

PEACE RIVER WATER QUALITY PROJECT

REPORT ON DATA ANALYSIS COVERING CONTRACT #DSS-07SBKL374-8-0316

for

Water Quality Branch Inland Waters Directorate Environment Canada Vancouver, B.C.

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PEACE RIVER WATER QUALITY PROJECT: DATA ANALYSIS

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PEACE RIVER WATER QUALITY PROJECT

INTRODUCTION

The Peace River water Quality project was initiated in late 1974 and a reconnaissance monitoring program was carried out from January 1975 to September 1976. The present report covers some of the data analysis of the project and is divided into two main sections, each of which is designed to be inserted as chapters into the main Peace River Water Quality Report to be completed later this year by Steve Sheehan.

The first section of the report deals with an assessment of sampling variability and the second section involves an overall assessment of chemical differences between the sampling stations selected for the study. The background and aims of the project, as well as the chemical loading results, and overall variability assessments will be described in detail in other chapters of the main report and only some explanatory information is provided here so as to facilitate an understanding of the data analysis.

Data were collected for five different stations in the Peace River drainage system: the Peace River at Taylor and at Clayhurst Ferry, the Pine River, the Kiskatinaw River and the Beatton River. The study was for reconnaissance and a complete data set for all five stations was available for the 1976 hydrological year. Replicate samples were collected at all five stations and were analyzed for total phosphorus, nitrate plus nitrite, ammonia nitrogen, total dissolved nitrogen, total organic and inorganic carbon, and dissolved iron. Single grab samples formed the basis for analysis of 28 other chemical parameters. The 1975-76 replicate data set was used as a basis for the variability assessment described in Section 1 while chemical differences between stations discussed in Section 2 were examined from the single grab sample data.

I. SAMPLE VARIABILITY ASSESSMENTS

The five stations selected in this study were sampled eight times during 1976. Each time six replicate samples were collected in a manner described by Oguss and Erlebach 1976, and Kleiber et al 1978. At two stations: the Peace River at Clayhurst Ferry and at Taylor, replicate samples were collected for river cross-sections. At the two, stations two to four sets of replicates were collected across each stream section. The laboratory results for the replicate samples were used as a basis for the variability assessment of the following parameters: total phosphorus, total dissolved nitrogen, ammonia nitrogen, total organic carbon and extractable iron.

(a) Replicate Sample Variability

Initially the variability between each set of six replicate samples was analyzed. The coefficient of variation (CV) which is derived from $CV = \frac{S \times 100}{\bar{x}}$ was used for the comparison. It should be noted that the use of this coefficient should be handled with some care since normally distributed data are needed. In many of the replicate data sets used in this study bi-modal distributions were common particularly in the case of nitrate plus nitrite, and the coefficient should therefore only be used as a relative rather than an absolute measure of variability. The replicate variability was calculated for each 1976 sampling period and the results of a comparison between the five stations is presented in Figures 1-5.

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Of the five parameters examined nitrate plus nitrite concentrations (Figure 2) generally showed the highest replicate variability. There is a tendency for nitrate plus nitrite and total organic carbon to exhibit greater variability during the period from June to September, but the overall variability of total organic carbon was considerably smaller. There is no consistent pattern with regard to replicate sample variability at different stations except that the iron variability was more uniform over the study period than any of the other parameters examined. However, additional information is needed to confirm the validity of these trends.

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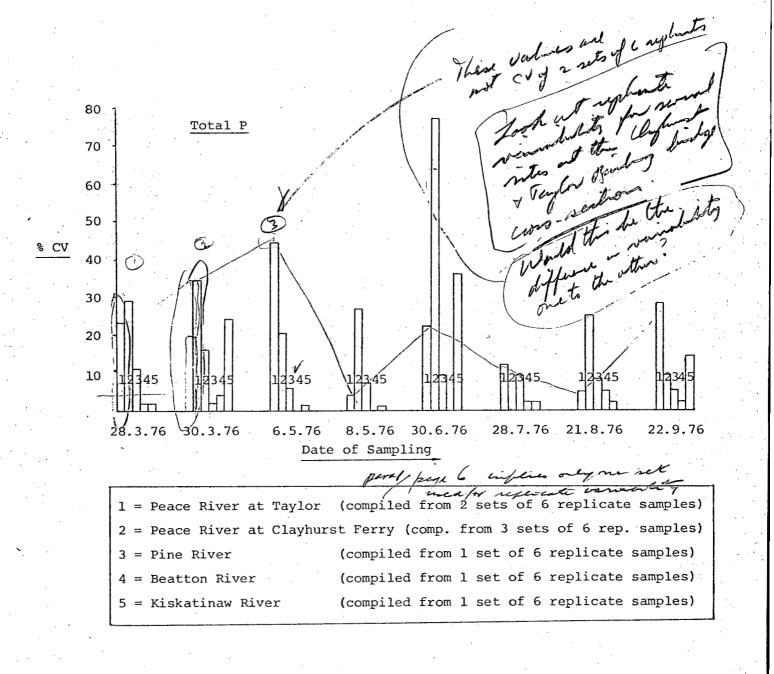


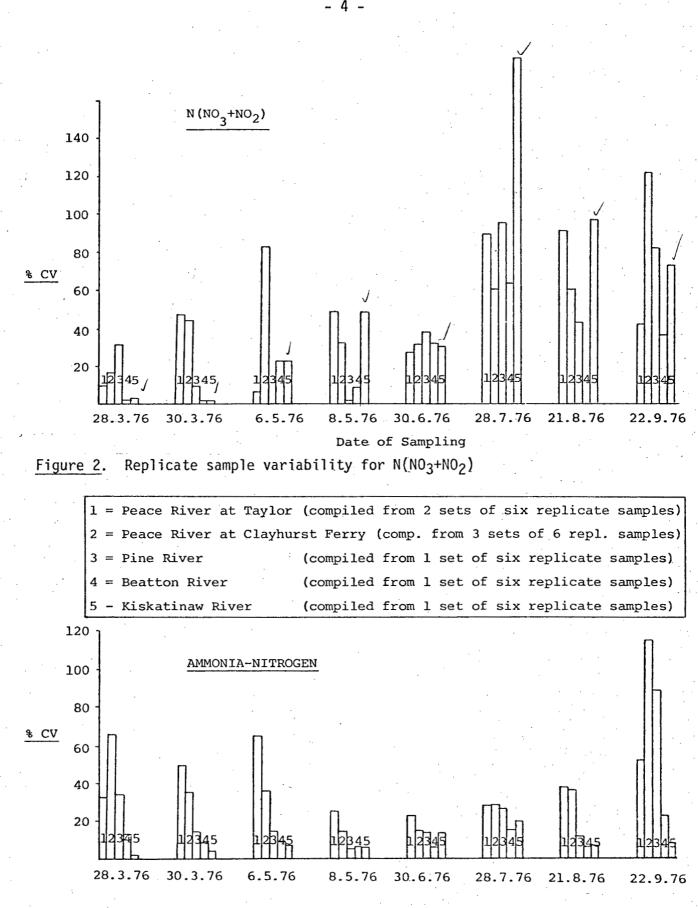
Figure 1. Replicate sample variability for total phosphorus.

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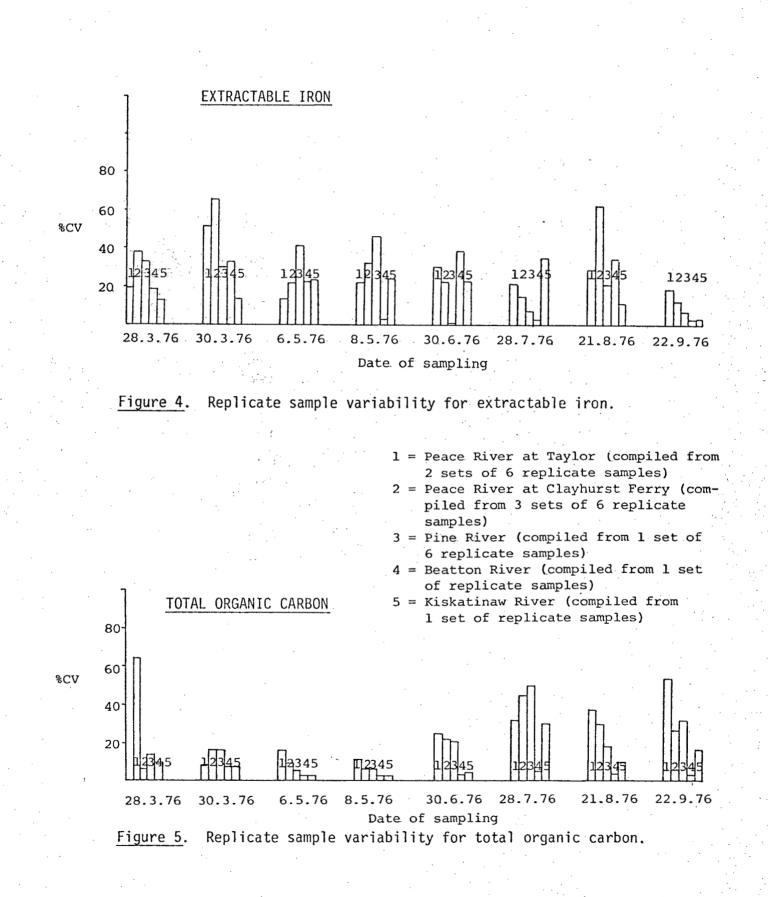
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B



Replicate sample variability for ammonia-nitrogen. Figure 3.



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(b) Cross-Sectional Variability

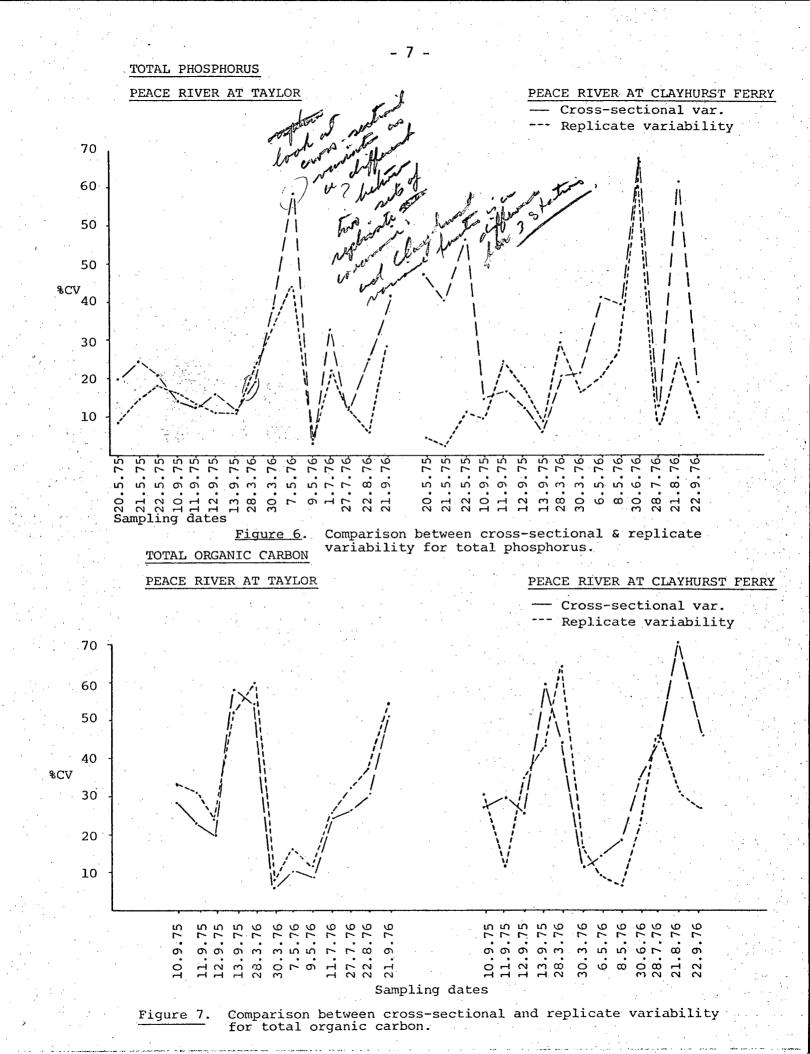
Cross-sectional analyses were made at the Peace River stations at Clayhurst Ferry and Taylor. In the first case three to four sets of replicates were collected across the stream section, while only two sets of replicates were collected at the Taylor site. The coefficient of variation was used for this analysis and it should be noted that a comparison between station replicates and cross-sectional variability is not completely adequate since the two data sets were only partially independent. Station replicate variability was determined from six coincidental samples while cross-section variability was determined from three sets of six replicates, one of the three sets being the same as the one used for the replicate variability assessment.

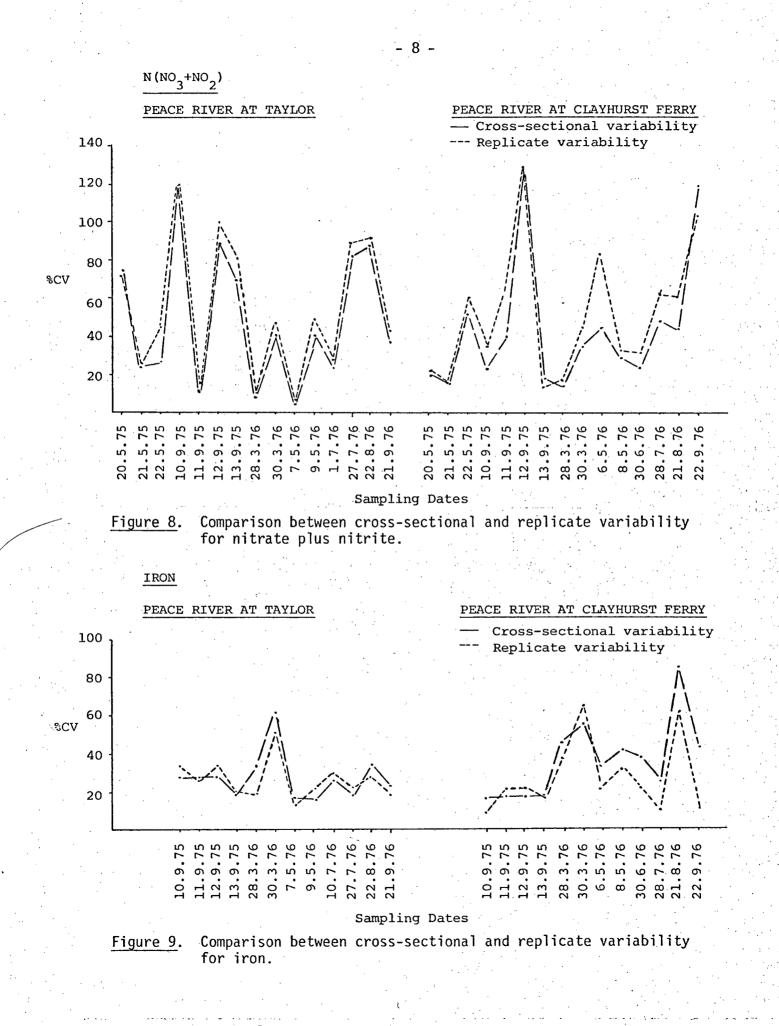
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On the basis of 15 independent sampling events over a 1½ year period, no consistent variability pattern could be observed. As is evident from Figures 6-9, cross-sectional variability of such chemical parameters as total phosphorus, total organic carbon, and extractable iron was at times slightly higher than replicate variability, while the reverse was true for nitrate plus nitrite variability. An independent data set is required however so as to perform a more rigorous test. when a ment by the last shift.

(c) Temporal Variability

Temporal variability was examined over the period from September 1975 to September 1976. Unfortunately the data set was not entirely complete for the Beatton and Kiskatinaw stations. First the parameters with replicate data were analyzed and the coefficient of variation was determined for total phosphorus, nitrate plus nitrite, total organic carbon and extractable iron using mean replicate values for seven to nine independent sampling dates over the one year study period (NAQUADAT data set). The results of this analysis are provided in Table 1 and indicate that total phosphorus exhibits the highest temporal variability.





SAMPLING STATIONS		PARAMETERS (VA	LUES IN % C	V)		
	Total P	N(N0 ₃ +N0 ₂)	ТОС	FE		
Peace River at Taylor	113 %	33 %	38 %	68 %		
Peace River at Clayhurst	119 %	70 %	73 %	105 %		
Pine_River	162 %	81 %	98 %	105 %		
Beatton River	106 %	125 %	. 39 %	81 %		
Kiskatinaw River	124 %	91 %	43 %	95 %		

Table 1. Comparison of Temporal Variability over the 1975-76 Period.

These four parameters seem to be subject to distinctly greater seasonal variation that geologically related parameters. This is substantiated by an analysis of the temporal variability of the single grab sample data presented in Table 2.

SAMPLING STATIONS		PAR	AMETERS	(VALUES	IN % CV)	
	Si Si	Ca	Mg	Na	C1	so ₄
Peace River at Taylor	10 %	15 %	37 %	15 %	33 %	17 %
Peace River at Clayhurst	9 %	10 %	31 %	9 %	16 %	13 %
Pine River	18 %	27 %	41 %	48 %	42 %	40 %
Beatton River	11 %	62 %	73 %	131 %	50 %	72 %
Kiskatinaw River	10 %	29 %	38 %	53 %	37 %	74 %

Table 2. Comparison of Temporal Variability of Parameters Determined from Single Grab Samples

In general total phosphorus and dissolved iron showed the greatest temporal variability while silica showed the smallest variability values. The former two are considered dynamic while the latter is a more conservative parameter. Also the Peace River stations exhibited smaller temporal variabilities for such parameters as sodium, chlorine, sulfate and calcium than the other three stations.

(d) Spatial Variability

A complete data set for all five stations was available for six time periods during 1976. The variability between the five stations was examined for each of the six periods and the results are presented in Table 3 below.

SAMPLING DATES		PARA	METERS (VAL	.UES IN % CV	1)
	Total P	N(N0 ₃ +N0 ₂)	NH3	тос	FE
31.3.76	157 %	147 %	167 %	86 %	115 %
7.5.76	70 %	67 %	60 %	57 %	62 %
10.5.76	111 %	70 %	48 %	43 %	54 %
27.7.76	54 %	36 %	80 %	101 %	127 %
22.8.76	125 %	48 %	160 %	67 %	110 %
21.9.76	78 %	51 %	70 %	138 %	134 %

Table 3. Comparison of Spatial Variability between Five Stations (derived from replicate data)

Again mean replicate data were used as a basis for the analysis of the above parameters while the variability for other parameters was once again determined from single grab samples. Some of the data from the latter analysis is provided in Table 4 below.

The highest spatial variability was observed in late winter and was most noticeable for nitrate plus nitrite, ammonia-nitrogen, total dissolved nitrogen, total phosphorus, sodium, chlorine and sulfate. The same parameter showed the smallest variability in May and this is probably related to the freshet where snowmelt and run-off water tends to dilute concentrations thus minimizing variability.

SAMPLING DATES PARAMETERS (VALUES IN % CV)						
	Si	Ca	Mg	Na	C1	so ₄
31.3.76	20 %	35 %	58 %	142 %	110 %	91 %
7.5.76	14 %	31 %	51 %	30 %	49 %	20 %
10.5.76	15 %	27 %	28 %	34 %	37 %	25 %
27.7.76	32 %	49 %	38 %	88 %	57 %	88 %
22.8.76	29 %	34 %	32 %	40 %	91 %	71 %
21.9.76	33 %	43 %	48 %	83 %	91 %	82 %

Table 4. Comparison of Spatial Variability between Stations (derived from single grab samples)

Again, total phosphorus, total dissolved nitrogen, total organic carbon and ammonia nitrogen showed significantly higher spatial variability than the more geologically related parameters such as silica, calcium, and magnesium.

(e) Comparison of Different Types of Variability

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The variability examined so far has been expressed in terms of the coefficient of variation and is thus suited to a relative comparison between different types of variability. For total phosphorus, nitrate plus nitrite, ammonia nitrogen, total dissolved nitrogen, extractable iron and total organic carbon a comparison between replicate, cross-sectional, temporal and spatial variability was made in Figures 10-15.

From Figure 10 it is evident that the replicate and cross-sectional variability of total phosphorus is considerably smaller than either the spatial or temporal variability. This means that differences and interpretations related to space and time are valid. In contrast nitrate plus nitrite, ammonia nitrogen, replicate and cross-sectional variability are so great that they cannot be separated from either the spatial or temporal components. This implies that no temporal or spatial interpretations

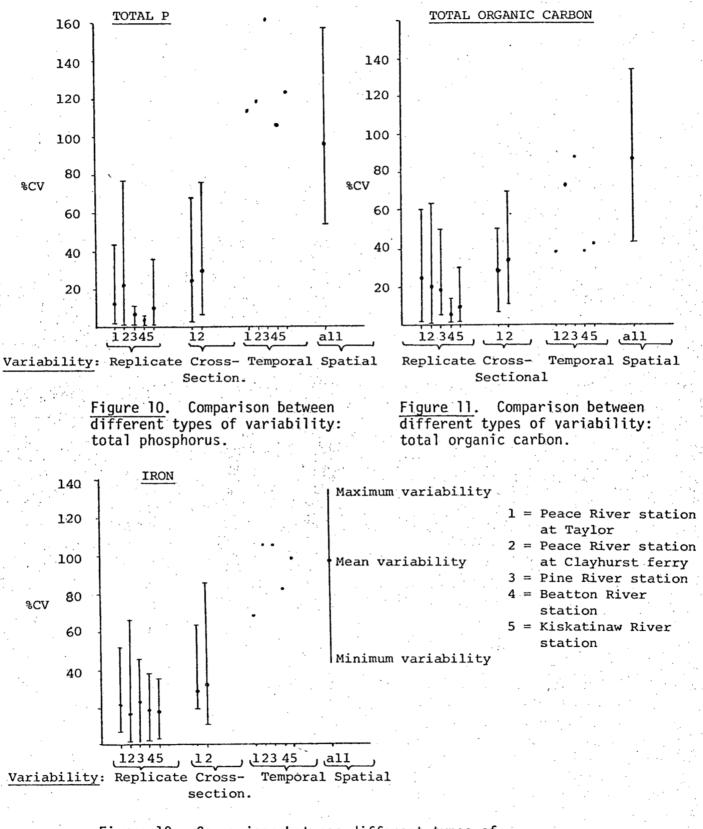


Figure 12. Comparison between different types of variability: dissolved iron.

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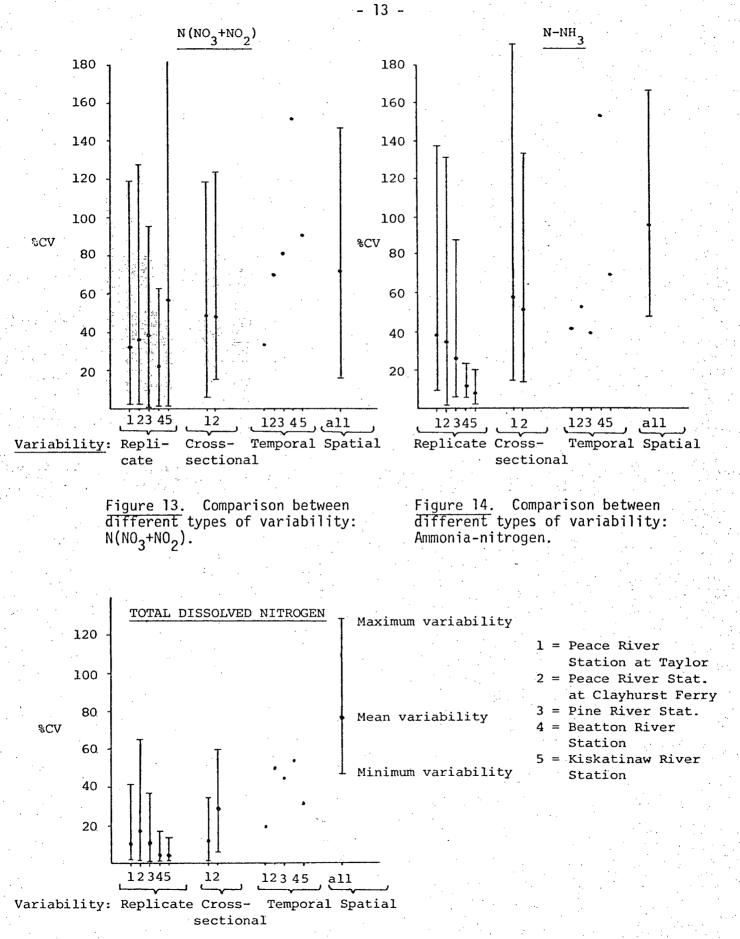


Figure 15.

. Comparison between different types of variability: total dissolved nitrogen.

can be made for these parameters on the basis of the present data set. This conclusion implies that other methods have to be found in order to quantify and separate the different nitrogen components in the waters of the Peace River system.

In general replicate and cross-sectional variability are of the same magnitude for all parameters. The temporal and spatial variability differ significantly only for total dissolved nitrogen and no separation between the two components is possible for the other parameters. Finally extractable iron and total organic carbon variability can only be partially separated into replicate and cross-sectional versus temporal and spatial variability components since there is considerable overlap in the variability range of the two categories. The fight a capito

(f) Summary of Variability Assessments

A comparison was made between replicate, cross-sectional, temporal and spatial variability for total phosphorus, total organic carbon, dissolved iron, nitrate plus nitrite, and ammonia nitrogen. In general variability for the above parameters was higher than for silica, calcium, magnesium, sulfate and chlorine which are more reflective of geological conditions.

Nitrogen compounds were particularly variable and nitrate plus nitrite had the highest replicate, cross-sectional, temporal and spatial variability. The replicate variation ranges for nitrate plus nitrite, and ammonia were equal or greater than that observed for cross-sectional, spatial, and temporal variability. This implies that cross-sectional, spatial and temporal variability can not be distinguished from replicate variability. No adequate separation was possible between replicate and cross-sectional variability but spatial and temporal variability were significantly higher for total phosphorus and marginally higher for extractable iron.

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Data from single grab samples and mean values from replicate samples were used to determine overall chemical differences between stations. Emphasis was placed on assessing the majority of chemical components analyzed during the study and significance tests, factor and cluster analysis were used for the data evaluation.

(a) Chemical Differences between Sampling Stations

Based on the data collected from eight sampling periods in 1976, a Mann Whitney significance test (Siegel 1956) was used to test the hypothesis of whether individual stations exhibited chemical compositions significantly different from one another. The test was performed for 15 chemical parameters, the results of which are provided in Figure 16 below.

STATIONS	Pine River	Beatton River	Peace River at Clayhurst	Kiskatinaw River		
Peace River at Taylor	1,2,12	3,4,6,8,9,10 12,13		1,2,3,4,6,8,9 10,12,14,15		
Pine River		4,6,9,10,12, 13	2			
Beatton River			6,8,10,12,13	10,13		
Peace River at Clayhurst				1,2,6,9,12,14		
1 = specific conductance6 = total diss. N.11 = F2 = alkalinity7 = total P12 = Si3 = diss. Fe8 = K13 = SO ₄ 4 = N-NH ₃ 9 = Na14 = Ca5 = N(NO ₃ +NO ₂)10 = C115 = Mg						
Explanation: Numbers in individual boxes indicate the parameters which are significantly different between individual stations over the 1976 sampling period.						

Figure 16. Results of Significance Test

The results shown in Figure 16 indicate the following:

- The two Peace River stations (Taylor and Clayhurst Ferry) could not be differentiated from one another on the basis of the 15 chemical parameters listed;
- Only a few parameters (alkalinity, silica and specific conductance) were found to differ significantly between the Pine and the Peace River stations;
- 3. The Beatton and Kiskatinaw Rivers are similar chemically, except for differences in chlorine and sulfate. The two rivers differ from the other rivers in a number of the same chemical parameters.
- Silica, chlorine, total dissolved nitrogen, alkalinity, sodium and sulfate were found to be the most useful differentiating parameters.

These results suggest that the Kiskatinaw and Beatton Rivers are controlled by a chemical regime which is significantly different from that observed in the other three sampling stations in the Peace River drainage system.

The overall contribution of these two rivers to the main channel is limited however since the Peace River downstream of the Kiskatinaw and Beatton confluence was not found to be significantly different from that observed at the station above these two confluences.

(b) Importance of Individual Parameters

Eleven water quality parameters were used in a detailed numerical analysis. They include specific conductance, alkalinity, sodium, chlorine, sulfate, dissolved iron, nitrate plus nitrite, total dissolved nitrogen, silica, calcium and magnesium. The samples used in this analysis are listed in Table 5 below.

SAMPLE IDENTIFICATION NO.	SAMPLING PERIOD	NO. OF SAMPLES CLASSIFIED	SAMPLING STATION
1 - 12	10.9.75 to 21.9.76	12	Peace River at Taylor
13 - 24	10.9.75 to 21.9.76	12	Pine River
25 - 30	29.3.76 to 21.9.76	6	Beatton River
31 - 45	22.5.75 to 22.9.76	15	Peace River at Clayhurst
46 - 52	29.3.76 to 21.9.76	7	Kiskatinaw River

Table 5. List of Samples used for the Numerical Analysis

The relationships amongst individual parameters were first assessed for the entire data set. A number of significant correlations were observed between chemical parameters and are presented in Figure 17 below.

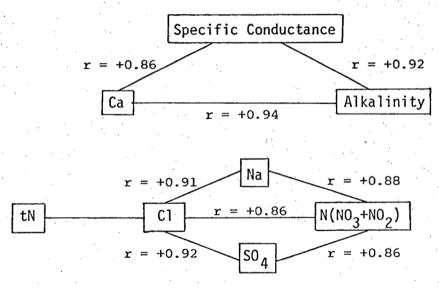


Figure 17. Significant correlation amongst chemical parameters $(\alpha = 0.005)$

It is important to identify the relationships amongst the main parameters for the numerical assessments since highly correlated parameters contain redundant information and thus can bias subsequent numerical classifications. The same set of data was examined with a factor analytical technique which is a method that describes complex interrelationships between multiple variables in terms of the simplest number of factors. If variables are intercorrelated they can be represented as a cluster of vectors and their projection length, known as factor loadings, can be used as weights to combine the original variables into fewer factors. A detailed discussion of factor analysis is provided by Cattel, 1965, and only the results of the analysis are presented below.

A 52 x 11 data matrix was subjected to factor analysis and the eleven original parameters were transferred to two factors with a loss of 19% of the total variance. The results of the transformation can be seen in Table 6.

PARAMETERS	FACTOR 1	FACTOR 2
C1	0.96*	0.20
total diss. N	0.93*	0.17
so ₄	0.84*	0.41
$N(NO_3 + NO_2)$	0.81*	0.37
Si	0.78*	0.11
Na	0.77*	0.52
Fe	0.61*	-0.05
Alkalinity	0.20	0.94*
Spec. conductance	0.51	0.84*
Ca	0.25	0.82*
Mg	0.06	0.81*
% of total variance accounted for by each factor	60%	21%

Table 6. Results of Factor Analysis

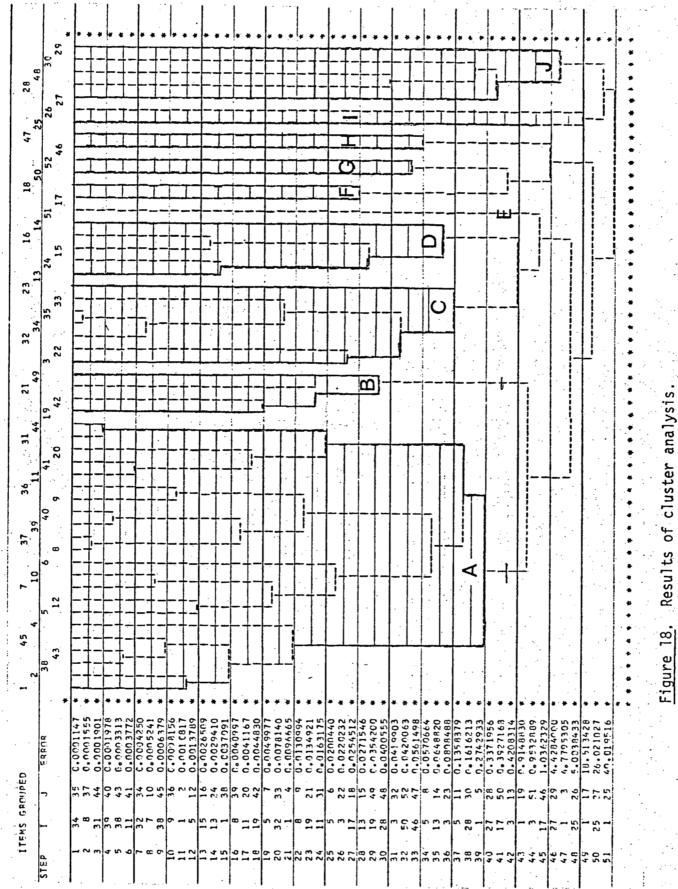
*Indicates those parameters which contribute significantly to the factor importance. This mathematical transformation successfully groups the two types of correlation structures identified in Figure 17 and the factor ratings of loadings were then used as weights prior to cluster analysis.

(c) Cluster Analysis of Individual Samples

An average distance clustering procedure based on Ward's (1963) method was used to determine the similarity between all samples in terms of the eleven chemical parameters listed in Figure 16. The original data set was multiplied by the factor loadings and the resulting factor score was classified with the UBC-C-Group cluster program (Patterson and Whitaker 1973). The results of the procedure are provided in the dendrogram in Figure 18 and the composition of the clusters is summarized in Table 7. The top numbers in Figure 18 indicate the individual samples from the different stations as described in Table 5.

CLUSTER-GROUP I.D. NUMBER	NO. OF SAMPLES IN GROUP	INDIVIDUAL SAMPLE NUMBERS IN CLUSTER	SAMPLING PERIOD
A	22	11 Peace River at Taylor 10 Peace River at Clayhurst 1 Pine River	entire year entire year May
В	4	2 Pine River 1 Peace River at Clayhurst 1 Kiskatinaw River	May and June May May
C	7	4 Peace River at Clayhurst 1 Peace River at Taylor 2 Pine River	September September July & August
D D	5	5 Pine River	all September
E	1	1 Kiskatinaw River	August
F	2	2 Pine River	March
G	2	2 Kiskatinaw River	July & September
Н	2	2 Kiskatinaw River	March
I	^s t 2	2 Beatton River	March
J	5	4 Beatton River 1 Kiskatinaw River	July, Aug., Sept. May

Table 7. Description and Composition of Cluster Groups



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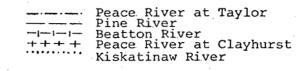
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A number of observations are possible from this cluster analysis:

- The chemical differences between the five stations, as shown by the significance test in Figure 16, were also confirmed by the cluster analysis. The Peace and Pine River stations were found to form clusters separate from those of the Beatton and Kiskatinaw Rivers.
- 2. A number of clusters were made up of samples collected during the same time period. For example, cluster group B consists of samples from three different rivers all collected during freshet (May June) and Group C is made up of late summer samples for the Peace and Pine River stations. This suggests that there is a definite relationship between discharge and overall chemical composition at least during some periods of the yearly hydrological cycle.
- 3. The Peace and Pine samples formed three distinct groups A, B, and C. The first is made up of samples covering the entire sampling period. Cluster B consists of May-June samples while cluster C covers late summer samples (July-September). This suggests that three distinctly different chemical regimes dominate the yearly cycles at these stations.
- 4. Three separate individual clusters were observed for the March samples from the Pine, Beatton, and Kiskatinaw River stations (clusters F, H, and I). This suggests that chemical differences between these streams are pronounced during late winter when groundwater and under-ice flow control the water quality.

(d) General Seasonal Trends

The mean concentrations were examined over the one year sampling period to determine whether obvious trends could be detected between the stations. Unfortunately no consistent pattern could be observed and a clear separation between the stations was only possible for the silica distribution indicated in Figure 19 below.



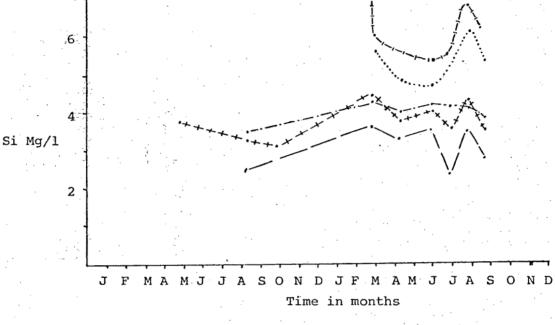


Figure 19. Silica distribution.

metals .

(e) Summary

The Pine and Peace River stations were found to exhibit a one-year chemical distribution which was significantly different from those of the Beatton and Kiskatinaw River stations and although these differences were substantial no significant change in the water quality could be detected in the main channel of the Peace River downstream of the Beatton and Kiskatinaw confluence.

Chlorine, silica, dissolved nitrogen, sodium, sulfate, alkalinity and specific conductance were found to be the most useful differentiating parameters. A cluster analysis using all individual samples indicated that, besides the overall differences between the stations, three distinctly different chemical regimes dominated the yearly cycle for the Peace and Pine River stations. The Beatton and Kiskatinaw River stations could best be differentiated during late winter (March) when groundwater and under-ice flow are dominant.

Finally, no consistent seasonal trend was found for the five sampling stations.

CONCLUSIONS

The data analysis for the Peace River project emphasized an assessment of sample variability and provided an examination of chemical differences between the sampling stations. The following conclusions were found to be of importance:

- A comparison between replicate, cross-sectional, temporal and spatial variability showed that the replicate variability for nitrate plus nitrite, and ammonia-nitrogen was equal to or greater than the variability observed from either cross-sectional, temporal or spatial sources. This implies that temporal and spatial interpretations for these parameters are dangerous to make and cannot be justified.
- Seasonal and spatial variability for total phosphorus and, to a lesser degree, for extractable iron were significantly larger and can thus be used for seasonal and spatial interpretations.
- In most cases replicate variability could not be differentiated from cross-sectional variability although an independent data set is needed for such an analysis.

- 4. Using a one-year data set significant chemical differences were observed between the Peace and Pine River stations on the one hand and the Beatton and Kiskatinaw River stations on the other hand and, although these differences were substantial no significant change could be detected in the main stream of the Peace River below the Beatton and Kiskatinaw confluence.
- 5. A cluster analysis using all individual samples from the five stations confirmed the chemical differences but also indicated that the hydrological regime has a profound influence on the water quality at different times of the year.
- Chlorine, silica, dissolved nitrogen, sodium, sulfate, alkalinity and specific conductance were found to be the most useful differentiating parameters.

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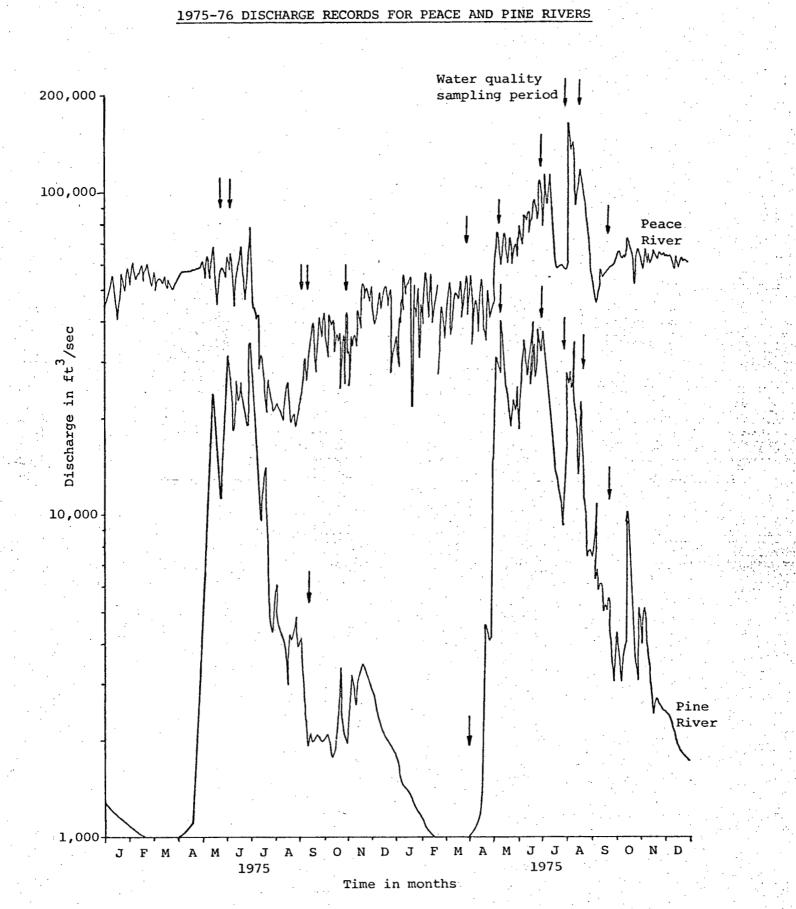
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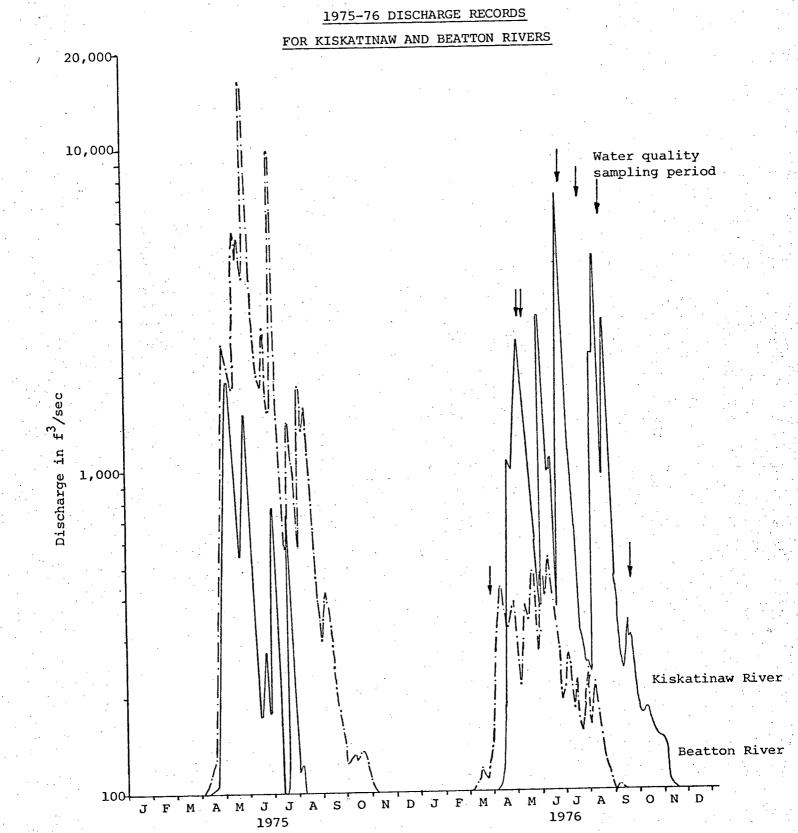
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APPENDIX I

1975-76 DISCHARGE RECORDS FOR PEACE, PINE, BEATTON AND KISKATINAW RIVER





Time in months

APPENDIX II. ANALYSIS OF SEDIMENTS

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Filterable and non-filterable residues were examined for the five sampling stations in the Peace River system over the 1975-76 period. The data were found to be insufficient for a detailed examination and only general observations are presented below.

(a) Non Filterable Residues

As can be seen from Figure 1, the Pine, Beatton, and Kiskatinaw River stations showed generally higher 1975-76 values than the two stations on the Peace River. Also fluctuations between sampling periods were lower in the Peace River than those found in the other three rivers. This can be attributed to the fact that the flow in the Peace River is regulated by a major hydroelectric dam.

Peak annual values were found to occur at various times of the year, the Beatton River station being the most variable of all five stations analyzed.

(b) Filterable Residues

From Figure 2 it is evident that filterable residues were highest for the Beatton and Kiskatinaw Rivers during late winter. The overall trends for the Pine and Peace River stations were similar and differed significantly from the values obtained for the Kiskatinaw River.

