

THE LIMNOLOGICAL CHARACTERISTICS  
OF THE BOW, OLDMAN AND SOUTH  
SASKATCHEWAN RIVERS (1979-82)

PART I. Nutrient and Water Chemistry

Prepared by:

P.M. Cross  
H.R. Hamilton  
S.E.D. Charlton

Alberta Environment  
Environmental Protection Services  
Pollution Control Division  
Water Quality Control Branch  
Edmonton, Alberta

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## EXECUTIVE SUMMARY

The objective of the research was to analyze nutrient and water chemistry in the Bow, Oldman and South Saskatchewan Rivers from May, 1979 to April, 1982. Particular emphasis was placed on phosphorus origins, budgets, and dynamics.

Water chemistry throughout the Basin showed typical seasonal changes related to climate, discharge and biological activity. In winter, climatological and physical factors controlled biological activity. In summer, climatological and physical factors were optimum for biological activity.

Conductivity, alkalinity, dissolved inorganic carbon, nitrogen and phosphorus were high in winter when temperature and pH were low. The opposite trend was shown in summer.

The spring high flow period had the greatest concentrations of particulate matter and turbidity. The Bow River, with its more regulated discharge, showed less extremes of particulate related variables than the other two rivers.

Dissolved phosphorus was the component of total phosphorus most available to biological systems. This form was used in Part II to develop functional relationships between phosphorus and aquatic plant and algal growth. In 1980 and 1981, city sewage treatment plants contributed 89% of the dissolved phosphorus input to the study area (70% from Calgary, 14% from Lethbridge and 5% from Medicine Hat).

Calgary contributed 91% of the dissolved phosphorus to the Bow River, Lethbridge contributed 78% to the Oldman River, and Medicine Hat contributed 12% to the South Saskatchewan River.

Phosphorus from sediments, from industry and from irrigation activities was not a major source contributing to plant growth.

Dissolved phosphorus was depleted most rapidly by plant growth in the Bow River downstream of Calgary. Low dissolved phosphorus was not the limiting factor for plant growth until the site at Bassano.

Dissolved phosphorus was the nutrient-limiting factor for plant growth for the remainder of the Basin. The possible exception was the short periods of nitrogen limitation in the Oldman River downstream of Lethbridge.

TABLE OF CONTENTS

	Page
EXECUTIVE SUMMARY .....	i
TABLE OF CONTENTS .....	iii
LIST OF TABLES .....	v
LIST OF FIGURES .....	viii
ACKNOWLEDGEMENTS .....	xi
1.0 INTRODUCTION .....	1
2.0 METHODS .....	4
2.1 Water Chemistry .....	4
2.2 Other Routine Data .....	10
2.3 Historical .....	10
2.4 Biologically-Available Phosphorus/Algal Assay .....	14
2.5 Nutrient Limitation .....	16
2.6 Sediments .....	16
2.7 Loading .....	18
2.8 Bonnybrook .....	21
3.0 RESULTS .....	24
3.1 Dissolved Oxygen .....	24
3.2 Water Temperature .....	27
3.3 pH .....	28
3.4 Conductivity .....	28
3.5 Alkalinity .....	31
3.6 Turbidity and Residues .....	35
3.7 Chloride .....	38
3.8 Silica .....	38
3.9 Carbon .....	42
3.10 Nitrogen .....	45
3.10.1 Nitrate/nitrite and Total Nitrogen .....	45
3.10.2 Dissolved Nitrogen .....	46
3.10.3 Ammonia .....	49
3.10.4 Particulate Nitrogen .....	51
3.11 Phosphorus .....	51
3.11.1 Bow River .....	54
3.11.2 Oldman River .....	59
3.11.3 South Saskatchewan River .....	60
3.11.4 Ratio of Phosphorus Forms .....	60

3.12	Biologically-Available Phosphorus .....	64
3.12.1	Dissolved .....	64
3.12.2	Sephadex-Gel Filtration .....	67
3.12.3	Particulate .....	67
3.13	Nutrient Limitation .....	74
3.14	Historical Nutrient Data .....	78
3.15	Other Water Chemistry Data .....	81
3.16	Sediment Phosphorus .....	82
3.17	Discharge .....	85
3.18	Phosphorus Loading .....	88
3.18.1	Site Loading .....	88
3.18.2	Loading Sources .....	96
3.18.3	Reach Loadings .....	102
3.19	Bonnybrook .....	111
4.0	DISCUSSION .....	121
4.1	Seasonal Variability .....	121
4.2	Historical Nutrient Data .....	127
4.3	Biologically-Available Phosphorus .....	129
4.4	Nutrient Limitation .....	134
4.5	Sediment Phosphorus .....	136
4.6	Phosphorus Loading .....	139
5.0	SUMMARY .....	142
6.0	CONCLUSIONS .....	151
7.0	REFERENCES .....	153
8.0	APPENDIX A .....	159
8.1	Technical Study Introduction .....	159
8.2	Methods .....	160
8.3	Results .....	162
8.3.1	Filter comparison .....	162
8.3.2	Precision .....	165
8.3.3	Diurnal variability .....	168
8.4	Discussion .....	176
8.4.1	Filter comparison .....	175
8.4.2	Precision .....	177
8.4.3	Diurnal variability .....	178
8.5	Summary .....	181
8.6	Report Appendix Tables and Figures .....	183
9.0	APPENDIX B - DATA VOLUME .....	Bound Separately

LIST OF TABLES

1.	Sampling bottle, analytical method, measurement unit and NAQUADAT codes for water chemistry variables. ....	5
2.	Site locations and NAQUADAT codes for water chemistry sampling in the South Saskatchewan River Basin. ....	7
3.	Location of Water Survey of Canada discharge measurement stations relative to water chemistry study sites in the South Saskatchewan River Basin. ....	11&12
4.	Equations used in the calculation of discharge at water chemistry sites which did not coincide with discharge measurement stations. ....	13
5.	Site number and location of sampling sites on Bow River for the Bonnybrook study. ....	23
6.	Comparison between 1980 and 1981 data using Mann-Whitney U tests, and between years for each season using Kruskal-Wallis one-way anova tests. Comparison between seasons (years combined) using Mann-Whitney U tests. Seasons not significantly different are tabulated. ....	32
7.	Annual and seasonal ratio of phosphorus forms in the basin overall and in each river separately. ....	61
8.	Ratio of biologically available phosphorus forms to chemically measured phosphorus forms. ....	65
9.	Ratio of dissolved nitrogen to dissolved phosphorus at each site in the study basin. ....	75
10.	Comparison of study data and historical data (1970 to 1979) for selected nutrient parameters. ....	79
11.	Summary of sediment phosphorus concentrations and proportional relationships between forms at each site. The estimate of areal distribution of fine particulate river bottom sediments in September, 1981, is also given. ....	83
12.	Comparison of annual phosphorus loading in tonnes including mean, standard deviation and coefficient of variation. ..	91

13.	Comparison of seasonal dissolved phosphorus loading in tonnes including mean, standard deviation and coefficient of variation. ....	95
14.	Bioavailability of particulate phosphorus in sewage treatment plant effluents. ....	100
15.	Return flow and tributary loadings and irrigation withdrawals of total and dissolved phosphorus on an annual and seasonal basis, including coefficient of variation. ....	103
16.	Net change in dissolved phosphorus loading within each river reach on an annual and seasonal basis. ....	107
17.	Inventory of annual total phosphorus and dissolved phosphorus loadings in tonnes directly into the Bow, Oldman and South Saskatchewan Rivers within the study area. ....	109
18.	Bonnybrook study loadings and net loading changes for dissolved phosphorus in summer, 1981. ....	120
19.	Literature review of percent availability of suspended particulate phosphorus in surface waters. ....	130
A-1	Sampling sites and dates for water chemistry diurnal variability study on the Bow River. ....	161
A-2	Summary of significance of Wilcoxon matched pairs test results for comparison of dissolved variables from GFC and 0.45 $\mu$ membrane filtrate. ....	164
A-3	Mean, standard deviation and coefficient of variation for data from water chemistry precision study on the Bow River below Bearspaw Dam. ....	166
A-4	Mean, standard deviation and coefficient of variation for data from water chemistry precision study on the Bow River at Stiers Ranch. ....	167
A-5	Mean, standard deviation and coefficient of variation of data from diurnal variability study on the Bow River. ....	169
A-6	Summary of F-ratios and ratio of maximum to minimum variance from one-way analysis of variance on diurnal variability study data. ....	173



A-7	Pearson's correlation between selected water chemistry variables. ....	184
A-8	Pearson's correlation between mean daily discharge and selected water chemistry variables. ....	185
A-9	Comparison of phosphorus loading values using study and Environment Canada data. ....	186

LIST OF FIGURES

1.	South Saskatchewan River Basin Limnological study sampling sites. ....	5
2.	Bonnybrook study sampling sites. ....	22
3.	Comparison of diurnal variability of dissolved oxygen between months and years at remote monitoring sites within the study basin. ....	25
4.	Monthly average temperature and dissolved oxygen at selected remote monitoring sites within the study basin from 1978 to 1982. ....	26
5.	Comparison of pH data from four sites in the study basin.	29
6.	Comparison of conductivity data from four sites in the study basin. ....	30
7.	Comparison of total alkalinity data from four sites in the study basin. ....	33
8.	Comparison of turbidity data from four sites in the study basin. ....	36
9.	Annual and seasonal average values of turbidity at each site in the study basin. ....	37
10.	Comparison of dissolved chloride data from four sites in the study basin. ....	39
11.	Comparison of reactive silica data from four sites in the study basin. ....	40
12.	Annual and seasonal average concentrations of reactive silica at each site in the study basin. ....	41
13.	Comparison of particulate organic carbon data from four sites in the study basin. ....	43
14.	Annual and seasonal average concentrations of particulate organic carbon at each site in the study basin. ....	44
15.	Comparison of dissolved nitrogen and nitrate + nitrite data from four sites in the study basin. ....	47

16.	Annual and seasonal average concentrations of dissolved nitrogen and nitrate + nitrite at each site in the study basin. ....	48
17.	Comparison of total ammonia nitrogen data from four sites in the study basin. ....	50
18.	Comparison of particulate nitrogen data from four sites in the study basin. ....	52
19.	Comparison of total and dissolved phosphorus data from four sites in the study basin. ....	55
20.	Annual and seasonal average concentrations of dissolved and dissolved reactive phosphorus data at each site in the study basin. ....	56
21.	Annual and seasonal average ratios of dissolved phosphorus to total phosphorus at each site in the study basin. ....	63
22.	Comparison between measurements of dissolved reactive phosphorus by chemical analysis and orthophosphorus by Sephadex-gel filtration. ....	68
23.	Annual and seasonal average ratios of particulate biologically available phosphorus to particulate phosphorus at each site in the study basin. ....	70
24.	Comparisons of the ratios of particulate biologically available phosphorus to particulate phosphorus, to the ratios of particulate phosphorus to total phosphorus, and to dissolved biologically available phosphorus. ....	71
25.	Comparison of annual and seasonal average values for biologically available phosphorus forms and total phosphorus at each site in the study basin. ....	73
26.	Comparison of algal growth potential with and without the addition of nitrogen at selected sites in the study basin. ....	77
27.	Comparison of annual and seasonal average concentrations of total phosphorus from study data and from historical data. ....	80
28.	Comparison of historical discharge values in the Bow, Oldman and South Saskatchewan Rivers. ....	86

29.	Monthly mean discharge in the Bow River at Calgary from 1970 to 1981. ....	87
30.	Comparison of annual loading of total phosphorus in 1980 and 1981 at each site in the study basin. ....	89
31.	Comparison of annual and seasonal loading of dissolved phosphorus at each site in the study basin. ....	93
32.	Population and sewage treatment plant effluent volume and phosphorus loading for Calgary from 1971 to 1981. ....	97
33.	Comparison between dissolved biologically available phosphorus and dissolved reactive phosphorus in sewage effluent. ....	99
34.	Comparison of calculated dilution concentrations of total phosphorus from city sewage treatment plants and measured concentrations of dissolved phosphorus in receiving river. ....	101
35.	Comparison of calculated and measured average annual loading of dissolved phosphorus at each site in the study basin. ....	104
36.	Comparison of calculated and measured average seasonal loading of dissolved phosphorus at each site in the study basin. ....	105
37.	Comparison between data collected from right and left river banks of the Bow River in the Bonnybrook study using the average of all sites on each date. ....	112
38.	Comparison between data collected from right and left river banks of the Bow River in the Bonnybrook study using the average of all dates at each site. ....	113
A-1	Diurnal variability study results for dissolved phosphorus, dissolved nitrogen, dissolved oxygen and conductivity. ..	170
A-2	Seasonal distribution of sediment biologically available phosphorus at selected study sites, 1980-81. ....	186
A-3	Seasonal distribution of sediment organic phosphorus at selected study sites, 1980-81. ....	187
A-4	Seasonal distribution of non-apatite inorganic phosphorus at selected study sites, 1980-81. ....	188

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## 1.0 INTRODUCTION

The purposes of the South Saskatchewan River Basin Limnological Study included the examination of the present state of the rivers; the development of relationships between plant growth and nutrients to determine the current response of the river to nutrients; and the development of phosphorus budgets for the Basin including inputs, storage, bioavailability, cycling dynamics and outputs.

This report deals strictly with water chemistry data, in particular, nutrient chemistry and loadings. The relationship between aquatic plant growth, nutrient levels and physical variables will be addressed in a separate report (Part II. The Primary Producers; Charlton et al., 1986).

The extensive information collected by regular sampling during the study (May, 1979 to April, 1982) forms the core of the water chemistry study. These data will be used to describe the conditions throughout the Basin as they change with seasons and sites. They also provide a basis for calculation of phosphorus loadings at different sites on the river. The results can be used, in turn, to determine changes within each reach of the river.

Loadings analysis has been used widely in eutrophication research on lakes to determine the relationship between phosphorus and primary production (Dillon, 1975a; Vollenweider, 1975; 1976; Jones and Lee, 1982) and is useful as a predictive management tool (Dillon, 1975b; Cross, 1978). Its application to rivers has been much less extensive, but provides a basis for study of river eutrophication (Peters, 1973; Hill, 1982; Brown et al., 1982).

Other sources of data were used to qualify and expand on the information derived from the core study. Dissolved oxygen and temperature, for example, were monitored by Alberta Environment remote continuous monitors at several locations within the Basin. The results provide a more comprehensive data base for these parameters. Similarly, daily discharges were monitored by Water Survey of Canada at a number of sites. Additional monthly water chemistry data were available from the Water Quality Branch, Environment Canada. These data, information from various tributary and irrigation return flow studies, sediment studies, stormwater studies, routine collections from sewage treatment plants, and industrial effluents were used to supplement the core data collection when defining the conditions in the Basin.

Water quality and discharge data have been collected in the South Saskatchewan River Basin for many years. This historical information provides a basis for comparison with data collected during the present study period. City of Calgary sewage treatment plant data were reviewed and an estimate of the relative impact on the receiving river of the sewage from Calgary, Lethbridge and Medicine Hat was made for the period from 1971 to 1981.

Phosphorus is generally considered to be the nutrient which limits or controls aquatic plant growth, although nitrogen has also been shown to have some influence (Wetzel, 1975). The ratio of nitrogen to phosphorus concentration, which indicates the relative supply of these nutrients, has been used to investigate nutrient limitation (Sakamoto, 1966; Schindler, 1976; Cross, 1978). However, absolute concentrations of each nutrient must also be considered.



Data collected during the study was used to determine which nutrient controlled plant growth.

Considerable controversy exists over the bioavailability of various forms of phosphorus (Paerl and Downes, 1978; Lee et al., 1980). An investigation of phosphorus bioavailability in the Basin will define which nutrient form to use in predictive relationships with plant growth.

The portion of the Bow River located between Calgary and Carseland shows the most dramatic impact of nutrients on the river system. The Bonnybrook study provides a more detailed look at the river in this one region. The nutrients entered the river at the right bank from Bonnybrook, the major sewage treatment plant, and at midstream from the Fish Creek sewage treatment plant. The gradient of nutrient concentrations downstream from the Bonnybrook plant provides natural experimental conditions for studying nutrient concentrations and primary producers within the mixing zone at varying concentrations.

## 2.0 METHODS

### 2.1 Water Chemistry

Acid washed sample bottles were obtained from the Water Quality Lab of Environment Canada in Calgary. Grab subsurface samples were collected into polyethylene and squirel bottles, filtered and kept cool while being transported back to the lab for analysis, using standard lab techniques (Table 1).

Thirteen sites were chosen for water chemistry sampling in the South Saskatchewan River Basin (Figure 1). Six of these sites were located on the Bow River, three were on the Oldman River and four on the South Saskatchewan River. The locations of several sites were changed during the study. A summary of station locations is given in Table 2.

Standard Water Quality Control Branch sampling techniques were employed. During the open water season, samples were collected either by wading into the river, or by lowering a bucket from a bridge. Methods varied at each site and throughout the year depending primarily on river discharge and access. Winter samples were collected either through a hole drilled in the ice, or at a flowing open lead if it was accessible. However, sampling methods differed at Sites 2 and 10. After January, 1980, Site 2, on the Bow River at Stiers Ranch, was sampled from the monitor's intake water pipe. During the period from May, 1979, to March, 1980, Site 10, on the South Saskatchewan River above Medicine Hat, was sampled from the monitor's intake water pipe.

TABLE 1 SAMPLING BOTTLE, ANALYTICAL METHOD, MEASUREMENT UNIT AND  
NAQUADAT CODES FOR WATER CHEMISTRY VARIABLES

<u>Variable</u>	<u>NAQUADAT<sup>*</sup> Code</u>	<u>Analytical Method</u>	<u>Units</u>	<u>Sample<sup>**</sup> Bottle</u>
Conductivity	02041L or S	conductivity meter	U Sie/cm	n/a
Temperature	02061S	mercury thermometer	°C	n/a
Turbidity	02073L	turbidimeter	JTU	1L poly
Dissolved Organic C (DOC)	06104L or D	infrared analysis, 0.45 u membrane filter	mg/L	2 oz poly
	06106L or D	as above, GFC filter	mg/L	2 oz poly
Dissolved Inorganic C (DIC)	06152L or D	infrared analysis, 0.45 u membrane filter	mg/L	2 oz poly
	06153L or D	as above, GFC filter	mg/L	2 oz poly
Particulate Organic C (POC)	06902L or D	thermal conductivity, CHN analyzer	mg/L	1L poly
Nitrate-Nitrite N (NIT)	07110L or D	colourimetry on autoanalyzer, 0.45 u membrane filter	mg/L	2 oz poly
	07119L or D	as above, GFC filter	mg/L	2 oz poly
Ammonia N (NH <sub>3</sub> )	07506L	ion selective electrode	mg/L	500 mL poly
Dissolved N (DN)	07651L or D	UV digestion, colourimetry on autoanalyzer, 0.45 u membrane filter	mg/L	2 oz poly
	07661L or D	as above, GFC filter	mg/L	2 oz poly
Particulate N (PN)	07902L or D	thermal conductivity, CHN analyzer	mg/L	1L poly
Alkalinity-Total (CaCO <sub>3</sub> )	10106L or O1L	infrared analysis	mg/L	1L poly
Alkalinity-Phenolphthalein	10151L	potentiometric filtration	mg/L	1L poly
pH	10301L	electrometric	pH units	1L poly
Residue - Non-filterable (NFR)	10401L	gravimetric	mg/L	1L poly
Residue - Non-filterable, fixed (NFR)	10501L	gravimetric	mg/L	1L poly
Silica - Reactive (Si)	14105L	colourimetry using heteropoly blue method on auto-analyzer	mg/L	1L poly
Dissolved P (DP)	15103L or D	colourimetry on autoanalyzer, 0.45 u membrane filter	mg/L	45 mL sov
	15113L or D	as above, GFC filter	mg/L	45 mL sov
Dissolved Reactive P (OP)	15256L or D	colourimetry on autoanalyzer, 0.45 u membrane filter	mg/L	2 oz poly
	15266L or D	as above, GFC filter	mg/L	2 oz poly
Total Inorganic P (TIP)	15301L	colourimetry on autoanalyzer	mg/L	45 mL sov
Dissolved Inorganic P (DIP)	15356L or D	colourimetry on autoanalyzer, 0.45 u membrane filter	mg/L	45 mL sov
	15346L or D	as above, GFC filter	mg/L	45 mL sov
Total P (TP)	15406L	colourimetry on autoanalyzer	mg/L	45 mL sov
Dissolved Chloride (Cl)	17206L	colourimetry on autoanalyzer	mg/L	

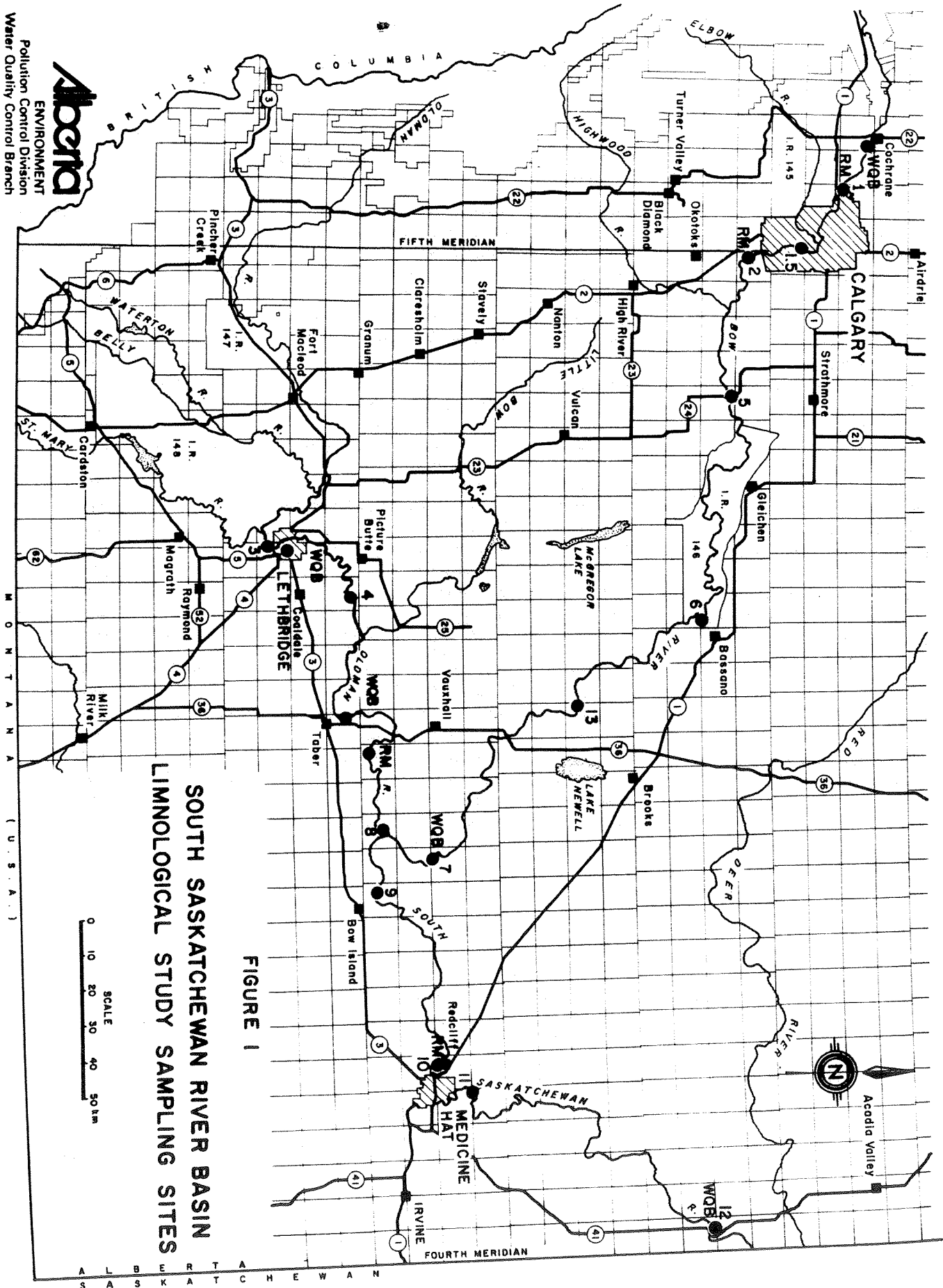
\* L - lab filtered (where applicable)

D - field filtered

S - site analysis

\*\* - filtered samples collected first in 1 or 2L poly bottle

- sovrel samples transferred from 1 or 2L poly bottles during winter



**SOUTH SASKATCHEWAN RIVER BASIN  
 LIMNOLOGICAL STUDY SAMPLING SITES**

**FIGURE 1**

M O N T A N A ( U . S . A . )

A L B E R T A S A S K A T C H E W A N

TABLE 2 SITE LOCATIONS AND NAQUADAT CODES FOR WATER CHEMISTRY  
SAMPLING IN THE SOUTH SASKATCHEWAN RIVER BASIN

<u>Site</u>	<u>Km</u>	<u>Code</u>	<u>Location</u>
1	5 0	00AT05BH2105 00AT05BH2090	Bow River at 85th Street Bridge, Calgary Bow River below Bearspaw Dam (from 10/03/80)
2	34 37	00AT05BM2161 00AT05BM2160	Bow River at Highway 22X, Calgary Bow River at Stiers Ranch, Calgary (from 22/01/80)
5	79	00AT05BM2215	Bow River below Carseland Weir
6	195	00AT05BM2240	Bow River below Bassano Dam
13	256	00AT05BN2245	Bow River at Bow City Bridge (from 24/09/79)
7	346	00AT05BN2270	Bow River at Ronalane Bridge
3	208	00AT05AD2035	Oldman River at Highway #3, Above Lethbridge
4	251	00AT05AD2050	Oldman River at Highway #845, Below Lethbridge
8	364	00AT05AG2095	Oldman River at the Mouth (Confluence with the Bow River)
9	382	00AT05AK2070	South Saskatchewan River at Highway #879
10	467	00AT05AK2080	South Saskatchewan River above Medicine Hat
11	499	00AT05AK2085	South Saskatchewan River below Medicine Hat
	501	00AT05AK2087	South Saskatchewan River below Medicine Hat (from 31/03/80)
12	624	00AT05AK2090	South Saskatchewan River at Highway #41

Duplicate samples were collected from May, 1979, to May 1980. Filtered variables were provided from filtrate collected through a 0.45  $\mu$  membrane filter for one sample and through a GFC filter for the duplicate. For numerous reasons, the number of samples collected was changed at this time. Starting in June, 1980, single samples were taken with one duplicate per 20 samples. Nucleopore membrane filters were used from May, 1979 till April, 1980. Sartorius membrane filters were then used from May, 1980, till the end of the project in May, 1982. Filtrate collected through a 0.45  $\mu$  Sartorius membrane filter provided the filtered variables except for dissolved nitrogen. Dissolved nitrogen was taken from the GFC filtrate from particulate nitrogen and particulate organic carbon analysis to ensure accurate calculation of total nitrogen.

The samples were collected onto ice and were generally field filtered within 16 hours of sampling. However, from November 1979 to June 1980 samples were returned to the lab for filtration, generally within 24-48 hours, but always within 60 hours.

For the first two years (May, 1979, to May, 1981), water samples were taken once every two weeks in the periods May to August, 1979, March to November, 1980, and March to May, 1981. Otherwise, samples were collected once in three weeks. In the third year, from June, 1981, to April, 1982, samples were collected once in three weeks from the Bow and Oldman River sites. Samples from the four South Saskatchewan River sites were taken once in six weeks (Sites 9 and 11 were sampled alternatively with Sites 10 and 12 at three week intervals).

The development of any routine sampling program requires a review of technical considerations related to analytical as well as sampling methods. Three studies, which were carried out to address several of these concerns, are reported in Appendix A.

For statistical purposes, seasonal definition at all 13 sites was based on three years of water chemistry and discharge data, and 20 months of benthic algal data. The dates of seasonal transition were chosen to avoid splitting of water chemistry sampling runs, thus making seasonal site means more comparable. Spring was defined as the period from March 20 to June 19, summer from June 20 to September 14, fall from September 15 to December 1 and winter from December 2 to March 19.

Seasonal and annual means were compiled using NAQUADAT (National Water Quality Data Bank) report formats, which give arithmetic averages of data. That is, when summer data from three years were combined, no attempt was made to weight each summer average equally. Similarly, annual averages are simply the average of all data collected during the study.

Pearson's correlations (SPSS) were calculated on a number of raw data sets to determine the strength of the relationship between different variables. Kruskal-Wallis anova tests and Mann-Whitney U tests were used to test for seasonal and yearly differences in selected variables.

## 2.2 Other Routine Data

Dissolved oxygen and temperature were measured by remote monitors on a continuous basis throughout the study: on the Bow River above Calgary at Baker Sanatorium and below Calgary at Stiers Ranch (from February 1980); on the Oldman River at Fincastle; and on the South Saskatchewan River at Medicine Hat (Figure 1). Diurnal curves of dissolved oxygen and temperature were generated from these data and compared among sites and seasons.

Water Survey of Canada measures of discharge at 47 stations in the South Saskatchewan River Basin were used directly in the study. Seven of the stations were on the main rivers. The remaining stations were on tributary streams, irrigation canals and return flows (Table 3). These data were used to calculate discharge at each regular sampling site and at other locations relevant to phosphorus input inventories. When discharge measurement stations were not at the same collecting sites as water chemistry sites, discharge was calculated according to the equations given in Table 4. The Water Quality Branch of Environment Canada under contract to Alberta Environment collects water chemistry data from five sites on the main rivers within the study area (Figure 1, Table 3). These data were used to supplement our data.

## 2.3 Historical

The most complete historical records of discharge, from 1900 to the present, are at Calgary on the Bow River, near Lethbridge on the Oldman River, and at Medicine Hat on the South Saskatchewan River.



TABLE 3 LOCATION OF WATER SURVEY OF CANADA DISCHARGE MEASUREMENT STATIONS RELATIVE TO WATER CHEMISTRY STUDY SITES IN THE SOUTH SASKATCHEWAN RIVER BASIN

<u>Station</u>	<u>Site</u>	<u>Location</u>
<u>BOW RIVER</u>		
05BH004	1	Bow River at Calgary
05BJ001		Elbow River below Glenmore Dam
05BH003		Nose Creek at Calgary
05BM003		Western Irrigation District Canal near Chestermere Lake
05BK001	2	Fish Creek near Priddis
05BL024		Highwood River near Mouth
05BM009		Twelve Mile Coulee Spillway near Carseland
05AC004		Bow River Development Main Canal
05BM002	5	Bow River below Carseland Dam
05BM005		Hammer Hill Spillway near Gleichen
05BM012		Cairn Hill Spillway near the Mouth
05BM014		West Arrowwood Creek near Arrowwood
05AC004		Bow River Development Main Canal
05BM008		Crowfoot Creek near Cluny
05CJ001		Eastern Irrigation District North Branch Canal near Bassano
05CJ003		Eastern Irrigation District East Branch Canal near Lathom
05CJ004		Eastern Irrigation District Springhill Canal near Lathom
05BM004	6	Bow River below Bassano Dam
05BN014	13	Coal Creek at Bow City
05BN010		Antelope Coulee Spillway
05BN024		Natural Flow C near Bow City
05BN009		Bow River Development Drain K near Vauxhall
05BN006		New West Coulee near Mouth
05BN023		Bow River Development Drain E near Vauxhall
05BN008		Bow River Development Drain D near Vauxhall

TABLE 3 CONT'D

<u>Station</u>	<u>Site</u>	<u>Location</u>
05BN015		Rolling Hills Canal No. 1 Spill
05BN002		Twelve Mile Creek near Cecil
05BN019		Rolling Hills Canal No. 2 Spill
05BN012	7	Bow River near the Mouth
05BN007		Ronalane Wasteway near Hays
05AG005		Bow River Development Drain A near Hays
<u>OLDMAN RIVER</u>		
05AD007	3	Oldman River near Lethbridge
05AD037	4	Piyami Drain near Picture Butte
05AD038		Battersea Drain near the Mouth
05AC023		Little Bow River near the Mouth
05AG007		Lateral 10 Spillway near Chin
05AG008		Bountiful Coulee near Cranford
05AG026		Bountiful Coulee Inflow near Cranford
05AG023		Drain T-2 near Taber
05AG003		Expanse Coulee near the Mouth
05AG025		Drain T-11 near Fincastle
05AG005	8	Bow River Development Drain T near Hays
<u>SOUTH SASKATCHEWAN RIVER</u>		
05AJ002	9	Drain S-4 near Grassy Lake
05AJ003		Drain S-10 near Bow Island
05AJ001	10	South Saskatchewan River at Medicine Hat
05AH005	11	Seven Persons Creek at Medicine Hat
05AK001	12	South Saskatchewan River at Highway No. 41

TABLE 4 EQUATIONS USED IN THE CALCULATION OF DISCHARGE AT  
WATER CHEMISTRY SITES WHICH DID NOT COINCIDE WITH  
DISCHARGE MEASUREMENT STATIONS

<u>Site</u>	<u>Equation</u>
2	$\frac{(\text{Site 1} + 4 \text{ d/s inputs}) + (\text{Site 5} - 3 \text{ u/s inputs})}{2}$
5*	Site 2 + 3 d/s inputs
6*	$\text{Site 5} + (\text{Site 7} - \text{Site 5}) \times \frac{117}{267}$
13	$\text{Site 7} - (\text{Site 7} - \text{Site 5}) \times \frac{90}{267}$
4	Site 3 + 1 d/s input
8	$\frac{(\text{Site 4} + 9 \text{ d/s inputs}) + (\text{Site 9} - 4 \text{ u/s inputs})}{2}$
9	Site 10 - 1 u/s input
11	$\frac{(\text{Site 10} + 1 \text{ d/s input}) + (\text{Site 12})}{2}$

\*required in winter

u/s - upstream

d/s - downstream

Historical nutrient data were compiled from January 1970 to April 1979 using the NAQUADAT summary and seasonal summary report formats from both provincial and federal data bases.

#### 2.4 Biologically-Available Phosphorus/Algal Assay

Phosphorus is found in particulate as well as dissolved fractions, and the dissolved fraction is measured in various chemical forms. There is considerable controversy over the techniques for measuring these forms (Rigler, 1966; Lean, 1973; Downes and Paerl, 1978; Stainton, 1980) and their bioavailability (Paerl and Downes, 1978; Lee et al., 1980). Therefore, measurements of dissolved and particulate bioavailable phosphorus were made using algal assay techniques to compare with chemical analyses.

Samples for biologically-available phosphorus analysis were collected on regular sampling trips. GFC filtered and whole water samples for dissolved biologically-available phosphorus and particulate biologically-available phosphorus analyses, respectively, were held on ice prior to initiation of the assay. Sample handling time after filtration in the field was usually 72 hours or less.

The algal assay technique was adapted from the USEPA bottle test for static bioassays (Miller et al., 1978) by Hamilton et al. (1981). Selenastrum capricornutum was used as the test alga. Triplicate bioassays were run on membrane filtered (0.45  $\mu$ ) samples. Samples were spiked with sodium nitrate to ensure that no nitrogen limitation occurred.

The treatment of particulate samples for analysis was a modification of the technique of Cowen and Lee (1976). The method is

given in detail in Hamilton et al. (1981). Mean values of dissolved biologically-available phosphorus and particulate biologically-available phosphorus were calculated from three values except when final cell density of one replicate was inordinately different from the other two.

Correlation analysis and paired student's t-tests were used to evaluate the relationship between dissolved biologically-available phosphorus and dissolved reactive phosphorus, dissolved inorganic phosphorus and dissolved phosphorus.

Algal growth potential was measured using the same technique as dissolved biologically-available phosphorus with the one exception that no nitrogen spiking was used.

A limited number of measurements of orthophosphate concentrations were obtained using Sephadex-gel filtration techniques. Comparison of these results with corresponding chemical data for dissolved reactive phosphorus would test the degree of interference from labile, high-molecular-weight organic phosphorus compounds (Downes and Paerl, 1978).

Sephadex-gel filtration was used to measure orthophosphate in samples from the Bow and Oldman Rivers in March and July of 1980. A column height of 70 cm, inside diameter of 1.6 cm, bed height of 55 cm and temperature of 25°C were used. Both Sephadex G-25 and eluent (0.2% NaCl, 0.03% NaN<sub>3</sub>) were degassed prior to use and the flow rate was maintained between 1.7 and 1.8 mL per minute. Effluent from the column was continuously sampled by Technicon proportioning pump sampling at 1.2 mL/min.

## 2.5 Nutrient Limitation

The nitrogen to phosphorus ratio, absolute concentrations, and algal growth potential studies with and without nitrogen additions were used to evaluate nutrient limitations.

The changing ratio of nitrogen to phosphorus has been used to indicate which nutrient was more limiting in a system (Schindler, 1976; Cross, 1978). That is, if the ratio increased through the system, then the biota were more limited by phosphorus. Other authors have used the absolute nitrogen to phosphorus ratio to determine nutrient limitation to algal growth. Dillon and Rigler (1974) suggested a ratio of 12 from work by Sakamoto (1966), while Grimm, Fisher and Minckley (1981) used 15 and Chacko et al. (1981) used 10 from work by Chiaudani and Vighi (1974).

Algal assays were performed with and without addition of nitrogen to the growth medium. When addition of nitrogen increased the growth potential, nitrogen was then assessed as limiting growth. When addition of nitrogen did not increase the growth potential, then another nutrient was in short supply. The other nutrient was often phosphorus.

## 2.6 Sediments

Bottom sediments in the river system represent a potential storage component for phosphorus (Reddy, 1978). In order to determine the magnitude of this potential under present conditions, sediment quantity as well as chemically and biologically determined phosphorus forms found in the sediment were measured.

Sediment samples were taken with an airlift sampler which used air pulsation to suspend the fine particulate sediment lodged among the larger gravel and cobble substrate. The sediment and water slurry were collected into a nalgene bucket. Composite sampling at each site, from the areas of the river channel with active flow up to a maximum depth of 1 metre, was carried out from April 1980 to September 1981. The Bow, Oldman and South Saskatchewan Rivers were sampled at five sites, three sites and one site, respectively.

After collection the slurry was filtered through an 80  $\mu$  filter and allowed to settle for 20 to 24 hours. The supernatant was then removed and the process repeated to obtain a concentrated slurry suitable for freeze-drying.

Phosphorus fractionation for apatite inorganic, organic and non-apatite inorganic forms was carried out according to the technique of Williams et al., (1976, 1980). Biologically-available phosphorus was determined by static Selenastrum capricornutum bioassays (Miller et al., 1978; Hamilton et al., 1981).

Five replicate quantitative estimates of fine particulate sediment were made in September 1981 at representative river sites. The fine sediments within a 0.1 m<sup>2</sup> closed cylinder, forced into the substrate, were subsampled for non-filterable residue analysis and the total volume of water in the cylinder overlying the substrate was calculated. These values were used to calculate fine particulate sediment per substrate area. No attempt was made to investigate the seasonality of sediment quantity.

To calculate total sediment phosphorus in the Bow River from Calgary to its confluence with the Oldman River and in the Oldman River from Lethbridge to its confluence with the Bow River, the arithmetic average of sediment data, from all sites within the reach, was multiplied by total river substrate area (from data supplied by Stanley Associates Ltd., 1982).

## 2.7 Loading

Discharge measurements and phosphorus concentration data were used to calculate phosphorus loading at routine sampling sites. Total loading was calculated as the average of the following two formulae:

$$L_1 = \frac{\sum c_i q_i}{\sum q_i} \cdot kQ \qquad L_2 = \frac{\sum c_i q_i}{n} \cdot k$$

where L = loading in tonnes  
c<sub>i</sub> = instantaneous concentration in mg/L,  
q<sub>i</sub> = mean daily discharge in cms  
n = number of observations of both variables  
Q = mean discharge in cms  
k = constant for unit adjustment.

The two formulae were averaged, since each is an acceptable calculation for use with both instantaneous and daily data but results, because of altering discharge information, can vary.

In the third year of data collection, phosphorus concentration data were collected less frequently at Sites 9 to 12 on the South Saskatchewan River than at other sites. Interpolated data, from the alternate site sampling strategy, were used in calculations of loading to provide more comparable information.



The calculation of net loading within each river reach had to include the effect of external loadings from tributaries, irrigation removal and return flows, sewage treatment plant effluents and other urban and industrial sources. Then, for comparison of different river reaches, loading from an upstream site plus external loadings was subtracted from loadings at a downstream site. This change in loading was expressed per unit of river length (Table 3; Kellerhals, Neill and Bray, 1972).

Tributary and irrigation loadings were calculated from discharge data from Water Survey of Canada stations (Table 3) and concentration data collected between 1977 and 1981. Irrigation return flow data were available at 27 sites from July to October 1977 for total phosphorus, and from May to October 1978 for both total and dissolved phosphorus. Eight return flows were sampled for total and dissolved phosphorus from June to September 1980 and 15 Bow River return flows plus the three withdrawal canals were sampled for total and dissolved phosphorus once in two weeks from June to October 1981. Some tributary data (Elbow, Nose, Fish and Highwood) were available from 1978. Elbow River was sampled for dissolved reactive phosphorus from May to December 1979. Nose Creek was sampled for total and dissolved phosphorus from April to September 1980, and Highwood River was sampled for dissolved and dissolved reactive phosphorus from May to November 1981.

Loadings were calculated for each season from spring 1979 to fall 1981 using average discharge for each season in cms and average

phosphorus concentration in mg/L. Average seasonal concentrations from each year were used when available, otherwise concentrations from other years or estimates from available data were used.

Loadings from sewage treatment plants were calculated from data collected by each city. Data from Calgary and Lethbridge were quite complete; Medicine Hat sewage plant loadings were estimated from Lethbridge values before spring 1981. Loadings of dissolved phosphorus were estimated from total phosphorus loadings, using ratios of dissolved to total phosphorus measured in Calgary/Bonnybrook effluent during the diurnal variability study. Urban stormwater and industrial total phosphorus loadings for 1980 are from Hamilton (unpublished) and other values are based on these figures. Industrial dissolved phosphorus loadings were estimated to be equal to total phosphorus loadings, since no data were available. Stormwater dissolved phosphorus loadings were based on the ratio of dissolved to total phosphorus from a 1981 stormwater retention pond study in Calgary and values were applied to stormwater runoff estimates from Medicine Hat. These estimates plus population ratios were used to calculate Lethbridge loadings.

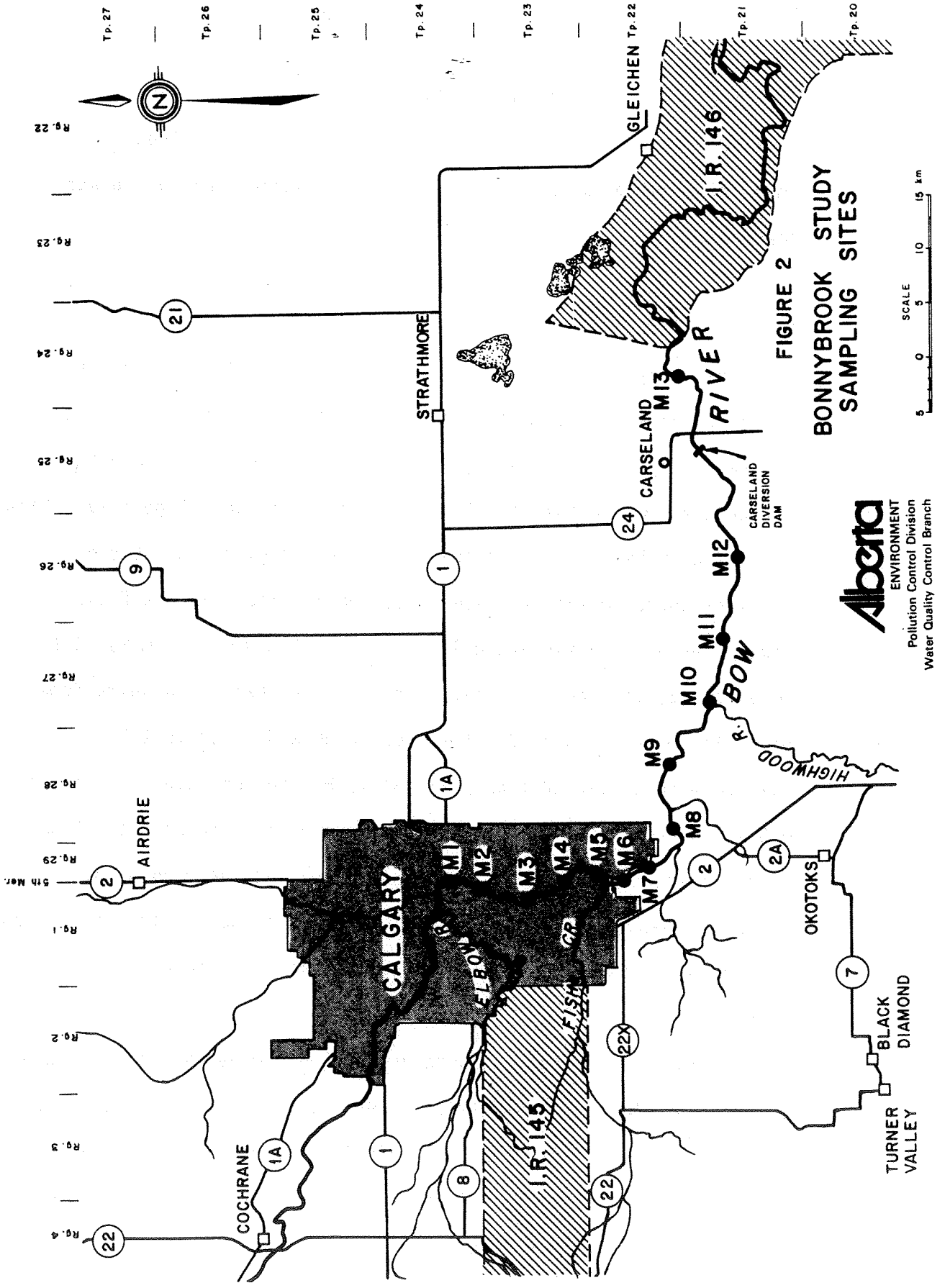
In order to compare the impact of phosphorus loading from the three cities in different years, mean dilution concentration values were calculated. Calgary population figures and sewage treatment plant effluent data were obtained from City of Calgary reports. Annual loading rate of total phosphorus from the City of Calgary sewage treatment plants was divided by mean, June to September discharge of the Bow River at Calgary to calculate a mean dilution concentration. Similar calculations were made with Lethbridge and

Medicine Hat data. However, estimates of phosphorus loadings were used for years 1971 to 1979. These estimates were derived from population estimates and relative Calgary sewage treatment plant loadings.

## 2.8 Bonnybrook

The Bonnybrook study provided a closer investigation of the one reach of the Bow River most strongly affected by nutrient inputs. Thirteen sampling sites were established from above the Bonnybrook sewage treatment plant to below Site 5 at Carseland (Figure 2). With Site M1 at 0 km, their downstream distance is given in Table 5. Site M8 is at approximately the same location as Site 2 in the Basin study. Water samples were collected every two weeks from May 4 to November 13, 1981 near the left and the right banks. Results from each site were designated R for right bank and L for left bank. Samples were collected from Sites M1 to M12 on the same day, and Site M13 was generally sampled on the previous or subsequent day. Samples were filtered within 16 hours of collection and analyzed using standard procedures for conductivity, pH, chloride, silica, dissolved phosphorus, dissolved reactive phosphorus and nitrate/nitrite (Table 1).

Pearson's correlations were used to determine the relationship between variables. Paired t-tests were used to compare left and right bank data at each site. Loading calculations during the summer period were made at Sites M1, M5, M9 and M13 using average left and right bank concentrations and discharge calculated from Water Survey of Canada data.



**FIGURE 2**  
**BONNYBROOK STUDY**  
**SAMPLING SITES**

**Alberta**  
 ENVIRONMENT  
 Pollution Control Division  
 Water Quality Control Branch

TABLE 5 SITE NUMBER AND LOCATION OF SAMPLING SITES  
ON BOW RIVER FOR THE BONNYBROOK STUDY

<u>Site Number</u>	<u>NAQUADAT Code</u>	<u>km</u>	<u>Location</u>
M1	BH2200	0	near Inglewood Golf Course
M2	BH2210	2	below Bonnybrook STP Outfall
M3	BH2220	4	near Acadia (Trailer Park)
M4	BH2230	8	near Queensland Downs
M5	BH2240	12	near Deer Run
M6	BM2159	14.5	below Fish Creek
M7	BM2165	17.5	near Academy
M8	BM2160	23	at Stiers Ranch
M9	BM2170	30	near Tree Nursery
M10	BM2175	37	below Highwood River
M11	BM2180	45	near Dalemead
M12	BM2185	52	above Carseland Weir
M13	BM2224	74	near Stangmuir

### 3.0 RESULTS

#### 3.1 Dissolved Oxygen

Dissolved oxygen (DO) results were erratic occasionally, because of problems with the dissolved oxygen probe or instrument calibration. The effect of calibration can be seen in the results collected at Stiers Ranch in February 1981 (Figure 3). Dissolved oxygen concentrations apparently dropped about 2.3 mg/L between measurements. This change was likely caused by manual resetting of the monitor equipment after dissolved oxygen calibration on site. Other difficulties arising from telemetry and equipment failure sometimes resulted in months with no data or an average monthly value calculated from relatively few data. However, the trends were apparent.

Dissolved oxygen trends on an annual basis were opposite to temperature trends (higher concentrations measured at low temperature) because of the dependence of oxygen solubility on temperature (Figure 4). In addition, dissolved oxygen showed variation over a 24 hour period (Figure 3). This diurnal variation was different between seasons and years at each site.

The largest diurnal change in oxygen concentration occurred on the Bow River below Calgary (Stiers Ranch). In August 1980 the oxygen concentration varied by as much as 7 mg/L during one day, but diurnal fluctuations were also evident to some degree for most seasons. The variation in size of diurnal fluctuation between different years is shown for February, April and August (Figure 3). Diurnal variation seemed to be more consistently low in June and moderate in November.

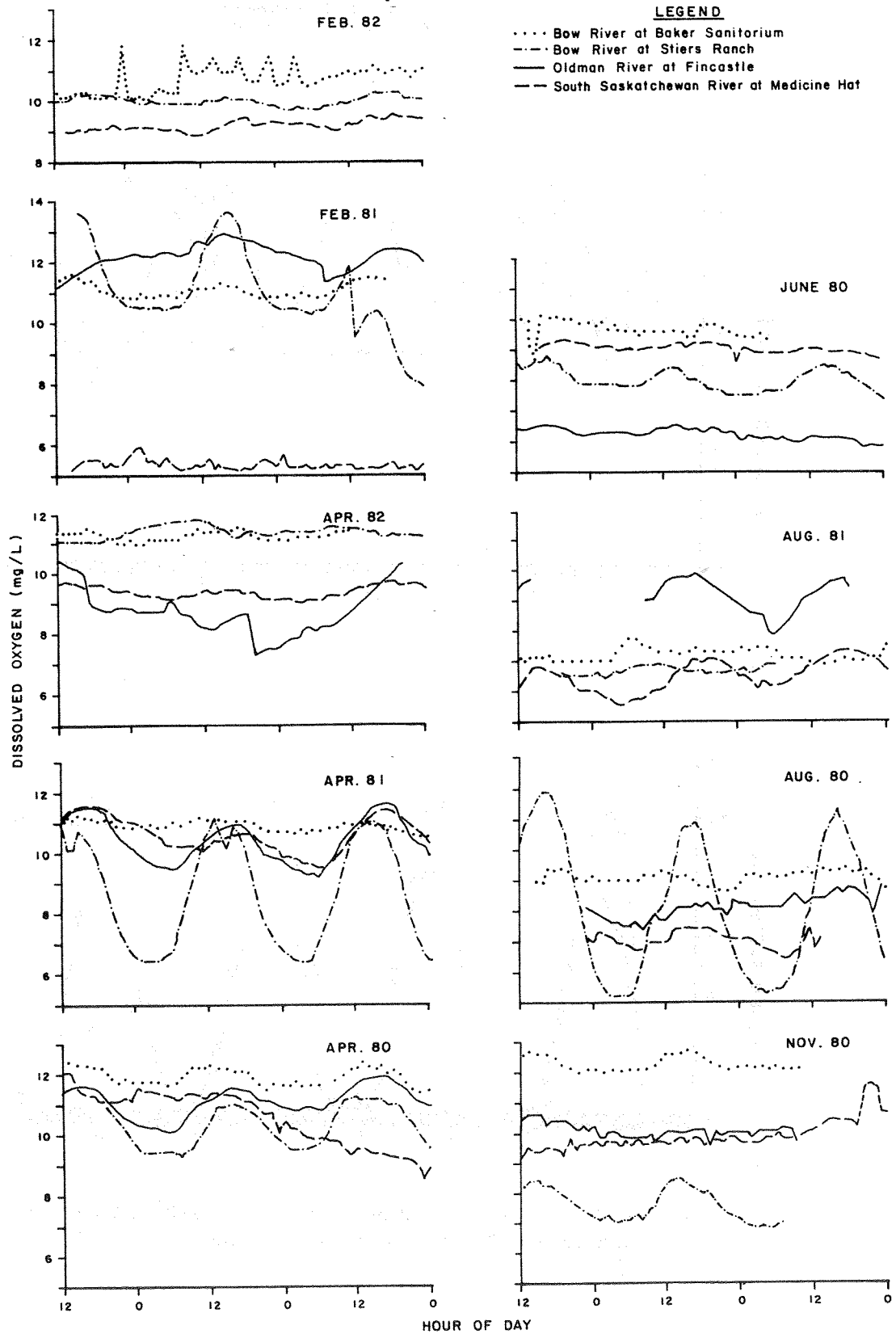


Fig. 3: Comparison of diurnal variability of dissolved oxygen between months and years at remote monitoring sites within the study basin.

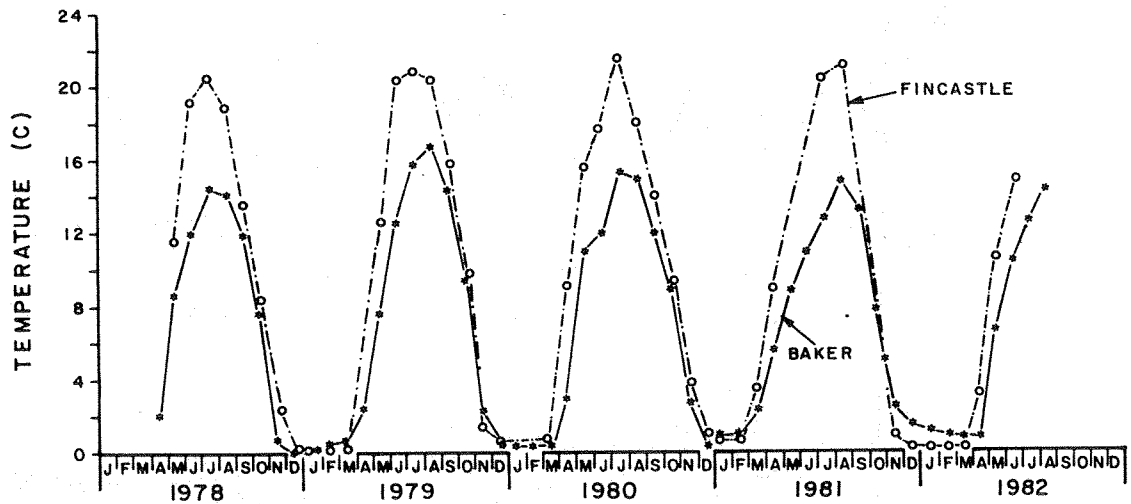
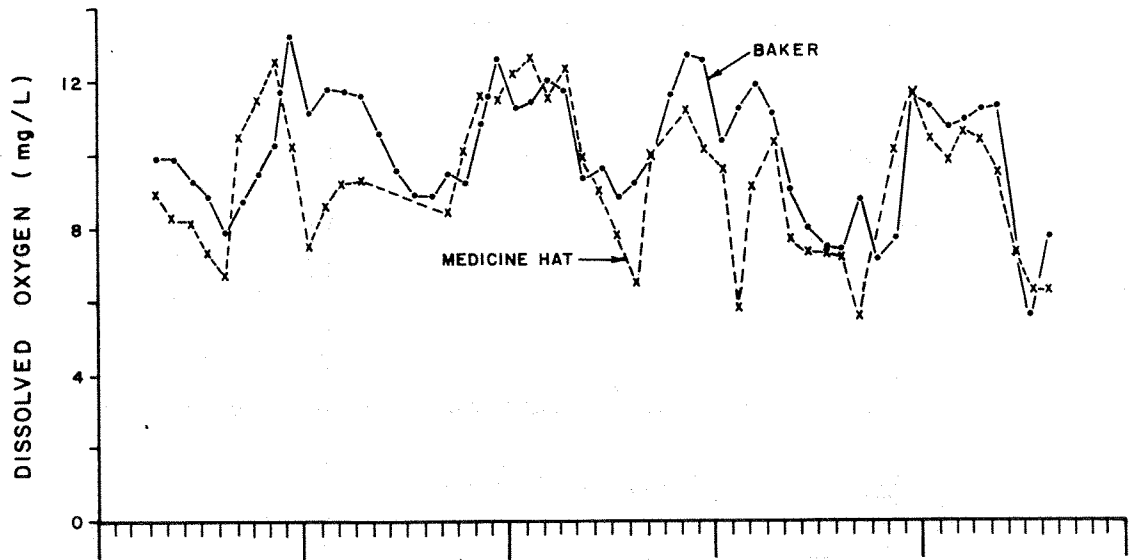


Fig. 4: Monthly average temperature and dissolved oxygen at selected remote monitoring sites within the study basin from 1978 to 1982.



In 1980, diurnal variation at Stiers Ranch was moderate in April and well developed in August, and in 1981 it was large in February and April, but small in August. This variation is affected by climate, flow and plant standing crop. Further studies were made in a technical study and results are reported in Appendix A.

Dissolved oxygen at Baker (on the Bow River above Calgary) was relatively high in all seasons and showed little diurnal variation. Results from Fincastle (on the Oldman River upstream of Site 8) and Medicine Hat (Site 10) showed moderate diurnal fluctuations in April and August, but were relatively constant in the other months.

### 3.2 Water Temperature

Water temperatures were generally highest in the South Saskatchewan River throughout the year, and the Oldman River was warmer than the Bow River through the spring and summer (Figure 4). July was generally the month with the highest mean monthly temperature in the Oldman and South Saskatchewan Rivers, while highest mean monthly temperatures in the Bow River occurred in either July or August. Summer mean temperatures were higher in the Bow River in 1979 than in 1978, 1980, 1981 and 1982.

Low winter temperatures were measured at all sites except Medicine Hat, which used recirculated warm water from the power plant to keep the intake pipe from freezing. The duration of low mean monthly temperatures (less than 1°C) varied each winter, but generally extended from December to March. The winter of 80/81 was quite mild and short, while that of 81/82 extended into April in the Bow River.

### 3.3 pH

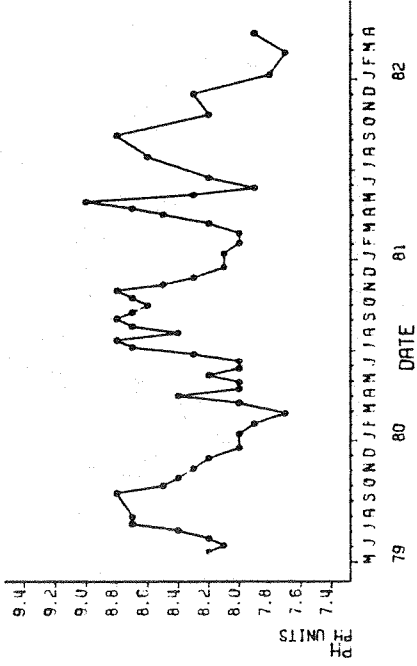
Values of pH in the Basin followed, roughly, a pattern of high values in late summer and low values in winter (Figure 5 and Appendix Table B-1). A second peak in pH occurred in about May 1980 and April 1981. These patterns were more pronounced in downstream sites. Over the three-year period, values ranged from 7.1 to 9.0 in the Oldman; 7.3 to 9.4 in the Bow; and 7.5 to 9.4 in the South Saskatchewan. The smallest site range in pH (7.9 to 8.4) was recorded at Site 1, Bow River above Calgary.

### 3.4 Conductivity

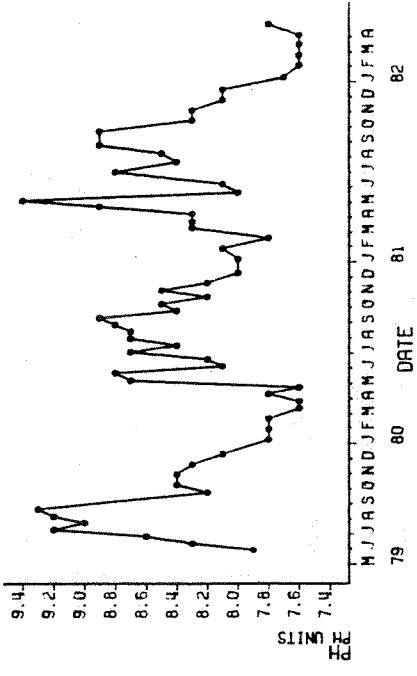
Conductivity in the South Saskatchewan River Basin was consistently highest in winter and lowest in summer (Figure 6 and Appendix Table B-1). Transition from high to low values occurred rapidly in spring at most sites. The return from low to high values was also rapid in fall at most sites. The exceptions were Site 1 (Bow River above Calgary) and Site 3 (Oldman River above Lethbridge), where the increase from low values in June to high values in winter was gradual. However, decrease to low values in spring was rapid at these two sites.

Conductivity was lower in the Bow River than in the Oldman and South Saskatchewan Rivers, with a mean value of 366  $\mu\text{S}/\text{cm}$  compared to 418 and 413  $\mu\text{S}/\text{cm}$ , respectively. Also, the pattern of conductivity trends at the Bow River sites was much smoother, particularly at upstream sites, than at Oldman River sites. Overall, conductivity was

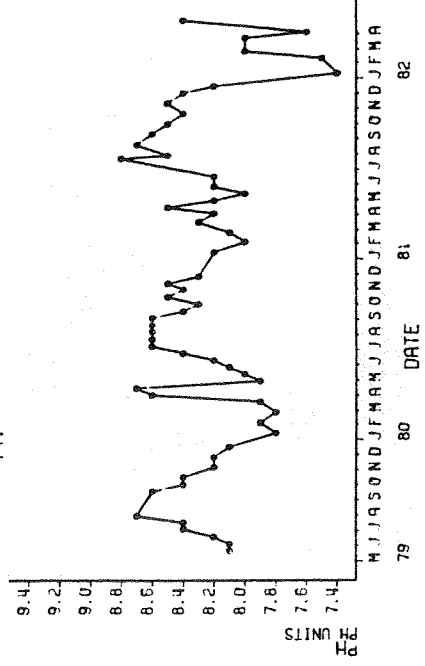
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 SOUTH SASKATCHEWAN RIVER  
 BELOW MEDICINE HAT  
 SITE 11  
 PARAMETER 10301L  
 PH



STATION OORT05BN2270  
 BOW RIVER AT THE MOUTH  
 SITE 7  
 PARAMETER 10301L  
 PH



STATION OORT05AG2095  
 OLDMAN RIVER AT THE MOUTH  
 SITE 8  
 PARAMETER 10301L  
 PH



STATION OORT05BM2215  
 BOW RIVER BELOW CARSELAND WEIR  
 SITE 5  
 PARAMETER 10301L  
 PH

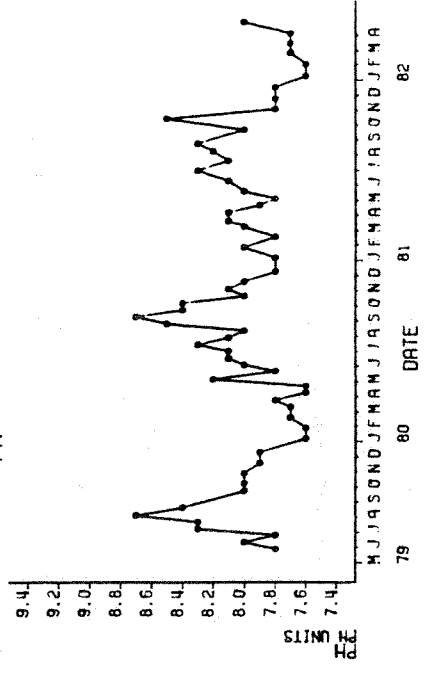
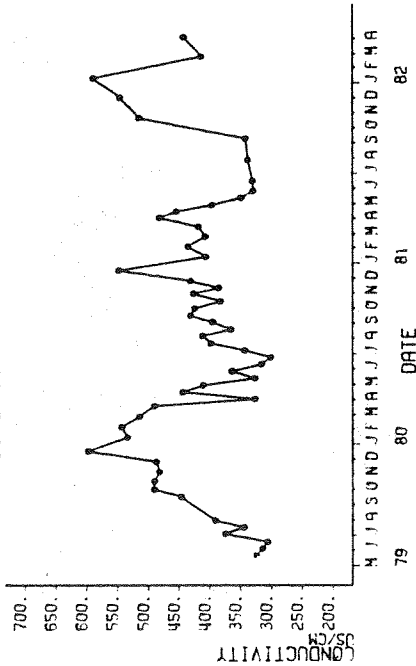


Fig. 5. Comparison of pH data from four sites in the study basin.

STATION 00A105AK2087  
SOUTH SASKATCHEWAN RIVER  
BELOW MEDICINE HAT  
SITE 11

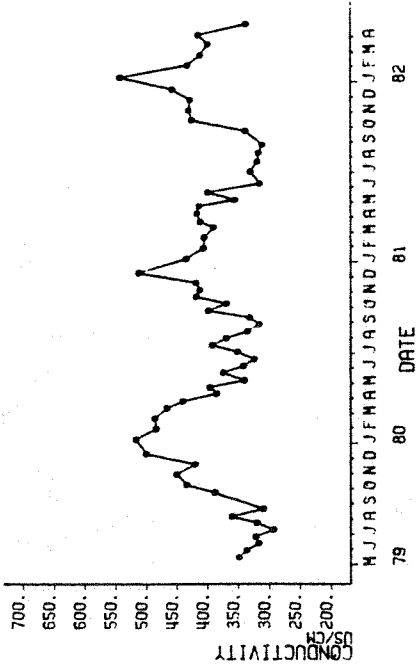
PARAMETER 020411  
CONDUCTIVITY



STATION 00A105BN2270

BOW RIVER AT THE MOUTH  
SITE 7

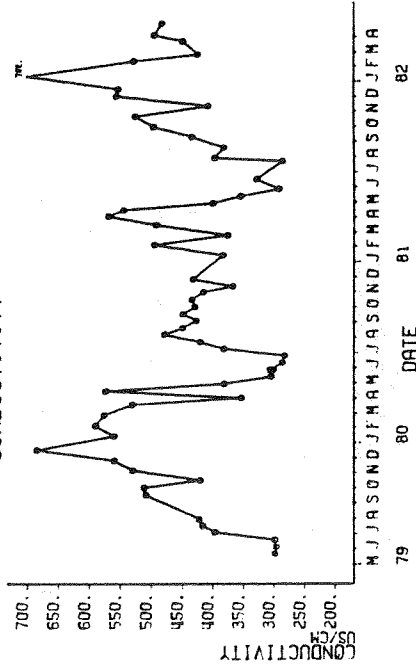
PARAMETER 020411  
CONDUCTIVITY



STATION 00A105AG2095

OLDMAN RIVER AT THE MOUTH  
SITE 8

PARAMETER 020411  
CONDUCTIVITY



STATION 00A105BM2215

BOW RIVER BELOW CARSELAND WEIR  
SITE 5

PARAMETER 020411  
CONDUCTIVITY

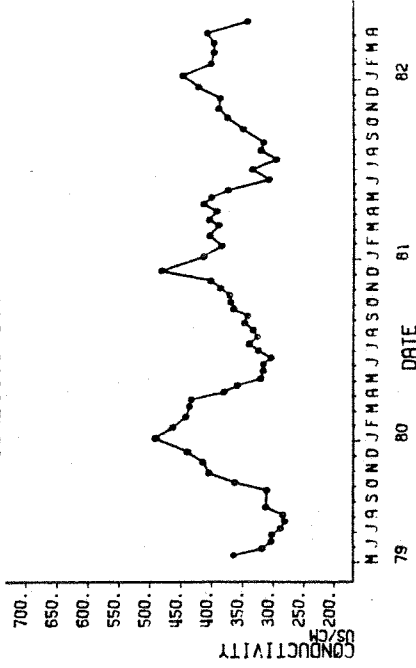


Fig. 6. Comparison of conductivity data from four sites in the study basin.

correlated with total alkalinity ( $r = 0.79$ ), dissolved inorganic carbon, ( $r = 0.70$ ) and chloride ( $r = 0.64$ ). Correlations of conductivity with dissolved inorganic carbon and chloride were improved for the Oldman and South Saskatchewan Rivers when each river was treated separately (Appendix Table A-7).

Statistical tests (Table 6) comparing data between years, showed that there was no significant difference between 1980 and 1981 values. However, when the seasons were compared separately, the differences between years were significant in most cases. A further test comparing data between seasons showed that the seasons were all significantly different with the exception of spring and summer in the South Saskatchewan River.

### 3.5 Alkalinity

Total alkalinity had a seasonal pattern of higher winter values and lower summer values (Figure 7 and Appendix Table B-1). The winter peak values were most pronounced in the Oldman, South Saskatchewan and lower Bow River sites. Small spring increases in concentration were also measured during April and May on all three rivers. Alkalinity values were correlated with dissolved inorganic carbon ( $r = 0.85$ ; Appendix Table A-7).

In the Bow River winter peak values increased at each downstream site from greater than about  $130 \text{ mg CaCO}_3/\text{L}$  at Site 1 to greater than  $160 \text{ mg CaCO}_3/\text{L}$  at Site 7. The increase to and decrease from the winter peak was gradual at Sites 1, 2, 5 and 6, though at Sites 5 and 6 a sharper winter peak was superimposed on this trend. At Sites

TABLE 6 COMPARISON BETWEEN 1980 AND 1981 DATA USING MANN-WHITNEY U TESTS AND BETWEEN YEARS FOR EACH SEASON USING KRUSKAL-WALLIS ONE-WAY ANOVA TESTS (\*p < .05, \*\*p < .01). COMPARISON BETWEEN SEASONS (YEARS COMBINED) USING MANN-WHITNEY U TESTS. SEASONS NOT SIGNIFICANTLY DIFFERENT ARE TABULATED (P-SPRING, S-SUMMER, F-FALL, W-WINTER).

	<u>TP</u>	<u>DP</u>	<u>DN</u>	<u>TURB</u>	<u>POC</u>	<u>COND</u>	<u>CL</u>	<u>Sl</u>
ALL DATA								
1980 vs 1981			**	**			*	
Spring	*		*	**		**	**	
Summer		*	*	**		*	**	**
Fall				**		**	**	*
Winter	**	**	**	**	*	**	**	**
Seasons	P-W S-F	none	P-F	S-F	S-F	none	P-S	P-W
BOW RIVER								
1980 vs 1981			*	**			**	
Spring				*		**	**	
Summer	*	**		**		**	**	**
Fall							*	
Winter	**	**	**	*		**	**	**
Seasons	P-F	P,S-F	P-F	S-F,W F-W	S-F,W F-W	none	P-F	none
OLDMAN RIVER								
1980 vs 1981			**	**				
Spring							**	**
Summer								
Fall				**		**	*	
Winter			**	**	**	**	**	
Seasons	S-F	P,S-F	P-F	S-F	S-F,W F-W	none	S-P,F,W F-P,W	P-W S-F
SOUTH SASKATCHEWAN RIVER								
1980 vs 1981							*	
Spring	**		**	**	*	**	**	
Summer		**	*	**		*	**	
Fall	**			**		**	**	**
Winter	**	**	**	**		**	**	
Seasons	S-F	S-F	P-F	S-F	S-F	P-S	P-S F-W	P-W S-F

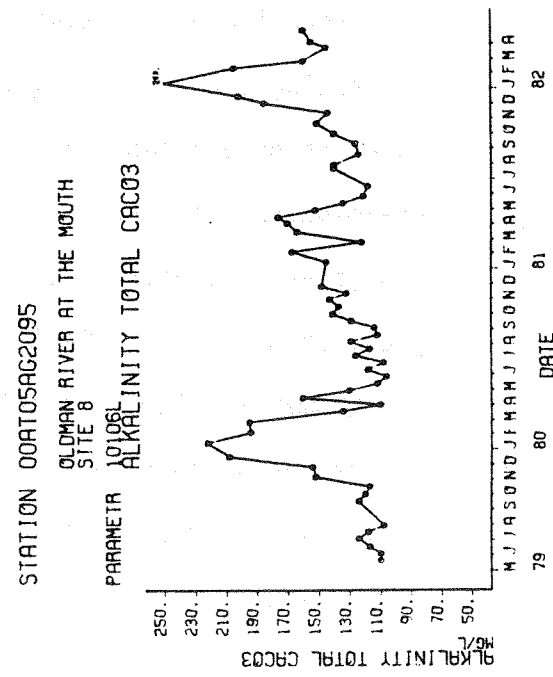
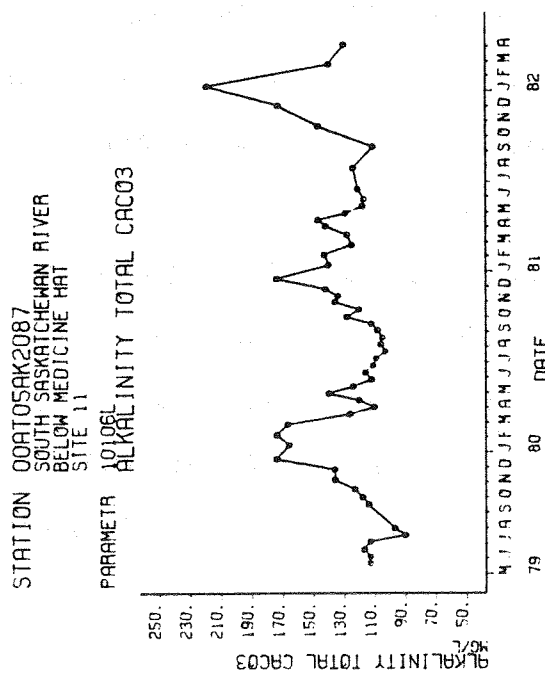
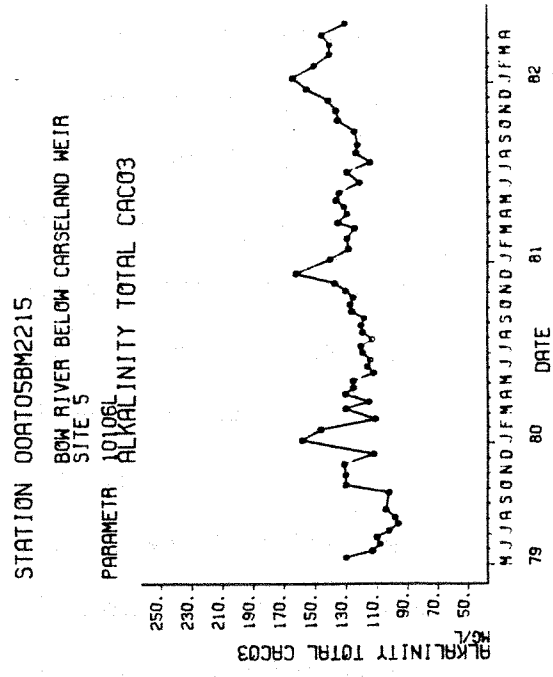
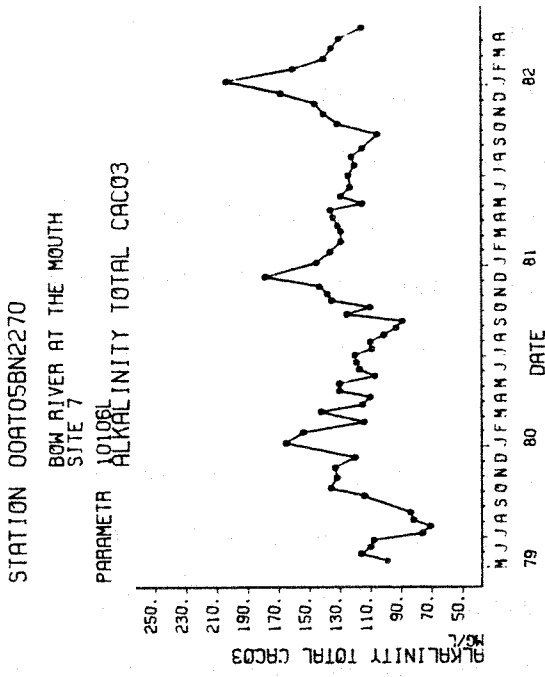


Fig. 7. Comparison of total alkalinity data from four sites in the study basin.

13 and 7, however, the decrease was gradual from the February high to the August low values (less than 100 mg CaCO<sub>3</sub>/L). The increase was more rapid to the winter high values at Sites 13 and 7.

In the Oldman River lowest values occurred around May. In 1979 and 1981 these were followed by constant to increasing values until October when concentration increased dramatically. In 1980, however, the concentration increase from May to winter was more gradual and the winter peak was less well-defined.

Alkalinity at the South Saskatchewan River sites showed a combination of Bow and Oldman River trends, with strongly defined winter highs and summer lows, and balanced, rapid-transition phases in spring and fall. Average alkalinity was 127 mg CaCO<sub>3</sub>/L in the South Saskatchewan River, 141 mg/L in the Oldman River, and 123 mg/L in the Bow River.

Phenolphthalein alkalinity values were highest in summer (averaging 0.6 to 21.2 mg/L) and lowest in winter (averaging 0 to 0.3 mg/L) (Appendix Table B-1). At Sites 1 and 2, in the Bow River, phenolphthalein alkalinity was detectable only in the summer. Further downstream, at Site 7, average summer values were 14.0 mg CaCO<sub>3</sub>/L, but phenolphthalein alkalinity was also detectable in spring and fall. In the Oldman and South Saskatchewan Rivers, the average summer values at six of the seven sites ranged from 3.3 (Site 3) to 7.0 mg CaCO<sub>3</sub>/L (Site 4). Values at Site 9 were higher than at the other sites (21.2 mg CaCO<sub>3</sub>/L).



### 3.6 Turbidity and Residues

Turbidity and residues, both non-filterable (NFR) and non-filterable fixed (NFFR), are highly correlated ( $r > 0.95$ , Appendix Table A-7). Highest turbidity values were measured in May/June of each year with lesser peaks in March/April (Figure 8, 9 and Appendix Table B-1). These two spring peak values were separated more distinctly in the Bow River than in the Oldman River. Within the Bow River, peak values at sites above the Bassano Dam were low, while those below Bassano were higher and more distinct. Smaller increases were also measured in October/November on the Bow River.

Turbidity values in the Oldman River (averaging 56 JTU) were much higher than those in the Bow River (averaging 7 JTU), and those in the South Saskatchewan River were intermediate (averaging 29 JTU). Residue peak values were more distinct in the Oldman than the Bow River, with non-filterable residue values greater than 500 mg/L occurring in May/June of each year (Appendix Table B-1). South Saskatchewan River sites reflected a combination of Bow and Oldman River characteristics with distinct residue peak values but reaching lower peak concentrations.

Statistical testing of turbidity data (Table 6) showed that values were significantly different in most cases between 1980 and 1981 and between years seasonally. A testing of seasonal differences showed that only differences in spring and fall values were not significant.

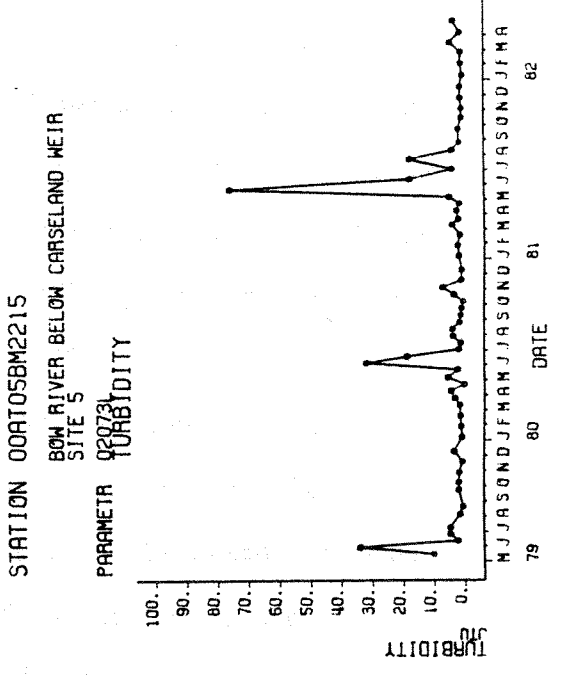
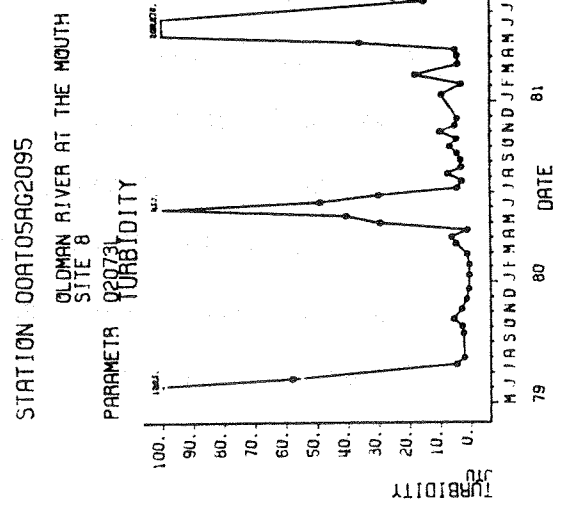
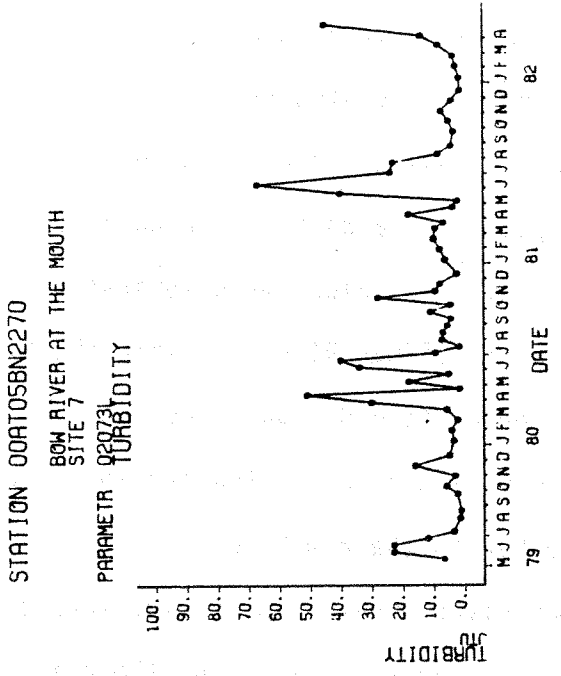
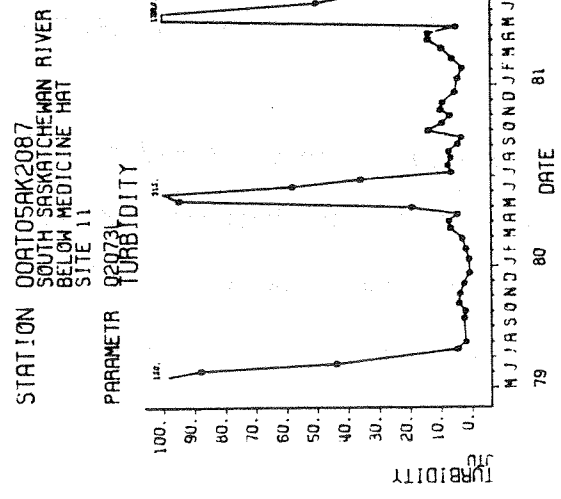


Fig. 8. Comparison of turbidity data from four sites in the study basin.

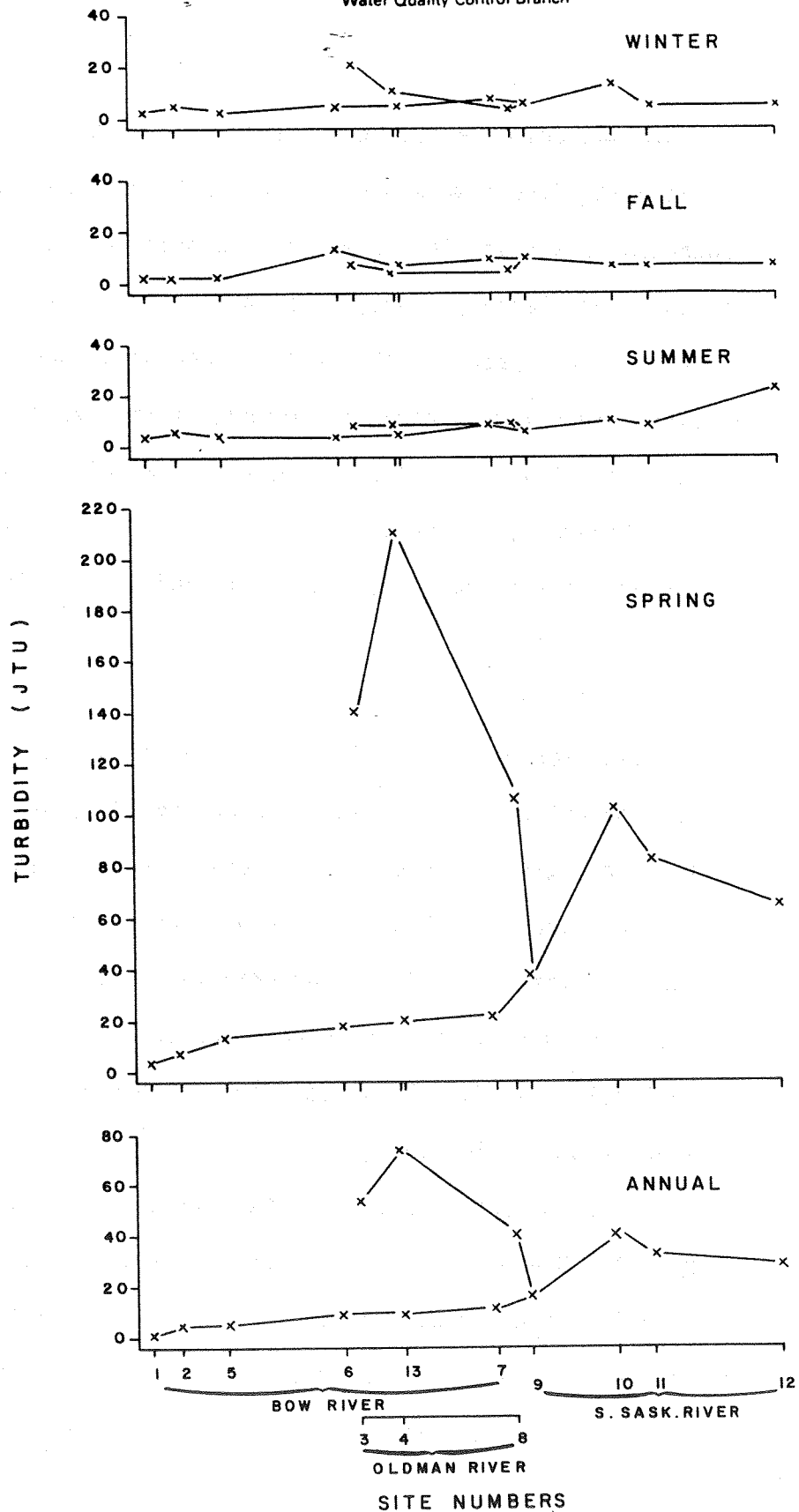


Fig. 9 : Annual and seasonal average values of turbidity at each site in the study basin.

### 3.7 Chloride

Average chloride (Cl) concentrations in the Bow, Oldman and South Saskatchewan Rivers were 4.4, 3.5 and 5.2 mg/L, respectively. Low concentrations (less than 2 mg/L) were measured in June/July in the Bow and South Saskatchewan, and slightly earlier in the Oldman River (Figure 10 and Appendix Table B-1). Concentrations increased rapidly at first, then more gradually from August to November, to higher winter concentrations. The drop-off to low values in spring was rapid. Generally, chloride concentrations were significantly different between years, both annually and seasonally (Table 6).

### 3.8 Silica

Collection of silica (Si) data began in January 1980. Peaks in silica concentration occurred twice during the year, in mid-winter and in late spring/early summer, at values of about 4 to 6 mg/L (Figure 11, 12 and Appendix Table B-1). Low values (less than 1 mg/L) were measured in late summer/fall and briefly in early spring. These fluctuations were less pronounced at upstream Bow River sites. Concentrations at Site 1 ranged from 3.0 to 4.8 mg/L and those at Site 2 ranged from 2.0 to 5.5 mg/L.

Silica concentrations were statistically similar between years (Table 6). Seasonally however, results were less consistent, with different seasons in each river showing statistically different results between years. When the seasons were compared, spring and winter results were similar, using the data from all three rivers combined. This was not true for Bow River data alone. In the Oldman and South Saskatchewan Rivers spring and fall were also similar.

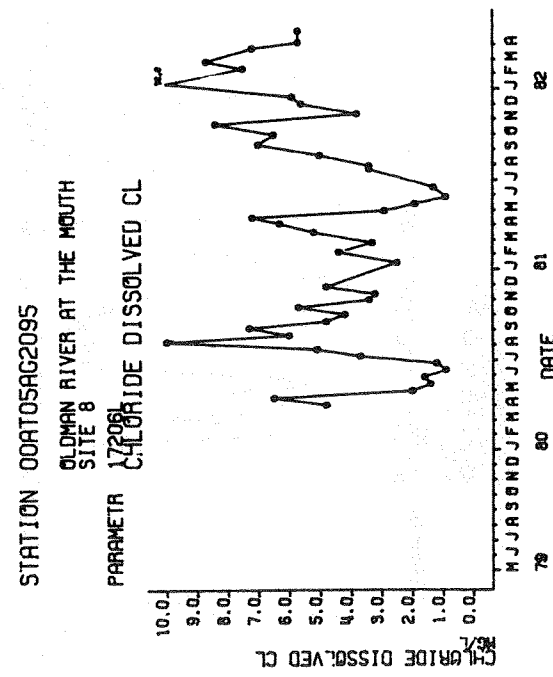
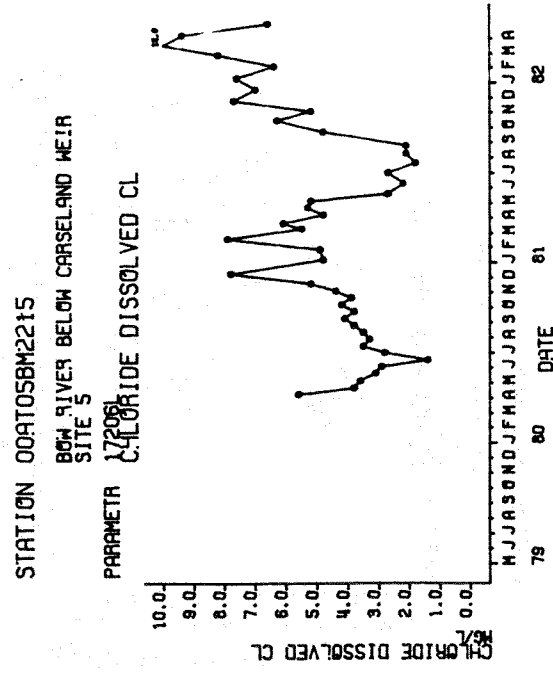
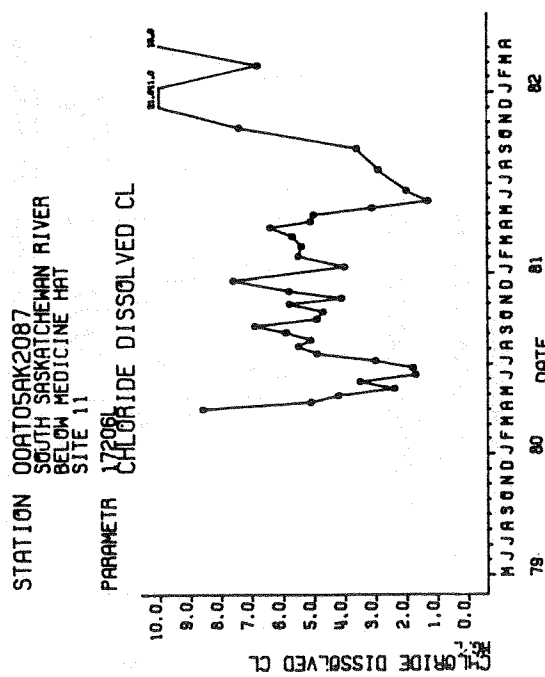
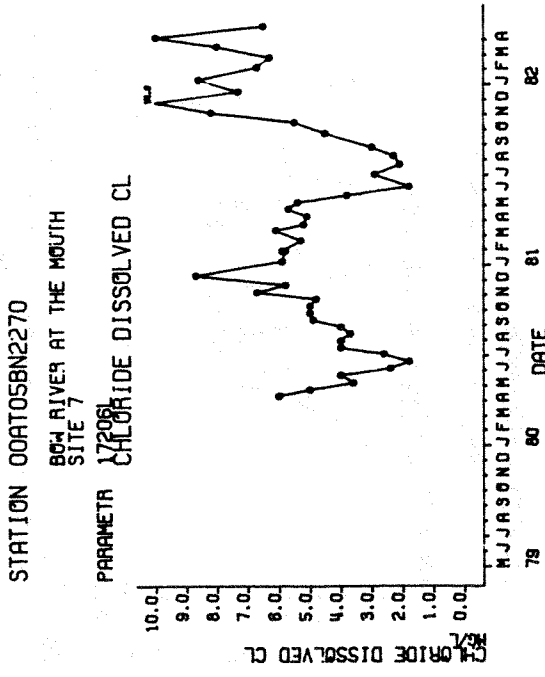


Fig. 10. Comparison of dissolved chloride data from four sites in the study basin.

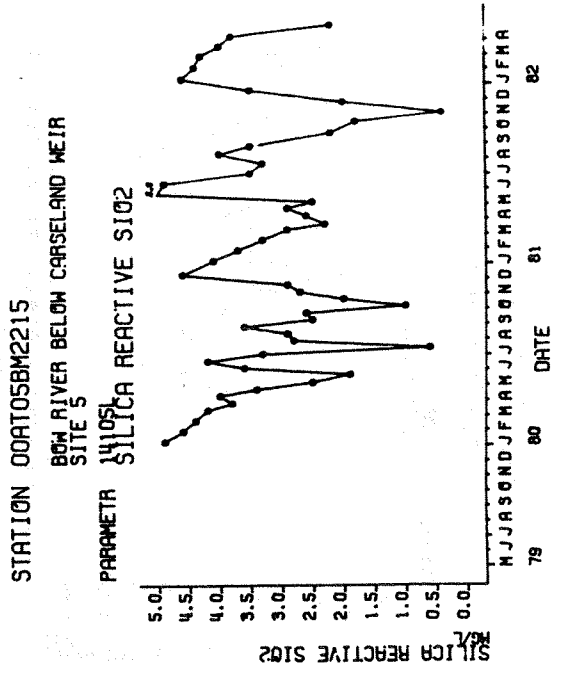
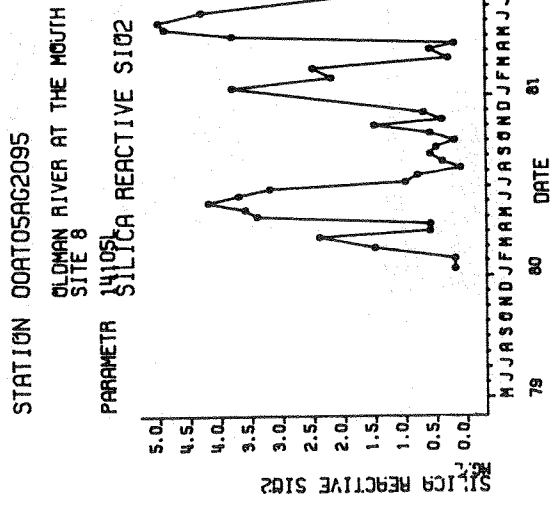
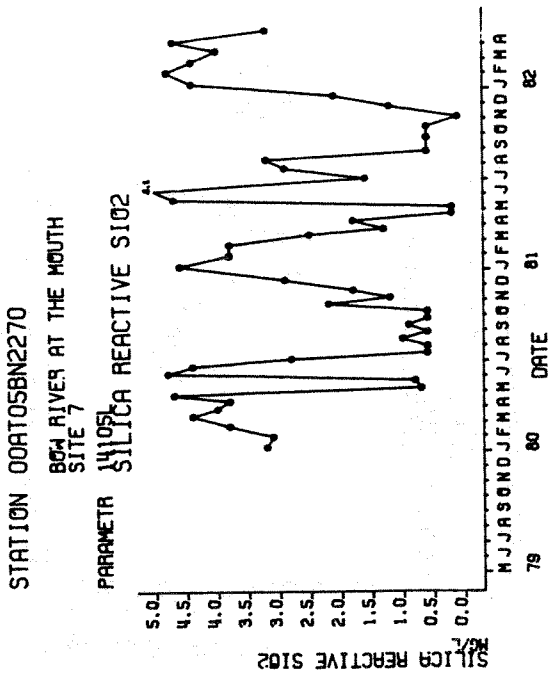
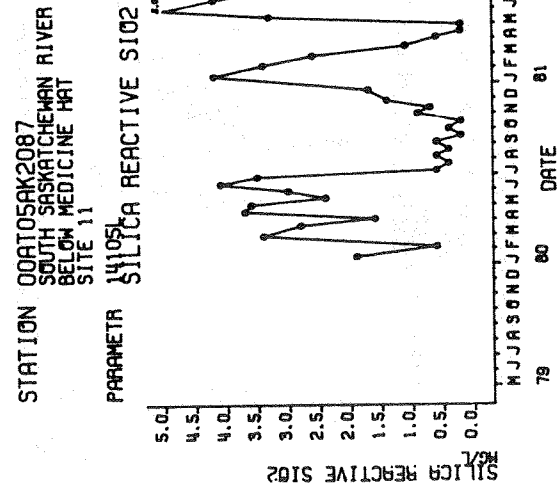


Fig. 11. Comparison of reactive silica data from four sites in the study basin.

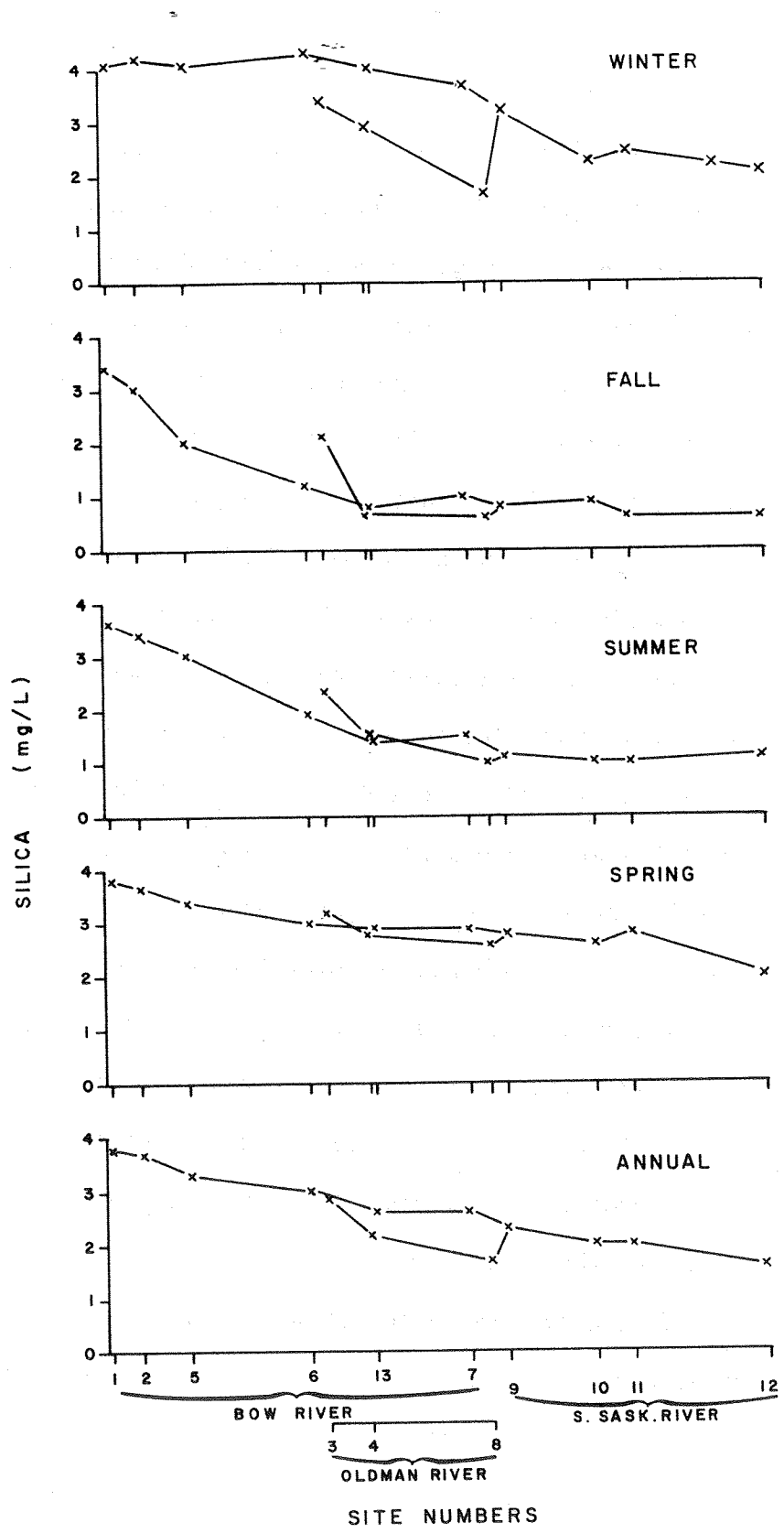


Fig. 12: Annual and seasonal average concentrations of reactive silica at each site in the study basin.

### 3.9 Carbon

Collection of three carbon forms, particulate organic (POC), dissolved organic (DOC), and dissolved inorganic (DIC) began in January 1980. Average concentrations of particulate organic carbon were higher in the Oldman (1.3 mg/L) and the South Saskatchewan Rivers (1.4 mg/L) than in the Bow River (0.9 mg/L). Particulate organic carbon was correlated with turbidity ( $r = 0.69$ ) and non-filterable residue ( $r = 0.72$ ). This correlation was stronger in the Oldman ( $r = 0.83$  and  $0.89$ ) than in the South Saskatchewan ( $r = 0.74$  and  $0.57$ ) or the Bow Rivers ( $r = 0.64$  and  $0.77$ ; Appendix Table A-7). The spring peak values of particulate organic carbon were apparent, however they were less pronounced in the Bow River than the turbidity peaks (Figure 13, 14 and Appendix Table B-1). One notable difference between turbidity peaks and particulate organic carbon patterns occurred at Site 2, Bow River below Calgary, where particulate organic carbon did not have any strong pattern over the sampling period. In fact, the correlation with turbidity was only 0.47, the lowest at any site.

Statistically, particulate organic carbon was not significantly different between years overall and seasonally in most cases (Table 6). Seasonal comparisons showed that spring was most often different from the other seasons.

Throughout the Basin, dissolved organic carbon followed a trend of higher values in April or May, but concentrations at other times of the year varied (Appendix Table B-1). Values at Site 1, Bow above Calgary, were generally lower than downstream sites, but this was not



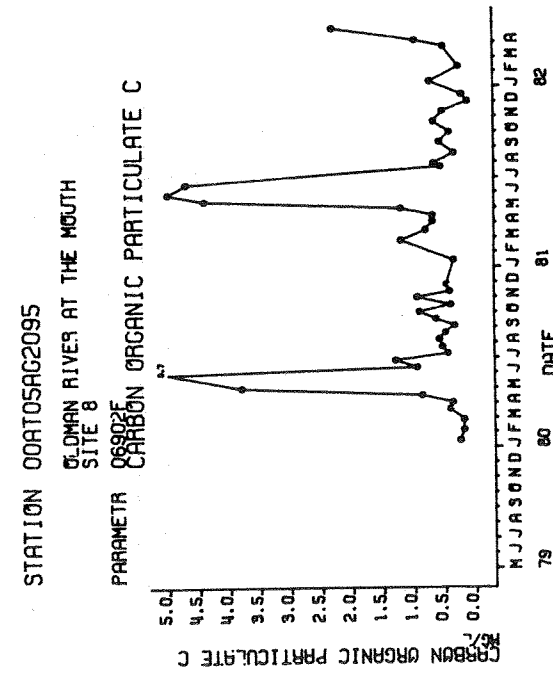
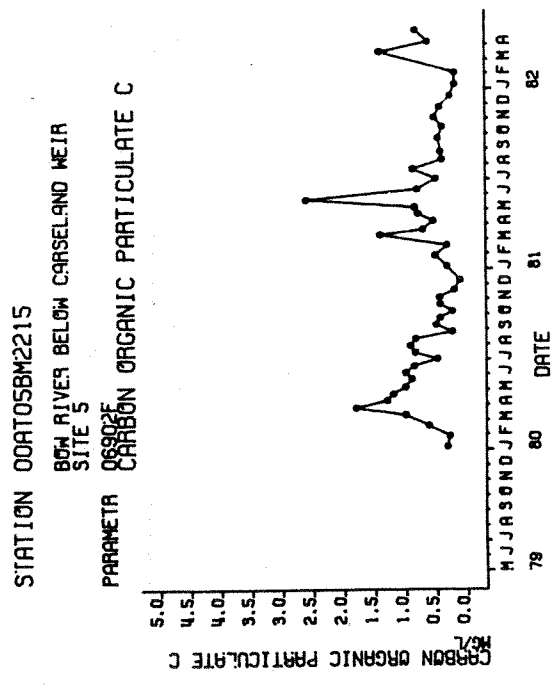
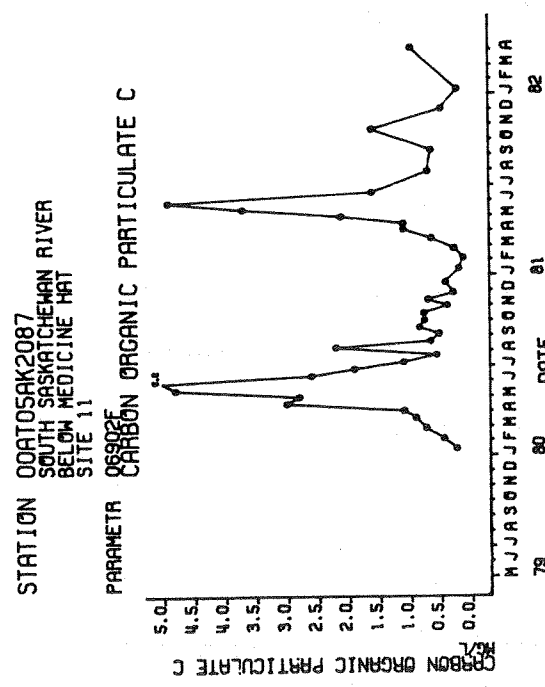
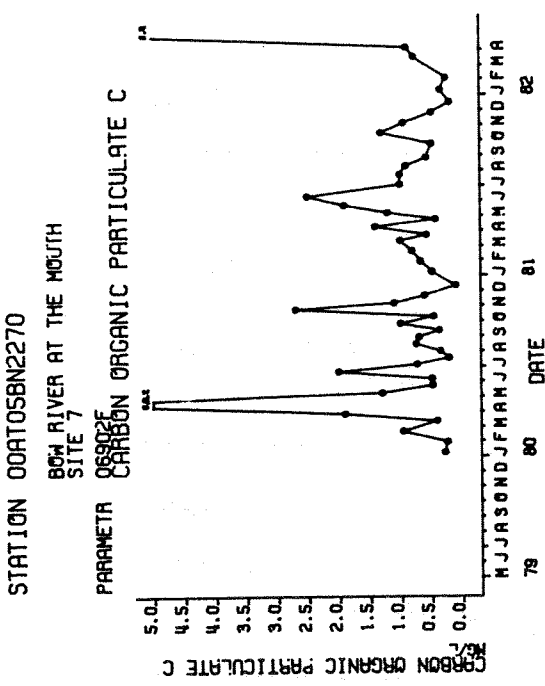


Fig. 13. Comparison of particulate organic carbon data from four sites in the study basin.

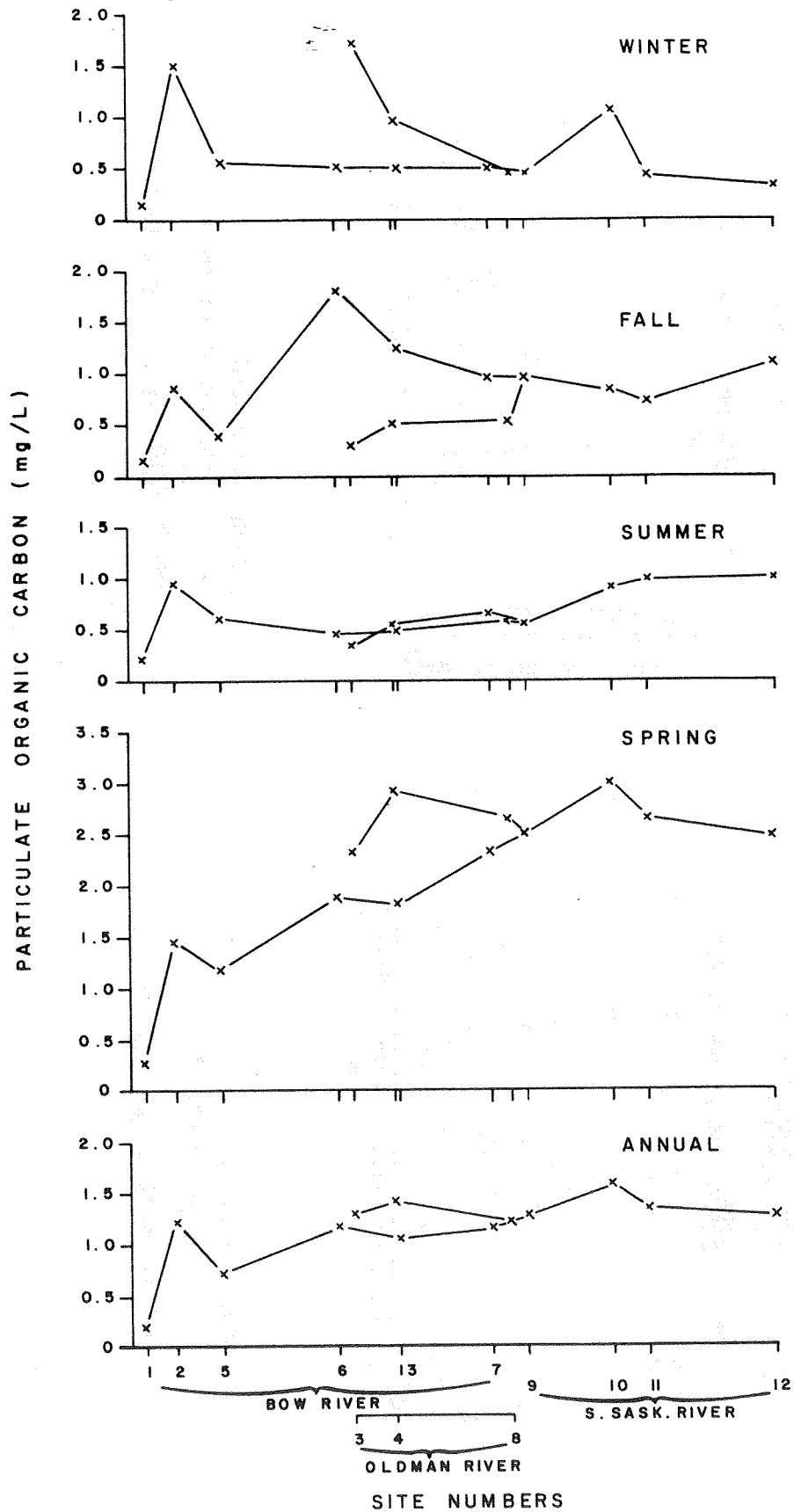


Fig.14 : Annual and seasonal average concentrations of particulate organic carbon at each site in the study basin.

as obvious at Site 3, Oldman above Lethbridge. Average concentrations of dissolved organic carbon in the Bow, Oldman and South Saskatchewan Rivers were 2, 3 and 3 mg/L, respectively.

Dissolved inorganic carbon concentrations were higher in winter and lower in summer, with variable transition patterns at different sites (Appendix Table B-1). Average concentrations in the Bow, Oldman and South Saskatchewan Rivers were 28.8, 32.5 and 29.2 mg/L, respectively.

### 3.10 Nitrogen

Nitrogen was collected and analyzed in several forms: nitrate plus nitrite (NIT); dissolved nitrogen (DN); ammonia ( $\text{NH}_3$ ); and particulate nitrogen (PN). Total nitrogen (TN) was the addition of dissolved nitrogen and particulate nitrogen.

#### 3.10.1 Nitrate/Nitrite and Total Nitrogen

Correlation coefficients between dissolved nitrogen (DN) and nitrate plus nitrite (NIT) were high, ranging from 0.87 in the Bow River to 0.94 and 0.96 in the Oldman and South Saskatchewan Rivers, respectively (Appendix Table A-7). Similarly, total nitrogen (TN) was correlated to dissolved nitrogen and nitrate/nitrite ( $r = 0.71$  for total nitrogen vs nitrate/nitrite in the Oldman River to  $r = 0.97$  for total nitrogen vs dissolved nitrogen in the Bow River). Since dissolved nitrogen and nitrate/nitrite were highly correlated only dissolved nitrogen trends will be discussed.

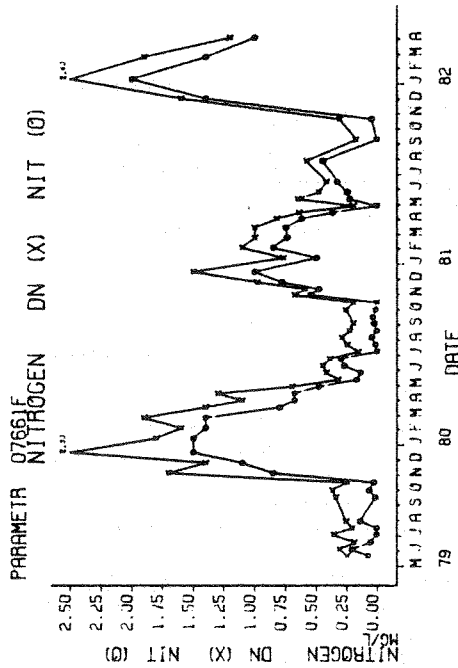
### 3.10.2 Dissolved Nitrogen

Throughout the Basin, dissolved nitrogen followed a general trend of high winter values and low summer values (Figure 15 and Appendix Table B-1). These seasonal fluctuations were strong in the Bow River, with the exception of Site 1, where dissolved nitrogen fluctuated between 0.05 and 0.32 mg/L. Otherwise, high winter values averaged from 2.16 to 1.84 mg/L and low summer values averaged from 1.12 to 0.28 mg/L (Figure 16). The winter values in 1981 were distinctly lower than winter values in 1980 and 1982.

In each season the highest concentrations of dissolved nitrogen were measured at Site 2 and values decreased at each downstream site to Site 7. A second trend was evident at these sites below Calgary. At Site 2 the low summer concentration was measured in July and began to increase immediately, but at each successive downstream site, the dissolved nitrogen concentrations stayed longer at the lower values. In fact, by Site 7, the low values were measured from July to the end of September.

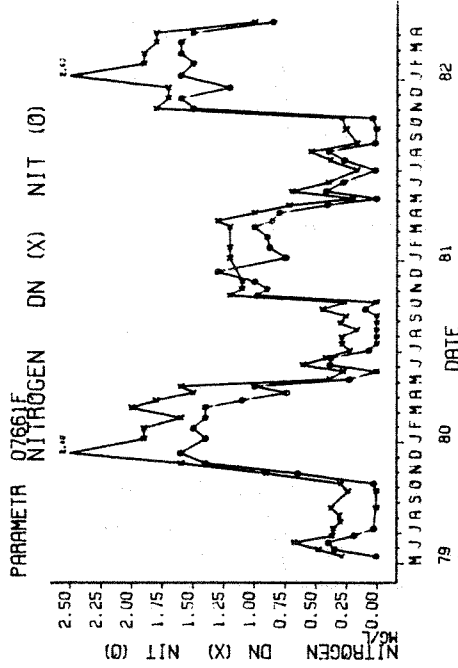
Dissolved nitrogen values in the Oldman River were generally lower than those in the Bow River below Calgary. Concentrations were less than 0.5 mg/L, in general, and the increase in concentration below Lethbridge was much less substantial than below Calgary. Higher values (averaging 0.69 mg/L) were measured over winter at each site, though these were not pronounced at Site 3 or in 1981 and were much lower than winter values in the Bow River.

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 SOUTH SASKATCHEWAN RIVER  
 BELOW MEDICINE HAT  
 SITE 11



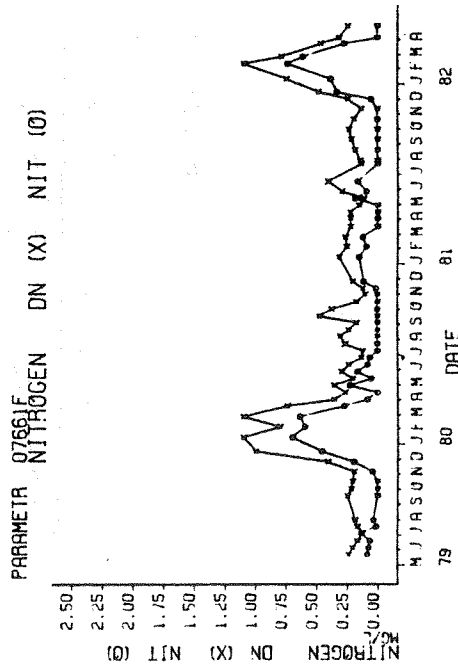
STATION 00AT05BN2270

BOW RIVER AT THE MOUTH  
 SITE 7



STATION 00AT05AC2095

OLDMAN RIVER AT THE MOUTH  
 SITE 8



STATION 00AT05BN2215

BOW RIVER BELOW CARSELAND WEIR  
 SITE 5

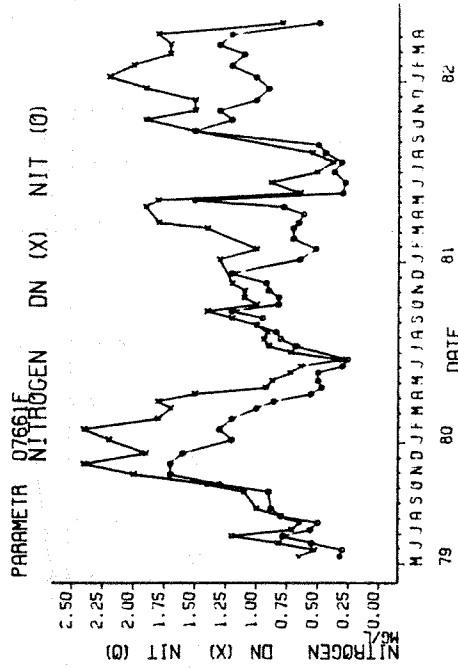


Fig. 15. Comparison of dissolved nitrogen and nitrate + nitrite data from four sites in the study basin.

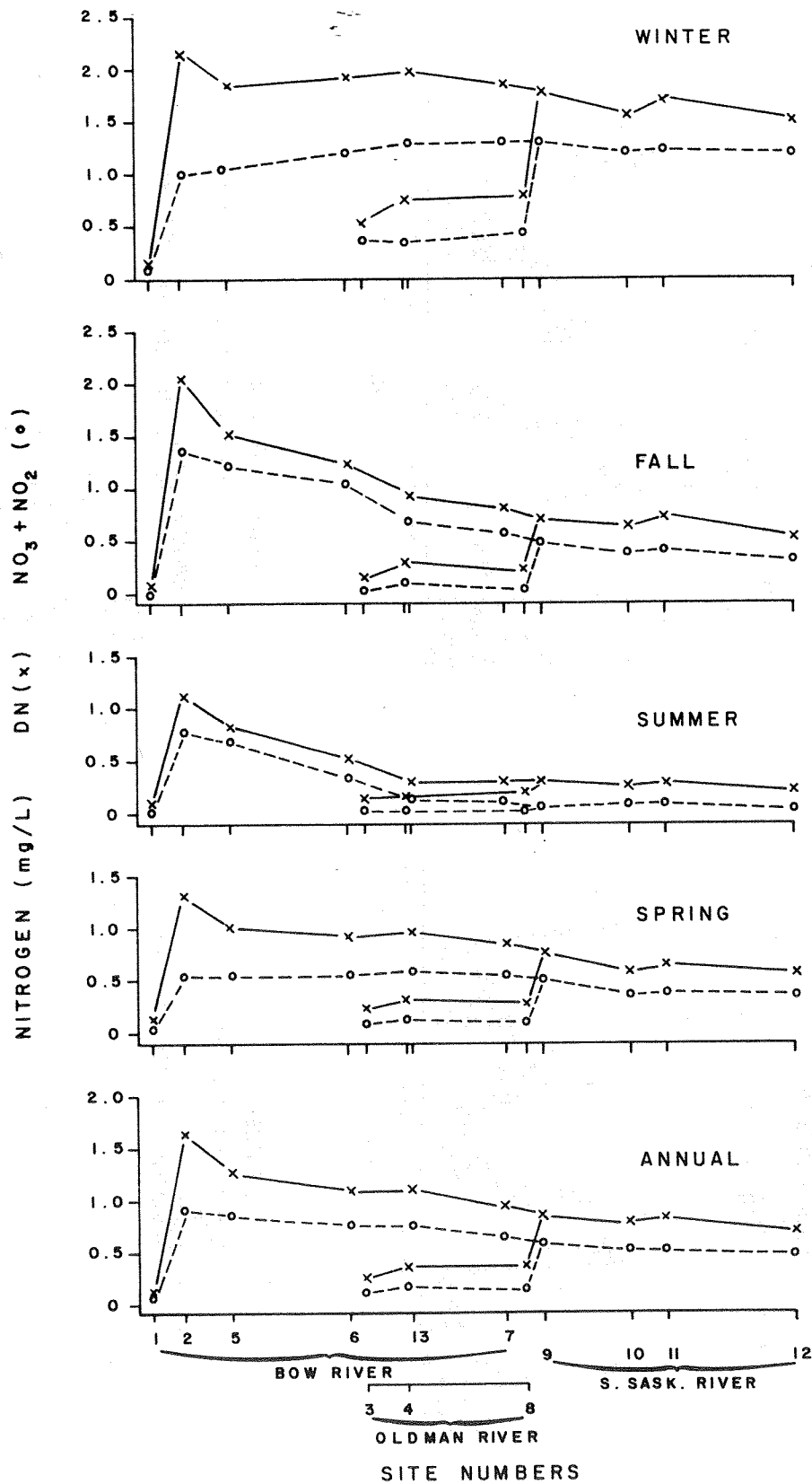


Fig. 16: Annual and seasonal average concentrations of dissolved nitrogen and nitrate + nitrite at each site in the study basin.

The South Saskatchewan River concentrations of dissolved nitrogen showed a seasonal pattern very similar to that in the lower Bow River sites. Longitudinally, there was very little change with only a slight reduction in concentration at each downstream site, except for a small increase below Medicine Hat.

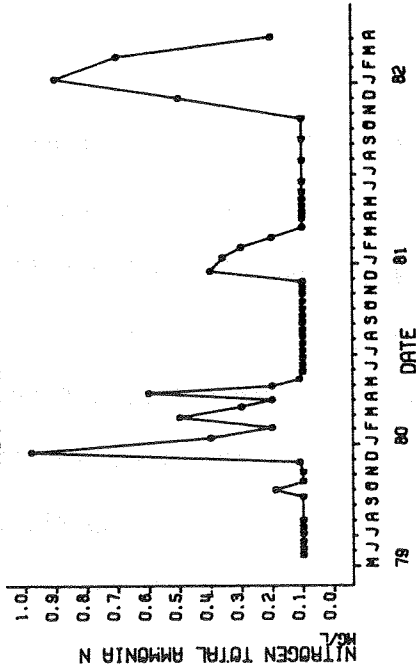
Statistical tests of dissolved nitrogen data (Table 6) showed that with data from all the rivers combined, there was a difference between 1980 and 1981 values. When the rivers were treated separately, however, comparisons between years and for each season were less consistent. Bow and Oldman River values were different between years and in winter; South Saskatchewan River values were not different between years, but were different in all seasons except fall. Comparisons between seasons showed consistently that spring and fall values were similar.

### 3.10.3 Ammonia

Ammonia concentrations at Site 1 and Site 3, upstream of Calgary and Lethbridge, were below detection ( $< 0.1$  mg/L) during the study except for three measurements. Highest ammonia concentrations were at Site 2, Bow River below Calgary, during winter and early spring (maximum of 2.9 mg/L). The size and duration of these high values decreased at successive downstream sites in the Bow River (Figure 17 and Appendix Table B-1) so that concentrations were mostly below detection for summer and fall. The peak in winter 1982 was much lower at Site 2 than in previous winters, though this was not true at downstream sites.

STATION 00AT05AK2087  
SOUTH SASKATCHEWAN RIVER  
BELOW MEDICINE HAT  
SITE 11

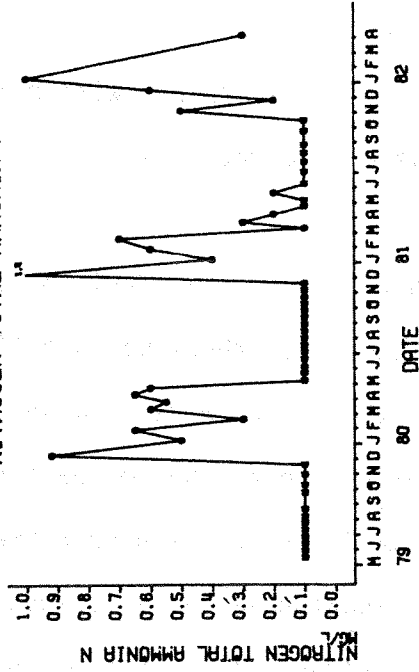
PARAMETER 07508  
NITROGEN TOTAL AMMONIA N



STATION 00AT05BN2270

BOH RIVER AT THE MOUTH  
SITE 7

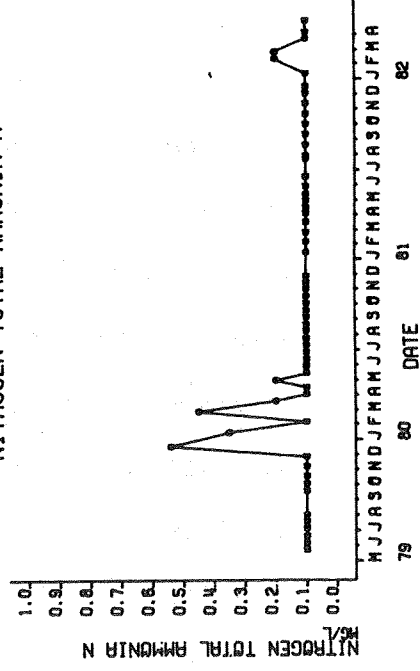
PARAMETER 07506  
NITROGEN TOTAL AMMONIA N



STATION 00AT05AG2095

OLDMAN RIVER AT THE MOUTH  
SITE 8

PARAMETER 07508  
NITROGEN TOTAL AMMONIA N



STATION 00AT05BM2215

BOH RIVER BELOW CARSELAND MEIR  
SITE 5

PARAMETER 07506  
NITROGEN TOTAL AMMONIA N

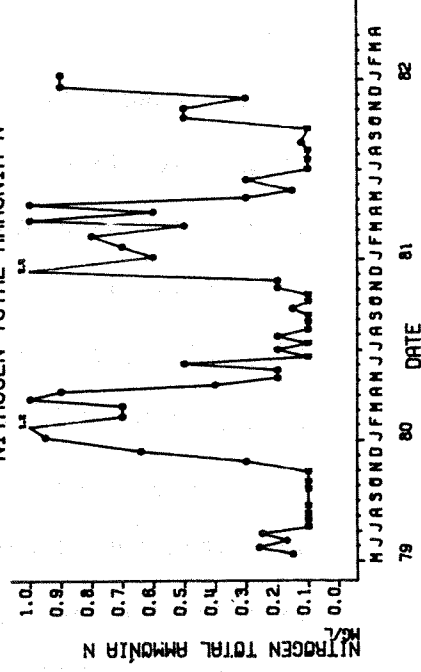


Fig. 17. Comparison of total ammonia nitrogen data from four sites in the study basin.



The trend of decreasing winter peaks of ammonia was continued through the South Saskatchewan River sites except at Site 11, below Medicine Hat, where peaks were slightly higher. In the Oldman River below Lethbridge at Sites 4 and 8, ammonia concentrations were at detection level except in winter and early spring. Peak values of 0.8 mg/L were measured except in winter 1981, when no peak developed.

#### 3.10.4 Particulate Nitrogen

Particulate nitrogen concentrations in the Bow River (Figure 18 and Appendix Table B-1) fluctuated with several single high value peaks (greater than 0.3 mg/L). These were inconsistent among sites, but tended to occur in spring and fall. Concentrations at Site 2 were generally higher throughout the study period (averaging 0.22 mg/L) than at the other Bow River sites (averaging 0.05 to 0.19 mg/L).

Peaks in particulate nitrogen were more consistent in the Oldman River, and recurred in May/June of each year at all sites. Additional high values were measured in winter 1981 and fall 1979. In the South Saskatchewan River, particulate nitrogen peaks in spring/early summer were well-defined, as was a peak in fall 1981. Average concentrations in both rivers ranged from 0.18 to 0.27 mg/L.

#### 3.11 Phosphorus

The five forms of phosphorus measured in the river - total (TP), total inorganic (TIP), dissolved (DP), dissolved inorganic (DIP) and dissolved reactive (OP) followed similar trends in many cases. This

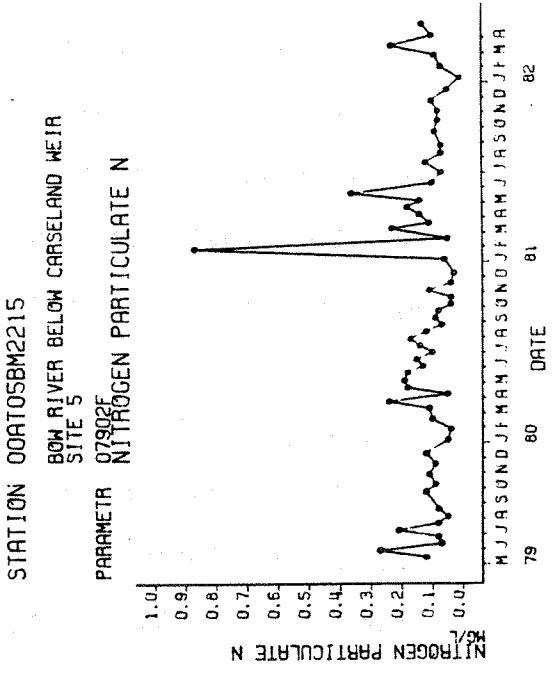
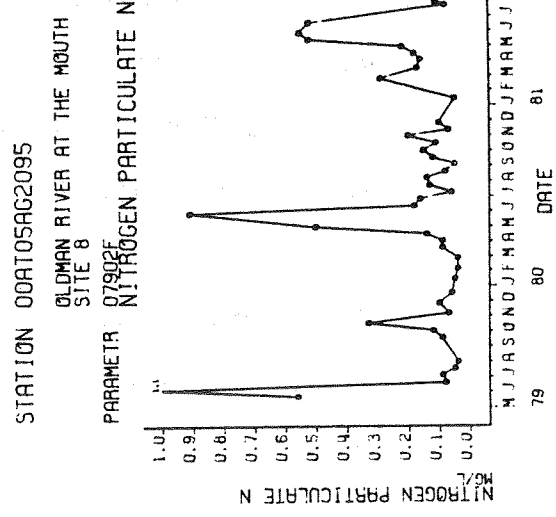
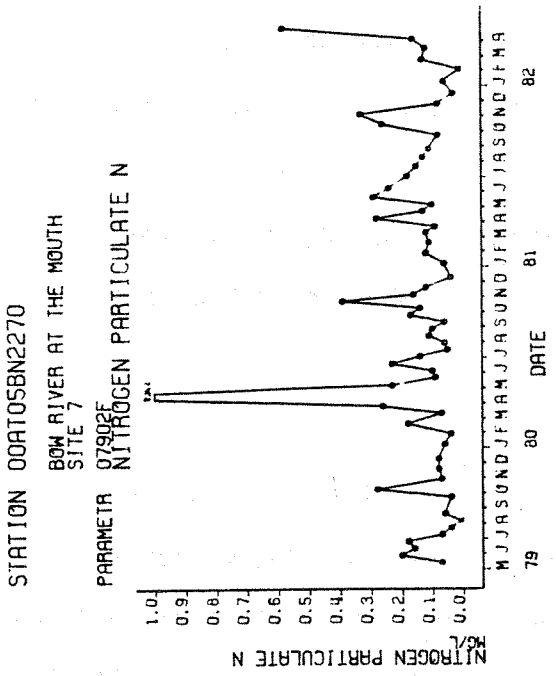
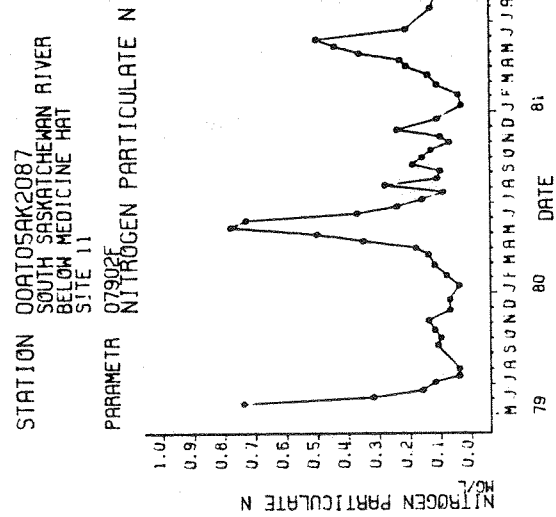


Fig. 18. Comparison of particulate nitrogen data from four sites in the study basin.

association was tested statistically using the combined data and treating each river separately (Appendix Table A-7). In all three rivers, total inorganic phosphorus and total phosphorus were highly correlated ( $r = 0.96 - 0.98$ ), as were dissolved reactive phosphorus, dissolved phosphorus and dissolved inorganic phosphorus ( $r = 0.96 - 0.996$ ). The dissolved forms were more highly correlated to total phosphorus in the Bow ( $r = 0.88 - 0.99$ ) than in the other two rivers ( $r = 0.04 - 0.29$ ). The most significant differences between the two groupings occurred during the spring high flow period in the Oldman and South Saskatchewan Rivers.

Data from the Basin were compared between years, and phosphorus concentrations were not significantly different (Table 6) between 1980 and 1981. Seasonal comparison, however, showed that winter values were different between years. When each river was considered separately results were quite different. The Oldman River showed no significant differences between years either annually or seasonally, while the Bow River values were different between years in summer and winter. South Saskatchewan River values were significantly different in every season for either total or dissolved phosphorus.

A second comparison was made between seasons, rather than between years (Table 6). For total phosphorus in the Bow River, spring and fall values were not significantly different, while summer and fall values were similar in the Oldman and South Saskatchewan Rivers. Seasonal comparisons for dissolved phosphorus were close to those of total phosphorus. In addition, summer and fall values for the Bow River, and spring and fall values for the Oldman River, were not significantly different.

Phosphorus concentrations throughout the Basin generally followed an annual pattern of high values in winter and low values in summer (Figure 19, 20 and Appendix Table B-1). There were, however, distinct differences between the rivers. For the purposes of description of trends, total and dissolved phosphorus concentrations will be discussed.

### 3.11.1 Bow River

At Site 1 above Calgary, phosphorus concentrations were low compared to all other Bow River sites, and annual patterns were not apparent. Total phosphorus fluctuated between 0.003 and 0.018 mg/L through the study period with a slightly higher average seasonal concentration in spring. Dissolved phosphorus remained at detection levels (0.003 mg/L) throughout most of the year.

Two longitudinal trends were apparent at the sites below Calgary. First, Site 2, consistently, had the highest phosphorus concentrations, and these concentrations decreased at each successive site downstream. Second, the annual pattern of high and low concentrations was slightly modified by the lengthening of time that low summer values were recorded at each downstream site.

At Site 2 highest total phosphorus concentrations were measured in November or December (from 0.43 mg/L in 1980 to 0.80 mg/L in 1979) and lowest concentrations (< 0.10 mg/L) were measured from May to August in different years. These peak high values were not maintained for long periods. The concentrations decreased from the peak winter value to relatively constant levels for most of the winter before

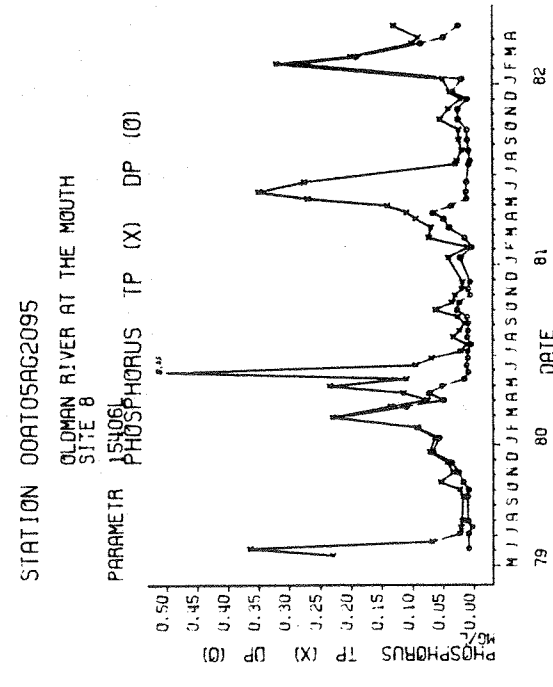
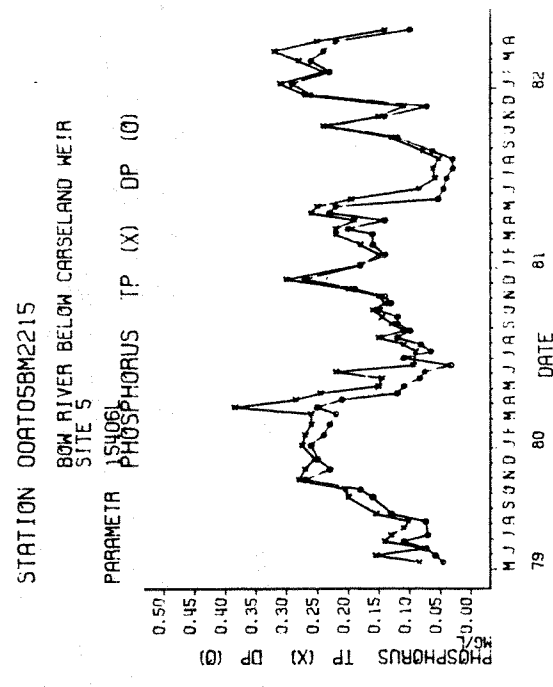
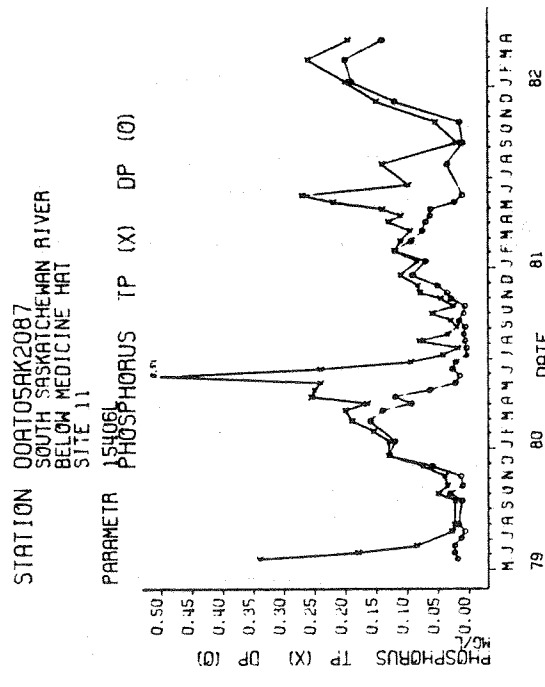
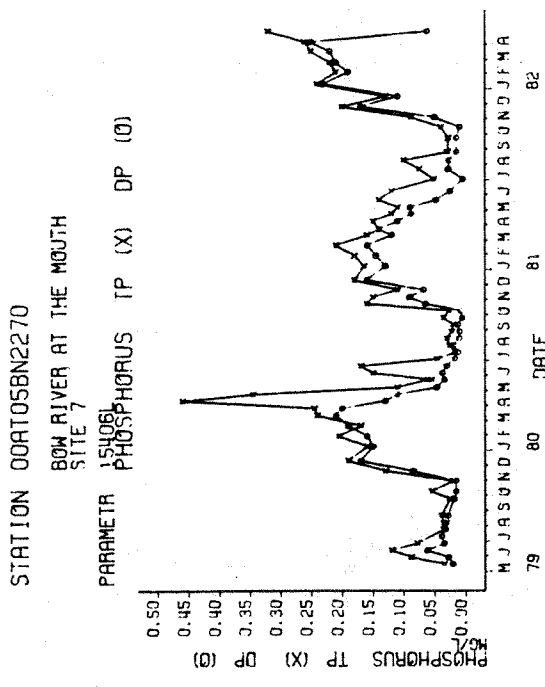


Fig. 19. Comparison of total and dissolved phosphorus data from four sites in the study basin.

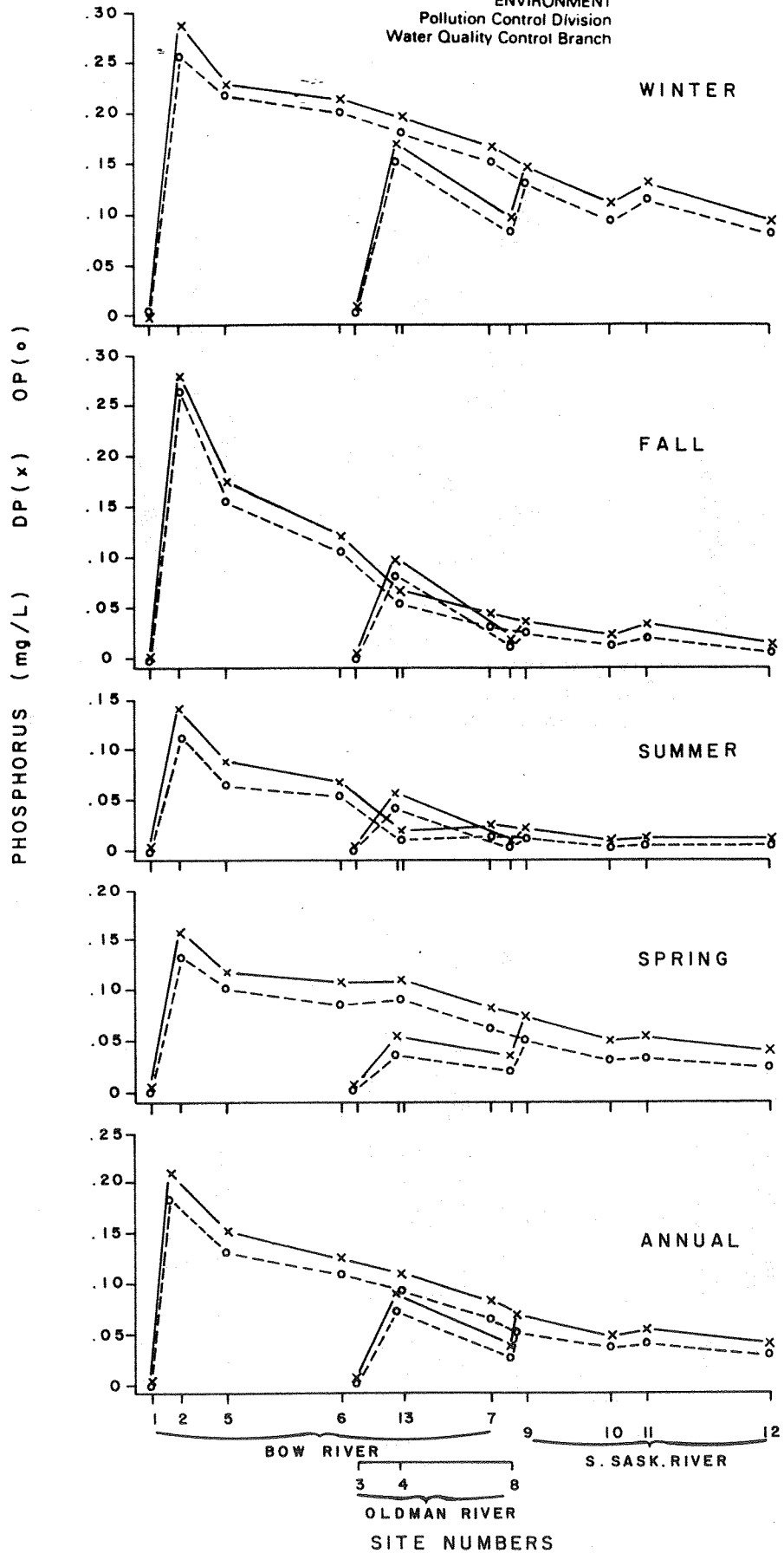


Fig. 20 : Annual and seasonal average concentrations of dissolved (DP) and dissolved reactive (OP) phosphorus data at each site in the study basin.

decreasing rapidly to low values in spring. The increase in concentrations from the low values to late summer/fall values was less consistent between years. In 1979, phosphorus increased from May through June, then decreased to low values for July and August before increasing to the December peak. In 1980, the concentration increased from a low in early June to constant levels for the months of September and October. There was also a small peak value in mid-July. In 1981, the low concentration was measured in early August and the increase to December was broken only by a drop in concentration in mid-November.

Concentrations of dissolved phosphorus followed the same trends as total phosphorus at Site 2, except in summer 1981, when they decreased to low levels earlier (May through July).

Total phosphorus concentrations at Site 5 below the Carseland weir increased less rapidly from summer low values (less than 0.05 mg/L) to winter high values than at Site 2 (Figure 19). In 1979, concentrations increased from August through October. Winter values of about 0.27 mg/L (with a peak total phosphorus value of 0.43 mg/L in April) decreased through spring 1980 to a low in June. Phosphorus concentrations in 1980 rose steadily from June to October, climbed rapidly to peak in December (0.30 mg/L), decreased to mid-January and increased again until April 1981. The summer low in 1981 extended through June and July. Concentrations rose from August to peak at 0.24 mg/L in October, dropped again in November before increasing to winter values of 0.24 to 0.32 mg/L. Dissolved phosphorus concentrations followed the total phosphorus trends except in the spring when they decreased to low values more rapidly.

Trends in phosphorus concentrations at Site 6 (below Bassano Dam) were similar to those at Site 5, though the concentration increase in the fall of 1979 was later, and did not reach winter values until December. Absolute values were generally lower (Appendix Table B-1). In addition, peak total phosphorus concentrations (greater than 0.40 mg/L) were measured in March and October 1981, but dissolved phosphorus did not show corresponding peaks.

Sites 13 and 7 showed similar trends in phosphorus concentration, with Site 7 concentrations slightly lower (Figure 19, 20 and Appendix Table B-1). Summer low values (averaging 0.042 mg/L) were separated from winter high values (averaging 0.202 mg/L) by rapid concentration changes. Spring and fall total phosphorus concentrations were less consistent between sites, and averaged 0.199 and 0.127 mg/L at Site 13 and 0.177 and 0.074 mg/L at Site 7, respectively.

As with concentrations at other sites, values of dissolved and total phosphorus diverged in spring, when those of dissolved phosphorus decreased before those of total phosphorus. There were also peak concentrations in total phosphorus at Site 13 in October 1980 and 1981, which dissolved phosphorus did not have. The decrease in dissolved phosphorus concentration began in March 1980 and in April 1981. This type of yearly variation results from variation in climate, discharge and biological activity.



### 3.11.2 Oldman River

Low phosphorus concentrations were measured above Lethbridge (Site 3) and the highest concentrations were measured below Lethbridge (Site 4). Values at Site 8 were less than those at Site 4. The relative peak value below Lethbridge was, however, much lower than that below Calgary in the Bow River.

Total phosphorus at Site 3 stayed at relatively low levels (0.01 - 0.03 mg/L) for most of the year. There were peak values in June 1979, in April to July and December 1980, and in February and April to June 1981 (Appendix Table B-1). Dissolved phosphorus did not have the same peak values but fluctuated from detection level (0.003 mg/L) to 0.019 mg/L.

At Sites 4 and 8 large peak values in total phosphorus concentration (greater than 0.3 mg/L) were measured in June 1979, May 1980 and May/June 1981. High values of total phosphorus, when dissolved phosphorus was also high, were measured throughout the winters of 1980 and 1982; there were peak values in January/February of both years (Figure 19, 20 and Appendix Table B-1). The 1981 winter peak value did not develop significantly. Concentrations of total phosphorus were lowest at Site 4 in July, and followed peak values immediately. In 1979 and 1981, concentrations increased until September and stayed relatively constant until November before increasing again. In 1980, phosphorus declined from September to November and increased to slightly higher concentrations in winter 1981. Concentrations of dissolved phosphorus deviated from total phosphorus trends in the spring. Dissolved phosphorus decreased to low values from May to July, when total phosphorus concentrations increased.

At Site 8 general trends in phosphorus concentration were similar, but values stayed lower for longer periods than at Site 4 (Figure 19). Phosphorus values at Site 8 remained below 0.05 mg/L from July to December for total phosphorus and from May to December for dissolved phosphorus.

### 3.11.3 South Saskatchewan River

Phosphorus concentrations in the South Saskatchewan River combine trends shown in the Bow and Oldman Rivers. Low concentrations of dissolved phosphorus were measured from May to October with a rapid increase in late fall to higher winter values (0.094-0.146 mg/L). These values decreased again in spring (Figure 19, 20 and Appendix Table B-1). Very large differences between total and dissolved phosphorus were measured from March to July, with total phosphorus values peaking, while dissolved phosphorus values decreased.

From upstream to downstream, concentrations of phosphorus decreased along the length of the river, with the exception of the site below Medicine Hat. However, the increase in phosphorus at Site 11 was much lower than those below the other two major cities.

### 3.11.4 Ratio of Phosphorus Forms

The ratios of several phosphorus forms were calculated both annually and seasonally (Table 7). Overall, the ratios of total inorganic phosphorus (TIP) to total phosphorus (TP), dissolved

TABLE 7 ANNUAL AND SEASONAL RATIO OF PHOSPHORUS FORMS IN THE BASIN OVERALL AND IN EACH RIVER SEPARATELY. VALUES MEASURED AT THE DETECTION LIMIT OF 3 µg/L WERE INCLUDED AND GIVEN THE VALUE 2.9 µg/L

<u>ANNUAL</u>	<u>TIP/TP</u>	<u>DIP/DP</u>	<u>OP/DP</u>
Basin	.79	.78	.69
Bow	.83	.85	.78
Oldman	.75	.75	.63
S. Saskatchewan	.75	.67	.57
<u>SPRING</u>			
Basin	.82	.76	.64
Bow	.84	.84	.77
Oldman	.81	.68	.52
S. Saskatchewan	.81	.68	.53
<u>SUMMER</u>			
Basin	.67	.69	.60
Bow	.73	.77	.65
Oldman	.64	.74	.67
S. Saskatchewan	.56	.50	.46
<u>FALL</u>			
Basin	.75	.74	.65
Bow	.81	.84	.77
Oldman	.72	.76	.63
S. Saskatchewan	.66	.55	.46
<u>WINTER</u>			
Basin	.90	.92	.86
Bow	.92	.95	.92
Oldman	.82	.85	.72
S. Saskatchewan	.92	.93	.85

inorganic phosphorus (DIP) to dissolved phosphorus (DP) and dissolved reactive phosphorus (OP) to dissolved phosphorus were 0.79, 0.78 and 0.69, respectively, and ratios in the Bow River were higher than those in the Oldman and South Saskatchewan Rivers. Seasonally, lowest ratios were measured in summer and highest ratios were measured in winter. The only exceptions were the low spring ratios of dissolved inorganic to dissolved phosphorus, and dissolved reactive to dissolved phosphorus, in the Oldman River.

The ratio of dissolved phosphorus to total phosphorus was calculated at each site both annually and seasonally (Figure 21). On an annual basis, Bow River sites had a larger component of dissolved phosphorus than Oldman and South Saskatchewan River sites. On a seasonal basis, however, Site 4 below Lethbridge, in summer and fall, had high ratios of dissolved to total phosphorus relative to Sites 13 and 7 in the Bow River. Overall, seasonal trends throughout the Basin are shown by combining data for each season from each site. Winter ratios were highest, and averaged 0.81, followed by fall (0.63), summer (0.52) and spring (0.43).

Sites 1 and 3, upstream of Calgary and Lethbridge, respectively, had lower ratios than Sites 2 and 4, downstream of each of these cities, respectively (Figure 1). The relationship between upstream and downstream sites was not as evident around Medicine Hat. The change in ratios at downstream sites was quite different between the rivers and between the seasons.

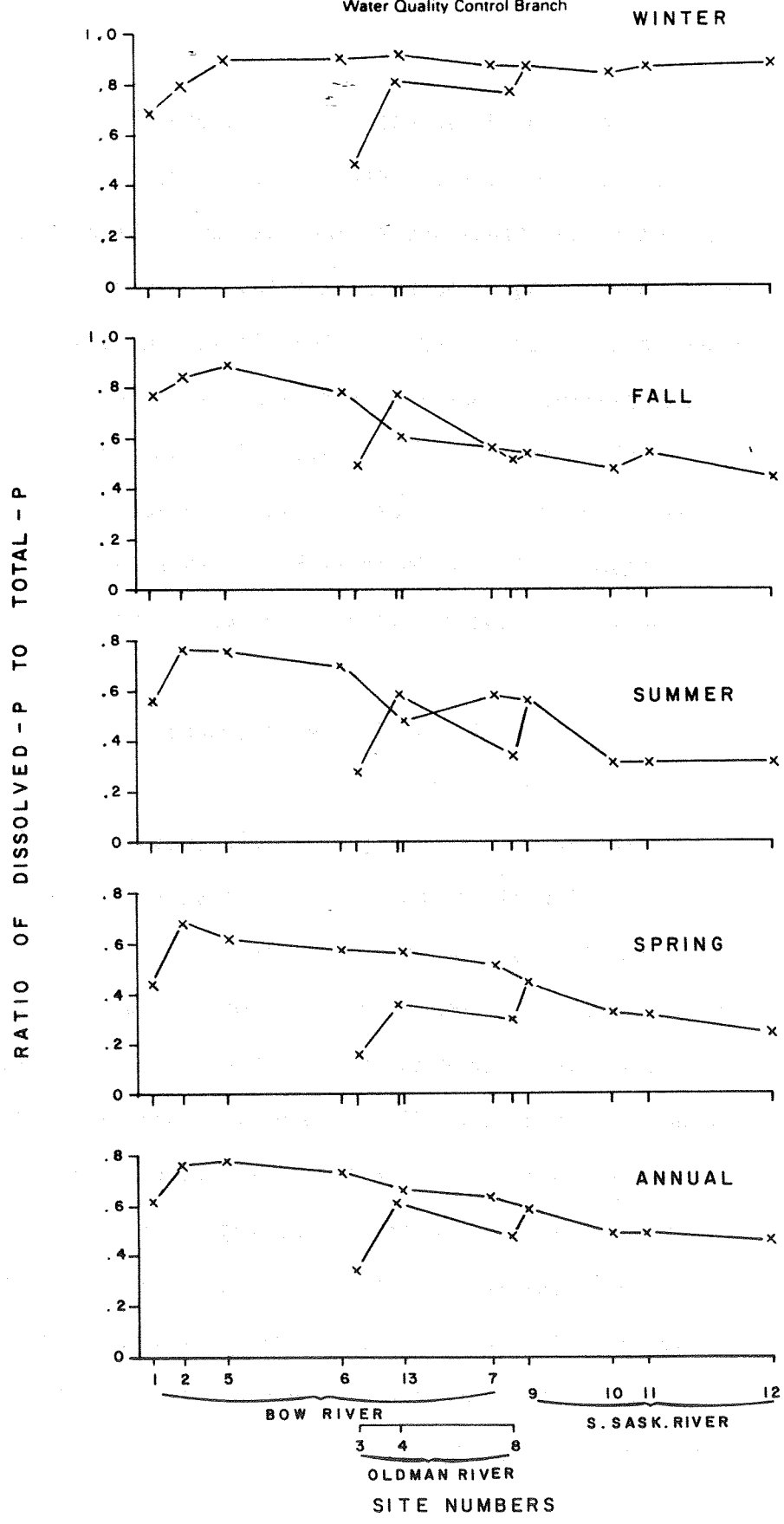


Fig. 21 : Annual and seasonal average ratios of dissolved phosphorus to total phosphorus at each site in the study basin.

The ratio of dissolved to total phosphorus was highest relative to other sites on the Bow River in the same season at Site 2 in spring and summer, but continued to increase below Site 2 in fall and winter before decreasing at downstream sites. This decrease was more pronounced in summer and fall than in spring, and in winter the ratio stayed relatively constant from Site 5 to Site 7.

In the Oldman River the ratio of dissolved to total phosphorus decreased below Site 4, but to a much smaller degree in winter than in other seasons. In the South Saskatchewan River, this ratio was relatively more constant than in the Bow or Oldman Rivers.

### 3.12 Biologically-Available Phosphorus

#### 3.12.1 Dissolved

Dissolved, biologically-available phosphorus (DBAP) is highly correlated with dissolved reactive, dissolved inorganic and dissolved phosphorus for each of the three rivers ( $r = 0.90$  to  $0.94$ ). These relationships are summarized as ratios in Table 8. The strong correlation means that any of the three forms of dissolved phosphorus can be used to predict dissolved biologically-available phosphorus.

The variable number of total data points between rivers reflects a difference in the number of sampling sites on each river. Seasonal variation in sample size (from 6 to 63) reflects the time distribution of sample collection and the exclusion of values at and below detection limit, since these were not used in ratio calculations. The summer and fall samples sizes for the Oldman and South Saskatchewan

TABLE 8

RATIO OF BIOLOGICALLY AVAILABLE PHOSPHORUS FORMS TO  
CHEMICALLY MEASURED PHOSPHORUS FORMS. VALUES AT  
THE DETECTION LIMIT WERE NOT USED IN RATIO CALCULATIONS.

		DBAP/CP			DBAP/DIP			DBAP/DP			PBAP/PP	
		Avg Ratio	n	Mean	Avg Ratio	n	Mean	Avg Ratio	n	Mean	Avg Ratio	n
ANNUAL	Bow	1.25	(138)	116+ 108	1.03	(143)	112 111	0.82	(150)	106+ 119	0.52	(162)
	Oldman	1.82	(40)	53+ 39	0.99	(48)	43 39	0.79	(56)	39 43	0.32	(86)
	SSR	1.61	(78)	61+ 49	1.07	(90)	52+ 48	0.69	(114)	43+ 49	0.43	(112)
WINTER	Bow	1.14	(30)	190+ 174	1.09	(30)	190 180	1.05	(30)	190 187	0.63	(40)
	Oldman	2.11	(9)	66+ 47	1.22	(8)	65 55	1.10	(10)	60 59	0.46	(20)
	SSR	1.26	(21)	109+ 91	1.08	(21)	109 100	0.99	(21)	109 107	0.64	(24)
SPRING	Bow	1.08	(63)	99 97	0.96	(62)	99 104	0.77	(63)	95+ 117	0.46	(62)
	Oldman	1.81	(16)	53+ 36	1.02	(19)	45 40	0.74	(22)	39 44	0.26	(31)
	SSR	1.94	(38)	49+ 38	1.26	(41)	44 41	0.82	(44)	42+ 53	0.40	(41)
SUMMER	Bow	1.93	(24)	76+ 58	1.10	(28)	61 55	0.69	(33)	54+ 63	0.51	(35)
	Oldman	1.11	(8)	53 45	0.81	(10)	42 41	0.76	(12)	38 41	0.29	(17)
	SSR	0.93	(6)	7 6	0.26	(12)	1+ 4	0.32	(25)	4+ 10	0.32	(27)
FALL	Bow	1.10	(21)	110 107	1.04	(23)	105 106	0.84	(24)	101+ 117	0.53	(25)
	Oldman	2.25	(7)	38+ 25	0.94	(11)	26 25	0.66	(12)	24 29	0.30	(18)
	SSR	1.16	(13)	47+ 34	1.14	(16)	39+ 31	0.55	(23)	27+ 33	0.40	(20)

\*indicates significant difference between means ( $p < 0.05$ )

Rivers, in particular, are reduced because of the frequent occurrence of dissolved reactive phosphorus and dissolved inorganic phosphorus concentrations of less than 3 µg/L.

Annually, there is a significant difference between dissolved, biologically-available phosphorus and dissolved reactive phosphorus for all three rivers. The greatest deviation between forms occurred in the Oldman River, and least deviation in the Bow River, while South Saskatchewan River results were intermediate. Seasonal means were significantly different for eight of twelve possible comparisons. The greatest deviation between dissolved, biologically-available phosphorus and dissolved reactive phosphorus for the Bow River occurred in summer. However, this average ratio is weighted by two extreme values. When these values are removed, the ratio is decreased from 1.93 to 1.18. Ratios for the Oldman River were greatest in fall and winter, then declined through spring to a summer low. In the South Saskatchewan, maximal difference occurred during spring.

The data show that dissolved, biologically-available phosphorus and dissolved, inorganic phosphorus values were generally most similar. The only data sets tested, which were significantly different, were those from the South Saskatchewan River on an annual basis, and again in summer and fall. Over the testing period average ratios ranged from 0.99 (Oldman) to 1.07 (South Saskatchewan) on an annual basis, though a greater range of ratios was measured when data were treated seasonally.

Annually, dissolved biologically-available phosphorus was significantly less than dissolved phosphorus for each river, with



average ratios of 0.69 to 0.82. A distinct pattern showed that dissolved biologically-available phosphorus closely approximated dissolved phosphorus in winter months. In other seasons, most of the dissolved phosphorus concentrations exceeded those of dissolved, biologically-available phosphorus.

### 3.12.2 Sephadex-Gel Filtration

Only 10 of 18 samples analyzed by Sephadex-gel filtration contained sufficient phosphorus to carry out the procedure. Comparison of orthophosphorus determined by Sephadex filtration and dissolved reactive phosphorus by chemical analysis on the same water (Figure 22) indicated very close correlation ( $r = 0.996$ ). Washing out (elution) of higher molecular weight phosphorus compounds (HMWP), which frequently caused the error in the orthophosphorus technique, did not occur in any of the March samples. Trace quantities of high molecular weight phosphorus were apparent and chemically analyzed as dissolved reactive phosphorus in the summer samples. This material was observed at void volume (molecular weight greater than 5000) but represented less than 5  $\mu\text{g/L}$  and therefore comprised only a fraction of the total measured dissolved reactive phosphorus.

### 3.12.3 Particulate

Particulate phosphorus (PP) was generally less available for biological uptake in the Oldman River and more available in the Bow River; South Saskatchewan River values were intermediate (Table 8).

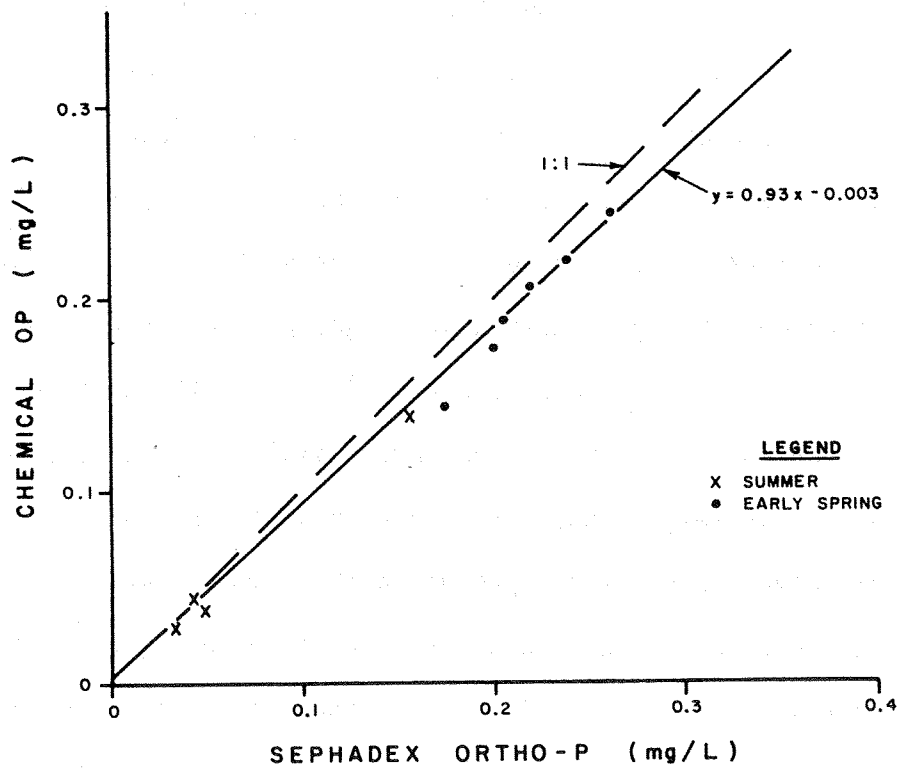


Fig. 22 Comparison between measurements of dissolved reactive phosphorus by chemical analysis and orthophosphorus by Sephadex gel filtration.

Seasonally, ratios of particulate biologically-available phosphorus (PBAP) to particulate phosphorus were higher in winter than in the other seasons.

When particulate phosphorus availability was investigated at each site separately, several trends were apparent (Figure 23). Low availability was shown at Site 1 upstream of Calgary. Site 3 upstream of Lethbridge had the lowest annual value of all sites studied. Generally, particulate phosphorus availabilities increased downstream of each of the three major urban centres, though this trend was least consistent in winter. Ratios further downstream of Calgary and Lethbridge were inconsistent between seasons, but stayed relatively constant on an annual basis. Highest particulate phosphorus availability in the South Saskatchewan River was measured at Site 9 below the confluence of the Bow and Oldman Rivers. Downstream on the South Saskatchewan River, proportions were lower and generally similar between sampling locations.

The relationship between particulate phosphorus availability (PBAP/PP) and three variables; particulate organic carbon, dissolved, biologically-available phosphorus and the ratio of particulate to total phosphorus; was tested. Though there was no relationship between availability and particulate organic carbon ( $r = 0.09$ ), there was a significant linear relationship with dissolved, biologically-available phosphorus ( $r = 0.37$ ) and the ratio of particulate to total phosphorus ( $r = -0.46$ ). Scattergrams of these relationships using seasonal average values are given in Figure 24. When particulate phosphorus comprised a major proportion of total

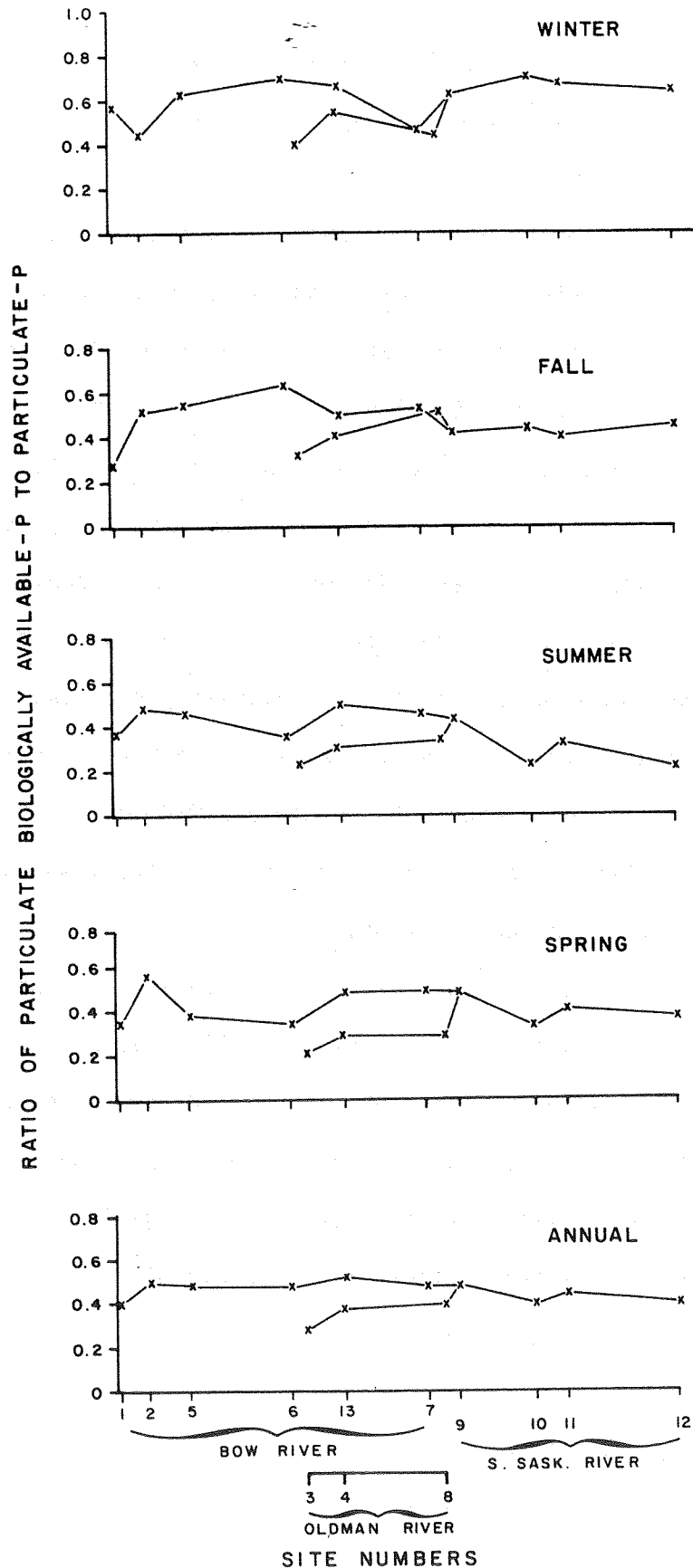


Fig. 23 : Annual and seasonal average ratios of particulate biologically available phosphorus to particulate phosphorus at each site in the study basin.

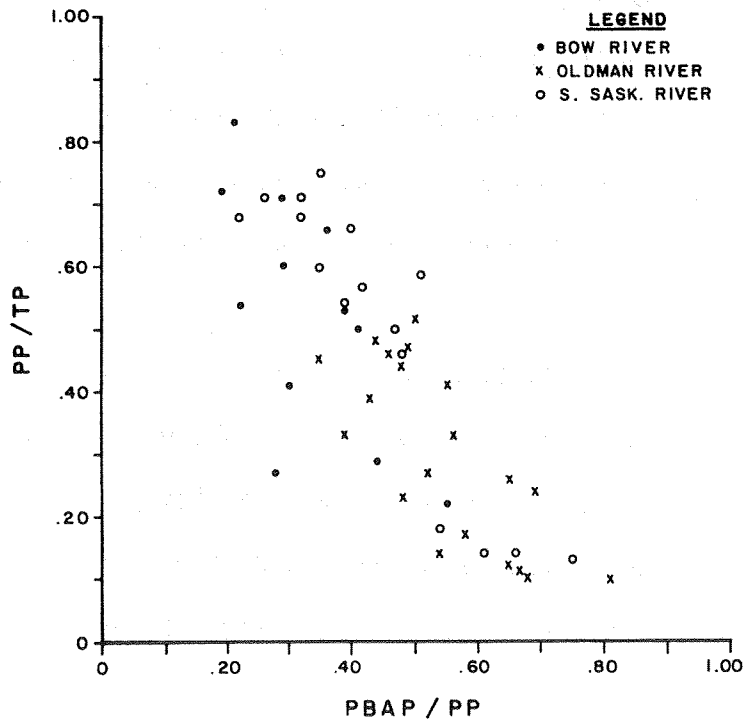
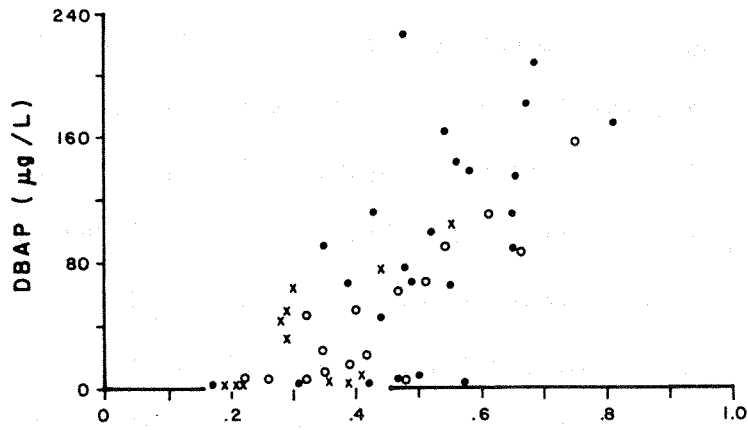


Fig. 24: Comparisons of the ratios of particulate biologically available phosphorus to particulate phosphorus, to the ratios of particulate phosphorus to total phosphorus, and to dissolved biologically available phosphorus.

phosphorus (0.60 - 0.85), availability was generally low (0.20 - 0.40). Availability was greatest when particulate to total phosphorus proportions ranged between 0.10 and 0.30.

Figure 25 summarizes the division of total phosphorus into biologically-available and unavailable forms, as well as the subdivision of available phosphorus into particulate and dissolved forms for the Basin. Annually, 80 to 90% of the total phosphorus in the Bow River downstream of Calgary is biologically-available. Most of the total biologically-available phosphorus was in the dissolved form (77-85%), since quantities of particulate phosphorus, though highly available, were small.

A very different relationship between phosphorus forms and availability occurred in the Oldman River, where more total phosphorus was in the particulate form. Dissolved, biologically-available phosphorus provided 68 to 82% of the total biologically-available phosphorus, but the overall availability of the total phosphorus transported in the Oldman River was less than in the Bow River (51-75%).

Overall proportion of biologically-available phosphorus in the South Saskatchewan River was about 70%, except for a higher percentage (82%) at Site 9. Phosphorus availability patterns in the South Saskatchewan reflected the combined effect of the two source rivers, that is, high dissolved, biologically-available phosphorus input from the Bow, and high particulate phosphorus from the Oldman. Calgary and Lethbridge had a significant influence on downstream phosphorus availability patterns in their respective rivers. The effect of Medicine Hat on the South Saskatchewan River was not as significant.

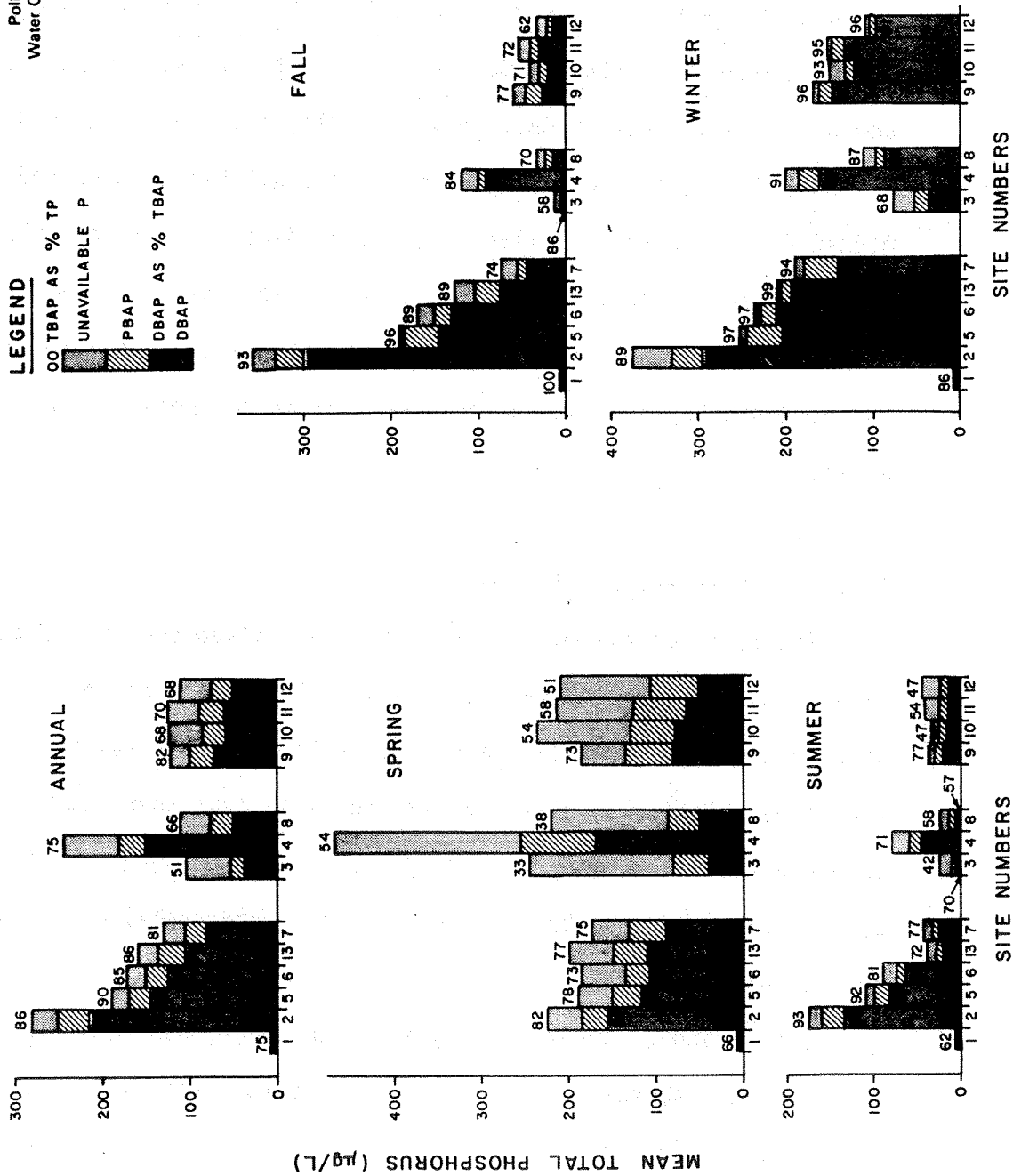


Fig. 25 Comparison of annual and seasonal average values for biologically available phosphorus forms and total phosphorus at each site in the study basin.

In the Oldman River, at Site 4 below Lethbridge, the ratio of dissolved nitrogen to dissolved phosphorus was low (4 to 8) in all seasons except spring, when the ratio was 19. Further downstream at Site 8, ratios ranged from 14 to 34 seasonally, and showed highest values in summer. Ratios in the South Saskatchewan River were generally high, but higher in summer and fall than in winter and spring.

Figure 26 and Appendix Table B-2 show the relationship between algal assay results with and without addition of nitrogen to the growth medium. When addition of nitrogen increased the growth potential, nitrogen was then assessed as limiting growth. When addition of nitrogen did not increase the growth potential, then another nutrient was in short supply. The other nutrient was often phosphorus.

At Sites 1 and 3 above the cities on the Bow and Oldman Rivers, respectively, results from the algal assays were very similar. In the Bow River below Calgary, the two algal assay results were similar only in May/June, but further downstream, by Sites 13 and 7, results were similar from June to September.

Results from the Oldman River below Lethbridge were somewhat different. At Site 4 algal assay results were similar in only May and October, but at Site 8, results were similar for the time period from May to November. In the South Saskatchewan River, results were similar from July to September at Site 9 and from May to October at the three downstream sites.



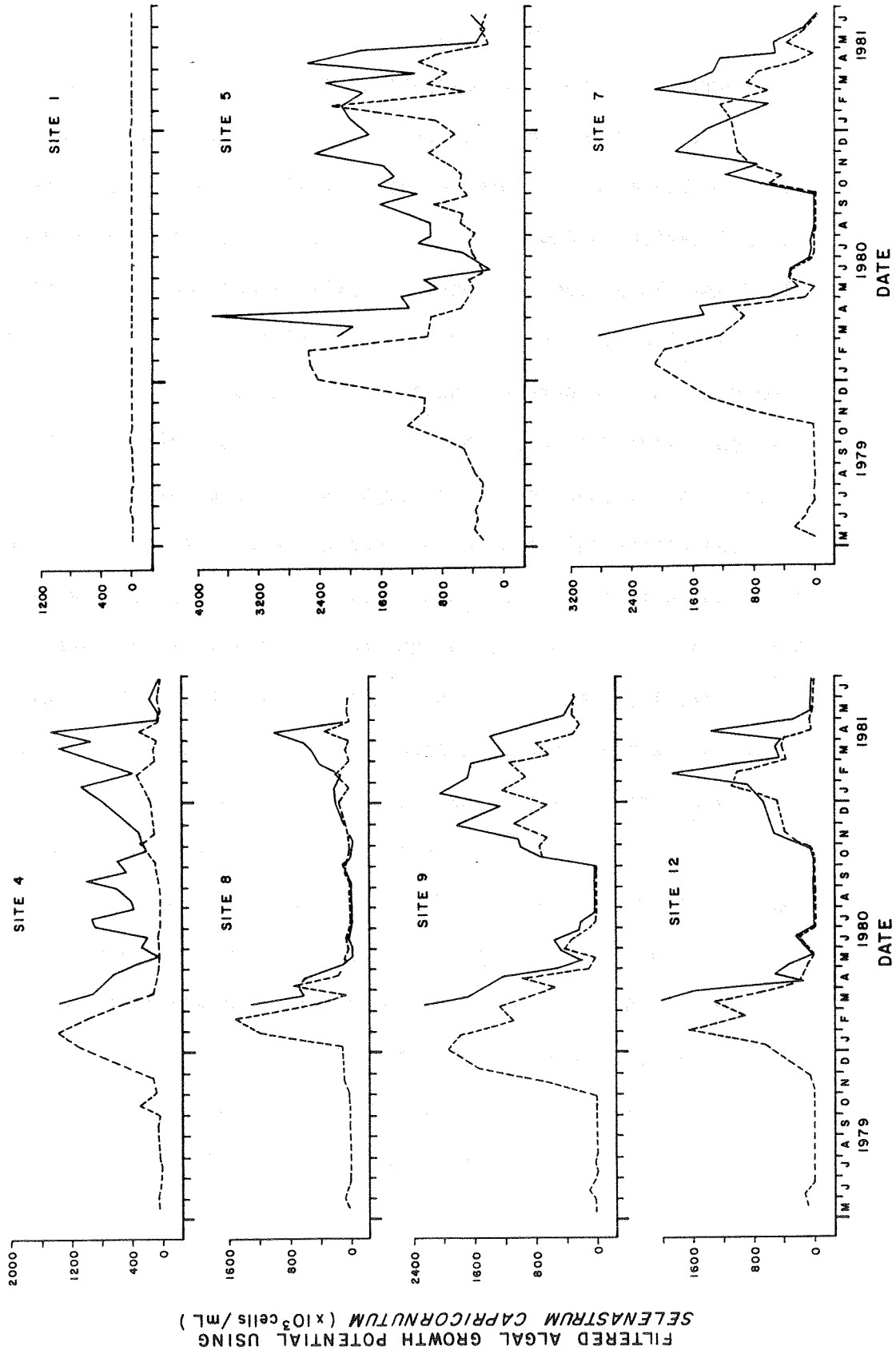


Fig. 26 Comparison of algal growth potential with (—) and without (---) the addition of nitrogen at selected sites in the study basin.

### 3.14 Historical Nutrient Data

Annual and seasonal concentrations of phosphorus (dissolved and dissolved reactive) and nitrogen (dissolved and nitrate + nitrite) are given in Table 10 for both the historical and this study data. Only three locations - Bow River near its confluence with the Oldman (Site 7), Oldman River above Lethbridge (Site 3) and South Saskatchewan River at Highway 41 (Site 12) - had sufficient data for a seasonal comparison of the nutrient parameters. The small number of samples that contributed to each seasonal mean were not sufficient for conclusions, though tentative comparisons are possible.

The historical data for phosphorus were consistently higher than the study data at Site 3, though values were close to detection. At Sites 7 and 12, annual study phosphorus concentrations were higher than historical concentrations. Seasonally, this relationship held in spring and winter when concentrations were highest, while historical means were often greater than study means in summer and fall.

Historical total phosphorus (TP) data are available for eight study sites in the basin, and a comparison was made with this study data in Figure 27. One extreme total phosphorus value of 8.2 mg/L was deleted from Site 10 data. Historical data were much higher than study data both annually and seasonally.

A comparison of historical and study data for nitrogen (Table 10) showed that historical annual means were greater than study means. Seasonal comparisons showed variable results except during winter when study concentration means exceeded historical means.

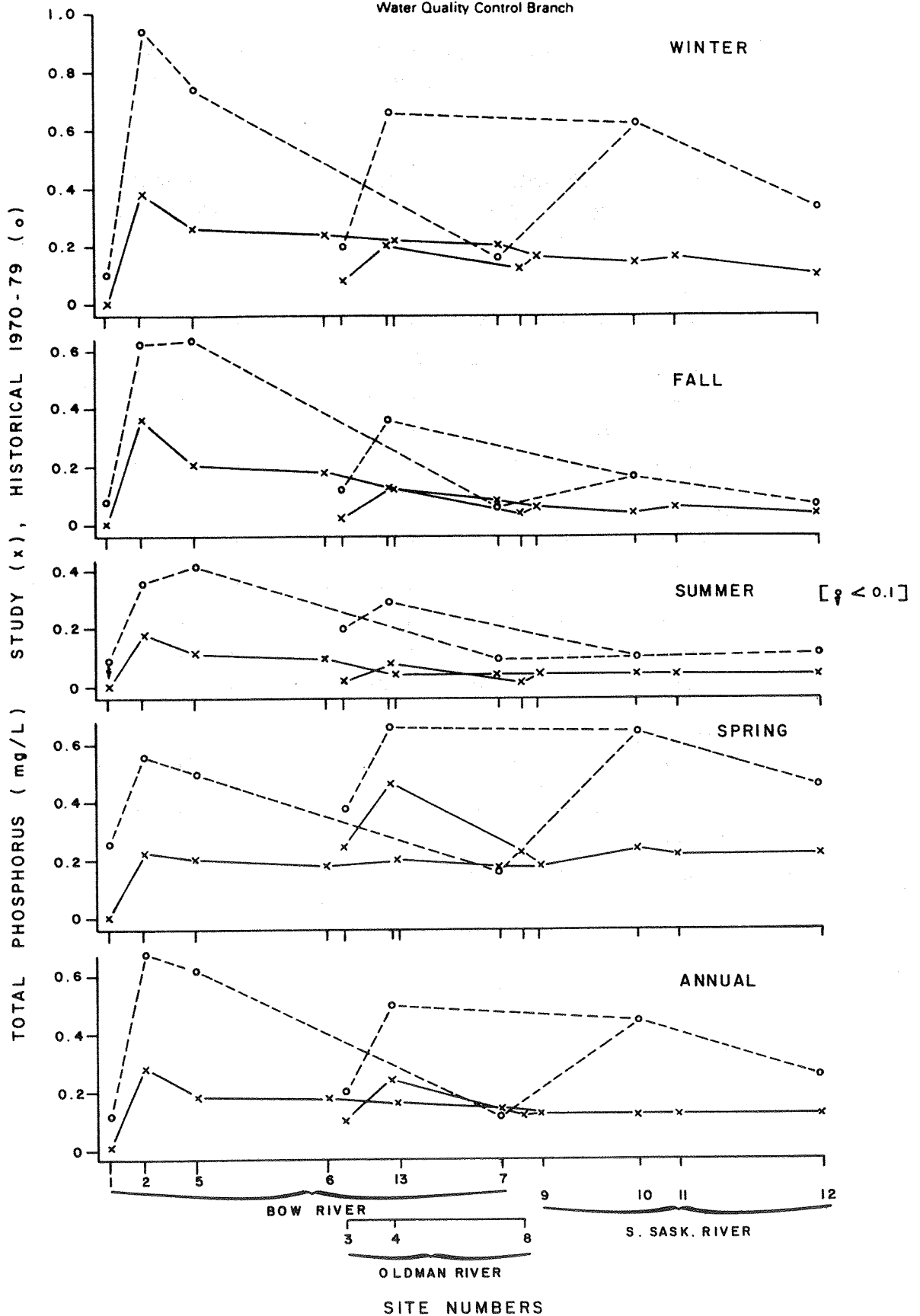


Fig. 27 Comparison of annual and seasonal average concentrations of total phosphorus from study data and from historical data.

TABLE 10 COMPARISON OF STUDY DATA AND HISTORICAL DATA  
(1970 TO 1979) FOR SELECTED NUTRIENT PARAMETERS

	DP ( $\mu\text{g/L}$ )				OP ( $\mu\text{g/L}$ )				DN ( $\text{mg/L}$ )				NIT ( $\text{mg/L}$ )			
	Study		Hist.		Study		Hist.		Study		Hist.		Study		Hist.	
	n	$\bar{X}$	n	$\bar{X}$	n	$\bar{X}$	n	$\bar{X}$	n	$\bar{X}$	n	$\bar{X}$	n	$\bar{X}$	n	$\bar{X}$
Site 3																
Annual	81	6	13	11	81	3	30	12	80	.26	13	.26	81	.12	18	.16
Spring	25	7	3	9	27	3	4	5	27	.23	3	.26	27	.07	3	.07
Summer	17	4	3	10	16	3	6	9	17	.14	3	.26	17	.02	3	.11
Fall	20	5	3	9	20	3	8	4	19	.16	3	.11	19	.04	4	.04
Winter	19	7	4	14	18	4	12	8	17	.53	4	.37	18	.36	8	.29
Site 7																
Annual	86	82	13	67	85	65	29	52	81	.95	13	.98	84	.64	22	.73
Spring	26	82	4	58	26	61	4	32	26	.84	4	1.15	26	.54	4	.57
Summer	20	25	2	19	20	11	5	15	18	.31	2	.27	18	.08	3	.07
Fall	18	44	3	41	18	30	8	34	18	.81	3	.76	18	.57	6	.76
Winter	22	166	4	121	21	151	12	85	19	1.84	4	1.35	22	1.29	9	1.00
Site 12																
Annual	75	40	38	33	75	29	13	28	73	.70	41	.84	75	.48	31	.51
Spring	24	40	11	32	24	24	1	8	23	.56	10	.55	24	.34	8	.40
Summer	15	9	8	12	15	4	4	41	15	.22	9	.25	15	.04	7	.04
Fall	18	12	6	17	18	5	4	26	18	.54	7	.82	18	.33	6	.40
Winter	18	94	13	53	18	81	4	23	17	1.51	15	1.39	18	1.20	10	.98

### 3.15 Other Water Chemistry Data

Data were collected by Environment Canada during the study period at sites comparable to Sites 1 and 7 in the Bow River, Sites 3 and 8 in the Oldman River, and Site 12 in the South Saskatchewan River (Appendix Table B-3). The annual and seasonal mean values for most variables were comparable with a few exceptions. At Site 3, total phosphorus, turbidity, non-filterable residue, particulate nitrogen and particulate organic carbon from this study data were higher on an annual basis than from Environment Canada's data, a discrepancy which was most pronounced in spring and winter when analyzed seasonally. A similar result was derived for non-filterable residue at Site 8 and Site 12 for spring data. These discrepancies were caused by a different sampling frequency of particulate variables. Study data were collected two to three times more often than Environment Canada's data. Spring and late winter were the times of most dramatic changes in particulate discharge related variables, and the higher sampling frequency in this study was more representative of average conditions at the time of high variation. This was reflected in the annual mean values.

The other exceptions occurred at Site 8 where dissolved phosphorus and chloride were lower for study data, and at Site 7 where silica was higher for study data. Again, these discrepancies were likely caused by sampling frequency, but discrepancies at Site 8 may have resulted because the locations were less comparable than other locations.

### 3.16 Sediment Phosphorus

Concentrations of total phosphorus in the sediments were lowest at sites upstream of Calgary and Lethbridge and substantially higher downstream, particularly below Calgary (Table 11). Levels decreased with distance downstream from these two major urban areas, and levels measured at Site 10 above Medicine Hat were almost as low as upstream levels. Seasonal variation was greatest below Calgary, and lowest at upstream sites (above Calgary and Lethbridge), and Site 10.

The apatite inorganic phosphorus (AIP) formed the largest fraction of total phosphorus (42% to 79%), but was the least variable both seasonally and between sites. The basin-wide variation in sediment total phosphorus was attributed largely to fluctuating concentrations of the organic (ORGP) and particularly the non-apatite inorganic (NAIP) phosphorus fractions. These fractions followed the same trends as the total phosphorus. They increased markedly below the urban centres, then decreased gradually downstream to low levels at Site 10.

The biologically-available fraction of sediment phosphorus (SBAP) was most similar to non-apatite inorganic phosphorus. The two fractions were highly correlated ( $r = 0.91$ ) and the ratio of sediment biologically-available phosphorus to non-apatite inorganic phosphorus (ranging from 1.04 to 1.56) indicated that non-apatite inorganic phosphorus underestimated bioavailable sediment phosphorus as measured by algal assays. The least deviation between forms occurred at the first two downstream Calgary sites. Non-apatite inorganic phosphorus

TABLE 11

SUMMARY OF SEDIMENT PHOSPHORUS CONCENTRATIONS ( $\mu\text{g/g}$ ) AND PROPORTIONAL RELATIONSHIPS BETWEEN FORMS AT EACH SITE, C.V. IS COEFFICIENT OF VARIATION,  $n=7$  EXCEPT AT SITE 1 ( $n=5$ ). THE ESTIMATE OF AREAL DISTRIBUTION OF FINE PARTICULATE RIVER BOTTOM SEDIMENTS IN SEPTEMBER, 1981 IS ALSO GIVEN,

Site	Total Phosphorus		Apatite Inorganic Phosphorus			Non-apatite Inorganic Phosphorus			Organic Phosphorus			Sediment BAP			Sediment Quantity g dry wt/m <sup>2</sup>	
	Mean	C.V.	Mean	C.V.	% of TP	Mean	C.V.	% of TP	Mean	C.V.	% of TP	Mean	C.V.	% of NAIP	Mean	S.D.
Bow River																
1	692	10	548	4	71	59	55	7	92	34	21	83	43	156	32	21
2	1735	34	667	5	42	660	60	35	407	45	23	609	38	104	103	22
5	1117	18	615	6	56	276	49	24	224	35	20	267	41	107		
13	794	19	512	12	65	160	54	19	122	30	15	207	37	142		
7	866	23	567	2	68	147	59	16	151	74	16	163	40	118	185	38
Oldman River																
3	615	11	485	6	79	48	37	8	81	41	13	49	57	113	293	60
4	793	17	534	6	59	151	47	18	108	44	12	233	69	142	368	264
8	770	22	507	5	68	110	74	13	154	59	19	155	82	127		
South Sask River																
10	710	4	530	7	75	90	29	12	81	66	11	119	42	139	297	56

was also highly correlated with dissolved inorganic phosphorus levels in the overlying river water ( $r = 0.88$ ).

Seasonally, highest concentrations of sediment organic phosphorus, sediment biologically-available phosphorus and non-apatite inorganic phosphorus often occurred in spring samples collected prior to the June high discharge period, while lowest levels were usually detected over the May to August interval (Appendix Figures A-2 to A-4). September and October concentrations were often higher than the summer lows, particularly for sediment organic phosphorus and sediment biologically-available phosphorus.

Estimates of areal amounts of fine particulate river bottom sediment were approximated and were derived from a single set of measurements in September. Spatial trends, however, are shown in these data (Table 11, Sediment Quantity).

The lowest quantity of sediment per substrate area was measured upstream of Calgary, as increasing levels occurred downstream at sequential sites along the Bow River. Overall quantities in the Oldman and South Saskatchewan Rivers are greater than in the Bow River and there is an increase between Sites 3 and 4.

These estimates of sediment quantity were used with average sediment chemistry to calculate relative amounts of phosphorus in the sediment 'pool' of the Bow and Oldman Rivers in fall 1981. The errors in this type of calculation are enormous, nonetheless, they are of interest for broad comparative purposes. The sediment 'pool' for the Bow River from Calgary to its confluence with the Oldman was estimated at 8300 kg total phosphorus, and 2100 kg sediment biologically-



available phosphorus. For the Oldman River from Lethbridge to its confluence with the Bow, the sediment 'pool' was estimated at 4600 kg total phosphorus, and 1900 kg sediment biologically-available phosphorus.

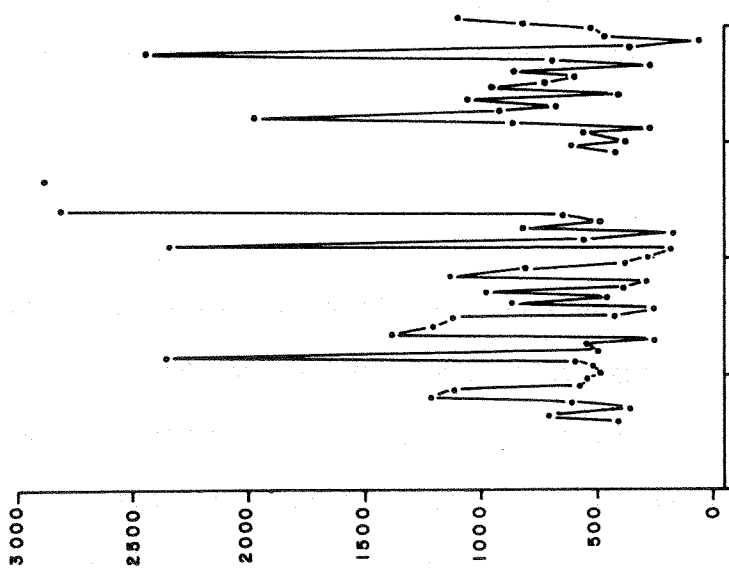
The net flux of available phosphorus from the sediments in each reach was calculated by using the average sediment biologically-available phosphorus decline observed from April to July 1981. Values were -1700 kg biologically-available phosphorus for the Bow River, and -1000 kg biologically-available phosphorus for the Oldman River.

### 3.17 Discharge

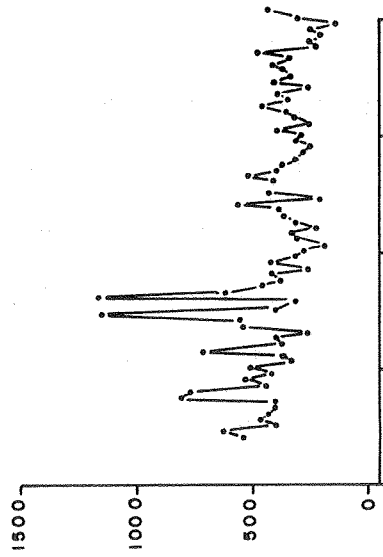
Figure 28 shows mean annual discharge in cms (cubic metres/second) and maximum daily discharge in cms from 1900 to 1981 for three Water Survey stations - Bow River at Calgary, Oldman River near Lethbridge and South Saskatchewan River at Medicine Hat. Average mean annual discharges for the period of record to 1979 were 92.1, 90.8 and 206 cms, respectively. The Bow River shows a smaller range of fluctuations than the Oldman River. Maximum daily discharge was variable at all three stations. Higher values were recorded in the Oldman than in the Bow River, and there was a long term trend of decreasing peaks in the Bow River. The South Saskatchewan River reflected the input of both rivers and the peaks in maximum daily discharge were influenced strongly by the Oldman River.

Monthly mean discharge for Bow River at Calgary (Figure 29) showed the yearly variation from 1970 to 1981 and the long-term average. The mean annual discharge exceeded the long-term average

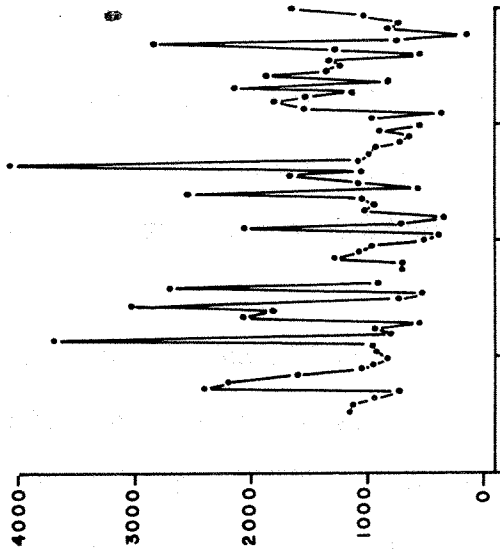
OLDMAN RIVER near LETHBRIDGE



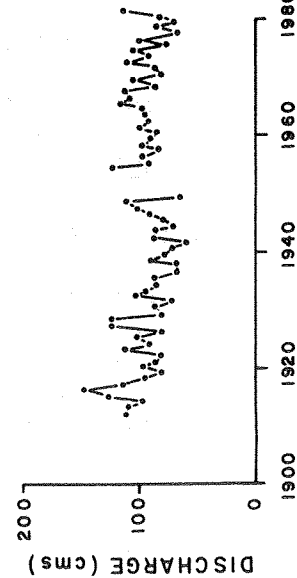
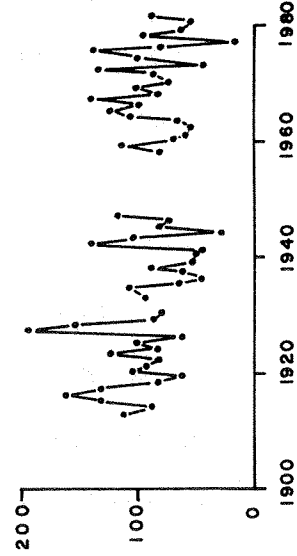
BOW RIVER at CALGARY



SOUTH SASKATCHEWAN RIVER  
 at MEDICINE HAT



MAXIMUM DAILY DISCHARGE (cms)



MEAN ANNUAL DISCHARGE (cms)

Y E A R

Fig. 28 Comparison of historical discharge values in the Bow, Oldman and South Saskatchewan Rivers.

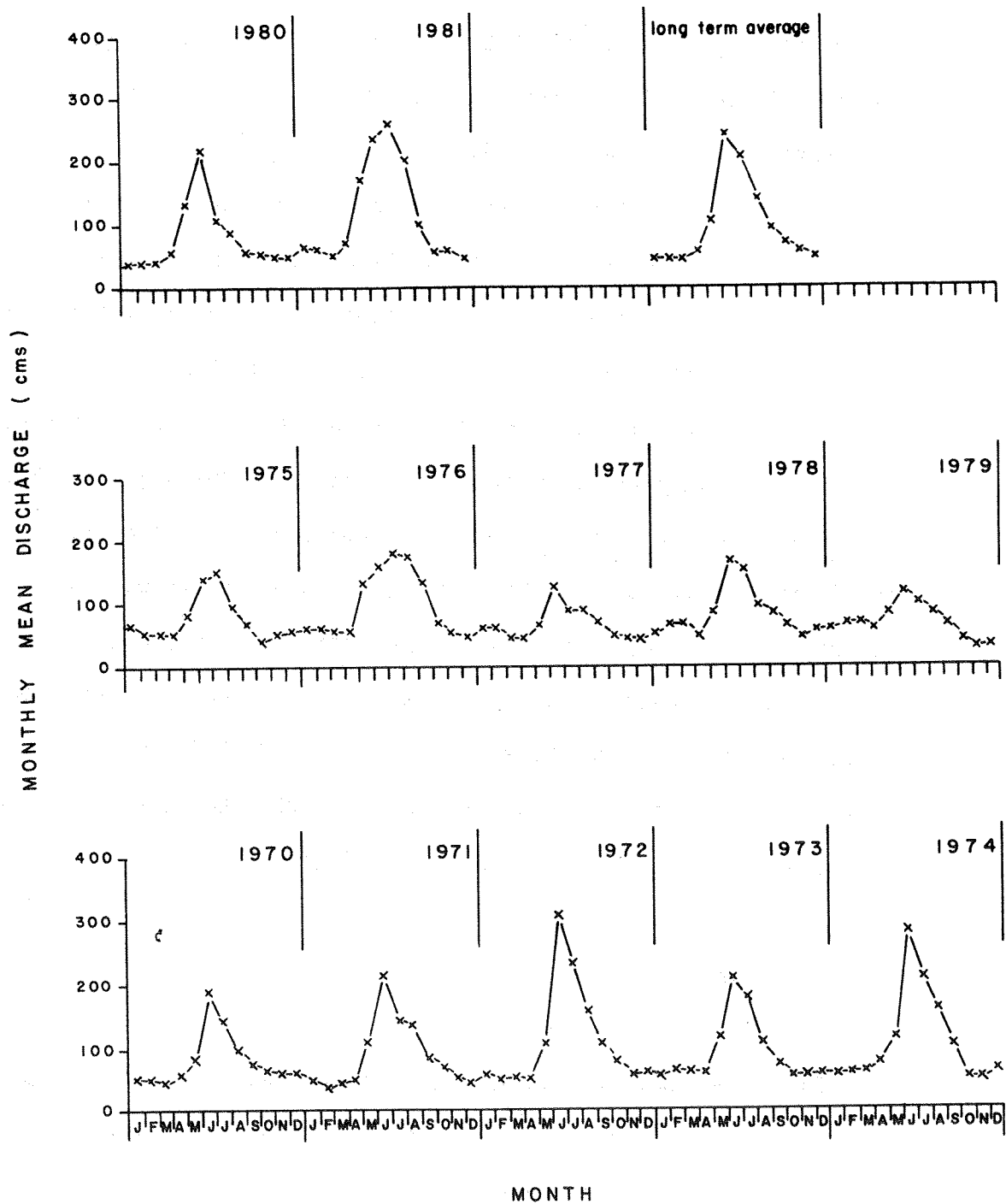


Fig. 29 Monthly mean discharge in the Bow River at Calgary from 1970 to 1981.

during the 1970s only in 1972, 1974 and 1976 (Figure 28). The years of lower than average flow were also reflected in the very low maximum daily discharge values for 1975 to 1979. In fact, the range of values recorded in these five years was equalled in only three previous years on record: 1941, 1944 and 1949.

Pearson's correlations were run between discharge and particulate phosphorus, particulate nitrogen, particulate organic carbon, turbidity, non-filterable residue, dissolved phosphorus and dissolved nitrogen for data from May 1979 to December 1981 (Appendix Table A-8). Combining all the data, the correlations with non-filterable residue ( $r = 0.59$ ) and turbidity ( $r = 0.53$ ) were the highest. When the data from each river were treated separately, the correlation with non-filterable residue in the South Saskatchewan River was the strongest ( $r = 0.82$ ). The highest correlation coefficients with particulate phosphorus, particulate nitrogen and particulate organic carbon were found in the Oldman River ( $r = 0.63, 0.71$  and  $0.75$ , respectively). Correlations with dissolved phosphorus and dissolved nitrogen were weak and negative ( $r = -.01$  to  $-.30$ ).

### 3.18 Phosphorus Loading

#### 3.18.1 Site Loading

Figure 30 shows the annual loading in tonnes of total phosphorus (TP) at each site during the study period. Throughout the Basin, the lowest values were measured at Site 1 on the Bow River in both years (22 and 29 tonnes) and the highest values in each year were measured at Sites 10 or 11 in the South Saskatchewan River. In most cases an increase in loading was shown from the upstream to downstream sites

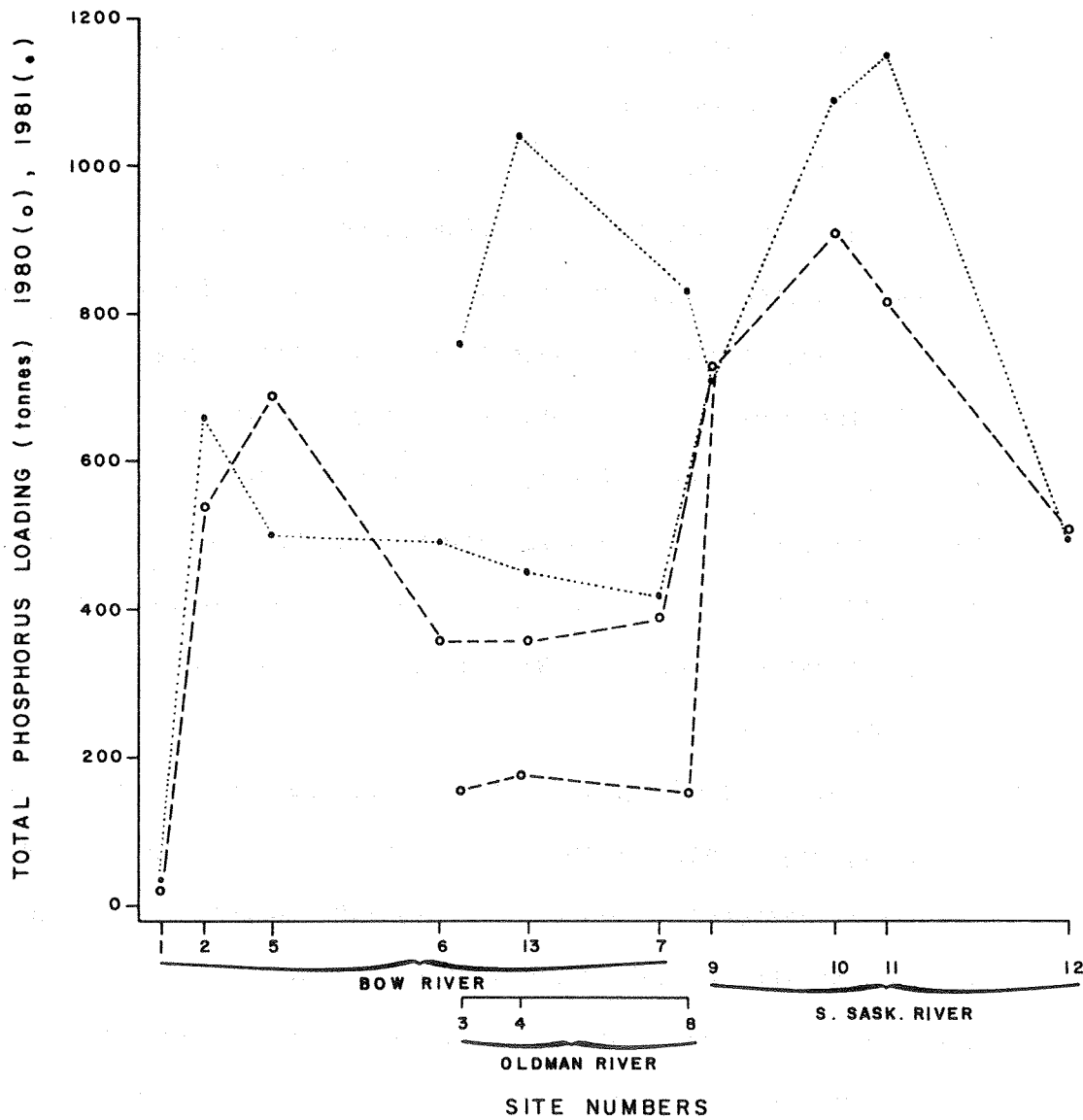


Fig. 30 Comparison of annual loading of total phosphorus in 1980 and 1981 at each site in the study basin.

for each city (Sites 1 to 2 for Calgary, Sites 3 to 4 for Lethbridge and Sites 10 to 11 for Medicine Hat), but the largest such increase was below Calgary. Generally, site loadings decreased in a downstream direction from these high values.

The variation in total phosphorus loading between years was very different for each river. Bow River values were quite similar, while Oldman River values differed dramatically and South Saskatchewan River values were intermediate.

In the Bow River, highest values were measured at Site 2 in 1981 (657 tonnes) and Site 5 in 1980 (688 tonnes). Loading values generally decreased at downstream sites. The coefficient of variation between years (Table 12) ranged from 5% at Site 7 to 23% at Site 5.

In the Oldman River, total phosphorus loading values at Site 3 were higher than those at Site 1 on the Bow River. However, the relative increase to Site 4 was lower than that to Site 2. Loadings decreased to Site 8 in both years. The absolute values were very different between years as 1981 values were five to six times higher than 1980 values (Table 12).

Calculations of total phosphorus loadings in 1980 excluded unusually high concentration of total phosphorus (0.85 - 3.5 mg/L) which were measured on May 27. These high concentrations occurred as a result of the variable deposition of ash over the study basin from the eruptions of Mount St. Helens in Washington. Since this unusual event occurred at a time of high discharge the effect on annual total phosphorus loading calculations was extreme. Had these values been included, total phosphorus loadings in 1980 would have been 1998, 3429 and 737 tonnes at Sites 3, 4 and 8, respectively.

TABLE 12 COMPARISON OF ANNUAL PHOSPHORUS (TP AND DP) LOADING  
 IN TONNES INCLUDING MEAN, STANDARD DEVIATION (SD)  
 AND COEFFICIENT OF VARIATION (CV)

Site	Year	Total Phosphorus				Dissolved Phosphorus			
		Loading	Mean	SD	CV	Loading	Mean	SD	CV
1	1980	21.8	25.6	5.37	21	8.4	9.9	2.12	21
	1981	29.4				11.4			
2	1980	543.7	600.6	80.40	13	461.4	438.4	32.53	7
	1981	657.4				415.4			
5	1980	687.6	592.8	134.14	23	370.8	357.4	19.02	5
	1981	497.9				343.9			
6	1980	359.9	424.4	91.29	22	227.8	236.0	11.60	5
	1981	489.0				244.2			
13	1980	357.2	404.1	66.33	16	191.4	213.0	30.62	14
	1981	451.0				234.7			
7	1980	389.0	404.3	21.64	5	161.6	187.9	37.19	20
	1981	419.6				214.2			
3	1980	155.7	459.2	429.25	93	10.4	22.3	16.83	75
	1981	762.8				34.2			
4	1980	177.5	608.8	609.88	100	47.6	61.2	19.23	31
	1981	1040.0				74.8			
8	1980	149.6	488.8	479.70	98	38.0	44.4	9.12	21
	1981	828.0				50.9			
9	1980	731.2	718.7	17.68	2	174.2	237.0	88.81	37
	1981	706.2				299.8			
10	1980	909.2	999.8	128.20	13	162.3	181.8	27.65	15
	1981	1090.5				201.4			
11	1980	816.7	983.6	235.96	24	178.4	196.9	26.16	13
	1981	1150.4				215.4			
12	1980	510.4	505.0	7.64	2	147.8	152.6	6.79	4
	1981	499.6				157.4			

Total phosphorus loading in the South Saskatchewan River was consistent between years (Table 12), but longitudinal patterns were different. In 1980, total phosphorus loading at Site 9 was greater than those of Sites 7 and 8 combined, while the opposite was true in 1981. Loadings increased to Site 10 in both years, but decreased to Site 11 in 1980 and increased in 1981. Loading at Site 12 was very consistent between years and showed a decrease from Site 11. The total phosphorus loading in 1981 had been adjusted, however, to remove the effect of one very high total phosphorus concentration during high flow. This deletion changed the annual total phosphorus loading from 2683 to 500 tonnes.

Annual and seasonal loading in tonnes of dissolved phosphorus (Figure 31) were calculated using all samples, unlike the total phosphorus loading values discussed above. The variability in dissolved phosphorus loading between years (Table 12) was generally lower than for total phosphorus loading, and the Bow River was the least variable, while the Oldman River was the most variable.

In the Bow River, dissolved phosphorus loading increased from low values at Site 1 to highest values at Site 2 and generally decreased in a downstream direction. The exception to this trend occurred in spring 1980 and 1981 when loadings increased from Site 2 to Site 5. Downstream of Site 5, not only the absolute loading decreased in a downstream direction, but also the rate of the reduction decreased, as indicated by the slope of the lines joining two sites. Seasonally, winter decreases in loading were smallest, while summer decreases were largest.



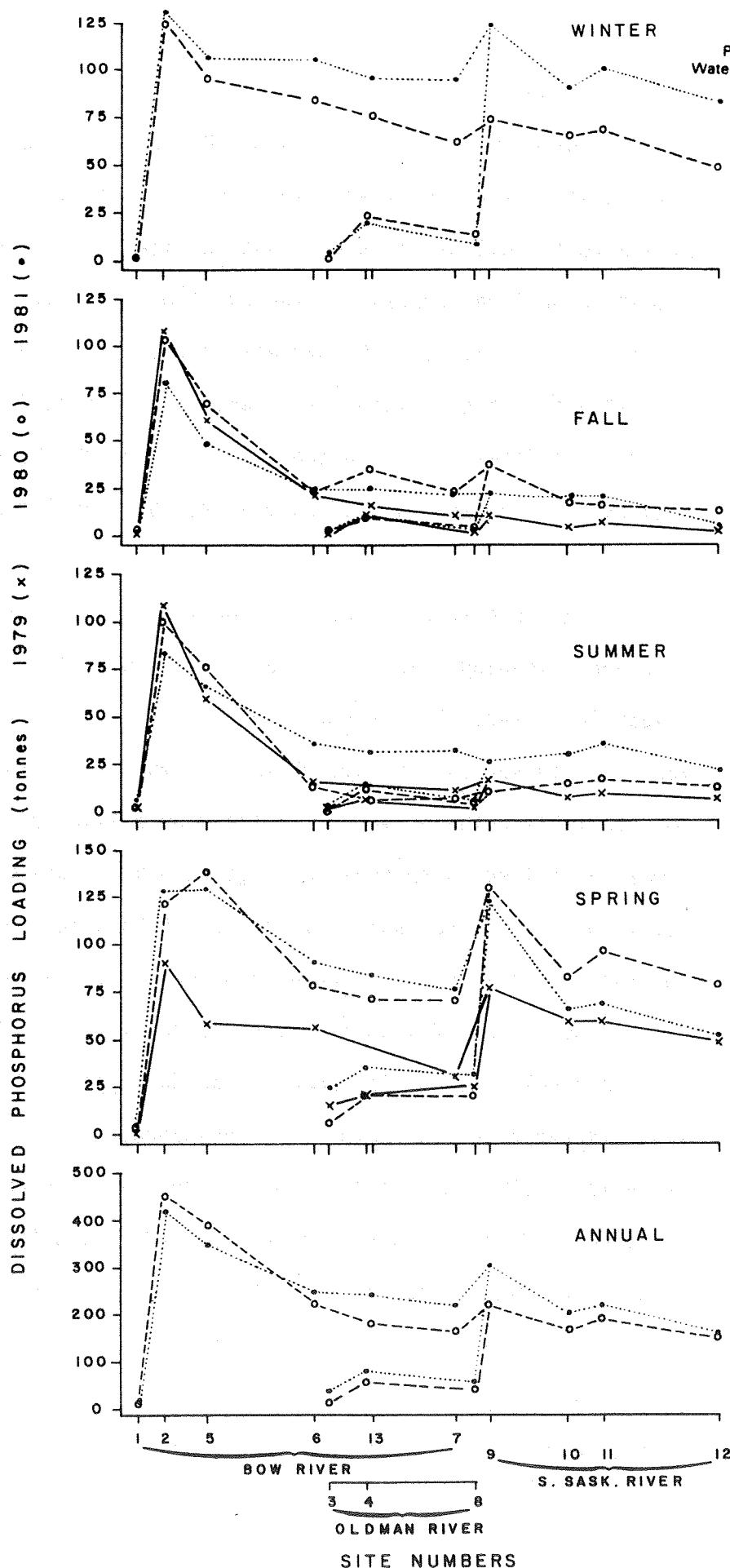


Fig. 31 Comparison of annual and seasonal loading of dissolved phosphorus at each site in the study basin.

In the Oldman River the dissolved phosphorus loadings were much lower than in the Bow River. There was an increase in loading from Site 3 to 4, followed by a decrease to Site 8. Site 9 on the South Saskatchewan River represents the addition of loadings from the Bow and the Oldman Rivers. The overall decrease in loading from Site 9 to Site 12 was at approximately the same rate as from Sites 13 to 7 in the Bow and Sites 4 to 8 in the Oldman, although there was an increase in dissolved phosphorus loading measured between Sites 10 and 11 in most cases.

Variation between years, considering seasonal dissolved phosphorus loading (Table 13), was highest overall in summer and lowest in winter. In the Bow River, Sites 2 and 5 showed highest variation in spring and fall while at downstream sites summer was the most variable between years. In the Oldman River at Sites 4 and 8, summer dissolved phosphorus loadings were most variable and fall values were least variable. In the South Saskatchewan River spring loading values were least variable between years at all sites.

A comparison of loading values calculated from the study data with data collected by Environment Canada (Appendix Table A-9) showed wide discrepancies for both total phosphorus (average coefficient of variation = 28%) and dissolved phosphorus (average coefficient of variation = 24%). This variation resulted from different sampling frequencies with differences in the discharge values sampled and the concentrations measured. A similar comparison was made between loading values from the study data and from the study data plus Environment Canada's data (Appendix Table A-9). In these cases

TABLE 13                      COMPARISON OF SEASONAL DISSOLVED PHOSPHORUS  
LOADING IN TONNES INCLUDING MEAN, STANDARD  
DEVIATION (SD) AND COEFFICIENT OF VARIATION (CV)

Site	Spring			Summer			Fall			Winter		
	Mean	SD	CV	Mean	SD	CV	Mean	SD	CV	Mean	SD	CV
1	2.4	0.91	38	3.6	1.50	41	1.2	0.32	26	1.4	0.05	4
2	113.3	19.62	17	96.6	12.75	13	97.0	14.33	15	127.1	4.62	4
5	108.6	44.25	41	66.4	7.99	12	59.0	9.98	17	101.0	8.31	8
6	74.9	17.55	23	21.1	12.13	57	21.6	0.51	2	93.9	15.96	17
13	77.5	9.67	12	18.2	17.54	97	25.0	9.57	38	85.4	14.62	17
7	59.1	25.11	42	15.7	13.06	83	18.9	7.26	38	78.1	22.78	29
3	15.9	8.92	56	1.0	0.38	37	0.6	0.35	56	1.7	1.51	87
4	26.4	8.37	32	9.8	3.29	34	9.9	0.55	6	21.8	1.69	8
8	25.8	5.34	21	3.1	1.43	46	2.6	0.97	4	10.9	3.58	33
9	109.8	28.54	26	17.3	7.47	43	23.4	13.89	59	98.4	35.08	36
10	69.1	12.18	18	17.0	11.40	67	14.1	8.16	58	77.9	17.59	23
11	74.8	19.56	26	19.6	13.89	71	14.6	6.22	43	84.0	23.43	28
12	59.7	15.78	26	13.1	7.72	59	7.2	5.68	79	67.3	25.60	35

discrepancies in loading values were generally higher for total phosphorus (average coefficient of variation = 10%) than for dissolved phosphorus (average coefficient of variation = 7%). The variation between loadings from the two data sets was generally less than the variation between the two years of study data at each site, particularly for dissolved phosphorus loadings.

### 3.18.2 Loading Sources

Over the past ten years the municipal input of phosphorus has changed as have populations. The City of Calgary grew from about 400,000 in 1971 to 590,000 in 1981 (Figure 32). The population growth was paralleled by an increase in sewage treatment plant effluent volume from 48 to 88 million gallons per day. From 1971 to 1974 the sewage treatment plant phosphate loading decreased, probably because of the restriction of phosphates in the manufacture of detergents. However, the loading increased since 1974, and exceeded the 1971 value in 1980. Lethbridge and Medicine Hat, with similar growth patterns, would show the same trends.

The form of phosphorus and its bioavailability are factors in determining the importance of sewage effluent as a loading source. Samples of effluent from Calgary's Bonnybrook sewage treatment plant were analyzed for phosphorus forms in connection with a study of diurnal variability (Appendix A). The phosphorus discharged from the plant was primarily in the dissolved form (90-97%), in which dissolved reactive phosphorus accounted for more than 90% of the soluble forms.

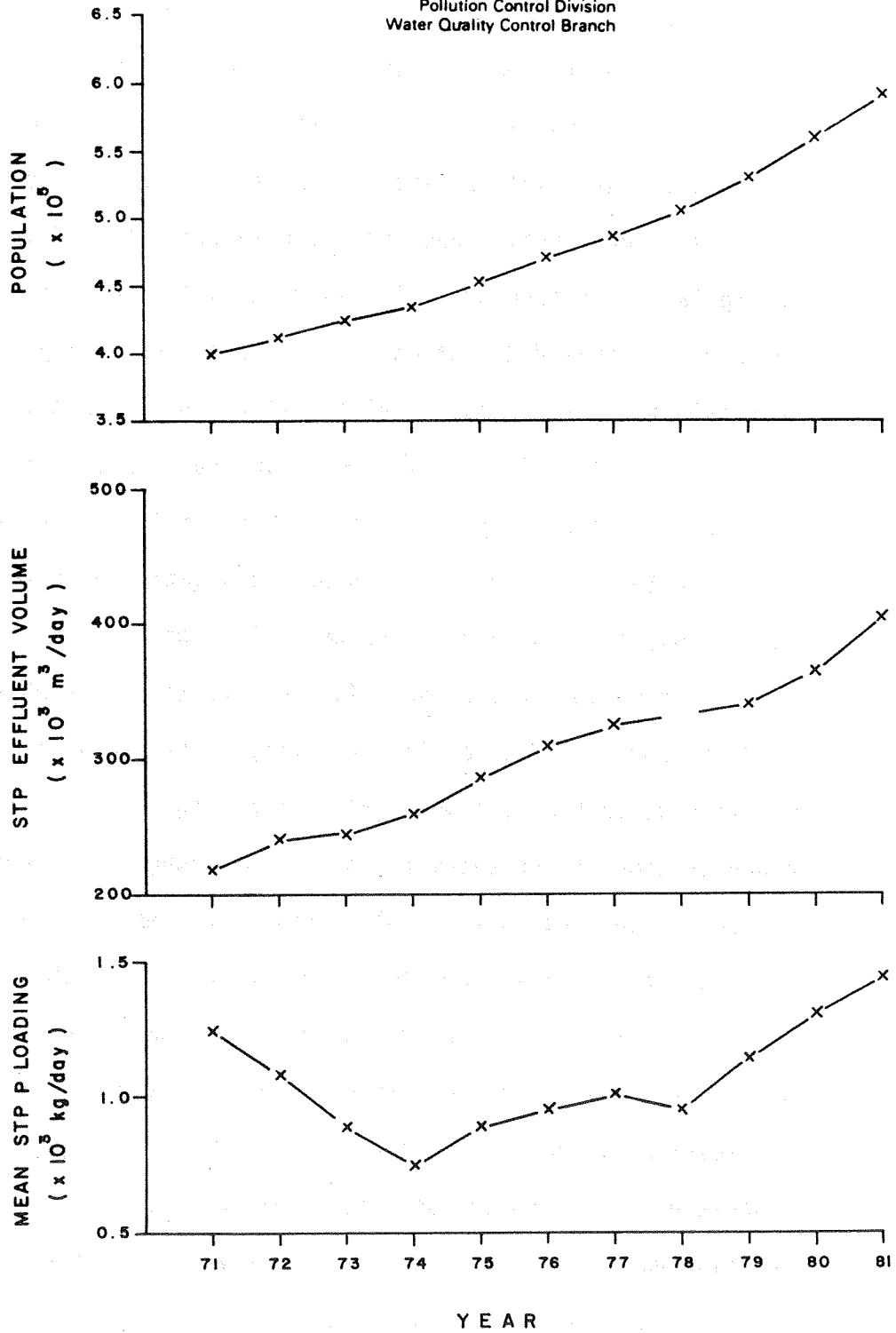


Fig. 32 Population and sewage treatment plant effluent volume and phosphorus loading for Calgary from 1971 to 1981.

A few dissolved biologically-available phosphorus estimates were carried out on sewage effluent in another study. Dissolved biologically-available phosphorus appeared to correlate fairly well with dissolved reactive phosphorus, both prior to and after alum precipitation (Figure 33). The large dissolved biologically-available phosphorus standard deviations may be caused partially by problems intrinsic to carrying out algal assays at very high nutrient levels (Hamilton et al., 1981). Extremely limited data on particulate phosphorus availability of Calgary sewage effluent (Table 14) suggested that particulate phosphorus availability in the effluent is low and may decrease after alum precipitation.

In order to compare the relative effects of the phosphorus loading from each city on its receiving river, total phosphorus dilution concentrations were calculated (Figure 34). These dilution concentrations represented the mixing of sewage treatment plant effluent with river water. Also shown for comparison are the measured mean summer dissolved phosphorus concentrations below the city inputs. Dissolved phosphorus was used for comparison to remove the bias in river water concentrations that resulted from seasonal fluctuations in total phosphorus in the Basin. Calgary has the highest dilution phosphorus concentrations, followed by Lethbridge and Medicine Hat. A large yearly variation was illustrated more strongly in the Calgary and Lethbridge data than in the Medicine Hat data. The effects of a low flow year such as 1977 were shown in high dilution

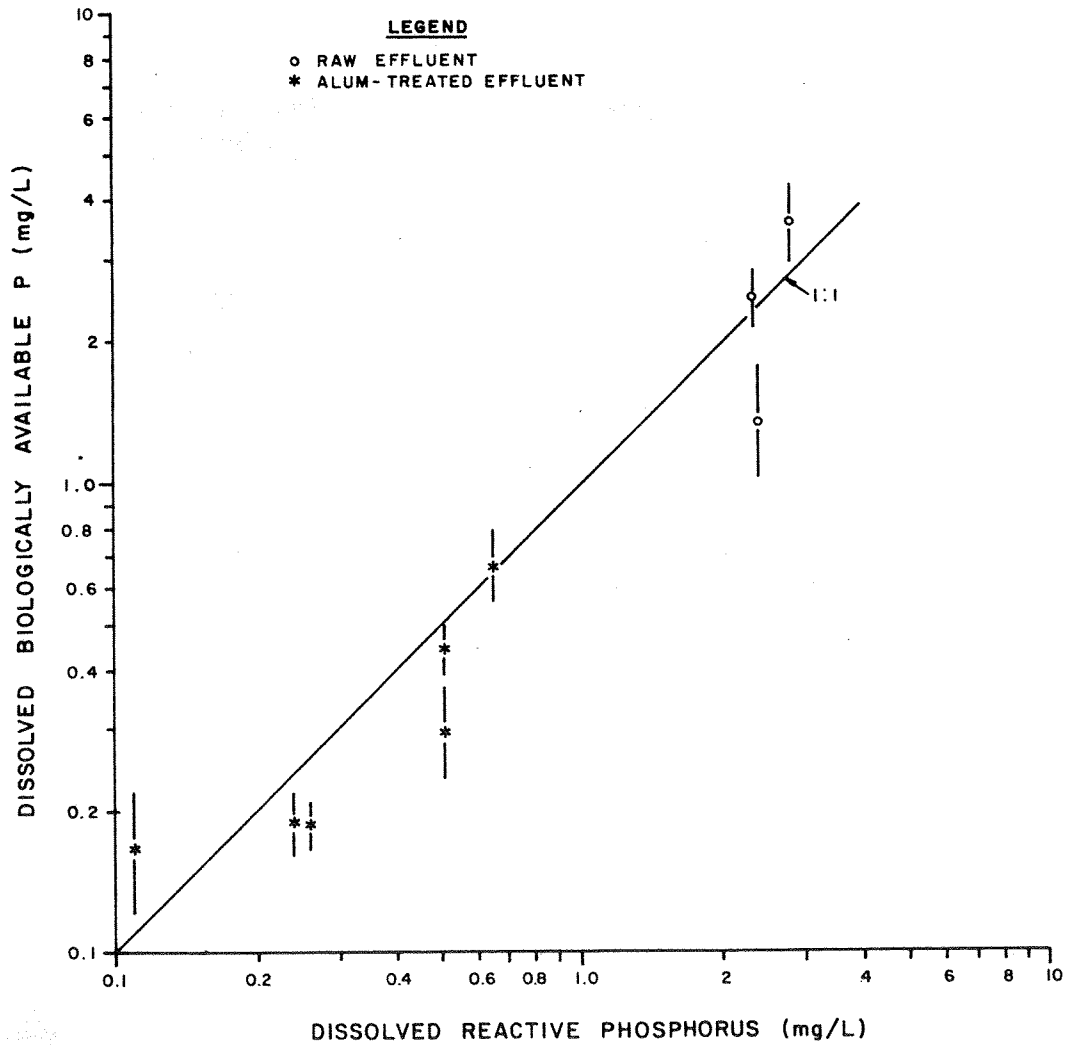


Fig. 33 Comparison between dissolved biologically available phosphorus and dissolved reactive phosphorus in sewage effluent.

TABLE 14      BIOAVAILABILITY OF PARTICULATE  
 PHOSPHORUS IN SEWAGE  
 TREATMENT PLANT EFFLUENT

	<u>PARTICULATE BAP*</u>	<u>S.D.</u>	<u>TOTAL PARTICULATE PHOSPHORUS*</u>	<u>PBAP/PP</u>
Raw Secondary	24.5	2.2	120	0.20
60 mg/L alum	14.6	1.5	870	0.02
100 mg/L alum	17.6	3.4	480	0.04

\* µg/L



**LEGEND**

- x CALGARY TP
- ..... x SITE 2 DP
- ..... o SITE 4 DP
- - - o LETHBRIDGE TP
- ..... o SITE 11 DP
- o MEDICINE HAT TP

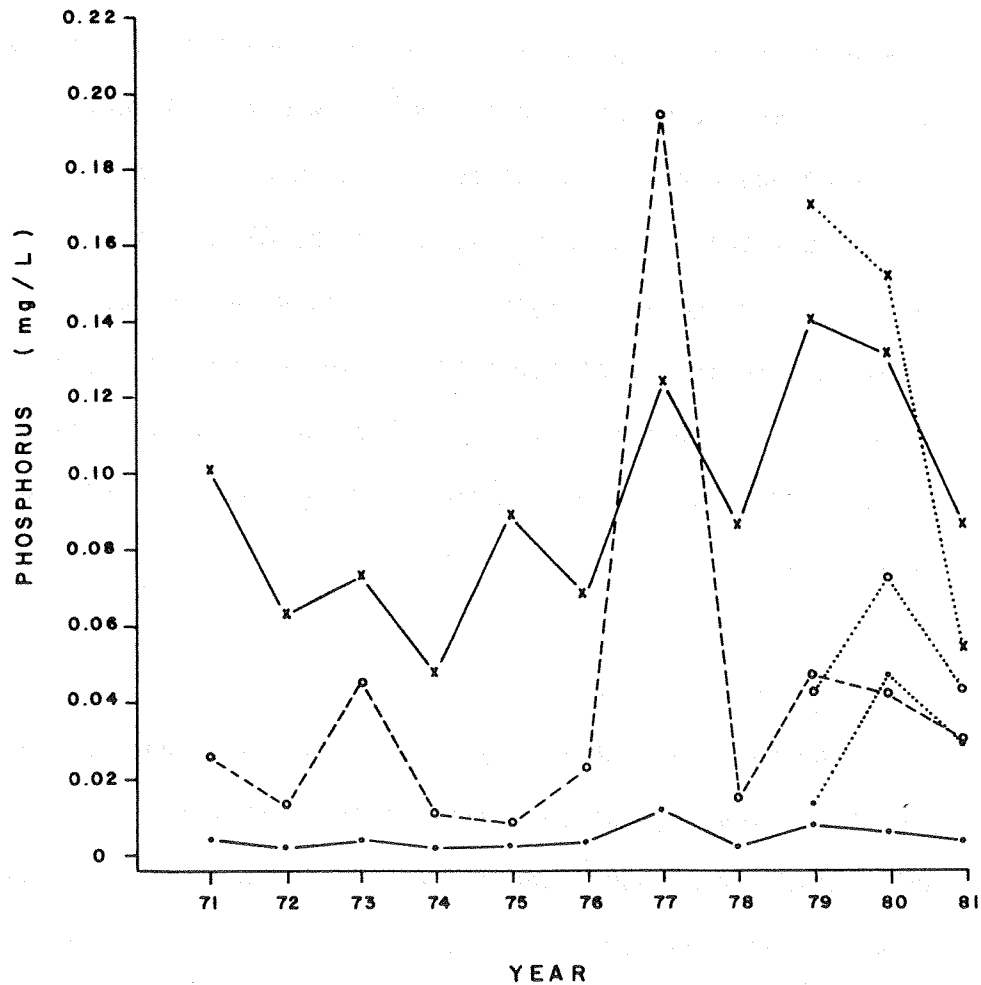


Fig. 34

Comparison of calculated dilution concentrations of total phosphorus from city sewage treatment plants and measured concentrations of dissolved phosphorus in receiving rivers.

concentrations, but the general trend of increasing impact was also shown. In 1978 and 1980 at Calgary, the mean June to September discharges were similar, but higher potential downstream concentrations of phosphorus occurred in 1980 because loading was higher.

Table 15 summarizes the seasonal and annual return flow and tributary loadings and irrigation withdrawals for total and dissolved phosphorus. Overall in the Basin, variation in tributary and return flow loadings was highest in winter and lowest in summer, with loadings varying by as much as 300% in winter. Annually, input variation was highest for dissolved phosphorus loading in the Bow River and total phosphorus loading in the Oldman River. Absolute seasonal loadings were higher in the Bow River in spring, and in the Oldman and South Saskatchewan Rivers in the summer. Irrigation withdrawal loadings from the Bow River were most variable in fall and least variable in summer. Absolute withdrawal loadings were highest in summer.

### 3.18.3 Reach Loadings

Figures 35 and 36 show average annual and seasonal dissolved phosphorus loadings at each site as the dark base of each 'bar'. The net loading from inputs and withdrawals within the downstream reach is shown as the clear upper portion of each 'bar'. This allows visual comparison of observed dissolved phosphorus loading at each site and

TABLE 15 RETURN FLOW AND TRIBUTARY LOADINGS AND IRRIGATION WITHDRAWALS  
OF TOTAL AND DISSOLVED PHOSPHORUS ON AN ANNUAL AND SEASONAL  
BASIS INCLUDING COEFFICIENT OF VARIATION (CV)

Return Flow and Tributary Loading (tonnes)

	Bow River				Oldman River				S. Saskatchewan River				Total			
	1979	1980	1981	CV	1979	1980	1981	CV	1979	1980	1981	CV	1979	1980	1981	CV
Dissolved Phosphorus																
Annual		32.15	21.28	29		3.10	3.72	13		1.84	2.25	14		37.09	27.25	22
Winter		1.46	4.83	76		0	0			0	0			1.46	4.83	76
Spring	12.05	20.09	6.99	51	0.36	0.70	0.82	38	0.27	0.30	0.39	20	12.68	21.09	8.20	47
Summer	5.36	6.08	7.69	19	1.90	2.03	2.34	11	1.23	1.13	1.33	8	8.49	9.24	11.36	15
Fall	1.79	2.91	2.88	48	0.37	0.38	0.65	34	0.26	0.52	0.53	35	2.42	3.81	4.06	26
Total Phosphorus																
Annual		83.48	95.10	9		9.20	13.58	27		3.55	4.02	9		96.23	112.70	11
Winter		3.87	12.79	76		0	0			0	0			3.87	12.79	76
Spring	33.16	54.42	58.96	28	1.46	2.32	3.14	36	0.50	0.51	0.72	22	35.12	57.25	62.82	28
Summer	11.13	14.25	17.53	22	6.36	5.54	8.06	19	2.07	1.86	2.20	8	19.56	21.65	27.79	19
Fall	4.29	7.21	8.73	33	1.44	1.34	2.38	33	0.63	1.17	1.10	30	6.36	9.72	12.21	31

Irrigation Withdrawals (tonnes)

	Dissolved Phosphorus				Total Phosphorus			
	1979	1980	1981	CV	1979	1980	1981	CV
Annual		58.81	74.81	12		78.90	93.30	17
Winter		0	0			0	0	
Spring	9.76	14.09	13.33	19	14.90	19.04	17.88	12
Summer	24.37	25.66	26.92	5	36.94	38.46	37.80	2
Fall	23.78	19.05	34.56	31	9.32	21.40	37.62	62

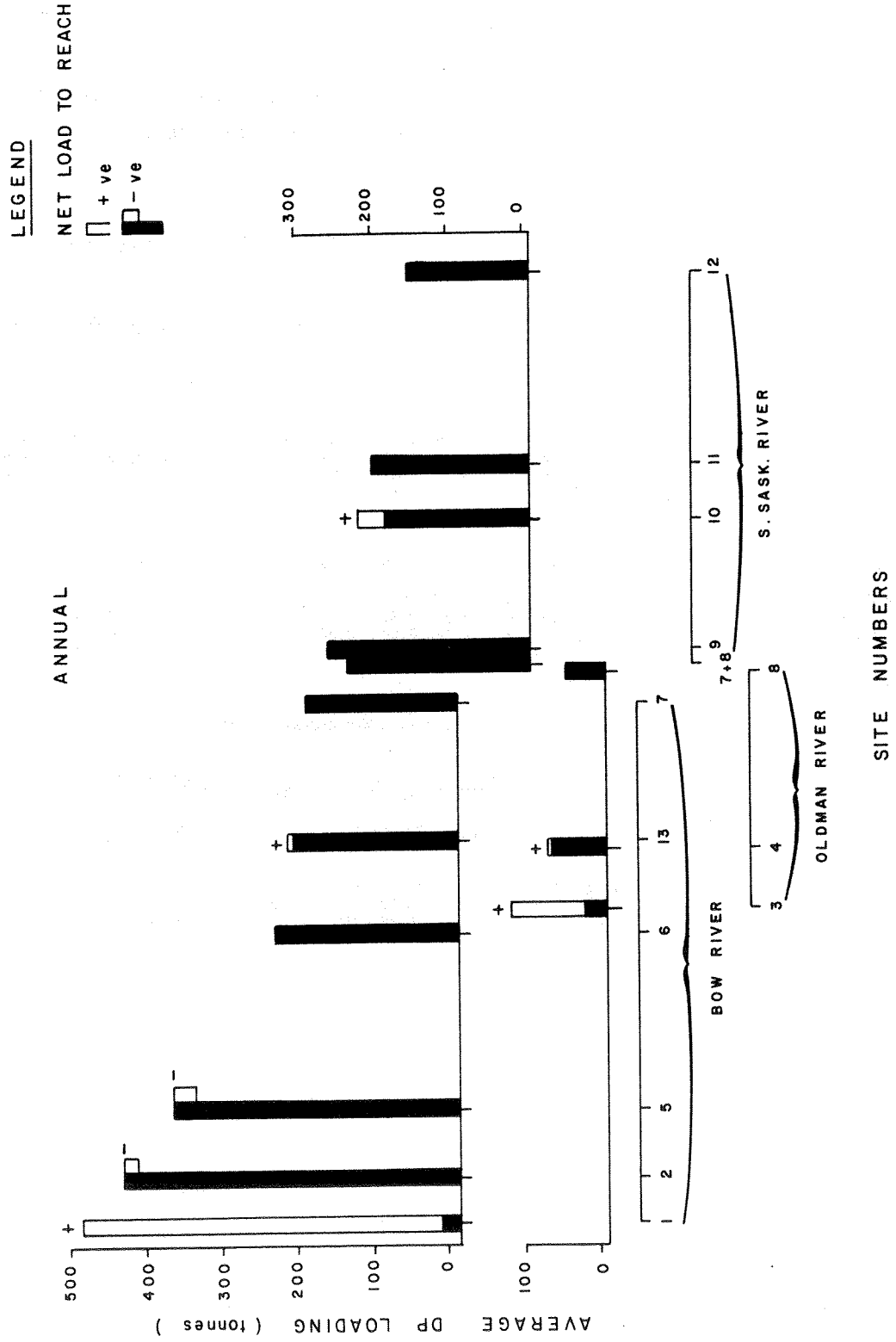


Fig. 35 Comparison of calculated and measured average annual loading of dissolved phosphorus at each site in the study basin.

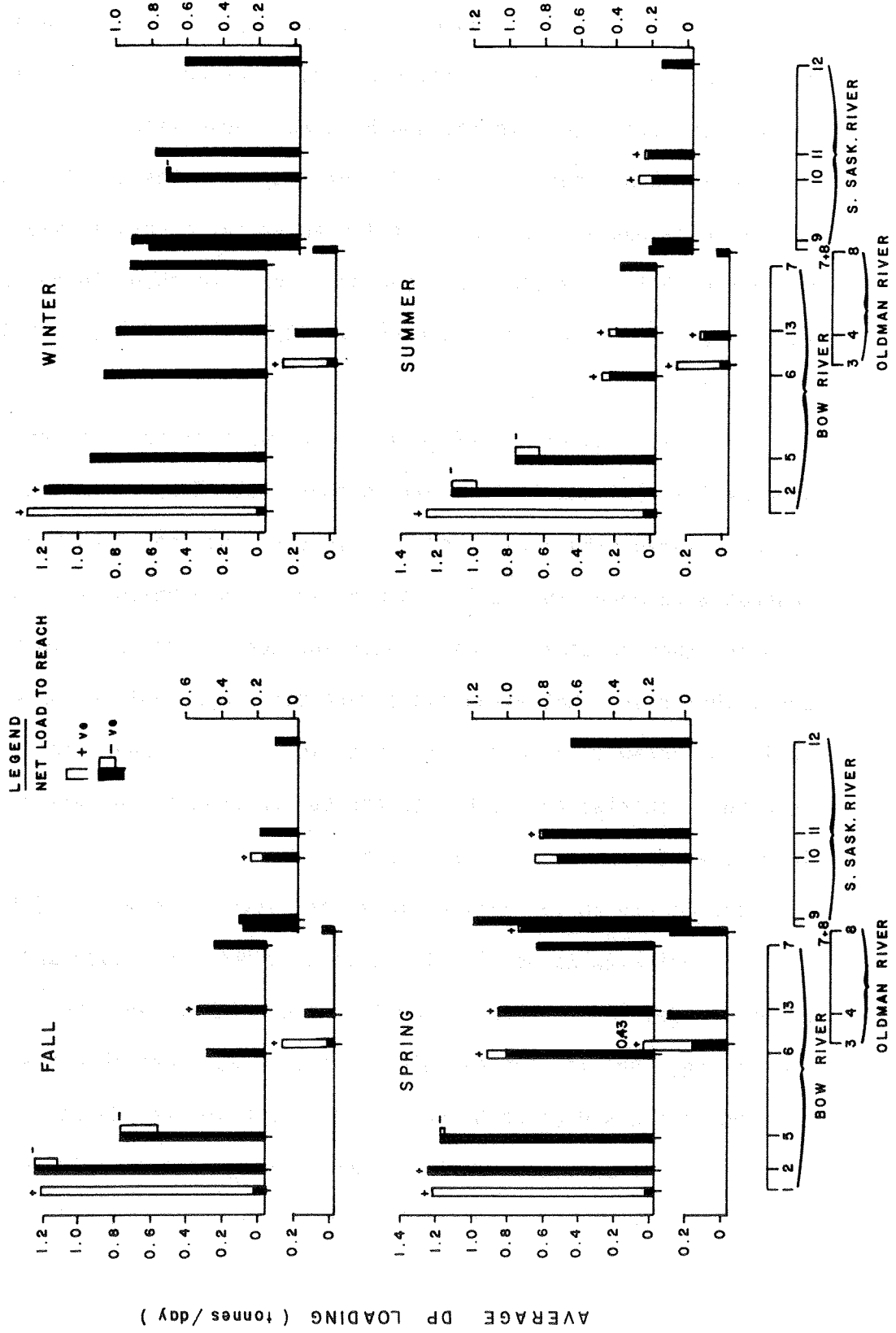


Fig. 36 Comparison of calculated and measured average seasonal loading of dissolved phosphorus at each site in the study basin.

mathematical 'expected' loading. The loading at Sites 7 and 8, at the confluences of the Bow and Oldman Rivers, were combined for ease of comparison with Site 9 in the South Saskatchewan River.

On an annual basis (Figure 35) net input in Reach 1-2 (from Site 1 to Site 2) was most dramatic, followed by net inputs in Reach 3-4 and Reach 10-11. Smaller net loadings were also shown in the reaches in the lower Bow and Oldman and net withdrawals were shown in Reaches 2-5 and 5-6.

Seasonal comparisons (Figure 36) showed that the net inputs in Reaches 1-2, 3-4 and 10-11 remained constant. These were the reaches which included city sewage inputs. In contrast, net inputs at other reaches were more important in summer and within Reach 6-13 in spring than in other seasons. These inputs include irrigation return flows and tributaries. Net withdrawals were more important in summer and fall. Withdrawals occurred at irrigation district headworks. Net loading calculated for each site can be compared to the measured loading at the next site downstream.

The discrepancies between these calculated and measured loadings can be considered as net loading changes within the reach and are given in Table 16. Annually, most reaches registered a net decrease in loading, that is, the calculated loading was less than the measured loading at the end of each reach. The exception was Reach 7-8-9 in both years. The reaches with the greatest net decrease (-2.1 to -1.0 tonnes/km) were 1-2 in 1981, 2-5 in both years, 5-6 in 1980, 3-4 in 1981 and 9-10 in 1981.

TABLE 16: NET CHANGE IN DISSOLVED PHOSPHORUS LOADING WITHIN EACH RIVER REACH ON AN ANNUAL AND SEASONAL BASIS

		River Reach Loading Change										
Reach	Reach Length (km)	1-2	2-5	5-6	6-13	13-7	3-4	4-8	7-8-9	9-10	10-11	11-12
Annual (tonnes/km)												
	1980	-0.63	-1.20	-1.27	-0.55	-0.25	-0.82	-0.20	+0.44	-0.57	-0.32	-0.30
	1981	-2.10	-1.03	-0.57	-0.16	-0.28	-1.60	-0.24	+0.93	-1.16	-0.72	-0.48
Seasonal (kg/day/km)												
	Spring 1979	-1.96	-9.35	+0.14	-1.88	-3.09	+0.41	+6.32	-2.32	-1.85	-0.92	
	Summer 1979	+4.90	-10.28	-3.22	-0.53	-3.46	-0.65	+1.17	-1.29	-1.62	-0.27	
	Fall 1979	+7.26	-12.09	-2.44	-1.33	-0.81	-2.35	-1.00	-0.71	-0.86	-1.14	-0.51
	Winter 1980	-1.13	-6.40	-1.00	-1.15	-1.34	-0.33	-0.79	-0.47	-0.89	-1.61	-1.26
	Spring 1980	+3.21	+3.22	-5.65	-1.30	-0.08	-2.22	-0.19	+11.54	-6.04	+2.13	-1.68
	Summer 1980	-5.97	-3.51	-4.97	-1.43	-0.27	-2.54	-0.87	+0.07	+0.58	-1.82	-0.41
	Fall 1980	+1.48	-7.41	-3.98	+2.80	-1.70	-2.28	-0.68	+3.77	-3.07	-2.24	-0.37
	Winter 1981	-5.52	-5.98	-0.15	-1.44	-0.15	-2.63	-1.01	+5.31	-3.58	+5.64	-1.24
	Spring 1981	-0.28	+1.56	-3.24	-1.14	-1.05	-4.68	-0.53	+4.51	-7.25	-2.36	-1.44
	Summer 1981	-11.99	-1.43	-1.95	-0.86	-0.35	-3.71	-1.06	-3.26	+0.54	-1.28	-1.36
	Fall 1981	-4.81	-5.45	-0.78	+0.68	-0.52	-3.92	-0.94	-1.44	-0.31	-3.10	-1.46

Seasonally, in the Bow River the largest net dissolved phosphorus decreases (-12.1 to -9.4 kg/day/km) occurred at Reach 1-2 in summer 1981 and Reach 2-5 in spring, summer and fall 1979. Somewhat lower decreases (-7.4 to -5.0 kg/day/km) were measured at Reach 1-2 in summer 1980 and winter 1981; at Reach 2-5 in fall and winter 1980 and 1981; and at Reach 5-6 in spring and summer 1980. Large net increases (2.8-7.3 kg/day/km) were measured at Reach 1-2 in summer and fall 1979 and spring 1980; at Reach 2-5 in spring 1980; and at Reach 6-13 in fall 1980.

In the Oldman River seasonal net changes were generally smaller than in the Bow. The only net increase (0.4 kg/day/km) occurred at Reach 4-8 in spring 1979. The net decreases in Reach 3-4 were fairly consistent between seasons (-2.3 to -3.9 kg/day/km). The exceptions were winter 1980 (-0.3 kg/day/km) and spring 1981 (-4.7 kg/day/km). This consistency was also shown in Reach 4-8 but at a lower range of values.

In the South Saskatchewan River net increases were highest (3.8 to 11.5 kg/day/km) at Reach 7-8-9 in spring of all years, fall 1980 and winter 1981, and at Reach 10-11 in winter 1981. Largest net decreases (-7.2 to -2.3 kg/day/km) occurred at Reach 7-8-9 in summer 1981; at Reach 9-10 in spring of all years, fall 1980 and winter 1981, and at Reach 10-11 in fall 1980, 1981 and spring 1981.

Table 17 summarizes the relative annual contribution of various phosphorus sources, both total and dissolved phosphorus, directly to the Bow, Oldman and South Saskatchewan Rivers within the three sub-basins. Irrigation withdrawals were not included in the loading



TABLE 17

INVENTORY OF ANNUAL TP AND DP LOADINGS IN TONNES  
DIRECTLY INTO THE BOW, OLDMAN AND SOUTH SASKATCHEWAN  
RIVERS WITHIN THE STUDY AREA

Study Basin	U/S	Cities		Irrigation		Trib.	Ind.	Total
		Sewage	S/W	W/D	Return			
<u>Bow River</u>								
TP - 1980	177.5	614.0	30.5	-78.9	38.6	57.3	6.2	924.1
- 1981	792.2	671.0	31.8	-93.3	38.8	73.8	6.2	1613.8
- %	34.2	54.0	2.6	(-7.2)	3.3	5.4	0.5	
DP - 1980	18.8	565.4	5.7	-58.8	16.7	20.4	6.2	633.2
- 1981	45.6	617.8	5.9	-74.8	14.6	12.6	6.2	702.7
- %	4.7	88.6	0.9	(-10.0)	2.4	2.5	0.9	
<u>Oldman River</u>								
TP - 1980	21.8	495.8	26.2	-78.9	26.0	57.3	3.4	630.5
- 1981	29.4	511.8	27.0	-93.3	21.2	73.8	3.4	666.6
- %	4.0	77.7	4.1	(-13.2)	3.6	10.1	0.5	
DP - 1980	8.4	456.6	4.9	-58.8	11.8	20.4	3.4	505.5
- 1981	11.4	471.3	5.0	-74.8	8.7	12.6	3.4	512.4
- %	2.0	91.2	1.0	(-13.1)	2.0	3.2	0.7	
<u>S. Saskatchewan River</u>								
TP - 1980	539.3	29.1	1.8	0	3.5	0	1.0	574.7
- 1981	1248.4	40.9	2.0	0	4.0	0	1.0	1296.3
- %	95.0	4.2	0.2		0.4		0.2	
DP - 1980	200.1	26.8	0.3	0	1.8	0	1.0	230.0
- 1981	265.6	37.6	0.4	0	2.2	0	1.0	306.8
- %	86.8	12.0	0.1		0.8		0.4	

U/S - upstream, S/W - stormwater, W/D - withdrawal

inventory, but irrigation withdrawal and returns flows caused a net reduction in phosphorus loading. In the Bow River sub-basin, large volumes of water are withdrawn at the three irrigation district headworks. Two of these withdrawals are located downstream of Calgary, thus the concentration of phosphorus in the withdrawal water was high. The return flow volumes are lower and in some cases the phosphorus concentrations are lower. Both of these factors contribute to lower phosphorus loading values.

In terms of the entire Basin, 34% of the total phosphorus loading was contributed from waters upstream of Calgary and Lethbridge and 54% from the sewage treatment plants of the three major cities. However, when similar calculations were made with dissolved phosphorus, the upstream contribution dropped to 5% and the sewage treatment plant contribution rose to 89%.

In the Bow River sub-basin, the Calgary sewage treatment plants contributed 78% of the total phosphorus and 91% of the dissolved phosphorus. In the Oldman River sub-basin, the Lethbridge sewage treatment plant contributed 24% of the total phosphorus, while upstream sources contributed 73% of the total phosphorus. Dissolved phosphorus from the sewage treatment plant contributed 78% and upstream sources contributed 17%. Most of the phosphorus in the South Saskatchewan River sub-basin came from upstream waters (the Bow and Oldman Rivers accounted for 95% for total phosphorus and 87% for dissolved phosphorus). The Medicine Hat sewage treatment plant contributed 4% of the total phosphorus and 12% of the dissolved phosphorus to the South Saskatchewan River sub-basin.

In 1981, referring back to calculations of sediment phosphorus, the total phosphorus 'pool' in the sediments along the full length of the Bow River downstream of Calgary (8.3 tonnes) was equivalent to 1.2% of the total phosphorus input to the reach from all sources (Table 17); the corresponding value for the Oldman River downstream of Lethbridge was 0.5%. The total sediment biologically-available phosphorus in each reach was equivalent to 0.4% of the dissolved phosphorus input to the lower Bow River and 1.3% of the total input to the Oldman. Relative to these values, the approximated 1981 flux of phosphorus from the sediments in each river was even less.

### 3.19 Bonnybrook

The main impetus behind the Bonnybrook study was to investigate further the nutrient concentrations in the reach directly downstream of the Calgary sewage treatment plants. Other variables were measured to help characterize the Bow River within this mixing zone. The Bonnybrook study sites are located by map on Figure 1 and by site and NAQUADAT Code on Table 5.

Temperature increased from May to peak values in August before decreasing more rapidly to low values by the end of October (Figure 37). Along the Bow River, the greatest difference between right and left bank temperatures occurred at Site M2R, which averaged 1.9°C higher than M2L (Figure 38). Temperature increased in a downstream direction by about 3°C to Site M11 and was lower at Sites M12 and M13. The rise in temperature was affected by the order of sampling

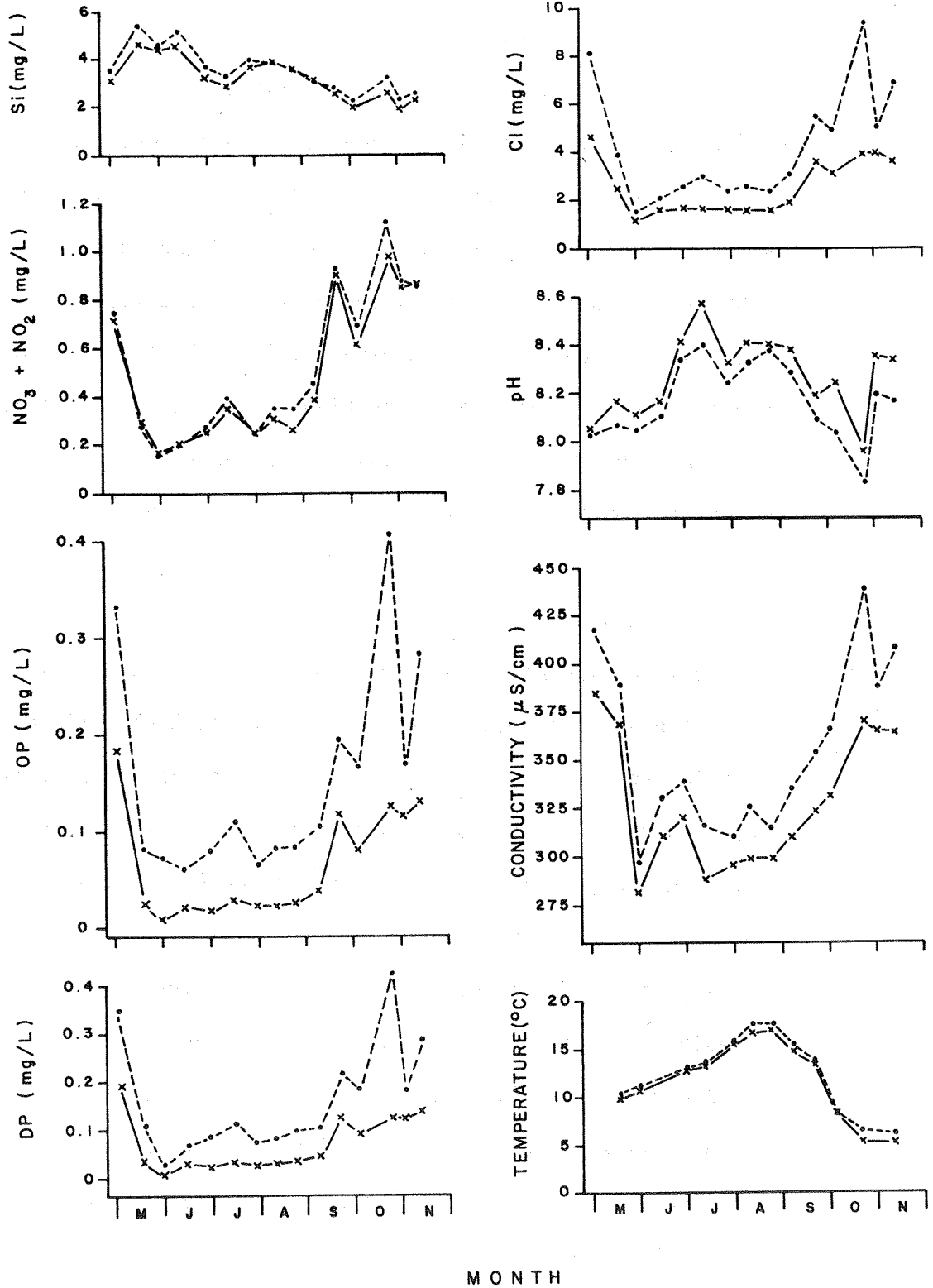


Fig. 37 Comparison between data collected from right (.) and left (x) river banks of the Bow River in the Bonnybrook study using the average of all sites on each date.

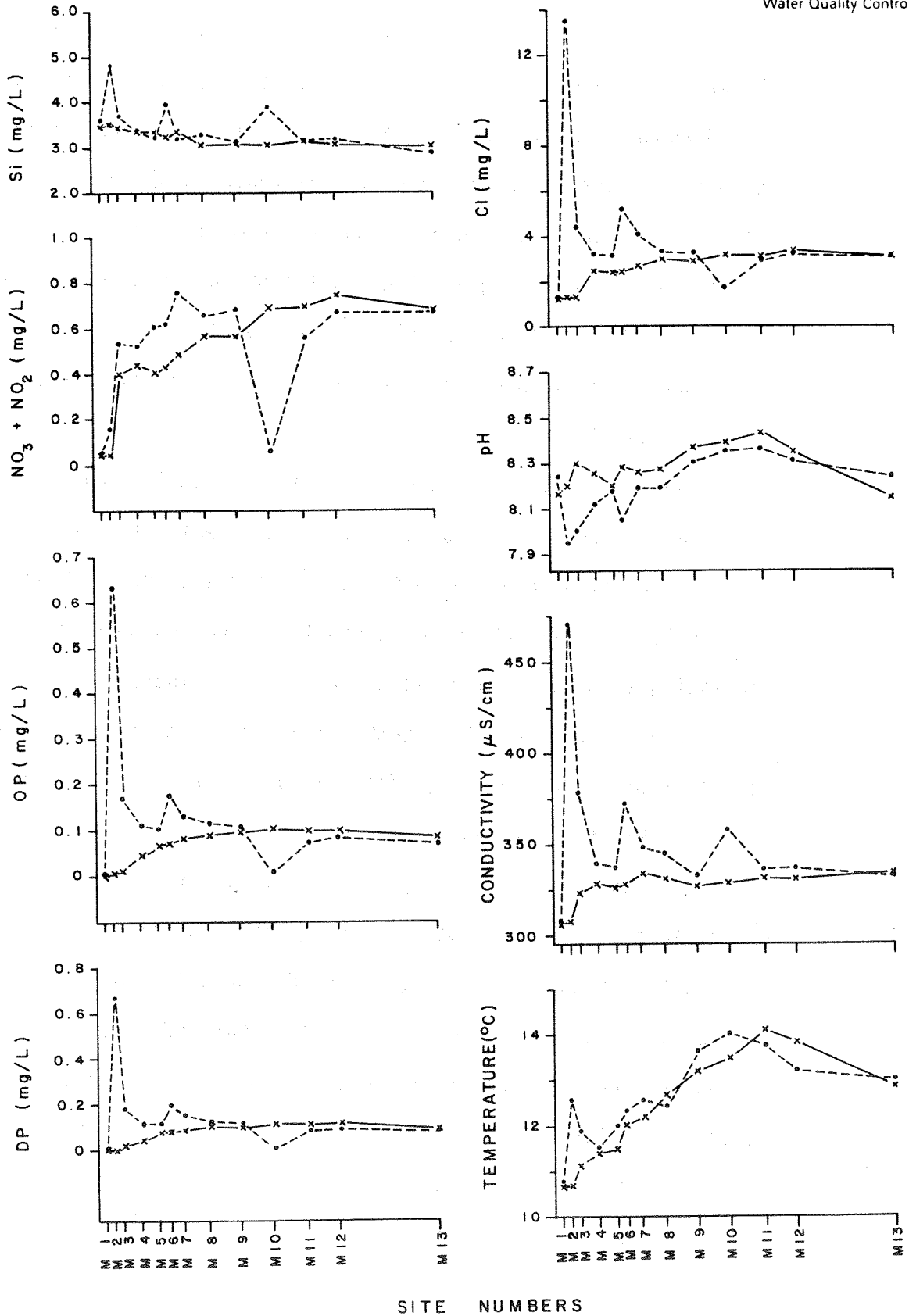


Fig. 38 Comparison between data collected from right (.) and left (x) river banks of the Bow River in the Bonnybrook study using the average of all dates at each site.

from upstream to downstream. The lower temperatures at Sites M12 and M13 were caused by a few missing values at times of high temperature.

Seasonally pH increased from May to July and decreased from September to October with higher values again in November (Figure 37). These trends were more pronounced from Sites M5 to M12. Left bank values averaged higher than right bank values with Sites M2 and M6 showing this most consistently throughout the study. The largest discrepancies between banks, however, was in September and October at Sites M3 and M4.

Longitudinally, left bank pH increased from Site M1L to M3L, decreased to M5L and increased again to M6L, while the opposite was true for the right bank pH, with lowest values at M2R and M6R (Figure 38). Below Site M7, pH followed similar trends on both banks, increasing to Site M11 and decreasing to M13. These trends were shown more strongly from July to November than in May and June. Right and left bank pH values were significantly different (t-test,  $p < 0.01$ ) at Sites M2, M3, M4, M11 and M13.

Chloride concentration and conductivity data had a correlation coefficient of 0.87 and both were correlated to phosphorus ( $r = 0.97$  and 0.83). Seasonally, average chloride concentrations and conductivity decreased from early to late May and lower values increased from September to November (Figure 37). From June to August, chloride concentrations were relatively constant at about 2 mg/L. During this period conductivity increased through June, then decreased to lower values for July and August. This trend was also

evident in chloride concentrations at Sites M2R, M3R and M6R but was masked in the average concentrations.

Chloride at M1, M2L and M3L was relatively constant during the study period, though slightly higher in May and from September to November. However, conductivity at these sites showed trends similar to, but less pronounced than the average trend.

Along the Bow River, chloride and conductivity showed peak values at M2R, M6R and M10R, though the peak at M10R for chloride was reversed (Figure 38). Left bank average concentrations increased from low values at M2L for conductivity and M3L for chloride to higher values which increased slightly through downstream sites. Right and left bank concentrations were similar at Site M9 and at M12. Using paired data for t-test, left and right bank concentrations were significantly different ( $p < .01$ ) from Sites M2 to M10 for chloride and M2 to M9 for conductivity.

Seasonal trends in silica concentrations were similar at all sites at both banks (Figure 37). Concentrations decreased from mid-May to October with fluctuations of lower values in early May and mid-July and higher values in June and August. The downward trend of concentrations through the season was more pronounced at downstream sites.

Average silica trends along the Bow River (Figure 38) showed the influence of the sewage treatment plants and Highwood River at Sites M2R, M6R and M10R with higher average concentrations. Sites M6R and M10R had lower silica concentrations than left bank samples from mid-August through September. A small downstream decrease in average

concentration resulted from different seasonal trends along the river. Concentrations were relatively constant in early May, constant to increasing downstream in May and June, and then decreased downstream from July to November. Right and left bank average concentrations were very similar at Sites M5, M9 and M12.

Seasonally, average nitrate/nitrite (NIT) concentrations for both banks followed the same trend: values decreased through May, increased to July, and then remained relatively constant before there was an increase with fluctuations from August to November (Figure 37). The exceptions were Sites M1R, M1L and M2L (Figure 38) which were unaffected by sewage treatment plant effluents and were low through the study period. Site M2R had relatively low nitrate/nitrite concentrations, though concentrations were slightly higher in May and from August to November.

In a downstream direction along the Bow River, average nitrate/nitrite increased from low values at Sites M1 and M2 to higher values at M3. The left bank concentrations increased gradually from Site M5L downstream, while the right bank concentrations increased from Site M4R to M7R, then stayed relatively constant with the exception of M10R which reflected Highwood River water and M11R with slightly lower values. Thus, the right bank had higher concentrations than the left bank from M2 to M9, particularly from M5 to M7 and lower concentrations from M10 to M12. Trends in nitrate/nitrite at each site varied between sampling times. For the left bank an initial peak



nitrate/nitrite concentration followed by a decrease occurred at Site M3 in May, October 23 and November 12, and at Site M4 on June 29, July 13 and from mid-August through September; at other sampling times the increase was more gradual and no drop-off was measured.

For the right bank the average concentrations masked distinct seasonal differences in trends along the river. The relatively constant average concentrations at Sites M8R, M9R, M12R and M13R were replaced by generally increasing values in early May and November. The initial increase in concentration to M3R was often less distinctly separated from the general downstream increase, particularly from June to mid-September, when highest relative concentrations were measured at Site M5R. The peak average concentration at Site M7R resulted from peak concentrations at M7R from mid-September to October when absolute concentrations were higher. Comparisons of right and left bank nitrate/nitrite concentrations using paired data showed a significant difference ( $p < .01$ ) at Sites M2 and M5 to M11.

Phosphorus forms (dissolved and dissolved reactive) followed trends similar to the nitrate/nitrite concentrations. In fact, the correlation coefficient ( $r$ ) for all data was 0.997. Seasonal trends in phosphorus concentration at all sites were similar except where there was low or minimal influence from the sewage treatment plant (Sites M1, M2L and M3L). Longitudinal trends were also similar though absolute concentrations varied.

Figure 37 shows average concentrations of all sites for right and left banks throughout the study period. High concentrations in early May decreased by the end of May. For the left bank, lower levels

persisted until early September when concentrations began to increase. Right bank average concentrations were higher than left bank, and concentrations through the summer increased from the low end-May concentration to a peak in mid-July. This was followed by lower concentrations until September when they started increasing again.

Figure 38 shows average phosphorus concentrations at each site for right and left banks down the length of the river. Highest concentrations were measured at Site M2R below Bonnybrook sewage treatment plant and at Site M6R below Fish Creek sewage treatment plant. Otherwise, right bank phosphorus concentration decreased in a downstream direction. Site M10R was below the input from the Highwood River and reflected low levels of phosphorus in the Highwood River water. Left bank concentrations increased gradually in a downstream direction. Left and right bank concentrations were essentially the same at Site M9. Using paired data for t-tests comparing right and left bank concentrations, results were significant ( $p < .01$ ) at Sites M2 to M11.

Despite the significant differences between right and left bank phosphorus concentrations, the average concentrations at Site M1, M5, M9 and M13 were used to calculate summer phosphorus loading. This allowed a more detailed investigation of the net loading changes within the mixing zone of the Bow River below the Calgary sewage treatment plants.

Net loading changes of dissolved phosphorus in the river reaches M1-M5, M5-M9 and M9-M13 were calculated for the summer period (Table 18) to be -1.2, -0.2 and -0.5 tonnes/km respectively. Thus, the greatest net loss of dissolved phosphorus from the river was shown in the reach from above the Bonnybrook sewage treatment plant to above the Fish Creek sewage treatment plant.

TABLE 18 BONNYBROOK STUDY LOADINGS AND NET

LOADING CHANGES FOR DP IN SUMMER 1981

<u>Reach</u>	<u>Length (km)</u>	<u>Loading (tonnes)</u>	<u>Loading Change (tonnes/km)</u>
<u>M1-M5</u>	12		-1.23
M1		3.78	
Bonnybrook STP		95.72	
Total		99.50	
M5		84.70	
<u>M5-M9</u>	18		-0.20
M5		84.70	
Fish Creek STP		15.82	
Fish Creek		0.14	
Total		100.66	
M9		97.00	
<u>M9-M13</u>	44		-0.51
M9		97.00	
Highwood River		1.74	
Twelve Mile Coulee		1.12	
Irrigation Diversion		-14.33	
Total		85.53	
M13		63.09	

## 4.0 DISCUSSION

### 4.1 Seasonal Variability

Water chemistry is influenced by a number of interrelated factors throughout the Basin which produces a recognizable seasonal variability. These factors are seasonally variable themselves, and include climatological factors, discharge, and biological activity. Groundwater and external inputs from cities, industry, tributaries and irrigation are also important to varying degrees. This variability is reflected in the differences in trends shown within each sub-basin and at each site.

Seasonal trends within the Basin were identified previously on the Oldman and South Saskatchewan Rivers (Davies et al., 1977). Ranges of concentrations differed in some cases but this is not unexpected because of yearly variation.

The solubility of oxygen is primarily determined by temperature, which in turn determines the basic seasonal trend of lower values in summer and higher values in winter. However, there is also a variation shown throughout the day which is dependent on plant photosynthesis and respiration. The size of the diurnal variation shown in the data reflected the relative degree of primary production both among seasons and among sites.

Hart and Exner (1979) reviewed the relationship between diurnal dissolved oxygen and macrophyte growth at sites above and below Calgary. They found that diurnal dissolved oxygen variation below

Calgary was much greater than above Calgary. In fact, the results of the 1979 - 1982 study indicated that the Stiers Ranch site showed the greatest effect of primary producers on dissolved oxygen of any other in the Basin. This effect was highest in summer 1980.

No direct comparison of the magnitude of dissolved oxygen variation between the site immediately below Calgary and that below Lethbridge was possible, since the remote monitor site on the Oldman River is farther downstream at Fincastle (Figure 1). However, Davies et al., (1977) found a diurnal pattern of dissolved oxygen saturation in summer on the Oldman and South Saskatchewan Rivers. Saturation values ranging from about 80% to 120% illustrate the daily rhythm in photosynthesis in the aquatic plants.

Many of the physical variables exhibit basic seasonal trends, with high or low periods over summer or winter and transitional periods through spring and fall. Variables with high winter and low summer values include conductivity, alkalinity, chloride and dissolved inorganic carbon. In fact, the correlation analysis confirmed the positive relationship between these variables overall. The improvement in correlation coefficient when rivers were tested separately reflects basic sub-basin differences in geology, climate, hydrology, land use and instream processes.

The changes in conductivity over a year reflect changes in ionic concentrations. The higher levels measured over winter during periods of base flow reflect the higher salinity of the groundwater within the Basin when undiluted by rainfall and snowmelt.

Chloride, a conservative ion, is a component of the conductivity measurement. Concentrations found in base flow are affected by influences external to the river and they tend to increase in a downstream direction. The influence of chloride input from sewage treatment plants was most evident at Site 2, but there was additional chloride input from irrigation return flows. The influence of discharge on this variable is also shown by the rapid drop-off of chloride concentration during high flow in spring.

The very high levels of chloride in December in the Bow River may have been caused by the freeze-out of salts during ice formation and higher proportional contribution of groundwater to base flow. The increase in chloride in the Bow River through summer and fall was moderated in the South Saskatchewan by the influence of the Oldman River, where chloride concentration decreased from August to November. This decrease may result from the reduction in irrigation return flows.

Alkalinity, as a measure of the buffering capacity of the river water, is affected by the changes in carbon dioxide utilization and release over a season. The changes were related to the biological activity of primary producers, and were reflected also by the trends of pH changes. In summer, pH was high and alkalinity was low when photosynthetic activities were greatest, and in winter pH was low and alkalinity was high when decompositional activities predominated.

Bow River results covered the widest range of pH values, and indicated the extremes of biological activity. A second trend of strong diurnal pH fluctuations measured at Site 2 below Calgary in the

summer indicated the significant local effect of a large plant population.

Turbidity and non-filterable residue give a measure of the particulate matter or suspended sediments which predominate during high flow periods in spring. During 1980 the volcanic ash from Mount St. Helens affected this measurement as well, both directly and when washed into the river after a rain. Other particulate variables of particulate organic carbon, particulate nitrogen and total phosphorus reflected the discharge levels in the rivers. The significant correlations amongst these variables and with discharge confirmed this relationship.

Higher concentrations of particulate variables were measured in the fall as a result of the addition of plant material during senescence. The variation among years was largely determined by climatic conditions, such as rainfall, snowmelt and temperature, which affected discharge. The Bow River, with a more regulated discharge, showed lower extremes of particulate variables than the Oldman or South Saskatchewan Rivers.

The concentration of reactive silica and the growth cycle of diatoms are inter-related. Peak values in diatom populations often match low values in silica concentrations. Low silica concentrations occurred in late summer/fall and briefly in early spring, and these should correspond to large diatom populations. Diatom populations in winter and during peak discharge would be expected to be low. These relationships are addressed in Part II (The Primary Producers; Charlton et al., 1986).



Carbon is an important nutrient for plant growth. Although particulate organic carbon showed seasonal trends related to discharge, the importance of the inputs from Calgary sewage treatment plants were apparent in the results for the Bow River at Site 2 below Calgary which showed little seasonal pattern. The seasonal pattern of dissolved inorganic carbon concentrations, like alkalinity, was affected by carbon dioxide utilization and release cycles of primary producers.

The changes in phosphorus and nitrogen concentrations over a year reflected changes in plant life cycles. Nutrients are utilized for growth and released upon senescence. These nutrient concentrations are correlated more strongly in the Bow than the Oldman River. At upstream sites on the Bow (Site 1) and Oldman (Site 3) Rivers, concentrations were generally low and seasonal changes were minimal. At Site 2 and 4, below Calgary and Lethbridge, the reduction of nutrients from high winter values caused by plant uptake was reinforced by the dilution effect of high discharge. In fact, the impact of plant utilization became more obvious at downstream Bow River sites as reduced nutrient concentrations were prolonged through the summer. By Site 13, low levels of phosphorus and nitrogen were maintained through the summer, a pattern which was shown also in the South Saskatchewan River. The contribution of phosphorus from the Medicine Hat sewage effluent appeared to have negligible additive effect to the concentration carried by the river, and was probably used very rapidly by plants within the reach below its input.

In the Oldman River, extreme peak values of total phosphorus occurred when large amounts of particulates were carried by the river during high discharge. Site 4 showed the effects of a major input of phosphorus from the Lethbridge sewage treatment plant, but phosphorus seemed to be less controlled by plant utilization than Site 2 in the Bow River. In 1980 a second distinct peak concentration of phosphorus in August indicated that less phosphorus was being taken up at that time, though the trend was reversed and utilization increased until October. The uniformly low concentrations of dissolved phosphorus from May to October at Site 8 indicated that plant utilization depleted the phosphorus within the reach of river from the Lethbridge sewage treatment plant input to Site 8.

Dissolved nitrogen patterns in the Oldman River were distinctly different from phosphorus patterns from May to October, 1980. At Site 4 when phosphorus increased from low values in May/June to August and then decreased to October, nitrate/nitrite was at or near detection levels. Under this circumstance, plant growth would be limited by nitrogen. At Site 8 the summer nitrogen was consistently low from July, as was the phosphorus.

Results from two other studies in Canada are discussed briefly to indicate comparability of this study. In another large river study, seasonal variation in nitrogen forms in the Red River, Manitoba (Chacko et al., 1981), was similar to that found in the South Saskatchewan River Basin Study with respect to lower summer values. The Red River study, however, put less emphasis on winter sampling, and highest values for nitrate were measured in late April rather than

December/January. All phosphorus forms showed a similar trend within the Red River data with higher values in June/July. This finding was in contrast to the results reported in our study. Our results showed that the peak concentrations were measured over winter, and that there was a second sharp peak value in spring for total phosphorus. Fluctuations in concentrations were generally less for all nitrogen and phosphorus forms in the Red River than in the South Saskatchewan Basin Study rivers.

Seasonal studies of nitrate plus nitrite on the Okanagan River, British Columbia (Kleiber, Whitfield and Erlebach, 1978) showed highest values in December and lowest in March, which was much more similar to the South Saskatchewan River Basin Study results. For total phosphorus, highest concentrations were measured in March on the Okanagan River and lowest concentrations were measured in September. These results were more similar to results for lower Oldman and South Saskatchewan River sites than Bow River sites. The absolute concentrations were much lower in the Okanagan River than in any of the Bow, Oldman and South Saskatchewan Rivers.

#### 4.2 Historical Nutrient Data

The comparison of historical and study nutrient data gave some indication of an increasing supply of nutrients. However, evaluation was complicated for several reasons. First, the database for the historical means was small; therefore, values could be strongly influenced by one extreme value. To use a current example (which will become part of historical record), during the eruption of Mount St. Helen's, the one very high value for total phosphorus would completely

dominate any calculation of an average value.

Second, the seasonal distribution of samples used to calculate annual mean could be very different between the two sets of data. Thus, the seasonal variation in concentration would bias the average concentration.

Finally, historical data were accepted at face value since verification was not feasible. Until relatively recently, total phosphorus was expressed chemically as mg PO<sub>4</sub>/L rather than mg P/L (1 mg PO<sub>4</sub>/L = 0.326 mg P/L). Often the distinction was not made clear in the results and could have led to entry of historical data onto NAQUADAT as mg P/L when, in fact, the values were mg PO<sub>4</sub>/L. Thus, some historical data could be interpreted as being about three times higher than were in fact measured.

Despite the difficulty of comparison, several factors indicated that the impact of Calgary sewage on downstream nutrient concentrations has increased. Firstly, although the historical total phosphorus data were higher than study values, the opposite was true for dissolved phosphorus at downstream river sites. The dissolved phosphorus data were less likely to have the first and third uncertainty factors, detailed above, and dissolved phosphorus was the main phosphorus form input to the river from the sewage treatment plant.

Secondly, in winter the study data for both dissolved phosphorus and nitrogen were higher than the historical data. Winter data provide a more comparable indication of 'diluted inputs' since flows were relatively similar between years and reduced biological activity allowed transport of nutrients to downstream sites.

#### 4.3 Biologically-Available Phosphorus

The bioavailability of particulate phosphorus has been evaluated for various surface water types in systems draining to the Great Lakes and in parkland streams of central Alberta (Table 19). Generally, the range of values observed in the South Saskatchewan River system appeared comparable to those derived elsewhere.

Although data were limited, Sephadex-gel filtration analysis indicated that the chemical dissolved reactive phosphorus test did provide a close approximation of orthophosphate for the basin in March and July. The deviation between forms measured to be significant elsewhere (Rigler, 1966; Downes & Paerl, 1978; Peters, 1978; Stainton, 1980) is not appreciable in these rivers. Dissolved reactive phosphorus, however, did not provide the best estimate of dissolved biologically-available phosphorus as measured by algal assay techniques. Dissolved inorganic phosphorus was the best predictor of dissolved biologically available phosphorus for all three rivers, and indicated that in addition to orthophosphate, the complex inorganic compounds in the system were readily available for biological uptake. The overestimation of dissolved biologically-available phosphorus by dissolved phosphorus implied that dissolved organic phosphorus was not available under these test conditions.

The greatest deviation between dissolved reactive phosphorus and dissolved inorganic phosphorus (and, therefore, dissolved biologically-available phosphorus if one assumes the two are equal) occurred in the Oldman when compared to the Bow River. The reason for

TABLE 19 LITERATURE REVIEW OF PERCENT AVAILABILITY OF SUSPENDED PARTICULATE PHOSPHORUS IN SURFACE WATERS

RIVER	LOCATION	% AVAILABILITY	TECHNIQUE	AUTHORS
Genesee	New York	19%	NaOH-P	Armstrong et al, 1979
Grand	Michigan	35%	NaOH-P	Armstrong et al, 1979
Nemadji	Wisconsin	14%	NaOH-P	Armstrong et al, 1979
Maumee	Ohio	35%	NaOH-P	Armstrong et al, 1979
Lake Ontario and Erie Tributaries	Ontario	8-50%	NaOH-P	Williams et al, 1980
Black Creek	Indiana	20%	Algal Assay	Dorich et al, 1980
Genesee	New York	38%	Algal Assay	Cowen et al, 1978
Niagara	New York	45%	Algal Assay	Cowen et al, 1978
Oswego	New York	38%	Algal Assay	Cowen et al, 1978
Black	New York	36%	Algal Assay	Cowen et al, 1978
Urban Runoff	Wisconsin	30%	Algal Assay	Cowen & Lee, 1976
Wabamun Streams	Alberta	49-70%	Algal Assay	Water Quality Control Branch

this greater relative abundance of complex inorganic compounds in the Oldman River is not fully understood. It may be simply a function of the overriding importance of the sewage treatment plant discharges on Bow River phosphorus chemistry, bearing in mind that dissolved reactive phosphorus accounted for 90% of sewage discharge phosphorus. Relative dissolved phosphorus availability and forms in the South Saskatchewan River appeared to be controlled by conditions in its two source rivers, the Bow and Oldman Rivers.

Seasonally, dissolved inorganic phosphorus tended to form a larger proportion of dissolved phosphorus in winter months and a lower percentage during summer and fall intervals. Thus, organic phosphorus was of greater significance to the dissolved phosphorus fraction during the open water season. Likely sources of this dissolved organic phosphorus were surface runoff and instream biological activity, both of which were maximal during summer and fall. Low dissolved organic phosphorus content in the system during winter also confirmed that the sewage treatment discharges were not a significant source of such material.

Although our results indicated that dissolved organic phosphorus was not immediately bioavailable, work elsewhere has shown that a certain proportion is ultimately degraded and made available because of bacteriological processing, ultraviolet irradiation and/or alkaline phosphatase activity (Franko & Heath, 1979). Peters (1978), using radioisotope techniques, concluded that 50% or more of the dissolved organic phosphorus in agricultural streams draining to Lake Memphremagog was actually bioavailable. Other investigators have

concluded that although certain forms of organic phosphorus are degradable, refractory organic compounds, entirely resistant to mineralization, do exist in aquatic systems (Lean, 1973; Lee et al., 1980). The observed non-availability of dissolved organic phosphorus in the South Saskatchewan River Basin Study may have been partially a function of the algal assay technique employed. Sample pretreatment by membrane filtration removed the natural bacteriological community from the test water, and thereby excluded any microbial processing of organic material during the test interval.

In light of the uncertainty surrounding dissolved organic phosphorus availability, Lee et al. (1980) recommend that the dissolved organic fraction be considered available for phosphorus management purposes, particularly when this fraction was of minimal overall significance relative to dissolved inorganic phosphorus. In the case of the South Saskatchewan Basin, this recommendation was confirmed since dissolved inorganic phosphorus comprised 75 to 85% of the dissolved phosphorus in the system.

The relationship between particulate phosphorus availability and dissolved biologically-available phosphorus implied that inorganic phosphate adsorption to suspended particulates is the major determining variable. Particulate phosphorus, where availability is low upstream of major dissolved phosphorus inputs, entered the system from erosional sources and was largely of the apatite form (Ongley and Blachford, 1982) which has been shown to be biologically inert (Williams et al, 1976, 1980; Millard et al., 1979). When brought in contact with dissolved phosphates, that is, downstream of Calgary and Lethbridge, phosphate was adsorbed to the particulate matter.



Desorption can occur as a result of chemical and biological mechanisms: simple chemical desorption results if the equilibrium is shifted by lowering the dissolved inorganic phosphorus concentrations (Stumm & Morgan, 1970); further desorption is possible if a high biological demand for phosphorus is present in the system. A phosphorus limited algal community functions as a sink for phosphorus which continually forces transfer of phosphates from the particulate to the dissolved phase (McColl, 1975; Golterman, 1977, Huettl et al., 1979).

The high proportion of dissolved phosphorus in sewage discharges ( $\approx 90\%$ ) and the high contribution of available dissolved reactive phosphorus to the dissolved component led to the conclusion that sewage effluent phosphorus is highly bioavailable. Young et al., (1982) undertook a detailed study of phosphorus availability in numerous sewage treatment plants and found that, on average, 82% of dissolved phosphorus and 55% of particulate phosphorus in sewage effluent was readily available for plant growth.

During the biologically-active summer and fall periods in the South Saskatchewan River system, dissolved biologically-available phosphorus formed 80 to 90% of the total biologically-available phosphorus in the high phosphorus content reaches downstream of Calgary and Lethbridge. This was also where nuisance aquatic weed growth was most acute. In the lower reaches of the Bow and Oldman Rivers, and throughout the South Saskatchewan River, particulate biologically-available phosphorus could comprise up to 40% of total

biologically-available phosphorus. However, these high proportions occurred at low overall phosphorus levels, when nuisance plant growth was not significant. This suggested that dissolved biologically-available phosphorus, rather than particulate biologically available phosphorus, and consequently dissolved phosphorus, was more significant in stimulating plant growth to nuisance levels. Particulate biologically-available phosphorus may have been utilized by the biological community, but it was likely of secondary importance.

#### 4.4 Nutrient Limitation

In the South Saskatchewan River Basin study, climatological and physical factors were more important than nutrient control of primary production during winter, as they were to varying degrees in spring and fall. Summer is the period when nutrient limitation of primary producers is most important. At Site 1 and 3 above Calgary and Lethbridge, respectively, the high ratios of dissolved nitrogen to dissolved phosphorus, low absolute nutrient concentrations and consistency between algal growth potential and nitrogen-spiked algal growth potential data, indicated that phosphorus was probably the nutrient which controlled primary production throughout the year. Similar conditions in the South Saskatchewan River from July to September at Site 9, and from May to October at the three downstream sites, suggested a similar conclusion.

The data from the Bow and Oldman Rivers below the cities were somewhat more complex and they changed with distance downstream from the cities. At Sites 2 to 6 below Calgary on the Bow River, ratios of dissolved nitrogen to dissolved phosphorus were relatively low, but absolute concentrations were high and algal growth potential data indicated that there was no nutrient limitation. The one exception occurred in May/June, although any growth at this time of peak discharge would be limited by physical conditions of light, temperature and abrasion. Further downstream, at Sites 13 and 7, high ratios in summer and fall, low absolute concentrations in summer but not fall, and agreement between algal growth potential and nitrogen-spiked algal growth potential data suggested that phosphorus was the controlling nutrient in summer in the lower Bow River.

The data from Site 4 below Lethbridge were quite different from those from Site 2 below Calgary. The two sets of algal growth potential data were only similar briefly in May and October, but dissolved nitrogen to dissolved phosphorus ratios were low in all seasons except spring, when discharge related factors predominated. Phosphorus and nitrogen concentrations were low during summer, but the other data indicated that it was not phosphorus, but nitrogen, which was the element controlling the primary production at Site 4 in summer.

At Site 8, high nutrient ratios, low concentrations in summer and fall, and consistency between the two sets of algal growth potential data from May to November suggested that phosphorus was the controlling nutrient in the Oldman River at its confluence with the Bow River.

#### 4.5 Sediment Phosphorus

Sediment phosphorus is a complex mixture of organic and inorganic forms (Armstrong et al., 1971; Stumm and Leckie, 1971; Syers et al., 1973). Apatite phosphorus is ortho-phosphate incorporated into the crystal lattice of apatite grains (Williams et al., 1976) and is the eroded form of sedimentary rock. The predominance of apatite phosphorus in sediments of South Saskatchewan Basin Rivers is understandable considering their mountain origin and the sedimentary nature of prairie soils. Ongley and Blachford (1982) found proportions of apatite phosphorus in suspended sediments of the Bow and Oldman Rivers similar to those measured in this study. The remaining inorganic phosphorus forms quantified by the non-apatite inorganic phosphorus test included iron and calcium phosphates and phosphate ions adsorbed to clays and organic compounds. Sedimentary organic phosphorus consisted of compounds of various complexity derived from decaying aquatic biota and input via surface runoff.

Laboratory studies (Golterman, 1977; McColl, 1975; Sagher et al., 1975) have shown some portion of aerobic sedimentary phosphorus to be available for algal growth. Of the various forms, apatite is usually considered unavailable while non-apatite inorganic phosphorus is considered the most available (Sagher et al., 1975; Williams et al., 1976, 1980). The very high correlation between sediment biologically-available phosphorus and non-apatite inorganic phosphorus for South Saskatchewan River Basin rivers substantiated this observation. However, the general underestimation of sediment biologically-available phosphorus by non-apatite inorganic phosphorus may indicate

that a portion of the sediment organic phosphorus pool was also available under assay test conditions. Although the sediments were freeze-dried prior to assay testing, they were not sterilized by autoclaving. Consequently, bacteriological activity was evident in the test flasks and subsequent biological breakdown of organic compounds could have occurred. There is no reason to believe that a certain proportion of the sediment organic phosphorus would not be made available under natural river conditions as well. However, complete utilization of sediment organic phosphorus was unlikely. Various studies have shown a certain proportion of organic compounds in aquatic systems to be resistant to all breakdown mechanisms (Lee et al., 1980).

The apparent buildup in fall and winter of non-apatite inorganic phosphorus and sediment organic phosphorus in river sediments downstream of Calgary, and to a lesser extent Lethbridge, was likely related to sewage treatment plant phosphorus inputs and the extensive summer aquatic plant populations which developed in these reaches. The high inorganic phosphorus levels during fall and winter in river water observed in these reaches would favour adsorption of phosphates to sedimentary material (Stumm and Morgan, 1970; Green et al., 1978). This would be measured as non-apatite inorganic phosphorus. The cobble nature of the substrate would favour this mechanism by ensuring river water contact with the imbedded fine particulate sedimentary material. Organic phosphorus accumulation during fall and winter can be attributed to death and decay of the macrophyte and benthic algal communities.

The summer decline in sediment non-apatite inorganic phosphorus and sediment organic phosphorus concentrations was probably caused by a combination of three factors: 1) reduced spring and summer ambient river phosphorus concentrations that favoured desorption of phosphate ions from the sediment phase in order to maintain sorption kinetic equilibria (the strong correlation between dissolved inorganic phosphorus and non-apatite inorganic phosphorus supports this hypothesis); 2) elevated spring flows that resulted in resuspension and transport of fine particulate sedimentary material accumulated during the low flow period during fall and winter. Deposition of upstream sediments, low in non-apatite inorganic phosphorus and sediment organic phosphorus, in turn, occurred as discharge levels dropped in late June or early July; 3) non-apatite inorganic phosphorus and sediment organic phosphorus was depleted by biological uptake during the summer growth period.

The latter mechanisms was likely not significant in the reaches where dissolved phosphorus levels remained high all summer. However, in the downstream reaches where dissolved inorganic phosphorus was depleted, greater non-apatite inorganic phosphorus dissolution than that caused by normal solubility product equilibria could result from a high biological demand for phosphorus (Huettl et al., 1979).

In spite of the latter mechanism, the low overall bioavailability of sediment phosphorus in the basin (12 to 35%), and small quantity relative to soluble phosphorus transported in the water column, it was concluded that sediment phosphorus was not currently a major phosphorus source that contributed to aquatic plant growth.

#### 4.6 Phosphorus Loading

The phosphorus loading concept was originally developed in relation to lakes and the biological response to inputs of phosphorus (Rawson, 1939; Edmondson, 1961; Vollenweider, 1976). The concept was also used in river basin studies to determine relative contributions of different sources of phosphorus (Peters, 1973; Alberta Environment, 1979) and to study the retention and transport of phosphorus through a river system (Aiba and Ohtake, 1977; Meyer and Likens, 1979; Rigler, 1979; Hill, 1982). Further developments in the loading concept included consideration of the bioavailability of the phosphorus which should be used in loading calculations (Schaffner and Oglesby, 1978; Sonzogni et al., 1982).

Calculations of phosphorus loading in the basin using total and dissolved phosphorus gave significantly different results. The source inventory for the Basin indicated that 34% of the total phosphorus came from upstream sources, compared to the sewage treatment plants (54%). However, when dissolved phosphorus is considered, the importance of the sewage treatment plant inputs rose to 89%. The shift from upstream sources to sewage treatment plant sources was shown most dramatically in the Oldman River where upstream sources dropped from 73% of total phosphorus to 17% of dissolved phosphorus and sewage treatment plant changed from 24% to 78%, respectively.

The change in emphasis from upstream sources was important, particularly when the two phosphorus forms are considered. Total

phosphorus included phosphorus contained in particles - particulate phosphorus, while the dissolved phosphorus was more readily available for use by the biological community.

When the dissolved phosphorus source inventory was separated into sub-basins, Calgary, Lethbridge and Medicine Hat sewage treatment plants contributed 91%, 78% and 12%, respectively, of the loadings. The highest relative return flow and industrial contribution was in the Oldman River at 3% and 2%, respectively. Considering the whole Basin, of the 89% source attributed to the sewage treatment plants, 70% was from Calgary, 14% was from Lethbridge and 5% was from Medicine Hat.

The impact of Calgary's sewage outflow on the Bow River in terms of nutrient input, though reduced in the early 1970s, has been increasing rapidly along with its population since 1974. During this same period, mean annual discharge in the Bow River was below average 7 out of 10 years. The low discharge was shown dramatically in the five consecutive years of very low maximum daily discharge from 1975 to 1979.

The coupling of rapidly increasing nutrient loading from the Calgary sewage treatment plant with consecutive years of extreme low flow hydrological conditions produced ideal conditions in summer for luxuriant growth of primary producers in the Bow River.

Phosphorus in the rivers below sewage treatment plants was attenuated by macrophyte and algal uptake and sediment adsorption. Our present studies have shown this, and so have others (Aiba and Ohtake, 1977; Anders, 1977; Brown et al., 1982). We found that the



most dramatic reductions in phosphorus loading by plant uptake occurred within the reaches from below Calgary to Bassano (Site 6) and below Lethbridge. These reductions were most apparent in summer and fall, and were the most indicative of maximum plant uptake of nutrients within the entire basin. Throughout the study period, the general trend was for net uptake of nutrients in the basin. Using the dissolved phosphorus loading inventory and the measured loading at Site 12, there was a net uptake in the basin of 75% of the dissolved phosphorus through 1980 and 1981.

The net uptake of dissolved phosphorus in the basin would be balanced somewhat by the nutrient loss from the basin in drifting of senescent macrophytes. This was not quantified. However, phosphorus retained in the basin would also be incorporated in secondary producers and more permanent primary producers.

## 5.0 SUMMARY

The purposes of the South Saskatchewan River Basin Study were to 1) examine the present state of the rivers, 2) determine the present response of the river to nutrients, and 3) develop phosphorus budgets for the basin. This report addresses the first objective, with respect to water chemistry, and the third objective.

Water chemistry data were collected routinely from May, 1979 to April, 1982 at thirteen sites throughout the South Saskatchewan River Basin: six sites were on the Bow River; three sites were on the Oldman River; and four sites were on the South Saskatchewan River. Additional data from remote monitors and from Water Quality Branch, Environment Canada, and Water Survey of Canada were used, as was information collected by the cities of Calgary, Lethbridge and Medicine Hat. Data from discharge studies of irrigation water, stormwater and industrial effluent were also incorporated.

Three studies were carried out to investigate sampling technique and additional studies were made of biologically-available phosphorus and sediment phosphorus. A closer investigation of the nutrient chemistry of the Bow River between Calgary and Carseland was undertaken in 1981.

Water chemistry was affected by the interrelated factors of climate, discharge and biological activity. Temperature related oxygen solubility showed basic trend of lower summer values and higher winter values. However, diurnal fluctuations of dissolved oxygen were

dependent on plant photosynthesis and respiration. The size of these fluctuations was greatest at Site 2 (below Calgary), and indicated the pronounced effect of primary producers at this site, particularly in the summer of 1980.

Water chemistry in the South Saskatchewan River often showed trends which were intermediate, or a combination of trends in the Bow and Oldman Rivers.

Correlated variables with high winter and low summer values included conductivity, alkalinity, chloride and dissolved inorganic carbon. Trends in pH values were opposite. Chloride and conductivity values reflected the freeze out of salts during ice formation, the higher salinity of groundwater base flow in winter, and the effects of inputs from the sewage treatment plants and irrigation return flows. Mean annual values of chloride and conductivity in the Bow, Oldman and South Saskatchewan Rivers were 4.4 mg/L and 366  $\mu$ S/cm, 3.5 mg/L and 418  $\mu$ S/cm and 5.2 mg/L and 413  $\mu$ S/cm, respectively.

Alkalinity, pH and dissolved inorganic carbon were affected by the changes in carbon dioxide utilization and release by primary producers. During summer photosynthetic activities predominate, and during winter decompositional activities predominate. Average alkalinity was 127 mg  $\text{CaCO}_3$ /L in the South Saskatchewan River, 141 mg/L in the Oldman River and 123 mg/L in the Bow River.

Measures of particulate matter (turbidity and non-filterable residue) and related variables (particulate organic carbon, particulate nitrogen and total phosphorus) correlated with discharge

and hence were high in spring. The more regulated Bow River showed lower turbidity values (averaging 7 JTU) than the Oldman River (averaging 56 JTU). The particulate nutrients were also high in the fall as a result of the addition of plant material during senescence.

The concentration of reactive silica was inversely related to the growth cycle of diatoms. Peak concentrations of silica (4-6 mg/L) were measured in mid-winter and in late spring/early summer and low values (less than 1 mg/L) were measured in late summer/fall and briefly in early spring.

Carbon was an important nutrient for plant growth. Average concentrations in the Bow, Oldman and South Saskatchewan Rivers, respectively, were: for particulate organic carbon 0.9, 1.3 and 1.4 mg/L; for dissolved organic carbon, 2, 3 and 3 mg/L; and for dissolved inorganic carbon 28.8, 32.5 and 29.2 mg/L.

Highest ammonia concentrations were measured below Calgary during winter and early spring (maximum of 2.9 mg/L).

Nitrogen and phosphorus concentrations throughout the Basin generally followed an annual pattern of high values in winter and low values in summer. The changes in concentrations over a year reflected changes in plant utilization for growth and release upon senescence.

Nutrient concentrations at sites upstream of Calgary and Lethbridge on the Bow and Oldman Rivers were generally low (dissolved phosphorus = 0.003 mg/L). Values increased below the cities, most dramatically at Site 2 below Calgary, which recorded the highest values (dissolved phosphorus = 0.43 mg/L) in December, 1980.

Two trends in changing concentration of nutrients were shown at the Bow River sites below Calgary: 1) concentrations decreased in a downstream direction; 2) the duration of low summer concentrations lengthened at each downstream site until low values were recorded at its confluence with the Oldman River from July to the end of September for dissolved nitrogen forms, and from May to October for dissolved phosphorus forms.

Changes in phosphorus loading within different reaches of the Bow River reflected the relative uptake of phosphorus by plants. The attenuation of phosphorus in the river was most dramatic from Calgary to Bassano during summer and fall.

Studies of water chemistry on both sides of the Bow River from the Calgary sewage treatment plant to Carseland (Bonnybrook Study) showed that phosphorus concentrations on the right bank were elevated below Bonnybrook sewage treatment plant and Fish Creek sewage treatment plant and then decreased at downstream sites. In contrast, on the left bank, concentrations increased gradually from low values at upstream sites until concentrations showed lateral mixing, and were comparable to right bank concentrations. This occurred at the approximate location of the downstream Calgary Site 2 of the routine sampling program.

Interpretation of historical river nutrient data must be made cautiously, but there is some evidence to suggest that the impact of Calgary sewage in downstream dissolved phosphorus concentrations has increased in recent years to the level found prior to phosphorus removal.

The nutrient input from Calgary sewage systems to the Bow River has increased rapidly since 1974. Increased loading in conjunction with low flow conditions produced ideal conditions in summer for luxuriant growth of primary producers in the Bow River.

The Bow River showed a smaller range of fluctuations in mean annual discharge than the Oldman River. During the 1970's, the long-term average annual discharge was exceeded only in 1972, 1974 and 1976. From 1975 to 1979 the very low maximum discharge values were equalled only in three previous years since readings were recorded.

Phosphorus ratio analysis showed that the relative proportion of inorganic to organic phosphorus was generally higher in the Bow River than the Oldman or South Saskatchewan Rivers, and high in winter and low in summer. Dissolved phosphorus, as a proportion of total phosphorus, was highest in the Bow River, and high in winter and low in spring.

Dissolved inorganic phosphorus concentrations were most comparable to dissolved biologically-available phosphorus. However, the long-term availability of dissolved organic phosphorus may not be adequately measured by the algal assay technique. Since dissolved organic phosphorus has been identified as available by other researchers, dissolved phosphorus, which includes both inorganic and organic forms, gave a good estimate of dissolved biologically-available phosphorus.

Phosphorus from sewage treatment plants was mostly (90%) in the dissolved form and hence available. On an annual basis total

phosphorus in the Bow River downstream of Calgary was 80% to 90% available, while total phosphorus in the Oldman River was only 51% to 75% available.

Information gathered by Sephadex-gel filtration techniques indicated that in March dissolved reactive phosphorus measurements did not include high molecular weight phosphorus compounds. Therefore, dissolved reactive phosphorus measurements did provide a good estimate of orthophosphate, which is biologically available.

The availability of particulate phosphorus was determined by inorganic phosphate adsorption to suspended particles. Particulate phosphorus was generally most biologically available in winter in all three rivers and in the Bow River in all seasons. Particulate phosphorus was least biologically available in spring in all three rivers, at sites above Calgary and Lethbridge in all seasons, and in the Oldman River in all seasons.

Particulate biologically-available phosphorus may be utilized by the biological community, but the mechanism is likely of secondary importance. Therefore, dissolved phosphorus was the form utilized to develop functional relationships for growth by aquatic weeds and algae. (Part II, The Primary Producers).

Climatological and physical factors predominated over nutrient limitations of primary production during winter, and to varying degrees in spring and fall. Nutrient limitation of primary producers was the controlling factor during summer.

In summer high ratios of nitrogen to phosphorus, low absolute concentrations and similarity of results between algal growth potential tests indicated that phosphorus was more limiting to growth above Calgary and Lethbridge. Phosphorus was also more limiting at sites in the lower Bow and Oldman Rivers nearer their confluence and at sites on the South Saskatchewan River.

Data from sites on the Bow River from below Calgary to Bassano had low nitrogen to phosphorus ratios and high absolute concentrations. These data, plus the algal growth potential data, indicated that there was no nutrient limitation at these sites.

In the Oldman River below Lethbridge, nitrogen to phosphorus ratios were low, and absolute concentrations were low. Nitrogen additions had a significant effect on algal growth potential tests. These results suggested that nitrogen could be controlling primary production at this location in summer.

Sediment phosphorus in the South Saskatchewan River Basin was not a major source contributing to plant growth because of its small quantity relative to phosphorus in the water column and low overall bioavailability (12 to 35%).

Concentrations of all phosphorus forms in sediments were lowest at sites upstream of Calgary and Lethbridge and substantially higher at downstream sites, particularly below Calgary. Concentrations returned to low values in the South Saskatchewan River at sites above Medicine Hat.



The non-apatite inorganic form of phosphorus was correlated to the biologically available fraction of the sediment, though some organic phosphorus should become available over the longer term. These fractions built up through fall and winter below Calgary and Lethbridge and decreased through spring and summer. This seasonal trend was related to adsorption and desorption of phosphates from the water column, decomposition of macrophytes and algae, and suspension and transport of sediments by high spring discharges.

Yearly variation in total phosphorus loading was highest in the Oldman River because of its higher component of suspended material, and the correlation of this material with discharge.

The phosphorus source inventory for the South Saskatchewan River Basin, derived from total phosphorus data, indicated that 34% of the total phosphorus came from upstream sources and 54% came from the sewage treatment plants. In contrast, using dissolved phosphorus data, the importance of the sewage treatment plant inputs rises to 89% (70% from Calgary, 14% from Lethbridge and 5% from Medicine Hat). The inventory that used dissolved phosphorus reflected the component of the total phosphorus which is more available for use by the biological community.

Within each river sub-basin, Calgary, Lethbridge and Medicine Hat sewage treatment plants contributed 91%, 78% and 12% respectively, of the dissolved phosphorus loadings. Upstream sources contribute 2%, 17% and 87% respectively. The highest contribution of phosphorus from irrigation return flow and industrial effluent was in the Oldman River at 3% and 2%, respectively.

Through 1980 and 1981, there was a net uptake in the basin of 75% of the dissolved phosphorus. The net uptake was incorporated into more permanent primary producers and secondary producers, but a substantial amount was lost from the basin in drifting, senescent macrophytes. This was not quantified.

In conclusion, water chemistry within the South Saskatchewan River Basin study area followed typical seasonal changes in concentration. Calgary had the most significant impact on the supply of plant nutrients to the river basin, although the contribution from Lethbridge to the Oldman River was substantial. The river below Calgary exhibited the most dynamic cycling of the plant nutrient, dissolved phosphorus.

## 6.0 CONCLUSIONS

Water chemistry throughout the Basin showed typical seasonal changes related to climate, discharge and biological activity. Water chemistry in the South Saskatchewan River often showed trends which were intermediate, or a combination of trends in the Bow and Oldman Rivers.

Changes in nutrient concentrations over a year reflected changes in plant utilization for growth and release upon senescence. The most dramatic uptake of phosphorus by plants occurred in the Bow River from Calgary to Bassano during summer and fall.

Dissolved phosphorus gave a good estimate of dissolved biologically-available phosphorus. Therefore, dissolved phosphorus was the form utilized in developing functional relationships between phosphorus and aquatic plant and algal growth (Part II, The Primary Producers, Charlton et al., 1986).

Climatological and physical factors predominated over nutrient limitations of primary production during winter, and to varying degrees in spring and fall. Nutrient limitation of primary producers was the controlling factor during summer. There was no nutrient limitation at the sites on the Bow River from below Calgary to Bassano. Phosphorus was more limiting to plant growth at all the other sites in the Basin except in the Oldman River below Lethbridge. Nitrogen could be controlling primary production at this location in summer.

The sewage treatment plants are the largest source of dissolved phosphorus in the Basin (89%). Calgary contributed 91% of the dissolved phosphorus to the Bow River, Lethbridge contributed 78% to the Oldman River and Medicine Hat contributed 12% to the South Saskatchewan River.

7.0 REFERENCES

- Aiba, S. and H. Ohtake, 1977. Simulation of  $PO_4 - P$  balance in a shallow and polluted river. *Water Research* 11:159-164.
- Alberta Environment, 1979. South Saskatchewan River Basin Eutrophication Control Study. Interim Report. Pollution Control Division, Water Quality Control Branch. 18 pp.
- Anders, C.G., 1977. Translocation and attenuation of wastewater phosphorus in streams. Ph.D. Thesis. 158 pp.
- Armstrong, D.E., R.F. Harris and J.K. Syers, 1971. Plant available phosphorus status of lakes. U. of Wisconsin, Water Resources Center. Final Technical Completion Report, OWRR B-022-WIS 27 pp.
- Armstrong, D.E., J.J. Perry and D.E. Flatness, 1979. Availability of pollutants associated with suspended or settled river sediments which gain access to the Great Lakes. Task D. Water Quality Impairment Studies for International Reference Group on Pollution from Land Use Activities. EPA-905/4-79-028. 102 pp.
- Brown, L., E.G. Belinger and J.P. Day, 1982. A case study of nutrients in the River Holme, West Yorkshire, England. *Environmental Pollution (Series B)* 3:81-100.
- Chacko, V.T., B.S.C. Chu and W.D. Gunner, 1981. Seasonal variation of nitrogen and phosphorus species in the Red River. *Scientific Series No. 128*. Inland Waters Directorate, Regina, Saskatchewan. 12 pp.
- Charlton, S.E.D., H.R. Hamilton and P.M. Cross, 1986. The limnological characteristics of the Bow, Oldman and South Saskatchewan Rivers 1979-82. Part II. The Primary Producers. Alberta Environment, Water Quality Control Branch.
- Chiaudani, G. and M. Vighi, 1974. The N:P ratio and tests with *Selenastrum* to predict eutrophication in lakes. *Water Research* 8:1063-1069.
- Cowen, W.F. and G.F. Lee, 1976. Phosphorus availability in particulate materials transported by urban runoff. *J. Water Poll. Control Fed.* 48:580-591.
- Cowen, W.F., K. Sirisinka and G.F. Lee, 1978. Nitrogen and phosphorus in Lake Ontario tributary waters. *Water, Air and Soil Pollution* 10:343-350.

- Cross, P.M., 1978. The application of nutrient loading-production models to the Qu'Appelle Valley Lakes of Saskatchewan. Environment Canada. Inland Waters Directorate. National Water Research Institute. Report W.N.R.-PR-78-1. 138 pp.
- Danielssen, L.G., 1982. On the use of filters for distinguishing between dissolved and particulate fractions in natural waters. *Water Res.* 16:179-182.
- Davies, R.W., J. Culp, R. Green, M. O'Connell, G. Scott and C. Zimmerman, 1977. River classification study of the South Saskatchewan River Basin. University of Calgary. 625 pp.
- Dillon, P.J., 1975a. The phosphorus budget of Cameron Lake, Ontario. The importance of flushing rate to the degree of eutrophy of lakes. *Limnol. Oceanogr.* 20:28-39.
- Dillon, P.J., 1975b. A manual for calculating the capacity of a lake for development. Ontario Ministry of Environment. 57 pp.
- Dillon, P.J. and F.H. Rigler, 1974. The phosphorus-chlorophyll relationship in lakes. *Limnol. Oceanogr.* 19:767-773.
- Dorich, R.A., D.W. Nelson and L.E. Sommers, 1980. Algal availability of sediment phosphorus in drainage water of the Black Creek Watershed. *J. Environ. Qual.* 9:557-563.
- Downes, M.T. and H.W. Paerl, 1978. Separation of two dissolved reactive phosphorus fractions in lake water. *J. Fish. Res. Board Can.* 35:1636-1639.
- Edmondson, W.T., 1961. Changes in Lake Washington following an increase in the nutrient income. *Verh. Int. Ver. Limnol.* 14:167-175.
- Francko, D.A. and R.T. Heath, 1979. Functionally distinct classes of complex phosphorus compounds in lake water. *Limnol. Oceanogr.* 24:463-473.
- Golterman, H.L., 1977. Sediments as a source of phosphate for algal growth. In: H.L. Golterman (ed.), *Interactions between sediments and fresh water.* Junk, The Hague. pp 286-295.
- Green, D.B., T.J. Logan and N.E. Smeck, 1978. Phosphate adsorption-desorption characteristics of suspended sediments in the Maumee River Basin in Ohio. *J. Environ. Qual.* 7:208-212.
- Green, R.H., 1979. Sampling design and statistical methods for environmental biologists. John Wiley and Sons, Toronto. 257 pp.

- Grimm, N.B., G. Fisher and W.L. Minckley, 1981. Nitrogen and phosphorus dynamics in hot desert streams of southwestern U.S.A. *Hydrobiologia* 83:303-312.
- Hamilton, H.R., unpublished. Bow River water quality 1970-1980, Alberta Environment. Pollution Control Division. 56 pp.
- Hamilton, H.R., B. Brown and E. Furnell, 1981. Algal bioassay: summary of technique development and methods manual. Alberta Environment. Pollution Control Division. 93 pp.
- Hart, C.J. and K. Exner, 1979. Primary productivity and community respiration measurement in the Bow River above and below Metropolitan Calgary using the open stream dissolved oxygen method. Alberta Environment. Water Quality Control Branch. 27 pp.
- Hill, A.R., 1982. Phosphorus and major cation mass balances for two rivers during low summer flows. *Freshwater Biology*, 12:293-304.
- Huettl, P.J., R.C. Wendt and R.C. Corey, 1979. Prediction of algal-available phosphorus in runoff suspensions. *J. Environ. Qual.* 8:130-132.
- Jones, R.A. and G.F. Lee, 1982. Chlorophyll - a raw water quality parameter. *Journal AWWA* September. pp. 490-494.
- Kellerhals, R., C.R. Neill and D.I. Bray, 1972. Hydraulic and geomorphic characteristics of rivers in Alberta. Research Council of Alberta. 54 pp.
- Keup, L.E., 1968. Phosphorus in flowing waters. *Water Research* 2:373-386.
- Kleiber, P., P.H. Whitfield and W.E. Erlebach, 1978. Limitations of single water samples in representing mean water quality. II. Spatial and temporal variation in nutrient concentrations in the Okanagan River, at Oliver, B.C. Technical Bulletin No. 107, Water Quality Branch, Inland Waters Directorate, Pacific and Yukon Region, Vancouver. 30 pp.
- Lean, D.R.S., 1973. Movements of phosphorus between its biologically important forms in lake water. *J. Fish. Res. Board Can.* 30:1525-1536.
- Lee, G.F., R.A. Jones and W. Rast., 1980. Availability of phosphorus to phytoplankton and its implications for phosphorus management strategies. In: *Phosphorus Management and Strategies for Lakes*, Ann Arbor, Science Ann Arbor, Michigan. pp. 259-308.

- McColl, R.H.S., 1975. Availability of soil and sediment phosphorus to a planktonic alga. *N.Z. J. Mar. Freshwater Res.* 9:169-182.
- Meyer, J.L. and G.E. Likens, 1979. Transport and transformation of phosphorus in a forest stream ecosystem. *Ecology* 60:1255-1269.
- Millard, E.S., C.C. Charlton and G.A. Burnison, 1979. Availability of phosphorus in different sources entering the Great Lakes for algal growth. Task Group D (Canadian Section) International Reference Group on Pollution from Land Use Activities. 38 pp.
- Miller, W.E., J.C. Greene and T. Shiroyama, 1978. The Selenastrum capricornutum Printz algal assay bottle test: experimental design, application and data interpretational protocol. U.S.E.P.A., Corvallis, Oregon, EPA-600/9-78-018, 126 pp.
- Oguss, E. and W.E. Erlebach, 1976. Limitations of single water samples in representing mean water quality. I. Thompson River at Shaw Springs, B.C. Technical Bulletin No. 95, Water Quality Branch, Inland Waters Directorate, Pacific and Yukon Region, Vancouver, B.C. 22 pp.
- Ongley, E.D. and D.P. Blachford, 1982. Nutrient and contaminant pathways in the Bow and Oldman Rivers, Alberta, 1980-1981. Report to Environment Canada, Contract OSU80-00056.
- Paerl, H.W. and M.T. Downes, 1978. Biological availability of low versus high molecular weight reactive phosphorus. *J. Fish. Res. Board Can.* 35:1639-1643.
- Peters, Robert H., 1978. Concentrations and kinetics of P fractions in water from streams entering Lake Memphremagog. *J. Fish. Res. Board Can.* 35:315-328.
- Peters, Roger H., 1973. Nutrient balances for the evaluation of nutrient sources in water quality management. *Water Resources Bull.* 9:49-53.
- Rawson, D.S., 1939. Some physical and chemical factors in the metabolism of lakes. In: *Problems of Lake Biology*. Publ. Amer. Assoc. Adv. Sci. 10:9-26.
- Reddy, M.M., 1978. Sediment nutrient and metal, and water column heavy metal characterization, in the Genesee River: Part of the Genesee River Pilot Watershed Study for Pluarg Task C. New York State Department of Environmental Conservation, Albany, New York, 49 pp.



- Rigler, F.H., 1966. Radiobiological analysis of inorganic phosphorus in lake water. *Ver. Int. Verein. Limnol.* 16:465-470.
- Rigler, F.H., 1979. The export of phosphorus from Dartmoor catchments: A model to explain variations of phosphorus concentrations in streamwater. *J. Mar. Biol. Ass. U.K.* 59:659-687.
- Sagher, A., R.F. Harris and D.E. Armstrong, 1975. Availability of sediment phosphorus to microorganisms. U. of Wisconsin, Water Resources Centre, Technical Report, WIS WRC 75-01.
- Sakamoto, M., 1966. Primary production by phytoplankton community in some Japanese lakes and its dependence on lake depth. *Arch. Hydrobiol.* 62:1-28.
- Schaffner, W.R. and R.T. Oglesby, 1978. Phosphorus loadings to lakes and some of their responses. Part I. A new calculation of phosphorus loading and its application to 13 New York lakes. *Limnol. Oceanogr.* 23:120-134.
- Schindler, D.W., 1976. Biogeochemical evolution of phosphorus limitation in nutrient-enriched lakes of the Precambrian Shield. In: J.O. Nriagu (ed.) *Environmental biochemistry*. Ann Arbor Science Publishers, Ann Arbor, Michigan, pp. 647-664.
- Sonzogni, W.C., S.C. Chapra, D.E. Armstrong and T.J. Logan, 1982. Bioavailability of phosphorus inputs to lakes. *J. Environ. Qual.* 11:555-563.
- Stainton, M.P., 1980. Errors in molybdenum blue methods for determining orthophosphate in freshwater. *Can. J. Fish. Aquat. Sci.* 37:472-478.
- Stanley Associates Engineering Ltd., 1982. Qual II Simulation: South Saskatchewan River Basin. Prepared for Alberta Environment, Water Quality Control Branch, 20 pp.
- Stumm, W. and J.J. Morgan, 1970. *Aquatic Chemistry. An introduction emphasizing chemical equilibria in natural waters.* Wiley-Interscience, New York. 583 pp.
- Stumm, W. and J.O. Leckie, 1971. Phosphate exchange with sediments; its role in the productivity of surface waters. In: *Proc. 5th Int. Water Poll. Res. Conf. July to August 1970.* 16 pp.
- Syers, J.K., R.R. Harris and D.E. Armstrong, 1973. Phosphate chemistry in lake sediments. *J. Environ. Qual.* 2:1-14.

- Verhoff, F.H. and D.B. Baker, 1981. Moment methods for analyzing river models with application to point source phosphorus. *Water Research* 15:493-501.
- Vollenweider, R.A., 1975. Input-output models with special reference to the phosphorus loading concept in limnology. *Schweiz. Zeits. fur Hydrologie* 37:53-84.
- Vollenweider, R.A., 1976. Advances in defining critical loading levels for phosphorus in lake eutrophication. *Mem. Ist Ital. Idrobiol.* 33:53-83.
- Wetzel, R.G., 1975. *Limnology*. W.B. Saunders Company, Toronto. 743 pp.
- Williams, J.D.H., J.M. Jaquet, and R.L. Thomas, 1976. Form of phosphorus in the surficial sediments of Lake Erie. *J. Fish. Res. Board Can.* 33:413-429.
- Williams, J.D.H., H. Shear and R.L. Thomas, 1980. Availability to Scenedesmus quadricauda of different forms of phosphorus in sedimentary materials from the Great Lakes. *Limnol. Oceanogr.* 25:1-11.
- Young, T.C., J.V. DePinto, S.E. Flint, M.S. Switzebaum and J.K. Edzwald, 1982. Algal availability of phosphorus in municipal wastewater. *Water Poll. Control Fed.* 54:1505-1516.

## 8.0 APPENDIX A

### 8.1 Technical Study - Introduction

The development of any routine sampling program requires a review of technical considerations related to analytical as well as sampling methods. Three studies were carried out to address these concerns.

In the first study, GFC-filtered and membrane-filtered samples were collected at each site to determine if results were comparable.

Sample filtering was often very time consuming and expensive since membrane filters clogged rapidly, especially in the spring.

Substitution of GFC-filtered water would reduce these effects. The second, a precision study, tested the variation introduced by sampling procedure and chemical analysis for each field sampler.

The third study tested the bias introduced into the routine water chemistry data from following a repetitive sampling route and schedule. Fluctuations in nutrients introduced into the Bow River by the Bonnybrook sewage treatment plant effluent were of particular interest. Variability in nutrient concentration may be complicated even further by variation in discharge flow rates and may differ seasonally. Therefore, the diurnal variation of selected variables was investigated at four sites on the Bow River, five times throughout the year.

## 8.2 Methods

Filter comparison tests were performed on duplicate samples collected at all regular sampling sites during the first year of data collection. The samples were treated equally in every way except for the use of a GFC filter in one case and a 0.45  $\mu$  membrane filter in the other. Wilcoxon matched pairs tests were carried out to test for significantly different results.

A precision study was carried out in spring 1980 and 1981 by each of the field personnel who collected regular water chemistry samples and data. Conditions of high and low nutrients were sampled on the Bow River at Stiers Ranch below Calgary (Site 2) and below Bearspaw Dam above Calgary (Site 1), respectively (Figure 1). Five discrete replicate samples were collected by each field sampler at each site. Sartorius membrane filters (0.45  $\mu$ ) were used for all filtrations with one exception - samplers #2 and #3 used GFC filtrate for dissolved nitrogen analysis. The mean, standard deviation, and coefficient of variation were calculated for each variable and sampler.

The diurnal variability study was carried out at four sampling locations (Figure 1): above Calgary (Site 1), in the Bonnybrook sewage treatment plant effluent (Site 1.5), at Stiers Ranch (Site 2) and below the Carseland Weir (Site 5). Locations and sampling dates are given in Table A-1. Ten samples were collected over a 24-hour period at four-hour intervals, with more frequent sampling during one 4-hour period at 15 minutes, 1 hour and 2 hours. The period of more intensive sampling was judged to be about the time of maximum sewage

TABLE A-1 SAMPLING SITES AND DATES FOR WATER CHEMISTRY DIURNAL

VARIABILITY STUDY ON THE BOW RIVER

<u>Sampling Location</u>	<u>Site</u>	<u>Late Spring 1980</u>	<u>Summer 1980</u>	<u>Fall 1980</u>	<u>Winter 1981</u>	<u>Early Spring 1981</u>
Below Bearspaw Dam or at 85th St. Bridge	1	02-03/06	11-12/08	06-07/10	05-06/01	23-24/03*
Bonnybrook Sewage Treatment Plant Effluent	1.5	09-10/06	05-06/08	27-28/10	15-16/01	25-26/03
At Stier's Ranch	2	05-06/05	28-29/07	20-21/10	12-13/01	30-31/03
Below Carseland Weir	5	12/13/05	21-22/07	13-14/10	20-21/01	18-19/03

\*Sampling repeated on 08-09/03/82

treatment plant effluent discharge, taking into account the lag time to downstream sites (Water Survey of Canada).

The variables measured were pH, conductivity, temperature, dissolved oxygen (DO), total phosphorus (TP), dissolved phosphorus (DP), dissolved reactive phosphorus (OP) and dissolved nitrogen (DN). During late spring and summer physical variables were measured in the field using a Hydrolab Surveyor Model 6D. The exception was at Site 1 in June when lab measurements of pH and conductivity were made. During fall, winter and early spring, pH and conductivity were measured in the lab, and temperature and dissolved oxygen were measured by thermometer and Winkler titration, respectively.

Dissolved nutrient variables were field filtered through 0.45  $\mu$  Sartorius membrane filters, and at Site 1.5 samples were prefiltered through GFC filters to reduce clogging of membrane filters.

A one-way analysis of variance was used to determine if sites or seasons were significantly different. The homogeneity of the variances between seasons was tested using the ratio of maximum to minimum variance. A level of 20 was used to determine significance (Green, 1979). The coefficient of variation was used to determine the variability within each test (10% level of significance).

## 8.3 Results

### 8.3.1 Filter Comparison

The filtrates from GFC and membrane filtered samples for the three dissolved phosphorus forms were significantly different when the

data from all the seasons were tested (Table A-2). Spring and fall data also show significant differences for two of the three forms. At individual sites - Sites 10 and 11 on the South Saskatchewan River and Sites 6, 13 and 7 on the Bow River - there were significant differences in at least one form. Each river individually showed a significant difference in one of the phosphorus forms. In all cases the average value for the GFC filtrate was greater than the average value for the membrane filtrate.

The nitrogen filtrate data were significantly different only in three cases: for dissolved nitrogen at Site 4 on the Oldman River; on the Oldman River data in total; and for nitrate/nitrite, at Site 2 on the Bow River. The membrane filtrate was greater than the glass fibre filtrate. This suggested that there were some contamination problems. Occasional ammonia contamination was noted previously (M. Korchinski, pers. comm.) and membrane filters without dividers were used to try to eliminate this problem.

The carbon filtrate data were available only from January to May 1980, and, therefore, summer and fall data were not tested. Dissolved inorganic carbon (DIC) showed a significant difference overall, and both dissolved inorganic carbon and dissolved organic carbon (DOC) showed significant filtrate differences in spring. The Bow River data showed a significant difference for dissolved inorganic carbon, as did Sites 12 on the South Saskatchewan River and Site 13 on the Bow River. Again, the membrane filter values were higher.

TABLE A-2 SUMMARY OF SIGNIFICANCE OF WILCOXON MATCHED  
 PAIRS TEST RESULTS FOR COMPARISON OF DISSOLVED  
 VARIABLES FROM GFC AND 0.45  $\mu$  MEMBRANE  
 FILTRATE (\*p < 0.05, \*\*p < 0.01)

<u>Dataset</u>	<u>n</u>	<u>DP</u>	<u>DIP</u>	<u>OP</u>	<u>DN</u>	<u>NIT</u>	<u>n</u>	<u>DIC</u>	<u>DOC</u>
ALL	257-272	**	**	*			113-115	**	
SEASONAL									
Spring	74-83		**	**			56-58	**	**
Summer	50-54						-		
Fall	54-58	**	**				-		
Winter	73-77						57		
RIVER									
Oldman	58-61		*		**		24-25		
S. Saskatchewan	80-85	**					35-36		
Bow	118-126	*		*			54	**	
SITE									
3	19-20						7-8		
4	19-21				**		9		
8	19-21						8		
9	21-22						9		
10	18-21	**	*				9		
11	19-21		*				8-9		
12	19-21						9	*	
1	20-22						9		
2	19-22					*	9		
5	21-22						9		
6	22-25	**					9		
13	13-14	*					9	*	
7	20-22		*	**			9		



### 8.3.2 Precision

A summary of means, standard deviations, and coefficient of variation for the precision study data are presented in Tables A-3 and A-4 for each sampler. A coefficient of variation greater than 10% was considered significant. Normal data scrutiny was carried out and resulted in enquiries about 44 individual results, 7.5% of the data. Ten results were omitted or rejected because of sample loss or obvious contamination. Seven results were corrected because of recording errors, and the remainder were confirmed to be accurate results.

At low nutrient levels (Table A-3), single outliers in the nitrate/nitrite data for Sampler #1 and in the dissolved nitrogen data for Sampler #3 were responsible for their low precision. The phenolphthalein alkalinity data for Sampler #1 cover a range of results, and suggested an inherent analytical imprecision near detection limits. The variables that depended on the suspended portion of the sample (non-filterable residue fixed, non-filterable residue, particulate nitrogen, particulate organic carbon, and turbidity) had a lower precision in many cases. This was not unexpected for analyses involving particulate matter and must be considered in interpretation of the routine water chemistry data.

Phosphorus concentrations that approached the detection limit would be expected to show poorer precision. In the case of total phosphorus (TP), however, another problem was encountered. When reviewing the data for Sampler #1, carry-over during lab analysis from

TABLE A-3 MEAN, STANDARD DEVIATION (SD) AND COEFFICIENT OF VARIATION (CV) FOR DATA FROM WATER CHEMISTRY PRECISION STUDY ON THE BOW RIVER BELOW BEARSPAW DAM

Variable	Sampler #1 n=5, 02/06/80			Sampler #2 n=4, 02/06/80			Sampler #3 n=5, 01/06/81		
	Mean	SD	CV	Mean	SD	CV	Mean	SD	CV
Conductivity	256.2	1.79	1	268.3	1.71	1	268.2	2.59	1
Turbidity	3.98	0.409	10	3.80	0.141	4	24.6	0.55	2
Carbon - DOC	2	0	0	2	0	0	2.4	0.14	6
- DIC	21.2	0.84	4	21	0	0	25	0	0
- POC	0.276	0.0251	9	0.205	0.0100	5	0.536	0.0702	13
Nitrogen - NIT	0.054	0.0261	48	0.055	0.0058	11	0.09 <sup>b</sup>	0	0
- NH <sub>3</sub>	L0.1	0	0	L0.1	0	0	L0.1	0	0
- DN	0.116	0.0055	5	0.165	0.0129	8	0.194	0.0709	37
- PN	0.044	0.0055	13	0.030	0.0141	47	0.052	0.0045	9
Alkalinity - total	105.4	4.93	5	101.8	1.26	1	108.8	0.45	0
- phenolphthalein	0.6 <sup>a</sup>	0.34	57	0	0	0	0	0	0
pH	8.5	0	0	8.2	0	0	8.1	0	0
Residue - NFR	3.8	0.45	12	4.0	1.15	29	25.8	1.64	6
- NFR	3.6	0.55	15	3.5	1.29	37	23.0	1.23	5
Silica - Si	3.88	0.179	5	4.05	0.100	2	4.3	0	0
Phosphorus* - DP	3.2	0.45	14	3.3	0.50	15	3.4	0.89	26
- OP	3	0	0	3.3	0.50	15	L3	0	0
- TIP	3	0	0	3.5	0.58	17	15.4	5.03	33
- DIP	L3	0	0	L3	0	0	L3	0	0
- TP	5.6	3.71	66	11.8	4.79	41	19.6	2.07	11
Chloride - Cl	0.92	0.045	5	0.93	0.050	5	0.9	0	0

	n=5, 12/09/80			n=5, 09/09/80		
Conductivity	307.0	0.71	0	303.3	2.06	1
Turbidity	2.04	0.297	15	1.93	0.222	12
Alkalinity - total	113.6	1.14	1	111.0	0	0
pH	8.22	0.045	0	8.3	0	0
Silica - Si	3.7	0	0	3.60	0.115	3
Phosphorus - TP	3	0	0	4.0	1.41	35
Chloride - Cl	1.0	0	0	1.0	0	0

Measurement units are given in Table 1

\* µg/L

<sup>a</sup><sub>n</sub> = 4

<sup>b</sup><sub>n</sub> = 1

TABLE A-4 MEAN, STANDARD DEVIATION (SD) AND COEFFICIENT OF VARIATION (CV) FOR DATA FROM WATER CHEMISTRY PRECISION STUDY ON THE BOW RIVER AT STIERS RANCH

	Sampler #1 n=5, 20/05/80			Sampler #2 n=4, 20/05/80			Sampler #3 n=5, 02/06/81		
	Mean	SD	CV	Mean	SD	CV	Mean	SD	CV
Conductivity	309.8	7.16	2	309.5	0.58	0	305.0	2.45	1
Turbidity	3.28	0.540	16	2.95	0.592	20	48.0	5.79	12
Carbon - DOC	2	0	0	2	0	0	3.5	0.19	5
- DIC	22	0	0	22	0	0	27.8	0.45	2
- POC	1.20	0.141	12	0.934	0.2549	27	1.18	0.164	14
Nitrogen - NIT	0.398	0.0045	1	0.393	0.0096	2	0.36	0	0
- NH <sub>3</sub>	0.46	0.152	33	0.40	0.163	41	0.1	0	0
- DN	0.792	0.0396	5	0.838	0.0050	1	0.744	0.2587	35
- PN	0.176	0.0230	13	0.135	0.0191	14	0.158	0.0164	10
Alkalinity - total	104.3 <sup>a</sup>	2.75	3	106.0	0.82	1	121.0	1.87	2
- phenolphthalein	0	0	0	0	0	0	0	0	0
pH	8.0 <sup>b</sup>	0	0	8.2	0	0	7.68	0.130	2
Residue - NFR	11.2	2.59	23	9.3	1.71	18	81.4	14.10	17
- NFFR	7.8	2.28	29	8.5	2.08	24	72.2	13.77	19
Silica - Si	3.72	0.303	8	3.33 <sup>b</sup>	0.115	4	4.96	0.548	11
Phosphorus* - DP	126.0	5.48	4	150	0	0	34.4	1.82	5
- OP	105.2	6.72	6	130	0	0	23.4	2.61	11
- TIP	162.0	13.04	8	170.0	21.60	13	78.8	3.77	5
- DIP	112.0	8.37	8	137.5	5.00	4	30.2	2.39	8
- TP	192.0	4.47	2	205.0	5.77	3	99.2	6.53	7
Chloride - Cl	2.66	0.089	3	3.0 <sup>b</sup>	0	0	1.74	0.055	3

Measurement units are given in Table 1

\* µg/L

<sup>a</sup><sub>n=4</sub>

<sup>b</sup><sub>n=3</sub>

a previous extremely high sample was not identified. Therefore, the analysis should have been repeated. No similar explanation was obvious for Sampler #2. Several variables were retested by Samplers #1 and #2 on September 9 and 12, 1980 (Table A-3). The results for total phosphorus indicated a low precision when levels were close to the detection limit.

At high nutrient levels (Table A-4) the poor precision in particulate nitrogen, particulate organic carbon, turbidity, non-filterable residue and non-filterable residue fixed reflected the same difficulty with particulate determination at high nutrient levels as at low nutrient levels. The consistently poor precision in ammonia was inherent to the lag time between sampling and analysis. The relatively poorer precision in total inorganic phosphorus for Sampler #2 was caused by a single outlier, while the poor precision in dissolved nitrogen for Sampler #3 was caused by a range of measured values.

### 8.3.3 Diurnal Variability

The mean, standard deviation, and coefficient of variation of each variable at each site is summarized in Table A-5, and the summer and early spring data for selected variables are presented graphically in Figure A-1. The remainder of the data are presented in Appendix Table B-1.

Site 1, which represented background levels, showed only minor fluctuations over each 24-hour period, particularly in conductivity and nutrients. Conductivity fluctuated with higher values from about

TABLE A-5 MEAN, STANDARD DEVIATION (SD) AND COEFFICIENT OF VARIATION (CV)  
OF DATA FROM DIURNAL VARIABILITY STUDY ON THE BOW RIVER

Variable	Site 1			Site 1.5			Site 2			Site 5	
	Mean	SD	CV	Mean	SD	CV	Mean	SD	CV	Mean	SD
<u>Late Spring</u>											
Conductivity	266.9	0.3	0	1095	69	6	365.5	8.0	2	321.0	10.5
Temperature	10.5	0.6	6	14.9	0.3	2	12.4	1.3	11	12.4	0.7
DO	10.3	0.1	1	3.9	0.2	5	10.4	2.1	21	10.8	1.6
pH	8.27	0.05	1	7.35	0.05	1	7.99	0.31	4	8.09	0.35
DN	0.108	0.006	6	16.98	2.97	18	1.13	0.17	15	0.875	0.126
DP	3.2	0.6	19	3410	600	18	181	20	11	101	12
OP	3	0	0	3300	640	19	141	20	14	62	13
TP	8.5	4.7	55	3730	760	20	237	21	9	142	8
<u>Summer</u>											
Conductivity	274.4	4.6	2	1015	64	6	308.5	14.0	4	296.0	11.0
Temperature	15.2	0.3	2	18.1	0.4	2	19.5	1.5	8	19.7	0.8
DO	10.3	0.4	4	3.9	0.2	4	7.1	2.2	31	7.8	1.7
pH	8.17	0.05	1	7.47	0.05	1	8.01	0.53	7	8.34	0.30
DN	0.038	0.004	11	12.45	2.29	18	1.23	0.18	14	0.891	0.100
DP	3	0	0	3680	580	16	169	38	23	121	14
OP	3	0	0	3430	60	31	146	40	27	98	8
TP	8.8	4.2	48	4100	770	19	189	42	22	153	14
<u>Fall</u>											
Conductivity	320.2	3.6	1	932	65	7	368.6	8.4	2	370.8	3.4
Temperature	4.7	0.8	17	16.4	0.7	4	10.8	0.4	4	6.7	0.8
DO	13.4	0.3	2	4.1	0.1	1	8.4	1.6	20	11.1	0.7
pH	8.32	0.04	0	7.72	0.04	0	7.79	0.14	2	8.19	0.12
DN	0.052	0.006	12	13.80	1.62	12	1.34	0.13	15	1.20	0.12
DP	3	0	0	3940	660	17	190	28	14	161	20
OP	3	0	0	3850	660	17	182	26	11	149	22
TP	3.2	0.6	19	4370	760	17	220	24	13	173	21
<u>Winter</u>											
Conductivity	350.9	1.5	0	822.6	116.1	14	396.4	7.1	2	399.1	6.9
Temperature	0	0	0	NV			1	0	0	0.7	1.2
DO	13.8	0.18	1	9.2	1.9	20	12.2	0.3	3	11.4	0.1
pH	8.21	0.06	1	7.79	0.12	2	7.85	0.07	1	7.87	0.12
DN	0.121	0.003	2	13.90	4.69	34	1.15	0.19	16	1.16	0.07
DP	3.5	1.6	46	3050	720	24	255	26	10	192	10
OP	3	0	0	2770	1060	38	244	28	12	182	10
TP	6.5	3.5	54	3330	760	23	286	28	10	207	18
<u>Early Spring</u>											
Conductivity	313.3	1.9	1	932.3	70.4	8	408.8	16.6	4	396.9	6.7
Temperature	3.2	0.3	10	9.8	0.8	8	4.7	0.7	14	1.8	0.8
DO	12.3	0.6	5	4.8	0.6	12	9.8	0.4	4	11.8	0.7
pH	8.05	0.05	1	7.60	0	0	7.63	0.07	1	8.50	0.16
DN	0.161	0.041	26	22.30	3.47	16	2.35	0.32	14	1.60	0.15
DP	3	0	0	3060	270	9	302	30	10	194	14
OP	3	0	0	2780	740	27	293	37	13	171	17
TP	5.4	2.0	37	3140	300	10	401	33	8	231	15

Measurement units for each variable are given in Table 1 except for phosphorus ( $\mu\text{g/L}$ )

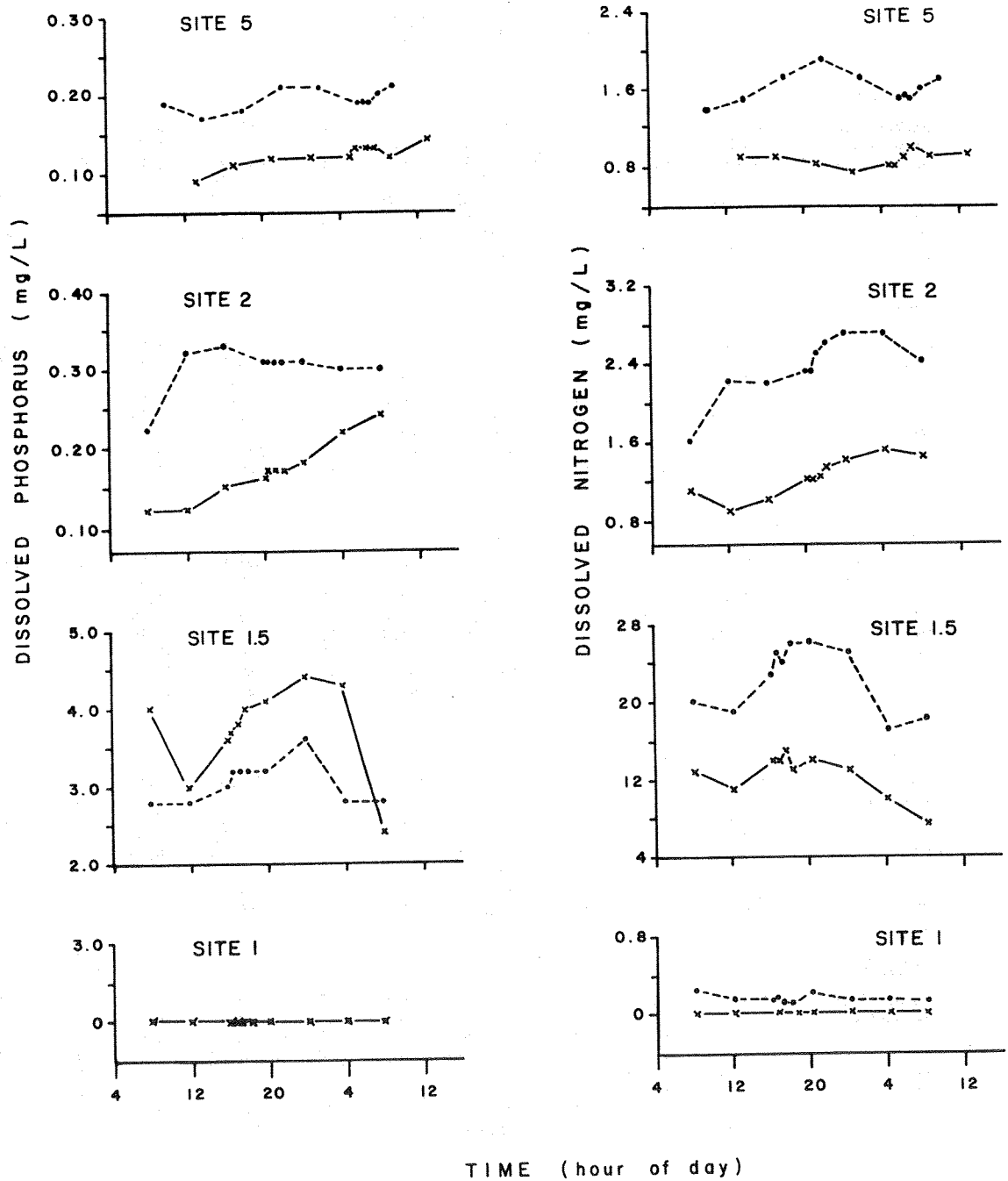


Fig. A-1 Diurnal variability study results for dissolved phosphorus, dissolved nitrogen, dissolved oxygen and conductivity. March (·-·-·-·), July/August (x—x)

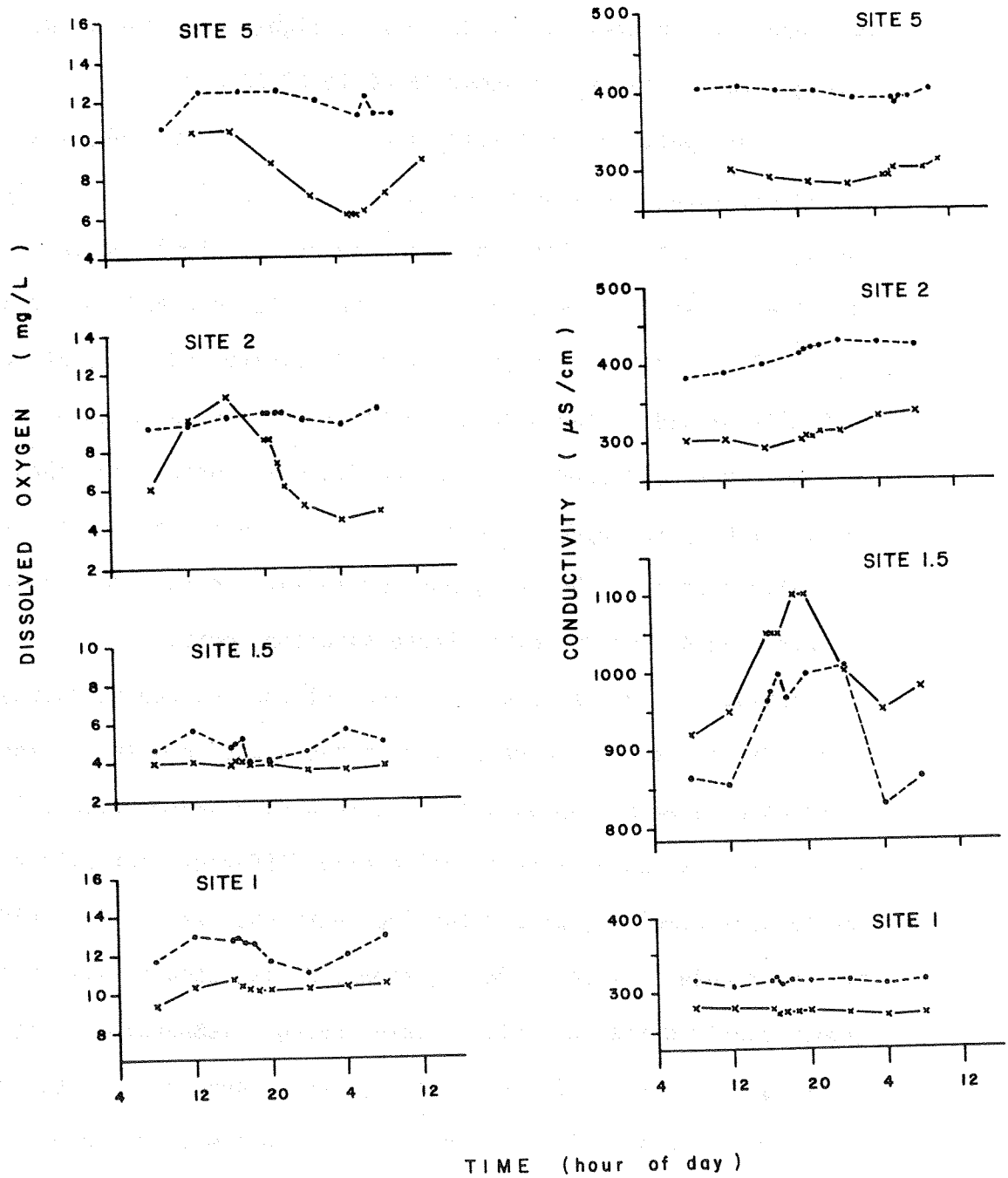


Fig. A-1(Continued)

16:00 to 24:00 hours and lower values at about 04:00 to 08:00 hours. Nutrient concentrations followed a similar pattern. Phosphorus values were generally highest at 24:00 hours (slightly earlier in winter) and nitrogen values peaked at about 16:00 to 20:00 hours.

Diurnal patterns were evident at Site 2 for most physical variables, though they were less pronounced in winter and early spring. Conductivity was generally highest at night, while pH and dissolved phosphorus were highest in the afternoon and lowest at night. The diurnal fluctuation of conductivity and nutrients was partially masked by the general upward trend over each sampling period.

Site 5 showed lower size in the diurnal fluctuations than Site 2, and masking by the upward trend was less evident. Nutrients were generally higher in the early morning in late spring and summer, and in late evening for the other three sampling periods.

Analysis of variance was carried out for the two downstream river sites, Sites 2 and 5, to determine if there was an overall significant difference between them as well as within each season (Table A-6). None of the variances were significantly different, but with all of the seasons combined, pH and the four nutrients were all significantly different between sites. On a seasonal basis, conductivity was significantly different only in late spring. Temperature, dissolved oxygen and pH were different in early spring and fall. Dissolved oxygen was also significantly different in winter. Phosphorus values were significantly different in all cases, except total phosphorus in summer and dissolved phosphorus in fall. Dissolved nitrogen values were significantly different except in fall and winter.



TABLE A-6 SUMMARY OF F-RATIOS AND RATIOS OF MAXIMUM TO MINIMUM VARIANCE  
 FROM ONE-WAY ANALYSIS OF VARIANCE ON DIURNAL VARIABILITY  
 STUDY DATA (\*F-RATIO  $p < 0.01$ , VARIANCE RATIO  $> 10$ )

Variable	ALL DATA		SITE 1		SITE 1.5		SITE 2		SITE 5	
	F-Ratio	Max:Min Variance	F-Ratio	Max:Min Variance	F-Ratio	Max:Min Variance	F-Ratio	Max:Min Variance	F-Ratio	Max:Min Variance
Temperature	205*	39*	1441*	6	351*	7	558*	12	864*	2
Dissolved Oxygen	12*	4	203*	12	61*	129*	16*	40*	19*	151*
pH	0.4	5	43*	2	76*	8	2	63*	11*	9
Conductivity	0.1	3	1490*	216*	17*	3	115*	5	319*	10
Total Phosphorus	0.2	2	5*	50*	5*	7	75*	4	54*	7
Dissolved Phosphorus	0.1	2	0.8	1457*	4*	7	38*	4	84*	4
Ortho Phosphorus	0.2	2			3	17	45*	4	115*	7
Dissolved Nitrogen	1.1	3	72*	168*	15*	8	61*	7	65*	5

F-RATIOS FOR SITES 2 AND 5

	All	Late Spring	Summer	Fall	Winter	Early Spring
Temperature	1.1	0.0	0.2	234.0*	0.4	78.0*
Dissolved Oxygen	5.2	0.2	0.6	23.3*	51.0*	62.4*
pH	25.9*	0.5	2.9	48.3*	0.1	261.0*
Conductivity	2.6	114.1*	4.9	0.6	0.7	4.4
Total Phosphorus	46.6*	185.9*	6.6	21.6*	57.0*	224.6*
Dissolved Phosphorus	42.7*	114.2*	14.0*	7.1	51.0*	107.1*
Ortho Phosphorus	35.2*	107.3*	13.8*	9.6*	44.4*	89.9*
Dissolved Nitrogen	12.5*	14.0*	27.4*	6.7	0.1	44.2*

The coefficient of variation (CV) can be used to compare the variability of measurements within each sampling series at different seasons and sites (Table A-5). Greater than ten percent was chosen as being significant. For the physical variables the coefficient of variation was never significant for pH and only once (winter at Site 1.5) for conductivity. Temperature was more variable, with significant values at Site 1 in fall, at Site 2 in late and early spring, and at Site 5 in fall, winter and early spring. However, these significant values are based on very low mean values and absolute variation was low.

The coefficient of variation for dissolved oxygen was significant at Site 1.5 in winter and early spring. However, at Sites 2 and 5 it was significant in late spring, summer and fall. In each case the coefficient of variation at Site 5 was lower than that at Site 2.

At Site 1 a significant coefficient of variation for the nutrient variables often indicated the difficulty in making measurements near the detection limits of the analyses. At Site 1.5, however, concentrations were high and the consistently significant coefficients of variation indicated clearly a high degree of variability within these nutrient variables over a 24-hour period.

The downstream effects at Sites 2 and 5 are different both among seasons and among variables. In late spring the coefficient of variation for total phosphorus was reduced below significance at both downstream sites. Dissolved phosphorus and dissolved nitrogen were lower downstream but showed no change between Sites 2 and 5, and the

coefficient of variation for dissolved reactive phosphorus increased within that reach. In summer the variability of nutrient measurements was high at Site 2 and markedly decreased by Site 5. Results from fall showed no strong change in the coefficient of variation in downstream sites. Winter coefficients of variation at Site 2 were similar to fall values, but at Site 5 no values were significant. In early spring results at Site 2 were similar to those in late spring, while Site 5 results had generally dropped below the level of significance.

An analysis of variance was run on all the sites combined and at each site individually to determine any significant seasonal differences (Table A-6). Overall, only temperature and dissolved oxygen were significantly different between seasons. However, when each site was treated individually, the seasonal differences between most variables were significant. The exceptions were dissolved phosphorus and dissolved reactive phosphorus at Site 1, dissolved reactive phosphorus at Site 1.5, and pH at Site 2.

The homogeneity of the variances (Table A-6) was used to determine any significant seasonal differences in variability overall and at each site. A ratio of maximum variance to minimum variance of greater than twenty was considered significant. When all the data were combined, only temperature variation was seasonally significantly different. When each site was treated separately, Site 1 showed the most seasonal differences in variation, with conductivity, total phosphorus, dissolved phosphorus and dissolved nitrogen all being

significant. At the other sites only variation for dissolved reactive phosphorus at Site 1.5, temperature and pH at Site 2, and conductivity at Site 5 were significantly different seasonally.

## 8.4 Discussion

### 8.4.1 Filter Comparison

The filter comparison testing showed that glass fibre filters are not always an acceptable substitute for 0.45  $\mu$  membrane filters for field filtering. The uses of membrane filter or glass fibre filter have their advantages and disadvantages. The effective pore size of the former changes when large particles are present and clogging occurs rapidly (Danielsson, 1982). The latter has a greater dirt-holding capacity, although contamination is a problem (pore size covers a range from 0.8 to 1.2  $\mu$  for GFC).

Results suggested that there was a fraction of both carbon and phosphorus in the size range from 0.45  $\mu$  to 0.8-1.2  $\mu$ . The significance of that fraction varied with season and by river and, therefore, results from GFC and membrane filtered water were not always interchangeable. Therefore, dissolved variables were measured on 0.45  $\mu$  membrane filtered water for the remainder of the project, since this was the more common functionally-defined determination of a dissolved parameter.

The results with dissolved nitrogen were less clear since the membrane filtered results were higher than the GFC filtered results. Significant results were restricted to the Oldman River for dissolved nitrogen, and Site 2 on the Bow River for nitrate/nitrite. Steps were

taken to remove possible ammonia contamination caused by membrane filter dividers; but dissolved nitrogen measurements were made on GFC filtered water for the remainder of the project, since particulate nitrogen was determined on GFC filters.

#### 8.4.2 Precision

A generally acceptable level of precision was attained for most variables in the routine water chemistry under conditions of both high and low nutrients. Only outliers which could be rejected on the basis of documented field or lab problems were excluded. Remaining outliers represented 0.5% of the data. This conservative data treatment ensures that data are not rejected simply for being difficult to explain.

There were three major factors affecting precision: 1) inherent instability caused changes between the time of collection and analysis (e.g., ammonia); 2) the discrete nature of suspended particles made them difficult to sample uniformly (e.g., particulate nitrogen, particulate organic carbon, turbidity, non-filterable residue, non-filterable residue fixed); and 3) precision was lost near the limits of analytical precision (e.g., low nitrogen and phosphorus forms). Similar conclusions about factors affecting precision have been reached by Chacko, Chu and Gummer (1981) on studies of the Red River in Manitoba and by Oguss and Erlebach (1976) on studies of the Thompson River in British Columbia.

Precision of a measurement is particularly important when the seasonal variation is considered. Precision study results indicated that samples collected throughout the limnological study have a precision of about  $\pm 5\%$ . Changes in concentration at the limits of detection are relatively less precise ( $\pm 10\%$ ), and trends should be interpreted with caution. Similarly, calculations of phosphorus loading that used concentrations near the detection limits should be used cautiously.

Trends in variables related to suspended particles must also be established beyond the levels of precision ( $\pm 15-20\%$ ) before they can be considered significant. Again, calculation of total phosphorus loading, under conditions of high suspended sediment load, would carry this qualification. Total phosphorus loading at sites where the total phosphorus concentration is near the detection limit would carry an uncertainty factor of  $\pm 25\%$  on the basis of precision alone.

#### 8.4.3 Diurnal Variability

Diurnal variability in phosphorus concentrations input by sewage treatment plants is a complicating factor in the understanding of the phosphorus removal process by the river (Verhoff and Baker, 1981). Our study showed that sewage treatment plant effluent is a seasonally variable source of nutrients to the river with a consistently high diurnal variation. The dissolved nutrients variability was evident most strongly in the summer at Site 2. It was reduced by Site 5.

particularly in summer, winter and early spring. Total phosphorus variation acted somewhat differently. It was reduced by Site 2, except in summer and fall, and remained significant only at Site 5 in fall.

The seasonal differences found in this study suggested that discharge and biological activity in the river were affecting the diurnal variability introduced by the sewage treatment plant effluent. Discharge acts in two ways. First, the degree of dilution of effluent reduced the variation during periods of high flow. This may have accounted for a basic diurnal variability in dissolved nutrients of about 10%, as shown in fall, winter and early spring (or 5% more than was accounted for by precision). Second, the amount of suspended material transported by the river varied with discharge. During periods of high flow, more suspended solids can be carried (Keup, 1968). This would affect the settling of the particulate fraction of the total phosphorus introduced at the sewage treatment plant.

Biological activity and uptake of dissolved nutrients for primary production was more evident in late spring, and particularly in summer. Studies on the Sandusky River below Bucyrus, Ohio, determined that 75% of the phosphate input at the sewage treatment plant was removed in 16 km (Verhoff and Baker, 1981). Biological utilization was a more significant factor than adsorption to particulate in this removal. Aiba and Ohtake (1977) studies the Tama-gawa River in Tokyo,

Japan, during August and found that 44% of the phosphate was retained in 20 km of river. They also found that 34% of the phosphate removal was attributable to algal fixation. The uptake may vary diurnally since it is related to plant photosynthesis, and this could act to reinforce the trends apparent in our variability study. This hypothesis, however, could not be evaluated with data from this study.

A second effect of biological activity was related to the large macrophyte community below the sewage treatment plant. This community senesced in the fall, and provided an additional source of particulate phosphorus to the river. This source contributed to total phosphorus variation at Sites 2 and 5, particularly in the fall.

The variability study provided valuable information for data interpretation. The consistently high diurnal nutrient variability at Site 2 must be considered when data trends are discussed. This consideration is less important at Site 5 in the summer, winter and early spring than it is in late spring and fall. The effect of nutrient variability introduced by the Calgary sewage treatment plant effluent would be expected to decrease at sites further downstream on the Bow River.

Lethbridge and Medicine Hat probably produced sewage treatment plant effluent with a similar diurnal variability. The strongest impact would have been at Site 4 below Lethbridge in summer. In general, however, the impact of these cities would be less severe since the relative nutrient input is much lower.



An additional factor must be considered when the results of the diurnal variability study are applied to the interpretation of the routine water chemistry results. The studies were conducted immediately after a weekend and reflect a maximum variation over a 24-hour period for two reasons: 1) sewage effluent flows are lower over the weekend (55-57 MIGPD on Saturday and Sunday versus 63-68 MIGPD on Monday to Friday); and 2) the quality of the weekend effluent was probably better than during the week because of the different contribution of light industry and household activities (Joe Kostler, personal communication).

The upper Bow River sites generally were sampled for routine water chemistry immediately following a weekend. Therefore, the concentrations of nutrients that were measured might be about 5% lower than if they were measured later in the week, and particularly if samples were collected in the early morning rather than the late afternoon. The largest potential underestimate would occur at Site 2 in summer (10%), a fact to be considered in discussions of seasonal variation as well as in interpretation of any calculations using the routine chemistry data to determine nutrient loadings and within reach characteristics.

#### 8.5 Summary

Filter comparison testing showed that glass fibre filters were not always an acceptable substitute for 0.45  $\mu$  membrane filters for field filtering.

A generally acceptable level of precision was attained for most water chemistry variables under conditions of both high and low nutrients. Levels of precision were about  $\pm 5\%$  for most variables,  $\pm 10\%$  for concentrations at the limits of detection and  $\pm 15-20\%$  for variables related to suspended particulates.

The Calgary sewage treatment plant effluent was a seasonally variable source of nutrients to the river with a consistently high diurnal variability. The effects of river discharge and biological activity in the river resulted in seasonal differences in the impact of this variability on the river. River flows provided variable dilution and suspended sediment carrying capacity. Biological activity included photosynthetic uptake of phosphorus by aquatic plants during summer and release because of senescence of macrophytes in the fall. The diurnal variability in nutrient concentrations was most pronounced at Site 2 (below Calgary) in general, and less so at Site 5 (Carseland) in summer, winter and early spring. As a consequence of sampling times, routine data may be about 5% low at these sites and potentially as much as 10% too low at Site 2 in summer.

## 8.6 REPORT APPENDIX TABLES AND FIGURES

TABLE: A-7 PEARSON'S CORRELATION BETWEEN SELECTED  
WATER CHEMISTRY VARIABLES

Variables	<u>ALL</u>	<u>BOW</u>	<u>OLDMAN</u>	<u>S. SASK.</u>
DIC vs ALK	.85	.76	.91	.84
ALK vs COND	.79	.74	.83	.76
DIC vs COND	.70	.60	.76	.72
COND vs CL	.64	.74	.77	.68
PN vs POC	.85	.70	.98	.95
PN vs PP	.66	.70	.79	.73
POC vs PP	.79	.87	.87	.91
NFR vs NFFR	.9999	.999	.99997	.999
TURB vs NFR	.96	.76	.97	.84
PN vs TURB	.53	.39	.70	.64
PN vs NFR	.56	.50	.78	.50
POC vs TURB	.69	.64	.83	.74
POC vs NFR	.72	.77	.89	.57
PP vs NFR	.95	.69	.98	.77
PP vs TURB	.95	.57	.98	.86
TP vs TIP	.97	.98	.96	.98
TP vs DP	.33	.89	.04	.29
DP vs DIP	.99	.99	.996	.97
DP vs OP	.99	.99	.99	.96
TP vs TN	.51	.89	.59	.50
DP vs DN	.84	.92	.55	.79
OP vs NIT	.71	.74	.38	.84
TN vs DN	.94	.97	.74	.92
DN vs NIT	.91	.87	.94	.96

TABLE: A-8 PEARSON'S CORRELATION BETWEEN MEAN DAILY DISCHARGE AND SELECTED  
WATER CHEMISTRY VARIABLES

DATA SET	PP	DP	PN	DN	POC	TURB	NFR
ALL	.46	-.21	.38	-.14	.49	.53	.59
Oldman R.	.63	-.21	.71	-.01	.75	.70	.68
S. Sask. R.	.58	-.20	.32	-.20	.36	.68	.82
Bow R.	.18	-.30	.05	-.29	.18	.57	.44
Site 3	.63	.28	.64	.23	.65	.74	.67
Site 4	.69	-.44	.81	-.05	.87	.72	.73
Site 8	.77	-.18	.69	-.08	.79	.89	.91
Site 9	.52	-.22	.31	-.19	.37	.83	.79
Site 10	.32	-.21	.24	-.21	.23	.60	.76
Site 11	.53	-.21	.42	-.23	.53	.74	.88
Site 12	.95	-.18	.50	-.16	.62	.86	.92
Site 1	.09	.05	-.11	-.04	.42	.48	.58
Site 2	-.18	-.75	-.20	-.70	.03	.70	.42
Site 5	.35	-.64	.09	-.64	.30	.59	.50
Site 6	.23	-.48	.24	-.38	.18	.56	.34
Site 13	.31	-.25	.17	-.23	.27	.74	.71
Site 7	.43	-.19	.13	-.21	.26	.74	.69

TABLE: A-9

COMPARISON OF PHOSPHORUS LOADING VALUES  
 USING STUDY AND FEDERAL DATA

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Site TP	Phosphorus Loading (tonnes)			Coefficient of Variation	
	Study (1)	Federal (2)	Combined (3)	1 vs 2	1 vs 3
#1	1980	21.8	22.4	6	2
	1981	29.4	25.8	26	9
#7	1980	389.0	413.8	12	4
	1981	419.6	497.4	28	12
#3	1980	155.7	122.0	60	17
	1981	762.8	580.6	71	19
#8	1980	149.6	129.0	0	10
	1981	828.0	760.5	17	6
#12	1980	510.4	598.2	28	11
	1981	499.6	598.5	31	13
<u>DP</u>					
#1	1980	8.4	9.4	21	8
	1981	11.4	10.1	25	9
#7	1980	161.6	167.9	7	3
	1981	214.2	205.6	8	3
#3	1980	10.4	9.5	22	6
	1981	34.2	26.4	67	18
#8	1980	38.0	41.0	33	5
	1981	50.9	48.6	9	3
#12	1980	147.8	156.1	12	4
	1981	157.4	138.2	34	9

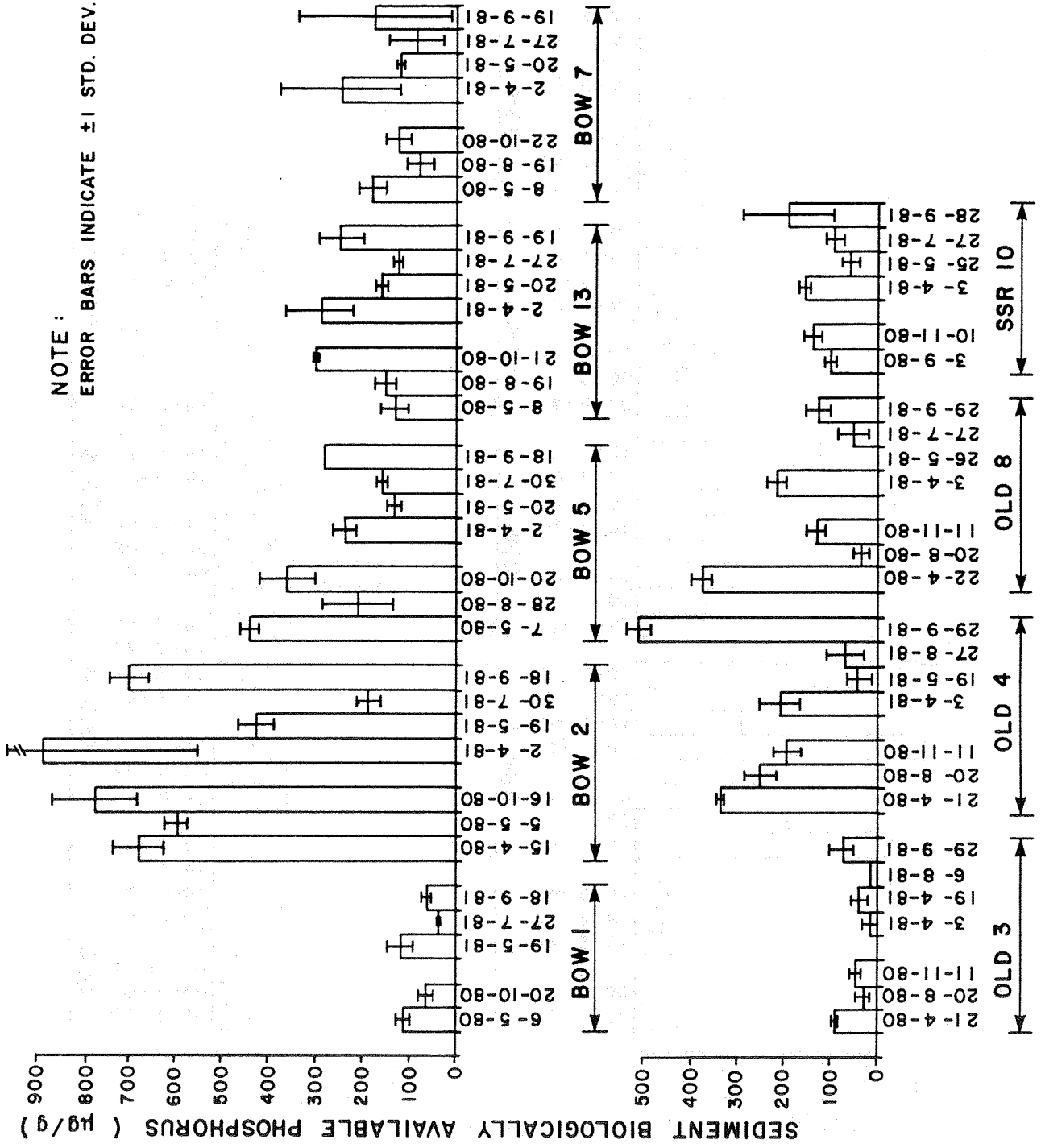


Figure A-2: Seasonal distribution of SBAP at selected study sites, 1980-81.

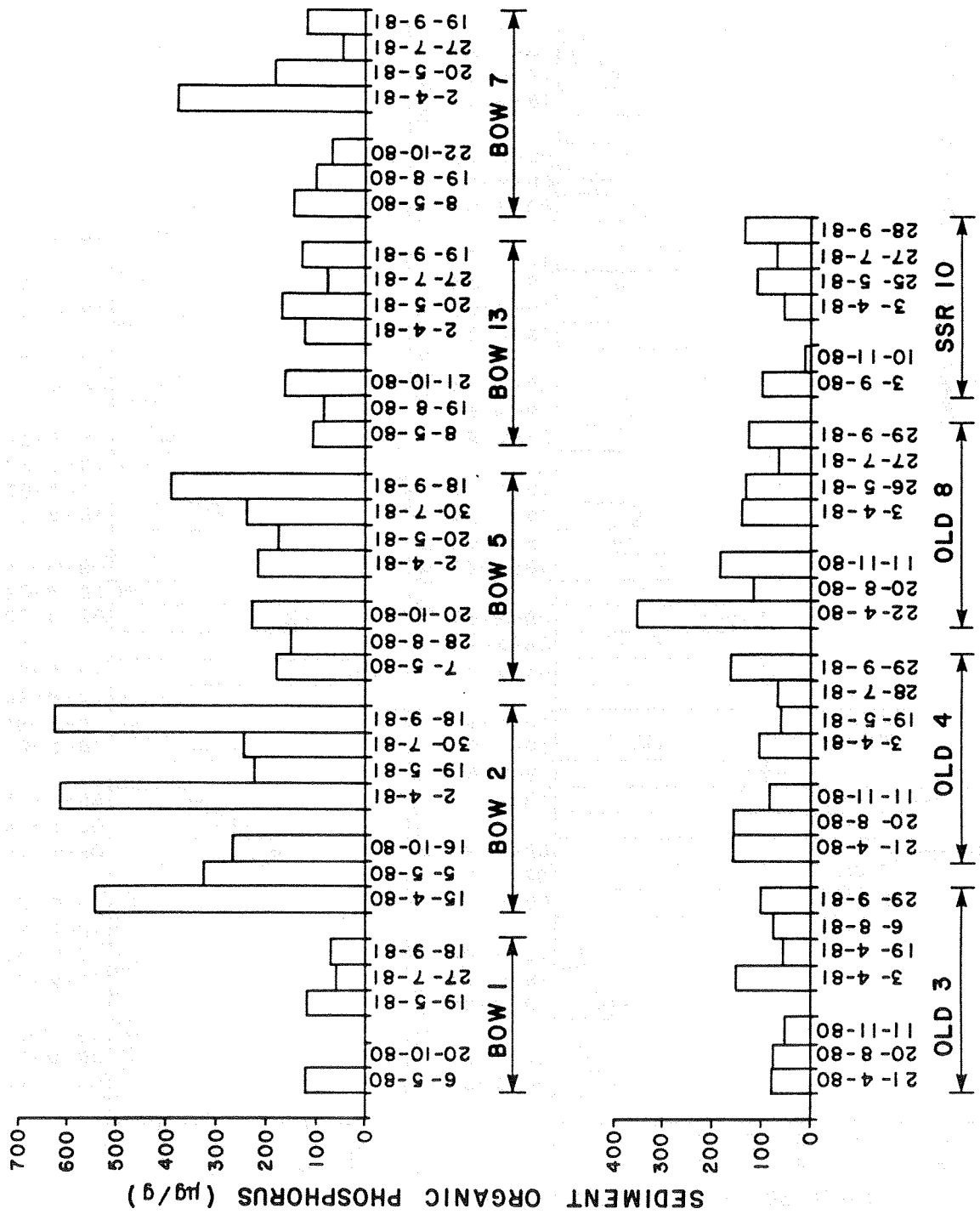


Figure A-3 Seasonal distribution of ORGP at selected study sites, 1980-81.



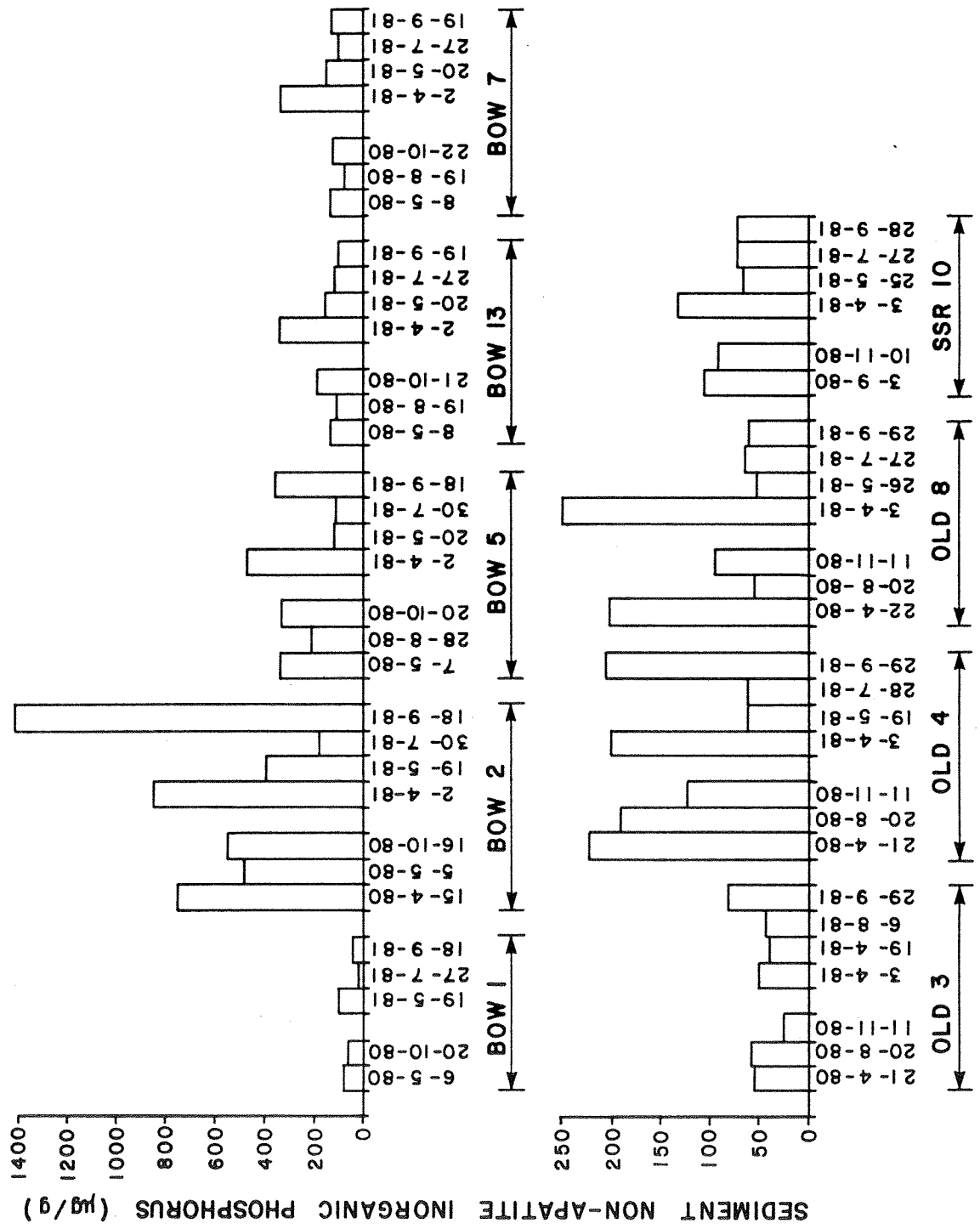


Figure A-4 Seasonal distribution of NAIP at selected study sites, 1980-81.

