation in water quality at selected monitoring stations in the region. This report concerns such an investigation at four stations located on the Okanagan River near Oliver, British Columbia. The objectives of the study are: (1) to determine representative values of water quality for the reach of river at which each station is located; (2) to ascribe confidence limits for the present values; (3) to estimate the confidence limits that can be applied to single grab samples collected at the station in the past; and (4) to determine the sampling effort necessary to detect year-to-year trends in water quality.

Résumé

La Direction de la qualité des eaux, région du Pacifique et du Yukon, a entrepris l'étude des variations spatiales et temporelles de la qualité des eaux à partir de certaines stations de contrôle de la région. Le rapport ci-après porte sur les travaux qu'elle a effectués à quatre stations de la rivière Okanogane, à proximité d'Oliver en Colombie-Britannique. Il a pour objectifs: (1) de fixer les valeurs qui correspondent à la qualité des eaux à l'emplacement de chacune des stations; (2) d'attribuer des seuils de confiance aux valeurs actuelles; (3) d'évaluer les seuils de confiance susceptibles de s'appliquer aux échantillons uniques prélevés au hasard par les stations dans le passé; et (4) de mesurer le travail d'échantillonnage nécessaire afin de déterminer les tendances de la qualité des eaux d'une année à l'autre.

Limitations of Single Water Samples in Representing Mean Water Quality

II. Spatial and Temporal Variation in Nutrient Concentrations in the Okanagan River at Oliver, B.C.

P. Kleiber, P.H. Whitfield and W.E. Erlebach

INTRODUCTION

Heterogeneities within a parcel of water limit the precision achievable with normal monitoring methods. Measurements of water quality made by Inland Waters Directorate in the Pacific and Yukon Region to determine how well single samples represent mean conditions over short spatial and temporal ranges have shown limitations (Oguss and Erlebach, 1976). Small-scale heterogeneities in conjunction with errors owing to sample handling and laboratory analysis cause within-sample variation, which affects the precision with which a single set of replicate samples represents a particular point along a river at a particular point in time. Temporal variation introduces an additional element of imprecision when the mean of a set of samples within a period of time is taken to represent the true mean value for that period of time. Furthermore, large-scale spatial variation along the course of a river affects the precision with which a set of sampling stations represents the average conditions over the reach of the river in which those stations are located. The present study is an investigation of these three sources of variation (within-sample, temporal and spatial) for four different seasons in the reach of the Okanagan River above and below Oliver, B.C.

STUDY AREA

The Okanagan River is dyked downstream from Oliver and flow is controlled with a number of weirs. The weirs serve to impound water for irrigation purposes. Land use in the area is limited primarily to orchards, with some hayfields and pasture along the lower reaches.

METHODS

Sampling Sites

The sampling stations and the river system are shown in Figure 1. The primary station at VDS (vertical drop

structure) control No. 3 was located immediately upstream from the weir. Three additional sampling sites were selected: at Inkaneep Park (from the highway bridge); at VDS No. 9 (below the weir) immediately downstream from Oliver; and at a location downstream from VDS No. 3 at VDS No. 1, immediately above Osoyoos Lake (below the weir).

Parameters Examined

Parameters chosen for examination were concentrations of total phosphate as phosphorus (TP), nitrate plus nitrite as nitrogen (N), and total organic carbon as carbon (TOC). These were considered to be suitable indicators of changes associated with remedial measures to reduce cultural eutrophication in the Okanagan basin. These parameters had also been measured in single biweekly or quarterly grab samples at the primary station for a number of years, and an assessment of the limitations of these earlier data was desired. Some additional parameters were measured on an infrequent basis. These data are available from NAQUADAT, Data and Instrumentation Section, Water Quality Branch, Inland Waters Directorate, Ottawa, Ontario K1A 0E7.

Sampling Techniques

Samples were collected at one-hour intervals at the primary station by an automatic sequential water sampler (ISCO 1391, Instrumentation Specialties Company, Fig. 2a) to examine temporal variation. The intake hose of the sampler extended approximately 3 m from the left bank facing upstream and was suspended 0.3 m from the bottom (1.3 m below the surface) by an iron cross frame (Fig. 2b). Subsequent to a water sample being taken, the ISCO unit reverses its pump and expels the water present in the intake hose.

Since this sampler was used for the first time by the Water Quality Branch, Pacific and Yukon Region, in this study, its usefulness in station evaluations was being assessed.

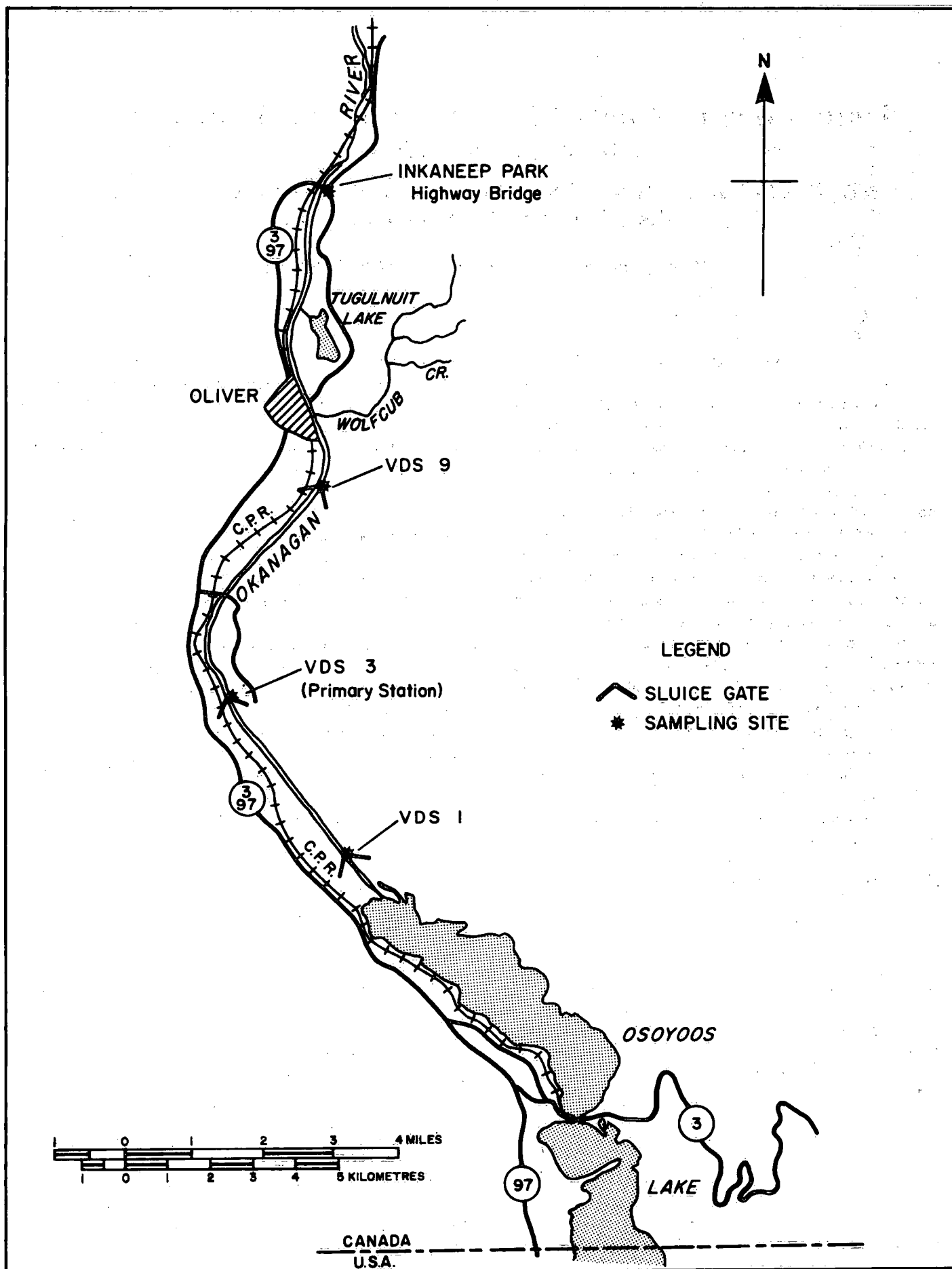


Figure 1. Sampling stations on Okanagan River near Oliver.



Figure 2a. Automatic (ISCO) sampler positioned on the shore at monitoring station VDS No. 3 at Okanagan River.

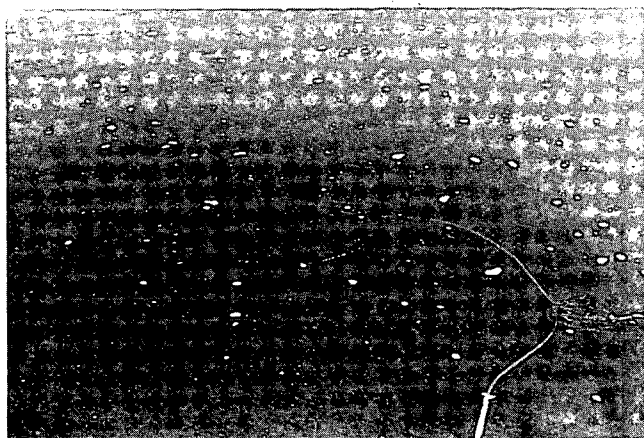


Figure 2b. Automatic (ISCO) sampler intake hose being held approximately 3 m into the stream and 0.3 m from the bottom by an iron rod arrangement.

The performance of this sampler has been examined by Lauch (1975). The values obtained from the samples collected automatically were verified with replicate samples collected at irregular intervals. The replicate sampler (Fig. 3) developed by the Water Quality Branch, Pacific and Yukon Region, collects six samples simultaneously from the upper metre of water. All samples at secondary stations were collected with the replicate sampler.

Samples for total phosphorus were taken directly into 50-ml glass bottles and digested in the original sample bottle in the laboratory. This procedure differed from the historical technique of digesting an aliquot of a subsample poured from a main sample bottle. Samples for nitrate plus nitrite analysis and for total organic carbon analysis were also taken directly into the bottles which were shipped

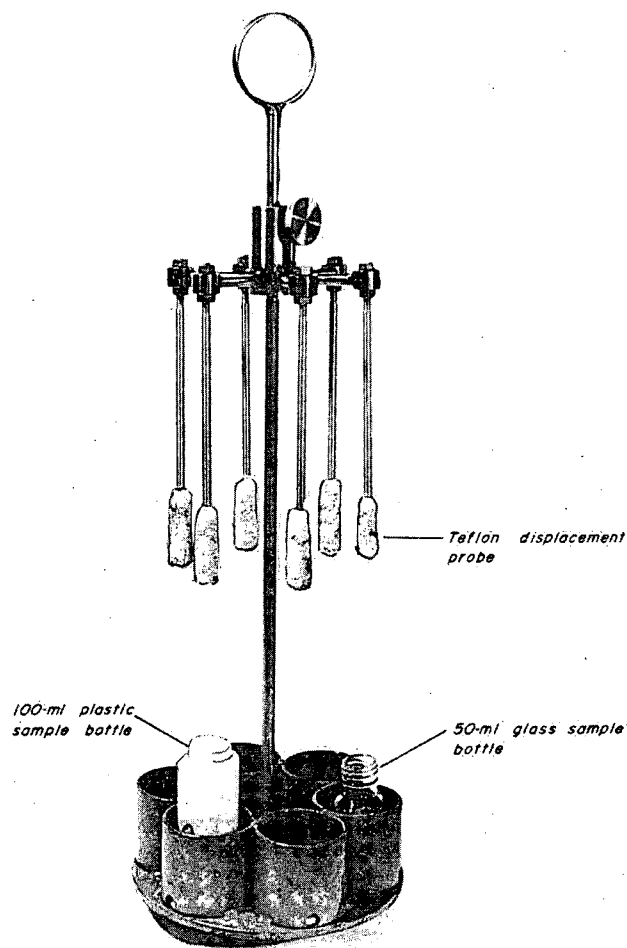


Figure 3. Inland Waters Directorate replicate sampler with Teflon displacement probes in raised position allowing access to cups holding sample bottles.

to the laboratory. Except for the filtration of some nitrate plus nitrite samples through a $0.45\text{-}\mu\text{m}$ filter, no field transfers were made. Samples collected for nitrate plus nitrite and total organic carbon analysis were maintained at a temperature as near to 4°C as possible. Most analyses were completed within one week of the sampling date.

Two- to four-day sampling periods chosen for each of the four seasons included the full range of flow conditions on the Okanagan River at this site, from 250 cfs in December to 1900 cfs in June. Information concerning sampling periods and the types of samples taken is given in Table 1. Analysis of total phosphate, nitrogen and total organic carbon was done using methods adapted by the Water Quality Branch, Pacific and Yukon Region (Environment Canada, 1974a and 1974b; Technicon AutoAnalyzer II Methodology, 1971 and 1972).

Table 1. Sampling Schedule

Sampling period	Stations	Number of samples collected				
		Automatic sequential sampler		Replicate sampler*		TOC
		TP	N	TP	N	
September 24 and 25, 1975	VDS No. 1			12	12	
	VDS No. 3	24†	24†	12	12	
	VDS No. 9			12	12	
	Inkaneep			12	12	
December 2-6, 1974	VDS No. 1			18	18	18
	VDS No. 3	48‡	48‡	54	54	54
	VDS No. 9			18	18	18
	Inkaneep			18	18	18
March 18-21, 1975	VDS No. 1			42	42	42
	VDS No. 3	36‡	36‡	42	42	42
	VDS No. 9			42	42	42
	Inkaneep			42	42	42
June 6-10, 1975	VDS No. 1			18	18	18
	VDS No. 3	25‡	25‡	48	48	48
	VDS No. 9			18	18	18
	Inkaneep			18	18	18

* Replicates were collected in sets of six samples.

† Collected at hourly intervals.

‡ Collected at two-hour intervals, each parameter in alternate hours.

Statistical Analysis

All statistical analyses were carried out on the log-transform of the original concentration values because the values can vary over two or three orders of magnitude with associated errors varying approximately in proportion. The log-transform in this case tends to even out the errors over the range of variate values, which is desirable for carrying out analysis of variance. Also, this assures that when mean values are transformed back, the lower confidence limits will not be less than zero as would surely be the case if untransformed values were analyzed directly.

RESULTS AND DISCUSSION

A detailed tabulation of the results is contained in Appendix B.

Seasonal Mean Values of Concentration

Total Phosphate

Figure 4 shows seasonal means of TP plotted against distance along the river for four different seasons. The

grand mean for all stations is also plotted for each season. These are geometric means, since they are antilogs of the mean of the log-transform of concentration. Ninety-five

Table 2. Analysis of Variance for Determination of Spatial, Temporal and Replicate Components of Variance

Sources of variation	Degrees of freedom	Mean squares	Expected mean squares
Spatial	$\nu_s = s - 1$	$MS_s = \frac{S_3 - S_4}{\nu_s}$	$\sigma_r^2 + b\sigma_t^2 + c\sigma_s^2$
Temporal	$\nu_t = \sum t_i - s$	$MS_t = \frac{S_2 - S_3}{\nu_t}$	$\sigma_r^2 + a\sigma_t^2$
Replicate	$\nu_r = \sum n_i - \sum t_i$	$MS_r = \frac{S_1 - S_2}{\nu_r}$	σ_r^2

s = number of stations.

t_i = number of times at station i.

r_{ij} = number of replicates at time j, station i.

$n_i = \sum r_{ij}$

$m_i = \sum r_{ij}^2$

$n_t = \sum n_i$

Y_{ijk} = log(concentration) for replicate k, time j, station i.

$$S_1 = \sum \sum \sum r_{ij} Y_{ijk}^2$$

$$S_2 = \sum \sum \left[\frac{1}{r_{ij}} \left(\sum Y_{ijk} \right)^2 \right]$$

$$S_3 = \sum \left[\frac{1}{n_i} \left(\sum \sum Y_{ijk} \right)^2 \right]$$

$$S_4 = \frac{1}{n_t} \left(\sum \sum \sum Y_{ijk} \right)^2$$

$$a = \frac{1}{\nu_t} \left[n_t - \sum \left(\frac{m_i}{n_i} \right) \right]$$

$$b = \frac{1}{\nu_t} \left[\sum \left(\frac{m_i}{n_i} \right) - \frac{\sum m_i}{n_t} \right]$$

$$c = \frac{1}{\nu_s} \left[n_t - \frac{\sum n_i^2}{n_t} \right]$$

Estimates of components of variance:

$$\sigma_r^2 = MS_r$$

$$\sigma_t^2 = \frac{1}{a} (MS_t - \sigma_r^2)$$

$$\sigma_s^2 = \frac{1}{c} (MS_s - \sigma_r^2 - b\sigma_t^2)$$

percent confidence limits for the values of the means are also plotted. It is evident that the main variability in TP is due to seasonal effects rather than spatial effects. This impression is confirmed by an analysis of variance which was designed as follows. The four seasons were treated separately. Table 2 gives the analysis of variance for a particular season. The main groups were the stations.

Sampling events were nested within stations, and replicates, within sampling events. The appropriate F statistic to test for significant differences among stations is the ratio of the station mean squares, MS_s , to the sampling time mean squares, MS_t . Values of this ratio are given in Table 3 along with the appropriate degrees of freedom. In the case of TP, none of these ratios are significant ($p = 0.05$).

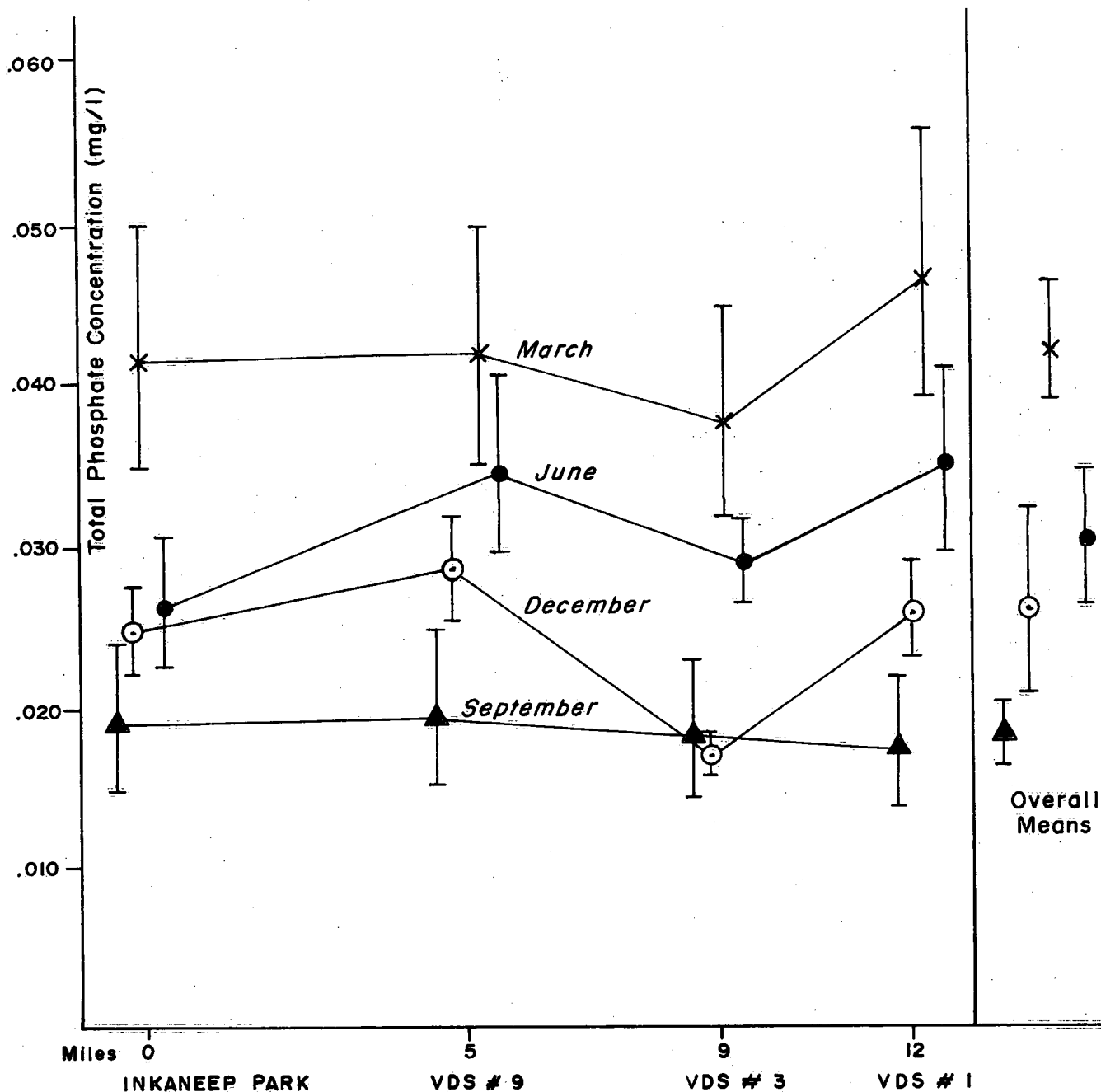


Figure 4. The geometric means of the total phosphate concentrations at the four stations on the Okanagan River at Oliver, for each of the four seasons from the fall of 1974 to the summer of 1975. Confidence limits at 95% are shown by the vertical bars.

Table 3. F Values for Differences among Stations

Parameter	September 1974	December 1974	March 1975	June 1975
TP	0.23 (3, 4)*	1.1 (3, 14)	0.29 (3, 14)	2.8 (3, 14)
N	93† (3, 4)	360† (3, 14)	17† (3, 14)	22† (3, 14)
TOC		0.029 (3, 14)	0.39 (3, 24)	0.16 (2, 15)

* Degrees of freedom are given in parentheses.

† Values showing a significant difference at $p = 0.05$.

Nitrate Plus Nitrite

The mean values of N are given in Figure 5. In this case, in addition to marked seasonal differences there is a pronounced increase in concentration from Inkaneep to station No. 3. The F ratios for N are significant ($p = 0.05$) for all seasons (Table 3).

Total Organic Carbon

Like TP, TOC appears to be more variable with season than with position along the river (Fig. 6). Again, none of the F ratios in Table 3 are significant ($p = 0.05$). The large confidence bands in Figure 6 are due to large temporal and within-sample variability which could mask real differences among stations.

Components of Variance

Table 2 gives formulas for the expected mean square values in terms of the replicate, temporal and spatial

components of variance (σ_r^2 , σ_t^2 and σ_s^2). Using these expressions and the observed values of the mean squares (MS_r , MS_t and MS_s), estimates of the components of variance (δ_r^2 , δ_t^2 and δ_s^2) were derived. The calculated results are given in Table 4.

Replicate Variance, δ_r^2

Estimates of replicate variance are given for the three parameters in Table 4. The percentage of total variance is also included. The variability at this level is partly due to the treatment of samples after they are collected, but spatial heterogeneities in the water on the size scale of the replicate sampler could also be a significant contributing factor.

For the most part, TP exhibits the smallest within-sample variance. The percentage figures, however, show that most of the variance in TP exists at the replicate level.

Temporal Variance, δ_t^2

Estimates of temporal variance are given in Table 4. These figures represent the variability with time within a season. In treating this quantity as a variance, it is assumed that the values obtained at different sampling times are independent, which may not be true if there is a non-random temporal pattern of variation within the season. To investigate the temporal pattern, TP and N samples were collected with a sequential sampler at VDS No. 3 for a time during each of the four seasons. The results are given in Figures 7, 8, 9 and 10.

Table 4. Components of Variance

Parameter	Sources of variance	September 1974	December 1974	March 1975	June 1975
TP	Replicate	0.044 (65%)*	0.019 (71%)	0.13 (80%)	0.030 (56%)
	Temporal	0.023 (35%)	0.0077 (28%)	0.034 (20%)	0.015 (27%)
	Spatial	-0.012 (0%)	0.00027 (1%)	-0.006 (0%)	0.0088 (17%)
N	Replicate	0.11 (9.1%)	0.028 (7%)	0.17 (15%)	0.43 (43%)
	Temporal	0.0052 (0.4%)	-0.0002 (0%)	0.28 (26%)	0.028 (3%)
	Spatial	1.1 (90.5%)	0.39 (93%)	0.63 (59%)	0.53 (54%)
TOC	Replicate		0.033 (17%)	0.049 (30%)	0.38 (53%)
	Temporal		0.16 (83%)	0.12 (70%)	0.34 (45%)
	Spatial		-0.04 (0%)	-0.01 (0%)	-0.08 (0%)

* The percentage figures in parentheses are percents of total for each parameter for each month. The negative variance components are taken to be zero.

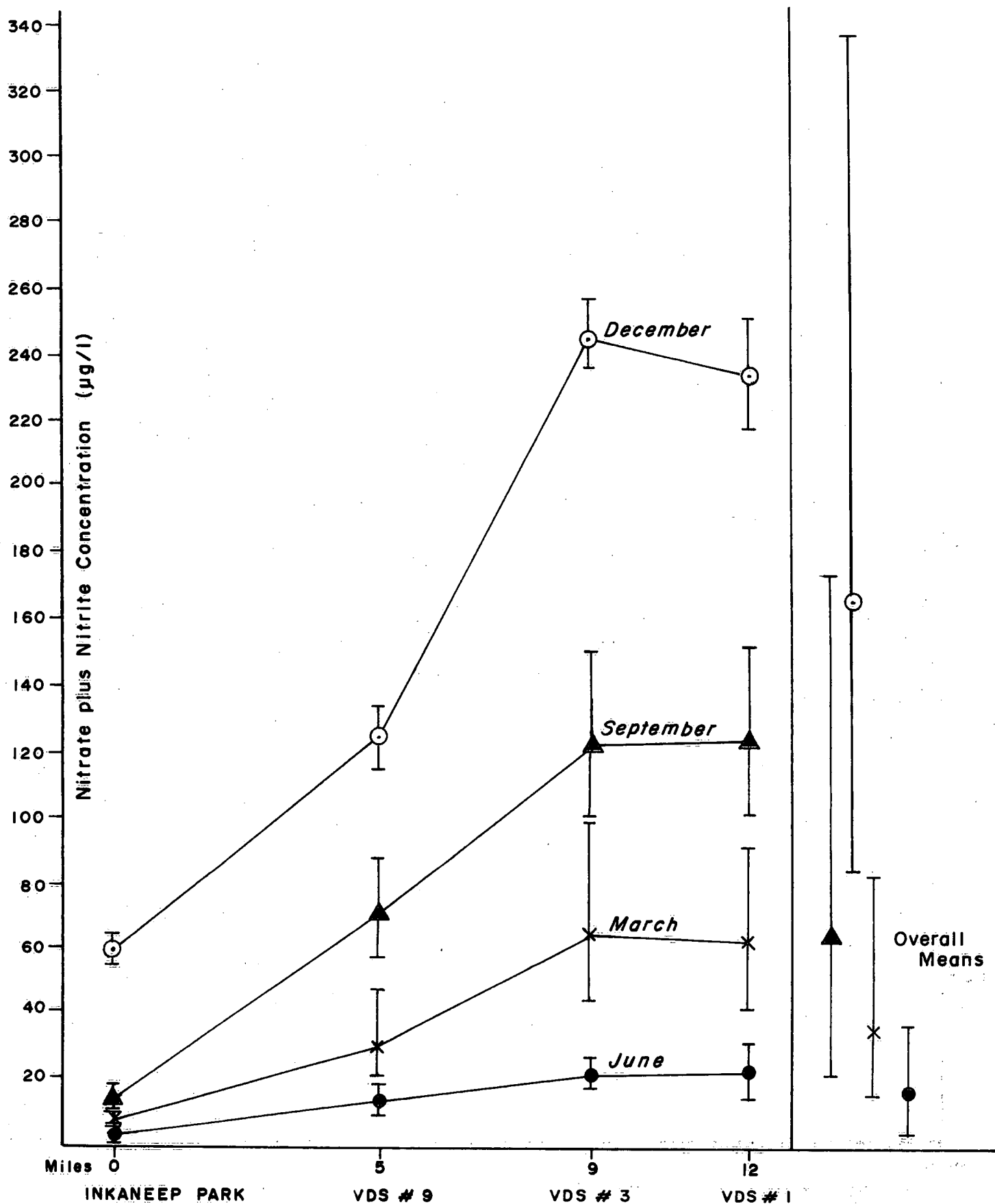


Figure 5. The geometric means of the nitrate plus nitrite concentrations at the four stations on the Okanagan River at Oliver, for each of the four seasons from the fall of 1974 to the summer of 1975. Confidence limits at 95% are shown by the vertical bars.

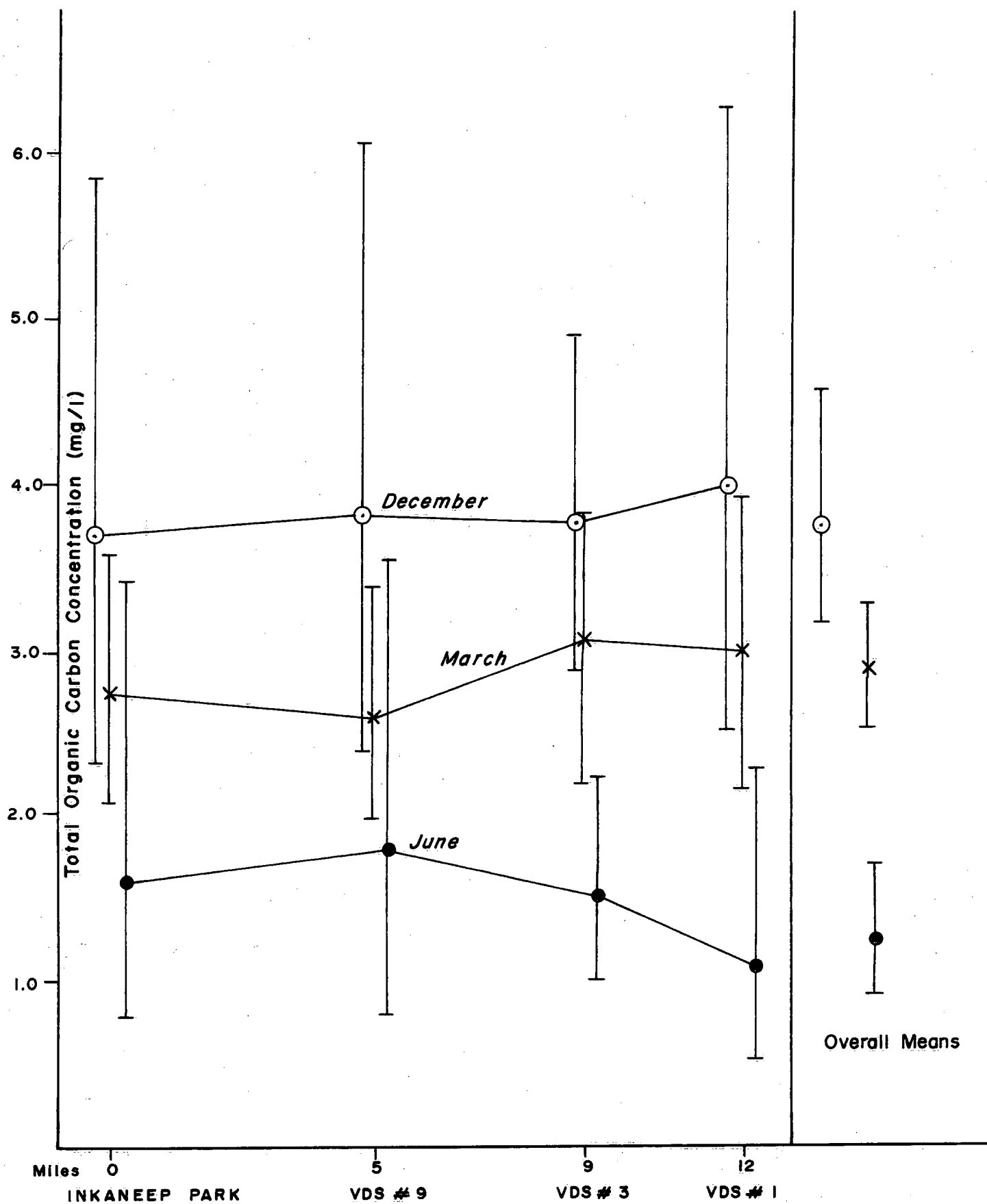


Figure 6. The geometric means of the concentrations of total organic carbon at the four stations on the Okanagan River at Oliver, for three seasons from the winter of 1974 to the summer of 1975. Confidence limits of 95% are shown by the vertical bars.

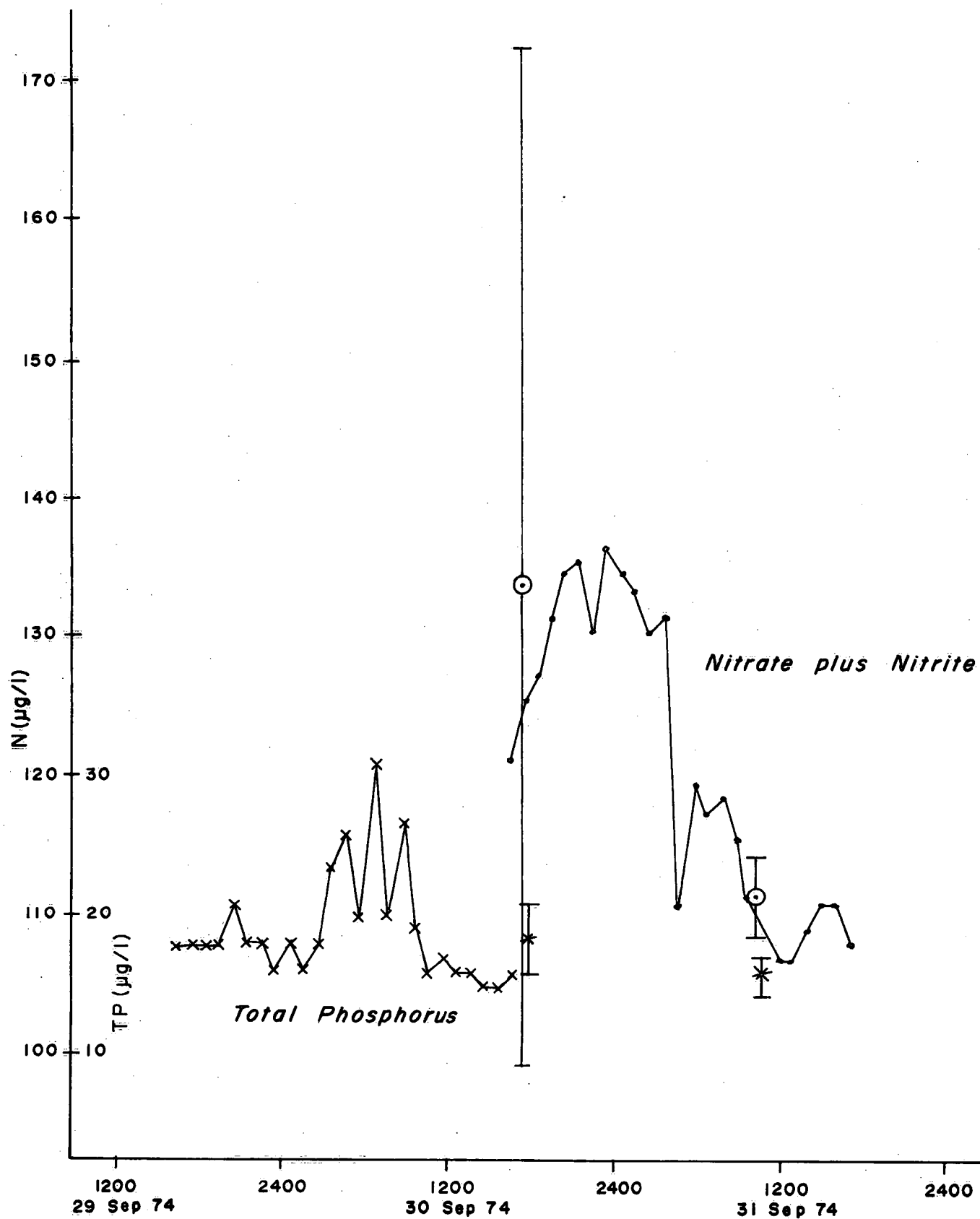


Figure 7. Sequential samples for total phosphate and nitrate plus nitrite during September 1974. Also shown are the means and 95% confidence limits for replicate samples collected at VDS No. 3.

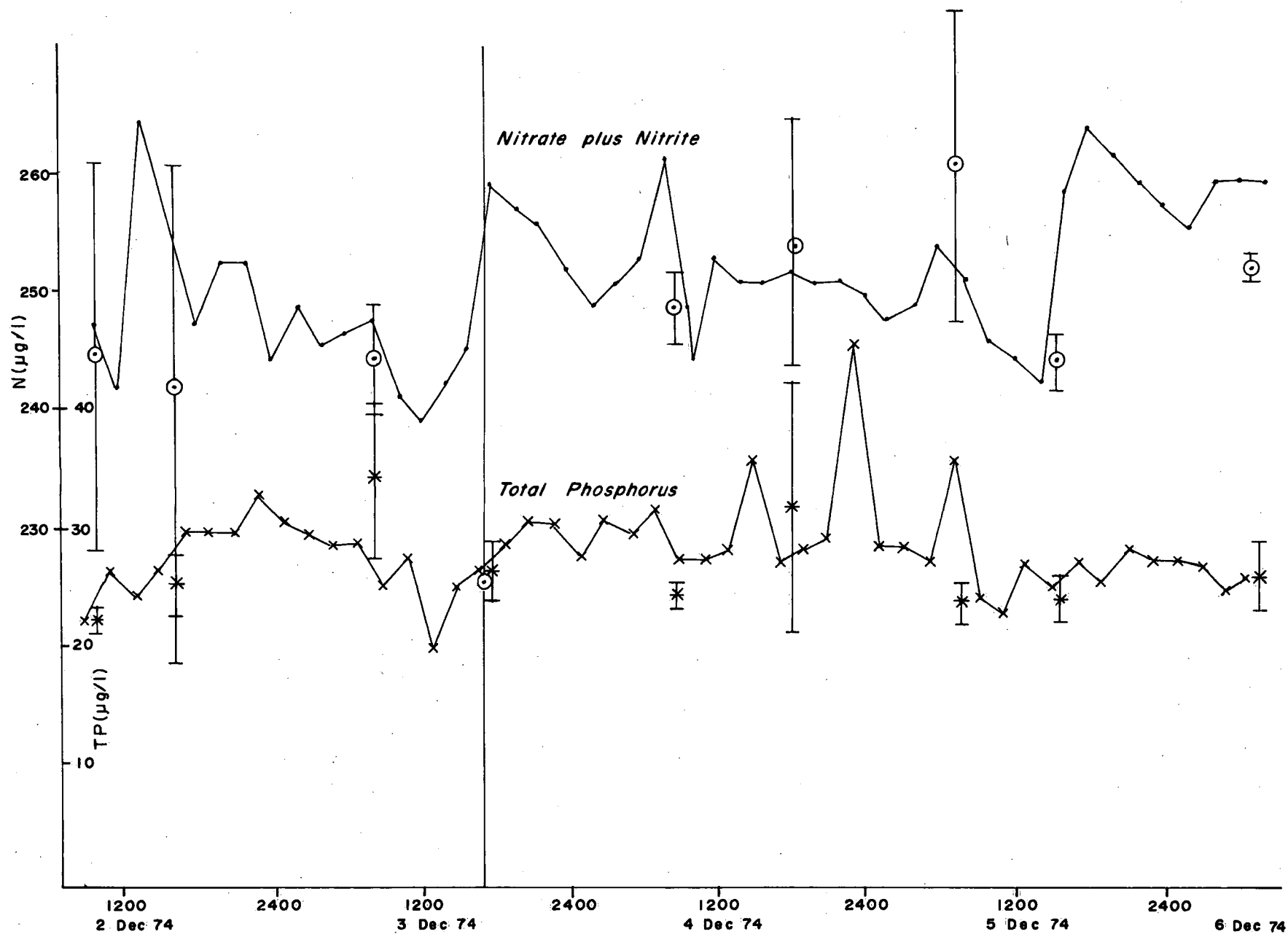


Figure 8. Sequential samples for total phosphate and nitrate plus nitrite during December 1974. Also shown are the means and 95% confidence limits of replicate samples collected at VDS No. 3.

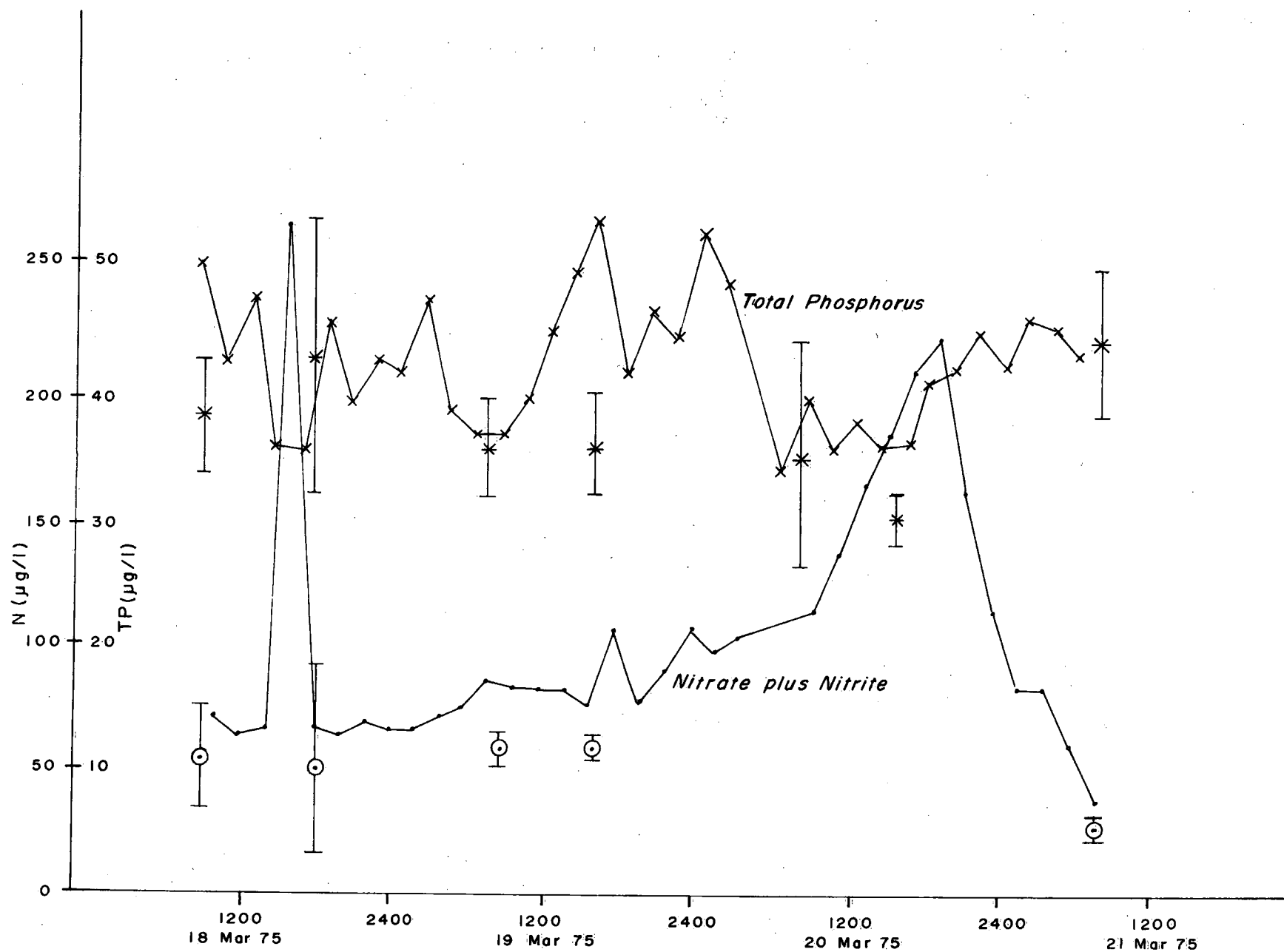


Figure 9. Sequential samples for total phosphate and nitrate plus nitrite during March 1975. Also shown are the means and 95% confidence limits of replicate samples collected at VDS No. 3.

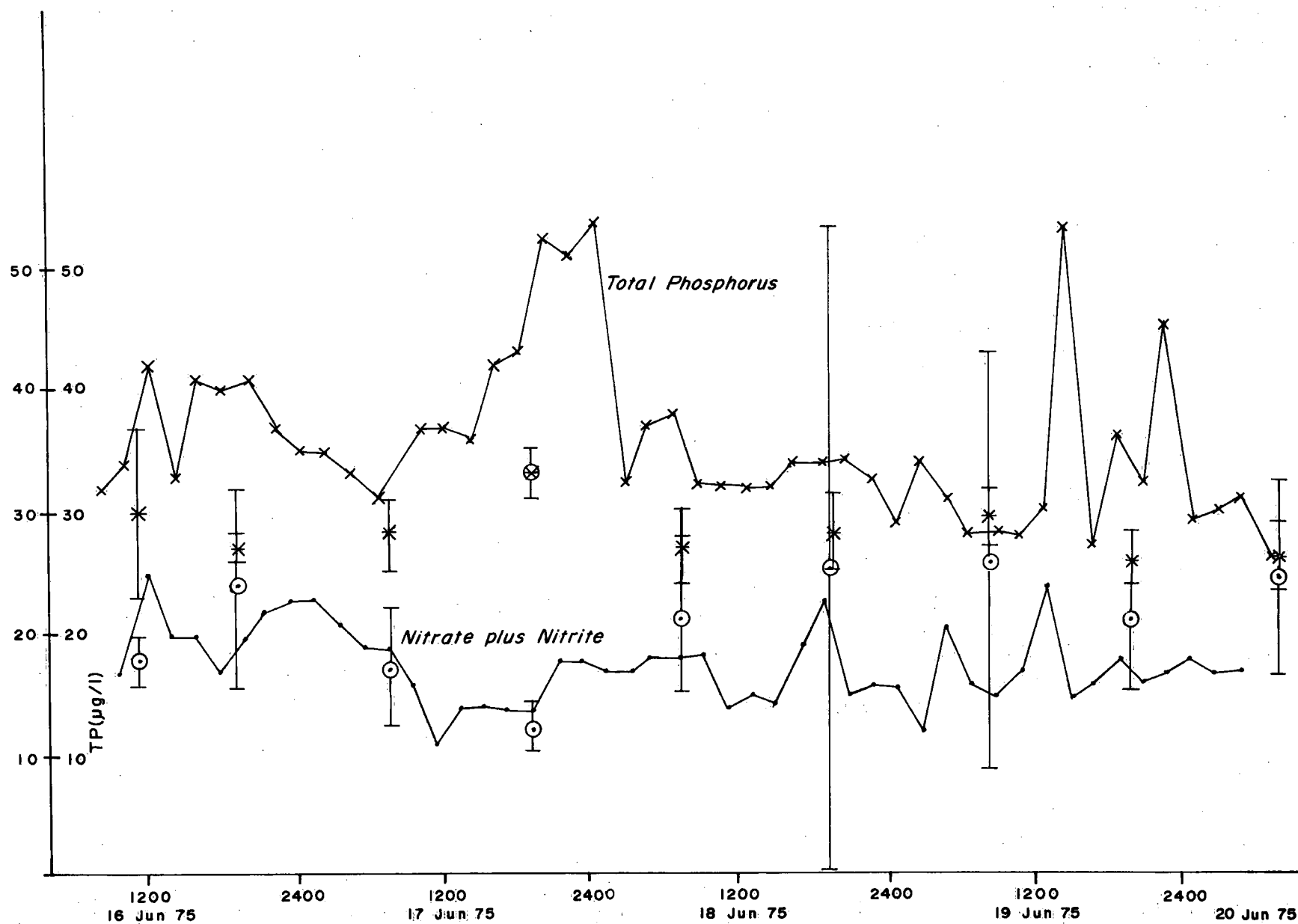


Figure 10. Sequential samples for total phosphate and nitrate plus nitrite during June 1975. Also shown are the means and 95% confidence limits of replicate samples collected at VDS No. 3.

To test for the existence of nonrandom temporal patterns, run tests were used (Sokal and Rohlf, 1969). The run test used in this case is based on comparing each determined value with the median value. All values that exceed the median are assigned a plus (+), and all values below the median are assigned a minus (-). Sequences of the same signs are called runs, the number of which is an indication of a significant temporal pattern. The results of the run tests are given in Table 5. Significant values were obtained in all but one case. Thus the concentrations tend to be correlated from one time to the next and the degree of correlation is presumably dependent in some way on the interval between samples.

Table 5. Results of Run Tests above and below the Median

Month	Parameter	Number of observations	Runs*	Significance at 5%
September	TP	24	6	Yes
	N	24	2	Yes
December	TP	46	15	Yes
	N	46	16	Yes
March	TP	34	15	No
	N	34	9	Yes
June	TP	48	17	Yes
	N	48	17	Yes

* Number of sequences of data points above or below the median.

Perhaps the best way to handle the situation above is to partition the temporal variance into a set of variances at various time intervals by spectral analysis (Kisiel, 1969). Serious errors, however, can result with this approach unless there is either a high sampling frequency or some sort of averaging mechanism in the sampling apparatus (Platt and Denman, 1975). In the present case there are only two to nine sampling times for each season, and each sample represents conditions at a point in time and not an average over a sampling interval. If the primary interest is in the average and its variance over the whole season, then another approach would be to take samples at random times during the season so that the sample values would be independently distributed about the seasonal mean. In this case the number of sample times would affect only the precision with which the mean and variance are determined. For the present analysis, it was assumed that sampling times were randomly distributed throughout the season. Actually, the sample times were clustered within a few days of each other (Table 1). It is therefore likely that the temporal variances reported here are underestimates if a "season" is taken to be more than a few days long.

Spatial Variance, σ_s^2

Estimates of the spatial component of variance are given for the three parameters in Table 4. This is the variability due to differences among stations located along the river. It tends to be low in most cases for TP and TOC, but it is consistently high in the case of N.

Confidence Limits

After estimates of the components of variance are obtained, it is possible to derive confidence limits for estimates of mean concentration based on various sampling schemes. In the most general case with varying numbers of replicates in each sample and varying numbers of sample times for each station, the variance estimate of the grand mean of log (concentration) over all replicates, times and stations would be

$$\sigma_{\text{mean}(\log)}^2 = \frac{\sum_i n_i^2}{(\sum_i n_i)^2} \sigma_s^2 + \frac{\sum_i m_i}{(\sum_i n_i)^2} \sigma_t^2 + \frac{1}{\sum_i n_i} \sigma_r^2 \quad (1)$$

where s = number of stations,

t_i = number of times at station i ,

r_{ij} = number of replicates at time j , station i ,

$$n_i = \sum_{j=1}^{t_i} r_{ij}$$

$$m_i = \sum_{j=1}^{t_i} r_{ij}^2$$

This variance defines a symmetrical confidence interval about the mean of logs. In taking antilogs the mean of logs becomes the geometric mean (GM) and the confidence interval becomes unsymmetrical and multiplicative. The 95% confidence interval would be:

$$\text{Lower limit} = \text{GM} \cdot f_1 \quad \text{Upper limit} = \text{GM} \cdot f_2 \quad (2)$$

where $f_1 = \exp \left(1.96 \sqrt{\sigma_{\text{mean}(\log)}^2} \right)$

$$f_2 = \frac{1}{f_1}$$

Table 6. Confidence Limits of Single Samples

Parameter	September 1974			December 1974			March 1975			June 1975		
	A	B	C	A	B	C	A	B	C	A	B	C
TP	1.5 0.66	1.7 0.60	1.7 0.60	1.3 0.76	1.4 0.73	1.4 0.72	2.0 0.49	2.2 0.45	2.2 0.45	1.4 0.71	1.5 0.66	1.6 0.64
N	1.9 0.52	1.9 0.52	8.3 0.12	1.4 0.72	1.4 0.72	3.6 0.28	2.2 0.45	3.7 0.27	7.6 0.13	3.6 0.28	3.7 0.27	7.0 0.14
TOC				1.4 0.70	2.4 0.42	2.4 0.42	1.5 0.65	2.2 0.45	2.3 0.44	3.4 0.30	5.3 0.19	5.3 0.19

Note: Each box in the table contains three pairs of values arranged in columns A, B and C. The values given in each pair are the upper and lower 95% confidence limits for the case of a single sample with a value of 1, i.e., these are the factors f_1 and f_2 as defined in Equation 2. Depending on what the sample is taken to represent, the applicable pair is chosen as follows:

Column	Sample Represents
A	Particular place and time
B	Particular place but entire season
C	Whole reach of river and entire season

Confidence Limits of Seasonal Means

The confidence limits shown in Figures 4, 5 and 6 for the grand means over all stations were derived from Equation 1. For the station means, the spatial component of variance, σ_s^2 , is not relevant in determining confidence limits. Dropping the term containing this variance component and setting $s = 1$ in Equation 1, the variance of a station mean of logs is

$$\sigma_{\text{station mean}}^2 = \frac{t}{(\sum r_j)^2} \sigma_t^2 + \frac{1}{t} \frac{1}{\sum r_j} \sigma_r^2$$

where t = number of sample times and
 r_j = number of replicates at time j .

The confidence interval for the grand means tends to be smaller than the intervals about the station means except when there is pronounced spatial variance as in the case of N (Fig. 5). The variances of the grand means and of the station means are partly dependent on the temporal components of variance, which in the present case are underestimates for "seasons" longer than a few days. Therefore the confidence limits shown in Figures 4, 5 and 6 would probably have been wider if the sampling activity had been distributed over longer "seasons" than those defined by the sampling periods given in Table 1.

Confidence Limits of Single Samples

Since routine water quality monitoring has traditionally been carried out on the basis of one sample per season, it is of interest to calculate the confidence limits for such single samples used to represent water quality in the Okanagan River. These confidence intervals for the various parameters and seasons were calculated using the estimated components of variance and are given in Table 6. The confidence limits in a particular case are obtained by multiplying the measured value by each of the pairs of factors given in the table, as in Equation 2.

The first pair of figures in each box of Table 6 (columns A) only accounts for the sample variance. Thus, they would be the confidence limits to apply if a particular sample is taken to represent only the particular point in the river where the sample was collected and only the particular time when it was taken. In the best possible case, if a single value of 0.100 ppm of TP was measured in December, it would be 95% sure that the true value at that point and time would be between 0.076 ppm and 0.13 ppm. The worst case is for TOC in June, for which a measured value of 1 ppm would have a 95% confidence interval of 0.30 ppm to 3.4 ppm for the particular point and time. The second pair of figures (columns B) accounts for temporal variance as well as sample variance. Thus, for the same hypothetical single measurement of 1 ppm for TOC in June, the 95% confidence interval for the seasonal mean at the particular sampling point would range from 0.19 ppm

to 5.25 ppm. Again these confidence ranges are underestimates except for short "seasons" of a few days. The same is true of the ranges given by the third pair of figures (columns C). For these, the spatial component of variance is included to give the confidence limits for a single value taken to represent an entire season and the whole reach of river from Inkaneep to VDS No. 1. The spatial component for TOC in June is a small negative value which is taken to be zero. There is, therefore, no increase in the confidence interval in this case. On the other hand, N tends to have a large component of spatial variance. Therefore, the confidence intervals for N expand considerably when a single sample station is taken to represent the whole reach of river.

Optimal Sampling Design

It is evident from the foregoing that a single water sample yields a poor estimate of concentration even if it is restricted to representing a particular point along the river and a particular instant in time. How many samples are required to get a "good" representation of concentration? This is a statistical question, the answer to which depends on the purpose of the survey. As an example it will be considered that the basic question is to determine whether or not there are trends from year to year in mean seasonal concentrations at a particular station. The concept of what is "good" in this case is the ability to determine whether a certain difference (discrimination level) between means for a particular parameter for a particular season in two different years is statistically significant. Appendix A outlines a procedure for determining the optimum sampling design (how many replicates to take on how many sampling trips) given a choice of a discrimination level, a probability level for the final statistical test, estimates for costs of sample taking and handling, and a pilot sampling study to determine temporal and sample variances. A somewhat more complicated procedure could be derived to help decide how many sampling stations to set up along the river, but for now it will be assumed that the concern is water quality at one particular site. Also a discrimination level of 0.1 will be assumed so that if there is a real difference between two different years of 10% or more it will be detectable. It will also be assumed that the desired probability level for the final test is 0.05.

The most extensive data sets available to serve as pilot studies are for TP, N and TOC for the periods March and June at station VDS No. 3. The results from running these data through the procedure in Appendix A are outlined in Table 7. Thus, for example, to detect a 10% difference in TP in March the most efficient sampling would be either more expensive or inadequate to discriminate a 10% difference. As expected, Table 7 shows that with greater overall variance more sampling effort is required. It can also

be seen that an increase in temporal variance relative to replicate variance requires the sampling effort to be distributed among a greater number of sampling trips. (As before, the temporal variances reported here are underestimates for "seasons" longer than a few days.) Three of the cases require an inordinate number of sampling trips. This would indicate either that less precision in order to reduce the sampling effort is acceptable or that alternative sampling logistics could be considered to facilitate collections of larger numbers of samples.

Table 7. Optimum Sampling Design for Detecting Trends at a Single Station (VDS No. 3) in March and June

Month	Parameter	σ_t^2	σ_r^2	Trip cost		Trips (t)	Replicates (r)
				Sample cost	Ω		
March	TP	0.025	0.0094	23	0.11	10	8
	N	0.054	0.30	38	0.56	201	3
	TOC	0.023	0.34	16	0.60	229	1
June	TP	0.020	0.0021	23	0.084	6	4
	N	0.23	0.0075	38	0.12	11	34
	TOC	0.37	0.20	16	0.52	173	5

Note: Discrimination level is 0.1 and probability level is 0.05.

SUMMARY

Total phosphate (TP), dissolved nitrate plus nitrite (N) and total organic carbon (TOC) were examined to determine components of spatial (longitudinal), temporal (within-season), and replicate variance in four different seasons of the year in the Okanagan River near Oliver, B.C. The pattern of variation was somewhat different in different seasons, but the general pattern is the following. Total phosphate showed the least overall variance because all three components of variance tended to be low relative to the other parameters. Dissolved nitrate plus nitrite was more variable than P partly because of increased replicate variance but mostly because of very large spatial variance, which is indicative of large changes in N with longitudinal position in the river. For TOC, increased replicate variance again tended to be higher than for P, but TOC also showed a marked within-season temporal variance, indicating large changes from time to time within a season.

The estimated variance components were used to calculate confidence limits for various mean values of the data obtained in this study. They were also used to estimate confidence limits for the traditional sampling scheme consisting of one sample taken at a single station, once per season. If the sample is taken to represent the whole reach of the river for the entire season, the worst case would be for N in September, for which the 95% confidence interval would range from 12% to 830% of the

measured value. The best case would be for TP in December, for which the 95% confidence interval would range from 72% to 140% of the measured value.

The components of variance can also be used to determine an optimal sampling scheme for the future. An example of such a determination is given, assuming that the purpose of the sampling scheme is to detect year-to-year trends in water quality. The number of sampling trips necessary to detect a 10% difference between two years was considerably lower for TP than for N and TOC. When there is a management question concerning eutrophication, it can be argued that TP is the single most relevant water quality parameter to measure. In this case it is shown that of the three parameters investigated, TP is certainly the most economical.

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Appendix A
Design of Optimal Sampling Program
for Detecting Trends in Water
Quality Parameters

Design of Optimal Sampling Program for Detecting Trends in Water Quality Parameters

To establish the existence of a trend in a water quality parameter, it is at least necessary to show a statistical difference in the mean value of that parameter for two different years. The mean could either be taken over the whole year or over a season of the year that is of particular interest.

The basic sampling program would be take t trips to a sampling station during the season of interest in each of two years, and to collect r replicate samples on each trip. The problem is to decide how many trips to take and how many replicates to collect. To make this decision it is necessary to know the expected variance which should be broken down into two components, the within-season temporal variance and the within set of replicates variance. It is also necessary to know or to estimate the ratio of the expense involved in making one sampling trip to the expense of analyzing a single sample in the laboratory. Also, two preliminary choices must be made. One is the discrimination level, d , which is the minimum proportional difference between the two years that is of interest to detect. The other choice is the probability level, p , for the statistical test. This is the probability of asserting that there is a difference between the two years when in fact there is not.

In order to obtain information about the variance to be expected, it is assumed that a pilot study has been made consisting of t' sampling times (trips) during one season with r' replicates collected on each trip. Table A-1 is an analysis of variance table which would be used to analyze the pilot study. Note that the log-transform of the parameter value is used. Table A-1 shows how estimates of within-season temporal variance, σ_t^2 , and replicate variance, σ_r^2 , can be calculated from the pilot study. Once these values are known and given an estimate of the ratio of trip cost to sample cost, it is possible (Cameron, 1951) to calculate an optimum number of replicates to take on each sampling trip.

$$r_{\text{opt}} = \sqrt{\frac{\sigma_r^2}{\sigma_t^2} \frac{\text{trip cost}}{\text{sample cost}}} \quad (\text{A-1})$$

Generally r_{opt} will not be an integer, but it is impossible to take fractional samples. To obtain an integer value for

r , i is set equal to the nearest integer less than r_{opt} . Then if $r_{\text{opt}} < \sqrt{i(i+1)}$, $r = i$ is chosen; otherwise $r = i+1$ is chosen. With this many replicates the precision of the mean value of the parameter for each year is optimized for a given cost, or alternatively, the cost is minimized for a given acceptable precision.

Table A-1. Analysis of Variance for Determination of Temporal and Replicate Components of Variance

Sources of variation	Degrees of freedom	Mean squares	Expected mean squares
Temporal	$t'-1$	$MS_t = \frac{S_2 - S_1}{t'-1}$	$\sigma_t^2 + r'\sigma_r^2$
Among replicates	$t'(r'-1)$	$MS_r = \frac{S_1 - S_3}{t'(r'-1)}$	σ_r^2

$$Y = \log(\text{concentration})$$

$$S_1 = \frac{t' r'}{\sum \sum Y^2}$$

$$S_2 = \frac{1}{r'} \sum \left(\frac{r'}{\sum Y} \right)^2$$

$$S_3 = \frac{1}{t' r'} \left(\frac{t' r'}{\sum \sum Y} \right)^2$$

Estimates of components of variance:

$$\sigma_t^2 = MS_t$$

$$\sigma_r^2 = \frac{1}{r'} (MS_t - MS_r)$$

It is now possible to determine the number of trips, t , necessary for a discrimination level, d , at a probability level of p . The derivation is as follows. It is assumed that an analysis of variance would be used to test for a difference between years. This would be a two-level nested design, as shown in Table A-2. In order to accept that there is a difference between years, the mean squares ratio, MS_r/MS_t , must be greater than the critical value of the F distribution, $F_p [1, 2(t-1)]$. Assuming a difference exactly at the limit of

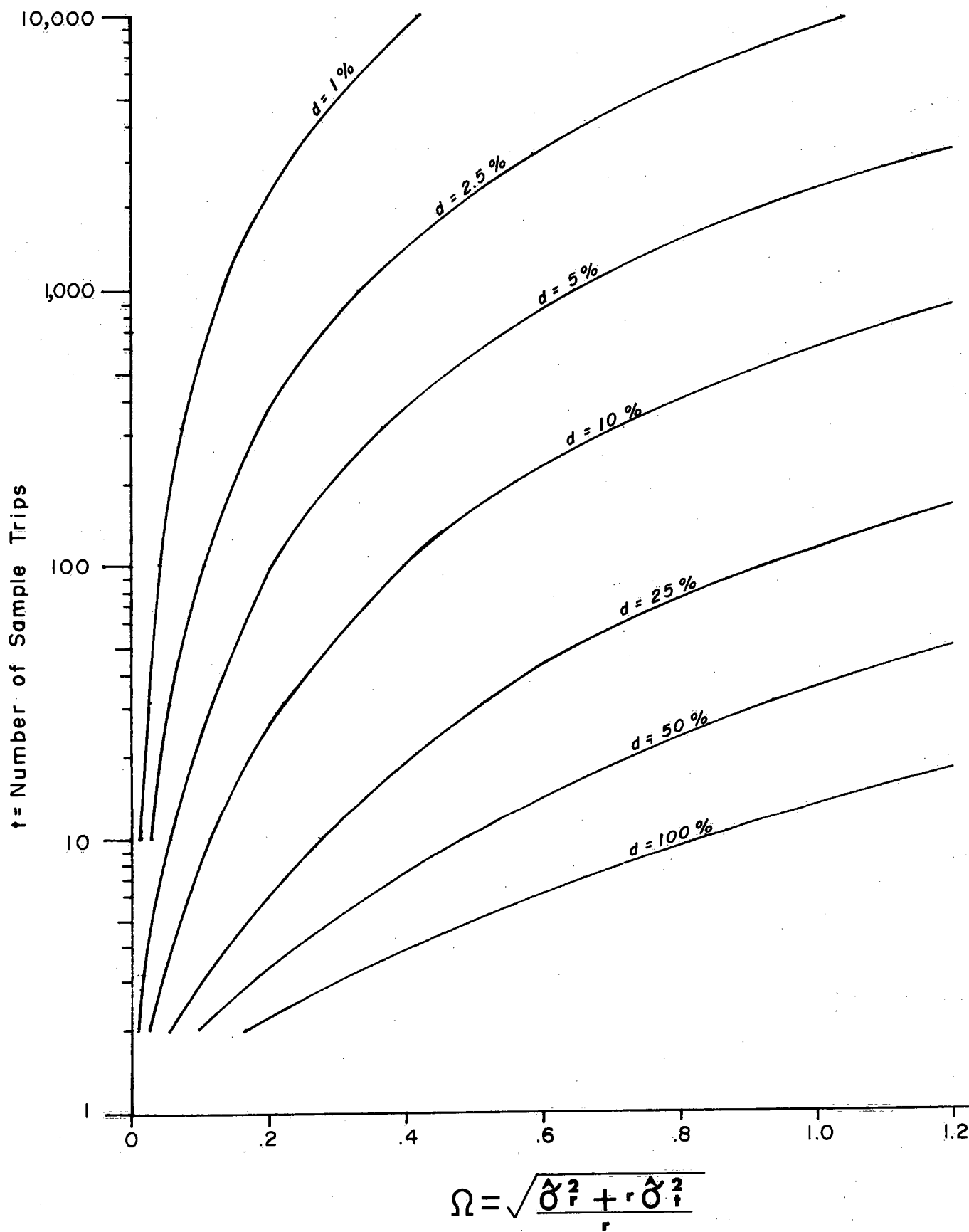


Figure A-1. Number of sampling trips required for different discrimination levels as a function of calculated Ω . The derivation of these curves assumes a probability level (p) of 0.05.

Table A-2. Analysis of Variance for Detecting Difference between Seasonal Mean Concentration in Two Different Years

Sources of variation	Degrees of freedom	Mean squares	Expected mean squares
Between years	1	$MS_y = S_3 - S_4$	$\sigma_r^2 + r\sigma_t^2 + \frac{1}{2}rt\Delta^2$
Within-season temporal	$2(t-1)$	$MS_t = \frac{S_2 - S_3}{2(t-1)}$	$\sigma_r^2 + r\sigma_t^2$
Among replicates	$2t(r-1)$	$MS_r = \frac{S_1 - S_2}{2t(r-1)}$	σ_r^2

t = number of sampling trips per season.

r = number of replicates per trip.

Y = log(concentration).

$$S_1 = \frac{2tr}{\sum \sum Y^2}$$

$$S_2 = \frac{1}{r} \sum \left(\sum Y \right)^2$$

$$S_3 = \frac{1}{tr} \sum \left(\sum Y \right)^2$$

$$S_4 = \frac{1}{2tr} \left(\sum \sum Y \right)^2$$

σ_r^2 = replicate variance.

σ_t^2 = within-season temporal variance.

Δ = difference between mean Y for two years.

resolution and substituting the previously obtained estimates of temporal and replicate variance, $\hat{\sigma}_t^2$ and $\hat{\sigma}_r^2$, for σ_t^2 and σ_r^2 , it would be expected that

$$F_p[1, 2(t-1)] = \frac{\hat{\sigma}_r^2 + r\hat{\sigma}_t^2 + \frac{1}{2}rt\Delta^2}{\hat{\sigma}_r^2 + r\hat{\sigma}_t^2}$$

where Δ is the difference in the means of the log-transformed variates, which is the same as the log of the ratio of geometric means of the untransformed variates. Therefore

$$F_p[1, 2(t-1)] = 1 + \frac{t}{2} \frac{\log GM_2 / GM_1}{\Omega}^2 \quad (A-2)$$

where

$$\Omega = \sqrt{\frac{\hat{\sigma}_r^2 + r\hat{\sigma}_t^2}{r}} \quad (A-3)$$

and GM_1 and GM_2 are the geometric means for the two years. By manipulating Equation A-2 it can be shown that the proportional difference between years is

$$\begin{aligned} \frac{GM_2 - GM_1}{GM_1} &= d \\ &= \exp \left(\Omega \sqrt{\frac{2(F_p[1, 2(t-1)] - 1)}{t}} \right) - 1 \end{aligned} \quad (A-4)$$

This equation can only be solved for t by numerical means. Figure A-1 is a plot of solutions for t as a function of Ω for various discrimination levels, assuming a probability level, p, of 0.05. By calculating Ω from Equation A-3, it is possible to obtain t by entering Figure A-1 with Ω along the x-axis and, using the curve with the desired discrimination level, read the value of t from the y-axis.

It should be pointed out that the t trips should be randomly distributed in time throughout the season of interest in order to avoid problems with periodicities in the value of the parameter. If, for example, sampling trips were to be taken at weekly intervals, then even with a rather weak periodicity of approximately one week it is obvious that the results would be biased. By the same reasoning, samples should not always be collected at the same time of day. In the event of very regular fluctuations, an even more efficient sampling program not based on random temporal sampling could be devised. But assuming that strong regular fluctuations do not exist, the method above of choosing r and t should yield a sampling program that would be able to detect a given degree of change from year to year at a minimum cost.

In summary, the procedure is as follows. Conduct a pilot study and calculate $\hat{\sigma}_t^2$ and $\hat{\sigma}_r^2$ by the analysis of variance given in Table A-1. Estimate the ratio for the cost per trip to the cost per sample, and choose the number of replicates, r, using Equation A-1. Calculate Ω from Equation A-3 and decide on the discrimination level, d. Assuming the desired probability level for the final statistical test is 0.05, the number of trips, t, can be obtained from the graph in Figure A-1. For other probability levels, Equation A-4 must be solved numerically for t.

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Appendix B
Results of Chemical Analyses

Results of Chemical Analyses

Table B-1. Concentrations of Various Parameters (mg/l) in Water Samples Collected with I.W.D. Replicate Sampler at Station at VDS No. 1 during September 1974

Parameter	Date and time	
	1974-09-25-18:40	1974-09-26-11:30
Total P	0.016	0.016
	0.014	0.017
	0.022	0.016
	0.022	0.015
	0.019	0.016
	0.020	0.016
NO ₃ +NO ₂	0.122	0.110
	0.121	0.110
	0.115	0.110
	0.121	0.110
	0.204	0.114
	0.118	0.113

Table B-2. Concentrations of Various Parameters (mg/l) in Water Samples Collected with I.W.D. Replicate Sampler at Station at VDS No. 3 during September 1974

Parameter	Date and time	
	1974-09-25-18:00	1974-09-26-10:45
Total P	0.020	0.014
	0.017	0.015
	0.018	0.022
	0.016	0.016
	0.016	0.018
	0.031	0.017
NO ₃ +NO ₂	0.140	0.115
	0.123	0.110
	0.123	0.115
	0.124	0.110
	0.150	0.110
	0.125	0.110

Table B-3. Concentrations of Various Parameters (mg/l) in Water Samples Collected with I.W.D. Replicate Sampler at Station at VDS No. 9 during September 1974

Parameter	Date and time	
	1974-09-25-16:20	1974-09-26-10:00
Total P	0.019	0.017
	0.019	0.017
	0.019	0.019
	0.019	0.017
	0.030	0.019
	0.024	0.018
NO ₃ +NO ₂	0.064	0.075
	0.066	0.058
	0.065	0.056
	0.091	0.057
	0.066	0.057
	0.232	0.057

Table B-4. Concentrations of Various Parameters (mg/l) in Water Samples Collected with I.W.D. Replicate Sampler at Station at Inkaneep Park during September 1974

Parameter	Date and time	
	1974-09-25-15:30	1974-09-26-09:20
Total P	0.016	0.015
	0.022	0.020
	0.024	0.013
	0.018	0.018
	0.051	0.014
	0.023	0.015
NO ₃ +NO ₂	0.009	0.012
	0.015	0.011
	0.014	0.009
	0.009	0.014
	0.024	0.049
	0.012	0.010

Table B-5. Concentrations of Various Parameters (mg/l) in Water Samples Collected with I.W.D. Replicate Sampler at Station at VDS No. 1 during December 1974

Parameter	Date and time		
	1974-12-02 15:43	1974-12-04 10:20	1974-12-05 15:00
Total P	0.025	0.028	0.027
	0.020	0.026	0.024
	0.023	0.023	0.026
	0.030	0.023	0.026
	0.022	0.024	0.032
	0.027	0.024	0.037
NO ₃ +NO ₂	0.223	0.234	0.230
	0.227	0.238	0.230
	0.224	0.270	0.230
	0.222	0.238	0.228
	0.229	0.235	0.232
	0.223	0.238	0.238
Total organic carbon	3.0	4.4	5.4
	3.2	3.5	6.2
	3.0	5.3	5.1
	2.4	3.9	5.8
	2.9	4.5	4.1
	2.7	4.7	5.1

Table B-6. Concentrations of Various Parameters (mg/l) in Water Samples Collected with I.W.D. Replicate Sampler at Station at VDS No. 3 during December 1974

Parameter	Date and time								
	1974-12-02 10:10	1974-12-02 16:20	1974-12-03 08:30	1974-12-03 18:00	1974-12-04 08:40	1974-12-04 18:10	1974-12-05 07:37	1974-12-05 15:35	1974-12-06 07:30
Total phosphorus	0.024	0.026	0.042	0.025	0.026	0.054	0.026	0.024	0.025
	0.025	0.023	0.040	0.027	0.025	0.026	0.025	0.023	0.033
	0.022	0.031	0.028	0.027	0.026	0.025	0.027	0.028	0.028
	0.023	0.025	0.036	0.026	0.027	0.026	0.021	0.027	0.025
	0.023	0.028	0.036	0.026	0.025	0.032	0.024	0.026	0.026
	0.023	0.024	0.026	0.032	0.024	0.030	0.025	0.024	0.026
NO ₃ +NO ₂	0.236	0.233	0.241	0.058	0.248	0.251	0.248	0.240	0.250
	0.245	0.234	0.242	0.254	0.245	0.246	0.249	0.247	0.250
	0.236	0.235	0.245	0.256	0.246	0.247	0.265	0.242	0.252
	0.277	0.237	0.243	0.274	0.248	0.248	0.282	0.244	0.251
	0.237	0.236	0.244	0.257	0.253	0.271	0.260	0.244	0.251
	0.238	0.280	0.253	0.261	0.248	0.246	0.250	0.244	0.252
Total organic carbon	3.6	2.7	2.1	2.6	4.4	4.9	4.0	6.6	5.2
	3.2	2.9	2.3	1.4	4.6	5.1	5.8	6.2	6.1
	3.5	2.3	2.3	1.6	4.6	4.4	5.2	5.1	4.7
	4.3	3.2	2.4	1.6	6.0	5.2	6.0	5.8	4.7
	4.0	2.9	2.1	1.8	5.0	5.0	5.4	4.1	5.2
	3.7	2.6	2.1	2.2	5.4	5.7	4.3	5.1	5.5

Table B-7. Concentrations of Various Parameters (mg/l) in Water Samples Collected with I.W.D. Replicate Sampler at Station at VDS No. 9 during December 1974

Parameter	Date and time		
	1974-12-02 17:00	1974-12-04 08:07	1974-12-05 16:05
Total P	0.029	0.026	0.029
	0.035	0.025	0.031
	0.028	0.023	0.033
	0.029	0.024	0.029
	0.031	0.029	0.032
	0.029	0.027	0.030
NO ₃ +NO ₂	0.120	0.157	0.125
	0.118	0.123	0.124
	0.123	0.127	0.124
	0.126	0.127	0.136
	0.117	0.112	0.124
	0.117	0.112	0.124
Total organic carbon	4.0	1.5	7.2
	3.0	2.0	6.2
	3.3	2.0	6.6
	3.6	3.7	5.9
	4.1	4.2	5.3
	2.6	3.8	5.2

Table B-8. Concentrations of Various Parameters (mg/l) in Water Samples Collected with I.W.D. Replicate Sampler at Station at Inkaneep Park during December 1974

Parameter	Date and time		
	1974-12-02 17:40	1974-12-04 07:20	1974-12-05 16:45
Total P	0.025	0.033	0.023
	0.022	0.022	0.032
	0.023	0.021	0.023
	0.044	0.023	0.024
	0.023	0.023	0.024
	0.026	0.022	0.022
NO ₃ +NO ₂	0.101	0.088	0.055
	0.060	0.066	0.055
	0.064	0.060	< 0.002
	0.054	0.064	0.054
	0.054	0.060	0.054
	0.055	0.060	0.054
Total organic carbon	1.4	3.0	5.9
	3.0	2.9	5.3
	3.7	2.9	6.6
	3.4	3.0	6.0
	3.6	2.8	6.1
	3.3	2.9	5.9

Table B-9. Concentrations of Various Parameters (mg/l) in Water Samples Collected with I.W.D. Replicate Sampler at Station at VDS No. 1 during March 1975

Parameter	Date and time						
	1975-03-18 09:50	1975-03-18 18:25	1975-03-19 08:20	1975-03-19 17:00	1975-03-20 09:35	1975-03-20 15:15	1975-03-21 07:30
Total phosphorus	0.116	0.051	0.032	0.036	0.038	0.031	0.580
	0.049	0.063	0.042	0.037	0.033	0.036	0.094
	0.053	0.080	0.038	0.033	0.032	0.032	0.054
	0.152	0.055	0.034	0.051	0.033	0.036	0.039
	0.036	0.048	0.037	0.042	0.033	0.036	0.043
	0.067	0.060	0.035	0.050	0.034	0.029	0.041
NO ₃ +NO ₂	0.060	0.039	0.051	0.061	0.084	0.123	0.035
	0.046	0.043	0.054	0.050	0.069	0.115	0.040
	0.049	0.033	0.062	0.055	0.073	0.120	0.044
	0.059	0.041	0.061	0.057	0.078	0.116	0.043
	0.050	0.044	0.063	0.059	0.098	0.117	0.044
	0.055	0.051	0.064	0.062	0.081	0.115	0.042
Total organic carbon	<1.0	<1.0	3.4	1.8	3.4	4.0	3.5
	<1.0	<1.0	1.8	<1.0	2.4	3.8	4.6
	<1.0	<1.0	1.3	<1.0	3.0	3.6	3.4
	<1.0	3.3	3.2	<1.0	2.9	4.0	4.6
	<1.0	3.7	2.4	<1.0	3.0	2.9	4.0
	<1.0	1.8	2.1	1.7	2.2	4.2	3.8

Table B-10. Concentrations of Various Parameters (mg/l) in Water Samples Collected with I.W.D. Replicate Sampler at Station at VDS No.3 during March 1975

Parameter	Date and time						
	1975-03-18 09:00	1975-03-18 18:00	1975-03-19 09:00	1975-03-19 16:30	1975-03-20 08:35	1975-03-20 16:00	1975-03-21 08:30
Total phosphorus	0.034	0.038	0.036	0.042	0.054	0.029	0.040
	0.042	0.034	0.034	0.038	0.030	0.029	0.053
	0.045	0.031	0.037	0.033	0.033	0.029	0.044
	0.038	0.047	0.045	0.033	0.031	0.030	0.042
	0.038	0.045	0.034	0.034	0.030	0.032	0.037
	0.037	0.065	0.034	0.036	0.035	0.034	0.049
NO ₃ +NO ₂	0.043	0.036	0.065	0.061	0.091	0.179	0.028
	0.052	0.039	0.050	0.058	0.085	0.210	0.030
	0.048	0.135	0.060	0.066	0.086	0.177	0.030
	0.048	0.044	0.062	0.062	0.093	0.175	0.024
	0.098	0.058	0.064	0.062	0.089	0.177	0.025
	0.063	0.040	0.068	0.065	0.087	0.188	0.021
Total organic carbon	<1.0	<1.0	2.4	<1.0	5.0	4.5	4.1
	<1.0	<1.0	2.3	1.7	3.8	5.0	3.9
	<1.0	<1.0	2.7	1.7	4.8	4.2	3.9
	<1.0	<1.0	2.5	1.5	4.3	3.9	3.8
	<1.0	<1.0	2.2	2.0	4.5	3.9	4.4
	<1.0	1.7	2.5	2.2	4.2	3.5	3.5

Table B-11. Concentrations of Various Parameters (mg/l) in Water Samples Collected with I.W.D. Replicate Sampler at Station at VDS No. 9 during March 1975

Parameter	Date and time						
	1975-03-18 10:30	1975-03-18 17:25	1975-03-19 09:45	1975-03-19 16:20	1975-03-20 10:00	1975-03-20 18:00	1975-03-21 08:15
Total phosphorus	0.033	0.038	0.035	0.043	0.038	0.320	0.043
	0.046	0.037	0.098	0.045	0.036	0.037	0.057
	0.035	0.030	0.041	0.044	0.033	0.035	0.042
	0.042	0.040	0.067	0.036	0.037	0.032	0.039
	0.044	0.068	0.040	0.036	0.045	0.033	0.040
	0.034	0.039	0.051	0.041	0.035	0.055	0.045
NO ₃ +NO ₂	0.037	0.033	0.086	0.042	0.044	0.109	0.012
	0.040	0.016	0.042	0.036	0.041	0.112	0.012
	0.059	0.016	0.040	0.030	0.041	0.109	0.010
	0.032	0.010	0.035	0.026	0.033	0.112	0.011
	0.035	0.020	0.039	0.036	0.046	0.116	0.012
	0.034	0.009	0.044	0.033	0.043	0.004	0.011
Total organic carbon	<1.0	1.2	4.3	2.0	<1.0	3.6	2.9
	<1.0	1.4	2.7	1.3	<1.0	3.4	2.8
	<1.0	1.4	2.8	2.3	3.7	3.3	4.2
	<1.0	2.1	2.0	<1.0	3.0	2.7	4.0
	<1.0	1.6	3.2	2.0	3.7	2.3	3.5
	<1.0	2.1	3.0	2.1	3.4	2.6	3.1

Table B-12. Concentrations of Various Parameters (mg/l) in Water Samples Collected with I.W.D. Replicate Sampler at Station at Inkaneep Park during March 1975

Parameter	Date and time						
	1975-03-18 11:00	1975-03-18 17:00	1975-03-19 10:15	1975-03-19 16:00	1975-03-20 10:30	1975-03-20 17:50	1975-03-21 08:00
Total phosphorus	0.033	0.040	0.030	0.038	0.035	0.045	0.034
	0.032	0.039	0.031	0.044	0.096	0.041	0.044
	0.042	0.034	0.036	0.037	0.029	0.049	0.068
	0.044	0.034	0.034	0.037	0.054	0.045	0.118
	0.032	0.040	0.040	0.040	0.029	0.062	0.043
	0.031	0.041	0.036	0.036	0.027	0.043	0.049
NO ₃ +NO ₂	0.032	0.033	0.016	0.021	0.008	0.021	0.004
	0.035	0.016	0.018	0.008	0.013	0.006	0.005
	0.042	0.016	0.018	0.009	0.013	0.005	0.006
	0.033	0.010	0.015	0.021	0.010	0.014	0.004
	0.034	0.020	0.012	0.007	0.010	0.004	0.005
	0.015	0.009	<0.002	0.007	0.008	0.004	0.004
Total organic carbon	<1.0	1.2	1.6	2.1	3.1	3.7	3.4
	<1.0	1.4	2.5	1.9	3.8	3.9	4.5
	1.5	1.4	2.5	1.3	3.1	4.5	4.5
	<1.0	2.1	1.4	<1.0	3.1	3.9	2.9
	<1.0	1.6	<1.0	4.8	3.5	3.3	5.2
	<1.0	2.1	<1.0	4.9	3.4	4.0	4.7

Table B-13. Concentrations of Various Parameters (mg/l) in Water Samples Collected with I.W.D. Replicate Sampler at Station at VDS No. 1 during June 1975

Parameter	Date and time		
	1975-06-06 10:15	1975-06-07 20:25	1975-06-09 07:15
Total phosphorus	0.033	0.072	0.029
	0.031	0.051	0.034
	0.028	0.045	0.028
	0.035	0.034	0.031
	0.029	0.034	0.028
	0.028	0.036	0.027
NO ₃ +NO ₂	0.018	0.009	0.047
	0.018	0.009	0.015
	0.031	0.033	0.014
	0.018	0.024	0.043
	0.018	0.014	0.028
	0.020	0.022	0.051
Total organic carbon	1.2	0.4	1.4
	1.8	2.4	1.4
	2.1	0.2	1.9
	1.7	0.4	1.5
	1.8	<1.0	0.9
	2.2	0.2	2.3

Table B-14. Concentrations of Various Parameters (mg/l) in Water Samples Collected with I.W.D. Replicate Sampler at Station at VDS No. 3 during June 1975

Parameter	Date and time								
	1975-06-06		1975-06-07		1975-06-08		1975-06-09		1975-06-10
	10:50	20:45	08:30	20:20	08:35	20:00	08:35	20:15	07:30
Total phosphorus	0.027	0.042	0.024	0.030	0.039	0.026	0.032	0.028	0.026
	0.026	0.026	0.027	0.036	0.028	0.030	0.029	0.029	0.026
	0.034	0.028	0.029	0.032	0.029	0.029	0.026	0.022	0.032
	0.043	0.028	0.032	0.038	0.025	0.027	0.032	0.027	0.025
	0.027	0.027	0.030	0.034	0.024	0.024	0.032	0.025	0.022
	0.026	0.024	0.029	0.038	0.027	0.034	0.029	0.028	0.029
NO ₃ +NO ₂	0.018	0.018	0.027	0.017	0.018	0.019	0.026	0.020	0.028
	0.020	0.039	0.017	0.012	0.027	0.017	0.016	0.020	0.016
	0.017	0.019	0.019	0.012	0.011	0.013	0.016	0.081	0.018
	0.017	0.031	0.017	0.012	0.026	0.013	0.021	0.015	0.038
	0.021	0.024	0.016	0.011	0.028	0.098	0.060	0.023	0.028
	0.081	0.018	0.015	0.011	0.019	0.048	0.017	0.016	0.019
Total organic carbon	2.9	2.6	1.9	0.6	0.4	1.8	1.7	0.9	2.5
	2.0	2.9	1.4	2.3	0	1.0	1.9	0.9	2.2
	1.8	3.2	1.7	2.0	0	2.1	2.3	1.7	1.9
	0.8	2.6	1.6	2.0	0	1.5	1.0	3.3	2.4
	2.3	2.4	2.7	2.7	1.4	1.0	1.5	2.1	0.9
	2.4	3.0	3.0	1.5	1.9	3.1	0.7	1.7	1.3

Table B-15. Concentrations of Various Parameters (mg/l) in Water Samples Collected with I.W.D. Replicate Sampler at Station at VDS No. 9 during June 1975

Parameter	Date and time		
	1975-06-06	1975-06-07	1975-06-09
	11:30	19:50	09:10
Total phosphorus	0.030	0.032	0.027
	0.035	0.033	0.052
	0.032	0.037	0.032
	0.026	0.045	0.035
	0.026	0.054	0.032
	0.025	0.056	0.027
NO ₃ +NO ₂	0.054	0.008	0.024
	0.018	0.007	0.009
	0.010	0.010	0.091
	0.039	0.016	0.009
	0.013	0.011	0.005
	0.010	0.007	0.016
Total organic carbon	2.6	1.2	1.9
	1.5	1.4	
	2.3	2.1	2.4
	3.1	1.9	1.7
	2.9	2.0	0.1
	2.6	2.6	1.7

Table B-16. Concentrations of Various Parameters (mg/l) in Water Samples Collected with I.W.D. Replicate Sampler at Station at Inkaneep Park during June 1975

Parameter	Date and time		
	1975-06-06	1975-06-07	1975-06-09
	12:15	19:10	09:50
Total phosphorus	0.024	0.043	0.026
	0.019	0.029	0.044
	0.023	0.028	0.024
	0.021	0.025	0.019
	0.025	0.033	0.023
	0.023	0.033	0.024
NO ₃ +NO ₂	0.005	0.002	0.003
	0.011	0.001	0.017
	0.003	0.010	0.007
	0.002	0.015	0.005
	0.001	0.003	0.002
	0.001	0.002	0.036
Total organic carbon	2.8	2.0	0.8
	3.1	1.9	0.1
	2.5	2.7	0.9
	3.3	2.2	0.7
	2.1	2.8	<1.0
	2.1	2.3	0.9

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