Field Sampling Methods and Precision of Nutrient Transport Estimation, Okanagan River, B.C.

L. John Zeman



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Water Quality Branch
Pacific and Yukon Region

#### **ABSTRACT**

Since 1976, a monitoring program of nutrient loading has been carried out by the Water Quality Branch, Pacific and Yukon Region as an integral part of the Canada-British Columbia Okanagan Basin Implementation Agreement. The primary goal of the program was to design a method for improving the precision of nutrient load estimation in order to provide water management with a reliable measure on nutrient transport by the Okanagan River to the valley lakes located downstream from the waste treatment plants.

Two sampling methods were used for measurements of concentration of primary nutrients, simultaneous and sequential methods. The simultaneous method, based on collection of sample replicates, permits the calculation of confidence limits of the concentration means and the total loads of nutrients passing through the channel cross-section. The sequential sampling method, used to obtain time series records of single point concentration measurements does not permit the calculation of confidence limits. Precision of the load data derived from sequential sampling method is, therefore, periodically compared with the results obtained by simultaneous methods. Consistency of load data is determined by the comparison of results obtained by these two sampling methods and statistically proved by correlation analysis.

#### INTRODUCTION

The goal of a water quality surveillance program is obtaining water samples that are representative of the original aquatic environment and that maintain the integrity of all chemical substances measured in each sample. However, the sample can be considered to be only an infinitestimal part of the total volume of water and is, therefore, representative of the total mass only to the degree that uniformity of chemical composition exists within the total mass (Rainwater and Thatcher, 1960). Because of local conditions, most water bodies do not have a uniform composition, and any sampling methodology should be related to the heterogeneity of the water body sampled and to temporal changes of variables measured.

In statistical discussions dealing with water quality sampling methods, the term representative sample refers to a single sample drawn from a population, for example in a channel cross seciton, that can be expected to exhibit average properties of that population. A considerable effort is required to ascertain the validity of the sample as a representative from such a variable medium as river water.

The heterogeneity of the chemical composition of surface water is the result of the geologic, hydrologic, biologic and cultural environments which undergo changes with the passage of time. Any procedure for collection of samples for chemical analysis should ultimately be related to the heterogeneity of the water body and variation of concentration

with time. The anticipated heterogeneity in chemical composition of river water, depending on the type of investigation, effects to a large degree the location of samling site, method and frequency of sampling.

The present report describes the approach undertaken in the determination of nutrient loads in the complex pollutant mixing system of the Okanagan River at Penticton. The study which has been carried out by the Water Quality Branch, Pacific and Yukon Region since 1976, is an integral part of the Canada — British Columbia Okanagan Basin Implementation Agreement. This agreement was signed after remedial actions had been undertaken to reduce phosphorus loads from the effluents of the municipal treatment plants built in the Okanagan River Basin.

## Objective

The major objective of the present study is to provide water quality management with a reliable measure of nutrient flux occurring downstream from the Penticton waste treatment plant and thus, to assess the effectiveness of remedial actions undertaken to reduce nutrient flux into Skaha Lake. In order to meet this objective, field sampling methods were designed for determination of precision and consistancy of nutrient loads estimates in the Okanagan River.

## Scope

The nutrient loading study program was subdivided into the two following components: (a) station selection study and (b) long-term nutrient monitoring project.

The aims of the station selection study are to: (a) determine nutrient mixing patterns in the Okanagan River below the municipal outfall and two tributaries to the river, (b) select a suitable station for a long-term monitoring program of nutrient loads to Skaha Lake.

The aims of the long-term nutrient monitoring program are to: (a) determinate temporal changes in concentrations of nutrients measured in the Okanagan River reaches below major point and non-point sources, (b) quantify, with known precision, the nutrient loads to lakes located downstream of treatment plants.

Two field sampling methods used to measure nutrient concentrations are described, the simultaneous and sequential methods. The precision of nutrient load estimates and their consistency are illustrated by the comparison of data derived by these two sampling methods.

#### BACKGROUND

# Data Need Categories

Basically, the approach to water quality sampling depends on the character of the river system examined and the needs for obtaining specific types of data. The data needs can be divided into two general categories, base level and surveillance data.

In evaluating sampling techniques for obtaining base level data the main

consideration will be the ability of the system to provide representative information of long term water quality levels. These levels and their changes can be statistically characterized by median and/or by mean concentration, standard deviation, confidence limits and other statistics identifying trends. In order to enhance the probability of obtaining representative data on concentration of chemical substances, selected for such a study, primary consideration is given to the design of sampling techniques, location of sampling sites, frequency of sampling, variability, and precision and consistency of obtained data. Prior to the design of a major river quality monitoring program, some knowledge of variability of the physical and chemical characteristics of the stream is required. This informaton should be obtained by conducting a short-term survey in selected reaches of the river under investigation.

In order to evaluate sampling techniques for obtaining surveillance data the major concern will be the assessment of the ability of the river monitoring system to detect short term chemical quality variations that are indicative of pollution events and violation of permissible limits or water quality requirements. In such a case, extreme concentration values and their persistency are of greater importance than the mean and its variability.

The number of chemical variables used in the water quality monitoring program depends on the purpose of the study, beneficial water uses and the environmental characteristics of a river basin. For example, the purpose can be to support the following activities: (a) planning and

management program (b) water quality baseline and trend evaluation, and (c) water quality objectives compliance and revision.

From the environmental point of view, data needs depend on the characteristics of the drainage basin, length of water course, slope, land use, and pollution problems. When waste treatment facilities are installed in order to maintain acceptable water quality levels in a stream, the basic water quality data requirements are related to the nature of the receiving stream and the applicable water quality criteria. However, the stream data requirements will vary greatly with water usage and the stream characteristics and processes promoting mixing of water pollutants. These factors have to be considered also in the process of the selection of sampling sites.

# Sampling Location

River water is subject to changes caused by natural forces promoting mixing and homogeneity of concentration of chemical substances in the channel cross-section. However, incomplete mixing and heterogeneities of water composition exist in many streams. Heterogeneous quality throughout the cross-sections results from upstream inflows from tributaries and groundwater, industrial, domestic and agriculture effluents, and upstream scouring of blank and bed associated with changes in water velocity sectors. Immediately below these intrusions a distinct physical separation of these inflows from the stream water exists and can remain discernible for a considerable distance downstream. The extent of mixing of chemical substances in the stream is governed by factors such

as the proximity of inflows and the degree of turbulence associated with the water movement in the channel. Lateral and vertical stream velocities generated by irregularities in the channel further promote the mixing process. This mixing process has to be examined systematically in a number of cross-sections along a river reach in order to select a suitable sampling site. Then, each sample or sets of samples simultaneously collected in a number of points across the channel must be representative of the whole volume of water passing through the cross-section.

In a sampling program in which adequate discharge data are required for the determination of loads of dissolved and suspended materials, the water quality sampling site should be located close to a stream gauging station or the hydrometric data obtained by direct measurements at the quality station. Hydrometric measurements combined water simultaneous sampling (Zeman and Slaymaker, 1981a) at a number of points of a channel cross-section are required for the calculation of the partial loads of solutes and suspended particulates, and their sum which represents the total cross-sectional loads. The method of simultaneous concentration and discharge measurements allows the calculation of confidence intervals of the load data, determined in the channel cross-section, if the simultaneous partial loads or the transformed values approximate a normal distribution and are homoscedastic. Also, this method assumes that there is no temporal change during the period of collection across the channel.

### Sampling Methods

The sampling methods involve either a manual method of samples collection or a mechanical method employing automatic devices.

#### Grab Sampling

A grab sample is defined as a single sample taken at a point in time and space.

### Simultaneous Sampling

For the purpose of determination of the precision of single point concentraion measurements a number of grab samples can be collected simultaneously. This procedure is appropriate when it is desired to measure heterogeneity of water composition in the channel cross-section at a particuar point and time. Simultaneous samples are usually collected by means of two devices, replicate sampler and portable sampling pump (Zeman et al., 1977). A replicate sampler is used for collection of sets of samples from upper stratum of the stream, at approximately one meter below the water surface. A portable sampling pump is used for collection of samples from the lower stratum of the stream in rapid sequence over a one—minute period to closely approximate true simultaneous sampling. In most situations in rivers, samples taken more than one hour apart would not be considered simultaneous. taken within a few minutes could be considered to exhibit short range spatial variation rather than temporal variation.

### Sequential Sampling

Automatic devices are used to collect sequential samples which are defined as a series of grab samples taken by a pump over a short period of time. Sequential sampling method can be used for the determination of temporal variation of concentrations at the point of sampling, and in time intervals in which a significant temporal change of concentration is likely to or does occur.

## Sampling Design

The following sampling design might be used in order to obtain a representative sample: (a) composite sample (b) random sample, and (c) sampling at evenly spaced intervals.

- (a) Theoretically, if the water in the cross-section is not uniform a sample representing the average composition might be obtained by compositing depth - integrated samples of equal volume taken at several points across the channel.
- (b) In the random sampling design, the simultaneous sampling method is used. Water samples should not be collected haphazardly. The channel cross-section is first divided into subsections, horizontally and vertically, and each subsection assigned a number. Random selection of those subsections from which samples are taken is made by following a sequence selected from a random number table (Kratochvil and Taylor, 1981). The results obtained from random

samples can be then statistically analyzed to determine whether apparent correlations exist because of systematic trends in the measurements.

(c) Sampling at evenly spaced vertical slices of the channel cross-section, both in the upper and lower stratum, can be used in place of random sampling. This sampling design is applied, particularly, in the combination of hydrometric measurements and simultaneous sampling in determining the partial loads of materials and their cross-sectional totals. The results from this type of sampling must be statistically analysed for homogeneity of variances before valid calculations of material loads with confidence limits can be made.

# Spatial and Temporal Variability

Earlier work on Thompson, Okanagan and Squamish Rivers (Oguss and Erlebach, 1976; Kleiber and Erlebach, 1976) has demonstrated the inadequacy of single water samples, taken from a river, in representing nutrient concentrations in time and over space. Erlebach (1975) stresses the need to establish confidence limits on nutrient loadings and the need for simultaneous sampling to determine short range spatial variation in nutrient concentration. This has been explicitly recognized in the literature previously (Taylor, et al., 1971; Gburek et al., 1974; Gale and Demayo, 1974), but there has been little evidence of attempts to modify sampling methodology until the work of Erlebach (1978) and his co-workers. The present study is a further extention of this initial effort.

## Precision, Consistency and Accuracy

In the literature, various load methodologies are suggested but with a little attempt to determine precision and consistency of the calculated loads.

The term precision refers to the reproducibility of a result when operations, for example chemical analyses, are performed repeatedly on a sample under controlled conditions. In the field, precision refers to the variability observed among numerous measurements of chemical concentration (Fritschen and Gay, 1979). The observed values can be widely displaced from a true mean value as a result of systematic errors present through the measurements. The precision, according to Eisenhart (1952) as an expression of the clustering of the data, is related to factors inherent to the measuring process.

Consistency of data can be determined when two or more measuring processes or methods are used over a finite time period and the resulting data are compared. If the results of one method are either always higher or lower than those of another method, a systematic bias can be assumed. However, it is not known which of the methods is more accurate. Nevertheless, if the bias shows a consistent pattern then the existance of temporal trends can be established.

Accuracy refers to the relation between the measured and "true" value or the closeness to an accepted standard such as those maintained by the National Bureau of Standards (American Society for Testing Materials, 1972). Accuracy expresses a relation to a value external to the measured process. An accurate method (Eisenhart, op. cit.) is a method that is both precise and unbiased in the sense that it yields measurements that are closely clustered and centered on the true value.

Laboratory standards are normally considered accurate. In field studies, on the other hand, the true field standards cannot be determined and indication of bias and defining levels of precision are, therefore, fundamentally important considerations in designing procedures of sampling and analytical interpretation.

#### STUDY AREA

# Okanagan River Basin

The topographic map (Figure 1) show the location of the Okanagan Basin. The Canadian portion of the basin has length of 176.9 km, with a maximum width of 96.5 km and covers an area of 8,197.35 km². The central drainage system consists of a chain of lakes stretching from Wood Lake, through Kalamalka, Okanagan, Skaha, Vaseux and Osoyoos Lakes to the international border. The theoretical water residence times, based on average total volume divided by the mean annual outflow, are 60, 1.2 and 0.7 years for Okanagan, Skaha and Osoyoos Lakes, respectively.

## Nutrient Sources

The investigated reach of the Okanagan River at Penticton, B.C. is a man

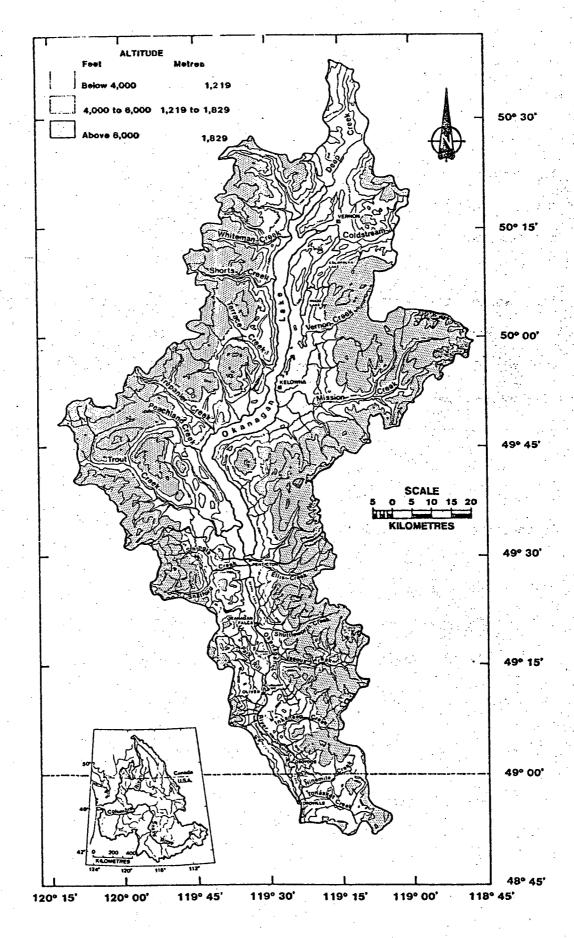


Figure 1. Okanagan Basin, British Columbia

made, 6.6 km channel connecting Okanagan and Skaha Lakes (Figure 2). The channel integrates the nutrient inputs from the waste treatment plant (Figure 3), agricultural and urban run-off via Shingle and Ellis Creeks, and seepage of groundwater and riparian water from backswamp areas drained by the meanders of the old stream which existed before the channel regulation.

The waste treatment plant at Penticton, B.C. commenced process modifications to remove 80 percent of the phosphorus removal from the effluent in 1972. However, the benefits of further phosphorus removal will depend on the relative contribution of all allochthonous sources of nutrient loads to Skaha Lake.

The Okanagan River between Okanagan and Skaha Lakes can be related to the following sources, pathways and sinks:

- (a) Allochthonous nutrient inputs from; Okanagan Lake, Ellis Creek, Shingle Creek, Penticton waste treatment plant, diffuse sources and direct bulk fallout from the atmosphere.
- (b) Autochthonous nutrient exchanges in the form of: turbulent mixing in vertical, lateral and downstream directions, bed and bank sediment and nutrient entrainment, chemical precipitation and adsorption of nutrients and organic sedimentation.
- (c) Storage in bed sediments.

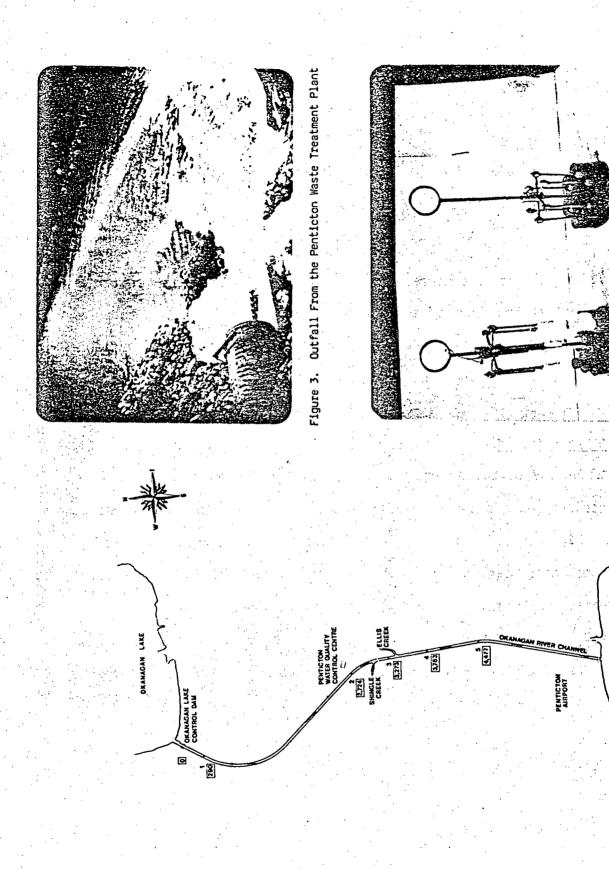


Figure 2. Okanagan River Channel, Penticton B.C.

(d) Net nutrient outputs measured at the lowest cross-section of the Okanagan River before it enters Skaha Lake and above major backwater effects.

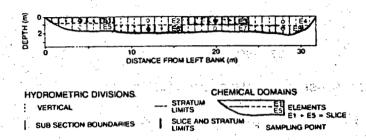
#### METHODOLOGY

Two field sampling procedures, the simultaneous and the sequential sampling methods are used to estimate nutrient flux. Data on total and dissolved phosphorus were selected from the six nutrient variables measured to illustrate the field sampling and interpretation methods.

### Simultaneous Sampling

The simultaneous sampling method, employing a manual sampler (Figure 4), enables collection of sample replicates at a number of points across the channel (Figure 5). Each set of replicates provides a measure of short-range heterogeneity of nutrient concentrations. The replicate measurements, in combination with hydrometric measurements, provide the possibility to determine the magnitude and precision of lateral and vertical variation of the partial and total nutrient loads in the channel cross-sections.

During December 9 and 10, 1976, hydrometric and chemical measurements were taken at the following five channel cross-sections (Figure 6); Station 1 (below Okanagan Lake dam); Station 2 (below the Penticton municipal outfall); Station 3 (below Shingle Creek); Station 4 (below



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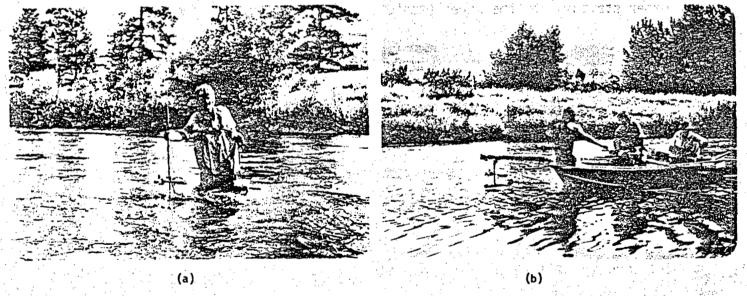


Figure 6. Combined Hydrometric and Chemical Measurements During Low Flow (a) and During High Flow (b)

Ellis Creek) and Station 5 (near the Penticton Airport). Each channel cross-section was divided into a minimum of twenty hydrometric subsections and four chemical slices. A standard, two point hydrometric method of velocity determination at 0.2 and 0.8 of the water depth (Ozga, 1971) was used for cross-section discharge calculation. Slices and strata in the cross-section were used to represent chemical domains. In these domains, slice-elements were the smallest sampling units defined by the stratum and slice boundaries, water surface and wetted perimeter of the cross-section. At one point of each element, approximately at the same depth as the hydrometric measurements, sets of three sample replicates were collected for chemical analysis of nutrients. A replicate sampler was used to collect three simultaneous samples in the upper stratum. In the lower stratum, a sampling pump was applied.

## Sequential Sampling

The sequential sampling method, employing a portable discrete sampling device (Figure 7 and 8), was used to obtain time series records of nutrient concentration measurements taken at a single point, approximately at 0.6 of the depth of water and at a fixed distance from the river bank, approximately one fourth of the channel width. Results obtained by this sampling method are periodically compared with results obtained by simultaneous sampling.

# Frequency of Sampling

Simultaneous measurements of nutrient concentration consisted of collection of three replicates at each sampling point across the

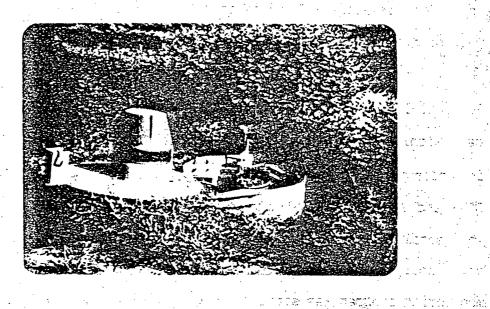


Figure 7. Portable Discrete Sampler



Figure 8. Housing of Portable Discrete Samplers

channel. This method was used once a day during the two-day nutrient dispersion study. During the long-term monitoring program, the simultaneous sampling method was applied once a month with the aim of comparing results of concentration measurements and nutrient load determinations with those based on sequential sampling.

Sequential sampling was carried out on two consecutive, randomly chosen days within each week. The time of sampling during the day was selected in order to observe concentration minima occurring at, approximately, 0300 and 1500 hours and maxima at, approximately, 0900 and 2100 hours. This sampling scheme is based on the diurnal variation, determined from a preliminary set of phosphorus concentration measurements taken before the monitoring program was started.

## Sample Pretreatment and Chemical Analysis

Water samples collected for the dissolved phosphorus analyses are immediately filtered after their collection through the pre-soaked and prewashed 0.45 micron cellulose acetate membrane filter of 47 mm diameter.

The concentration of total phosphorus (P) and total dissolved phosphorus (P) were measured, after digestion in persulfuric acid, by the automated colorimetric phosphomolybdate method utilizing ascorbic acid as the reducing agent (Murphy and Riley, 1962). Results are reported as total phosphorus (P) and total dissolved phosphorus (P) in mg  $1^{-1}$ , and the detection limit of this method is 0.002 mg  $1^{-1}$ .

## Data Registration

A registration form was designed and used for recording field measurements by simultaneous and sequential methods and for coding laboratory analysis data. Figure 9 shows an example of the registration of measurements obtained by the use of the replicate sampler. On the left hand side of the form there are columns designated for identification of sampling station and the period of sampling. The other columns contain information on week-day, year-day and the chemical domains in the channel cross sction, such as slice, stratum and the number of replicates. All these control numbers are useful during the process of data interpretation by the application of various statistical subroutines.

Also, the data register is very useful for the preparation of the field trip, by labelling sample hottles and entering their numbers into the register form. During the field measurements, the reading of the gauge heights is registered. The major advantage of this data register is that laboratory results are entered directly into this form and thus avoiding additional coding of the results of the chemical analysis.

# Data Reception

Data reception is an intermediate step between registration of laboratory results and their interpretation. The diagram (Figure 10) shows the procedure which is used for comparison of the results of chemical analysis of total dissolved phosphorus with the results obtained for total phosphorus. An error message is printed when the results of

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Figure 9. Data Register

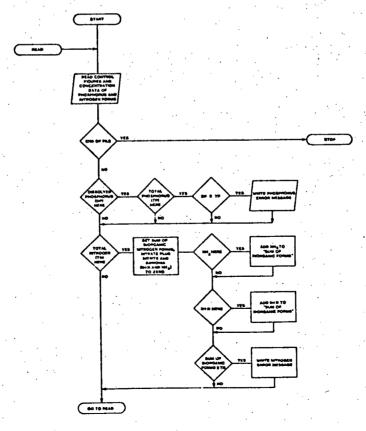


Figure 10. Diagram of data reception comparing concentrations of total dissolved phosphorus and total phosphorus and inorganic nitrogen forms with total nitrogen

dissolved phosphorus are greater than the results of total phosphorus. Similarly the results of chemical analysis of nitrogen forms are checked to ensure that the sum of inorganic forms of nitrogen are not higher than the results obtained for total nitrogen. This type of the raw data control has been found to be essential for their acceptance for further statistical analysis.

#### DATA INTERPRETATION

The techniques used to interpret data obtained from the short-term station selection study and from the long-term nutrient monitoring program are shortly discussed.

# Station Selection Study

During the station selection study, conducted in the Okanagan River at Penticton on December 9 and 10, 1976, the simultaneous measurements of nutrient concentration were performed in combination with hydrometric measurements. Samples for chemical analysis were collected at five channel cross-sections, located above and below the outfall from the waste treatment plant and below two tributaries, Shingle and Ellis Creeks (Figure 2). The results were interpreted in terms of nutrient concentrations and loads. Nutrient concentration data were used for the selection of a representative station and to illustrate spatial changes occurring along the river reach. The graphs of discharge and velocities plotted versus distance from left bank of the river were used to

illustrate the flow patterns at each cross-section. The symmetrical patterns of flow and velocities were applied as a further criterium for the selection of representative Station (Zeman et al., 1977).

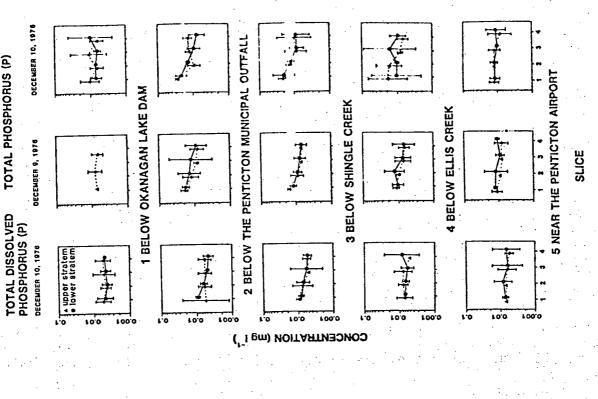
Concentration of nutrients were subject to analysis of variance in order to determine statistically significant differences between the mean concentration of nutrients determined in each slice-element of the investigated channel cross-sections (Zeman et al., op. cit.). Some of these mean concentrations were significantly different, therefore, the multiple range test (Miller, 1966) was applied to sort the slices into groups whose means were not significantly different and thus indicate the degree of mixing.

Results in terms of total phosphorus concentration (Table 1) indicate that almost complete vertical and lateral mixing is achieved at Station 5. Also, the flow and velocities (Zeman et al., 1977) were symmetrical at this station. Thus, this station, located approximately 1.7 km downstream from the outfall, has been selected as representative station for the long-term monitoring of nutrient loads to Skaha Lake.

Spatial changes, in terms of lateral, vertical and longitudinal variation of concentrations of total phosphorus and total dissolved phosphorus observed at the five channel cross-sections are shown in Figure 11. The mean total phosphorus concentration, measured at Station 1 increased from 0.008 mg  $1^{-1}$  to 0.014 mg  $1^{-1}$  below the outfall on December 9 and 10, respectively, and slightly declined downstream to 0.011 mg  $1^{-1}$ , at Station 5. On the other hand, concentration of total dissolved

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TOTAL PHOSPHORUS (P)



Lateral, Vertical and Longitudinal Variation of Concentration of Total Dissolved Phosphorus and Total Phosphorus, Okanagan River, Penticton, B.C. Figure 11.

REFERENCE: Miller, R.G., Stmuttangous Statistical Inference, McGraw-Hill Inc., New York, 1966, pp. 1-272 SOURCE: Zeman, L.J., Erlobach, W.E., and Siaymaker, H.O., Nutrient Loadings Okanagan Bash., Okanagan Rivor at Pentiction, Protiminary Survey and Station Selection, Progress Report, pland Waters Directorate, Vancouver B.C., Canada, 1977, pp. 1-95

NOTE: NS - Statistically not significant

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4 BELOW ELLIS CREEK

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phosphorus, ranging from 0.005, 0.006 and 0.007 mg  $1^{-1}$  at Station 1. Station 2, and Station 5, respectively, showed a steadily increasing downstream gradient.

Nutrient loads are calculated by the partial load method (Zeman and Slaymaker, 1981a,b) using combined hydrometric and simultaneous concentration measurements in the channel cross-sections. The method consists of the calculation of loads in slice-elements and the sums for each pair, which give the partial loads in slices. Then, the sum of the partial loads gives the total nutrient load passing through the channel cross-sections.

Graphical and statistical methods are used to examine the distribution of the load data (Zeman and Slaymaker, op. cit.). The Levene test (Levene, 1960) confirmed the existence of significant heterogeneities of the partial load variances. The Brown-Forsythe test (Brown and Forsythe, 1974), which does not assume the homogeneities of variances, indicates that there are significant differences between the partial loads in the channel cross-sections. In such a case variances of the partial loads and the cross-sectional loads have to be determined. Further, the method proposed by Satterthwaite (1946), which is implemented in some of the University of B.C. statistical programs (Bjerring and Seagraves, 1972), is applied to the calculation of degrees of freedom in the process of estimating confidence limits for the partial loads and the cross-sectional loads of nutrients (Zeman and Slaymaker, 1981 a, b).

Figure 12 shows lateral variation of the partial loads of total

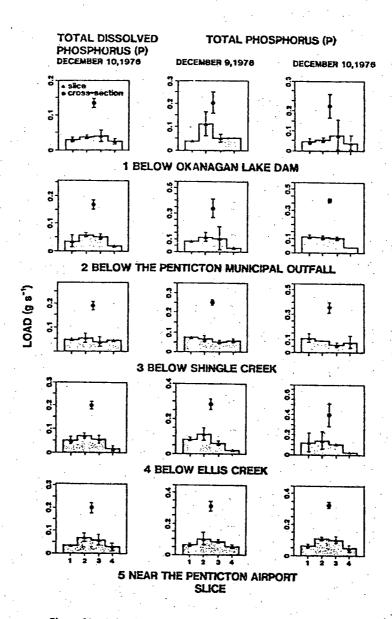


Figure 12. Lateral, Vertical and Longitudinal Variation of the Parital Loads of Total Dissolved Phosphorus and Total Phosphorus, Okanagan River, Penticton, B.C. Total loads are shown in the upper portion of the figure.

phosphorus and total dissolved phosphorus, with their 95 percent confidence intervals, along the investigated river reach. The downstream gradients of these load data are statistically significant. Further results are shown in Table 2. This table shows the cross-sectional loads of the two phosphorus forms, number of samples and the calculated degrees of freedom used to estimate precision of the loads in the channel cross-sections. On December 9, 1976, the cross-sectional load of total dissolved phosphorus determined at Station 1 is 0.134 (95% confidence intervals  $\pm$  0.016) g s<sup>-1</sup> and increases to 0.168 (95% confidence intervals  $\pm$  0.017) g s<sup>-1</sup> at Station 2, below the outfall. The load of this phosphorus form increases further downstream, particularly below Ellis Creek, and at Station 5, near the airport, the load is 0.201 (95% confidence intervals  $\pm$  0.024) g s<sup>-1</sup>. These data indicate that the contribution of the tributaries to the load of dissolved phosphorus can be as great as that from the treatment plant.

In contrast to dissolved phosphorus, the longitudinal changes of total phosphorus are smaller. During the two day study, at Station 1, the cross-sectional load of total phosphorus levels were from 0.206, on the first day, and 0.226 on the second (95% confidence intervals  $\pm$  0.046 and  $\pm$  0.061) g s<sup>-1</sup> and increased to the levels of 0.340 and 0.373 (95% confidence intervals  $\pm$  0.074 and  $\pm$  0.019) g s<sup>-1</sup>, at Station 2, below the outfall. Below tributary creeks, total phosphorus loads showed no statistically significant further change in terms of the cross-sectional means. Although, the longitudinal increase of total phosphorus load during this study varies from 35 to 44 percent, the major source of total

Table 2 Longitudinal Variation and Precision of Phosphorus Loads, Okanagan River, Penticton, December 9 and 10, 1978.

	Station	Sampling Date	Discharge m <sup>3</sup> s <sup>-1</sup>	Number of Observations	Number of Replicates	Degrees of Freedom	Cross- Sectional Load	95% Confidence Interval
-		. 1	otal Dissolve	d Phosphor	us (P)			
1	Below Okanagan Lake Dam	10-12-78	26.75	24	3	5.484	0.134	± 0.016
2	Below the Penticton Municipal Outfall	10-12-76	26.75 (est.)	24	3	5.338	0.168	± 0.017
3	Below Shingle Creek	10-12-76	28.26	24	3	5.487	0.189	± 0.019
4	Below Ellis Creek	10-12-76	28.34	24	3	8.082	0.203	± 0.017
5	Near the Penticton Airport	10-12-76	28.67	24	· . 3	6.565	0.201	± 0.024
			Total Ph	osphorus (F	<b>)</b>			
1	Below Okanagan	9-12-76	26.75	9	3	2.509	0.20	± 0.048
	Lake Dam	10-12-78	26.75	24	3	3.353	0.22	± 0.061
2	Below the Penticton Municipal Outfall	9-12-76	26.75 (est.	) 24	3	3.560	0.34	D ± 0.074
	Mullicipal Oditali	10-12-76	26.75 (est.	) 24	3	10.484	0.37	3 ± 0.019
3	Below Shingle Creek	9-12-76	28.26	24	3 ·	6.178	0.25	3 ± 0.013
		10-12-78	26.75 (est.	) 24	3	6.516	0.35	4 ± 0.047
4	Below Eilis Creek	9-12-76	28.34	24	3	4.615	0.28	3 ± 0.030
		10-12-76	28.34	24	. 3	6.413	0.39	9 ± 0.111
5	Near the Penticton Airport	9-12-76	28.67	24	3	3.076	0.27	9 ± 0.031
	Airport	10-12-76	28.67	24	3	8.704	0.32	6 ± 0.019

phosphorus load is from Okanagan Lake. The implication is that nonpoint sources, including Okanagan Lake, make a greater contribution than point sources as far as total phosphorus loadings to Skaha Lake are concerned. However, it should be realized that point sources to Okanagan Lake can be a major part of its output to the Okanagan River.

The results illustrated here indicate that the simultaneous sampling method, employing sample replicates permits the determination of precision in terms of confidence limits around the load means of phosphorus based on concentration measured across the channel. Errors associated with the load mean can be expressed as follows: mean + (a) short range spatial error + (b) cross-sectional error + (c) analytical error and + (d) discharge error. Errors (c) and (d) are estimated to be one fifth to one tenth of errors (a) + (b).

## Monitoring Program

Since 1976, a monitoring program of nutrient loading has been carried out in the southern part of the Okanagan Basin. Examples of results discussed here are drawn from the stations located below Okanagan Lake, above and below Skaha Lake. As indicated in the section on methodology, two sampling methods are used for collection of samples for chemical analysis, the simultaneous and sequential methods. Consequently, two methods are used to determine nutrient loads in the channel cross-sections, the partial load method and the flow interval method (Zeman and Slaymaker 1981 a,b)

The partial load method utilizes data obtained from the combined simultaneous chemical sampling and the hydrometric measurements in a channel cross-section. Results obtained by this method are compared with results obtained by the flow interval method (Zeman and Slaymaker 1981 a).

The loads estimated by the flow interval methods are based on the concentration data derived from sequential sampling and discharge determined for each of four quarter-day intervals. The time period for the first interval extends from 0000 to 0600 hours. According to this procedure the discharge for a flow interval is calculated from the original hourly discharge data (m³s-1), converted into hourly discharge and cumulated over the six-hour interval which encompasses the time of chemical sampling. The cumulated discharge and concentration data are used to calculate the nutrient loads for the daily flow intervals. The sum of the load intervals provides, then, the daily nutrient loads passing through the channel cross-section.

Results obtained during the sampling period from 1976 to 1979 are discussed in detail by Zeman and Slaymaker 1981 c. In the present report, the consistency and precision achieved in terms of total phosphorus loads, is further emphasized.

## Consistency and Precision

Data obtained from the measurements of phosphorus concentrations are used

to demonstrate consistency and precision of the calculated loads. The consistency of nutrient load data is determined by comparing results obtained by the simultaneous and sequential sampling methods. A time series record of the daily loads of total phosphorus, obtained by the two sampling methods at the station located in Okanagan River at Penticton near the airport, is illustrated in Figure 13. Each point represented by triangle indicates the daily load of phosphorus based on concentraton measurements taken at quarter-day intervals on each sampling day at one single point in the river channel. Each square symbol, on the other hand, is the arithmetic mean of the total phosphorus load derived from all simultaneous samples collected in the channel cross-section. The bar represents the 95 percent confidence interval about the mean. If the bar is absent this indicates that it would be smaller than the square used to indicate the magnitude of the load.

There are some differences in the load data derived from the simultaneous and sequential methods. These differences were examined on sets of nutrient load data obtained at all sampling stations at the same time. This examination was performed graphically and by the use of statistical tests. Figure 14 shows the graphical comparison of loads of total phosphorus derived from simultaneous and sequential methods at four sampling stations of the investigated river reach. In the case of perfect correlation the data points would be aligned on the 45° line. But the scatter of data points shows that load data obtained by sequential sampling are higher in more cases than data derived from simultaneous sampling. This graph shows that data obtained by any of the



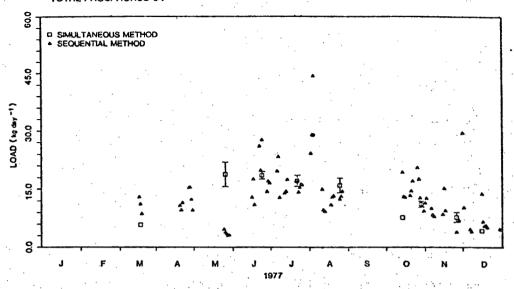


Figure 13. Loads of Total Phosphorus Derived from Simultaneous and Sequential Methods, Okanagan River near the Penticton Airport

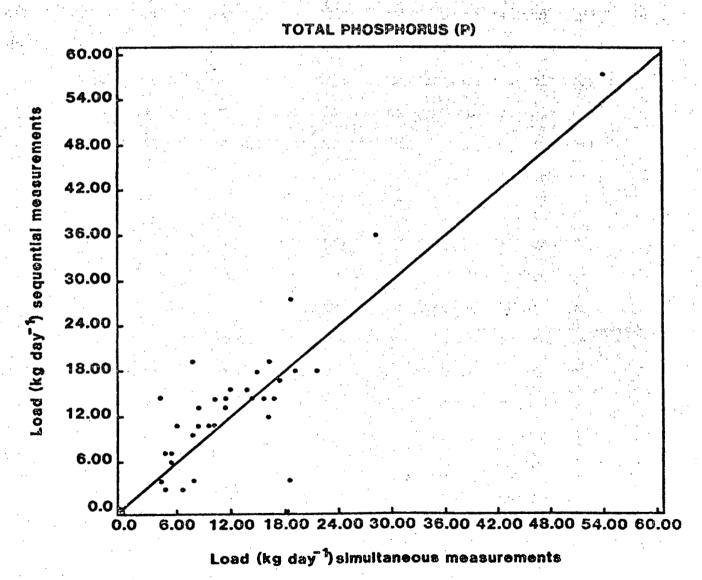


Figure 14. Comparison of Load Data Derived from Simultaneous and Sequential Measurements taken at the same time. Okanagan River, 1976-1978

sampling methods may be subject to random and systematic errors of measurements. Nevertheless, the consistency of the higher load data derived from sequential method are indicative of the prevailance of a systematic error between repeated measurements.

A correlation test (Table 3) indicates that there is agreement between the results obtained by the simultaneous and sequential methods. Highly significant correlation coefficients are obtained for the load data of all nutrients analysed. Also, results obtained by the t-test confirms that there are no significant differences between means of nutrient loads derived from simultaneous and sequential measurements. Because of the significant correlation that is achieved between the results obtained by the simultaneous and sequential sampling methods it is, therefore, legitimate to lump all information derived from these two sampling methods.

Combined data on concentrations and loads of total phosphorus and dissolved phosphorus, are taken from the monitoring program conducted during 1976 to 1979. Concentrations of these nutrients exhibited pronounced seasonal variations while the load data are characterized by significant annual changes. Table 4 shows the variations of these concentrations during two distinct sub-periods, from April to September (spring - summer) and from October to March (fall - winter), and for the entire period, 1976 to the end of March 1979. Data in this table indicate that at the stations located below Okanagan and Skaha Lakes significantly higher concentrations of total phosphorus are observed

Table 3 Correlation of Nutrient Loads Derived from Sequential and Simultaneous Sampling Methods

Sampling Methods	Number of Obser- vations	Over-all Mean	Standard Deviation	Standard Error	(Difference) Mean	Standard Deviation	Standard Error	Corr. Coeff.	2-Tall Prob.	T	Degrees of Freedom	2-Tail Prob.
					Total Phos	phorus (P)		•				
Sequential		14.4870	10.334	1.799	1.4121	4.875	0.849	0.882	0.000			
Simultaneous	33 <u>.</u>	13.0748	9.381	1.833						1.66	32	0.106
				To	otal Dissolved	Phospho	rus (P)					٠.
Sequential		5.8887	7.369	1.345	- 0.7743	2.184	0.399	0.955	0.000			
Simultaneous	30 B	6.8610	7.177	1.310						1.94	29	0.062
•					Nitrata plus	Nitrite (N	)					
Sequential		40.8859	39.571	6.171	4.679 <del>8</del>	•						·
Simultaneous	41 B	38.2063	38.678	6.040		12.668	1.978	0.948	0.000	2.37	40	0.023
					Ammo	nia (N)					•	
Sequential		85.7085	95.738	14.952	2.5005	: ·	• • •		Section 1			
Simultaneou	41 B	83.2080	99.781	15.583		69.058	10.785	0.751	0.000	0.23	40	0.818
					Organic N	itrogen (N)	)				: ,	
Sequential		208.3148	113.914	17.790	8.1561		· · · · · · · · · · · · · · · · · · ·					
Simultaneou	41 8	202,1585	114.092	17.818		41.581	6.494	0.933	0.000	0.95	40	0.349
to year			. ".		Total Nit	rogen (N)						
Sequential	-	334.8073	190.252	29.712	13.2634		•				. ,	
Simultaneou	41 3	321.5439	190.457	29.744		88.940	13.890	0.891	0.000	0.95	40	0.345
	-				Sili	ica	· · · · ·					
Sequential		4274.0938	3296,362	582.720	311							:
Simultaneou	32	4028.9375	2530.411	447.318	245.1563	1016.881	179.757	0.973	0.000	1.38	31	0.182
	•		_000.411									

Table 4 Seasonal Variation of Nutrient Concentration Measured by Simultaneous and Sequential Sampling Methods

Sampling Period	Number of Samples	Arithmetic Mean mg/l	95% Confidence Interval	Number of Samples	Arithmeti Mean mg/l	c 95% Confidence Interval	Number / of Samples	Arithmetic Mean mg/l	95% Contidence Interval
				•			•	Ratio	
	Total Phosphorus (P)			Total Dissolved Phosphorus (P)			Total Dissolved Phosphorus (P) Total Phosphorus (P)		
		-	Okanagan Ri	ver Below C	kanagar	Lake Dam		. · .	
1976-78 AprSept.	484	800.0	± 0.001	378	0.004	± 0.0002	378	0.527	±0.018
1978-79 OctMar.	192	0.010	± 0.001	173	0.004	± 0.0002	173	0.481	±0.023
1976-79 AprMar.	658	0.009	± 0.0001	551	0.004	±0.0002	551	0.508	± 0.015
			Okanagan	River Near	Penticto	n Airport			
1976-78 AprSept.	857	0.017	± 0.001	695	0.005	±0.0001	645	0.331	± 0.013
1976-79 OctMar.	499	0.017	± 0.002	467	0.006	± 0.0001	468	0.389	± 0.017
1978-79 AprMar.	1358	0.017	± 0.001	1161	0.005	± 0.0001	1111	0.347	± 0.011
			Okanaç	jan River at	Okanaga	n Falls			
1976-78 AprSept.	370	0.015	± 0.001	347	0.008	± 0.0001	323	0.399	± 0.018
1977-79 OctMar.	248	0.031	± 0.002	239	0.014	± 0.001	238	0.455	± 0.029
1978-79 AprMar.	618	0.021	± 0.001	586	0.009	± 0.001	581	0.423	± 0.016
						,			

during the fall-winter period than during the spring-summer period. This in total phosphorus pattern of seasonal changes established below the two lakes, is disturbed at the station near the airport. This disturbance is ascribed to the effect of total phosphorus inputs from the municipal outfall and the tributaries. Shingle and Ellis On the other hand, the bi-seasonal differences of total Creeks. dissolved phosphorus concentration are statistically significant at the station near the airport and below Skaha Lake. At these stations concentration of total dissolved phosphorus is higher during fall-winter periods than during spring-summer periods. The downstream increases. between the station below Okanagan Lake and that near the airport, of the overall means of total phosphorus and total dissolved phosphorus concentrations are, approximately, 89 and 25 percent, respectively. Further downstream, the concentration increases between the station near the airport and that below Skaha Lake are, for total phosphorus and total dissolved phosphorus, approximately 24 and 80 percent, respectively. Further, this table shows variation of the compositional content of total phosphorus. The overall ratio, and its confidence intervals, of total dissolved phosphorus to total phosphorus, varies in the range of 0.506 (+0.015), 0.347 (+0.011) and 0.423 (+0.016) at the stations below Okanagan Lake, near the airport and below Skaha Lake, respectively.

Load data are interpreted on the annual basis. Table 5 shows annual variation of loads of total phosphorus and total dissolved phosphorus observed at the three sampling stations for the calendar yars, 1976 to 1978. This table indicates that the most pronounced changes occurring in

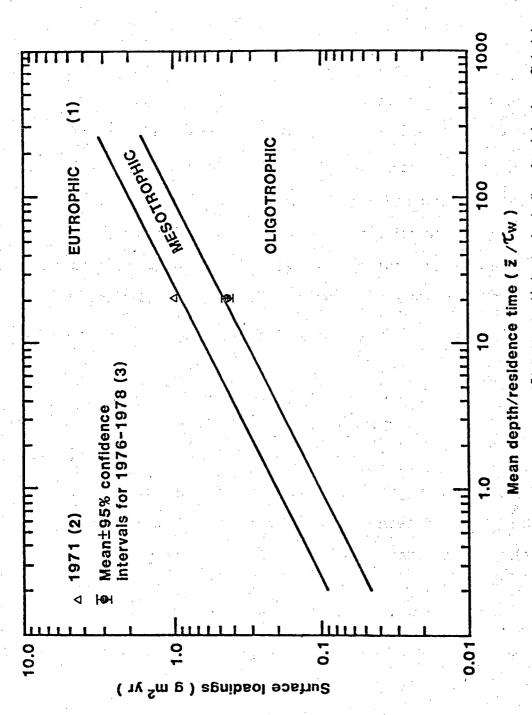
Table 5 Annual Variation in Nutrient Loads Derived From Simultaneous and Sequential Sampling Methods

Year	Month	Number of Observations	Arithmetic Mean kg/day	95% Confidence Interval	Month	Number of Observa- tions	Arithmetic Mean kg/day	95% Confidence Interval
	Total	Phosphorus	(P)	:	Total Di	ssolved P	hosphorus	(2)
		Oka	nagan Riv	er Below O	kanagan Lake D	am		
1976	Feb. Apr. J Aug. Sept. De	ul 12 c	23.175	± 4.084	Jul. Sept. Dec	. 4	15.000	±7.458
1977	Mar. Apr. Mr. Jun. Jul. Au Sept. Oct. No	g.	5.250	±0.522	Mar. May Jun Jul. Aug. Oct Nov. Dec.		2.460	± 0.262
1978	Jan. Feb. Ma Apr. May Ju		13.843	± 2.945	Jan. Feb. Mar		5.499	± 0.878
	Apr. May Ju Jul. Aug. Sep Oct. Nov. De	st.	•		Apr. May Jun Jul. Aug. Sept Oct. Nov. Dec	•		
1976 (	to 1978	160 _	10.837	±1.704	· · ·	144	4.476	± 0.831
	er e	, 0	kanagan I	River Near I	Penticton Airpor	t		
1976	Jul. Aug. Ser Dec.	ot. 10	28.330	± 4.946	Sept. Dec.	2	17.000	± 5.082
1977	Mar. Apr. Mar. Jun. Jun. Au Sept. Oct. No	9.	13.153	±1.438	Mar. May Jun Jul. Aug. Oct Nov. Dec.		3.509	± 0.362
1978	Dec.  Jan. Feb. May Ju Apr. May Ju Jul. Aug. Seg	n.	29.314	± 4.984	Jan. Feb. Mar Apr. May Jun	•	6.702	± 0.831
	Oct. Nov. De	c.			Jul. Aug. Sept Oct. Nov. Dec			
1978	lo 1978	182	21.357	± 2.640		172	5.207	± 0.534
			Okanaga	n River at C	kanagan Falls			
1978	Jul.	3	31.667	± 6.723				
1977	Mar. Apr. M. Jun. Jul. Au Oct. Nov. De	g.	12.152	± 0.938	Mar. May Jun Jul. Aug. Oct Nov. Dec.		5.706	± 0.854
1978	Jan. Feb. Ma Apr. May Ju Jul. Aug. Sep Oct. Nov. De	n. ot.	41.547	±8.511	Jan. Feb. Mar Apr. May Jun Jul. Aug. Sept Oct. Nov. Dec	•	13.875	± 3.219
1978	to 1978	163	26.217	± 3.785		155	9.712	± 1.722

the river reach are the year-to-year changes in loads of total phosphorus and total dissolved phosphorus. These changes are largely caused by variation in the discharge. The downstream increase, between the station located below Okanagan Lake and that near the airport, in terms of means of total phosphorus and total dissolved phosphorus is, approximately, 97 and 16 percent, respectively. The increase, between the stations near the airport and that below Skaha Lake is, for total phosphorus and total dissolved phosphours, approximately, 22 and 87 percent, respectively. The contrasting increases of loads of these phosphorus forms evidently underline the differing behaviour of river reach compared with lake Sources of the two phosphorus forms analysed include effluent from the Penticton waste treatment plant, and a number of non-point sources, such as Okanagan Lake, Shingle and Ellis Creeks watersheds and Skaha Lake. The major increase in total phosphorus loading is associated with the point source from the waste treatment plant and the non-point sources, Shingle and Ellis Creek watersheds. The non-point source Skaha Lake contributes the major increase in total dissolved phosphorus.

## Relevance to Earlier Studies

Further use of the load data of total phosphorus obtained during the monitoring program is illustrated in Figure 15. This figure shows the Vollenweider relationship between phosphorus surface loading and relative eutrophication—related water quality conditions of a lake. This relationship is used to compare results of nutrient loading to Skaha Lake



The relationship between trophic state, mean depth ( z̄ ), flushing time (tw ) and surface loadings of total phosphorus, Skaha Lake

(z), flushing time (τw) Figure 15. The Relationship between trophic state, mean depth

and Surface Loadings of Total Phosphorus, Skaha Lake

<sup>(1)</sup> Vollenweider, R. A. 1968. The Scientific Basis of Lake and Stream Eutrophication of Lakes and Flowing Waters with Particular Reference to Nitrogen and Phosphorus as Factors in Eutrophication. OECD. Paris, pp. 1 - 159.

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obtained from the previous Okanagan Basin water quality study (Canada-British Columbia Okanagan Basin Agreement. 1974) with the results obtained during the current water quality monitoring program. The surface loads of total phosphorus reported in 1974 are plotted in the upper part of the figure indicating eutrophic condition. The results from the present study, shown as the overall mean and its 95 percent confidence intervals of total phosphorus load derived form 182 observations during the period 1976 to 1978, indicate the trophic status of the lake to be positioned between mesotrophic and oligotrophic portion of the graph. However, from the statistical point of view since the earlier surface loading data are not reported with confidence limits, the conclusion of a change cannot be statistically validated.

## SUMMARY

Two sampling methods are used for the collection of water samples for chemical analysis: (a) simultaneous and (b) sequential methods. These methods were applied during the nutrient loading study program in the Southern part of the Okanagan Basin, B.C.

The simultaneous sampling method engages a replicate grab sampler or a pump for the collection of sample replicates, three in this study. Concentration measurements are taken usually at four sampling points across the channel cross-section, approximately one meter below the water surface at monthly intervals. This procedure is designed to provide

information on the short range heterogeneities of point concentration measurements of nutrients and in combination with hydrometric measurements provides a basis for calculation of their partial loads. The sum of these partial loads gives the total nutrient loads passing through the channel cross-section.

The sequential sampling method employs a portable discrete sampler for collection of single pumped samples. Concentration measurements are taken at a sampling point, approximately 0.6 of the depth below the water surface. Water samples are drawn at quarter-day intervals, at 0300, 0900, 1500 and 2100 hours, during two consecutive days randomly chosen within a week. These concentration measurements combined with discharge, determined for four daily intervals, provide a basis for calculation of loads by the flow interval method. The time period for the first flow interval extends of 0000 to 0600 hours. According to this procedure the discharge for a flow interval is calculated from the original hourly discharge data cumulated over the six-hour interval which encompasses the time of chemical sampling. The cumulated discharge and concentration data are used to calculate the nutrient loads for the flow intervals. The sum of these loads gives the daily nutrient load passing through the channel cross-section.

Data on concentration measurements of total phosphorus (P), total dissolved phosphorus (P) nitrate plus nitrite (N), ammonia (N), total nitrogen (N) and dissolved silica were obtained during the two types of studies (a) a short-term evaluation study and (b) a long-term monitoring

program. In this report concentration data of total phosphorus and dissolved phosphorus are used to illustrate the methodology applied to evaluate concentration measurements and to calculate loads of these nutrients.

The purpose of the evaluation study was to obtain information on the pattern of the lateral and vertical mixing of nutrients along the Okanagan River channel linking Okanagan and Skaha Lakes and select a suitable sampling cross-section for the long-term monitoring of nutrient loads to Skaha Lake. The simultaneous sampling method was used to determine the precision, in terms of confidence intervals, of concentration measurements of nutrients and their loads determined at the channel cross-sections.

During the long term monitoring program both simultaneous and sequential sampling methods were applied. The use of these two sampling methods facilitated the determination of consistency and precision in the calculation nutrient loads. Graphical comparisons and the correlation test indicated a precise agreement between the load data derived from the simultaneous and sequential sampling methods. Because of this agreement it was legitimate to lump all data obtained from these two sampling methods.

Examples, in terms of phosphorus concentration measurements, illustrate the pattern of the statistically significant seasonal variation of concentration observed at sampling stations located below Okanagan and Skaha Lake. However, this pattern of seasonal changes is disturbed at station located downstream from the Penticton waste treatment plant. Loads of phosphorus are characterized by statistically significant annual variations introduced by changes of the discharge regulated by control dams below Okanagan and Skaha Lakes.

Information provided by the results from the monitoring study are used in the evaluation of the trophic status of Skaha Lake and thus in the assessment of the effectiveness of remedial actions initiated in 1971, to reduce nutrient loadings from point source to this lake.

## **CONCLUSIONS**

Location of sampling stations must be representative of the water body being sampled and indicative of the changes occurring in the variable being monitored.

The simultaneous sampling method revealed very pronounced short range spatial heterogeneities of point concentration measurements of nutrients at investigated channel cross-sections.

The determination of nutrient loads based on a single grab sampling procedure, therefore, cannot provide a reliable estimate of the amounts of nutrients passing through a channel cross-section.

Concentration measurements, obtained by the sequential sampling method, show significant long range seasonal changes of nutrient concentration at stations located below Okanagan and Skaha Lakes. However, this pattern, of seasonal changes is disturbed at stations located below the outfall from waste treatment plant and tributary creeks.

Calculation of nutrient loads during widely varying discharges indicate that major changes in flow can produce large changes in nutrient flux without substantial change in nutrient concentration. In this river system a concentration – discharge relationship approach to nutrient loading determination on a temporal basis is, therefore, not feasible.

The overall mean load of phosphorus determined on lumped data from these two methods during the three year sampling period indicates a reduced input of total phosphorus to Skaha Lake, by comparison with load data reported in the previous study, conducted under the Canada-British Columbia Okanagan Basin Agreement, 1974. Nevertheless, since the earlier data are not reported with confidence limits, the conclusion of a change cannot be statistically validated.

According to the previous study, phosphorus loads came mainly from point sources. But, the present study indicated that the major contribution of phosphorus loads came from non-point sources such as Okanagan Lake, via Shingle and Ellis Creeks, and from Skaha Lake itself.

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