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Abstract

The Red River flows from the United States through Manitoba and into the south basin of Lake Winnipeg. Significant seasonal variations in nitrogen and phosphorus species, concentration and ratios occurred in the Red River during a study conducted at the border between Canada and the United States.

Nitrate-N was as much as 60% of total-N during the spring high flow. During summer nitrate-N was so low that it might have been a limiting factor for phytoplankton growth (the inorganic-N to ortho-P ratio exceeded 10 on one occasion only). Particulate-N was usually less than 30% of total-N. Ammonia was up to 30% of total-N in February.

The ortho-P concentration constituted between 25% and 80% of total-P. Dissolved organic-P never exceeded 16% of total-P, and particulate-P was as much as 70% of total-P.

Particulate P:N:C ratios differed from the stoichiometric ratios of plant cells. On this basis, it is concluded that much of the particulate-P was in mineral form.

Résumé

La rivière Rouge prend naissance aux États-Unis, traverse le Manitoba et se jette dans la cuvette méridionale du lac Winnipeg. On a observé à la frontière internationale des variations saisonnières significatives des formes d'azote et de phosphore, de leurs concentrations et de leur rapport dans cette rivière.

Au cours de la crue printanière, l'azote sous forme de nitrates représentait jusqu'a 60 % de l'azote total. En été, sa concentration s'est abaissée tellement que l'azote sous forme de nitrates a pu devenir un facteur limitant de la croissance du phytoplancton (le rapport azote minéral/phosphore sous forme d'orthophosphates n'a dépassé 10 qu'en une fois seulement). L'azote particulaire représentait habituellement moins de 30 % de l'azote total. En février, l'ammoniac s'est élevé à 30 % de l'azote total.

La concentration de phosphore sous forme d'orthophosphates se situait entre 25 et 80 % du phosphore total. Le phosphore organique dissous n'a jamais dépassé 16 % du phosphore total, et le phosphore particulaire s'est élevé jusqu'à 70 % du phosphore total.

Les rapports P/N/C particulaires différaient des rapports stœchiométriques des cellules végétales; d'après cela, on conclut qu'une grande partie du phosphore particulaire se trouvait sous forme minérale.

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INTRODUCTION

The Red River drainage basin (~170 000 km^2) lies almost entirely within the agricultural areas of Manitoba, North Dakota and Minnesota and receives nitrogen (N) and phosphorus (P) enrichment from point and non-point sources. The non-point sources include precipitation, drainage from agricultural and pasture lands, urban land drainage, decaying vegetation and wastes from wildlife; point sources consist of municipal and industrial effluents.

The implementation of the Garrison Diversion Project (Fig. 1) will result in the diversion of part of the Missouri River flow to the Souris and Red rivers and eventually into Lake Winnipeg. The south basin of Lake Winnipeg into which the Red River drains is already suspected of nearing eutrophic state (Brunskill, 1974). Runoff from the Garrison Diversion or other future irrigation schemes could modify nitrogen and phosphorous species, concentrations and ratios in the Red River. The International Joint Commission (1976), in its report to the Canadian and United States governments, recognized that better understanding of the nutrient forms (species) was essential for determining "the nature and extent of the complex nitrogen transformations in the Souris and Red Rivers."

Future changes in nitrogen and phosphorus species in the Red River will only be interpretable if the present pattern is established. Thus, Canada has a major interest in determining the nature of the nutrients, their concentrations and their ratios in the Red River as it enters Canada at the international border. Accordingly, a study was conducted on the Red River near Emerson, Manitoba, during the period of April 1978 to March 1979. The objectives were to determine: (1) the relative abundance of nitrogen and phosphorus species, (2) the seasonal variability of these species, and (3) the N:P ratios in the Red River.

METHODS

A cross section of the Red River near Emerson (Fig. 1) was divided into grids of 1 m^2 (about 150). Water samples were collected from 12 randomly selected grids during the 12 sampling trips conducted between April 1978 and March 1979. Samples were collected in the same order in which the random grids had been selected. During the winter low flow period, it was necessary to reduce both the size and the total number of grids, but the sample size (12 samples) always constituted no less than 10% of the total number of grids. The random generation of grids and the 10% design criterion were selected to obtain a representative sample of the river cross section. The methods used for random generation were those described by Youmans (1973).

Samples were collected with a weighted horizontal alpha sampler.[1] Immediately after collection the samples were transferred to polypropylene bottles and transported to Winnipeg in ice-packed containers. In Winnipeg, the samples were analyzed at the Freshwater Institute Laboratory, Department of Fisheries and Oceans, for ammonia (NH_3), nitrite (NO_2), nitrate (NO_3), total dissolved nitrogen (TDN), particulate nitrogen (PN), ortho-phosphorus (*o*P), total dissolved phosphorus (TDP), particulate phosphorus (PP), particulate carbon (PC) and suspended sediments (SS). Analyses for dissolved constituents and filtration for particulates were completed within 24 h after sampling. Concentrations of total dissolved organic nitrogen (TDON), total nitrogen (TN), dissolved inorganic nitrogen (DION), total dissolved organic phosphorus (TDOP) and total phosphorus (TP) were calculated from the results. The analytical procedures used were those described by Stainton *et al.* (1974).

RESULTS AND DISCUSSION

Variability of Replicate Samples

During the study the mean velocity of the Red River near Emerson was 27 m/min (personal communication, Water Survey of Canada, Winnipeg, Manitoba). The average sampling time for each set of 12 sequential samples was 33 min. This time period therefore represents a volume of

[1] Alpha style bottle, based on the original design by W. Van Dorn, available from WILDCO Instrument and Aquatic Sampling Supplies, Saginaw, MI.

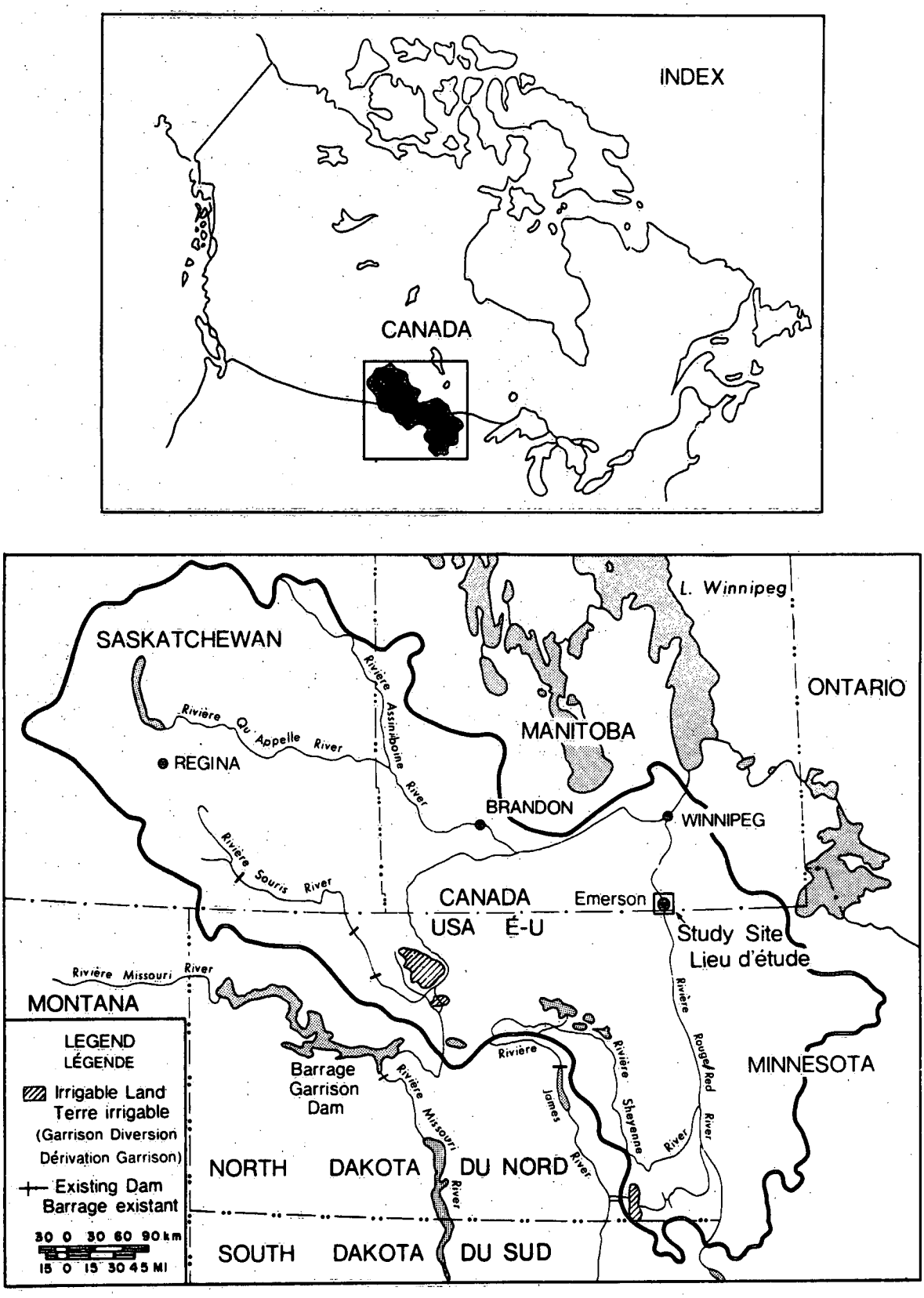

Figure 1. Red River drainage basin in relation to the Garrison Diversion Project.

Table 1. Replicate Sample Precision Compared with Laboratory Analytical Precision

	Nitrogen species					Phosphorus species	
	NH_3	NO_2	NO_3	TDN	PN	TDP	PP
Analytical precision	2	20	6	2	8	N.V.	8
Sampling date							
78-04-25	9.0	3.0	2.6	2.4	11.2	1.8	6.8
78-05-15	41.0	5.8	1.2	6.6	20.2	3.6	4.8
78-06-06	60.8	19.2	13.2	4.2	17.4	4.0	15.4
78-06-26	45.8	28.4	1.8	7.8	36.6	2.8	4.8
78-07-17	68.2	26.8	1.2	4.0	42.0	1.8	6.0
78-08-08	46.4	<0.1	4.6	3.6	51.0	1.2	8.6
78-08-28	63.8	35.2	18.6	4.8	78.0	4.0	19.0
78-09-18	149.2	<0.1	2.0	8.8	49.2	2.4	5.4
78-10-10	52.4	<0.1	2.8	3.2	18.0	2.6	17.0
78-11-06	104.2	<0.1	N.V.	7.0	9.0	2.2	3.0
78-12-11	37.4	<0.1	4.8	14.2	22.2	3.2	5.2
79-02-12	3.4	<0.1	1.4	6.2	43.2	6.2	5.4

Note: Precision is reported as twice the coefficient of variation in percent ($\frac{s}{\bar{x}} \times 200$); n = 12 for each sampling date.

N.V. – No value.

water occupying an 890-m reach of the river from which the sequential samples were collected. These sequential samples henceforth are referred to as replicate samples of this reach. Analytical precision and the precision of the 12 replicate samples are given in Table 1. Small precision values for replicate samples suggest homogeneity of the river water, while large values suggest heterogeneity.

Replicate variability (sample precision) of nitrite-N, nitrate-N and particulate-P was, for the most part, within the analytical variation, suggesting homogeneous distribution of these parameters throughout the 890-m reach of river during the entire study period.

Although not large (Table 1), replicate sample precision of total dissolved-N consistently exceeded the analytical precision. Replicate precision of particulate-P was consistently better than that of particulate-N. This suggests that particulate-P was more evenly distributed in the river reach than particulate-N. Because poor replicate precision was observed for ammonia and particulate-N during the early stages of the study (Table 1), the effect of sample storage on replicate precision was investigated. In the case of particulate-N, replicate precision decreased 7% after three days of storage, whereas for ammonia the decrease was as much as 45%. Therefore, poor ammonia precision is attributed not only to heterogeneity in the river reach but also to changes taking place in the sample bottle. The poor particulate-N precision suggests heterogeneous distribution of this constituent in the river reach.

Seasonal Variability of Nitrogen Species

To observe seasonal variability in the nitrogen species, it is necessary that seasonal variability be greater than the variability within each set of replicate samples. The 95% confidence mean concentration limits given in Table 2 and Figure 2 show that except for ammonia and particulate-N, the variability within the replicate samples was small in comparison with the seasonal variability. One-way analysis of variance and multiple comparisons at a 95% confidence level (Nie *et al.*, 1970) were used to determine whether temporal variability in the data existed. Since high replicate variability masked temporal variability (Fig. 2), only four distinct groupings (subsets) were evident for ammonia. There were six groupings for particulate-N, seven for nitrite-N and total dissolved organic-N, and eight for total dissolved-N and total-N. The fact that the data are not confined to only one or two groupings substantiates that temporal variability in the nitrogen species is significant. The seasonal variability of the species is shown in Figure 2.

Nitrate-N in the Red River fluctuated between 1 μg/L in November and 1295 μg/L in April with an annual mean of 365 μg/L. High nitrate-N during spring could have resulted from overland runoff (Logan, 1977). Agricultural drainage water can contain nitrogen concentrations ranging from 1 to more than 100 mg/L, mostly in the form of nitrate-N (McCarty *et al.*, 1970). Nitrate-N constituted about 60% of the total-N during spring runoff in April and

Table 2. Mean Concentration (μg/L) of Phosphorus, Nitrogen and Carbon (1978-79)

Parameter	Sampling date												Mean for the study period	Percent of total P or N
	Apr. 25	May 15	June 6	June 26	July 17	Aug. 8	Aug. 28	Sept. 18	Oct. 10	Nov. 6	Dec. 11	Feb. 12		
*o*P	148 (1)	94 (1)	95 (1)	131 (1)	184 (2)	123 (0)	89 (1)	80 (1)	48 (1)	142 (1)	66 (1)	145 (3)	112	40
TDOP	21 (1)	17 (2)	19 (1)	10 (1)	10 (1)	14 (1)	15 (1)	13 (1)	14 (1)	22 (1)	19 (1)	13 (1)	16	6
TDP	169 (1)	111 (1)	114 (1)	141 (1)	194 (1)	137 (1)	105 (1)	93 (1)	61 (1)	164 (1)	85 (1)	158 (3)	128	46
PP	90 (2)	244 (4)	264 (13)	331 (5)	285 (5)	146 (3)	66 (4)	109 (2)	79 (4)	109 (1)	33 (1)	21 (1)	148	54
TP	259 (3)	355 (4)	378 (13)	472 (5)	479 (6)	283 (4)	170 (3)	202 (2)	141 (5)	273 (2)	118 (1)	179 (3)	276	100
NH_3	176 (5)	64 (8)	42 (8)	51 (7)	44 (10)	33 (5)	25 (5)	74 (35)	48 (8)	56 (19)	157 (19)	396 (4)	97	7
NO_2	45 (0)	10 (10)	10 (1)	6 (1)	4 (0)	4 (0)	3 (0)	6 (0)	5 (0)	1 (1)	3 (0)	3 (0)	8	<1
NO_3	1295 (10)	177 (1)	177 (8)	654 (4)	610 (2)	124 (2)	32 (2)	486 (3)	224 (2)	1 (0)	92 (1)	402 (2)	356	26
TDN	1928 (14)	833 (18)	881 (12)	1 191 (30)	1 186 (15)	843 (10)	655 (10)	985 (27)	799 (8)	743 (16)	855 (39)	1252 (25)	1013	73
TDON	413 (18)	582 (11)	652 (14)	480 (28)	528 (17)	682 (9)	595 (11)	419 (41)	522 (14)	686 (25)	603 (39)	451 (23)	551	40
PN	284 (10)	698 (45)	674 (37)	538 (62)	504 (67)	382 (62)	247 (55)	172 (27)	308 (18)	517 (15)	173 (15)	58 (8)	380	27
TN	2213 (13)	1532 (36)	1555 (39)	1 729 (80)	1 690 (62)	1224 (59)	888 (57)	1157 (46)	1107 (22)	1260 (25)	1021 (41)	1310 (29)	1390	100
PC	3405 (84)	9060 (346)	9706 (417)	11 310 (928)	10 093 (450)	5088 (360)	2580 (91)	3306 (146)	3257 (150)	4225 (90)	1898 (50)	970 (57)		

Note: The 95% confidence limits are given by (±) value in parentheses. These limits are calculated from the student *t* distribution: $\left(\bar{x} - \frac{(s)(t)}{\sqrt{n-1}}\right) < \bar{x} < \left(\bar{x} + \frac{(s)(t)}{\sqrt{n-1}}\right)$

where $\bar{x}$ = sample mean,
s = standard deviation,
t = student *t* value, and
n = number of samples (12).

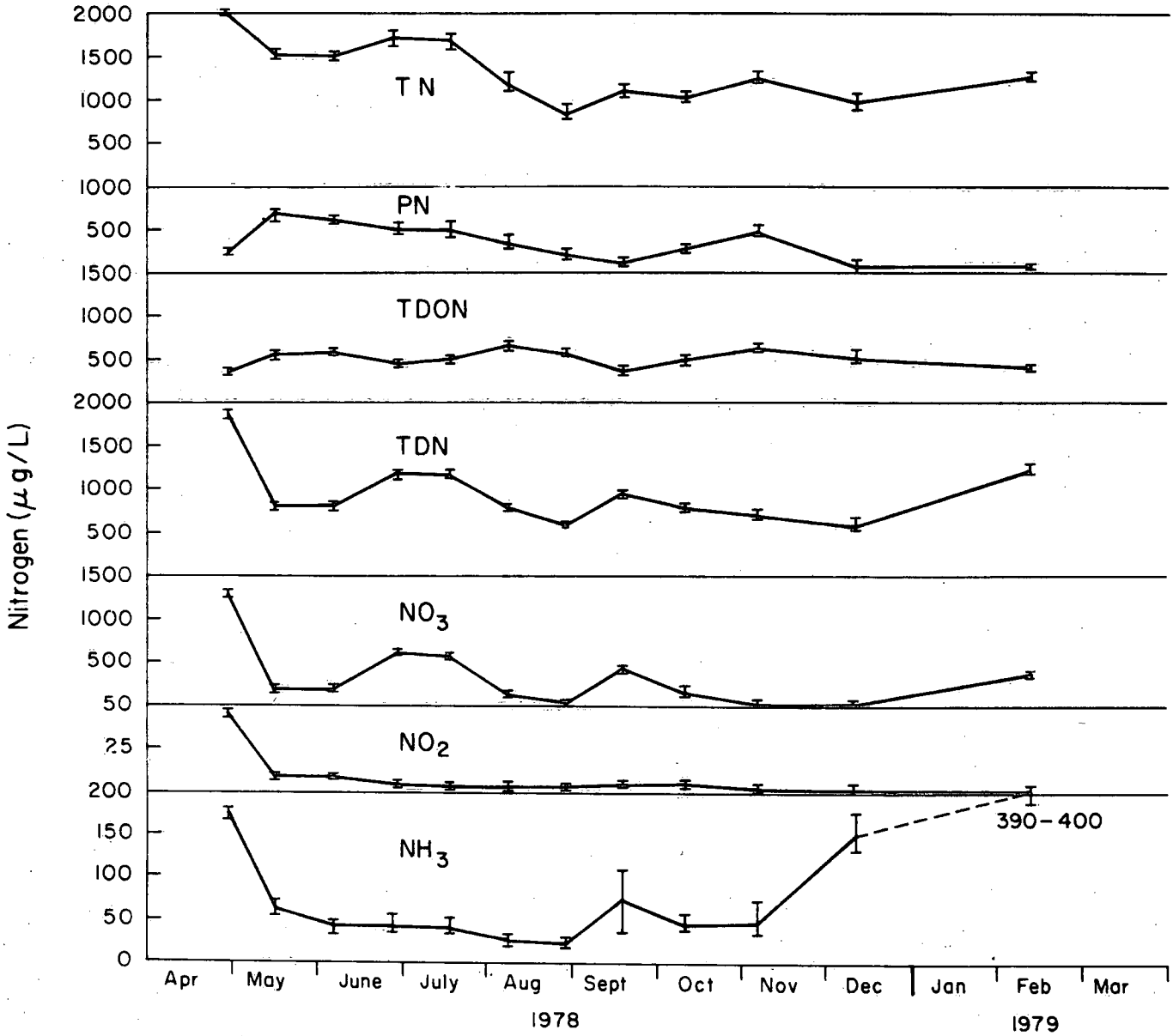

Figure 2. Temporal variability in mean concentration of nitrogen species (95% confidence limits shown).

about 1%-40% during the summer, autumn and winter months (Figs. 3 and 4). Since the Red River drainage basin lies almost entirely within the agricultural areas of Manitoba, North Dakota and Minnesota, the high April concentration can probably be attributed to agricultural runoff. Historical data on file (NAQUADAT) also show that the nitrate-N concentration between March and May is about twice the concentration observed during other seasons of the year. Since the hydrograph remains virtually constant between September and February (Fig. 3), the fluctuation in the nitrate concentration is attributed primarily to biological transformation (Logan, 1977).

The nitrite-N level was low except for April (45 μg/L). As with nitrates, the highest nitrite-N concentration occurred during spring runoff.

Ammonia was less than a tenth of the total nitrogen for most of the year, but was as much as 30% of the total nitrogen in February under ice cover. An increase in ammonia concentration in lakes and rivers during winter has been documented before (Johannes, 1968; Keeney, 1973).

Total dissolved organic-N constituted only 20% of the total-N during spring runoff, but it was the most constant

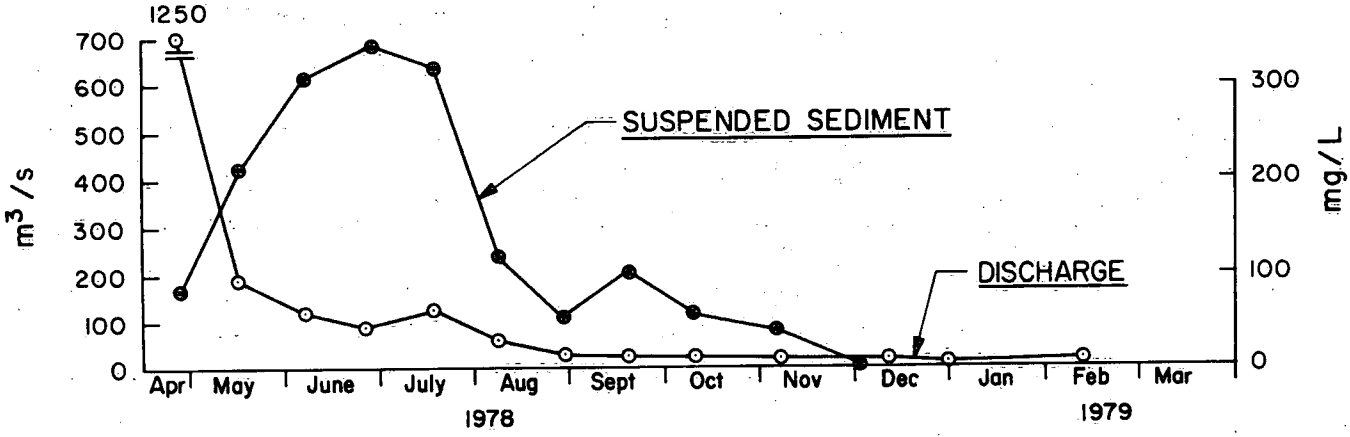

Figure 3. Hydrograph and suspended sediment concentration.

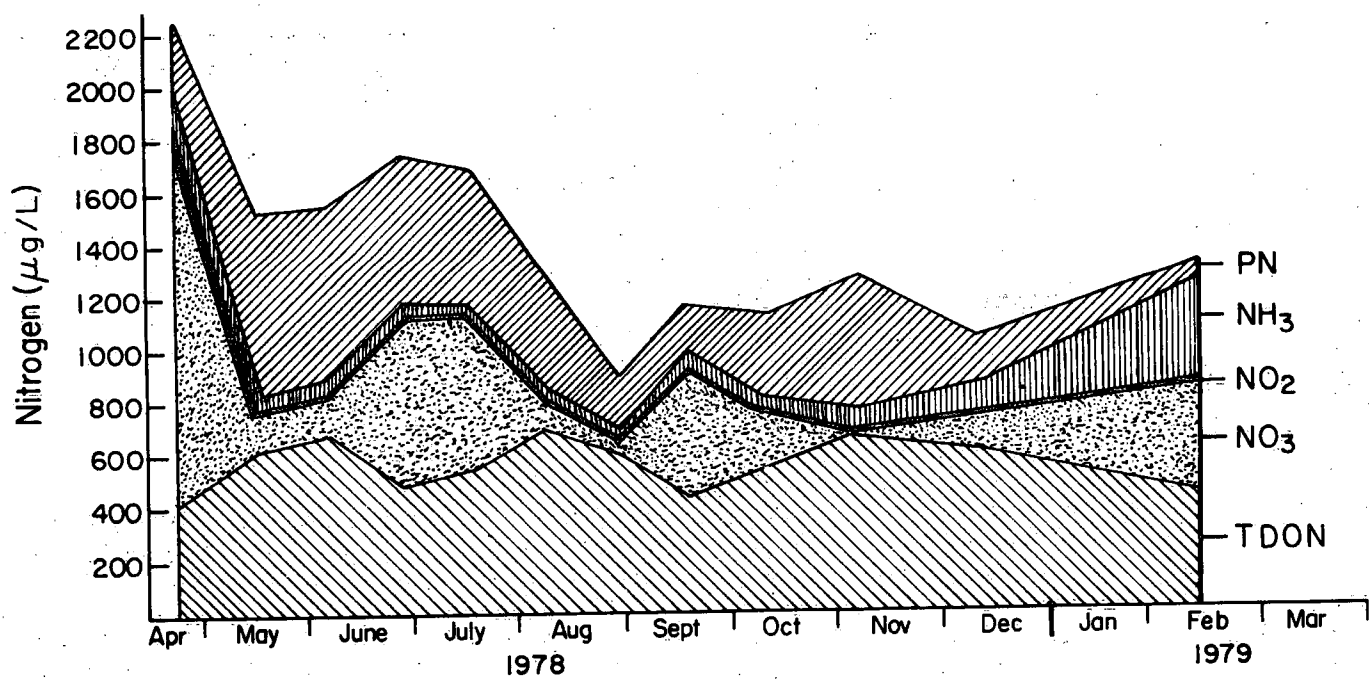

Figure 4. Temporal variability in the cumulative concentration of nitrogen species.

nitrogen species during the hydrologic period under study (Fig. 4). It varied between 413 and 686 μg/L with an annual mean of 551 μg/L.

Particulate-N concentrations varied from 58 μg/L in February to 698 μg/L in May. Maximum levels occurred during the declining peak flows of spring runoff. Low February values probably corresponded to low algae and suspended sediment concentrations present in the water under ice cover. With the exception of peak spring flow, particulate and total nitrogen concentrations increased with increasing streamflow and suspended sediments (Figs. 5 and 6).

Seasonal ratios of nitrogen species also varied in the Red River during the study period (Fig. 4). The particulate-N to inorganic-N (NO_3, NO_2, NH_3) ratio was about 1:5 in April, 4:1 in August, and 1:14 in February. This seasonal variation in the particulate-N to inorganic-N ratio reflects varying hydrologic and biological conditions in the Red River. The higher inorganic-N level in April probably resulted from land runoff, and the lower level in August and the proportionally higher level in February likely resulted from biological assimilation and mineralization, respectively (Keeney, 1973). Although in winter, under ice cover, biological transformation is reduced, it is probably a dominant factor affecting the ratio of the nitrogen species.

The nitrogen loading was calculated for each species. Nitrate-N constituted 48% of the total nitrogen loading during the study. If April and May values are taken to represent the spring runoff and the sum of the 12 trips to represent the annual loadings, 90% of nitrate-N was transported during spring runoff when the water temperature was low and biological transformation was minimal. Similarly, nitrite-N, ammonia and total dissolved organic-N constituted 2%, 7% and 25% of the annual load, respectively, with 92%, 85% and 66% of the loading, respectively, occurring during April and May. Particulate-N was only 19% of the annual nitrogen loading, 65% of which was transported during the high discharge of April and May.

Seasonal Variability of Phosphorus Species

Except for particulate-P and total dissolved organic-P, replicate sample variability for phosphorus species was small in comparison with seasonal variability (Table 2 and Fig. 7). One-way analysis of variance and multiple comparisons at a 95% confidence level produced five data groupings (subsets) for total-P, six for total dissolved organic-P, nine for particulate-P, ten for ortho-P and eleven for total dissolved-P. Because there were five or more significantly different data groupings during the study period, temporal variability was significant for the phosphorus species.

During the study, ortho-P concentrations ranged from 48 to 184 μg/L with an annual mean of 112 μg/L. Ortho-P concentrations in the Red River were relatively constant and abundant for potential biological uptake. If the critical ortho-P level for the production of algae is considered to be 10 μg/L (Sawyer and McCarty, 1967), then it was not a limiting factor in the Red River. Depending on the time of year, ortho-P constituted between 25% and 80% of the total phosphorus concentration in the Red River (Fig. 8). Unlike the inorganic-N species, ortho-P did not change significantly with the hydrograph (Figs. 3 and 8).

Total dissolved organic-P remained virtually constant between 10 and 22 μg/L. In contrast with reports that total-P consists of 30%–60% dissolved organic-P in lakes (Hutchinson, 1957) and up to 30% in rivers (Englebrecht and Morgan, 1959), the dissolved organic-P level in the Red River was most often less than 10% of the total-P.

Polyphosphate was determined for a number of sample sets and the values were always less than 4 μg/L.

The particulate-P level in the Red River varied from a low of 21 μg/L in February to a maximum of 331 μg/L in June. The maximum levels of particulate-P occurred after the peak spring flow during the period of May to July. The lowest concentrations of particulate-P occurred in the winter under ice cover (Fig. 8). With the exception of peak spring flow, particulate-P and total-P increased with stream discharge and suspended sediment content (Figs. 9 and 10), a phenomenon that has been observed elsewhere (Cahill, 1977).

The particulate-P to ortho-P ratio was about 2:3 in April, 2:1 in June, and 1:7 in February (Fig. 8). Since the ortho-P level was relatively constant, the change in the particulate-P to ortho-P ratio resulted primarily from varying particulate-P. The relative abundance of the phosphorus species shown in Figure 8 also shows that particulate-P and ortho-P are the dominant phosphorus species in the Red River.

Loading was calculated for each of the phosphorus species. While particulate-N was only 19% of the annual nitrogen load, particulate-P constituted 48% of the phosphorus annual load and 57% was transported during spring runoff. The ortho-P constituted 46% of the annual load, and 75% was transported during spring runoff. Comparable figures for total dissolved organic-P were 6% and 76%, respectively. The phosphorus loading in the Red River is not as strongly influenced by river discharge as the nitrogen loading.

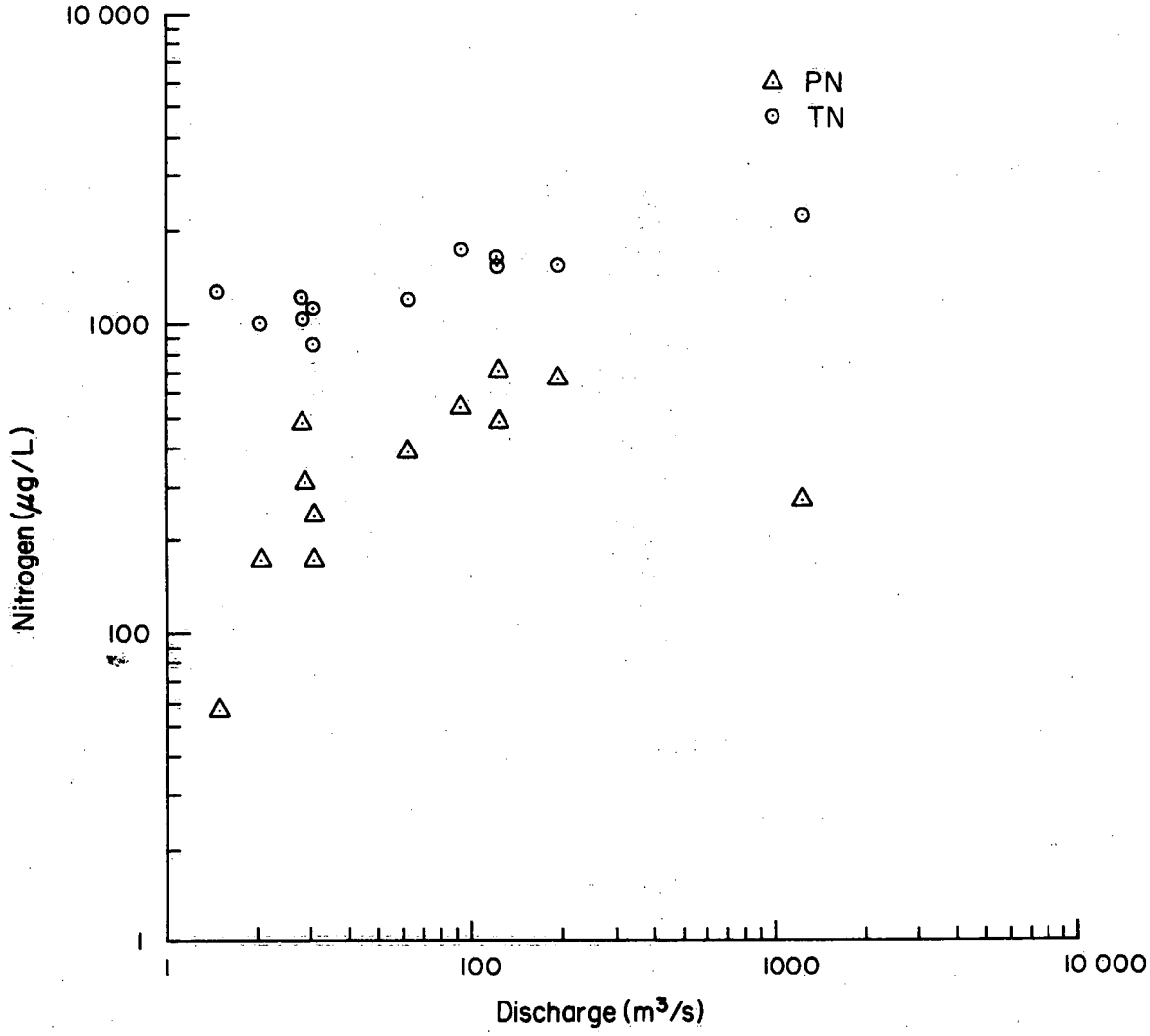

Figure 5. Particulate-N and total-N vs. streamflow.

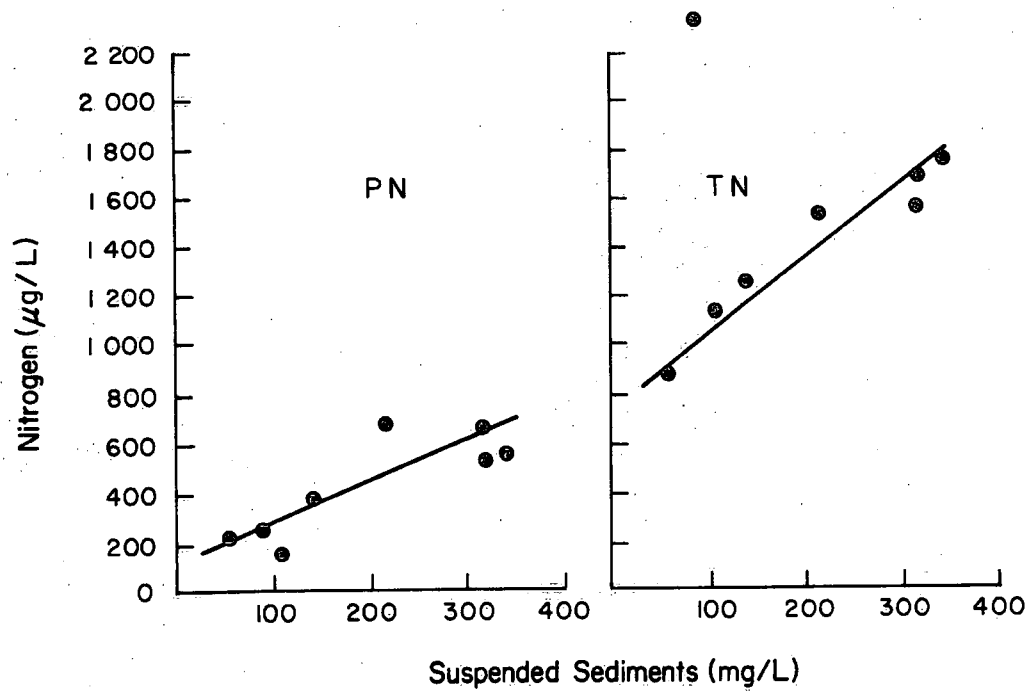

Figure 6. Particulate-N and total-N vs. suspended sediments.

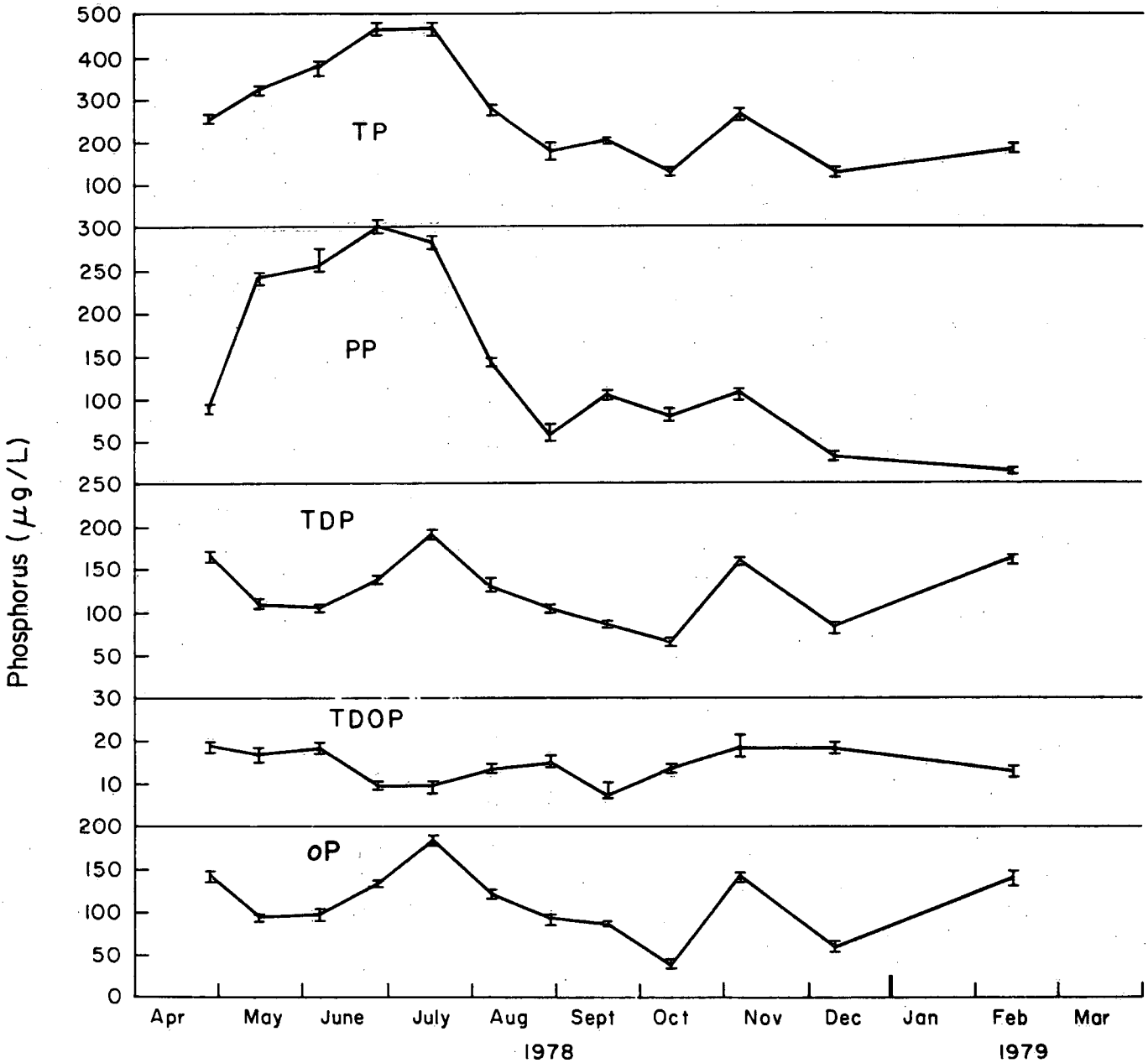

Figure 7. Temporal variability in mean concentration of phosphorus species (95% confidence limits shown).

N:P Ratio in the Red River

Phosphorus may be a limiting factor for algal growth when the stoichiometric ratio of inorganic-N to ortho-P (N:P) exceeds 10 (Chiaudani and Vighi, 1974). The N:P ratios (Table 3) show that except for the peak spring flow, the ratios were always substantially below 10. On two occasions the ratio was even less than 1. Similar, very low TN:TP ratios have been reported for lakes in the Qu'Appelle River basin of the prairie region of southern Saskatchewan (Allan and Roy, 1980). Variations in the N:P ratio occurred primarily as a result of the fluctuation in levels of inorganic-N (Table 3). Spring and precipitation runoff events and biological uptake appear to be major factors affecting inorganic-N levels in the Red River. There is no clear seasonal pattern in the N:P ratios (Table 3).

The stoichiometric plant cell (algae and bacteria) ratio of P:N: carbon reported by McCarty *et al.* (1970) is 1:16:106. The particulate-P:N:C ratios given in Table 3 indicate that much of the particulate-P was not of plant origin. Much of the particulate phosphorus was probably

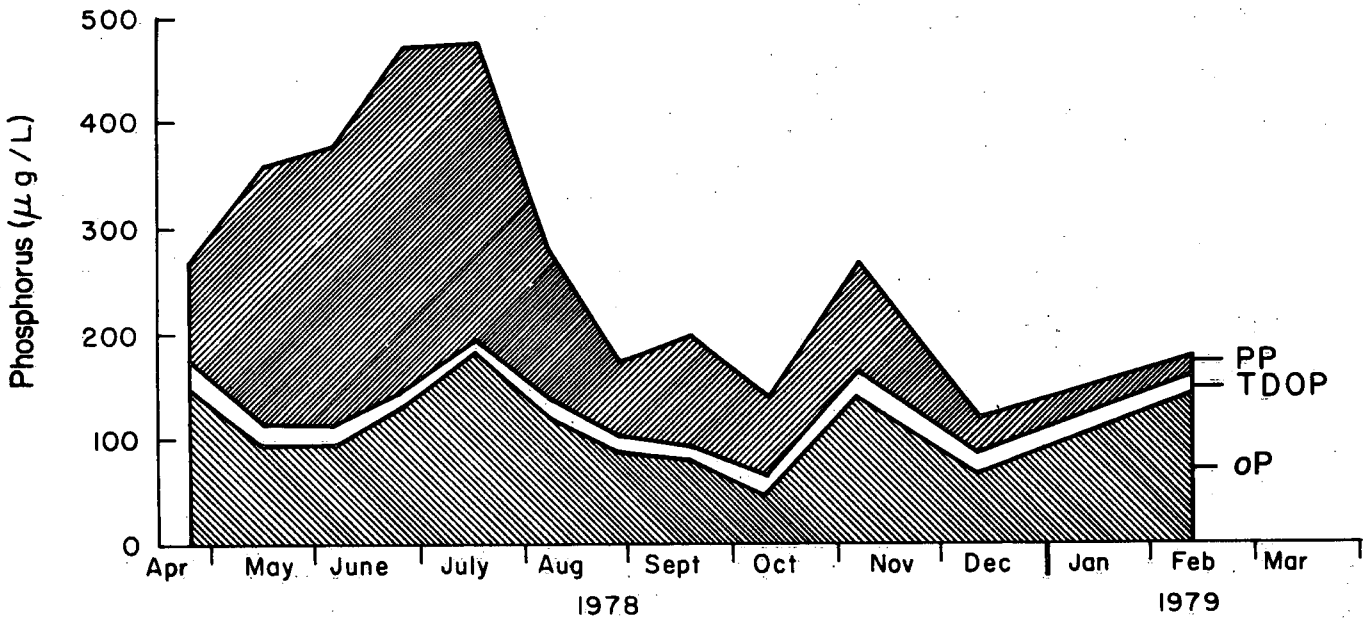

Figure 8. Temporal variability in the cumulative concentration of phosphorus species.

Table 3. Inorganic-N to Ortho-P Ratio and the Particulate P:N:C Ratio

Sampling date	Inorganic-N (μg/L)	Ortho-P (μg/L)	N:P*	PP (μg/L)	PN (μg/L)	PC (μg/L)	P:N:C*
78-04-25	1516	148	10:1	90	284	3 402	1:3:38
78-05-15	251	94	3:1	244	698	9 061	1:3:37
78-06-06	229	95	2:1	264	674	9 706	1:3:37
78-06-26	711	131	5:1	331	583	11 316	1:2:34
78-07-17	658	184	4:1	285	504	10 093	1:2:35
78-08-08	161	123	1:1	146	382	5 088	1:3:35
78-08-28	60	89	1:2	66	247	3 154	1:4:48
78-09-18	566	80	7:1	109	172	3 306	1:2:30
78-10-10	277	48	6:1	79	308	3 257	1:4:41
78-11-06	58	142	1:3	109	517	4 225	1:5:39
78-12-11	252	66	4:1	33	173	1 898	1:5:58
79-02-12	801	145	6:1	21	58	970	1:3:46

* Ratios are by weight.

transported as apatite during the high flows of spring and following heavy precipitation events (Ongley, 1978). Although the concentration of particulate-P, N and C changed during the study period, the ratio remained relatively stable. Even during spring runoff in April when the inorganic-N to ortho-P ratio increased substantially, the particulate P:N:C ratio did not change.

CONCLUSIONS

Seasonal variability in nutrient species concentrations was greater than the variability between samples collected from an 890-m reach of the Red River.

During February, ammonia-N concentrations were high and about equal to the nitrate-N concentrations, or about 30% of the total-N. The majority of nitrate-N load occurred during the spring flow when nitrate-N constituted as much as 60% of the total-N. During the growing season the nitrate-N level became so low that it could have limited phytoplankton growth. Except for high spring runoff, particulate-N and total-N concentrations increased with increasing streamflow and suspended sediment. Particulate-N ranged from 4.4% to 45% of the total-N, with highest levels occurring during May to July on the descending peak of the high spring flow. The ratio of the particulate-N to inorganic-N was about 1:5 in April, 4:1 in August and 1:14 in February.

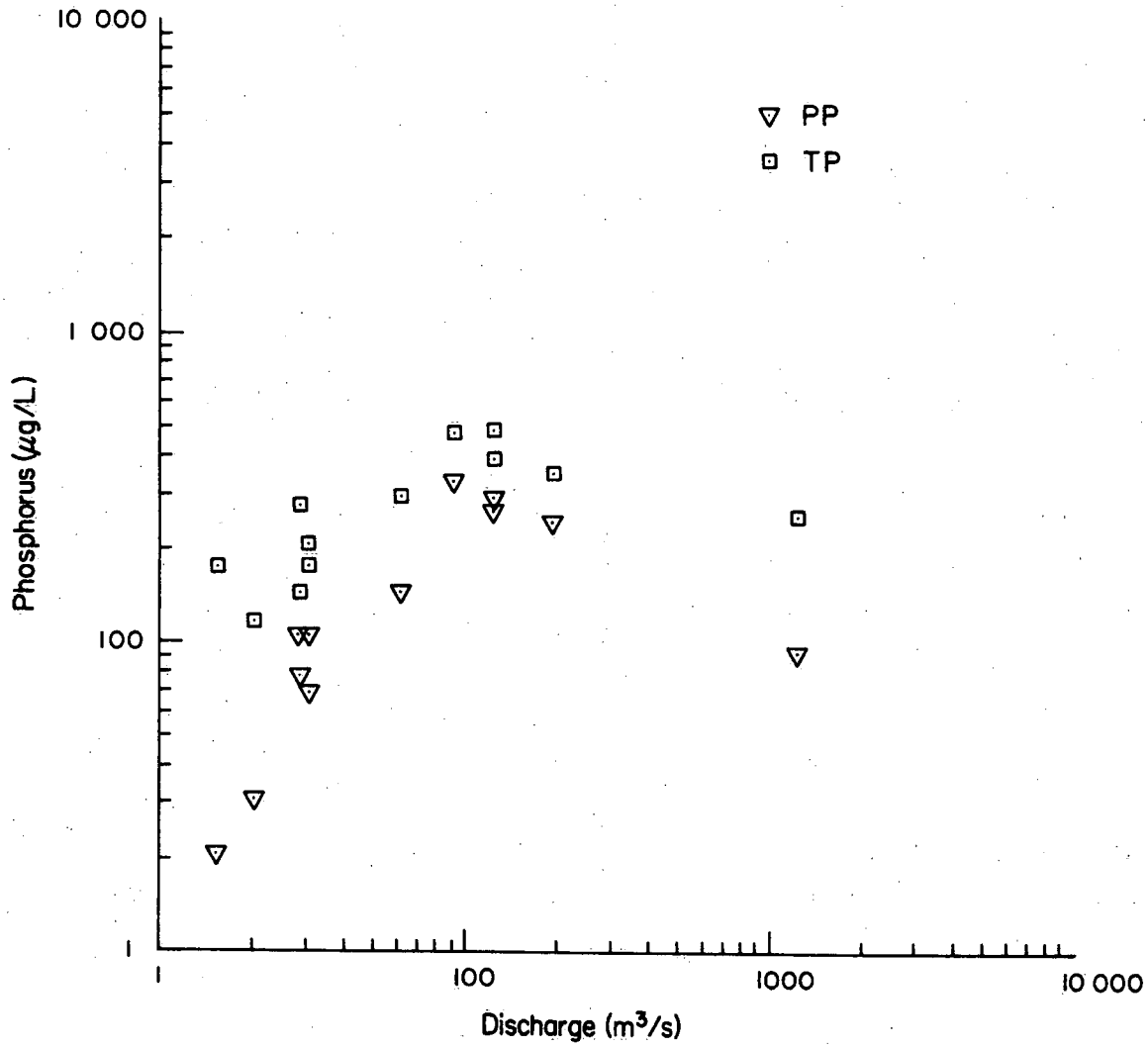

Figure 9. Particulate-P and total-P vs. streamflow.

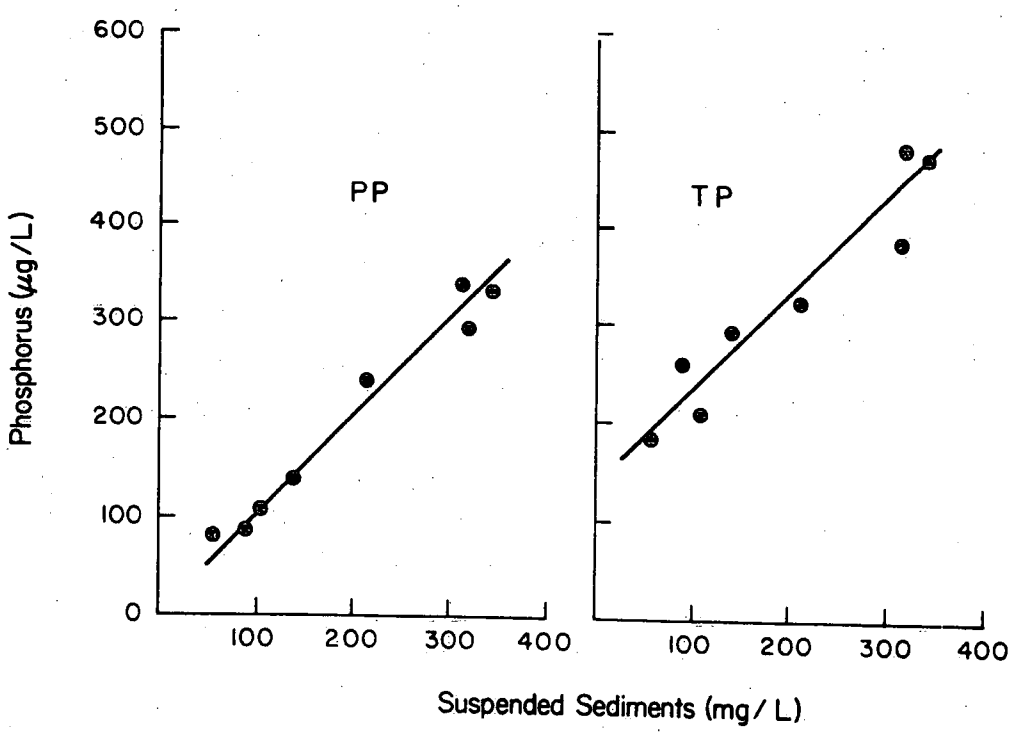

Figure 10. Particulate-P and total-P vs. suspended sediments.

Of the total-P, ortho-P constituted between 25% and 80%, dissolved organic-P never exceeded 16%, and particulate-P ranged from 12% to 70%. The highest particulate-P levels occurred during May to July on the descending peak of the high spring flow. With the exceptions of peak spring flows, particulate-P and total-P levels increased with increasing discharge and suspended sediments. Particulate-P and ortho-P were the dominant phosphorus species in the Red River.

The inorganic-N to ortho-P ratio exceeded 10 only once, indicating that inorganic phosphorus was abundant and not a limiting factor for phytoplankon growth. The particulate P:N:C ratio of about 1:3:40 indicated that much of the particulate-P was not planktonic and was probably present in mineral apatite.

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