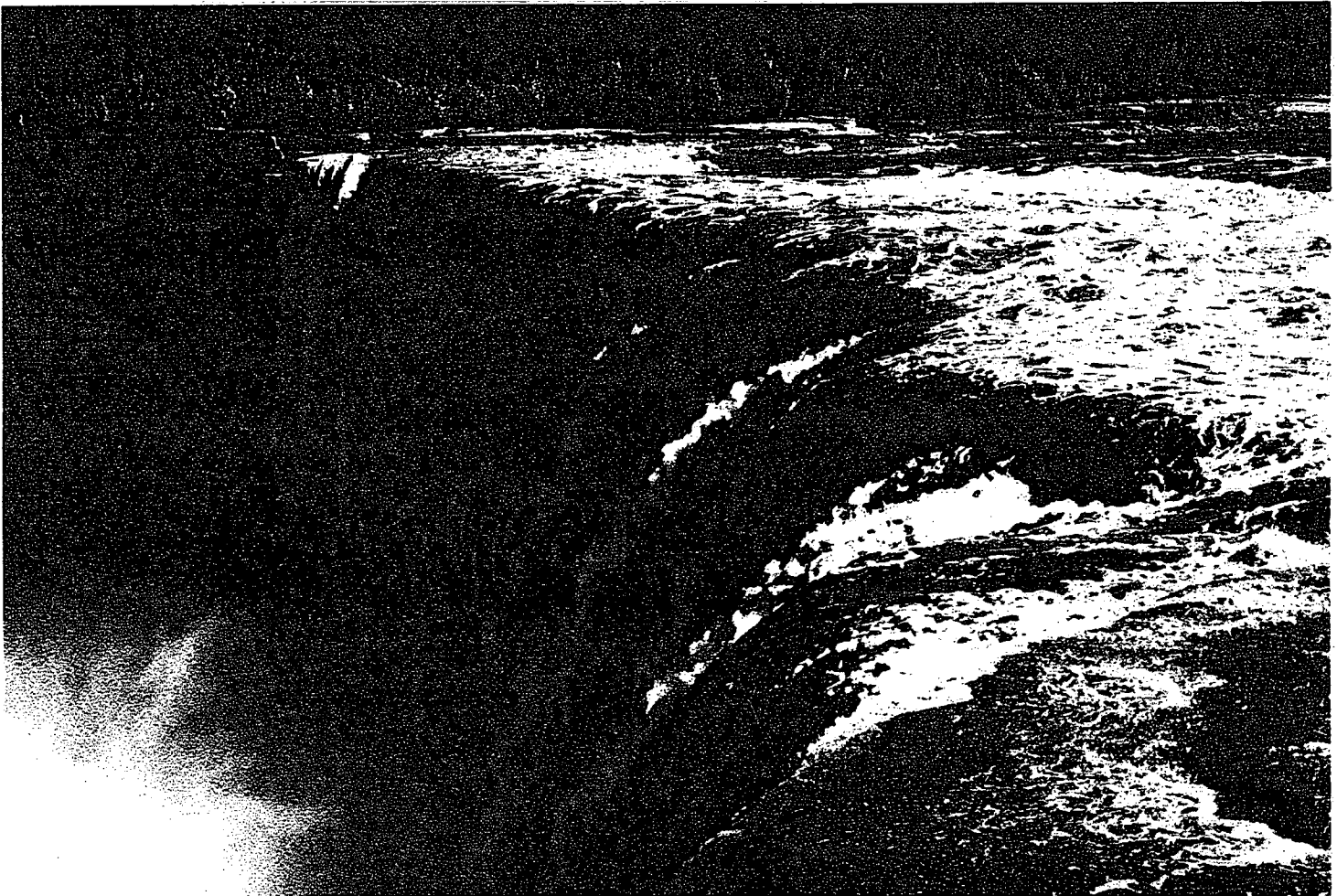


# Limitations of Single Water Samples in Representing Mean Water Quality

III. Effect of Variability in Concentration Measurements on Estimates of Nutrient Loadings in the Squamish River, B.C.

P. Kleiber and W.E. Erlebach



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WATER QUALITY  
LOADING ESTIMATES  
SQUAMISH RIVER  
B.C.



Fisheries  
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**P. Kleiber and W.E. Erlebach**

**TECHNICAL BULLETIN NO. 103**  
*(Résumé en français)*

**INLAND WATERS DIRECTORATE,  
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## **Abstract**

An examination of the effect of variability in concentration measurements on estimates of nutrient loadings in the Squamish River and its tributaries has shown the limitations that result from the use of data derived from infrequent single grab samples. By the use of Monte Carlo techniques, the precision and accuracy of various measurement approaches were assessed. Correlations between discharge, measured continuously, and nutrient concentration, measured intermittently, provide a means of generating precise and accurate loading estimates.

## **Résumé**

Une étude de l'effet de la variabilité des dosages sur les estimations des charges d'éléments nutritifs dans la rivière Squamish et ses affluents a montré les limites qui proviennent de l'utilisation de données dérivées d'échantillons simples d'eau prélevés au hasard et de façon intermittente. En ayant recours aux techniques de Monte Carlo, la précision et l'exactitude des diverses méthodes d'échantillonnage ont pu être évaluées. Les corrélations entre le débit, mesuré à des intervalles réguliers, et la concentration des éléments nutritifs, déterminée à l'occasion, fournissent un outil permettant d'établir des estimations précises et sûres quant aux charges d'éléments nutritifs.

# Limitations of Single Water Samples in Representing Mean Water Quality

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### INTRODUCTION

In routine water quality monitoring, single samples are often taken at monthly or longer intervals. With such scant data, it is difficult to adequately assess the variability associated with the water quality measures or the degree to which this variability might limit the usefulness of the data. To deal with this question of variability, a program of intensive replicate sampling for nutrients was carried out on the Squamish River and its major tributaries, the Cheakamus River and the Mamquam River. As an example of the use of water quality data, nutrient loadings were estimated and statistical confidence limits of the estimates were determined. Estimates were obtained using all the data and also using selected subsets of the data in order to mimic a one-datum-per-month sampling program.

The Squamish River is the major freshwater input to Howe Sound, a coastal inlet in southern British Columbia. To make this study a useful adjunct to an ongoing investigation of primary production in Howe Sound, it was decided to concentrate on algal nutrients. Three water quality parameters were chosen for this study with regard both to their relevance to phytoplankton nutrients and to the ease with which large numbers of samples could be collected in the field and processed in the laboratory. The parameters were concentrations of total phosphorus, dissolved nitrate plus nitrite, and dissolved silica, hereafter referred to as P, N and Si, respectively.

All sampling sites shown in Figure 1 were close to, but upstream of tributary confluences, and were also upstream of tidal influences and major human settlement or industrial activity. This study is, therefore, concerned primarily with natural nutrient loadings from diffuse sources. Discharge data used to calculate loadings at the selected sites were obtained at hydrometric gauging stations by Water Survey of Canada. The close proximity of these gauging stations to the sampling sites allowed the use of discharge data without correction.

### METHODS

All nutrient samples were taken in sets of six replicates except for Si. The silica concentrations determined initially

from sets of six samples collected simultaneously showed such low variability that the sets were reduced to duplicates. Samples were taken from near the mid-point of the rivers at the locations indicated in Figure 1. Water samples were brought to the laboratory for processing within a day or two of sampling. They were maintained at 2-4°C while in transit or while awaiting analysis. Nutrient concentrations were measured by automated methods (Technicon Instruments Corporation, 1971; Technicon Instruments Corporation, 1972; Environment Canada, 1974).

In a preliminary sampling, six replicate samples were taken serially within several minutes in 2-litre plastic bottles. Six subsamples were then decanted from each main sample, with care taken to shake the main sample thoroughly between each subsample. A problem peculiar to the P samples emerged as is shown in Figure 2, where P is plotted against subsample number. Evidently a significant amount of phosphorus was associated with rapidly settling material and, in spite of the vigorous mixing, appeared disproportionately in the final subsamples when the main sample bottle was almost empty. To solve this problem the sampling rack shown in Figure 3 was designed, allowing replicate samples to be taken directly without the need for decanting. Six sample bottles are held in this rack by stainless steel and Teflon plungers. These plungers displace some of the volume in the sample bottles so that reagents can subsequently be added without decanting some of the sample. Samples to be analyzed for P were collected in 50-ml glass bottles, which could be placed in an autoclave following the addition of sulphuric acid and potassium persulphate. In this way reactions to convert particulate and adsorbed phosphate to the dissolved orthophosphate form can be carried out in the original sample bottle.

Samples to be analyzed for N and Si were collected in 100-ml polyethylene bottles placed in the rack. Subsamples were removed for N and Si analysis without pretreatment of the collected sample. When the concentration of nutrient in a sample from a set of six deviated substantially from the mean of the concentrations in samples from the set, the analysis was repeated on a second subsample. With few exceptions the second analysis confirmed the measurement from the first.

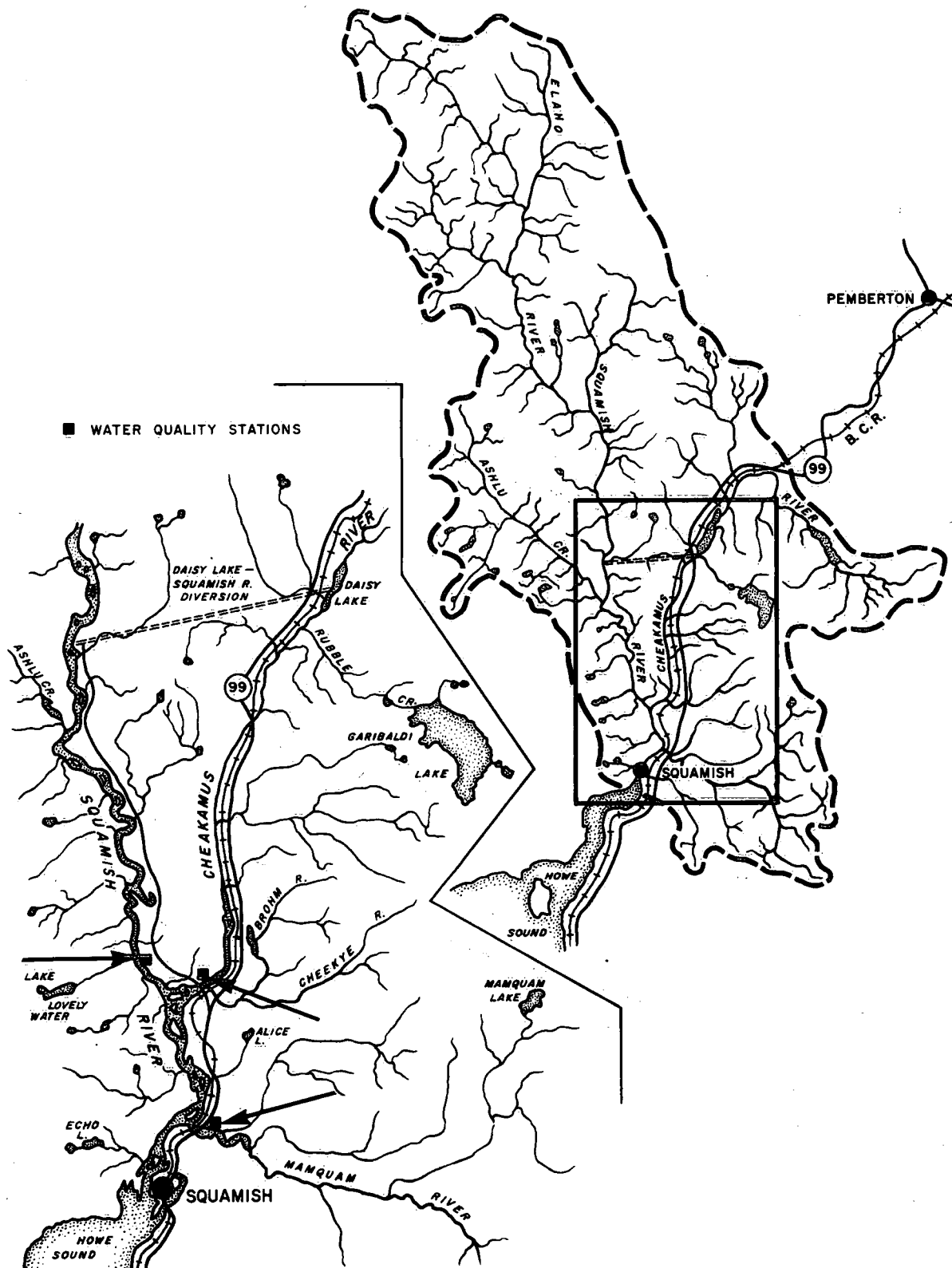


Figure 1. Location of sampling stations on the Squamish, Cheakamus and Mamquam rivers.



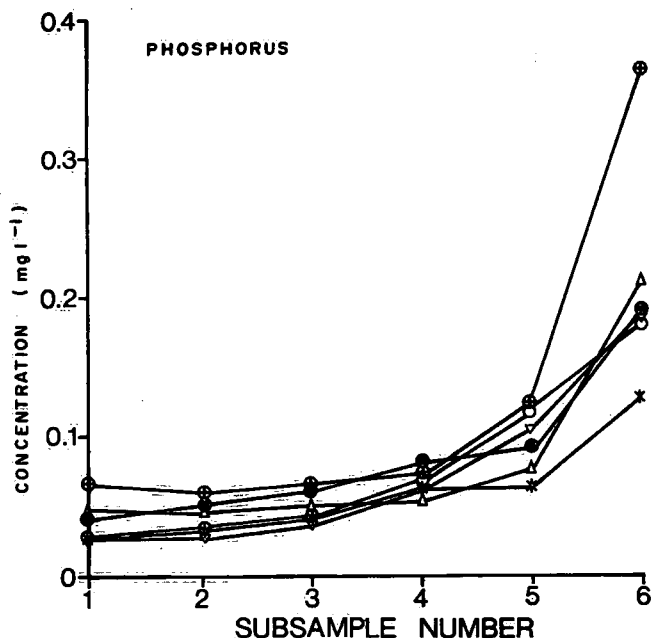


Figure 2. Preliminary replicate sampling results. P is plotted against the order in which six subsamples were decanted from each of six main sample bottles. The 2-litre main samples were collected in quick succession from one point in the river.

## RESULTS AND DISCUSSION

### Nutrient Concentrations

The plots in Figure 4 show the raw concentration data for the three nutrients in all samples taken from the three rivers over the period March to December, 1974. Data were not obtained during January and February, 1974. Considerable scatter is evident within individual sample sets for P and N, and very little scatter for Si. It is apparent from the temporal variation within a month or a quarter that single samples would provide imprecise measures of the mean monthly or quarterly values for these rivers.

### Loading Calculations

To investigate the consequences of this variability on the use of the data, cumulative loading estimates were calculated in various ways from concentration and discharge data for the period March to December, 1974. The statistical distributions of the resulting estimates were estimated by using Monte Carlo techniques, that is, by making repeated loading estimates based on "samples" from an appropriately tuned random number generator. Although the precision of the mean daily discharge measurements has not been established, a review of the methodology suggests that the variance is small relative to the variance of the concentration measurements. It was, therefore, assumed that discharge variance did not make a significant contribution to the loading variance.

The continuous line in Figure 5 shows the seasonal pattern of daily average discharge for the Squamish River. The plotted points (+) indicate the dates when nutrient samples were taken. These points also indicate estimates of discharge based on manual readings of stage height at the sampling times. The Mamquam and Cheakamus rivers, which were also sampled on these dates, have discharge records showing a similar pattern to the Squamish, but with approximately one tenth of the discharge. Since the concentrations are not much higher on average than in the Squamish River, it is evident that the Squamish accounts for most of the nutrient loading from the river system. Therefore, the following discussion will concentrate primarily on the Squamish data.

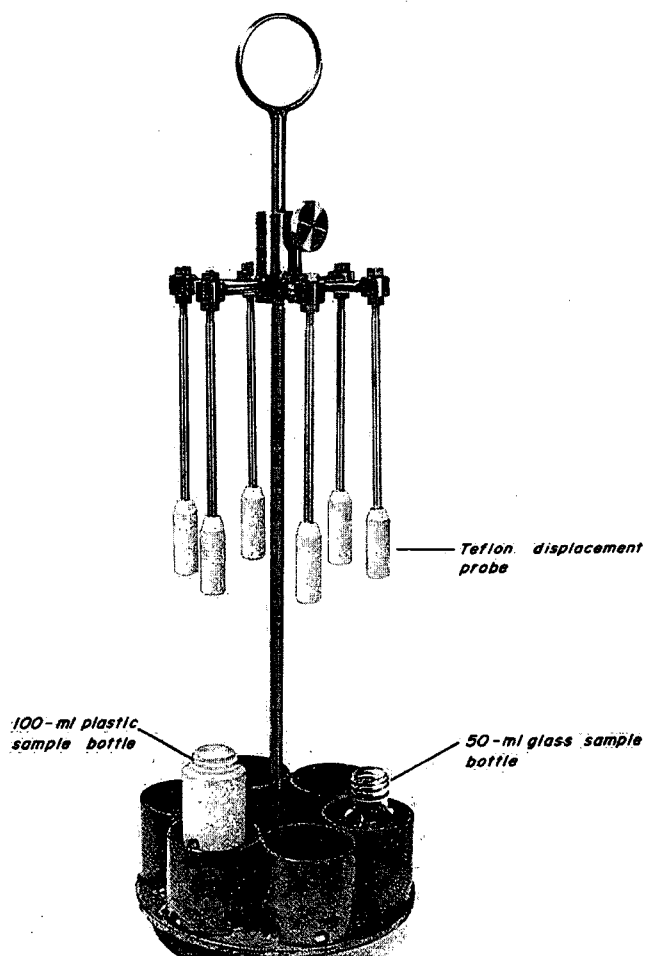


Figure 3. Inland Waters Directorate replicate sampler with Teflon displacement probes in raised position allowing access to cups holding sample bottles.

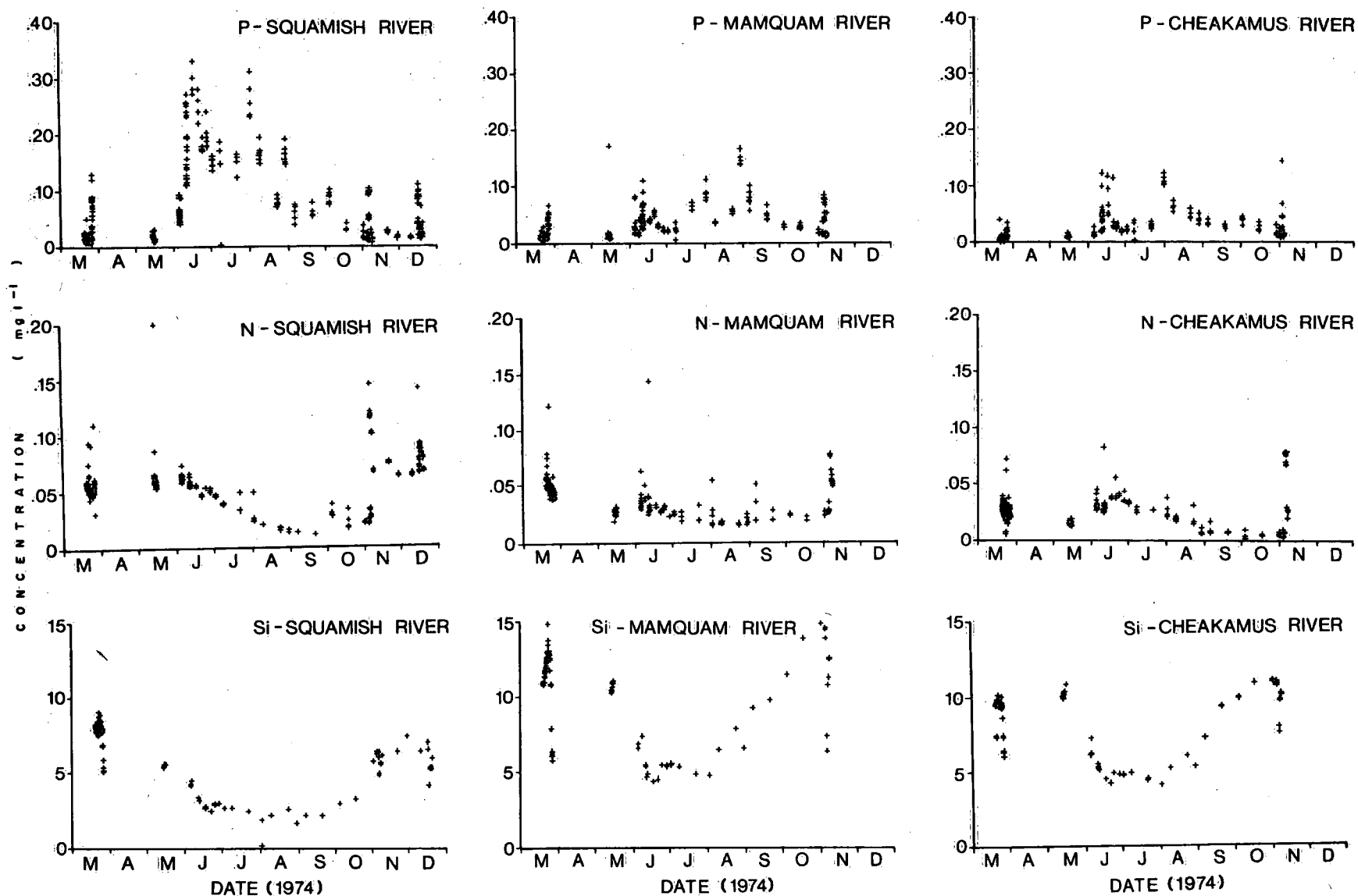


Figure 4. Measured concentrations of P, N and Si in the Squamish, Mamquam and Cheakamus rivers.

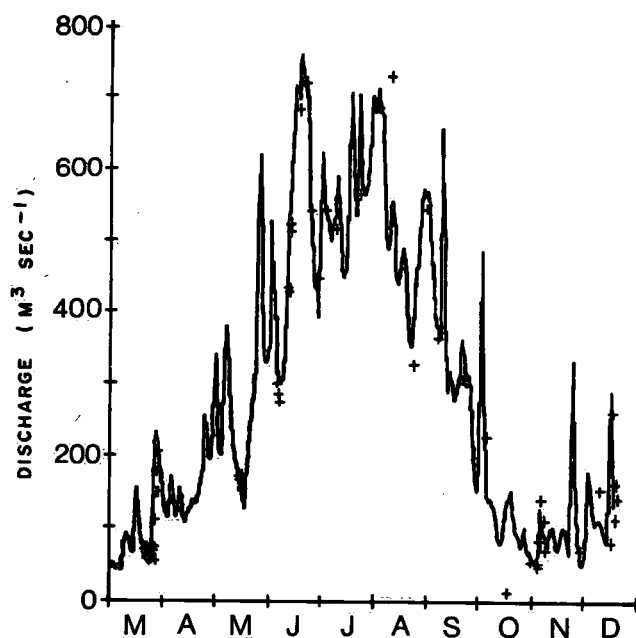


Figure 5. Daily average flow record for the Squamish River. Sampling times for nutrient concentration are indicated by + marks.

#### Loading Based on One Datum per Month

For the first loading calculation it was assumed that only a single monthly sample had been taken. To do this, a concentration datum was randomly chosen from among the data available for the month. These concentrations were then multiplied by the monthly discharges and the resulting monthly loads summed. This process was repeated 200 times giving 200 separate estimates. The distributions of estimates obtained by this Monte Carlo procedure are shown as Curve A in Figure 6. The width of these distributions reflect both the scatter within sample sets and the temporal variability. Thus P has the widest distribution. A quarterly sampling regime would be expected to give correspondingly wider distributions.

#### Loading Based on All Data Available

The distributions in Figure 6 marked as Curves B and C are for loading estimates based on all the data available. To generate these distributions it was necessary to know the underlying distributions of the concentration data. The data from a set of six replicates do not adequately define the shape of a distribution. Therefore, all the data were combined in one distribution by dividing each datum by the mean for its set. Since the degree of scatter appeared to be proportional to the mean, division by the mean rather than subtraction of the mean was preferred.

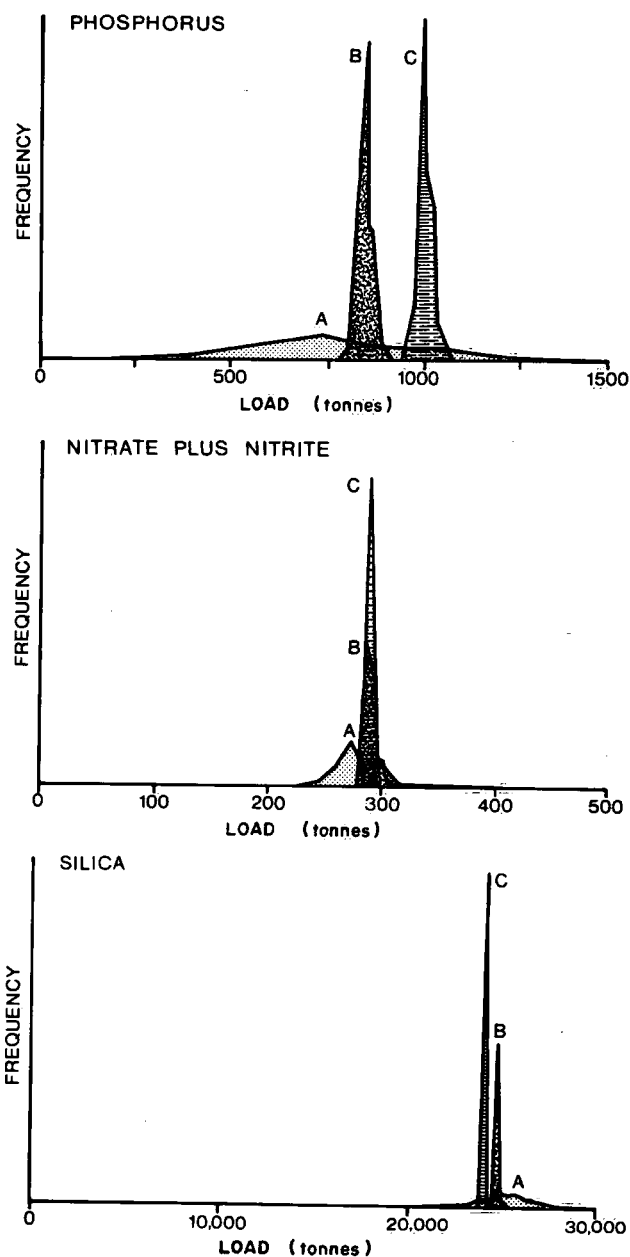


Figure 6. Monte Carlo distributions of cumulative loading estimates (March - December, 1974) for the Squamish River obtained by three different methods: A - one datum per month; B - all data, direct; and C - regression equations. The frequency axis is scaled so that the areas under Curves A, B and C are the same.

The results for the Squamish River are given in Figure 7, where it can be seen that P has the greatest within-sample variability and Si has the least. A random number generator was tuned to produce numbers distributed like these empirical distributions. Then each set of replicates in the original data record could be matched with a new set of

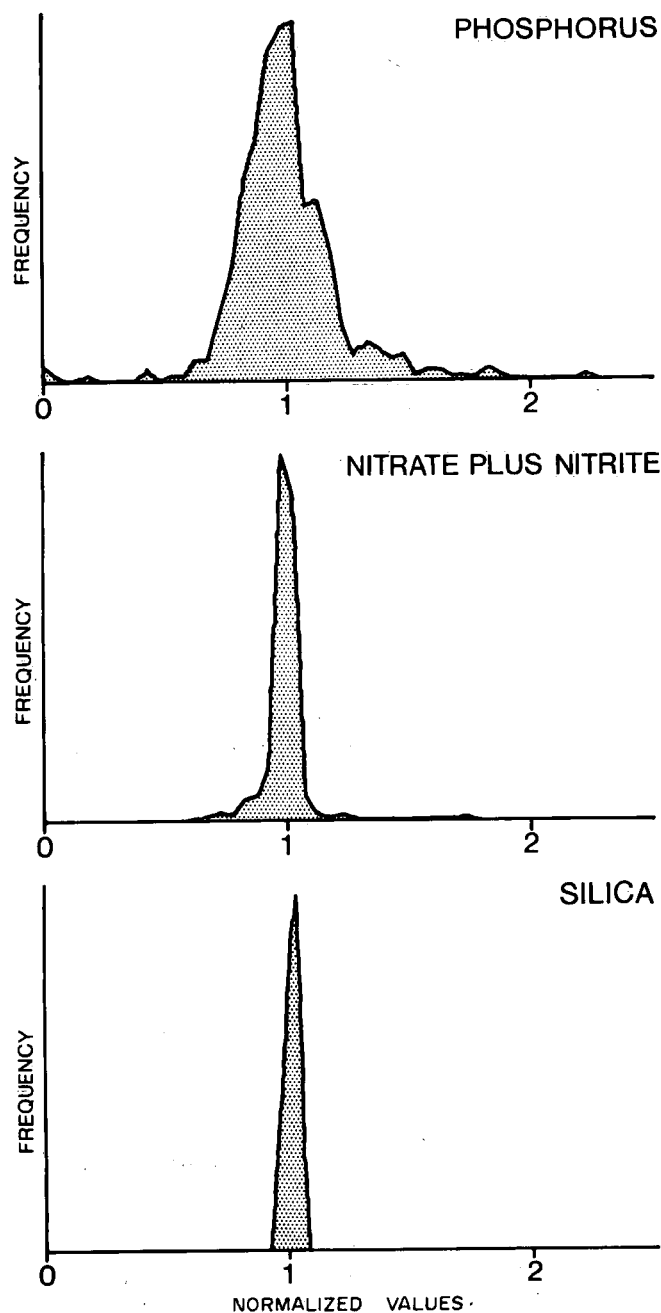


Figure 7. Distribution of concentration within sample sets. All Squamish River data were combined as described in text.

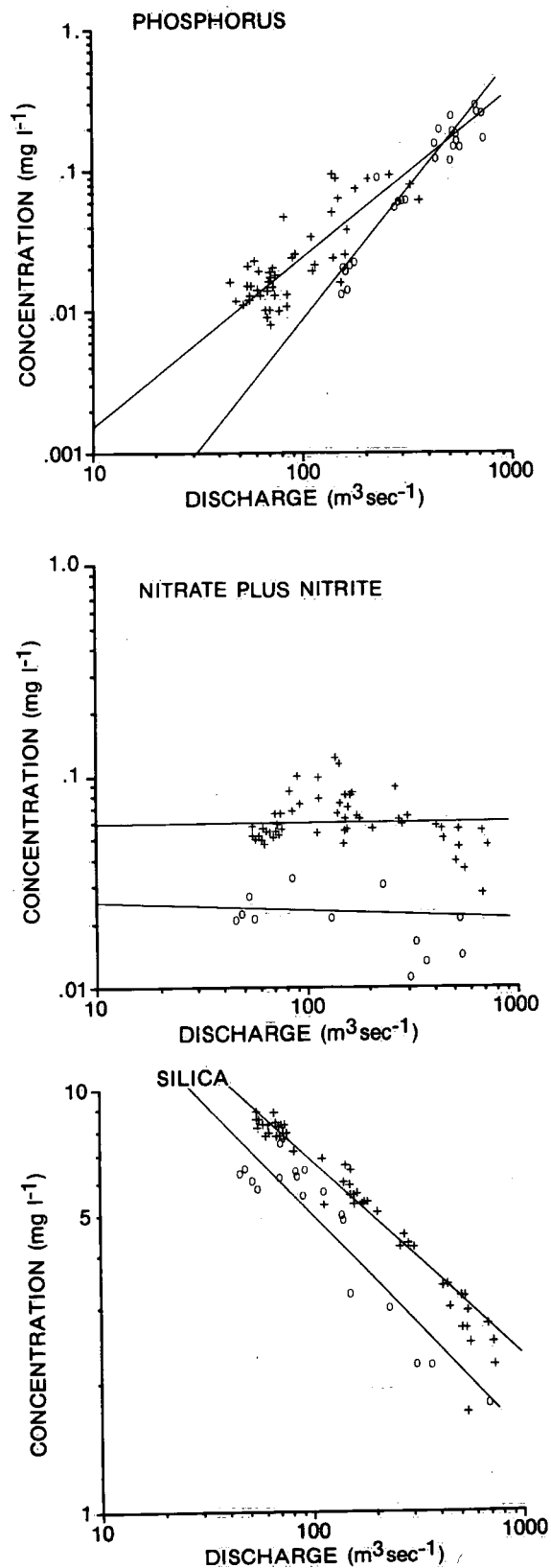


Figure 8. Concentration discharge relationships, Squamish River data. Regression lines are included for the two seasonal periods. The points indicate mean concentration values derived from replicate samples and instantaneous discharge at the time of sampling.

generated data, which were obtained by multiplying a set of randomly chosen numbers from the distribution by the mean of the original set. In this way 200 complete concentration data records were generated, each with statistical properties similar to the original data record.

*Direct Loading Estimates* — Loading estimates from the complete data records were first calculated by multiplying the mean of each generated set of replicates by the discharge for the period since the last sampling. The resulting loadings for all periods were then summed. Curves B in Figure 6 are the distributions of loading estimates obtained in this way. These distributions are narrower than Curves A because they are based on the complete data record, which has more frequent sampling times than once per month and which, in addition, has replicates at each sampling time.

*Loading Estimates Based on Regression Relationships* — The validity of either of the foregoing methods for calculating loading depends on the point concentration determination being representative of concentration during the period of continuous discharge to which it is applied. In Figure 5 it can be seen that the river flow is highly episodic; that is, there tend to be narrow peaks of high flow with wider valleys of lower flow between. Thus, uniform or random sampling over time would tend to emphasize conditions during the periods of lower flow. If concentration were independent of flow, this would be no problem, but if concentration were to vary with flow, the estimate of load would be biased toward low flow conditions. Figure 5 clearly shows that for the sampling regime of this study the peaks of flow received less sampling attention than the valleys. Fortunately, enough samples were taken during periods of high flow to check for a relationship between concentration and flow.

Figure 8 shows log-log plots of concentration against flow, with regression lines included. If these plots are drawn at a large enough scale to include codes for dates of sampling, the data seem to fall into two more or less distinct groups representing two portions of the year. A separate regression was carried out for each group, hence the two regression lines. Statistically significant relationships ( $p < .05$  for null hypothesis of zero slope) exist for P and Si but not for N. The increase in P with discharge could be related to the increase in concentration of suspended solids containing the bulk of the phosphates present. These phosphorus-containing solids are resuspended from the river bed by the increased turbulence and entrained by increased surface runoff accompanying high flows. The opposite behaviour of Si, which is dissolved, is presumably related to a dilution effect. The relationship between flow and N may represent a balance between the opposing effects shown by P and Si, but it more likely results from the input of

nitrogen from rain and snow. If precipitation were the main nitrogen source, N would be independent of flow and dependent only on the value of N in the original precipitation. Rain samples in a neighbouring drainage basin gave N values in the same range as those reported here (Zeman and Nyborg, 1974).

Having obtained an empirical relationship between concentration and discharge, one is able to generate a continuous concentration record using the continuous discharge record. Loading can then be integrated over the year using appropriate values of concentration for all conditions of discharge. This was done with the regression lines shown in Figure 8, using the appropriate regression for each of the two seasonal periods. To obtain Monte Carlo distributions, estimates were also made using regressions based on each of the 200 sets of generated concentration data. The resulting distributions are shown by the Curves C in Figure 6. Distributions for the regression estimates were originally produced by using the regression on the real data (measured concentration against instantaneous discharge at the time of sampling, see Fig. 8) and by adding a random error based on the confidence band of the regression. This method deals directly with the scatter around the regression line, which is large, particularly for P and N. The resulting distributions of loading estimates were actually narrower than those shown in Figure 6, Curves C. This occurs because the regression line is consulted 306 times for the 306 days of the cumulative loading period, and errors on one side of the line are likely to be balanced by errors on the other side of the line. For the 200 separate regression lines, however, the differences persist for all 306 concentration predictions obtained from each regression.

For the sake of comparison, the daily loading as predicted by the regression equations based on the original data is plotted in Figure 9 along with the instantaneous daily loadings calculated directly from the original data. The arrows indicate the times when seasonal shifts were assumed to take place. Other shift times were tried, but the ones in Figure 9 seemed (by eye) to give the best fit of predicted instantaneous loadings. The fit is good for the most part except for N in the summer months. During this time, N shifted slowly from one grouping to the other on the plot of concentration versus discharge (Fig. 8). Thus neither of the regression equations would be a good predictor during this transition period. The other two nutrients appeared to undergo more rapid shifts. To improve the predictive power for the transition periods would require a more complicated model than the two-part regression scheme presented here. The model would probably have to incorporate mechanisms for the seasonal shifting, which at present would be highly speculative.

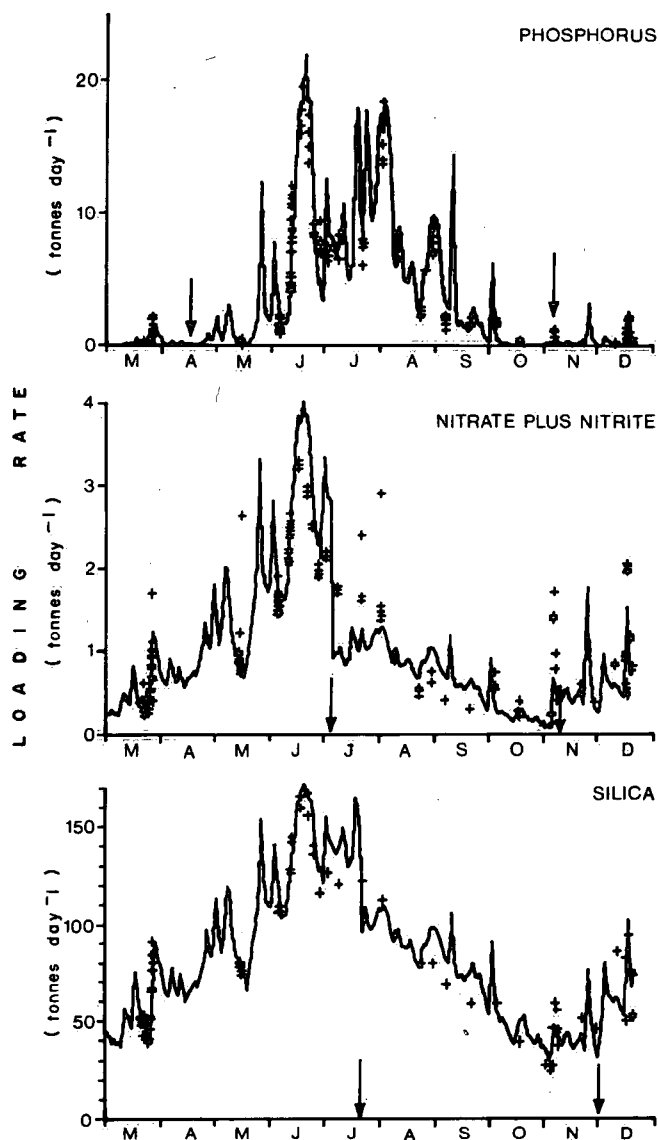


Figure 9. Daily loading record in the Squamish River predicted by regression equations. The instantaneous daily loadings calculated directly from the concentration data are also plotted (+ marks). The arrows indicate when seasonal shifts appeared to occur.

## Comparison of Loading Estimates

### Precision

Differences in precision (i.e., width of the distribution) among the different nutrients reflect the inherent within-sample variabilities shown in Figure 7, P being the most variable and Si the least. For a given nutrient, there is little difference in precision between the regression estimates and the direct estimates, as would be expected because both are based on the same number of data.

### Accuracy

There is an apparent bias in the monthly and direct estimates for P and Si because the correlation between concentration and flow is ignored in these methods of calculating loading. The direct estimates for P are all lower than the regression estimates (Fig. 6). Since the combination of flow regime and sampling regime tended to emphasize low flow conditions, and since P is positively correlated with flow, the concentration figures used in the direct estimates would tend to be lower than average, hence the negative bias. The mode of the monthly estimates is shifted even further, indicating that the effect of this bias is stronger for longer intersampling periods. Silica shows the opposite tendency because it is negatively correlated with flow, and N, which has little or no correlation with flow, has little or no bias in the direct estimates.

In the above paragraph it is implicitly assumed that the direct estimates are biased and not the regressions estimates. Given that the regression procedure eliminates a source of bias in the direct estimates, it is probable that the regression estimates are more accurate. However, it is possible to introduce bias in these estimates if the regression tends to consistently overpredict or underpredict the concentrations. In Figure 9 this is seen to be true in some cases, particularly for N during July and September. It is to be hoped that the periods of overprediction more or less balance the periods of underprediction. The choice of when to shift from one regression to the other affects this balance. Altering the time shifts by about a month had the effect of moving the distributions of regression predictions by approximately the widths of the distributions. Thus, in the absence of other unknown sources of bias it appears that the inaccuracy of the regression estimates owing to the "eyeball" choice of shift times is on the same order as the imprecision.

### Seasonal Loading Pattern

Figure 9 shows the effect of the concentration-flow relationship on the seasonal pattern of loading. The positive correlation of P causes the seasonality of the river flow to be accentuated in the loading, so that the bulk of the phosphate loading occurs during the summer months. The loading of silica is more evenly distributed throughout the year because of the negative correlation of Si with flow.

### Yearly Nutrient Input to Howe Sound

Table 1 summarizes the cumulative regression estimates of loading for the three nutrients and the three rivers. Ninety-five per cent confidence intervals were obtained from the Monte Carlo distributions based on regression equations (Curves C, Fig. 6). These confidence intervals

reflect only the precision of the determinations and not the accuracy (see "Accuracy"). To help the reader appreciate the impact of this loading on Howe Sound, estimates of the total tonnage of these nutrients in the Sound are also included, along with the approximate average turnover owing to the input from the Squamish River system.

Table 1. Summary of Nutrient Loading Estimates in the Squamish River System for March–December, 1974

Nutrient loading	P	N	Si
Squamish River (tonnes)	984	296	24 400
Mamquam River (tonnes)	38	35	6 900
Cheakamus River (tonnes)	39	41	6 900
Total (tonnes)	1 061	372	38 200
95% Confidence interval (%)	±5	±2	±1
Average concentration in Howe Sound * (mg/l)	0.05	0.2	1.0
Total amount in Howe Sound † (tonnes)	200	800	4 000
Approximate turnover per year	5	0.5	10

\*John Stockner, 1975, personal communication.

†Based on volume for Howe Sound of  $4 \times 10^9 \text{ m}^3$  (Pickard [1961]).

## CONCLUSIONS

For the rivers studied, temporal variation and replicate variation in the concentrations of total phosphate, nitrate plus nitrite and reactive silica show that single samples collected monthly or quarterly would provide imprecise measures of mean monthly or quarterly concentrations. Loading estimates derived from these concentration values would also be imprecise.

The estimates of loadings of total phosphate and reactive silica would be biased, as well as imprecise, because of two factors: (1) the pattern of discharge in the rivers is episodic, and (2) the concentrations of these nutrients

correlate with discharge. The bias is negative for total phosphate and positive for reactive silica. The use of the regression relationships between concentration and discharge and the availability of continuous discharge data eliminate this source of bias.

## RECOMMENDATIONS

The study should be repeated soon to confirm that the empirical relationships between concentration and discharge are unchanged. Then the data for both studies would define existing loadings with a specified degree of confidence, and statistically significant changes could be identified in the future.

## ACKNOWLEDGMENTS

The contributions of the Monitoring and Surveys Division and the Analytical Services Division of the Water Quality Branch to all phases of the study are gratefully acknowledged. The timely provision of discharge data by Water Survey of Canada was also appreciated.

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