AN INTENSIVE SURFACE WATER QUALITY STUDY

OF THE MUSKEG RIVER WATERSHED

Volume I

WATER CHEMISTRY

by

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for

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HY 2.5

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ABSTRACT

Seasonal and areal variations in significant water quality parameters in the Muskeg River basin of northeastern Alberta are described.

Specific conductances and the concentrations of major ions (Ca^{+2}, Mg^{+2}, HCO_3^-, and, to some extent, Na^+ and Cl^-) generally exhibited relatively stable seasonal levels, except for occassional fluctuations caused by storm events or deep groundwater flows.

The relationship between physiographic features and watershed water quality indicated that water and chemical storage/movement in muskeg areas play a major role in maintaining or influencing observed patterns, levels, and loadings of Ca and Mg, as well as Na:Cl ratios.

Longitudinal relationships, between key sub-basin sites and the watershed focal point, for specific conductance and the concentrations of major ions, were significant enough to allow basic water quality information on the sub-basin sites to be deduced by monitoring the focal point.

Good regression relationships, between index variables (specific conductance and discharge) and the concentrations of major ions and related parameters, were found. It was possible to calculate annual loads discharged through the major sampling sites. The use of these relationships to monitor degradation or improvement in chemical water quality was proposed.

Fluctuations in the dissolved oxgyen regime were influenced by sub-basin dependent physical factors (turbulence, turbidity, and temperature) as well as changes in algal and microbial populations. "Free" CO_2 (and pH) variations reflected fluctuations in biotic

respiration, biochemical decomposition, and photosynthetic processes.

Changes in microbial communities were also analysed in relation to macronutrient concentrations and the assimilative capacity of the streams. Orthophosphate phosphorus and nitrite- + nitrate-nitrogen (NO_2^--N + NO_3^--N) concentrations were generally low, especially during the ice-free period. This may be due to low watershed release and/or microbial uptake.

The dissolved organic carbon (DOC) and ammonia-nitrogen (NH_3-N) concentrations peaked at approximately the same time (dissolved organic nitrogen, DON, peaked a month earlier); the coincidence appeared to inhibit nitrification. DOC:DON and NH_3-N:(NO_2^--N + NO_3^--N) ratios, along with variations in NH_3-N concentrations, indicate that bacterial communities in streams of the Muskeg River basin are, at present, effective in converting organic substances to nutrients.

Levels of K, B, Co, Ni, Hg, Pb, Cu, and Zn were found to be influenced by biotic factors.

The observed levels of certain metals were lower than Alberta Surface Water Quality objectives, while for As, Hg, Ni, Zn, Fe, and Mn, the objective levels were exceeded. The higher baseflow concentrations of extractable Cr, Pb, Zn, V, Ni, Fe, Al, Mn, Cu, and Co were associated with the particulate rather than the dissolved phase.

ACKNOWLEDGEMENTS

1. THE MUSKEG RIVER BASIN

1.1 INTRODUCTION

Water quality/quantity studies of rivers and
lakes within the Alberta Oil Sands Environmental
Research Program (AOSERP) study area have been a major
undertaking since the inception of AOSERP in 1975.
This report (AOSERP Project HY 2.5 Report, Volume 1),
on an intensive study of the surface water quality of
the Muskeg River watershed, is a part of a long range
AOSERP program of basin-wide reconnaissance.
Specifically, this report documents and appraises
baseline water chemical quality conditions of a lake
and streams within the Muskeg River watershed.

Because water is both a medium for and
reactor in the series of dynamic physical, biological,
and chemical processes that maintain (or influence) the
ecological conditions of the watershed, the discussions
in this report have emphasized the relationships
between water quality parameters, streamflows, and
several environmental factors and their variations,
both in area and with time.

1.1.1 Study Objectives

The intensive water quality/quantity study of
the Muskeg River watershed was conducted to establish
baseline conditions of water quality, streamflow,
suspended sediments, and channel regime, and to obtain
an understanding of the natural water quality loadings
and processes in this basin for current and future
studies. It is hoped that the information collected by
this study will contribute to a reduction in the
environmental impact of oil sand developments.

The specific objectives of the water quality
portion of the study were to:

1. Obtain measurements of water quality conditions throughout the basin on a monthly (or bimonthly) basis starting July 1976, to complete one year of observation at the end of July 1977, and to continue three sites for another full year;

2. Determine the relationships between streamflow, conductivity, and some inorganic water quality parameters throughout the basin;

3. Estimate the temporal variation, over the year, of some water quality parameters at a large number of sites in the basin; and

4. Identify the types and sources of significant water quality unit loadings in the streams of the basin.

Hydraulics, water quantity, and suspended sediments are covered in Volume II (Froelich in prep.).

1.1.2   Field Work

The field work for AOSERP project HY 2.5 began on 27 July 1976 and ceased on 17 August 1977. A few visits were subsequently made to several sites; including monthly water quality samplings at the two main sampling sites which have been maintained as part of the AOSERP regional water quality program.

1.1.3   Concurrent Studies

Water Survey of Canada operated, since 1974, a hydrometric station on the Muskeg River about 16 km above its mouth, and began, in 1976, the operation of another station on the Hartley Creek near its confluence with the Muskeg River.

Several AOSERP biological studies were
carried out concurrently with this study. The aquatic
invertebrates were studied in the Hartley Creek by
Hartland-Rowe et al. (1979) and throughout the basin by
Barton and Wallace (in prep.). Lock and Wallace (in
prep.) investigated the lower trophic levels in the
Muskeg River; Bond and Machniak (1977) conducted an
intensive study of the fish fauna in the Muskeg River.

Schwartz (1979) conducted hydrogeological
investigations of muskeg and shallow groundwaters in
the basin.

Turchenek and Lindsay (1978) conducted soil
analyses and compiled an ecological classification of
soils in the AOSERP study area, including the Muskeg
River basin.

1.2   DESCRIPTION OF THE STUDY AREA

1.2.1   <u>Location</u>
The Muskeg River watershed is located some
60 km north of Fort McMurray and approximately 470 km
northeast of Edmonton (Figure 1).

1.2.2   <u>Drainage Pattern, Hydraulic, and</u>
           <u>Physiographic Features</u>
A network of tributary streams feeds the
Muskeg River and, together, drain a total area of
1520 km² (Figure 2). Except for Stanley Creek, which
drains the Fort Hills Upland area on the west side of
the basin, the general pattern of drainage by the other
tributary streams involves northwesterly flows. The
latter streams originate from the treed and poorly
drained Muskeg Mountain (maximum elevation 536 m)
Upland area located on the eastern boundary of the
watershed.

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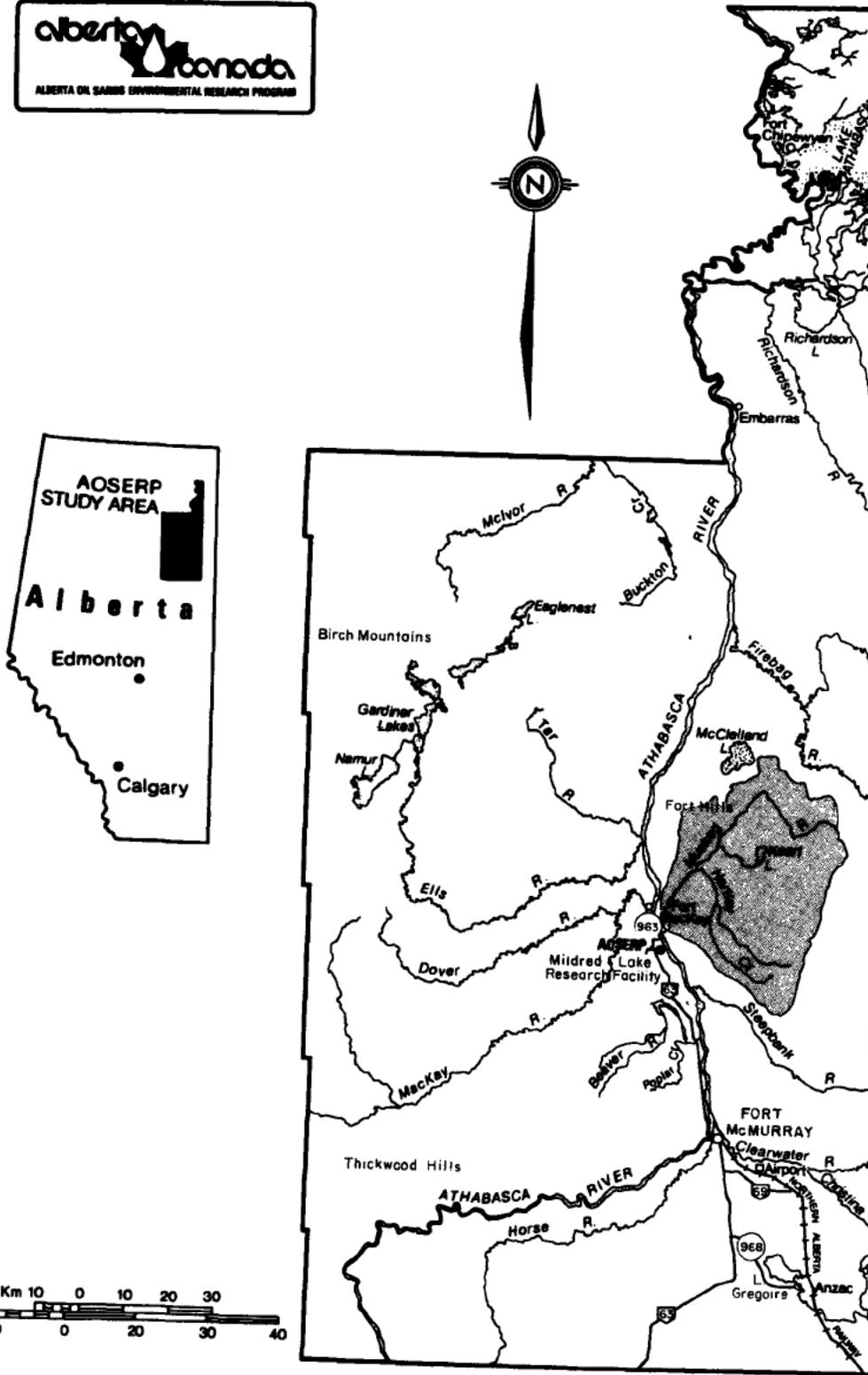
Figure l. The AOSERP study area and the Muskeg River watershed.

LEGEND

- Ground moraine
- Ice - contact deposits
- Outwash sand & gravel
- Outwash sand
- Aeolian sand, dunes
- ● Water quality sampling sites
- ▲ Water quality sampling sites & hydrometric gauges

SCALE
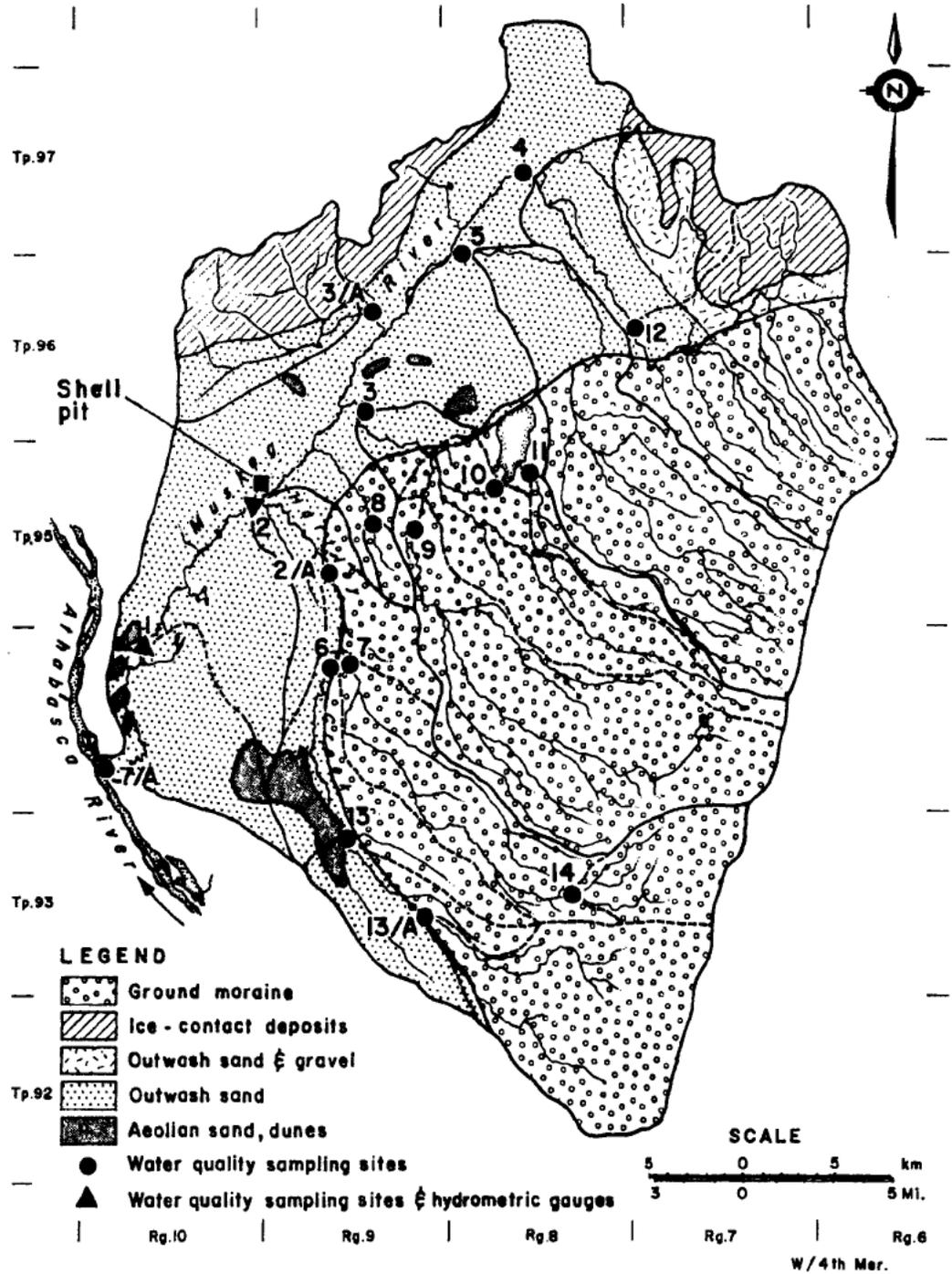
Figure 2. Surficial geology (Bayrock 1971) and water quality sampling sites of the Muskeg river watershed.

Hartley Creek, draining an area of 373 km², is the major tributary to the Muskeg River.

Tributary streams flow along steep channel slopes on the upland area but change abruptly to very low slopes on reaching the foothills. In general, the central area has very few steep slopes along stream channels. These low slope channels are often associated with adjacent bogs which are subject to frequent floodings. Changes in the hydraulic characteristics (Appendix 7.1) and surficial geology are reflected in the bed material size distribution (Appendix 7.2, Table 17).

The headwaters of the mainstem Muskeg River are also in the Muskeg Mountain Upland area. Channel slopes are the steepest here. After an initial steep drop (200 m within a 10 km stretch), the main channel of the Muskeg River flows through moderate slopes (through Site 12) along the base of the uplands. After passing through Site 4, the channel flattens out to a slope of only 0.001 and maintains this for the 58 km northeast-southwest flow to Site 1. This reach contains a flat, broad, and very poorly drained lowland.

Below Site 1, the Muskeg River channel slope increases again until the river joins the Athabasca River at an altitude of 235 m. Between the confluences with Hartley Creek and the Athabasca River, the Muskeg River channel is characterized by very steep banks; the river has penetrated the drift materials, the McMurray formation, and reached the Waterways limestone. And, because of the unstable nature of alluvial bank materials, erodability along this and other steep reaches is high; except where the channel is stabilized by vegetation or bedrock outcroppings.

1.2.3   Geologic Materials and Chemical Sources

The Muskeg River watershed was developed by
the erosion of beds that lie nearly flat and that are
composed chiefly of limestone and shale. Limestone
consists mainly of calcite ($CaCO_3$) with admixture of
magnesium and other impurities; while shale is
composed, in large part, of clay minerals and other
particulate matter resulting from the chemical reaction
between water and silicates.

Surficial materials, which include organic
deposits, soils, and mantle materials (eg., glacial and
post glacial deposits of till, silt, and sand; Bayrock
1971) (Figure 2) etc., dictate, to a large extent, the
kinds of substances that will be dissolved by surface
flowing waters. The thicknesses of the mantle
materials were detailed in an AOSERP report by Schwartz
(1979). Greater thickness of soils (Turchenek and
Lindsay 1978) (Figure 3) and glacial and alluvial
deposits reportedly (Tables 1 and 2) occur on rolling
and flat lands rather than on steep hillsides where
erosion is active.

Underlying the recent deposits are a number
of erosional unconformity formations of the Cretaceous
age. These formations contain shale, sandstone,
siltstone, quartz sands, and oil-cemented fine-to-
coarse-grained sands. Most of the shale contains
considerable amounts of soluble calcareous material.
Sandstone forms a small part of this bedrock, probably
most (80 to 90%) of it contains sand, silt, and clay.
The cementing materials may be calcium carbonate or
iron oxide. Weathering of sandstone consists chiefly
of leaching of the more soluble cementing materials,
leaving behind the less soluble sand, silt, and clay .
The Cretaceous formation and the overlying glacial and
post-glacial deposits (mostly Pleistocene) have also
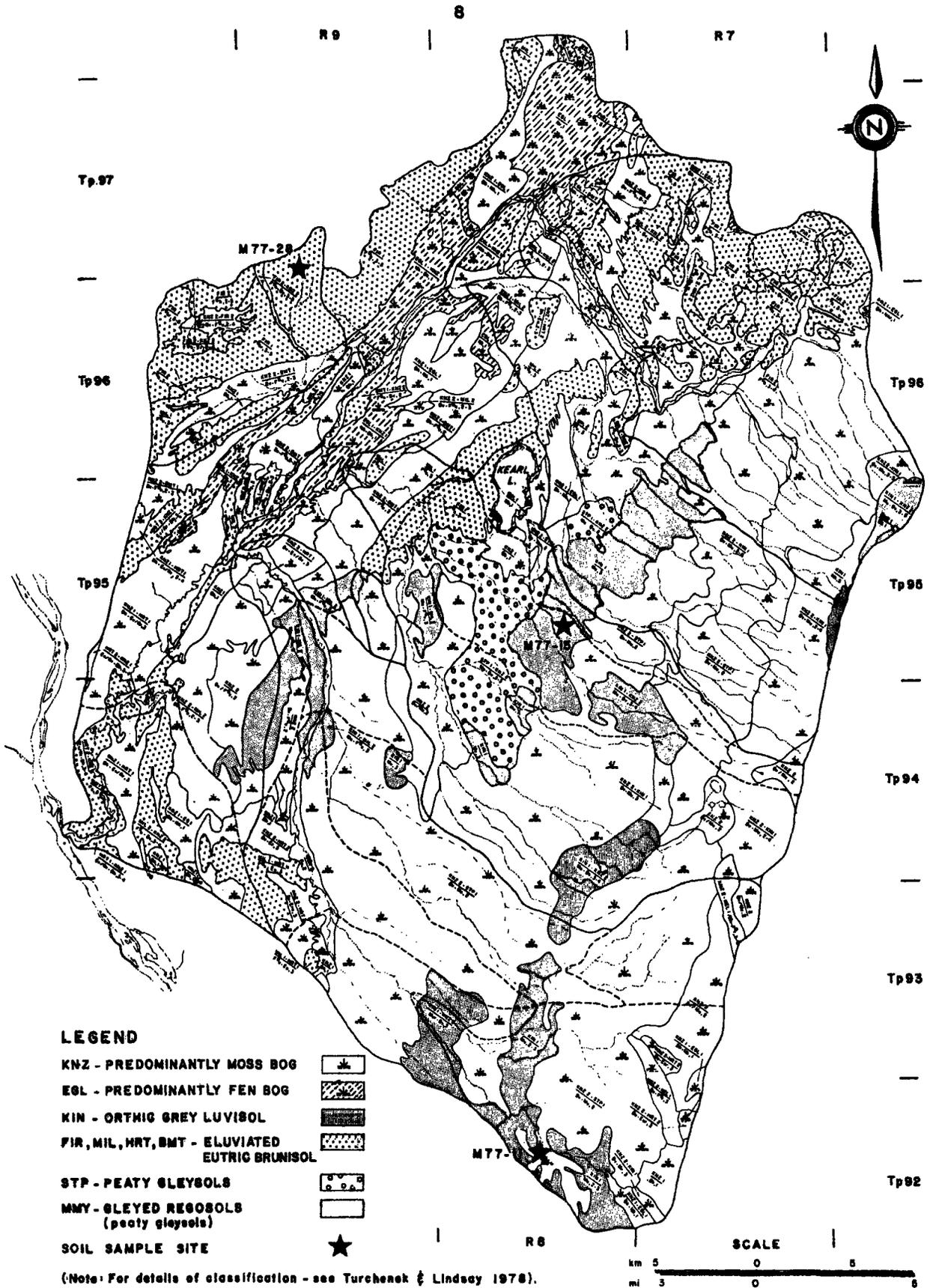
Figure 3. Muskeg River basin: soils (adapted from Turchenek & Lindsay 1978).

Table 1. Sub-basin area and dominant (%) soil classification.

| Sub-Basin | | Bog | | Orthic Grey | Eluviated Eutric | Gleyed | Peaty |
Site #	Area (Km^2)	Moss	Fen	Luvisol	Brumisols	Regosols	Gleysols
1	1520	62	6	11	16	2	3
2	373	80	-	16	3	2	-
2/A	344	81	-	15	2	Small	-
3	290	63	2	17	7	-	11
3/A	68	24	-	-	76	-	-
4	275	54	3	4	35	4	-
5	242	66	1	13	15	Small	4
6	168	75	-	19	3	3	Small
7	209	94	-	Small	-	-	6
8	7	>90	-	10	-	-	-
9	≈162	≈75	-	≈25	-	-	-
10	≈67	53-64	3-6	11-16	4-8	-	-
11	≈57	≈75	-	≈20	≈4	-	-
12	159	≈65	-	5	30	-	-
13/A	108	82	Small	18	Small	-	-
14	40	100	-	-	Small	-	Small

Table 2. Soil types and soil characteristics (Turchenek and Lindsay 1979).

	Soil Classification	Predominant Particles %	pH Ca Cl₂	pH H₂O	Organic Carbon	Total N	C/N	TEC meg/100g	Exchangeable Cation (meg/100gm)				Base Saturate %
									Na	K	Ca	Mg	
N 77-11	(0-4 cm) Slightly to moderately decomposed leaves and needles	-	4.6	5.1	31.67	0.88	36	-	-	-	-	-	-
	(0-6 cm) Light gray, fine sandy loam	21% medium sand 30% fine sand 34% silt	4.0	4.8	0.62	0.02	31	2.8	0.02	0.09	0.9	0.2	43
	(6-15 cm) light yellowish, brown loamy fine sand	15% medium sand 59% fine sand 11% very fine sand 14% silt	4.6	5.4	0.12	0.01	12	2.0	0.04	0.06	0.6	0.2	45
	(15-27 cm) Light yellowish brown fine sand	16% medium sand 57% fine sand 10% very fine sand 12% silt	4.5	5.2	0.14	0.01	14	1.9	0.0	0.5	0.6	0.2	45
	(27-60 cm) yellowish brown sand clay	16% medium sand 21% fine sand 27% silt 12% clay 14% fine clay	5.3	5.6	0.41	0.02	21	9.2	0.05	0.3	7.4	2.4	100
	(60-100 cm) brown, loam	15% medium sand 22% fine sand 32% silt 18% clay	7.0	7.2	-	-	-	6.9	0.06	0.2	5.5	2.3	100
N 77-15	(0-8 cm) Spongy matt mainly of moss composition, with some needles and leaves, permeated with fungal hyphae	-	-	-	-	-	-	-	-	-	-	-	-
	(0-7 cm) Light gray silt loam	10% fine sand 65% silt 10% clay	4.4	5.1	0.45	0.03	15	4.1	0.02	0.1	1.4	0.6	52
	(7-12 cm) Light gray, silt loam	9% fine sand 56% silt 20% clay	4.4	5.0	0.31	0.02	16	4.2	0.3	0.08	1.5	0.8	64
	(12-17 cm) Light grey, clay loam	43% silt 36% clay 11% fine clay	4.5	4.7	-	-	-	10.9	1.0	0.4	4.2	3.3	82
	(17-59 cm) Pale brown, clay	29% silt 54% clay 23% fine clay	4.5	4.7	-	-	-	18.8	0.3	0.5	7.4	6.4	78
	(59-63 cm) Brown, clay loam	12% fine sand 42% silt 30% clay 11% fine clay	4.7	4.5	-	-	-	16.7	0.2	0.4	7.9	6.4	89
	(63-73 cm) Brown, clay loam	15% fine sand 34% silt 31% clay 17% fine clay	5.1	5.4	-	-	-	14.3	0.3	0.3	7.6	5.6	97
	(73-85 cm) brown, loam	13% medium sand 19% fine sand 27% silt 30% clay	6.6	7.0	-	-	-	11.1	0.3	0.2	7.6	5.0	100
N 77-28	(0-2 cm) Slightly to moderately well decomposed needles and lichens	-	4.2	4.5	32.9	0.79	42	-	-	-	-	-	-
	(0-7 cm) Grayish, brown sand	61% medium sand 28% fine sand	4.5	5.3	1.07	0.02	54	3.2	0.02	0.03	0.4	0.2	20
	(7-16 cm) Light yellowish brown, sand	32% fine sand 57% medium sand	4.5	5.2	0.21	0.01	21	1.2	0.02	0.02	0.0	0.05	8
	(16-37 cm) Yellowish brown sand	59% medium sand 31% fine sand	5.0	5.9	0.14	0.01	14	0.9	0.01	0.02	0.0	0.2	26
	(37-55 cm) Brown, sand	53% medium sand 30% fine sand	5.1	6.1	-	-	-	0.5	0.1	0.01	0.0	0.0	22
	(55+ cm) Brown, sand	58% medium sand 35% fine sand	4.9	6.1	-	-	-	0.4	0.02	0.02	0.0	0.5	23

been identified by Kramers and Brown (1976) as the natural sources of heavy metals, such as Pb, Zn, Fe, Al, V, Ni, Co, Cd, Ti, Hf, and Zr, in the Athabasca Oil Sands area. These authors reported that the highest Fe (up to 38%) and Si concentrations occur in coarser size mineral fractions: predominantly, sidevite ($FeCO_3$), pyrite (FeS_2), and quartz (SiO_2); while leucoxene, a mineral carrying mainly iron and titanium, exists in the finer fractions.

Although iron and aluminum are reportedly evenly distributed, predominantly in layer ferric alumino-slicates (e.g., hornblende $Ca(MgFe)_3Si_4O_{12}$ + $NaAlSi_2O_6$), aluminum is found in higher concentrations in the finer size fractions. The manganese concentrations in the heavy minerals were found to be uniform but low (0.06 to 0.77%).

The other minerals identified (Kramers and Brown 1976;Carrigy 1966) include hematite (Fe_2O_3), magnitite (Fe_3O_4), apatite ($Ca_5(PO_4)_3F(or\ Cl)$), and garnet $(Ca,Mg,Fe)_3(Al,Fe)_2(SiO_4)_3$. The majority of these and other heavy minerals found in the Athabasca deposit, reportedly, range from ultrastable to moderately stable with regard to chemical weathering. Other natural heavy metals, specifically vanadium and nickel, occur in the bituminous oil sands.

1.3   WATER CHEMISTRY

Precipitation falling on the Muskeg River basin typically contains small amounts of dissolved gases (e.g., N_2, O_2, CO_2, SO_2, and nitrogen oxides) and airborne particulates. Where rainwater falls through a forest canopy and down vegetation stems during the growing season, the water is generally enriched with potassium, phosphorus, magnesium, and calcium (Likens et al. 1977).

On reaching the ground, water containing dissolved carbon dioxide dissolves available soluble salts (e.g., calcareous materials) and dissolves or reacts with clay minerals and metal sulphides, further modifying the chemical character of the water. Although a part of the cation content of natural water may be derived from non-lithologic sources, the importance of these other sources on cation concentrations in the Muskeg River basin is rather small.

1.3.1 Transformation Processes

The chemical composition and the thickness and texture (affected by plant roots and decaying detritus) of the surficial material influence the rate and the chemical character of the waters perculating through them. For instance, clay minerals with high cation-exchange capacities (e.g., Site M77-15) (Table 2) may exert considerable influence on the proportionate content of different cations carried by the water.

Physical processes involving dissolution of substances and adsorption-desorption interactions with solid surfaces are very important means of regulating chemical constituents in streams. Temperature, turbulence, light, and medium changes also affect water chemistry by shifting chemical equilibria. The change in equilibrium may involve dissolved gas reactions, changes in oxidation states, and/or precipitation reactions.

The magnitude of the change to the ecosystem also depends on biological components utilizing the nutrients (organic carbon, phosphorus, nitrogen, silicon, or sulphur containing compounds) and/or converting them to organics (eg., phenolics),

organometallics (eg., methylmercury), or gaseous
compounds.

1.3.2   Water and Chemical Storage/Movement
        The Muskeg River watershed includes extensive
areas of muskeg (bog, fen, swamp, marsh, etc).
Numerous studies have attempted to understand the water
chemistry of muskegs in Canada (Terasmae 1977; Radforth
1969). Muskeg waters contain significant amounts of
organic substances and debris derived from the
decomposition of leaves and plankton. The effects of
evapotranspiration, organic and inorganic solute
concentrations, and the timing of muskeg drainage on
the water quality of streams draining areas containing
appreciable muskeg may not be easily separated from
those due to shallow groundwater. The muskeg storage
capacity of the Muskeg River basin has not, however,
been determined; as a result, the contribution of
muskeg drainage to streamflow, especially during dry
periods, is not entirely clear.

        As waters descend into the ground, they
become increasingly more mineralized and generally
undergo changes in the relative amounts of different
constituents. These percolating waters may also
deposit some of the dissolved materials in openings in
rocks or soils or may leave them on the surface when
the groundwater is discharged by interflow.

        However, the ultimate disposal of most of the
dissolved material is the removal from the region as
the dissolved load of streams. Thus, this report will
establish areal and seasonal variations in the
concentrations of significant water quality parameters,
relate, where possible, the observed levels to probable
sources (e.g., surficial geology), biological,

processes, and/or significant (adsorption or complexation) interactions.

2.   <u>MAJOR IONS, INDEX VARIABLES, AND DERIVED</u>
        <u>FUNCTIONAL RELATIONSHIPS FOR THE MUSKEG RIVER</u>
        <u>WATERSHED</u>

2.1   INTRODUCTION

    This discussion of the major ion chemistry
emphasizes the temporal and areal variations of the
concentrations of major ions (Na^+, Ca^{+2}, Mg^{+2}, Cl^-,
SO_4^{2-}, and HCO_3^-) and the specific conductances of the
waters of the Muskeg River watershed; and, where
possible, functional interparameter relationships.

    Except for some of the water quality data
collected from the Muskeg River, Sites 1 and 7/A, it
was assumed that all chemical quality characteristics
and variations at all sites are due to natural causes.
The Shell (Canada) Ltd. Pit, located approximately
10 km upstream from Site 1, inevitably contributed
considerable loadings of chemical constituents during
pit pumping events. These and other aspects of water
pollution will be considered when discussing parameters
affected by Shell Pit pumpings.

2.2   BACKGROUND

    Most of the calcareous rocks and alluvial or
glacial deposits of this region are high in major
anions and calcium but low in magnesium. Information
(Table 2) (Turchenek and Lindsay, 1979) on soil
analysis for samples obtained from sites (Figure 3)
within the Muskeg River basin gave Ca:Mg concentration
ratios ranging from 1.5:1 to 4.5:1. The relatively
high Ca:Mg ratios in the rocks are reflected to some
degree in the Ca:Mg ratios in the soil, and surface and
groundwater.

    The possibilty exists for calcium and
magnesium ions, derived from the solution of limestone,

to exchange for sodium or potassium ions that are
loosely held in clay minerals.

Potassium appears, however, to be liberated
with greater difficulty from silicate minerals and
exhibits a strong tendency to be re-incorporated into
solid weathering products, especially clay minerals.
This observation is supported by the fact that the
concentrations of exchangeable potassium in the soil
materials collected from Sites M77-11 and M77-28 (Site
M77-15 has no definite order) are equal to or higher
than those of sodium, while the concentrations of
sodium are always much greater than those of potassium
in surface waters of the Muskeg River watershed.

Because seasonal variations in the surface
water potassium concentrations appear to be closely
related to biological activity, detailed discussions
will be carried out in Section 3.4.2.2

2.3   METHODS AND SOURCES OF DATA
           See Appendices 7.3 and 7.5 and Table 18.

2.3.1   Procedure for Loadings Calculations
           The following procedure was used in
estimating the annual loadings through Sites 1, 2, and
4.

           A regression analysis was performed, using a
double log scale, on the data for major ion
concentrations and stream discharges.   In the case of
Site 1, the data collected during Shell Pit pumping
periods were excluded during the regression analysis.

           Each parameter was correlated against stream
discharge and each relationship checked for
significance. Magnesium, calcium, chloride, sodium,
and bicarbonate ions concentrations gave significant
relationships with streamflow, while total organic
carbon (TOC) and sulphate did not.   Where the

relationship was significant, a value for flow, which
was used in the construction of unit flow-duration
curve (Froelich in prep.), was used to predict the
concentration. The flow was then multiplied by the
corresponding predicted concentration to give the daily
load. These daily loads were plotted (ROSCOE program
WQNB P001) against the frequency (number of days) of
occurrance of the daily loadings to obtain annual unit
loadings.

Unfortunately, because of insufficient data,
the loading duration method could be used only for data
for Site 1 (1976, 1977, and 1978), Site 2 (1976, 1977,
and 1978), and Site 4 (1977). Annual unit loadings (in
kg/ha/yr) of each ion for each sub-basin were
determined by dividing the annual load by the sub-basin
area (in hectares).

Loadings from Shell Pit pumpages were also
estimated using the ROSCOE program WQNB P002 on
available records of the Shell Pit pumping period. The
average discharge rate was multiplied by the ionic
concentrations of the effluent and integrated over time
to obtain an estimate of loadings (in kilograms).

2.4   RESULTS AND DISCUSSION

2.4.1   Variations in the Concentrations of Major
         Ions

2.4.1.1 Calcium. Figure 4 shows plots of the
concentrations of calcium verses time at Sites 1 and 2.
In both cases, the calcium concentrations display
distinct seasonal patterns; similar patterns exist for
other sites (Figure 5). In a few cases, exact or
similar values were observed the following year during
the same season. For example, the highest calcium
value recorded at Site 2 was 91.0 mg/L (7 March 1977),
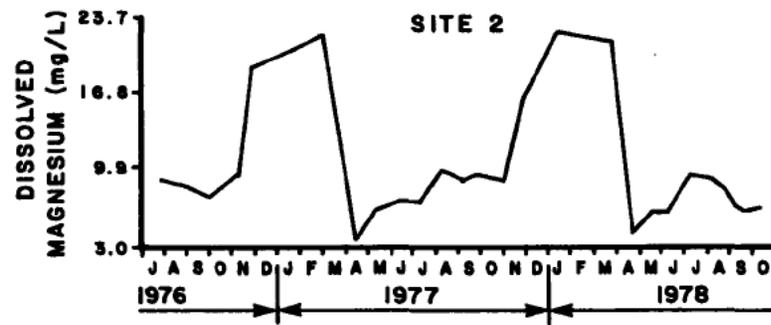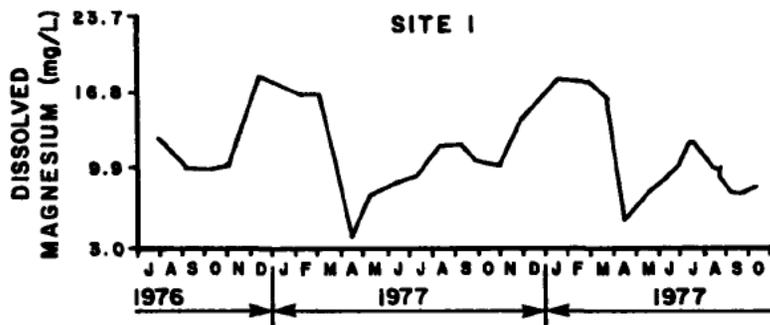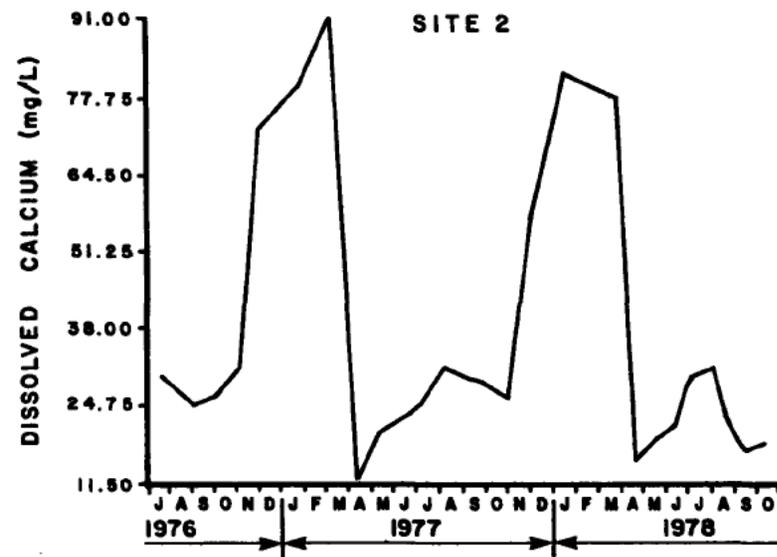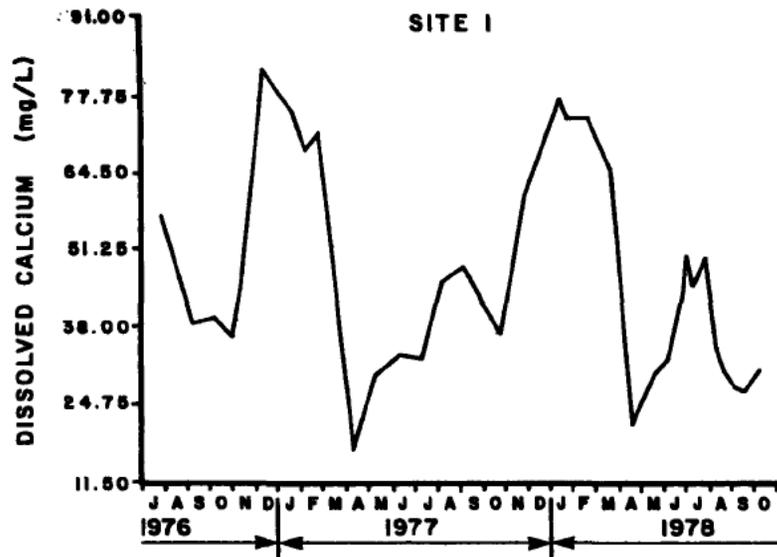
Figure 4. Variations in dissolved calcium and magnesium concentrations (Sites I and 2).

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Ca^{++} (mg/L)

4-29 OCTOBER 1976

24-26 JANUARY 1977

18-28 APRIL 1977

13-20 JULY 1977
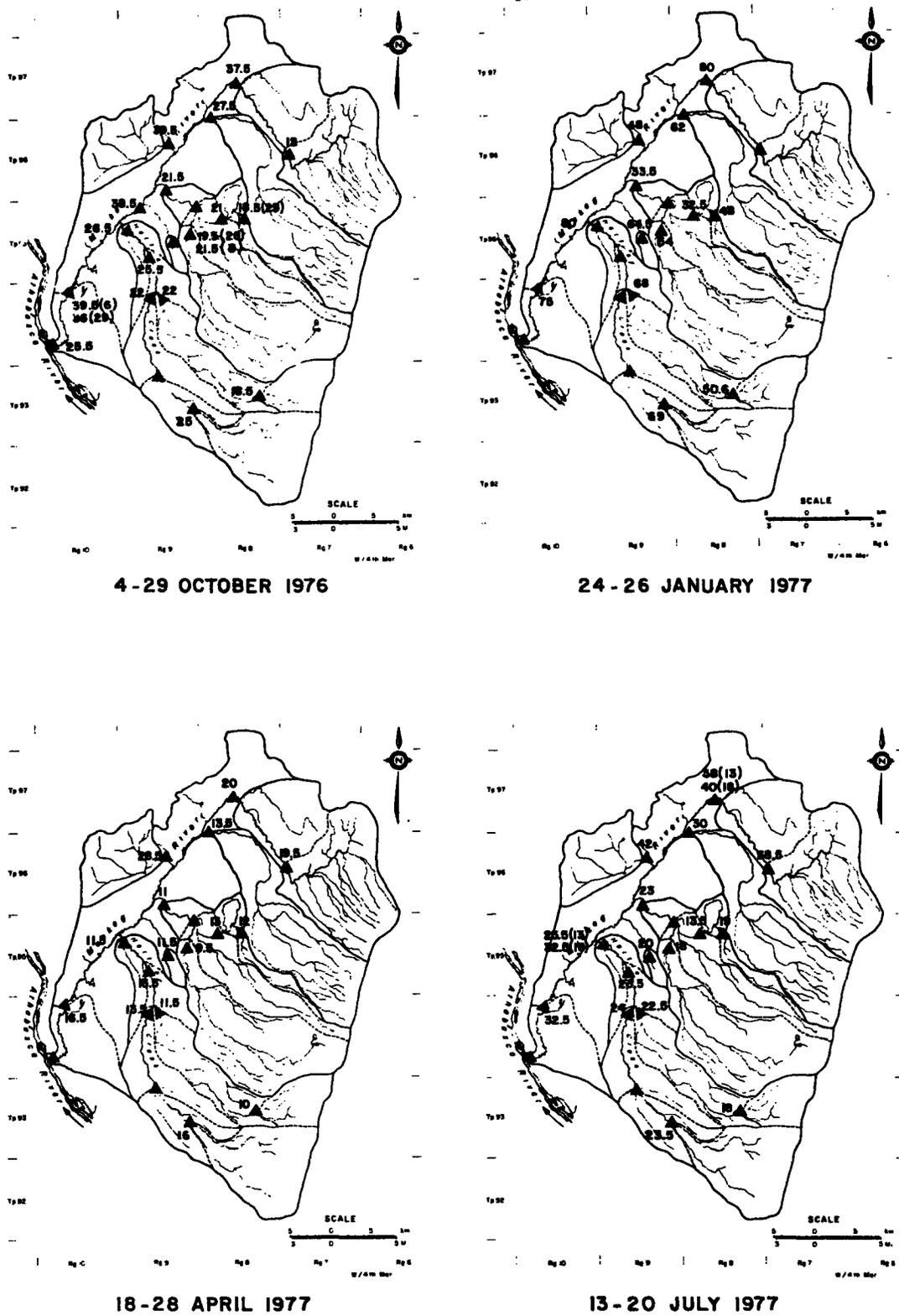
Figure 5. Areal variations in calcium concentrations.

and the next highest values, 82.5 mg/L and 80.0 mg/L,
were observed on 24 January 1978 and 26 January 1977,
respectively. Between 1976 and 1978, there also
appears to emerge a midsummer seasonal level of
approximately 30 mg/L as demonstrated by the analyses:
30.0 mg/L (27 July 1976), 25.5 mg/L (13 July 1977),
32.0 mg/L (16 August 1977), and 30.0 mg/L (20 July
1978).

Most sites observed sharp drops in the
concentrations of calcium during September and October
1976 in response to a series of rainstorms. Minimum
calcium concentrations observed during the study ranged
between 10 and 20 mg/L at all sites, except Sites 3/A
and 7/A where the minima ranged between 20 and 30 mg/L.

The maximum values of calcium ranged from 32
to 36 mg/L at Sites 6 and 10, 40 to 60 mg/L at Sites
3/A, 3, 9, 11, and 12, and 60 to 95 mg/L at Sites 1, 2,
2/A, 4, 5, 7, 8, 13/A, and 14. A value of 160 mg/L was
recorded at Site 7/A on 25 February 1977, and another
high value (144.0 mg/L, 4 March 1977) was observed at
Site 12.

The mean daily loadings, determined from
yearly loadings of calcium during the study period,
were 6550 kg (1976), 7230 kg (1977), and 13 115 kg
(1978) for Site 1; the corresponding values at Site 2
were 1445 kg (1976), 1294 kg (1977), and 2564 kg
(1978). The mean daily loading similarily obtained for
Site 4 in 1977 was 1478 kg of calcium.

2.4.1.2   Magnesium. The concentrations of magnesium
at most sites, including Sites 1 and 2, (Figures 4 and
6) showed the same seasonal pattern observed for
calcium.

The minimum magnesium concentrations at all
sites, except Sites 3/A, 4, 7/A, and 12, ranged between

21

Mg^{++}(mg/L)
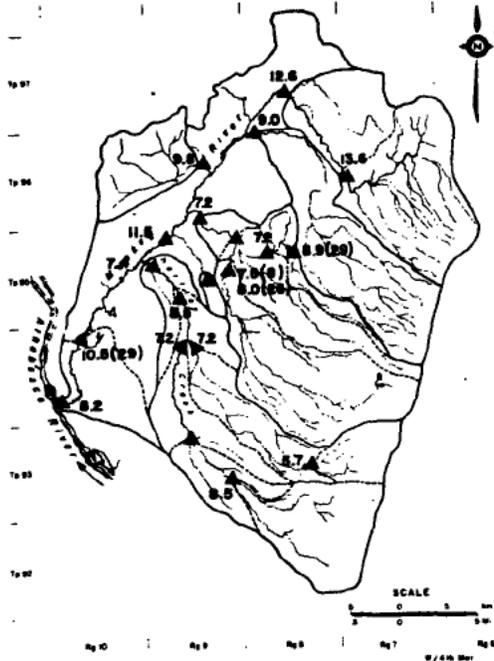
4-29 OCTOBER 1976
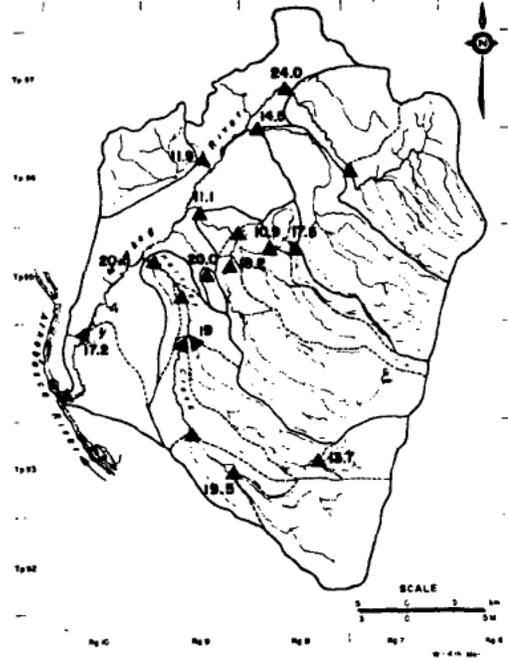
24-26 JANUARY 1977
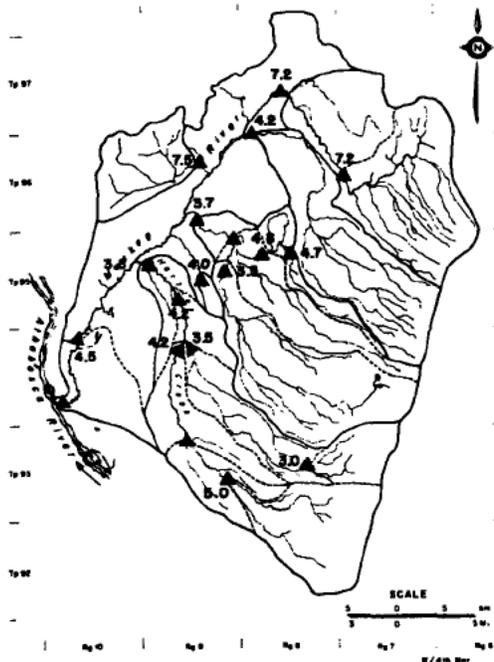
18-28 APRIL 1977
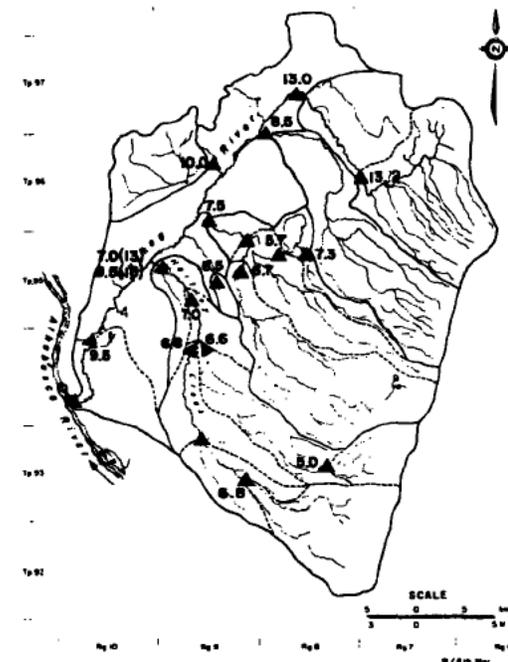
13-20 JULY 1977

Figure 6. Areal variations in magnesium concentrations.

3.0 and 5.0 mg/L; the range at Sites 3/A, 4, 7/A, and 12 fell between 5.0 and 10.0 mg/L.

The maximum values ranged between 13.0 and 20.0 mg/L at Sites 1, 2/A, 3, 3/A, 5, 7, 9, 10, 11, 12, 13/A, and 14, and between 20.0 and 26.5 mg/L at Sites 2, 4, and 8. Two unusually high values were recorded at the Muskeg River, Site 7/A (58.0 mg/L) on 25 February 1977 and Site 12 (72.0 mg/L) on 4 March 1977.

Except for sharp drops associated with spring runoffs, the magnesium concentrations at Site 4 generally remained at relatively high levels throughout the open water season. The only interruption in the seasonal pattern was caused by a series of autumn 1976 precipitation events. Site 4 is located within a muskeg area and the lack of significant change in the calcium and magnesium concentrations could be a reflection of stable major ion chemistries in muskeg areas.

The mean daily loadings of magnesium, similarily determined, were 1754 kg (1976), 1933 kg (1977), and 3701 kg (1978) for Site 1; 431 kg (1976), 384 kg (1977), and 778 kg (1978) for Site 2; and 487 kg (1977) for Site 4.

2.4.1.3. Bicarbonate. Bicarbonate concentrations exhibited areal (Figure 7) and seasonal patterns parallel to those of calcium. Generally, the lowest values were observed during spring runoffs, moderate values during spring, summer, and fall, and high (300 to 500 mg/L) to very high (>800 mg/L) values during baseflow periods. In most cases, there were strong seasonal differences between baseflow and open water seasons.

As was the case with calcium and magnesium, the seasonal pattern described above was also slightly

23

HCO$_3^-$(mg/L)

4-29 OCTOBER 1976

24-26 JANUARY 1977

18-28 APRIL 1977

13-20 JULY 1977
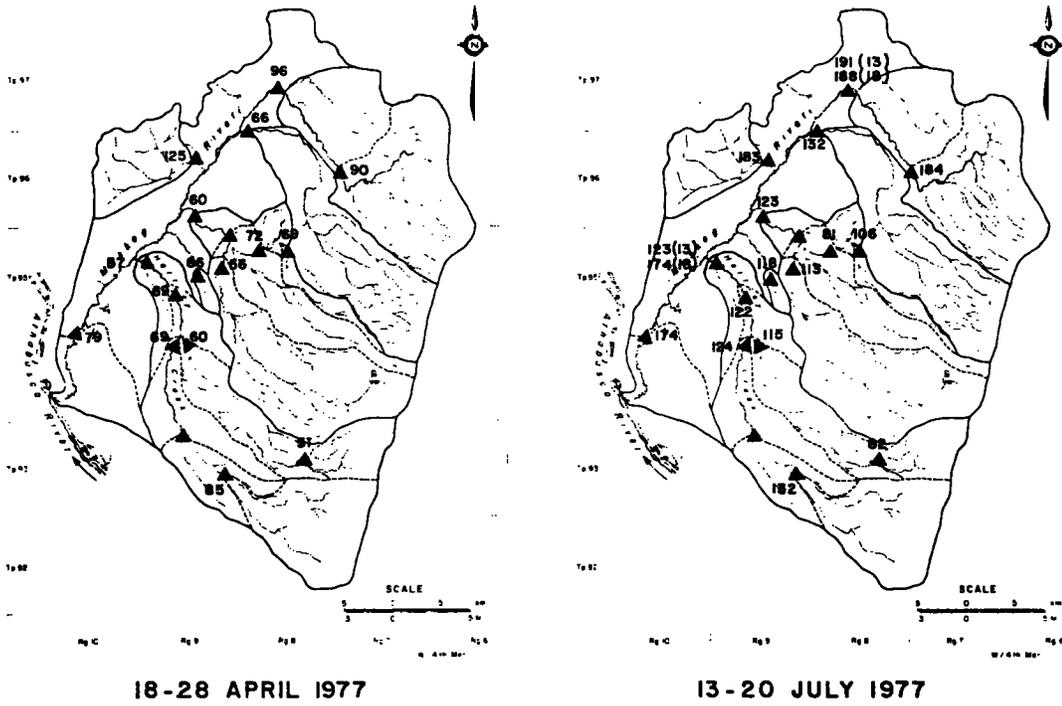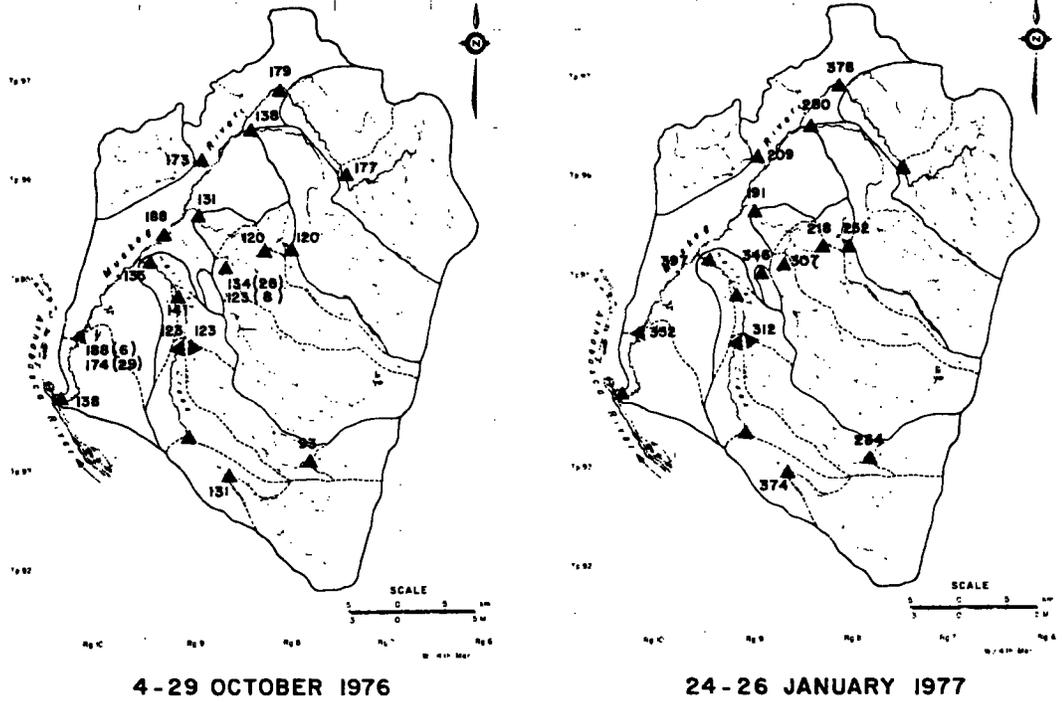
Figure 7. Areal variations in bicarbonate concentrations.

modified by the autumn 1976 rainstorms and exaggerated by contributions of groundwater, specifically groundwater of the Ca-Mg/HCO_3-SiO_2 type (see Section 2.4.2.2) at Site 12 (HCO_3^-, 878 mg/L) on 4 March 1977.

The minimum values at Sites 2, 2/A, 3, 5, 6, 7, 9, 11, and 14 ranged between 50 and 70 mg/L and between 70 and 96 mg/L at Sites 1, 4, 8, 10, 12, and 13/A. Moderately higher concentrations were observed at the mouth of the Muskeg River, Site 7/A (138 mg/L), and Stanley Creek, Site 3/A (125 mg/L), during spring runoffs.

Maximum values in the concentration of bicarbonate ranged between 300 and 400 mg/L at Sites 1, 2/A, 4, 5, 7, 7/A, 8, 9, and 11, 13/A, and between 200 and 300 mg/L at Sites 3/A, 3, 10, and 14. The maxima at Sites 2, 6, and 12 were 424, 164, and 878 mg/L, respectively.

As was the case with calcium, the seasonal patterns for bicarbonate appeared relatively constant between years at certain sites. For instance, at Site 2, the maximum value of 424 mg/L observed on 7 March 1977 compares closely with the 395 mg/L observed on 6 April 1978. Similarily, at Site 1, values of 352 mg/L (16 December 1976) and, two years later, 351 mg/L (7 Feburary 1978) were observed.

The mean daily loadings of bicarbonate during the study period were 4425 kg (1976), 7719 kg (1977), and 12 104 kg (1978) at Site 1; 7564 kg (1976), 6743 kg (1977), and 13 443 kg (1978) at Site 2; and 7188 kg (1977) at Site 4.

2.4.1.4   Sulphate. The range and seasonal variations (Figure 8) in the concentrations of sulphate observed in this study did not show a discernable pattern.

$SO_4^=$ (mg/L)

4-29 OCTOBER 1976

24-26 JANUARY 1977

18-28 APRIL 1977

13-20 JULY 1977
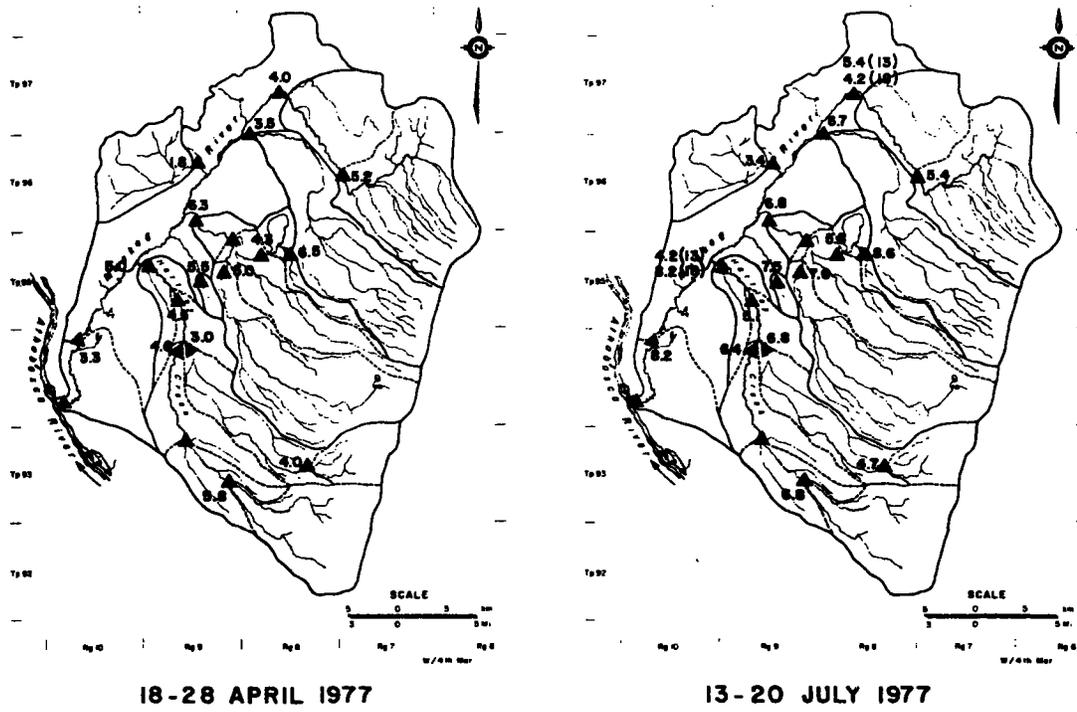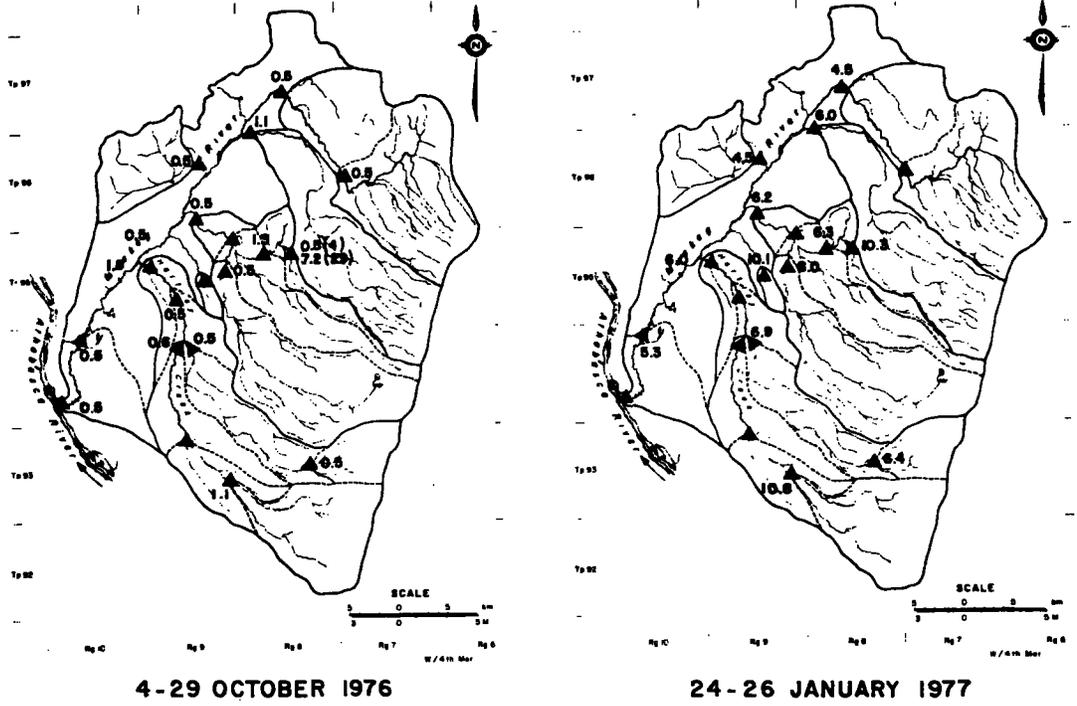
Figure 8. Areal variations in sulphate concentrations.

Sulphur can occur in stream waters in any of the following forms: sulphate (SO_4^{2-}), sulphite (SO_3^{2-}), sulphide (S^{2-}), hydrogen sulphide (HS^-), and gaseous di-hydrogen sulphide (H_2S). The conversion of oxidized to reduced species or vice-versa is generally slow and often associated with biochemical processes. Intermediate products [specifically, pyrite (FeS_2), elemental sulphur, and poly-sulphides species] in the oxidation of sulphide have been observed (Cloke 1963).

Hem (1977) reported that most sulphide-bearing groundwater, especially some of the brines associated with petroleum, may contain several hundred milligrams of dissolved hydrogen sulphide per litre. In these waters, the process of anaerobic sulphate reduction reportedly required the presence of a certain species of bacteria and organic matters. For instance,

$$SO_4^{2-} + CH_4 \longrightarrow HS^- + HCO_3^- + H_2O + energy$$
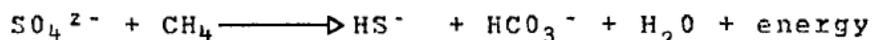
Another method by which dissolved sulphate concentration in water samples could be lowered is by the formation of insoluble ion pairs (e.g., $CaSO_4$ or $BaSO_4$) or metal complexes.

It is reasonable to believe that the combined effect of these processes was responsible for the variable sulphate concentrations observed in this study.

2.4.1.5 Sodium_and_Chloride. Except where the sodium and chloride levels were influenced by Shell Pit pumpages, these two ions appear to exhibit seasonal patterns similar to calcium and bicarbonate ions. Of all the major ions considered so far, Na and Cl experienced, proportionally, the largest drops in concentration as a result of the September and October 1976 precipitation events. Figures 9 and 10 show areal

Na$^+$(mg/L)
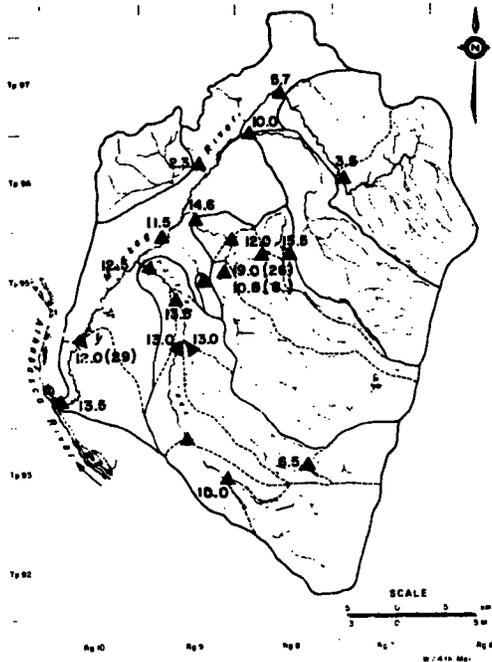
4-29 OCTOBER 1976
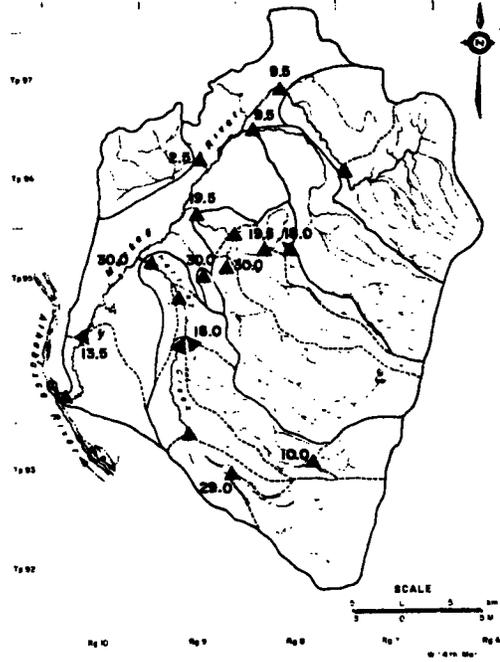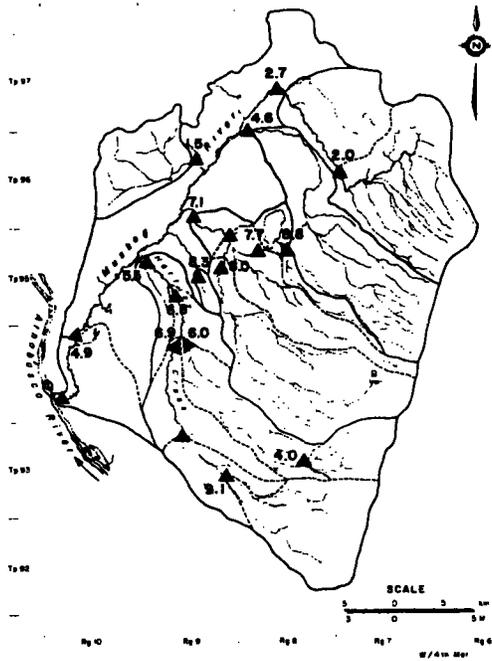
24-26 JANUARY 1977
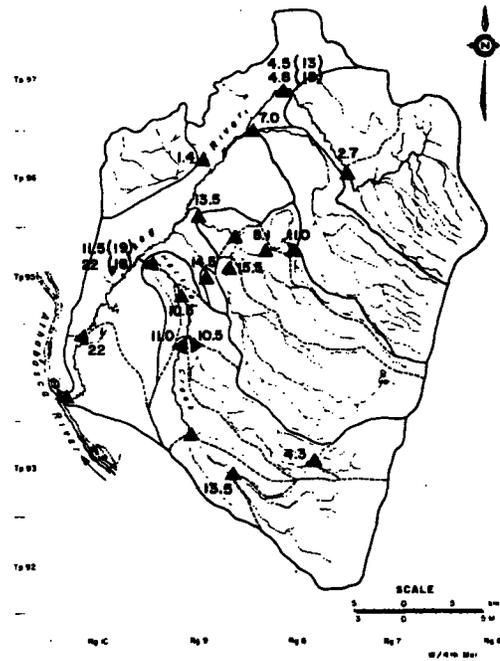
18-28 APRIL 1977

13-20 JULY 1977

Figure 9. Areal variations in sodium concentrations.

28

Cl⁻ (mg/L)
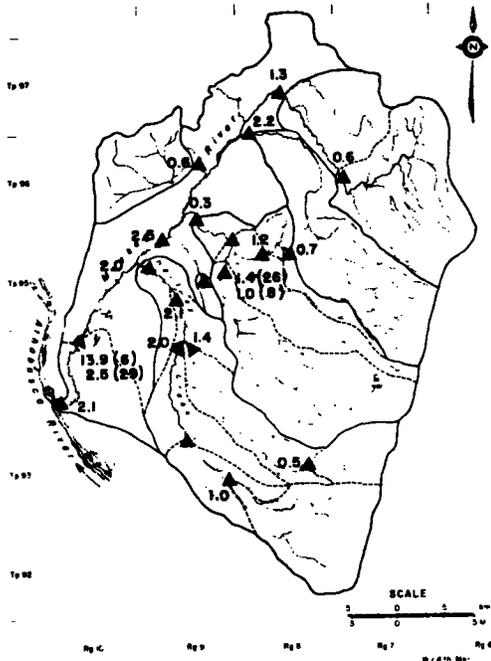
4-29 OCTOBER 1976
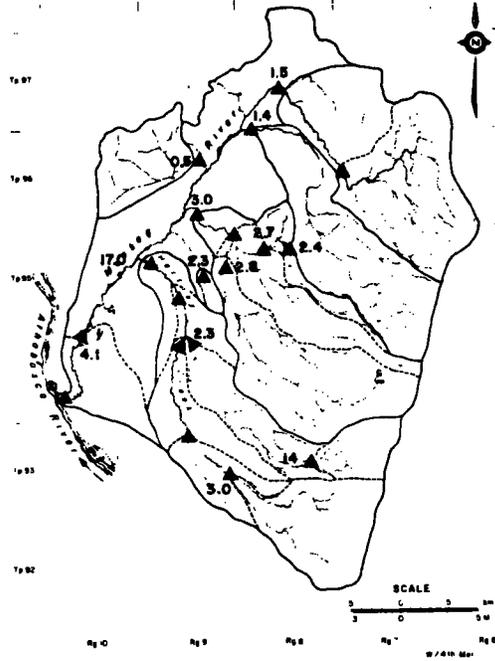
24-26 JANUARY 1977
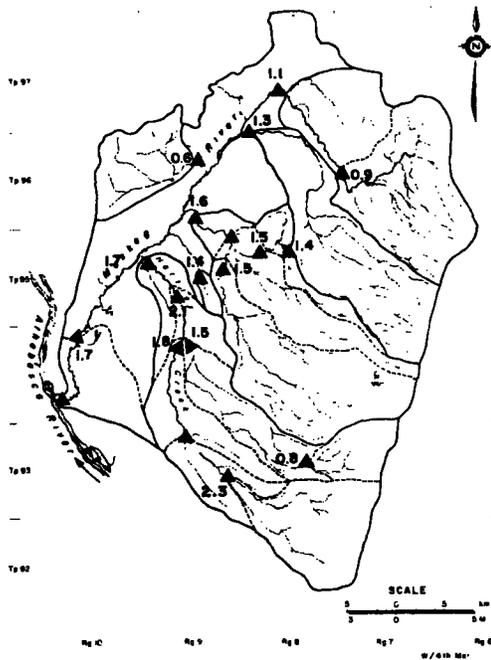
18-28 APRIL 1977
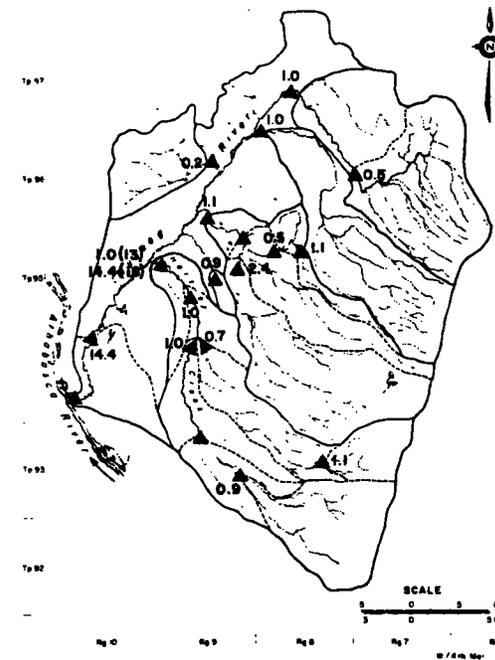
13-20 JULY 1977

Figure 10. Areal variations in chloride concentrations.

and (some) seasonal variations in the concentrations of sodium and chloride.

The minimum values of sodium concentration ranged from 1.5 to 4.9 mg/L at Sites 1, 3/A, 4, 5, 12, and 14. The range at Hartley Creek, Sites 2, 2/A, 6, and 7, was 5.5 to 6.9 mg/L; while the minima at Sites 3, 7/A, 8, 9, 10, 11, and 13/A varied between 7.1 and 9.1 mg/L.

The lowest minima for chloride, ranging between 0.1 and 0.6 mg/L, were observed at Sites 3/A, 3, 5, 7, 8, 10, 12, and 14. The next lowest set, ranging between 0.7 and 1.0 mg/L, occurred at Sites 2, 2/A, 4, 6, 9, 11, and 13/A. Even without the Shell Pit pumpages, the lower Muskeg River, Sites 1 and 7/A, showed the highest minima, at 1.6 and 2.1 mg/L, respectively.

The maximum values of sodium and chloride concentrations were found to be greatly influenced by Shell Pit pumpages (at Sites 1 and 7/A) and ground-water contributions. The natural maximum sodium concentrations at Sites 3/A and 12 were only 2.5 and 8.5 mg/L, respectively; while the natural (disregarding data collected at Sites 7/A and 1 during Shell Pit pumping periods) maxima at Sites 1, 4, 5, 6, 7, 11, and 14 ranged between 12.0 and 20.0 mg/L; and those at Sites 2, 8, 9, 10, 11, and 13/A ranged between 29.0 and 30.5 mg/L. Sites 2/A and 3 both reported maxima of 24.0 mg/L; while the highest value, 50.0 mg/L, was recorded at Site 7/A on 25 February 1977.

The natural maximum concentrations of chloride at Sites 3/A, 5, 6, 7, 12, and 14 ranged between 1.0 and 3.5 mg/L, and between 5.0 and 9.2 mg/L at Sites 1, 2/A, 3, 4, 8, 9, 10, 11, and 13/A. The highest natural maxima were recorded at Sites 7/A (20.2

mg/L, 25 February 1977) and 2 (17.0 mg/L, 26 January 1977 and 6 April 1978).

When the Shell Pit pumping dates (Table 3) were included, the effluent discharges raised the sodium concentrations at Site 1 to 22.7 mg/L (6 October 1976), 22.0 mg/L (18 July 1977), 38.5 mg/L (13 September 1977), and 18.7 mg/L (21 June 1978). The chloride concentrations for these same dates were 13.9, 14.4, 29.7, and 9.4 mg/L, respectively. The only data available for Site 7/A (27 September 1976) gave 26.5 mg/L for sodium and 18.1 mg/L for chloride.

2.4.2 Specific Conductance

2.4.2.1 Introduction. Generally, the relationship between the specific conductance and the total dissolved substances appears to remain constant only when the water is dominated by a strong electrolyte in relatively high concentrations. For most natural waters, where the chemical composition is likely to change drastically, the value of specific conductance serves only as an approximate index (of the amount of total dissolve solids, calcium, chloride, etc.) for that body of water. As shown in Sections 2.4.1.5 and 2.4.2.2 and Figure 12, the relationship between concentration and specific conductance can be influenced by the composition and concentration of run-off waters, groundwaters, and industrial effluents.

2.4.2.2 Seasonal and Areal Variations. During spring runoffs, the stream waters in this drainage basin have characteristics of surface flows, generally low in total dissolved solids. But the specific conductances and chemical data showed drastic increases during baseflows, especially at Sites 2, 4, 7, 8, and 13/A (Figure 11).

Table 3. Shell pit pumpage analyses (at the settling pond).

| Parameters	Codes	26 July 1976	9 Sept. 1976	30 Sept. 1976	14 Oct. 1976	29 June 1977	14 Sept. 1977	21 June 1978	Units
Calcium	20103L	12.0	28.5	37.0	39.0	27.5	57.5	10.000	mg/L
Magnesium	12102L	42.0	32.5	34.0	35.0	33.5	32.5	35.00	mg/L
Sodium	11102L	410.0	500.0	860.0	730.0	500.0	900.0	785.00	mg/L
Potassium	19102L	13.5	14.5	15.0	14.0	18.2	23.80	11.00	mg/L
Chloride	17203L	380.0	460.0	825.0	710.0	430.0	805.0	750.00	mg/L
Sulphate	16306L	71.0	57.4	58.0	86.0	73.0	65.0	70.00	mg/L
Total Alkalinity	10101L	418.0	620.0	875.0	850.0	589.6	980.4	948.0	mg/L
PH	10301L	8.2	8.0	7.9	8.0	8.0	7.64	7.67	Units
Carbonate	06301L	0.0	0.0	0.0	0.0	0.0	0.0	0.0	mg/L
Bicarbonate	06201L	509.5	755.8	1066.6	1036.2	718.7	1195.1	1156.0	mg/L
Total Hardness	10603L	302.9	205.0	232.4	241.5	206.6	277.4	169.0	mg/L
Fluoride	09105L	0.72	0.58	1.80	1.00	0.82	1.25	1.02	mg/L
Silica	14101L	7.5	6.6	6.7	7.0	5.2	6.0	5.80	mg/L
Conductance	20401L	2200.	2950.	4200.	3700.	2720.	3790.	3900.0	µm/cm
Threshold Odor #	02001L	8.	4.	64.	4.	32.	64.	128.	Units
Color	02011L	10.	10.	<5.	<5.	<5.	<5.	<5.	Units
Tannin & Lignin	06551L	0.02	<0.2	0.40	0.70	0.3	0.9	<0.1	mg/L
Total Filt. Residue	10451L	1752.	1505.	2465.	2105.	1640.	2550.	2574.	mg/L
Total Filt. Residue Fixed	10551L	1264.	1390.	2175.	1875.	1394.	2260.	2477.	mg/L
Total Non-Filt. Residue	10401L	12.4	23.2	24.0	38.0	14.4	19.0	6.8	mg/L
Total Non-Filt. Residue Fixed	10501L	6.8	18.0	18.0	26.4	6.0	11.6	<0.4	mg/L
Turbidity	02073L	20.0	-	-	-	10.3	6.05	9.1	Units
Surfacants	10701L	0.21	0.20	0.10	0.07	0.135	0.69	0.52	mg/L
Humic Acids	06581L	<2.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	mg/L
Total Organic Carbon	06001L	20.	32.	50.	40.	17.	45.	22.0	mg/L
Total Inorganic Carbon	06051L	150.	120.	250.	220.	59.	205.	173.5	mg/L
Nitrate + Nitrite Nitrogen	07110L	0.01	<0.01	<0.01	<0.01	0.013	0.007	0.010	mg/L
Ammonia Nitrogen	13302L	0.19	0.94	2.20	1.80	0.39	1.85	2.450	mg/L
Total Kjeldahl Nitrogen	07013L	1.40	5.50	4.85	2.68	0.80	2.63	2.31	mg/L
Total Phosphorous	15406L	<0.005	0.02	0.05	0.06	0.021	0.049	0.042	mg/L
Ortho Phosphorous	15256L	<0.005	<0.01	0.03	0.02	0.006	0.039	0.037	mg/L
Phenol	06532L	0.004	<0.001	<0.001	0.020	<0.001	-	<0.001	mg/L
Oil & Grease	06521L	2.8	3.0	1.0	1.70	2.9	-	0.6	mg/L
Sulphide	16101L	<0.05	<0.05	<0.05	<0.05	-	-	5.96	mg/L
Cyanide	06601L	<0.01	<0.01	<0.01	<0.01	-	-	0.001	mg/L
Chemical Oxygen Demand	08301L	36.6	111.0	59.8	234.	121.	124.	128.	mg/L
Cadmium	48302L	<0.001	<0.001	0.004	0.003	0.001	<0.001	<0.001	mg/L
Hexavalent Chromium	24101L	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	0.003	mg/L
Copper	29306L	0.002	0.004	0.010	0.012	0.002	0.005	<0.001	mg/L
Iron	26304L	0.41	1.15	0.45	0.85	0.11	0.45	0.330	mg/L
Lead	82302L	0.008	0.012	0.031	0.031	<0.002	<0.002	<0.002	mg/L
Manganese	25304L	0.04	0.162	0.193	0.238	0.043	0.135	0.360	mg/L
Silver	47301L	<0.005	0.015	<0.005	0.005	<0.001	<0.001	<0.001	mg/L
Zinc	30304L	<0.001	0.009	0.001	0.008	0.001	0.012	0.001	mg/L
Vanadium	23301L	<0.01	<0.001	0.001	0.002	<0.001	<0.001	<0.001	mg/L
Selenium	34302L	0.0027	<0.0005	<0.0005	<0.0005	0.0008	0.0005	<0.0002	mg/L
Mercury	80011L	<0.0002	<0.0002	<0.0002	<0.0002	<0.0001	<0.001	0.0002	mg/L
Arsenic	33004L	<0.005	0.010	0.010	0.005	0.0012	0.0007	0.0004	mg/L
Nickel	28302L	0.011	0.018	<0.002	0.013	0.006	0.005	0.005	mg/L
Aluminum	13302L	0.20	0.36	0.38	0.50	0.06	0.33	0.14	mg/L
Cobalt	27302L	0.006	0.013	0.011	0.007	<0.002	0.004	0.004	mg/L
Boron	05105L	0.92	0.95	0.20	0.88	1.42	2.1	1.50	mg/L
Chlorophyll A	06711L	-	<0.001	<0.001	<0.001	<0.001	-	-	mg/L
Titanium	92500L	-	-	-	-	-	-	0.15	mg/L

32
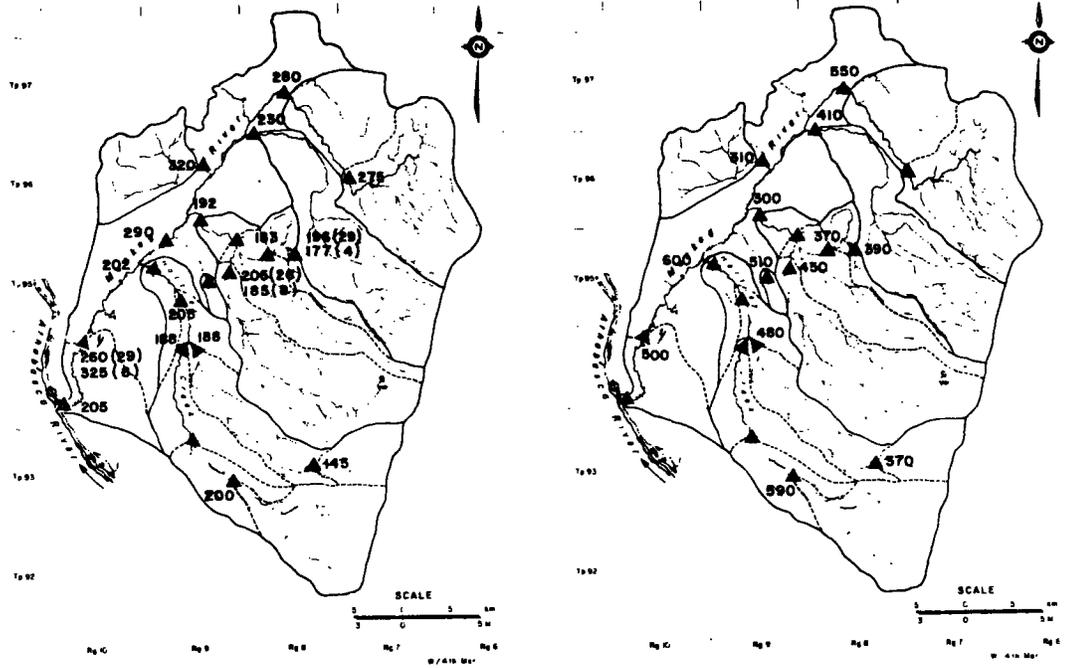
4-29 OCTOBER 1976

24-26 JANUARY 1977
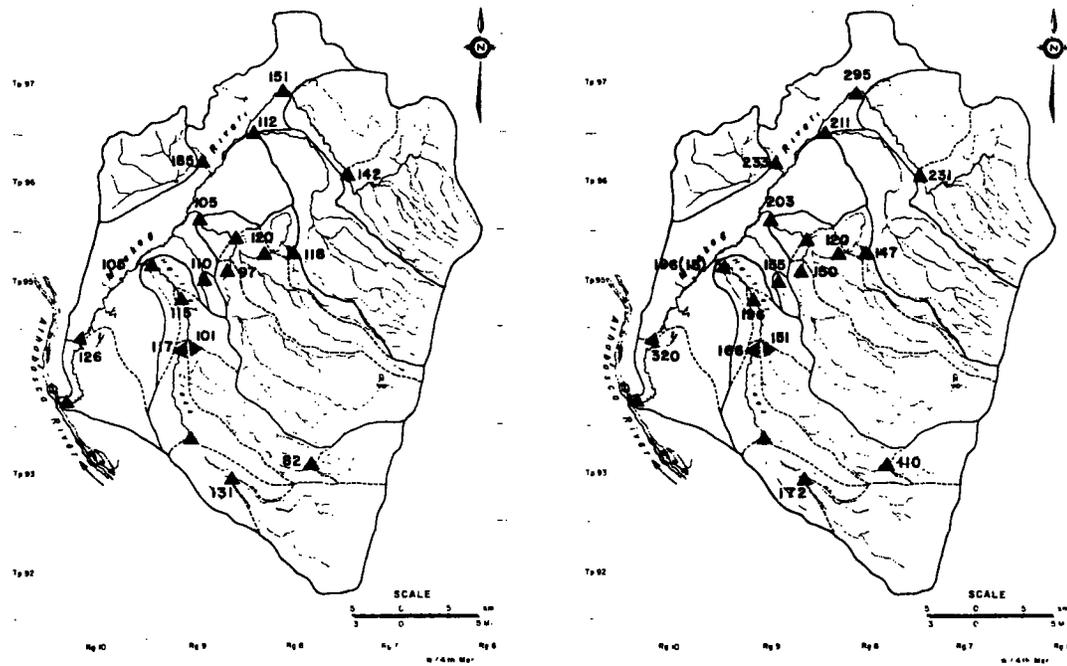
18-28 APRIL 1977

13-20 JULY 1977

Figure II.   Areal variations in specific conductance (μ S/cm).

The specific conductance values recorded in the Muskeg River basin showed maxima ranging between 250 and 1360 μS/cm and minima ranging between 82 and 290 μS/cm. The wide ranges indicate the extremely large variations in the dissolved solids contents. Two sites along the Muskeg River, Sites 7/A (25 February 1977) and 12 (4 March 1977), had exceptionally high conductance values (1360 and 1200 μS/cm, respectively) during late winter 1977. Without these two high values, the specific conductance maxima only varied from 250 to 660 μS/cm, and the range in mean values varied from 184 to 380 μS/cm.

Griffiths (1973) reported that, except for two sites on the Christina River, the specific conductances of other streams and rivers in the AOSERP study area generally ranged from 27 to 550 μS/cm. The similarity between the Muskeg River basin results and the levels observed by Griffiths suggests that similar levels of controlling constituents may occur during baseflow.

The highest specific conductance reading (1360 μS/cm) during the study was recorded at Site 7/A, at the mouth to the Muskeg River. The concentrations of major ions, Ca^{+2} (160.0 mg/L), Mg^{+2} (58.0 mg/L), Na^+ (50.0 mg/L), HCO_3^- (963 mg/L), Cl^- (20.2 mg/L), and SO_4^{2-} (10.9 mg/L), analysed from the same sample, suggest groundwater inflows of the $Ca-Mg-Na/HCO_3$ type. In addition to the major ions, the concentrations of reactive silica, total Kjeldahl nitrogen, oil and grease, total and dissolved organic carbon, and certain heavy metals [Cr(+6), Cd, Cu, Fe, Pb, Mn, Zn, Hg, Ni, and B] were also found to be higher than values observed during open water seasons. The high value recorded at Site 12 occurred with a different distribution of dissolved substances; Ca^{+2} (144.0

mg/L), Mg^{+2} (72.0 mg/L), Na^+ (8.5 mg/L), Cl^- (2.0
mg/L), HCO_3^- (878 mg/L), SiO_2 (72.0 mg/L) and SO_4^{2-}
(8.5 mg/L); and except for Cr(+6), Cu, Mn, As, and Ni,
were the only other parameters that appeared to be
moderately higher. The major ion concentrations
suggest contributions from groundwater of the
$Ca-Mg/HCO_3-SiO_2$ type.

2.5   FUNCTIONAL RELATIONSHIPS

2.5.1   Introduction

The present study examined the relationships
between sites; and between the concentrations (C_i) of
the major inorganic solutes (Ca^{+2}, Mg^{+2}, Na^+, HCO_3^-,
SO_4^{2-}, Cl^-, and total dissolved solids), at sites
within the basin, and appropriate independent variables
[e.g., specific conductance (K_{sc}), stream discharge
(Q), or both], where relatively stable regression
relationships exist.

2.5.2   Longitudinal Relationships in Major Ion
            Concentrations

The specific conductances or concentrations
of major ions at certain sites were plotted against the
specific conductances or concentrations of the same ion
at a reference site, for samples collected at or on
approximately the same date. These plots showed
significant correlations. Site 1 (samples known to be
affected by Shell Pit pumpages were excluded) was used
as a reference focal point for drainages through Sites
2, 3, 4, and 5. Schwartz (1979) has already reported
similar plots using Site 2 as a reference point for
Sites 6, 7, 13/A, and 14.

In most cases (Figures 12 and 13), the
correlations gave smooth linear plots. There were,
however, some tendencies (eg. Ca^{+2}, HCO_3^-, and specific
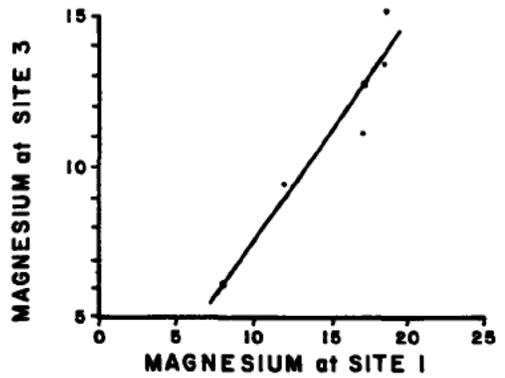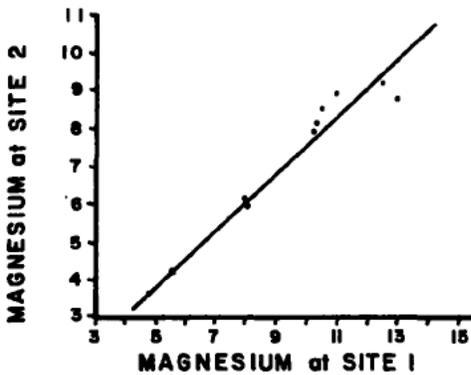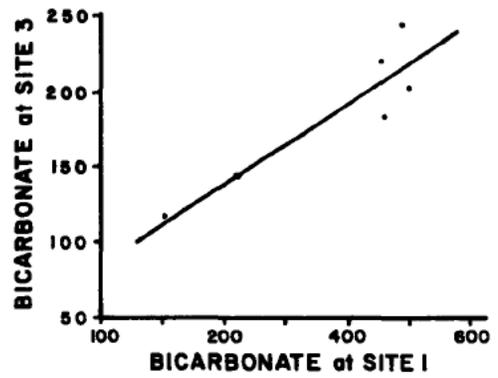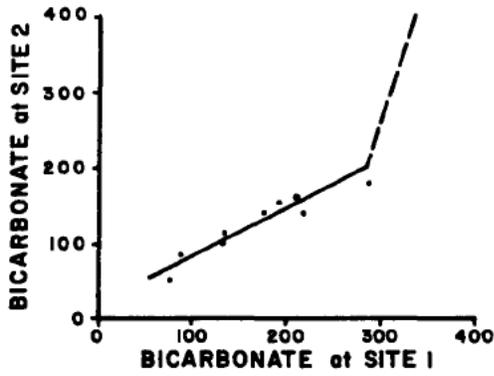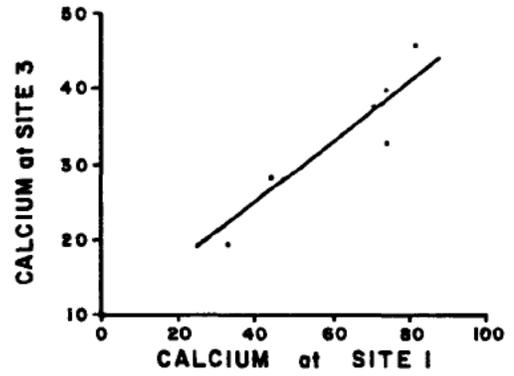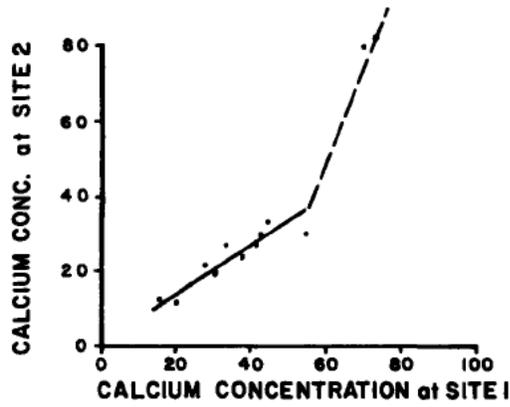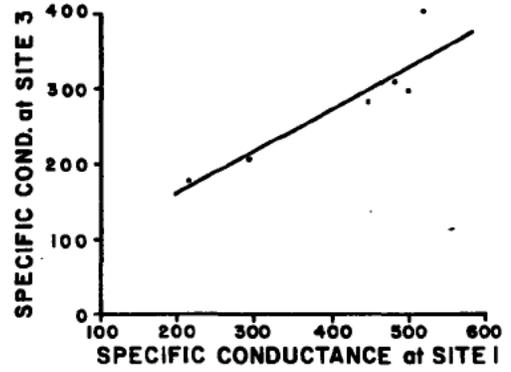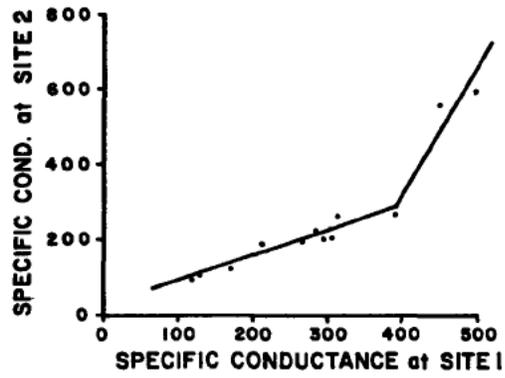
Figure 12. Relationship of parameter concentrations at Sites 2 and 3 to values at Site 1.
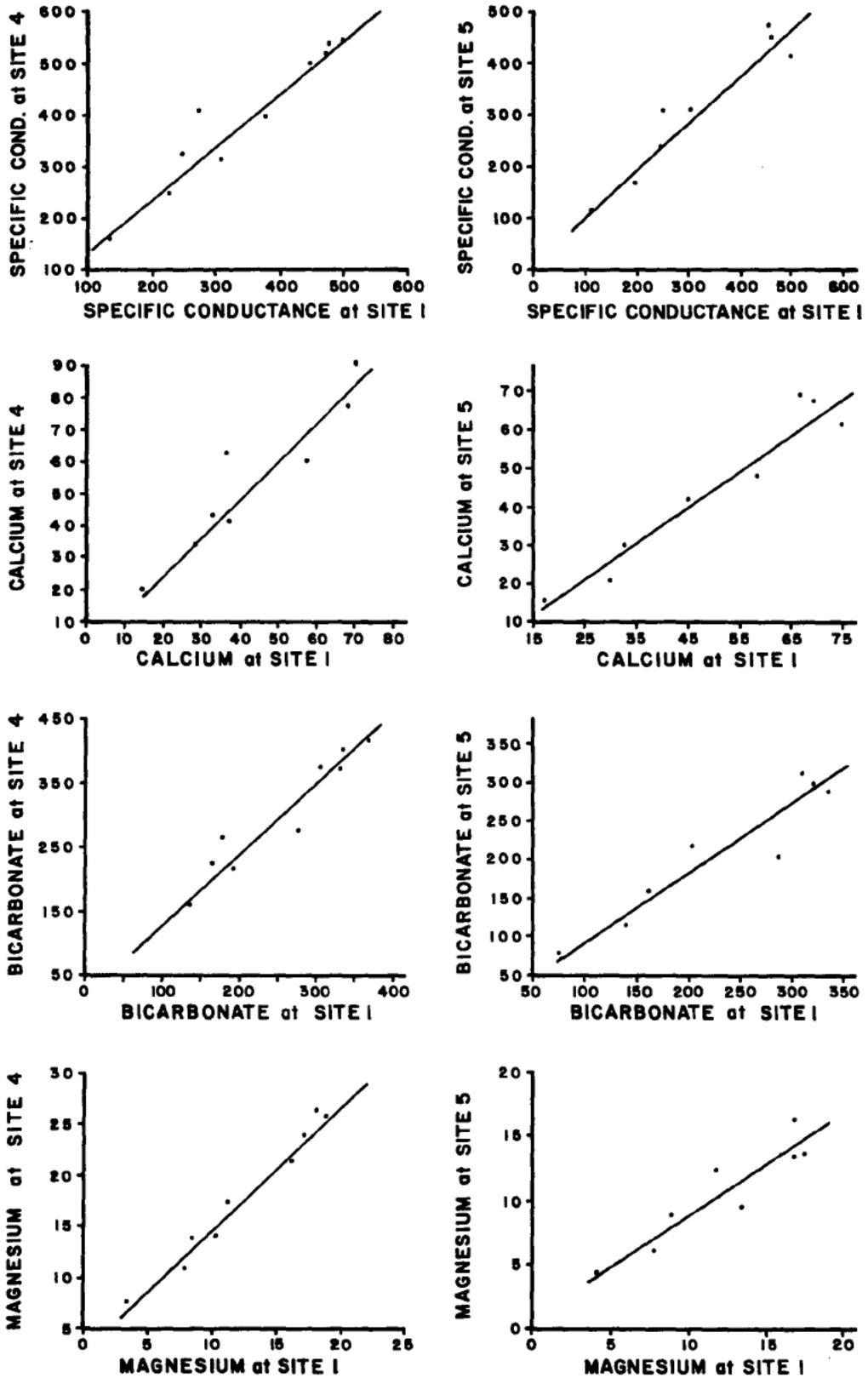
Figure 13. Relationship of parameter concentrations at
Sites 4 and 5 to values at Site I.

conductance at Site 2) for drastic deviations during
baseflow periods.

Of the parameters considered, calcium,
magnesium, bicarbonate, and specific conductance gave
good correlations while sodium and chloride gave poor
relationships. The poor showing in sodium and chloride
was probably caused by differences in sub-basin water
quality characteristics, groundwater inputs,
exchange/mixing processes, or incomplete removal of
Shell Pit pumping effects.

The Site 2 sub-basin, reported by Schwartz
(1979), showed similar results.

Unfortunately, the limitations imposed by
non-simultaneous samplings reduced the number of
correlatable sampling dates available for these plots.

2.5.3   Specific Conductance as an Index Variable

Although natural waters are very complex
electrolytic solutions, the effects of dominant solutes
(e.g., Na^+, Cl^-, Ca^{+2}, and HCO_3^-) generally overshadow
those of other dissolved substances, and significant
relationship between specific conductance and the
concentration of certain strong electrolytes still
emerge. The relationships between specific conductance
and the ionic concentrations of weak electrolytes, or
sparingly soluble salts, are, however, often not very
good.

According to Steele (1968, 1971), the
relationship between the concentrations, C_i, of a
strong electrolyte and specific conductances, K_{sc},
follow the algebraic equation:

$$C_i = a_i + b_i K_{sc}$$

where a_i and b_i are regression parameters corresponding
to the intercept (on the y-axis) and the slope,
respectively.

Except for cases involving waters of highly
variable chemical composition (e.g., upstream spillage
of brines), the C_i-K_{sc} relationship is generally
preserved over time.

Analyses of the C_i-K_{sc} relationship in this
study produced good correlations (Figures 14 and 15),
with positive slopes for all sites (Sites 1 and 7/A
data affected by Shell Pit pumping were excluded) for
the parameters:

1. bicarbonate   5. magnesium

2. alkalinity   6. filterable residue

3. hardness   7. total dissolve solids

4. calcium   8. sodium

but poor correlations for most sites for the
parameters:

1. potassium   5. zinc

2. sulphate   6. copper

3. aluminum   7. iron

4. manganese   8. total phosphate
                       phosphorus

2.5.4   Streamflow as an Index Variable

It is commonly observed that the
concentrations of most dissolved solids decrease with
increased stream discharge.

Assuming environmental changes upstream from
a station have not significantly altered the streamflow
related relationships over the period of the record,
the dilution model (Steele 1968) relationship between
concentration, C_i, or specific conductance, K_{sc}, and
stream discharge, Q, can take the logarithmic form:
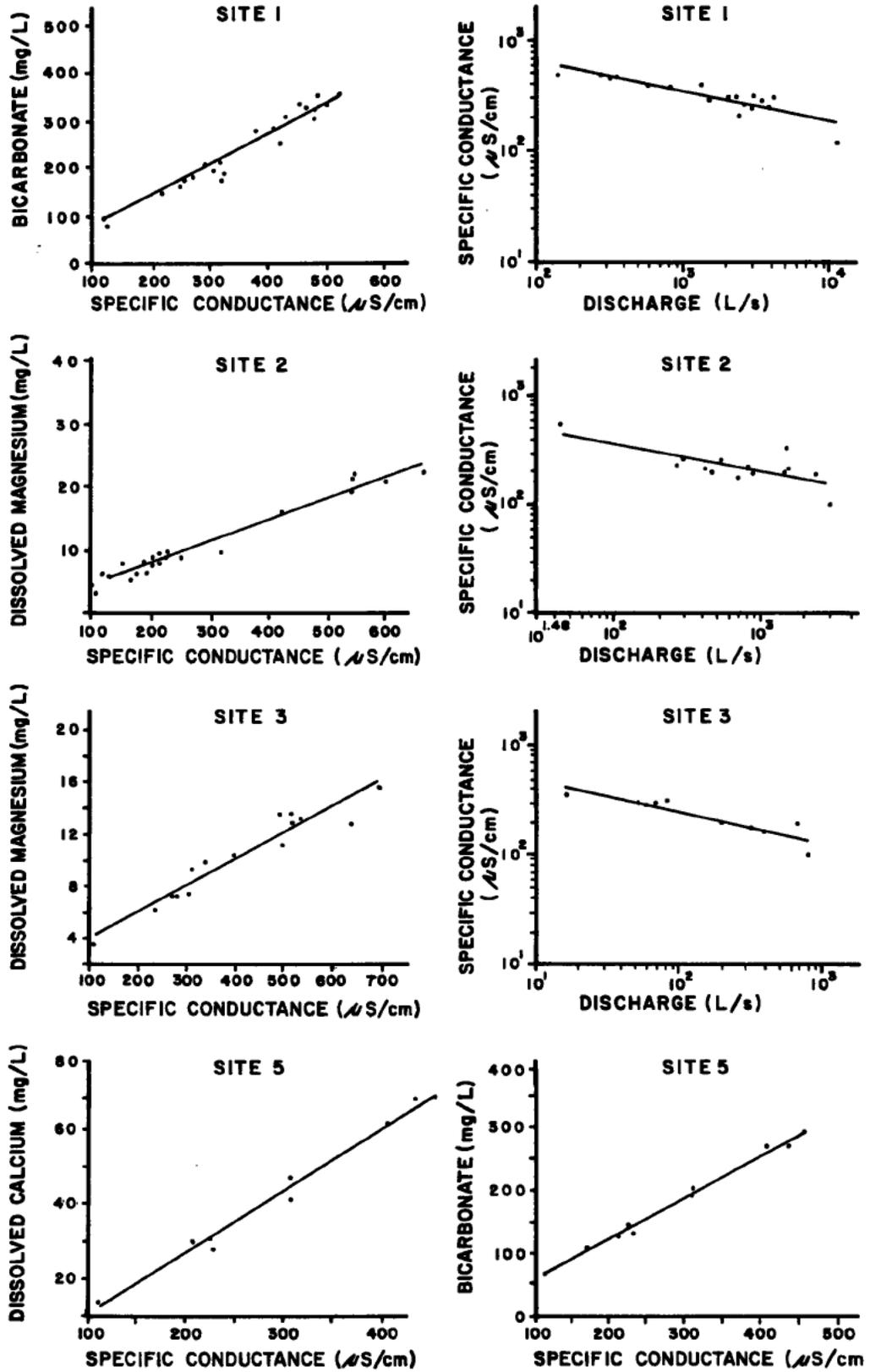
Figure 14. Interparameter relationships at Sites 1, 2, 3, and 5.
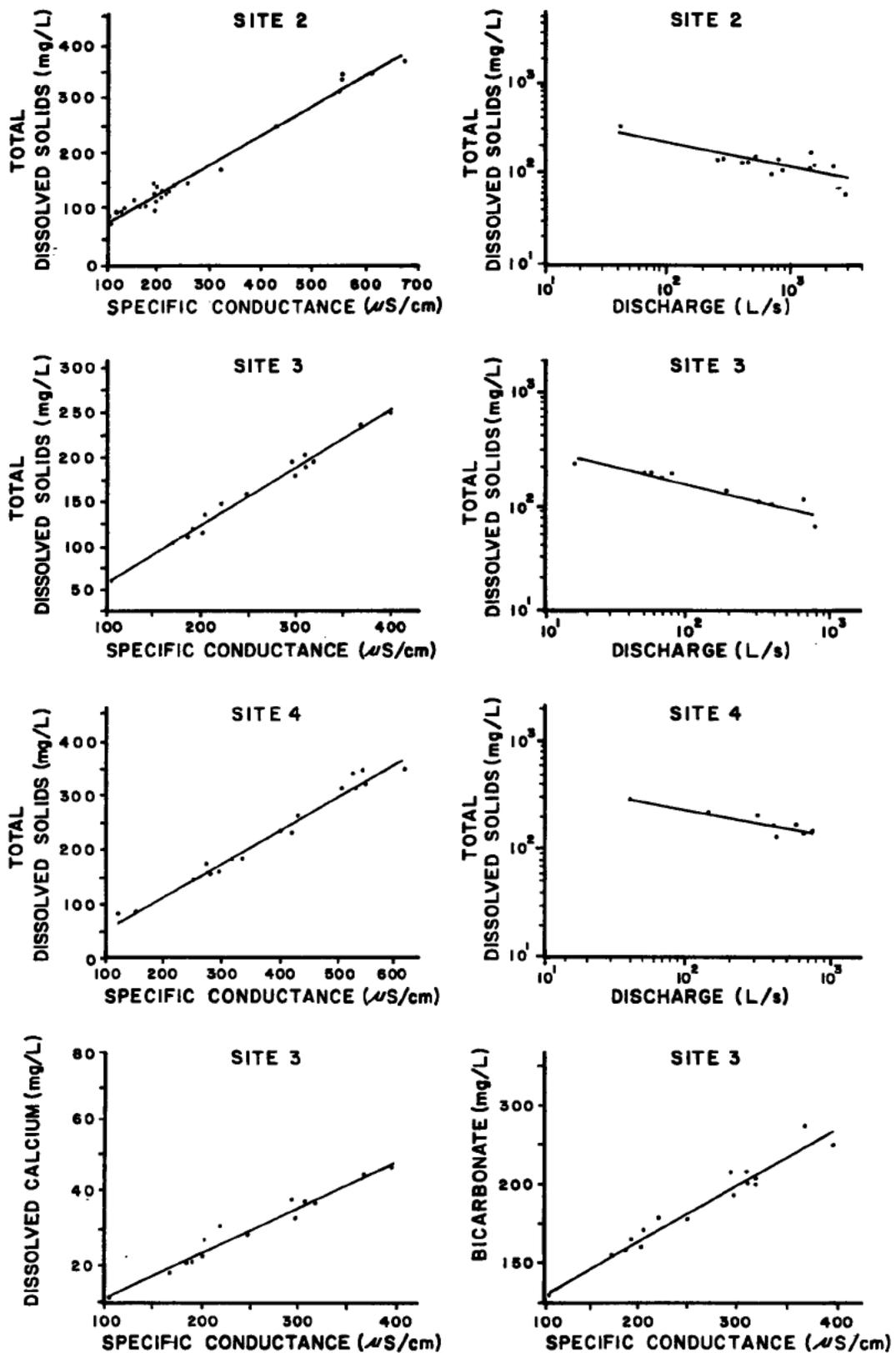
Figure l5. Interparameter relationships at Sites 2, 3, and 4.

$$\log C_i = \log k_i - n_i \log Q$$

where k_i is a constant and n_i a dilution factor.
The above equation gives a straight line plot with a
slope of n_i, a factor which allows for all values for
slope including 1.0. Because the parameter n_i tends
to vary, Steele (1971) has suggested that this means
increasing flows tend to accompany concentrations of
solutes higher than anticipated from a strict dilution
model.

Similarily, the equation:

$$\log K_{sc} = \log k_{sc} - n_{sc} (\log Q)$$

where k_{sc} and n_{sc} are regression parameters, relates
the specific conductance to streamflow.

Some of the data sets collected from the
Muskeg River watershed were subjected to C_i-K_{sc} (Figure
15), C_i-Q, and K_{sc}-Q (Figures 14 and 15) graphical
analyses. Analyses of appropriate dependent and
independent variables yielded regression equations
which, together with daily records of the selected
independent variable [and flow duration curves
(Froelich in prep.)] were used, according to the method
described in Section 2.3.1, to determine individual
solute concentrations and natural loads (Table 4).

2.5.4.1 Possible Use of the Dilution Model in the
Muskeg River Basin. Plots of log C_i verses log Q
(Figures 14 and 15) showed that certain sets of
concentrations fit the dilution model and showed no
drastic variations in n_i (the slope) for alkalinity,
filterable residue fixed, or total dissolved solids;
suggesting that the relationship:

$$\log C_i = \log k_i - n_i \log Q$$

Table 4. Chemical loading.

	Parameters	1976 Loading kg/yr	1976 Unit Loading kg/ha/yr	1977 Loading kg/yr	1977 Unit Loading kg/ha/yr	1978 Loading kg/yr	1978 Unit Loading kg/ha/yr
Site 1	Cl	188 927.49	1.55	211 622.23	1.74	415 898.08	3.42
	HCO$_3$	1 615 144.36	13.29	2 817 537.20	23.18	4 418 068.27	36.36
	Ca	2 390 691.75	19.67	2 638 807.67	21.71	4 786 797.56	39.39
	Mg	640 190.84	5.26	705 608.51	5.80	1 350 686.56	11.11
	Na	679 635.26	5.59	750 989.75	6.18	1 623 126.11	13.35
Site 2	HCO$_3$	2 760 851.49	74.01	2 461 171.88	65.98	4 906 873.45	131.55
	Cl	39 868.55	1.06	37 227.59	0.99	58 886.90	1.58
	Na	251 679.32	6.74	223 420.79	5.98	471 240.71	12.63
	Mg	157 480.76	4.22	140 194.21	3.75	284 038.58	7.61
	Ca	527 422.61	14.14	472 236.12	12.66	935 903.58	25.09
Site 4	HCO$_3$			2 623 683.19	108.42		
	Cl			15 966.11	0.66		
	Na			71 193.76	2.94		
	Mg			177 982.16	7.35		
	Ca			539 452.20	22.29		

	Parameters	9 Sep. 76 to 14 Oct. 76	23 Jun. 77 to 2 Aug. 77	3 Sep. 77 to 14 Sep. 77	7 Jun. 78 to 5 Jul. 78	24 Sep. 78 to 20 Nov. 78
Shell Pit	HCO$_3$	165 549.97	140 577.72	64 284.43	158 279.52	256 347.98
	Cl	118 521.38	84 108.00	43 032.00	102 690.00	-
	Na	124 254.90	97 800.00	48 411.00	107 482.20	-
	Mg	5 776.30	6 552.60	1 748.18	4 792.20	9 755.55
	Ca	5 964.57	5 379.00	3 092.93	1 369.20	-

applies to conditions in the streams considered. It
also appears that such relationships could be used to
compare equations between different solute
concentrations and stream discharges in different
streams or at different points along the same stream.
Such comparisons have been used by other workers
(Steele 1971) to obtain an index from which assessments
of degradation or improvement in chemical quality can
be made.

2.6   WATER SOURCES AND TYPES

2.6.1   Sub-basin Variations

        As can be expected, a general relationship
between drainage basin geology (or soil) and the
composition of natural water in contact with it is not
always simple or obvious. Minor components may control
the major features of the composition of circulating
waters. For instance, a carbonate cemented sandstone
might be largely composed of silicates in the form of
quartz, but yield water containing calcium and
bicarbonate ion. This is caused by carbonic acid
(dissolved carbon dioxide) reacting with silicates to
form bicarbonate and silica.

        Processes involving organic soil materials,
muskeg, and groundwater may also have profound
influences on streamflow water quality. These
processes occur alongside those involving the mixing of
different kinds of waters, chemical (cation exchange)
reactions, adsorption, and biological processes.

        A comparison of the 1977 unit loadings of
sub-basins drained by Site 2 (80% moss bog and 16%
Orthic Grey Luvisol) and Site 4 (54% moss bog and 35%
Eluviated Eutric Brunisols) show that loadings of
calcium, magnesium, and bicarbonate were higher through
Site 4 (22.29, 7.35, and 108.42 kg/ha/yr, respectively)

than through Site 2 (14.14, 4.22, and 74.1 kg/ha/yr, respectively).

Table 2 also shows that the ratio of Ca:Mg unit loadings by Site 2 and Site 1 sub-basins remained relatively constant at 3.34 ± 0.04 and 3.67 ± 0.08, respectively, through the three years, 1976, 1977, and 1978.

The influence of moss bog (eg., the sub-basin drained by Site 2) on the chemical characteristics of waters draining areas covered by base saturated parent materials is caused, in part, by the acidic and/or organic properties of the bog. The extent of the modification also depends on factors (slope, porosity, and geologic material) which influence water residence time or "flushing" rate. Waters draining larger areas of bog would therefore be expected to carry slightly less basic material than waters draining larger areas of Eluviated Eutric Brunisols (or Orthic Grey Luvisol).

This simple comparison and pattern emerging between dominant sub-basin soil types and unit loadings for Sites 2 and 4 do not, however, hold for bicarbonate, sodium, or chloride. For instance, the 1977 bicarbonate unit loading through Site 1 (62% moss bog, 11% Orthic Grey Luvisol, and 16% Eluviated Eutric Brunisol) was only 23.18 kg/ha/yr (Table 4). The significantly lower bicarbonate unit loadings through Site 1 compared to Site 2 were also observed in 1976 and 1978. It appears that bicarbonate-carbonate equilibrium reactions were a major factor. In fact, bicarbonate loadings from Shell Pit pumpings seldom showed in analyses of samples collect at Site 1.

Although loadings calculations were only possible for a limited number of sites and years, other attempts to relate surficial materials to water quality

characteristics were made using levels of major ion
concentrations in uniform non-overlapping watersheds.

Figures 2 and 3 and Table 1 show that sub-
basins drained by Sites 6, 7, 8, 9. 11, 13/A, and 14
are covered by 75 to 100% moss bog overlying ground
moraine (composed of gravel, sand, silt, and clay)
derived from limestone and shale. The minimum calcium
(and bicarbonate) concentrations ranged between 10.0
and 13.5 mg/L (HCO_3^-, 51 to 72 mg/L) at all sites,
except Site 13/A (Ca^{+2}, 16.0 mg/L). The maxima ranged
between 54.5 and 69.0 mg/L (HCO_3^-, 252 to 312 mg/L) at
Sites 7, 11, 13/A, and 14 which have some areas of
Orthic Grey Luvisol; and the maximum concentration
dropped to 32.0, 36.0, and 48.0 mg/L (HCO_3^-, 164, 218,
and 252 mg/L, respectively) at Sites 6, 8, and 9, where
significant areas of moss bog exist along stream
channels.

While trends in levels of magnesium mimic
those of calcium and bicarbonate in most sub-basins,
those of sodium and chloride were less distinct. This
is probably caused, in part, by ion (cation or anion)
exchange reactions occurring at mineral surfaces. For
instance, clay, which generally has high cation-
exchange capacities, could exert considerable influence
on the proportionate content of different cations
(Ca^{+2}, Mg^{+2}, Na^+, and K^+) in waters in contact with it.

2.6.2   Sodium/Chloride Ratios and Muskeg Drainage
Of the major ions considered in this report,
sodium and chloride ions were probably the least
utilized or changed in form and bicarbonate one of the
most labile. This section will investigate trends in
ratios of sodium/chloride concentrations (together with
bicarbonate concentrations and levels of specific
conductance) to identify water sources and types.

The Na/Cl concentration ratio in a solution of pure sodium chloride is approximately 0.65.

Representative seasonal and areal trends in this ratio are given in Table 5. Almost all sites (except Sites 2, 3/A, 4, 5, and 7) showed a decreasing trend in the Na/Cl ratios going from October 1976 to January 1977 to April 1977, but increasing again in July 1977. A series of high precipitation events (in September and October 1976) which followed a very dry summer must have washed into the streams compounds higher in sodium content, e.g., $NaHCO_3$. This would influence the Na/Cl ratio (refer to Section 2.5) and could explain the relatively higher ratios observed in October 1976 and summer 1977 at most sites. A plot of the Na/Cl ratios versus time at Site 2 (Figure 16) shows the above trend very clearly.

Considering the whole basin, Site 1 appears to, generally, have one of the lowest Na/Cl ratios. When Shell Pit pumping periods were added to the plot for Site 1 (Figure 17), the character of Shell effluent (Table 6) appeared more drastic than baseflow. It is, however, possible that the baseflow groundwater effecting Site 1 could be of the Na/HCO_3 or $Ca-Mg-Na/HCO_3$ type. So that muskeg (or shallow groundwater) drainage of the Na/HCO_3 or $Ca-Mg-Na/HCO_3$ type dominating baseflow at Site 1 would not give the Na/Cl ratio characterized by the Shell Pit pumpage.

Calculations of Na/Cl ratios of aquifer test data obtained from the Alberta Research Council (Schwartz 1979) clearly indicate that muskeg drainage or shallow groundwater (specific conductance 560 to 860 $\mu S/cm$) of the Na/HCO_3 and $Ca-Mg-Na/HCO_3$ type, and orginating from glacial and post-glacial drift, are probably the main contributors of baseflow at most sites in the Muskeg River watershed (Table 7). The

Table 5. Seasonal variations in Na/Cl ratios.

Site Number	October 1976	January 1977	April 1977	July 1977
1	4.8	3.3	2.9	—
2	6.3	1.8	3.2	11.5
2/A	4.1	—	3.2	10.5
3	48.7	6.5	4.4	12.3
3/A	3.8	5.0	2.5	7.0
4	4.4	6.3	2.7	4.5
5	4.5	6.8	3.5	7.0
6	6.5	—	3.8	11.0
7	9.3	2.8	4.0	15.0
7/A	6.4	—	—	—
8	—	13.0	5.9	16.1
9	13.6	10.7	5.3	12.9
10	10.0	7.2	5.9	16.2
11	22.1	7.5	6.3	10.0
12	5.8	—	2.2	5.4
13/A	10.0	6.7	3.9	15.0
14	13.0	8.3	5.0	3.9
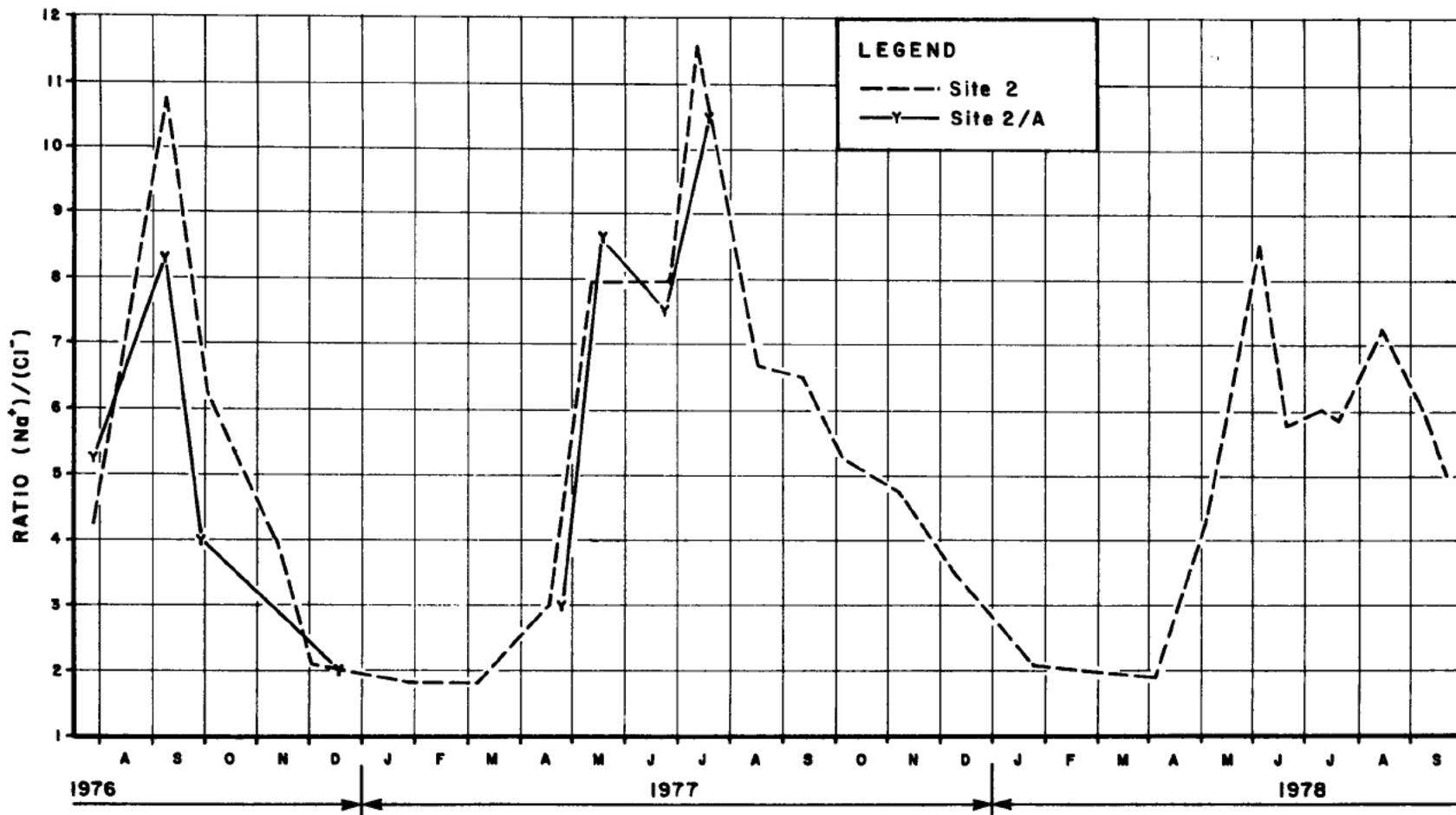
Figure 16. Variations in Na/Cl ratios (Sites 2 and 2/A).

48
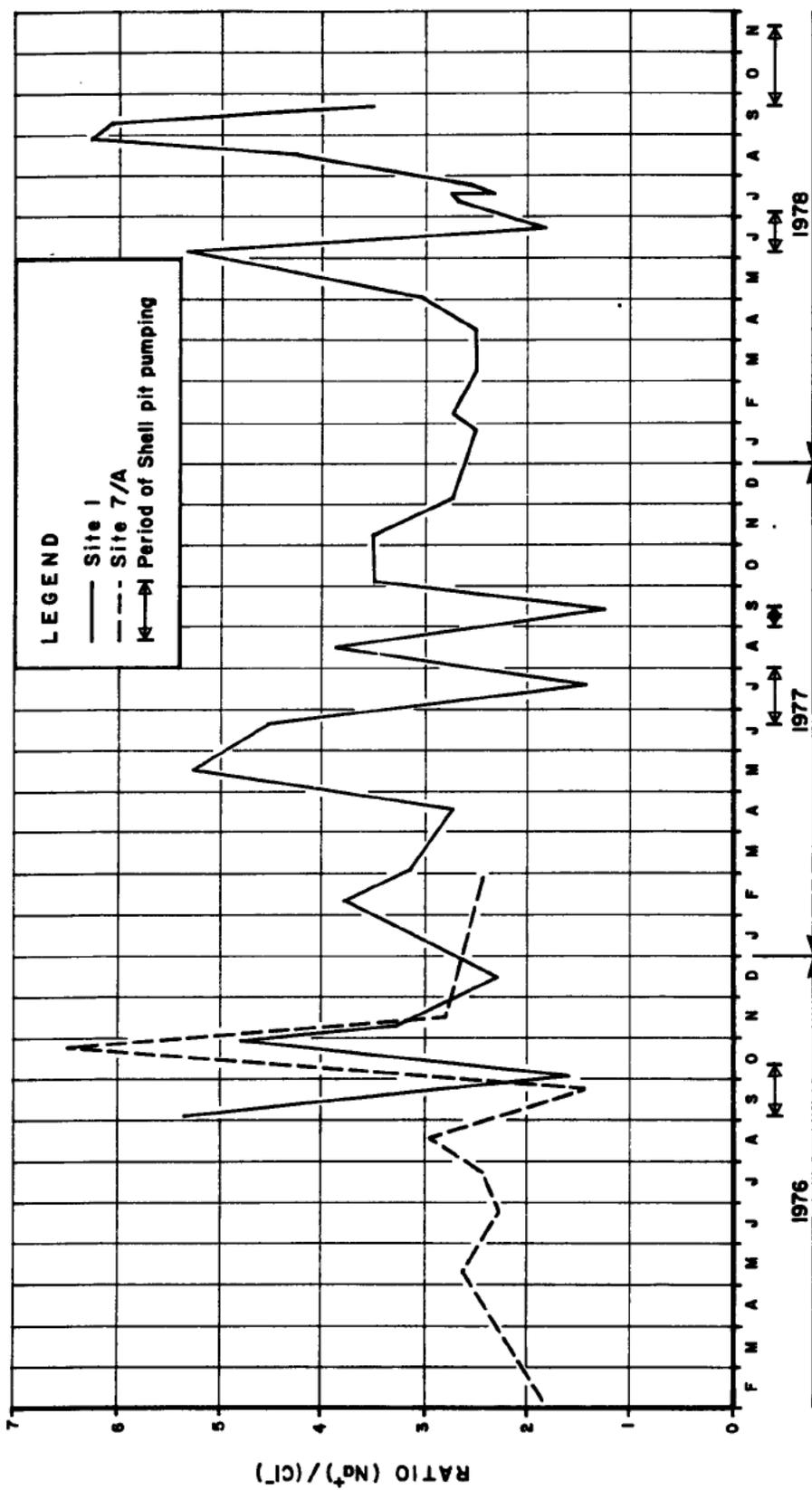
Figure 17. Variations in Na/Cl ratios (Sites 1 and 7/A).

Table 6. Index parameters from Shell Pit pumpage
          analyses.

Date	Conductivity μS/cm	HCO$_3$	Na (mg/L)	Cl (mg/L)	Na/Cl
28 Jul 1976	2200	509.5	410	380	1.08
9 Sep 1976	2950	755.8	500	460	1.09
30 Sep 1976	4200	1066.6	860	825	1.04
14 Oct 1976	3700	1036.2	730	710	1.02
29 Jun 1977	2720	718.7	500	430	1.16
14 Sep 1977	3790	1195.1	900	805	1.12
21 Jun 1978	3900	1156.0	785	750	1.04

Average Na/Cl ratio   1.08 ± 0.08

Table 7. Summary of chemical data (from Alberta Research Council).

Formation	Well No.	Lithology	Date	Concentrations (mg/L)			Type	Conductivity (µS/cm)	Na/Cl Ratio
				HCO_3	Na^+	Cl^-			
DRIFT	7-32	Sandy Till	31 Jan. 75	408.0	101.0	5.0	Na/HCO₃	660	20.2
			10 Sep. 75	322.0	108.0	14.0	Na/HCO₃	610	7.71
	8-34	Sand	22 Feb. 75	517.0	146.3	44.0	Na/HCO₃	860	3.32
			10 Sep. 75	444.0	133.0	22.0	Na/HCO₃	820	6.05
	9-161	Sandy Clay Till	8 Mar. 75	325.0	40.0	25.0	Ca-Mg-Na/HCO₃	560	1.6
CLEARWATER	8-114	Clay	22 Feb. 75	525.0	239.0	54.0	Na/HCO₃	1100	4.43
	8-220	Clay	6 Mar. 75	1898.0	700.0	4.0	Na/HCO₃	1800	175.0
	8-370	Clay	23 Feb. 75	1054.0	409.0	27.0	Na/HCO₃	1710	15.15
McMURRAY	6-21	Tar Sand	18 Feb. 75	378.0	6.3	44.0	Ca/HCO₃	640	0.14
			11 Sep. 75	137.0	17.5	12.0	Ca/HCO₃	280	1.46
	6-220	Tar Sand	18 Feb. 75	1715.0	1431.0	1320.0	Na/Cl	6500	1.08
			11 Sep. 75	2079.0	1400.0	658.0	Na/HCO₃	-	2.13
	7-135	Tar Sand	2 Feb. 75	947.0	355.0	31.0	Na/HCO₃	1550	11.45
			10 Sep. 75	1017.0	345.0	14.0	Na/HCO₃	1600	24.64
	7-337	Water Sand	6 Feb. 75	1235.0	583.0	321.0	Na/HCO₃	2780	1.82
			7 Feb. 75	1369.0	586.0	315.0	Na/HCO₃	2900	1.86
			8 Feb. 75	1171.0	585.0	323.0	Na/HCO₃	2780	1.81
			9 Sep. 75	1239.0	575.0	218.0	Na/HCO₃	3200	2.64
			10 Sep. 75	1239.0	575.0	218.0	Na/HCO₃	3200	2.64
	Home #2	Water Sand	18 Feb. 75	965.0	-	1800.0	Na/Cl	-	-
	Home #4	Water Sand	10 Mar. 75	1625.0	-	3150.0	Na/Cl	-	-
	Tenneco 1	Water Sand	6 Mar. 74	453.0	114.0	2.0	Na/HCO₃	-	57.0
	Tenneco 3	Water Sand	27 Feb. 74	560.0	190.0	Trace	Na/SO₄	-	-
	Tenneco 4	Water Sand	18 Feb. 74	431.0	161.0	Trace	Na/SO₄	-	-
BEAVERHILL LAKE (Devonian)	6-310	Limestone	10 Feb. 75	1720.0	1469.0	1480.0	Na/Cl	6800	0.99
			19 Feb. 75	1708.0	1563.0	1440.0	Na/Cl	7000	1.08
			11 Sep. 75	1996.0	2850.0	2238.0	Na/Cl	-	1.27
	8-532	Clay	24 Feb. 75	1396.0	775.0	511.0	Na/HCO₃	3500	1.52
			7 Mar. 75	1161.0	813.0	717.0	Na/Cl-HCO₃	3600	1.13
	8-716	Limestone	7 Mar. 75	215.0	738.0	895.0	Na/Cl	-	0.82
			10 Sep. 75	1491.0	2125.0	2838.0	Na/Cl	-	0.75
	9-1150	Limestone	4 Mar. 75	83.0	21.3	54.0	Ca/Cl	330	0.39
PRAIRIE EVAPORITE	7-594	Gypsum	19 Feb. 75	422.0	1688.0	2875.0	Na/Cl	8000+	0.59
PRECAMBRIAN	7-933	Granite	11 Mar. 75	146.0	251.0	300.0	Na/Cl	1480	0.84

only occasion when stream water specific conductance
was very high (1360 µS/cm), and the Na/Cl ratio rather
low (2.5), was at the mouth of the Muskeg River (Site
7/A) on 25 February 1977. This high specific
conductance value, however, suggests that the
groundwater source is probably deeper than drift
formation.

The dissolved solids concentrations in
muskegs and shallow groundwater depend on chemical
reactions, the rates of atmospheric inputs
(precipitation) and losses (directly as evaporation and
indirectly as vegetative transpiration), and the
porosity of the surficial geology. It is possible, for
example, for the concentrations of major ions in
muskegs and shallow groundwaters to be diluted and to
approach spring runoff levels. Alternatively, the
other factors and Ca-Na exchange reactions could alter
the Na/Cl ratios and the concentration of the other
major ions to the level generally observed during low
streamflow periods. Figure 17 appears to indicate the
effects of such exchange processes by slight mid-summer
(especially June and July) drops in the Na/Cl ratios.
But the exchange processes do not appear to cause
changes in the levels of the other major ions to
conditions as severe as those observed during baseflow.

Thus, muskegs or shallow groundwater could
have the character (as shown by solute ratios) of
surface flows or low flow periods depending on which of
the modifications detailed above is predominant.

2.7   POSSIBLE EFFECTS OF HIGH CONCENTRATIONS OF
         MAJOR IONS

2.7.1   Total Dissolved Solids
         A number of inorganic ions appear to be
necessary for the normal functioning of freshwater

fish. Of these ions, Na^+, Cl^-, HCO_3^- , K^+, and Mg^{+2} are involved in osmotic balance. Inland waters are usually dominated by the four major cations Ca^{+2}, Mg^{+2}, Na^+, and K^+ and the major anions CO_3^{2-}, SO_4^{2-}, and Cl^-. It is known that in hard waters, calcium and magnesium affect the efficiency of osmoregulation as well as the rate of respiration (Schlieper et al. 1952).

An AOSERP report (Hartland-Rowe et al. 1979) has suggested that most invertebrate species in the Hartley Creek over-winter as larvae in pools while others appear to over-winter as eggs. The authors indicated that this may be a mechanism by which these organisms can reduce the effects of severe winter water quality conditions.

The limitations of the stream winter conditions may have even greater effect on fish than on invertebrates. But whether the fish migrating from the Athabasca River into the Muskeg River are capable of over-wintering in the deep pools created by beaver dams is, however, not yet known.

2.7.2   Sodium and Chloride

Machniak (1977) cited a number of studies on the effects of high concentrations of chlorides. The general attitude of the literature review appeared to be that physiological toxicity of chlorides was attributed to the cations (K, Na, Ca, Sr, Mg, Cu, Hg, Cd, Zn, and Pb) with which the chloride anion is associated.

A study by Vosjan and Seizan (1968) reported that chloride, in the form of NaCl, played a major role in limiting the distribution of diatoms and determining the kinds and growth of algae and photosynthetic rates in the water. Zeimann (1968) also found a quantitative relationship between salinity and biological conditions

of diatom communities in several inland waters. More
recently, Seddon (1972) reported correlations between
groups of aquatic macrophytes and water quality
parameters (specifically, specific conductance and
total dissolved solids); and of toxicity symptoms, and
the frequency and severity of these symptoms, to levels
of salinity.

Shell Pit discharges and the potential for
saline conditions to occur during a dry open water
season raise concern about the extent to which many
aquatic plants, invertebrates, and vertebrates may
tolerate such discharges. The review by Machniak
(1977) indicates that species composition shifts have
resulted from saline discharges. Thus, a need to
investigate toxic and inhibitory effects of major ions
in the AOSERP study area is suggested.

2.8   SUMMARY

Areal and seasonal variations in major ion
concentrations were described and analysed. The
analyses, based on limited data, produced some very
strong functional relationships between parameters and
between sites. These relationships, especially the
longitudinal relationships, allow information on basic
water quality data, at certain sites within the basin,
to be obtained by monitoring a limited number of sites
for a limited set of parameters.

Attempts were also made to relate surficial
materials with natural major ion chemistry and ion
ratios in surface flows. Source identification
analyses in this report and studies by Schwartz (1979)
appear to suggest that muskeg and shallow groundwater
drainage are the major contributors of streamflow
during low flow periods; the magnitude and timing being

influenced by the porosity of surficial geology and atmospheric input and output processes.

The potential toxic effects of major ions on aquatic biota were discussed in light of baseflow and Shell Pit pumping chemical analyses.

3.   PHYSICOCHEMICAL PARAMETERS RELATED TO
      BIOLOGICAL ACTIVITY

3.1   INTRODUCTION
       Nutrients in surface waters are, by
definition, chemical substances which support the
growth of aquatic fauna and flora. These substances,
indirectly, influence the oxygen content and the
assimilative capacity of the water.

       This chapter describes the macronutrient
chemistry of the Muskeg River drainage basin, the
spatial and temporal distribution of these nutrients
(carbon, potassium, silica, phosphorus, and nitrogen),
and those physical and biological factors which exert
major controls on the water quality.

3.2   METHODS AND SOURCES OF DATA
       See Appendices, Sections 7.3 and 7.3.1 and
Table 18.

3.3   RESULTS AND DISCUSSIONS: PHYSICOCHEMICAL
       PARAMETERS

3.3.1   Water Temperature
         Water temperature recorded during the study
period in the Muskeg River and its tributaries ranged
from 0°C during the period November to March, to 20°C
during June and July (Figure 18). The period November
to March also corresponds to the freeze-over period.
The lowest air temperatures occur during January and
February.

       A maximum water temperature of 22°C was
recorded at Site 10 in June. This site is located on
the major outlet from Kearl Lake. The high temperature
is probably a result of the warming up of accumulated
water in this shallow lake whose average depth is
1.5 m.
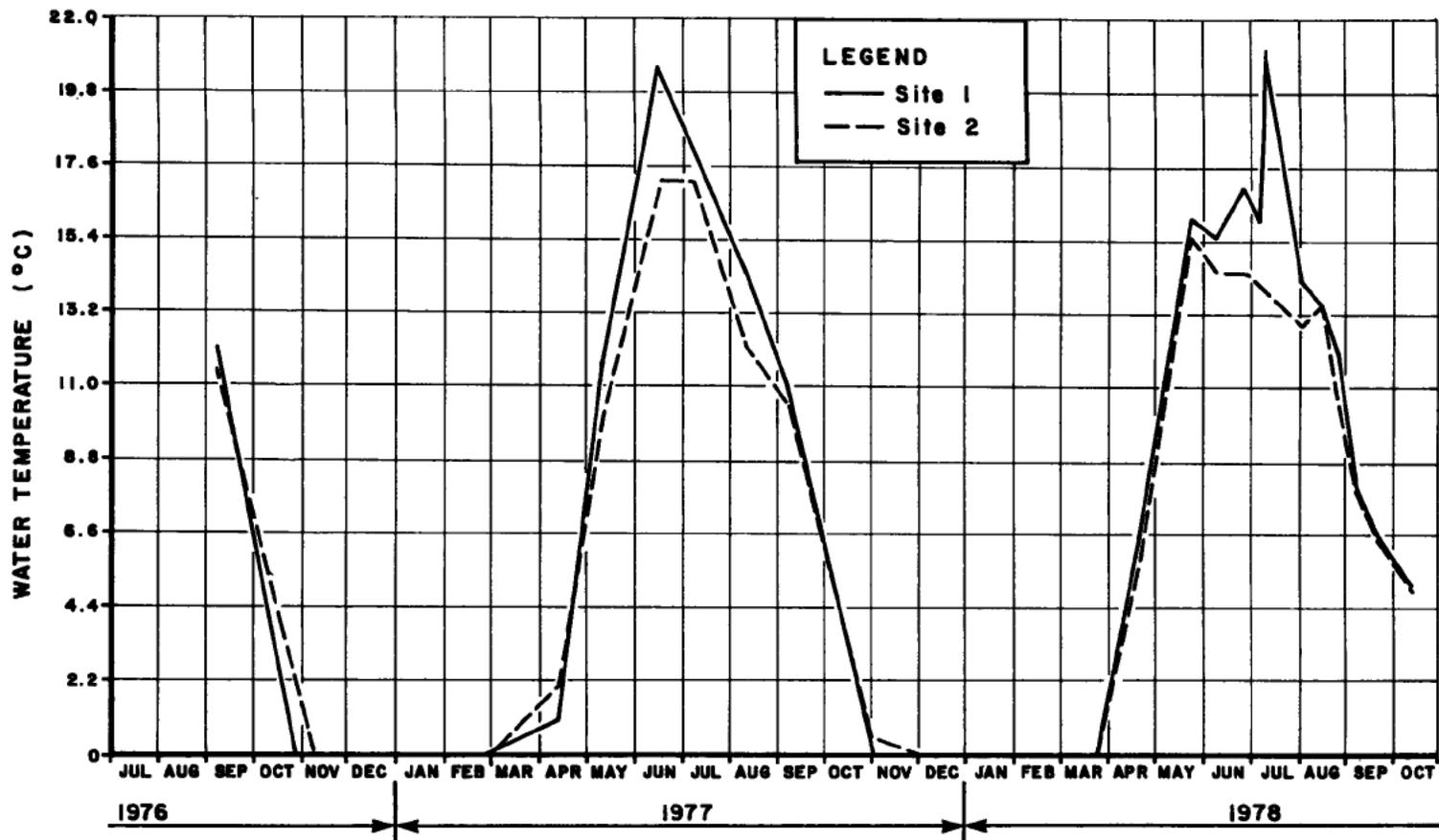
Figure 18. Variations in temperature at Sites 1 and 2.

There is evidence that considerable cooling occurs in the basin at night. Diurnal water temperature fluctuations of up to 8°C were reported by Bond and Machniak (1977).

3.3.2   Turbidity and Non-filterable Residues

Numerous studies (references in Froelich in prep.) have attemped to relate streamflows with turbidity, quantities of non-filterable residue, and of suspended sediments.

Turbidity data reflect the amounts of flocs, mineral and rock fragments, and organic and other materials, while suspended sediment concentrations (most closely associated with non-filterable residue fixed) reflect amounts of mineral and rock fragments only.

Several environmental factors control the movement of residues into and by streams; of these, the surface drainage system and soil characteristics, land slope, land use or vegetation cover, precipitation, and direct runoff are probably the most significant.

Most of the waters in the Muskeg River basin are turbid, especially during the winter and during all surface runoff events (Tables 8 and 9), when the loadings of silt and organic particles are high. These high loadings of particulate materials decreased the amounts of dissolved oxygen in these waters via increased biochemical oxygen demand and reduced photosynthesis. Oxygen is a by-product of photosynthesis.

Although turbidity values were relatively high during the dry summer of 1976 and winter months, much of the turbidity was caused by fine particles which were not readily settleable. There were, however, a few samples collected (e.g., Sites 2, 5,

Table 8. High turbidity (JTU) events.

SITE	1976							1977			
	June	July	Aug	Sept	Oct	Nov	Dec	Jan	Feb	Mar	Apr
1		17.0		14.6				10.3			
2		25.0		21.0				320.0			
2/A		19.0					12.6				
3											
3/A		10.6								11.1	
4											
5								12.7	180	47.0	
6		25.0									
7		23.0						10.0			
7/A	16.0	15.0							11.6		
8										92.0	
9			40.2					11.7			
10			52.5								
11			34.0					10.8			
12										5.9	
13											
14											

Table 9. High non-filterable residue (mg/L) events.

SITE	1976							1977				
	June	July	Aug.	Sept	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.	Apr.	May
1							10.0					9.6
2				14.4			12.4	459.0			15.6	
2/A				20.0			18.4				16.4	
3												
3/A				58.0	12.0	29.2		73.0	24.8	36.0	12.6	7.2
4												
5				22.4	9.6	14.4		22.0	59.0	50.0	12.4	
6					12.8						12.8	7.6
7						7.6		82.0			8.0	8.8
7/A	9.2		7.0						20.4			
8								14.0		114.4		6.8
9			21.0					11.6			8.4	
10			82.0		19.6					12.4	10.0	
11			30.0					48.0			7.2	
12										37.2	8.4	
13												
14												

and 8) during the winter months which had extremely
high turbidity values. It is possible that, because of
the winter ice-cover, samples were collected from close
to the bottom of the river where suspended solids
concentrations are high. Furthermore, bottom
disturbances could occur during sample collection.

Along the mainstem of the Muskeg River,
turbidity mean values were 2.4, 6.7, and 5.5 JTU at
Sites 12, 4, and 1, respectively; while at Sites 13/A,
6, 14, 7, and 2, turbidity mean values were 26, 6, 11,
7, and 23 JTU, respectively. The sub-basin draining
Sites, 11, 10, 9, and 3, showed turbidity mean values
of 10.0, 10.0, 14.0, and 4.7 JTU, respectively.

Low visibility affects the growth rate of
sight feeders; and reduced light penetration affects
photosynthetic reactions associated with algae and
other aquatic vegetation. Where turbidity is caused by
loadings of organic materials, microbial activity
associated with the decomposition of these materials
removes dissolved oxygen from overlying waters. The
depletion of dissolved oxygen would affect aquatic
invertebrate population.

In the case of Kearl Lake, high turbidity
(Site 10, maximum 52.5 JTU) probably resulted in
increased heat absorbancy (Figure 19) by the water body
and a stabilized water column. Such stratification
could then decrease the dispersion of dissolved oxygen
to the lower portions of the lake (See Section
3.3.4.3).

3.3.3   pH

Most of the pH values recorded during this
study of the Muskeg River and its tributaries were only
slightly (7.1 to 8.2) alkaline. These pH values are
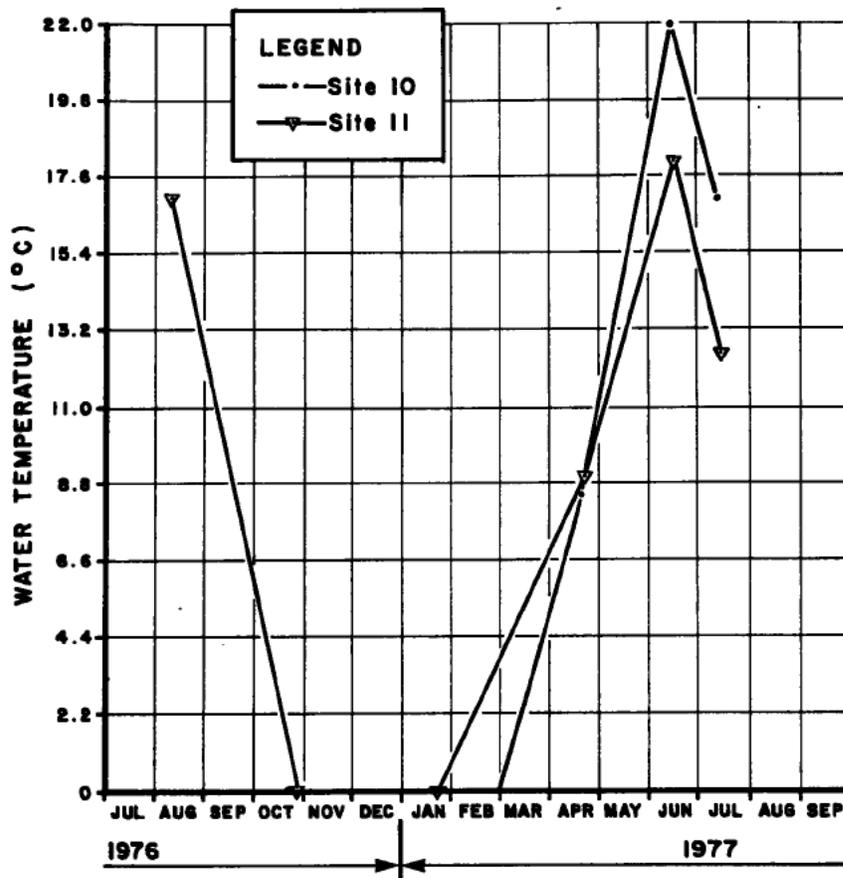
Figure 19. Variations in temperature at Kearl Lake, Sites 10 and 11.

normal for the rivers in this part of the province
(Griffith 1973).

Seasonal variations indicate generally lower
pH values during the winter months and slightly higher
values during the other seasons of the year. Along the
Muskeg River, the recorded pH values ranged between 7.1
and 8.2 (Sites 1 and 4). Variations in the pH values
at Sites 1, 2, and 4 are shown in Figure 20. pH values
ranged from 6.5 to 7.9 at Site 7, and from 7.0 to 8.3
at Sites 2, 2/A, 6, 13/A, and 14. Kearl Lake outlet,
Site 10, always (Figure 21) reported values lower than
the inlet, Site 11. A basin minimum pH value of 6.5
was recorded at Site 10, and a basin maximum value of
8.4 at Site 3/A. pH values at sites (2, 3/A, 4, and
12) draining bogs ranged from 6.9 to 8.4.

3.3.4   Dissolved Oxygen

3.3.4.1   Introduction. Biological degradation of
putrescible organic matter and reactions of reducing
chemical agents result in the depression of dissolved
oxygen concentrations in streams. A depletion of
oxygen can be directly or indirectly deleterious to the
growth, survival, reproduction, and movement of aquatic
biota.

Although this discussion is presented in
terms of oxygen, it should be understood that because
of the photosynthetic and respiratory activities of the
biota, carbon dioxide behaves similarily but with a
reversed sign.

As a first approximation, one would expect,
at ambient temperatures, a direct increase in dissolved
oxygen with runoff and turbulence, an inverse
relationship between dissolved oxygen concentrations
and temperature, a direct relationship between
temperature and bacteria count, and a direct increase
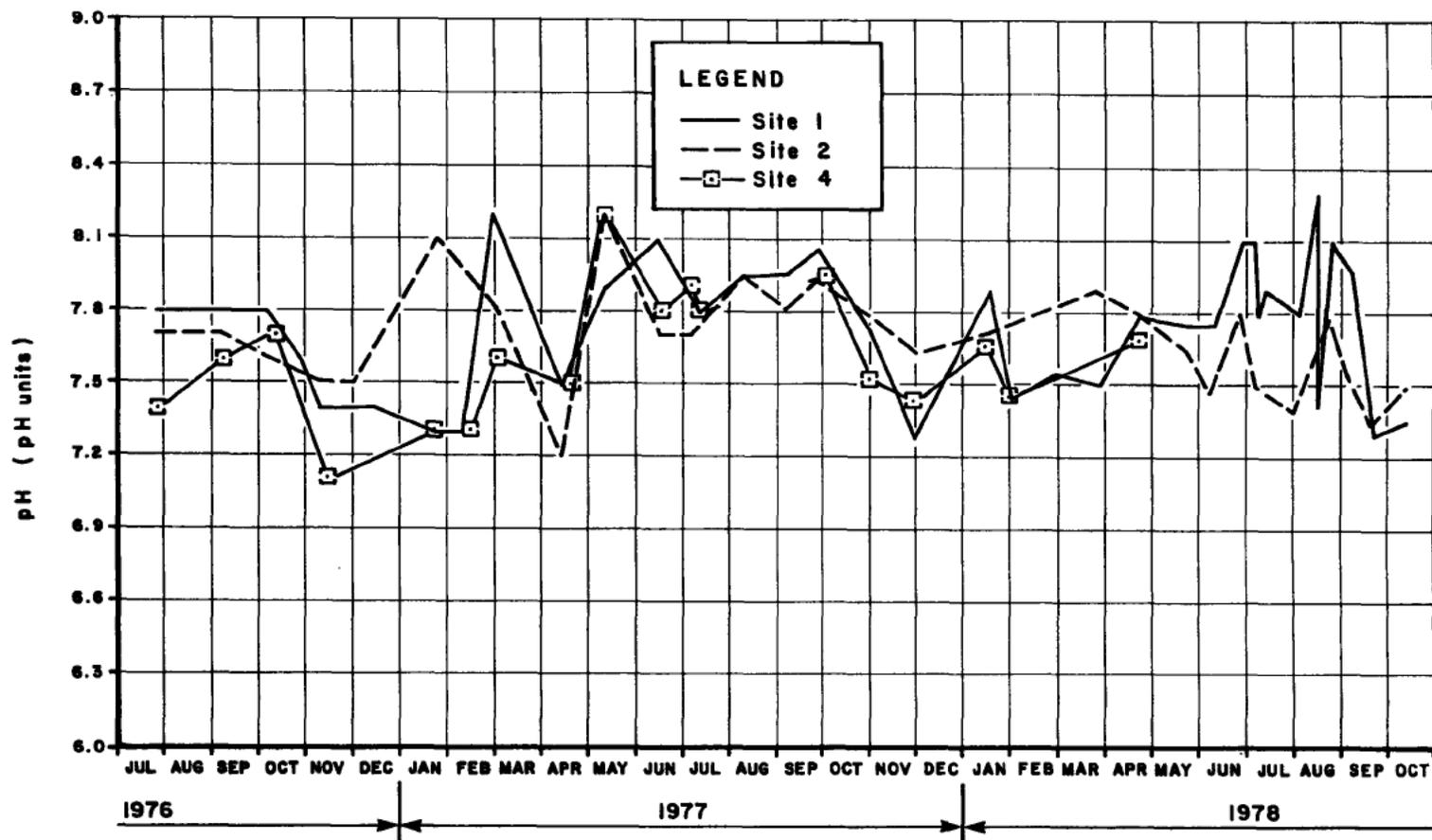
Figure 20. Variations of pH at Sites 1, 2, and 4.

64
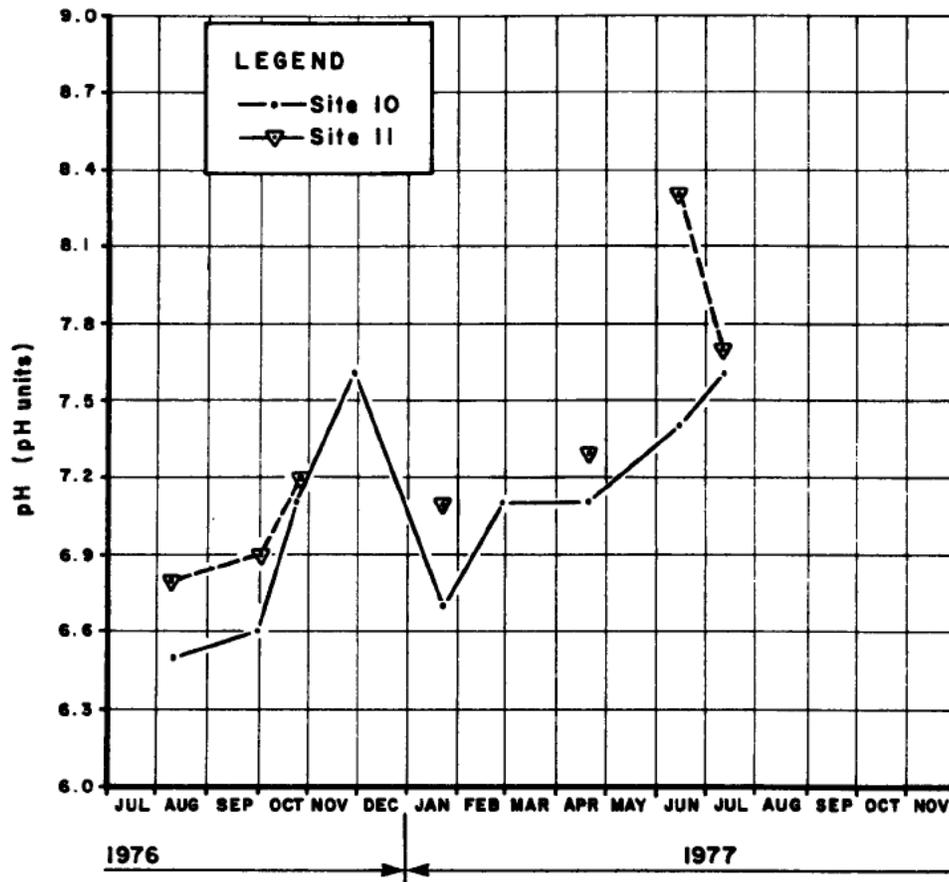
Figure 21. Variations of pH at Kearl Lake, Sites 10 & 11.

in rates of biochemical decomposition of organic matter
with increases in temperature.

The observed relationships are, however, not
so direct or simple.

3.3.4.2   Turbulence and Dissolved Oxygen Regime Along
turbulent reaches of streams in this watershed, the
concentrations of most dissolved chemical constituents,
during spring runoff periods, are at a minimum while
the dissolved oxygen concentrations are normally near
or above saturation. Presumably, this is a result of
aeration of water along these turbulent reaches, since
sites (3/A, 4, 7, and 10) draining bogs and Kearl Lake
showed (Table 10) substantially lower values of
dissolved oxygen (in percent saturation).

The data collected from most sites during the
study period also indicate that the stream waters were
undersaturated with oxygen during late spring and late
summer. The decrease in percent saturation, following
the spring runoff and summer (e.g., summer 1977) storm
runoff periods, is probably a result of increased
biotic respiration associated with biodegradation of
previously deposited organic materials, including
fallen autumn leaves, and/or (because of high
turbidity) decreased photosynthetic activity.

Unfortunately, attempts to correlate
discharge rates with percent saturation of DO for Sites
1 and 2 disclosed no obvious correlation.

3.3.4.3   Temperature and Dissolved Oxygen Regime
Surface water temperatures in this basin remain at or
near 0°C from November to March and rise to a maximum
of about 20°C during late June-early July.

Generally, the dissolved oxygen concentra-
tions started off quite high (Figures 22 and 23,

Table 10. Spring temperature and dissolved oxygen
          levels.

Site Number	Date in Spring	Temp (°C)	DO (mg/L)	DO (% Saturation)
11	26 Apr 77	9.0	7.9	69
2/A	25 Apr 77	6.0	12.0	97
10	25 Apr 77	8.5	3.1	27
3	26 Apr 77	4.5	13.4	103
1	16 May 77	11.5	9.5	89
1	3 May 78	6.5	11.8	97
2	18 May 77	2.0	14.4	104
2	3 May 78	6.0	13.0	105
6	25 Apr 77	4.6	12.2	95
7	25 Apr 77	4.5	6.0	46
5	25 Apr 77	15.0	8.1	80
3/A	26 Apr 77	3.5	5.4	40
8	25 Apr 77	9.4	12.2	105
4	26 Apr 77	4.5	8.4	65
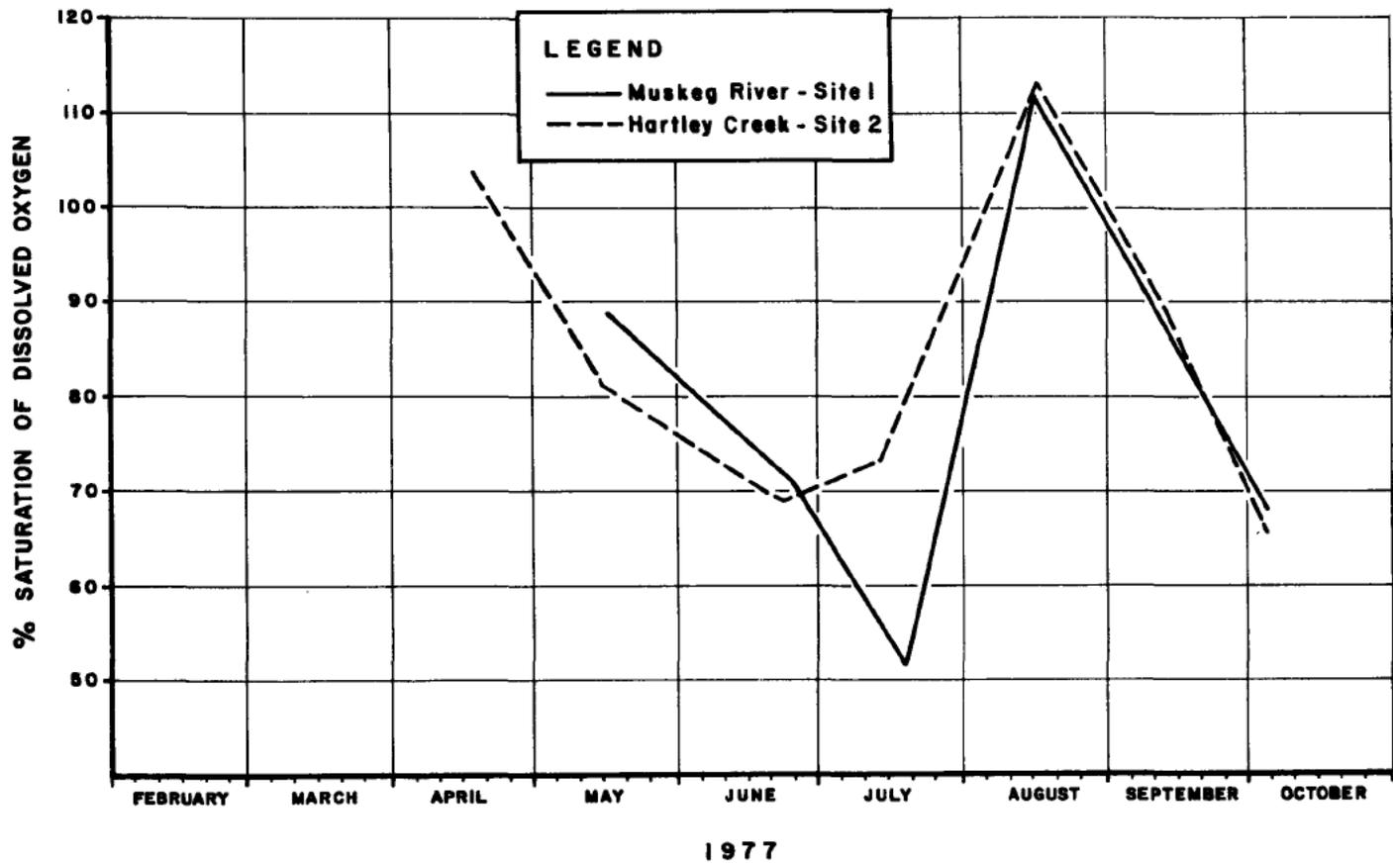
Figure 22. Variations of dissolved oxygen (% saturation) at Sites
1 and 2 (1977).
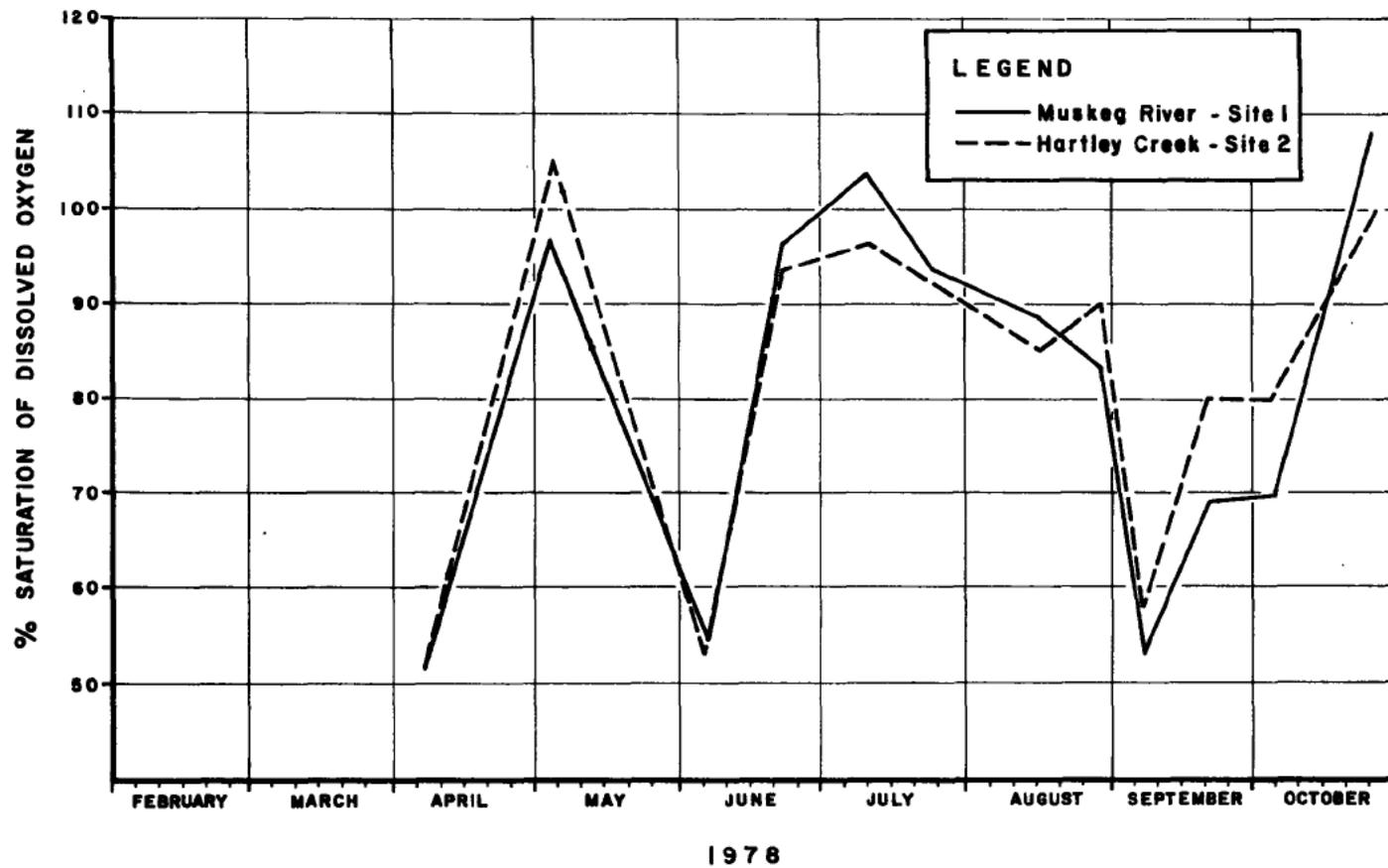
Figure 23. Variations of dissolved oxygen (% saturation) at Sites 1 and 2 (1978).

Table 9) at the start of the spring runoff period
(April or early May), and dropped steadily to an annual
midsummer low. The percent saturation curves for 1977
(Figure 22) showed that the streams at Site 1 and 2
were undersaturated from approximately 22 April 1977,
immediately following the start of the high flow
period, to 5 August 1977 and again after 1 September
1977. The late summer period of supersaturation lasted
approximately three weeks. On 18 June and 4 October
1977, the dissolved oxygen content dropped below 70% at
Site 2. The summer minimum for dissolved oxygen (51%)
for Site 1 occurred on 18 July 1977.

The 1978 data show that both Sites 1 and 2
were undersaturated, on 6 April, 5 June, and 7
September, to values as low as 51%, 53%, and 55%,
respectively.

The watershed maximum temperature of 22°C was
recorded in June at Site 10, located on the outlet to
Kearl Lake; the dissolved oxygen concentration measured
at the sampling time indicated the lowest value (1.8
mg/L) in the total study area. It is conceivable that
the timing of this, and other lows, is affected by
biological processes occurring within the watershed.

For shallow-running streams separated from
bogs, the heating of the water body is more efficient
and the equilibrium dissolved oxygen concentration is
easily achieved. Thus, the summer dissolved oxygen
minimum generally occurred at approximately the same
time as the maximum water temperature. But for streams
draining bogs or those with deeper channels (Table 11
and Appendix 7.1), the minimum dissolved oxygen
concentrations occur about one month (approximately end
of July to mid August) after the thermal high.

After the summer low, the dissolved oxygen
concentrations appear to shoot back up in mid-August

Table 11. Dates of thermal highs and dissolved
oxygen minima.

Site Number	Date of recorded Thermal High	Date of recorded DO Minimum
7/A	—	—
10	21 Jun 77	21 Jun 77
3	20 Jun 77	16 Aug 77
8	21 Jun 77	21 Jun 77
5	21 Jun 77	18 Jul 77
1	20 Jun 77	18 Jul 77
2	22 Jun 77	22 Jun 77
6	20 Jul 77	20 Jul 77
3/A	21 Jun 77	21 Jun 77
9	21 Jun 77	21 Jun 77
7	21 Jun 77	21 Jun 77
2/A	20 Jun 77	18 Jun 77
11	21 Jun 77	21 Jun 77
4	24 Jun 77 (18 Jul 77)	24 Jun 77
12	—	—
13	—	—
13/A	—	—
14	—	—

(at sites monitored, e.g., 1, 2, 3, 3/A, 6, and 9), and
then undergo gradual declines through the autumn.
Although no dissolved oxygen measurements were taken
during the winter time at any of these sites, because
of instrument freeze-up, it is probable that the
percent saturation under ice-cover is low (see Section
2.3.4.4). This is partly because of biotic respiration
and partly because the winter ice-cover reduces re-
aeration and photosynthesis.

3.3.4.4   <u>Variation of Calculated "Free" CO_2</u>. These
waters generally have lower dissolved carbon dioxide
and slightly higher pH (field measured values) during
the summer when photosynthetic activity by aquatic
vegetation is depleting dissolved carbon dioxide, than
in the winter, when photosynthetic processes are less
effective.

The calculated values for CO_2 were
consistently high in winter at all sites. Maximum
reported values for the winter ranged from a low of
26 mg/L (2 December 1977) at Site 2, on Hartley Creek,
to a high of 78.8 mg/L (18 February 1977) at Site 8.

Mid-winter flows, carrying high CO_2, indicate
microbial respiration and/or suggest the possibility of
inputs from muskeg drainage or groundwater. This
hypothesis is supported by data obtained from a
27 February 1977 sampling of the Muskeg River at the
mouth (Site 7/A), which showed a specific conductance
of 1360 µS/cm, a pH of 7.4, and a large amount of CO_2
(60.8 mg/L).

As indicated earlier, seasonal trends for
dissolved oxygen or carbon dioxide have not lent
themselves to easy interpretations. Anomalies do
exist. For instance, high CO_2 values were observed
during the summer of 1976 at Sites 7, 9, and 10. The

dry summer of 1976 gave rise to water quality
conditions reflecting summer lowflows.

In the case of Sites 7 and 9, the low pH (6.5
and 6.9, respectively) and high iron and humic acid
concentrations suggest the presence of organic acids
and other products of biochemical reactions, which tend
to be acidic, being carried into the streams. The iron
could be retained in solution as a complex with the
organic acids.

The anomaly (in values of chemical oxygen
demand, turbidity, and non-filterable residues)
observed at the Kearl Lake outlet (Site 10) is probably
caused by the decomposition of phytoplankton and the
respiration of aquatic organisms within the lake.

3.3.4.5   Variation of Dissolved Oxygen and Organic
Carbon Concentrations. Variations in total and
dissolved organic carbon concentrations and chemical
oxygen demand (COD, expressed in terms of oxygen
equivalent) were determined to assess the magnitude of
oxidizable material load being carried in these
streams.

It appears that, for a significant number of
samples, at most sites, only a small amount of the
organic carbon was tied up in suspended matter, since
the values of total organic carbon (TOC) and total
dissolved organic carbon (TDOC) at Sites 1, 2, 3, 3/A,
4, 5, 6, 7, 7/A, 8, 9, 10, and 11 were very close
(Figures 24 to 26) and showed seasonal patterns
resembling most dissolved substances in the study
period. These patterns (Figures 24 and 25) are
characterized by relatively higher winter values, a
sharp decline during the March-April spring runoff
period, and a recovery by mid-May. These parameters
(TOC and TDOC) underwent slight but steady declines

14 - 29 OCTOBER 1976

24 - 26 JANUARY 1977

18 - 28 APRIL 1977

18 - 20 JULY 1977
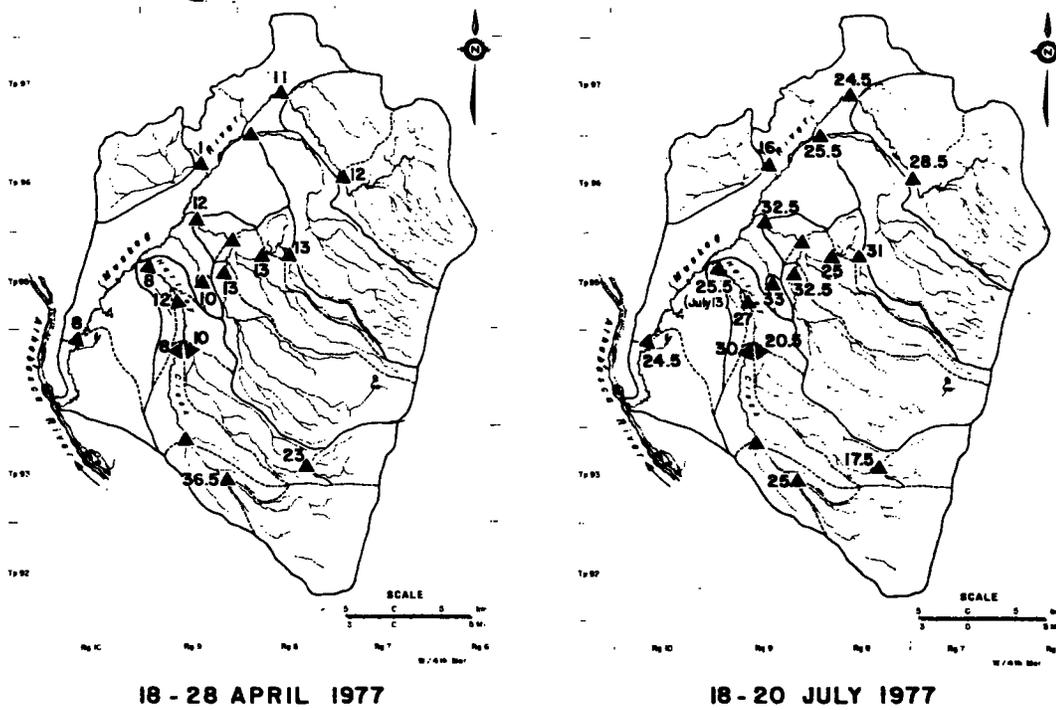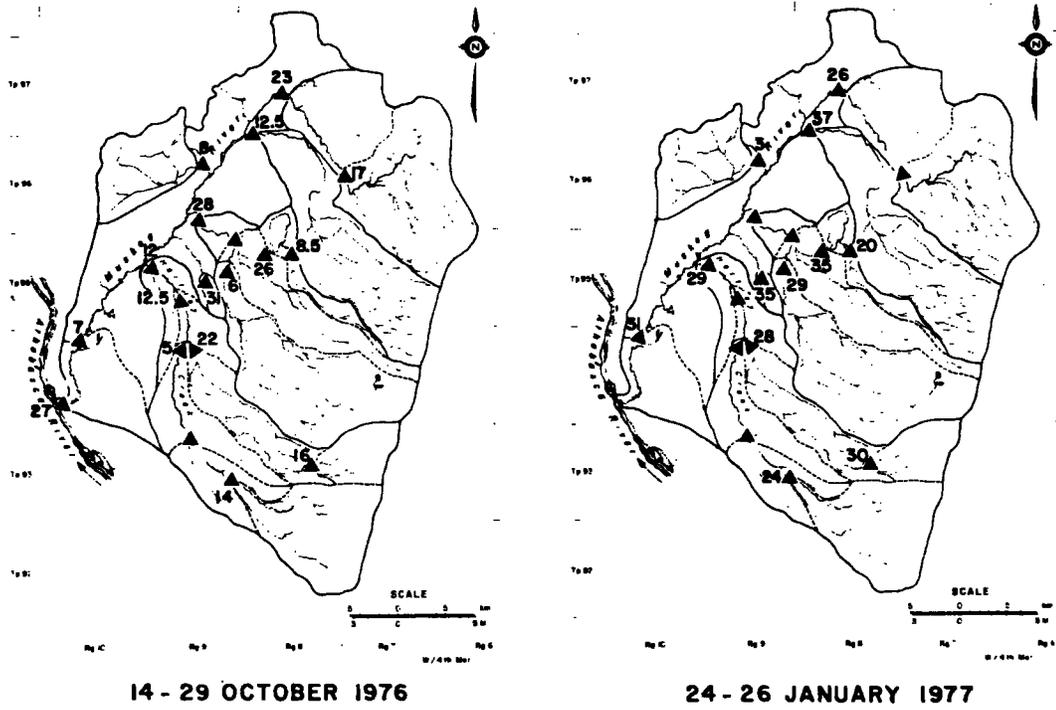
Figure 24. Areal variations in total dissolved organic carbon.
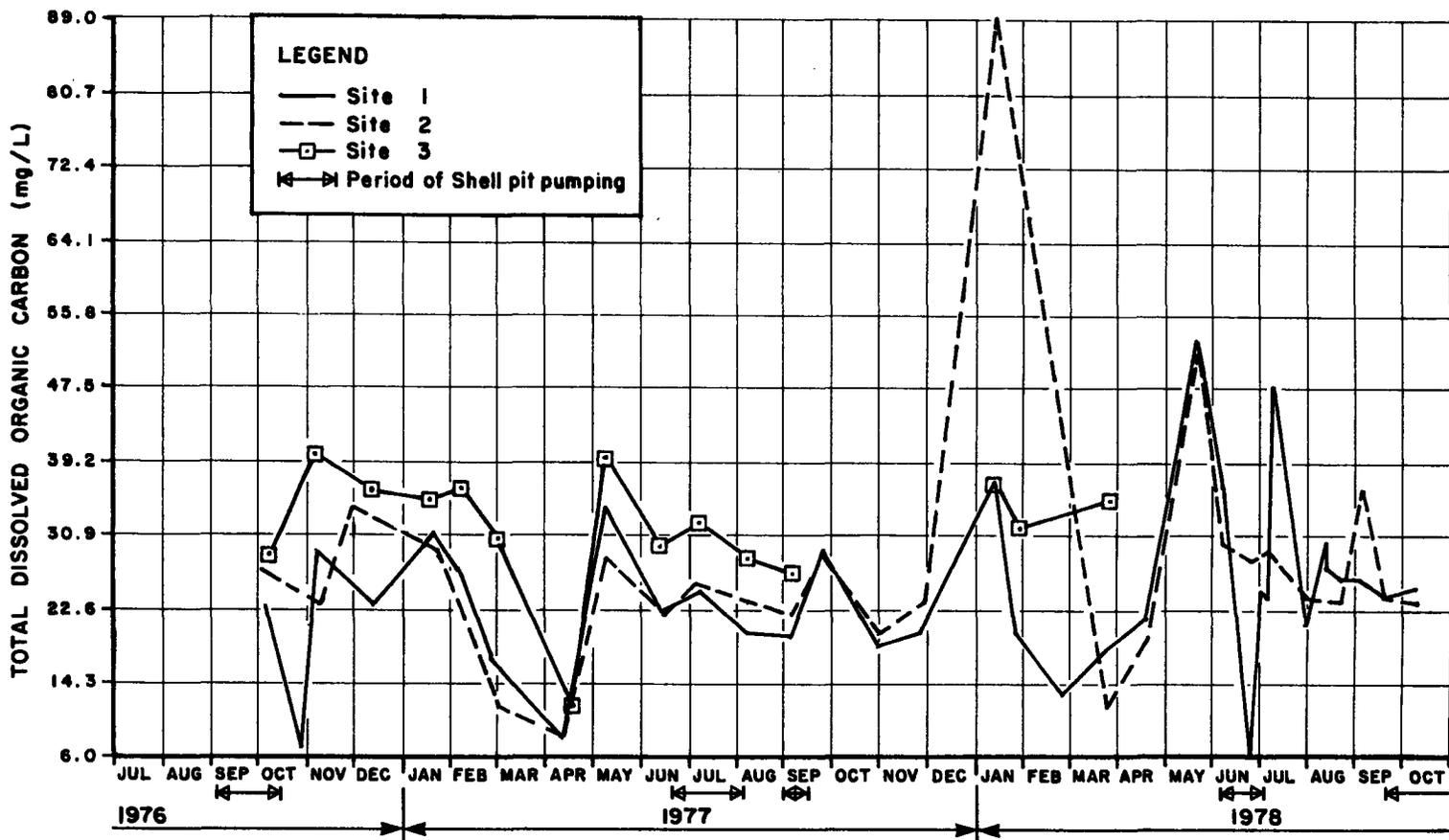
Figure 25. Variations in dissolved organic carbon at Sites 1, 2, and 3.

14 - 29 OCTOBER 1976

24 - 26 JANUARY 1977

18 - 28 APRIL 1977

18 - 20 JULY 1977
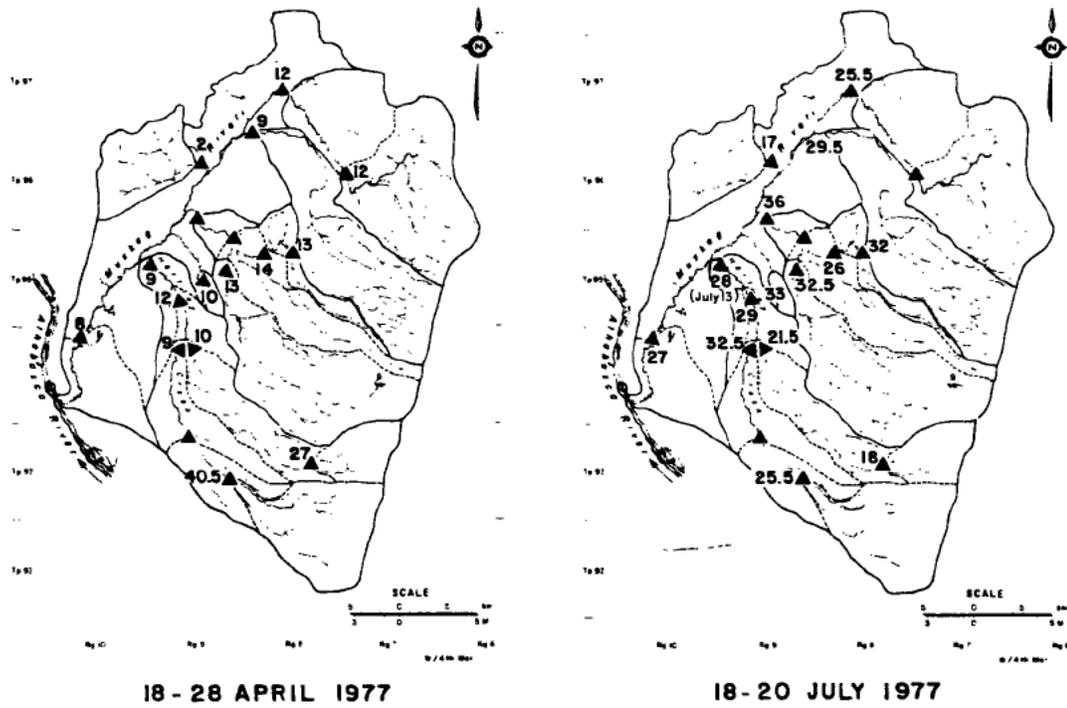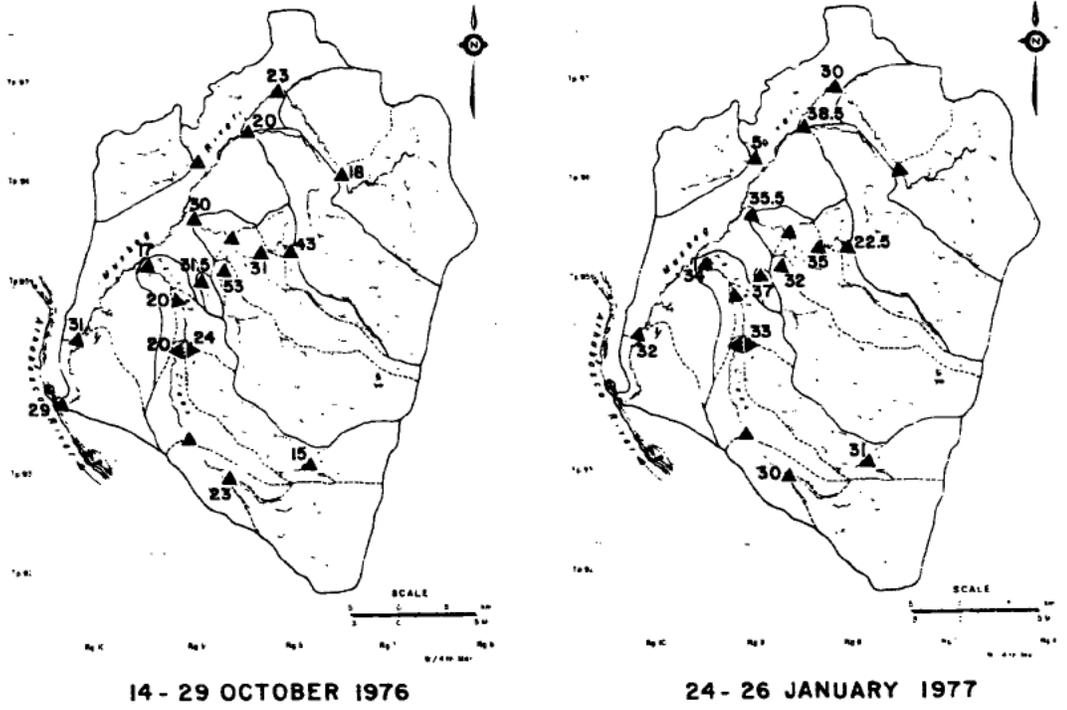
Figure 26. Areal Variations in total organic carbon.

(interrupted occasionally by storm runoffs) through the summer and fall, but with no apparent correlation with microbial biomass.

Although variations in the carbon content of the waters at most sites were found to be relatively small, those of the COD (Figures 27 and 28) were much larger. The relationship between TOC and COD values were not strong enough to obtain estimates of organic loads from COD determinations. Furthermore, trends in the results of COD determinations did not bear any relationship to those of dissolved oxygen and may not correspond to values obtainable by BOD determinations.

3.4   VARIATIONS OF MICROBIAL POPULATIONS AND
           NUTRIENTS CONCENTRATIONS

3.4.1   Introduction

Micro-organisms, which utilize organic matter as food and decompose them to simpler compounds, need oxygen to maintain these biochemical reactions at maximum rates:

$$\text{Organic Matter} + O_2 \xrightarrow[\text{micro-organisms}]{} \begin{array}{l}\text{Biochemical} \\ \text{Decomposition Products} \\ \text{(primary products include)} \\ CO_2, \ NO_2^-, \ NO_3^-, \ \text{and} \ SO_4^{2-}\end{array}$$
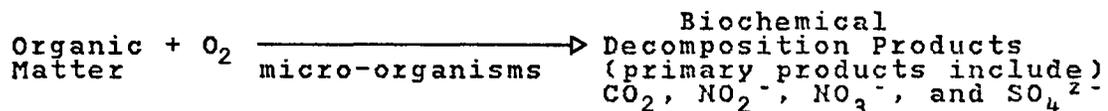
Thus, the activity of microbial components (bacteria, algae, fungi, etc.) is, in some respect, the principle agent determining the water chemistry and, therefore, the assimulative capacity of a stream.

3.4.1.1   Microbial Biomass. The data collected by this study was limited to determining the number of planktonic (floating) bacteria per millilitre, as represented by the standard plate count.

AOSERP studies (Lock and Wallace in prep.; Costerton and Geesey 1979) have determined sessile and sedimentary populations and shown that these may exceed
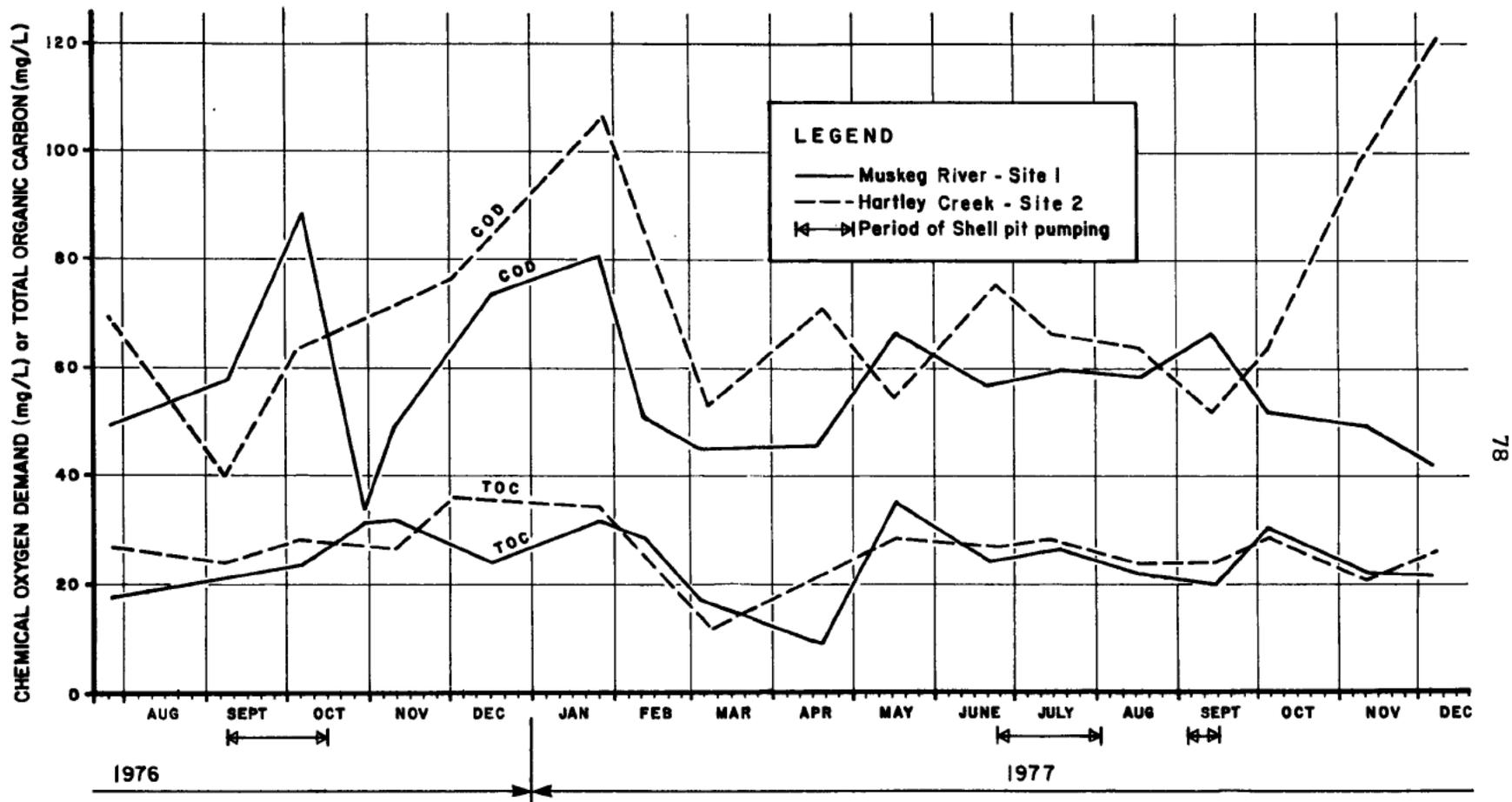
Figure 27. Seasonal variations of COD and TOC (Sites 1 and 2).
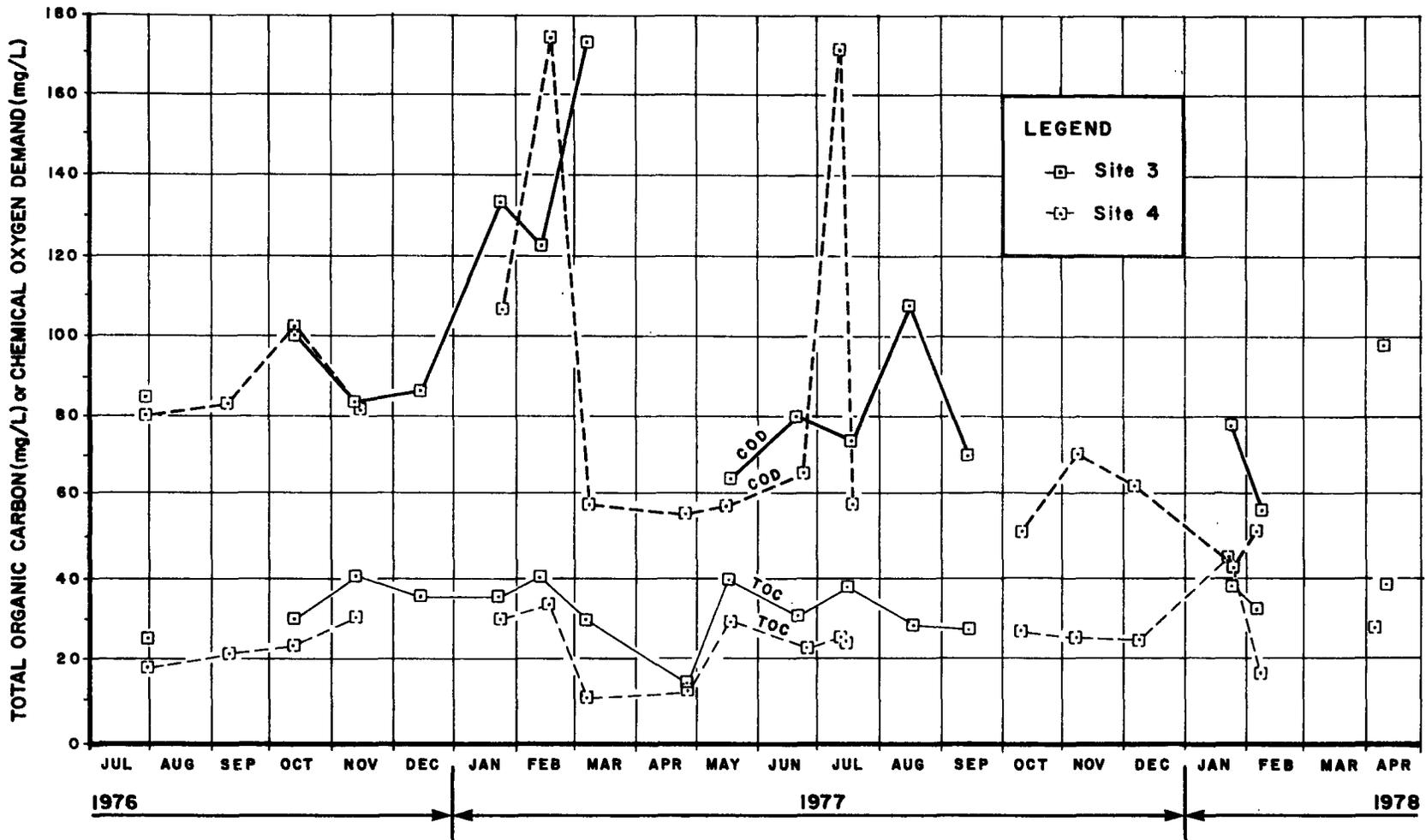
Figure 28. Seasonal variations of TOC and COD (Sites 3 and 4).

the planktonic by several orders of magnitude. Results
of some of these studies have been cited to supplement
the present data.

An inverse relationship seems to emerge
(Figures 29, 30, and 31) between planktonic bacteria
and dissolved oxygen, at Sites 1 and 2 but not at Site
3.

The data from Site 1 were very limited and
probably influenced by effluents from the Shell Pit.
What data were available showed trends similar to those
of Hartley Creek, Site 2.

In contrast to Sites 1 and 2, Site 3 (Figure
31) registered sharp declines in both the total plate
count and dissolved oxygen on 16 August 1977. On that
same day, the water at Site 3, located in a bog,
registered a high COD (108 mg/L) and a peak in the
percent (30%) ammonia-nitrogen in total Kjeldahl
nitrogen. The percent of ammonia-nitrogen in total
Kjeldahl nitrogen on 16 August 1977 were 25% and 8.3%
for Sites 1 and 2, respectively; and both corresponded
to peaks. (See section 3.4.2.5.3, Figures 52 and 53
for further detail.)

Two AOSERP studies (Hartland-Rowe et al.
1979; Lock and Wallace in prep.) (Figure 32) have
established that the epilithon, attached communities,
of Hartley Creek (study site located on Hartley Creek
at approximately 4 and 6 km, respectively, from the
confluence with the Muskeg River), increased after ice-
out up to a maximum of around 1 to 2 x 10^8 bacteria
cm^{-2} in July, then fell dramatically to below 10^7
bacteria cm^{-2} by mid-August. The population remained
this low for about two weeks before rising gradually
again to a maximum of 1 x 10^8 bacteria cm^{-2} in mid-
December.
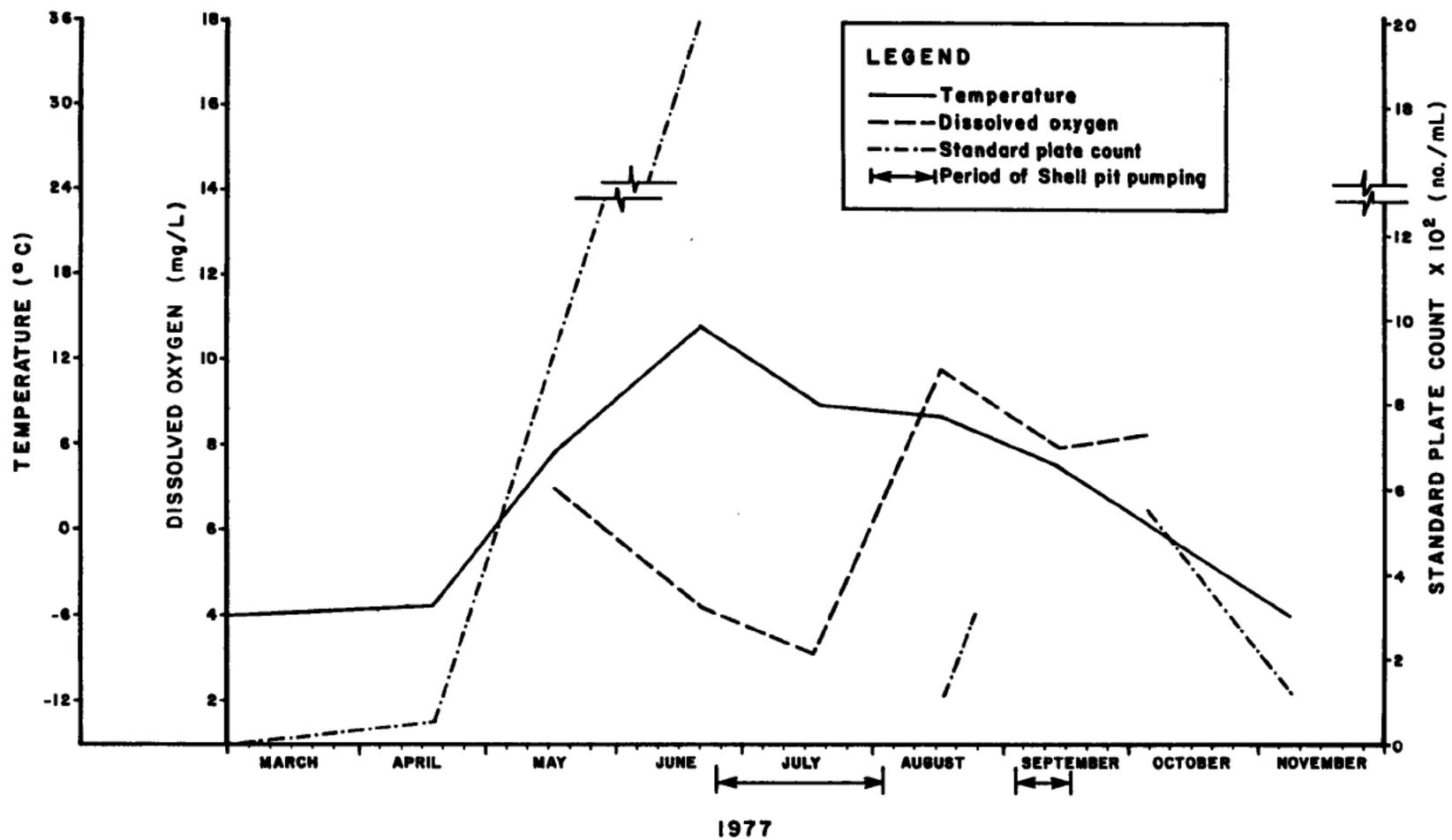
Figure 29. Variations in temperature, dissolved oxygen, and standard plate count during open water season (Site I).
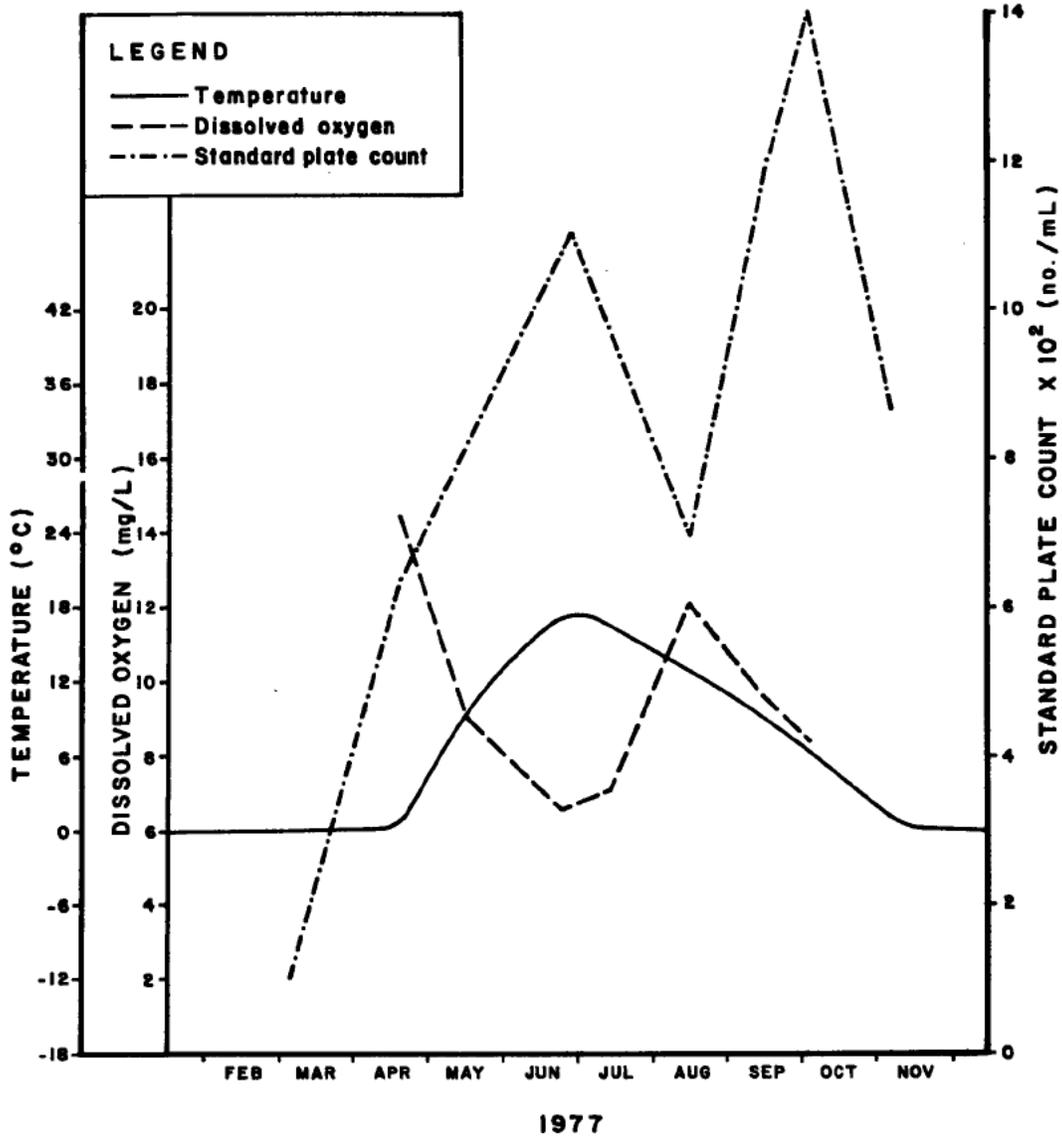
Figure 30. Variations in temperature, dissolved oxygen, and standard plate count during open water season (Site 2).
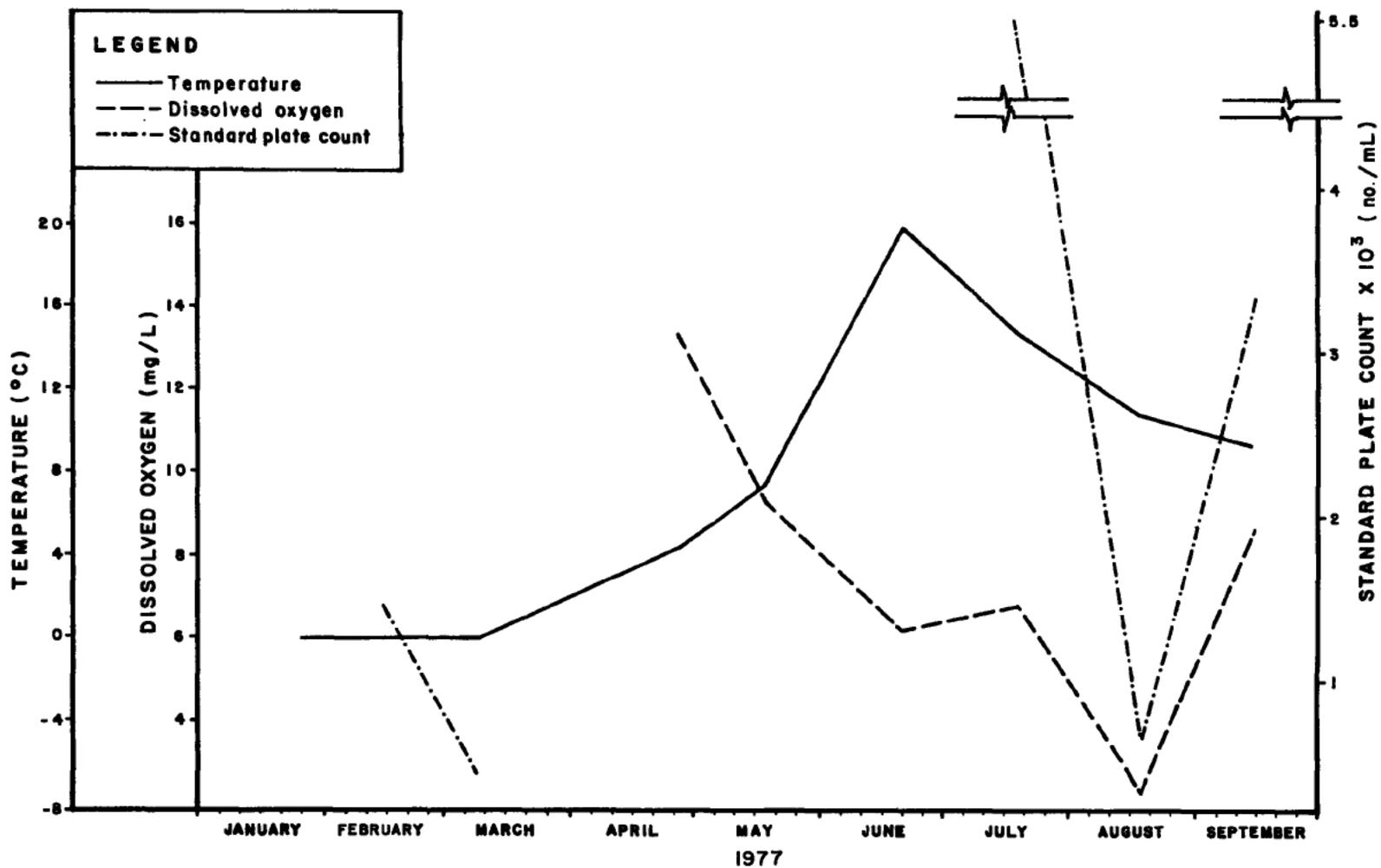
Figure 31. Variations in temperature, dissolved oxygen, and standard plate count (Site 3).
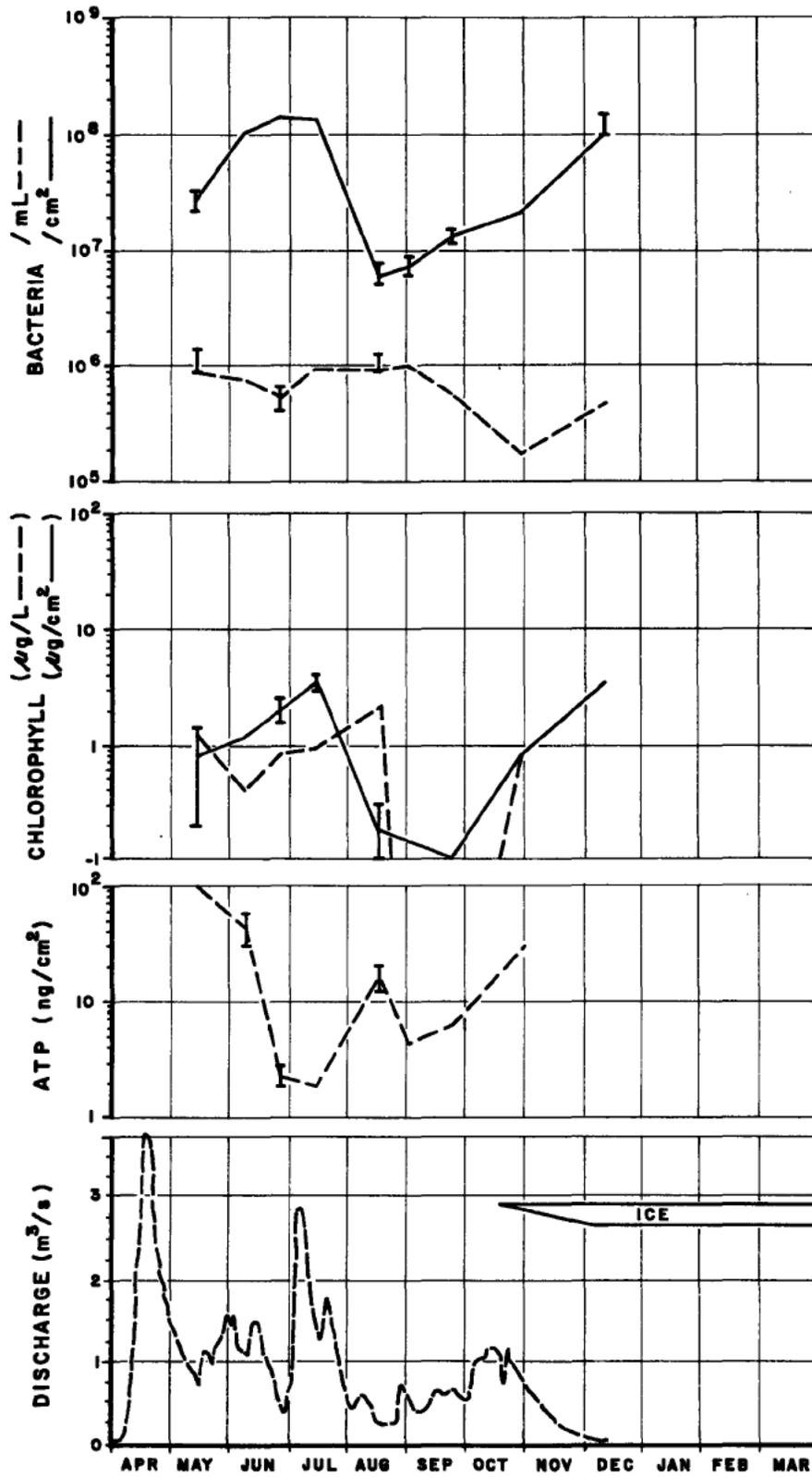
Figure 32. Epilithic and suspended microbial biomass determinations and discharge measurements for Hartley Creek (Lock & Wallace in prep.).

The Lock and Wallace (in prep.) study also
reported trends for the algal biomass as determined by
chlorophyll 'a', showing that chlorophyll 'a' reached a
peak around mid-July of 3.3 g cm^{-2} and declined from
early August to less than 0.1 g cm^{-2} in September.
The chlorophyll 'a' reading then rose again and reached
3.0 g cm^{-2} on 8 December 1977.

The living biomass indicator, ATP (adenosine
tri-phosphate), which responds to all organisms that
are living and thus contain a pool of ATP (i.e.,
bacteria, algae, fungi, protozoa, micro- and
macroinvertebrates), showed (Lock and Wallace in prep.)
a pattern parallel to the dissolved oxygen curve
recorded in the present study; starting relatively
high, just after ice-out, and then declining until the
end of June (early July) followed by an increase which
lasted until mid-August. After the August peak, the
ATP dropped slightly before rising again.

Similar studies conducted (Lock and Wallace
in prep.) at the Muskeg River Site 1 found the same
trends established for Hartley Creek.

3.4.2   Nutrients Chemistry

3.4.2.1   Introduction. The period (May through August)
of moderate temperatures is generally accompanied by
microbial production, decomposition of organic
materials, and lower dissolved oxygen due, mostly, to
biotic respiration and lower oxygen solubility.

A number of studies have attempted to
identify factors that influence rates of processing of
leaves or dissolved organic matter by stream bacteria.
Kanskik and Hynes (1971) and Egglishaw (1968) have
shown that temperature and calcium and nitrate
concentrations in the water affect decomposition rates.
It was also indicated that phosphate phosphorus has a

greater effect than nitrogen, as a limiting agent, in increasing microbial production than the rate of decomposition of some leaves. An AOSERP study by Costerton and Geesey (1979), however, found no apparent correlation between total organic carbon, total Kjeldahl nitrogen or total phosphate phosphorus, and bacterial numbers in the Athabasca River.

Various components of the nitrogen, phosphorus, and carbon cycle, with corresponding figures of dissolved oxygen (when available), will be presented and discussed for Sites 1 and 2. The discussion will show that some of the fluctuations in the concentration of individual parameters are interrelated and in most cases reflect intimately the changes in the oxygen regime and phytoplankton biomass or vice-versa.

3.4.2.2 Potassium. Analyses of soil samples collected (0 to 120 cm deep) from within the watershed showed moderately high (0.1 mg/100 mg is considered normal) exchangeable potassium ion concentrations; the values ranged from 0.01 to 0.5 mg of potassium per 100 gm of soil (Turchenek and Lindsay 1979) Table 2. Furthermore, the precipitation that passes through the forest canopy during the growing season and reaches the soil as throughfall or stemflow is reportedly (Likens et al. 1977) greatly enriched in potassium and other nutrients.

The measured concentrations of potassium ion in stream waters of this watershed do not follow the pattern established for the other major dissolved ions. In relationship to seasonal biological control, stream water concentrations of potassium are generally low during periods of plant growth, because the biotic portion of the ecosystem is actively extracting

potassium from the soil and drainage waters (Figures 33 to 36).

In the autumn and winter, aquatic plants die and deciduous plants enter a dormancy period and lose their leaves. In general, potassium ion concentrations in the stream waters begin to rise in the autumn, when there is a reduction in biological activity, and attain maximum concentrations in the early spring. Kearl Lake Outlet (Site 10) attained its maximum concentration in mid-winter (Figure 34). The fact that the highest potassium ion concentrations normally occur at the same time as the stream spring runoff is considered only coincidental and should not be construed to suggest a direct relationship between stream discharge and concentrations of potassium ion. In fact, this study did not find any such relationship at any of the study sites.

In the Muskeg River basin, the following values (Figures 33 to 36) provide some idea on the temporal range for potassium concentrations during the growing season: May (0.6 to 1.4 mg/L), June (0.1 to 1.7 mg/L), July (0.01 to 0.8 mg/L), August (0.49 to 0.8 mg/L); while January (0.9 to 4.6 mg/L), March (1.2 to 3.5 mg/L), and April (1.1 to 2.6 mg/L) represent the dormancy period. Except for the periods September 1976 and March, April, and June 1977, Kearl Lake Outlet recorded the highest concentrations of potassium in the basin.

3.4.2.3 Phosphorus. Numerous studies have singled out phosphorus as the nutrient most frequently controlling eutrophication. The most predominant forms of phosphorus found in water are: phosphorus anions ($H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}), complex phosphate compounds (inorganic polymers and organic phosphate compounds),
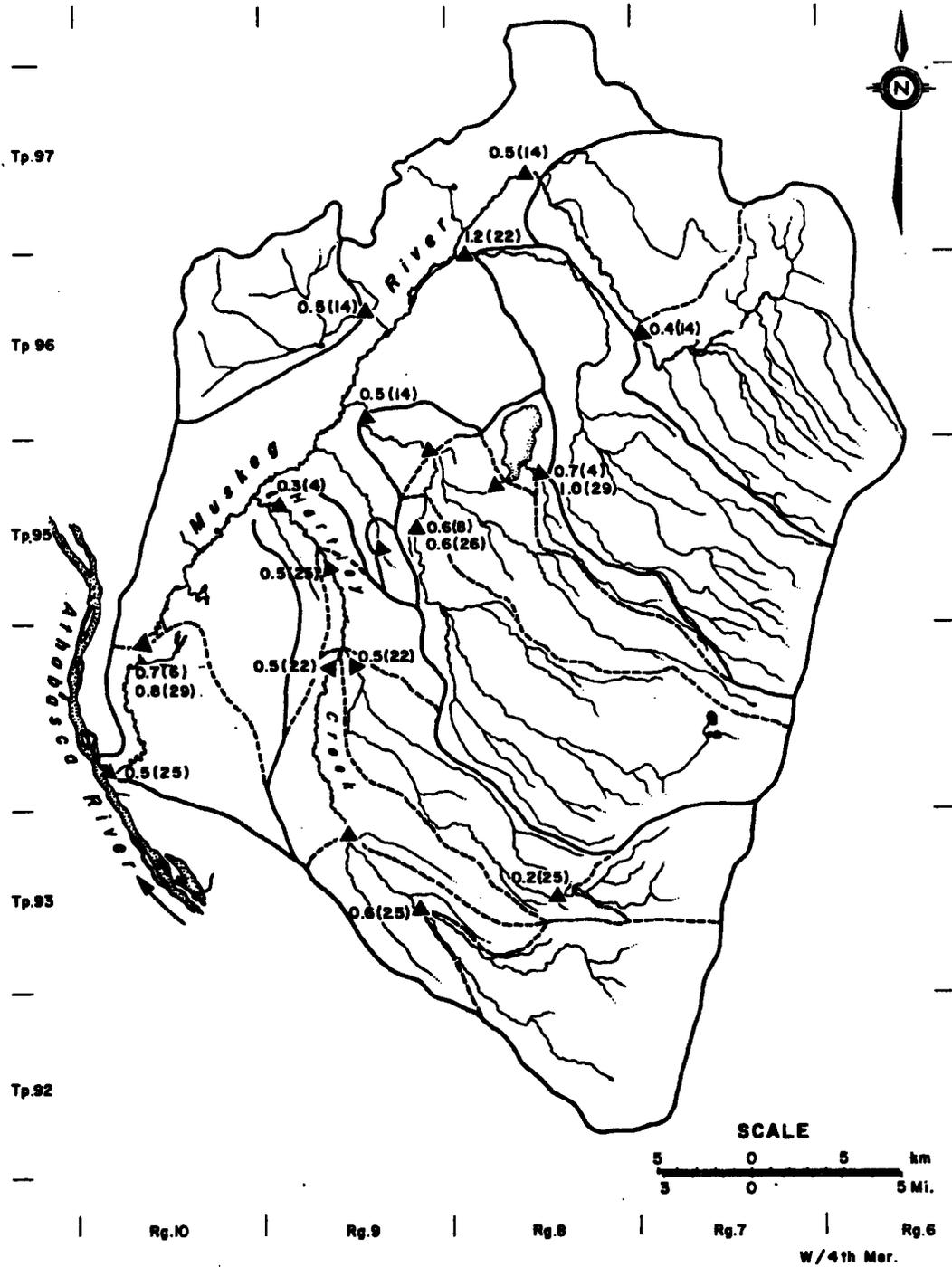
4 - 31 OCTOBER 1976

Figure 33. Areal variation in potassium concentrations; October 1976.
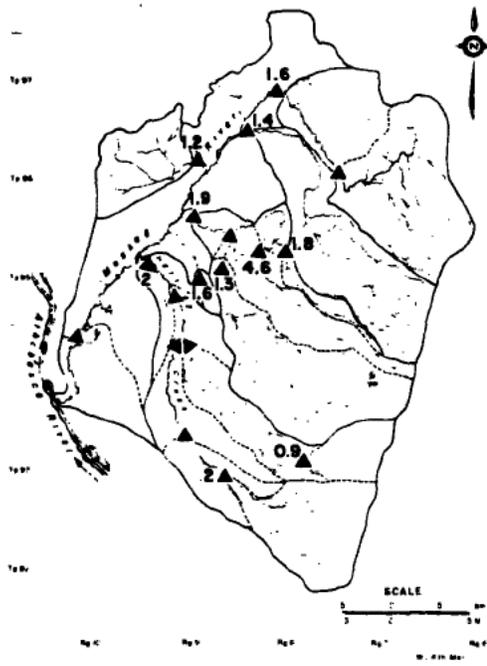
24 - 26 JANUARY 1977

3 - 18 MARCH 1977

18 - 28 APRIL 1977

Figure 34. Areal variation in potassium concentrations;
January, March, April 1977.

16-18 MAY 1977

20-24 JUNE 1977

13-20 JULY 1977

4-11 OCTOBER 1977
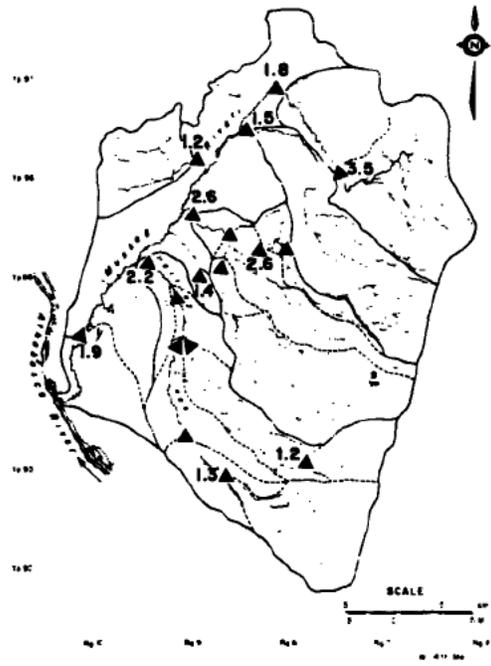
Figure 35. Areal variation in potassium concentrations;
May, June, July, October 1977.
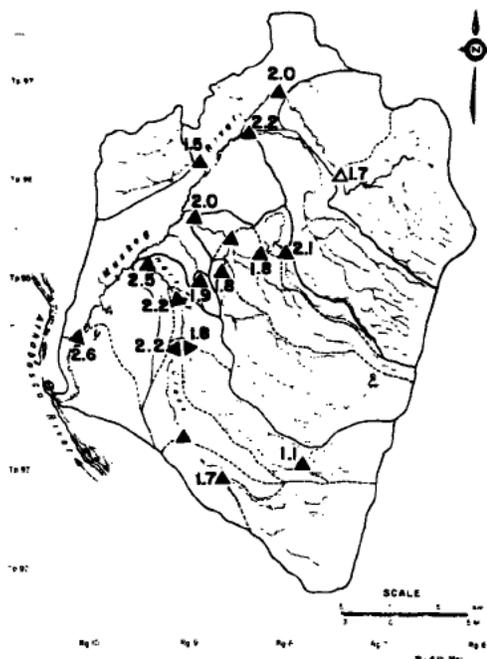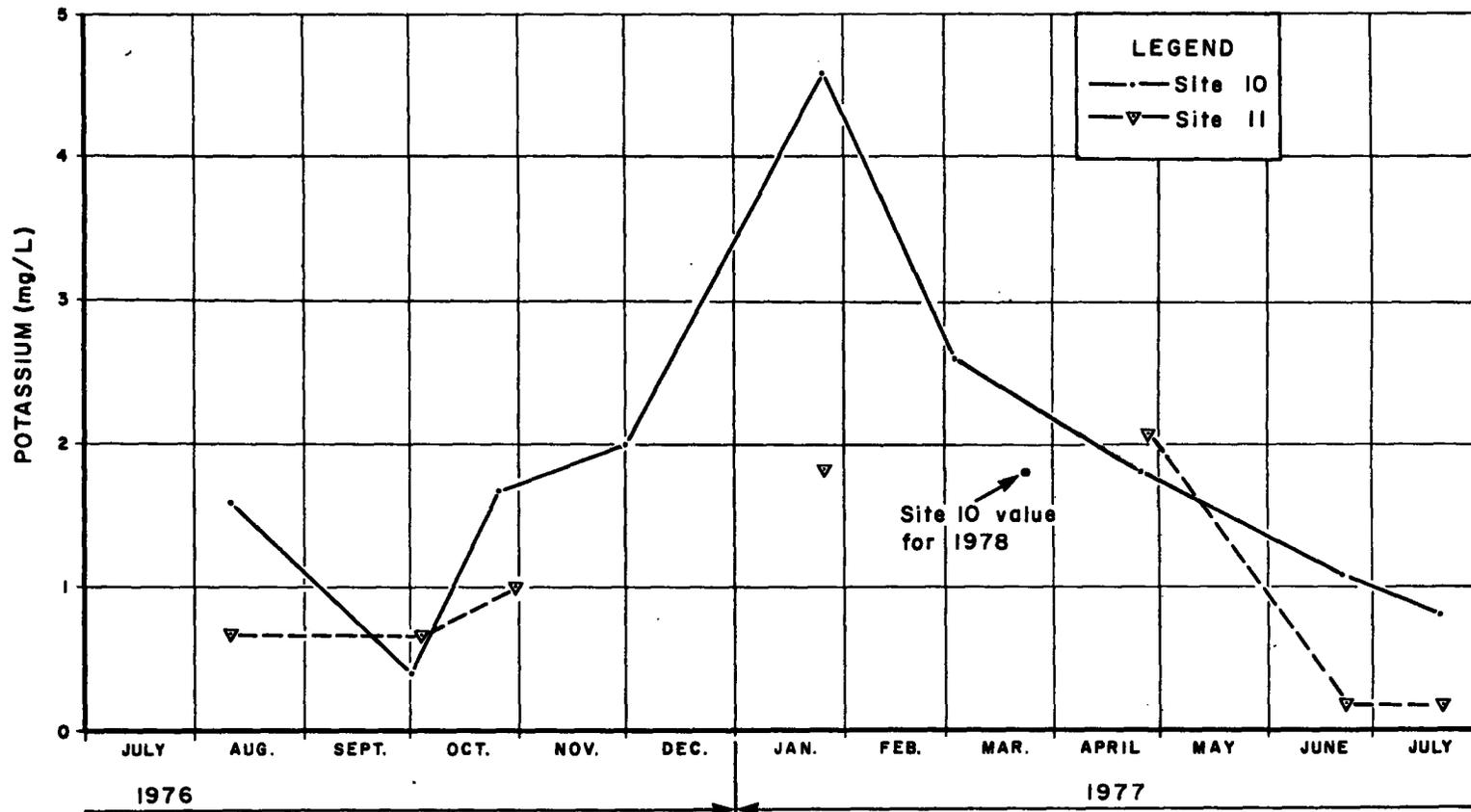
Figure 36. Variations in potassium concentrations at Kearl Lake, Sites 10 and 11.

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complexes with metal ions, and colloidal particulate
material. The concentration of phosphorus in these
forms vary daily, seasonally, and with flows.

The low dissolved phosphorus concentrations
observed in the summer at most sites in this watershed
were partly because of the adsorption of phosphate ions
on sediments, and partly because of the utilization of
phosphorus by aquatic vegetation (especially free
floating types, e.g., algae) which depend on the
presence and availability of dissolved phosphorus and
nitrogen compounds for its nutrient supply.

Orthophosphate phosphorus values in this
watershed ranged from less than 0.003 mg/L to 0.09
mg/L; the higher values being recorded at Sites 2, 3,
3/A, 8, 10, and 12.

The total phosphate phosphorus values, on the
other hand, ranged from less than 0.005 mg/L to
0.56 mg/L, with the higher maximum values occurring at
Sites 8 (0.56 mg/L), 13/A (0.50 mg/L), 9 (0.47 mg/L), 2
(0.33 mg/L), 5 (0.34 mg/L), 3/A (0.32 mg/L), 12 (0.32
mg/L), and 11 (0.31 mg/L). It appears that these
nutrients are greatly utilized, precipitated, or
diluted by the time they reach the Muskeg River, Sites
1 and 7/A. The maximum total phosphate phosphorus
concentrations recorded at these sites were 0.09 and
0.07 mg/L, respectively.

Generally, the highest total phosphate
phosphorus was found in the winter when suspended
matter, such as inorganic sediments and plant debris,
is highest in the streams. This is partly because
soluble phosphates, which are generally returned to the
water by dying algae, tend to be adsorbed by suspended
material. The release of phosphate by algae is
especially noticeable after a cold temperature die-off,
a process that could start sometime in October (Lock

and Wallace in prep.). Because the sediments, especially hydrous Fe and Al oxides, $CaCO_3$, and apatite (Syers et al. 1973), serve as a "sink", the release of inorganic phosphorus from sediments plays a vital role in controlling the levels to which overlying waters can replenish dissolved inorganic phosphorus.

This study found that seasonal trends in, and values of, total phosphate phosphorus at the Muskeg River, Site 1, paralleled (or matched) those of Hartley Creek, Site 2 (Figures 37 and 38), except for the 24 January 1978 sample, when Site 2 gave a very high total phosphate phosphorus value (0.170 mg/L).

In addition to seasonal trends, dominated by biotic utilization and/or sedimentation, there appear to be some coincidences between slightly higher total phosphate phosphorus values and Shell Pit pumping periods (Figure 37). The concentration of total phosphate phosphorus in the Shell Pit discharges differed only slightly from the stream values recorded for the Muskeg River, Site 1. Shell Pit pumpages are low in sediments but could carry carboxylic acids which would react with particulate Ca^{+2-}, Al^{+3-}, or Fe^{+3-} phosphates to form soluble hydrogen phosphate ($HPO_4{}^{2-}$) or dihydrogen phosphate ($H_2PO_4{}^{-}$) ions. The only occasion when total phosphate phosphorus did not increase at Site 1 during a Shell Pit pumping period was between 20 June and 13 September 1977. The field measured pH, temperature, and dissolved oxygen at Site 1 during this period (Table 12) ranged from pH 7.9 to 9.0, 11.0 to 20.5°C, and 52 to 12%, respectively. The high alkalinity and aerobic conditions probably resulted in sulphide oxidation or precipitation. Furthermore, dilution by summer storm runoffs and utilization of phosphate phosphorus by aquatic
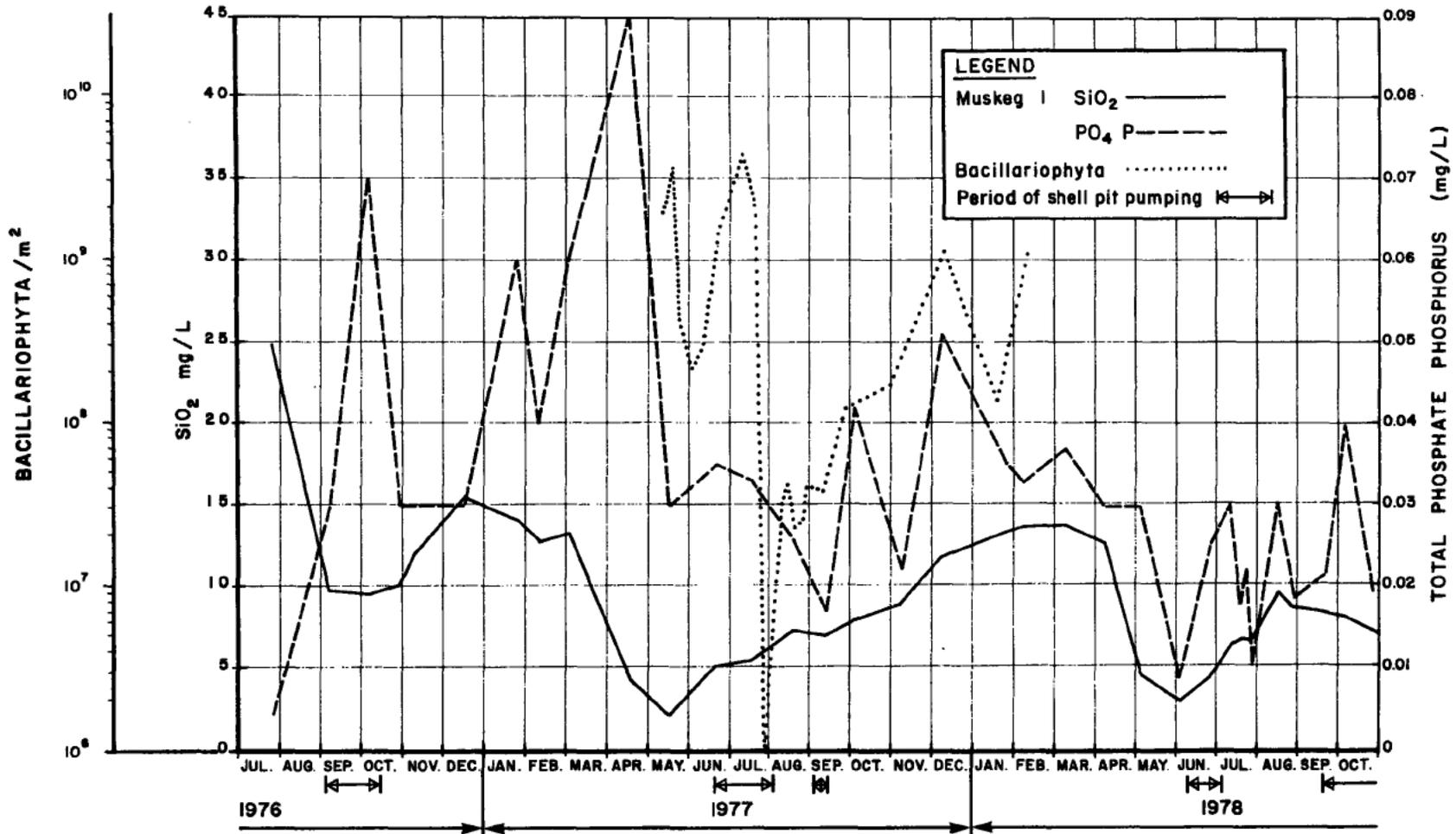
Figure 37. Variations of total phosphate phosphorus, reactive silica concentration, and numbers of bacilleriophyta (Site I).
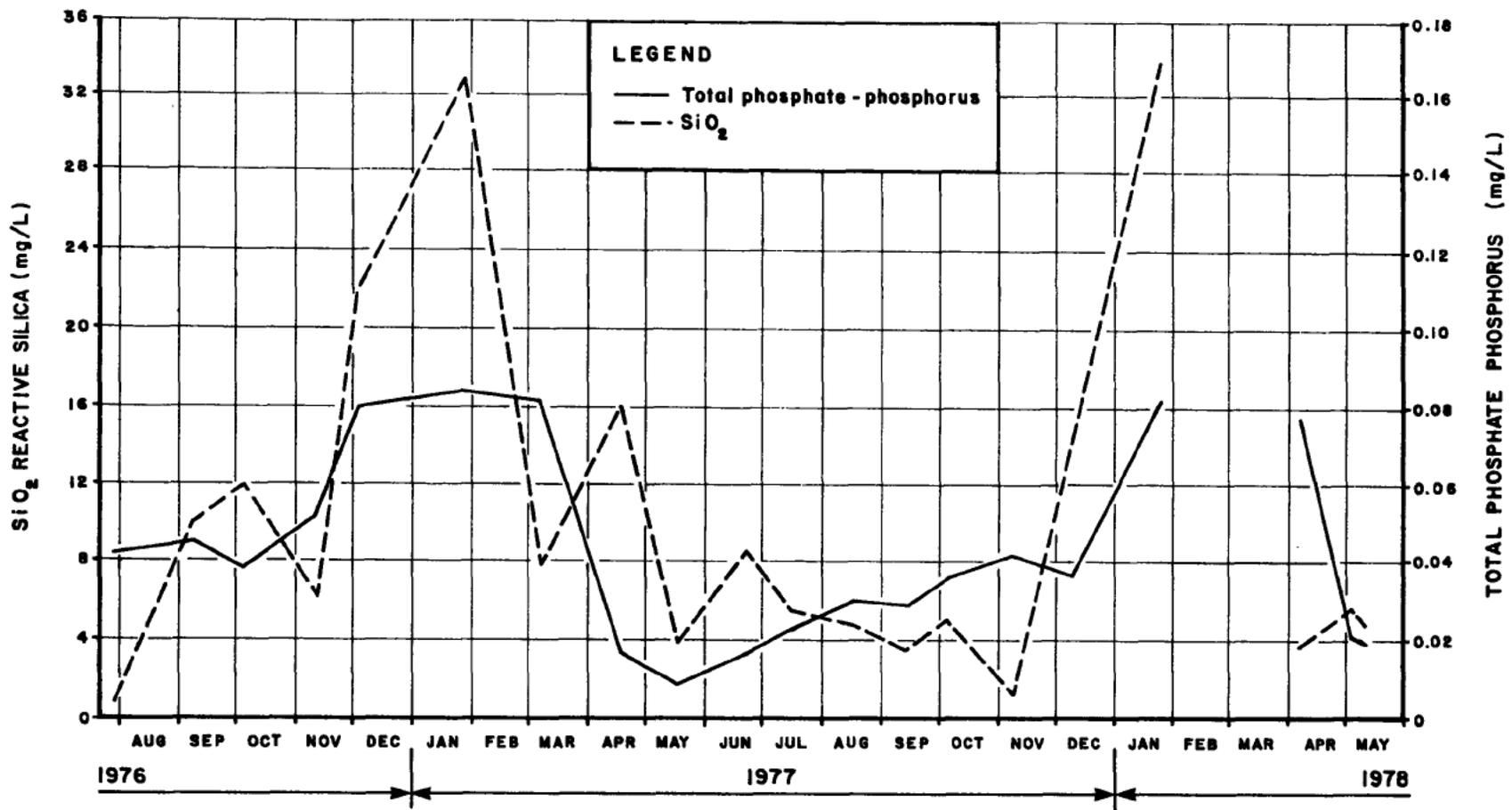
Figure 38. Variations of total phosphate phosphorus, and reactive silica concentration (Site 2).

Table 12. Field measured pH, temperature and
            dissolved oxygen (Site 1).

Date	pH	Temp.	DO(mg/L)	DO(% Saturation)
16 May 77	—	11.5	9.5	88
20 Jun 77	8.7	20.5	6.3	71
18 Jul 77	7.9	15.0	5.2	52
16 Aug 77	9.0	14.5	11.5	112
13 Sep 77	7.9	11.0	10.0	91

vegetation would tend to reduce the amount of dissolved phosphate phosphorus.

While there appear to be complete sets of data for phosphorus (as total phosphate and orthophosphate) at all sites monitored in the study, problems related to analyses of the samples do not justify efforts to develop seasonal and areal patterns for phosphorus. The accuracy and precision of the analytical data reported between July 1976 and June 1977 cast doubts on their usefulness. The data for orthophosphate seldom showed variations above the "coefficient of variation" produced in duplicate analyses. After June 1977, the analytical laboratory lowered its detection limits for phosphorus. Yet, there still appeared to be no strong seasonal pattern to the data.

In an effort to extract valuable information from the available data, the phosphorus data will be discussed in further detail along with the nitrogen analysis data.

3.4.2.4   Reactive Silica. Silica (dissolved or colloidal) is a major nutrient for the diatom algae, Bacillariophyceae. As a result, diatoms have significant impact on silica cycling (Carlisle 1974).

The major source of silica is from the degradation of alumino-silicate minerals. The amount of silica in solution is chemically modified by surface adsorption (on inorganic particulates) of silicic acid which reduces solubility; and biochemically, by diatoms which utilize large quantities of silica in the synthesis of their cell structure. The effects of these processes are apparent in the relative levels of silica at the inlet compared to those at the outlet of

Kearl Lake (Figure 39). Kearl Lake does not receive
significant inflow from other sources.

Unlike other dissolved substances in the
watershed, concentrations of reactive silica tended to
follow a relatively stable cycle (Figure 40 and 41), a
cycle only slightly affected by streamflow.

Following the spring runoff period, there is
a very rapid decline in the concentration of dissolved
silica. Spring lows, observed between late April and
early June (Figure 41), varied between 0.5 and
9.0 mg/L. This period is probably dominated by
intensive assimilation by diatoms and subsequent
sedimentation by them. The process appears to be
removing silica more rapidly than is being supplied by
surface and groundwater flows. Other studies (Wetzel
1975) have reported that drops in silica concentrations
reflect a response by the grazing diatom populations to
changes in other nutrients (possibly nitrogen and
phosphorus) (Figure 37), intensity of light, and
temperatures. Therefore, the mid-May minimum values of
silica, observed in the Muskeg River basin sites,
should reflect the timing of the maximum number of
diatoms. Unfortunately, the only site monitored (Lock
and Wallace in prep) for diatom populations was Site 1,
and attempts at direct analogy were interrupted by
Shell Pit pumpages.

After spring, and consequent declines in the
population of diatom algae, silica is very gradually
(Figures 37, 38, and 40) released to the overlying
waters in the watershed. The concentrations finally
reach a maximum value in the winter. The winter highs
varied between 9.4 and 29.8 mg/L (Figure 40). The
chemical desorption reaction, contributing to the
recovery, is diffusion-controlled and thus very slow.
But the dissolution of suspended silica can be
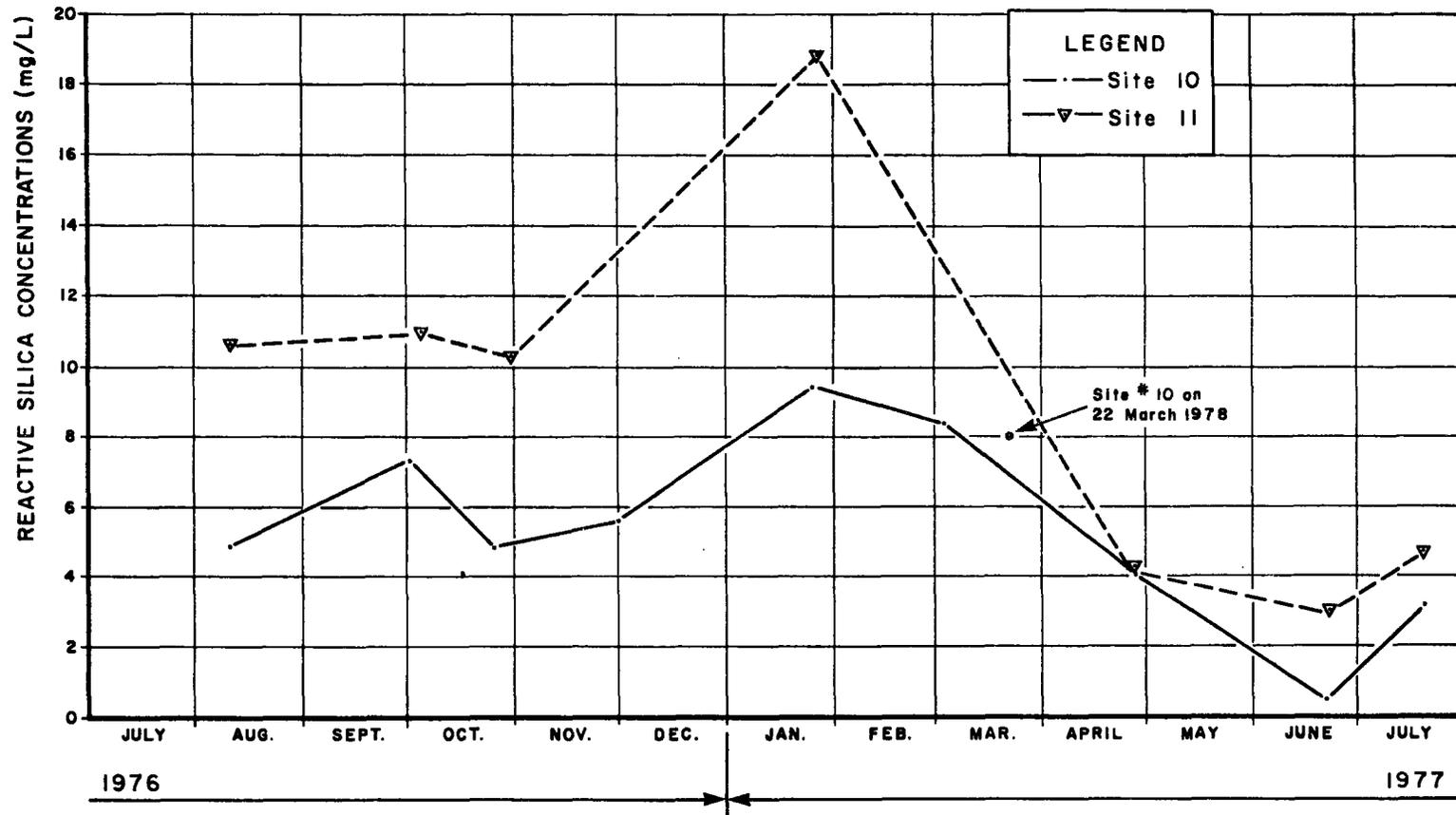
Figure 39. Variations of reactive silica concentrations at Kearl Lake, Sites 10 and 11.

14-29 OCTOBER 1976

24-26 JANUARY 1977

18-20 JULY 1977

Figure 40. Areal variations in reactive silica concentrations; October 1976; January, July 1977.
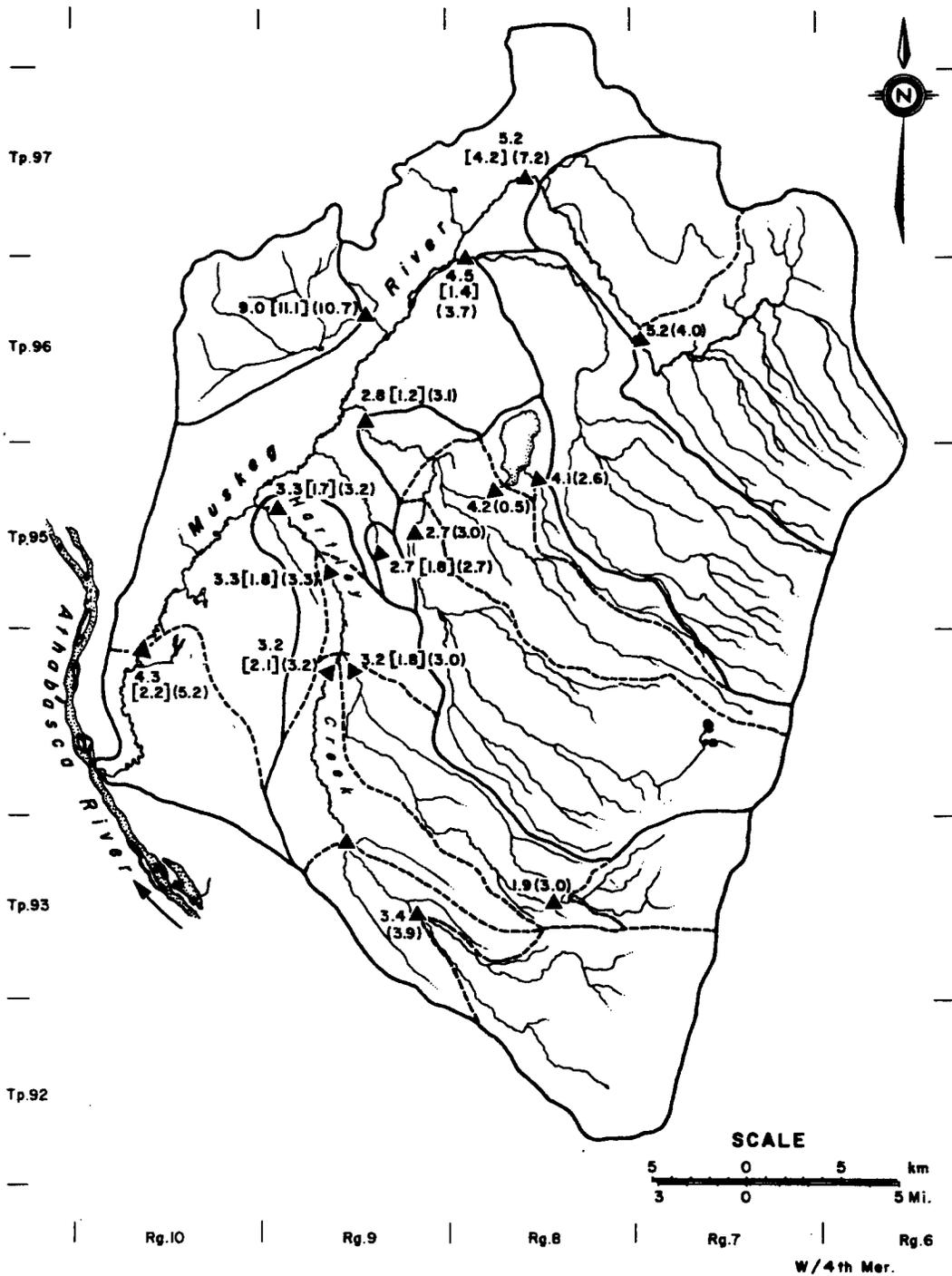
18 - 28 APRIL [MID MAY] (20 - 22 JUNE) 1977

Figure 41. Areal variations in reactive silica concentrations;
April, May, June 1977.

accelerated by the consumption of diatom cells by invertebrates. Other factors influencing the equilibration process are temperature, turbulence, and the difference in silica concentrations between the sediment and dissolved phases. In addition to these factors, muskeg drainage or shallow groundwater entering streamflow during baseflow periods could add to the levels of silica observed in basin streams.

Except for the unusually high silica concentrations observed at Site 12 (72 mg/L, 4 March 1977) and Site 7/A (57.0 mg/L, 25 February 1977), most maximum silica values in the watershed occurred in mid-winter.

The trend in dissolved silica concentrations observed at Site 1 and the trend in diatom populations reported in the Lock and Wallace (in prep.) report show (Figure 37) a definite relationship. While it appears that diatom populations at Site 1 were affected by Shell Pit pumpings (23 June to 2 August and 3 to 14 September 1977) and possibly the July 1977 storm events, the effects of these pumpings were probably caused by constituents other than silica.

3.4.2.5 Nitrogen: Nitrification and Nitrogen Removal

3.4.2.5.1 Introduction. A variety of micro-organisms in soils and streams can, conditions permitting, oxidize ammonia and nitrite to nitrate. The biochemical process for the oxidation of ammonia to nitrate (nitrification) has been represented (Sharma and Ahlert 1977) by the overall reactions:

$$NH_3 + 1.5O_2 \longrightarrow 2H^+ + H_2O + NO_2^- + 58 \text{ to } 84 \text{ kcal}$$
$$NO_2^- + 0.5O_2 \longrightarrow NO_3^- + 15.4 \text{ to } 20.9 \text{ kcal}$$
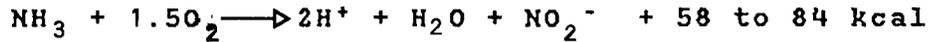
Nitritification = ammonia oxidation to nitrite;

Nitratification = nitrite oxidation to nitrate;

Nitrification = ammonia oxidation to nitrate.

It is generally believed that two autotrophic bacteria, Nitrosomonas sp. and Nitrobacter sp., contribute most significantly to nitrification. Kiesow (1964) reported that, while Nitrosomonas sp. and Nitrobacter sp. are obligate aerobes as far as growth on their respective substrates is concerned, in the absence of oxygen, Nitrobacter sp. is capable of becoming a nitrate reducer. In fact, a recent study by Voets et al. (1975) found evidence that denitrification (reduction of nitrite-nitrogen to gaseous nitrogen) takes place under both anaerobic and aerobic conditions.

3.4.5.5.2 Nitrogen Compounds: Seasonal Variations. The distribution of nitrogen compounds in streams of the watershed was found to be highly variable, spatially and seasonally.

Total Kjeldahl Nitrogen. The general annual range of total Kjeldahl nitrogen concentrations, 0.3 to 3.2 mg/L (ten-fold for most sites), appeared small and relatively uniform throughout the basin. But a number of exceptionally high values were recorded at Site 4 (5.50 mg/L, 10 September 1976), Site 2 (4.05 mg/L, 24 January 1978), Site 10 (3.5 mg/L, 10 August 1976), Site 7 (3.74 mg/L, 24 January 1977), and Site 12 (4.90 mg/L, 22 June 1977). Autumn 1976 (also July 1977) high values coincided with precipitation events. Unfortunately, the above exceptions and seasonal correlations of total Kjeldahl nitrogen show (Figures

42 to 44) that, except for the slightly higher winter values, there are no definite seasonal patterns.

Attempts to draw correlations between fluctuations in total Kjeldahl nitrogen and biological phenomena have not been conclusive.

Ammonia-Nitrogen. Ammonia-nitrogen is produced in the biochemical decomposition of organic nitrogen compounds (e.g., proteins, amino acids, amines, nucleic acids, purines, and products of their biochemical transformation, e.g., humic and fulvic acids). Most of the organic compounds are formed as a result of photo- and biosynthetic processes of aquatic organisms, mainly phyto-, zoo-, and bacterioplankton.

Ammonia-nitrogen concentrations appear to exhibit more definite patterns (Figures 45 to 47). Almost all sites showed high NH_3-N concentration in the winter, a sharp decline in the spring (April, May), a moderate peak in August, followed by another decline in the early autumn (September, October). Furthermore, ammonia-nitrogen concentrations appear to be low in well-oxygenated reaches of the streams, and high in bogs and sections of streams containing appreciable amounts of organic matter. This is due to the fact that under anaerobic conditions, the reduction of NO_2^- and NO_3^- is increased, oxidation of NH_3 to NO_2^- and NO_3^- is retarded, and the absorptive capacity of the sediments is greatly reduced. The result is a marked release of NH_3 from the sediments and colloidal particles. The release continues until the microzone at the sediment-water interface is oxygenated (also see Section 3.4.2.5.4).

For the major sites (1, 2, 3, and 4), the widest range of NH_3-N (<0.01 to 1.06 mg/L) occurred at Site 4 and the smallest (0.01 to 0.29) at Site 2. The
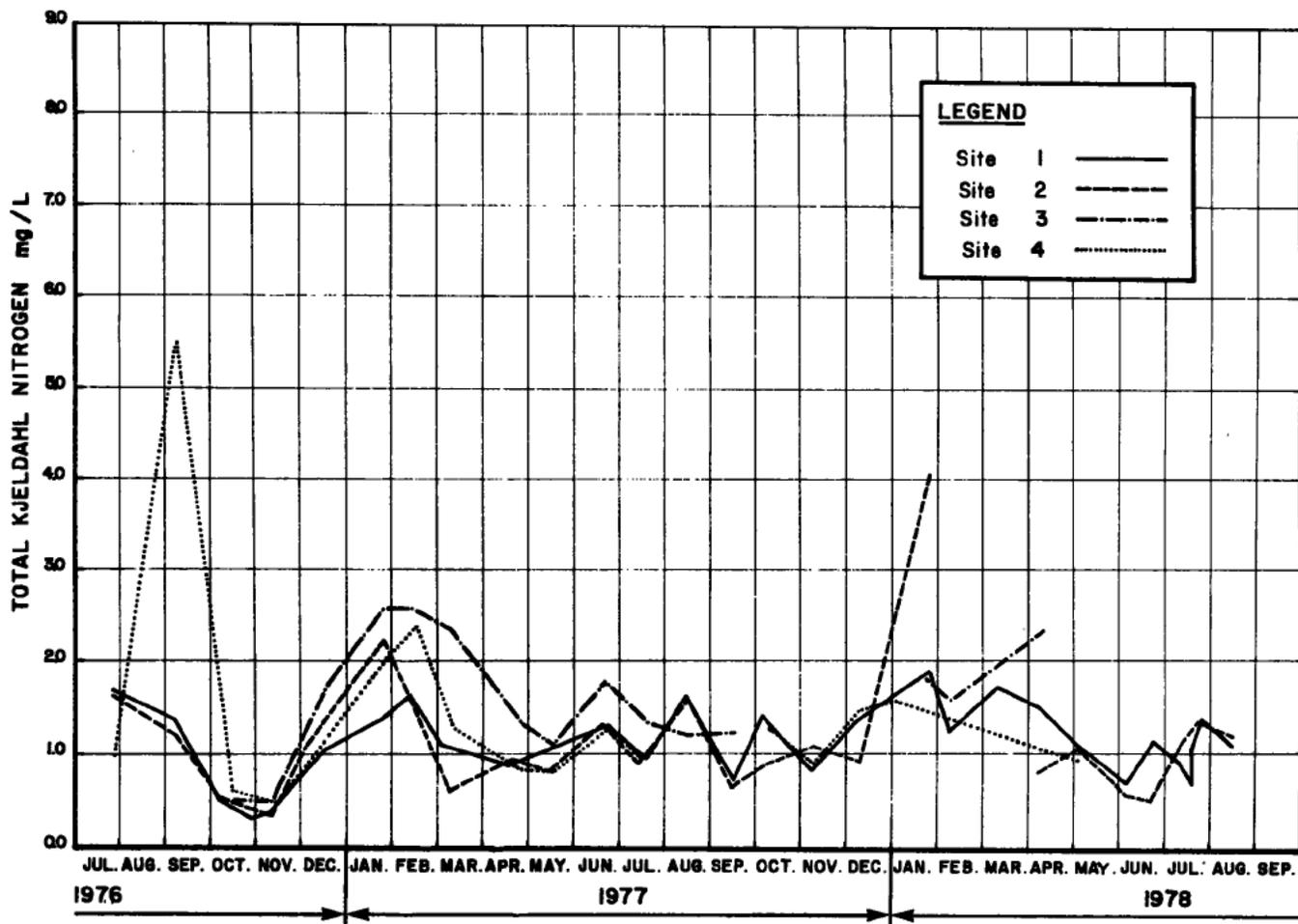
FIGURE 42. Variations in total Kjeldahl nitrogen concentrations (Sites 1,2,3,and 4).
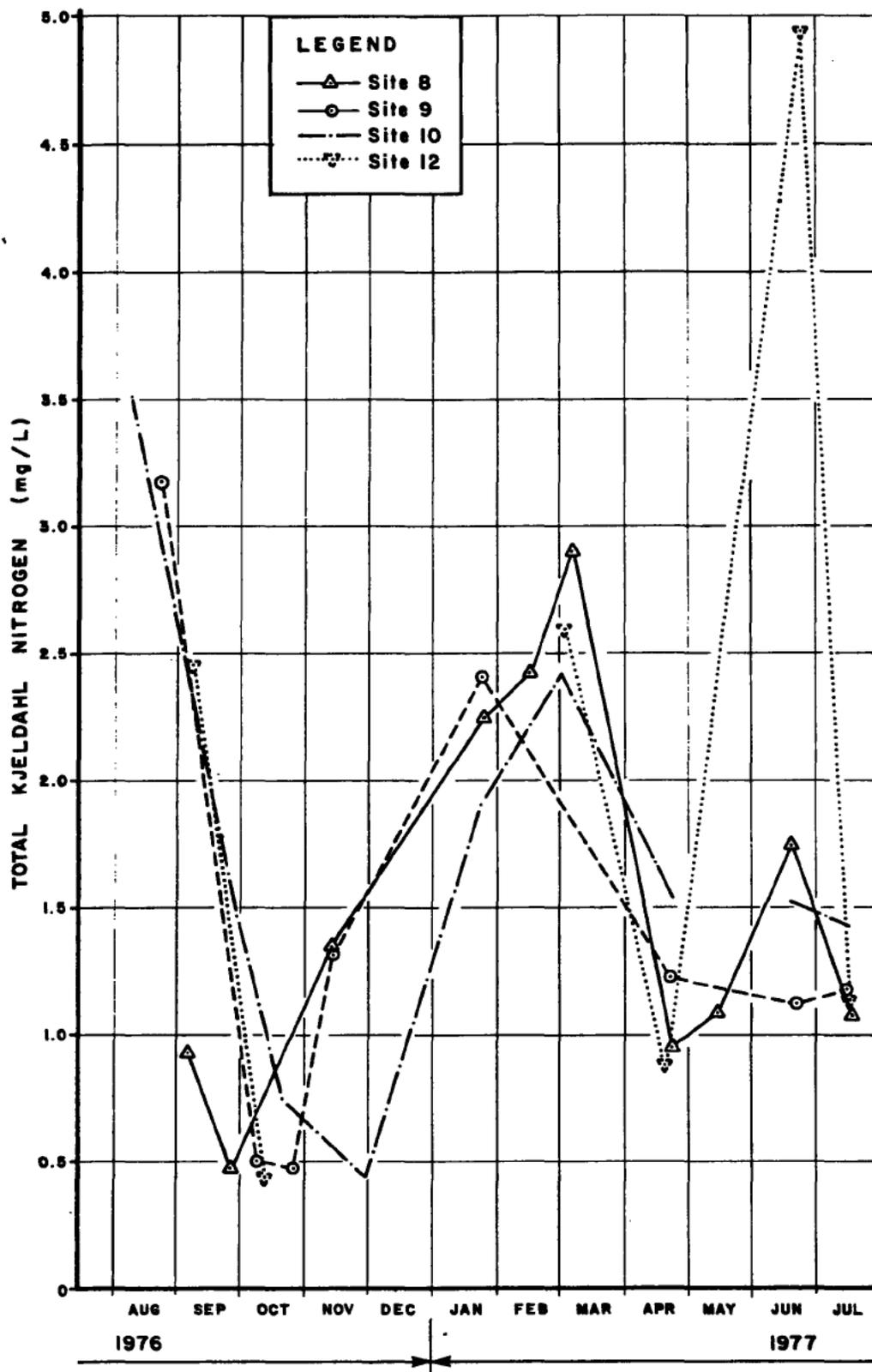
FIGURE 43. Variations of total Kjeldahl nitrogen concentrations (Sites 8, 9, 10, and 12).
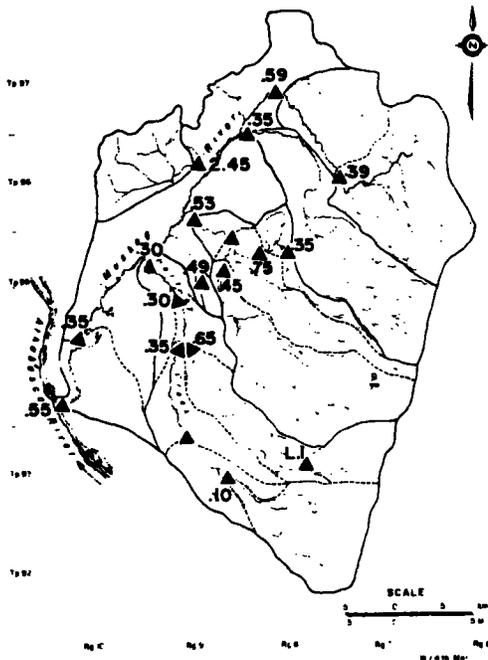
14 - 29 OCTOBER 1976
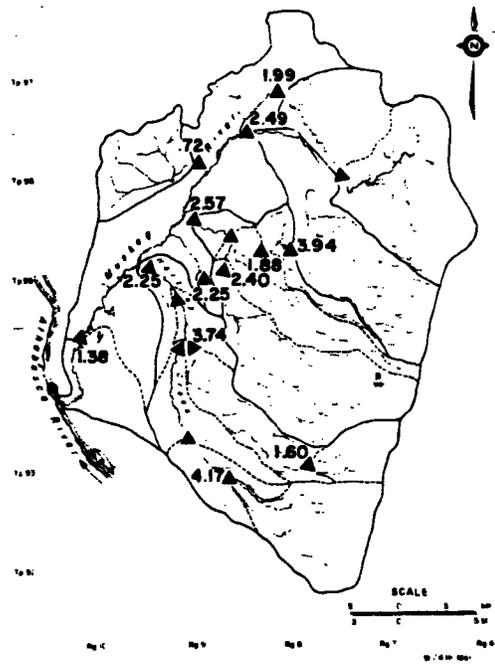
24 - 26 JANUARY 1977
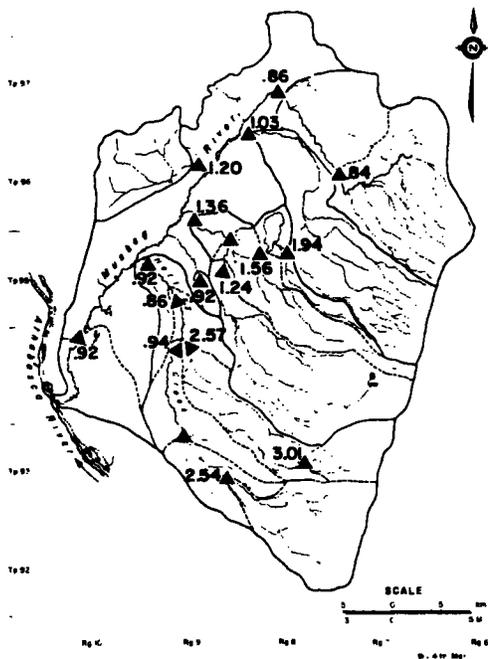
18 - 28 APRIL 1977
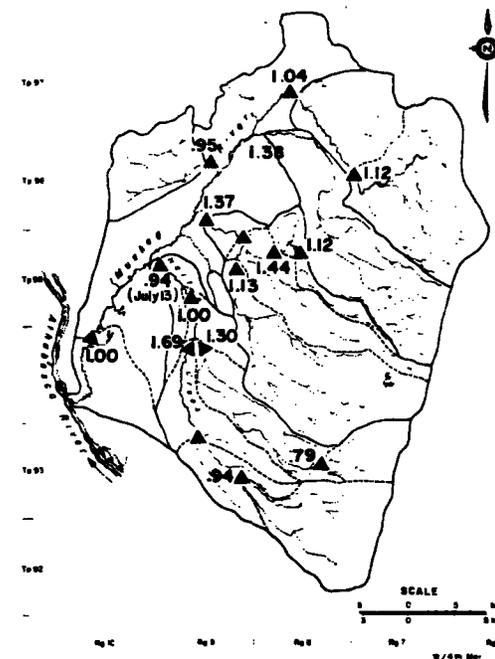
18 - 20 JULY 1977

FIGURE 44. Areal variations of total Kjeldahl nitrogen concentrations.

range in NH_3-N concentrations was moderate at Site 8
(0.01 to 0.89 mg/L), Site 9 (0.01 to 0.56 mg/L), and
Site 10 (0.05 to 0.59 mg/L). Exceptionally high winter
values for NH_3-N were observed at Site 11 on 25 January
1977 (1.28 mg/L) and at Site 12 on 4 March 1977
(1.69 mg/L).

3.4.2.5.3 Winter Nutrient Levels

Ammonia-Nitrogen and Orthophosphate
Phosphorus Levels. Figures 45 to 47 show that during
winter freeze-up, which usually lasts from early
November to mid-March, the concentrations of NH_3-N are
generally at their maximum levels at most sites. This
is not unexpected since winter chlorophyll levels are
low (see Figure 32) and nitrification proceeds better
during warmer seasons. The growth constants of
nitrifying bacteria are affected greatly by
temperature. Buswell et al. (1954) reported that
little or no growth of nitrifying bacteria is expected
below 4°C.

The high dissolved ammonia concentrations are
particularly pronounced in stagnant water bodies,
including muskeg areas (Sites 3, 4, 10, 11, and 12),
where substantial under-ice release of ammonia-nitrogen
is accompanied by elevated levels of soluble reactive
phosphate (o-PO_4). Values as high as 1.69 mg/L NH_3-N
and 0.06 mg/L o-PO_4 (Site 12, 4 March 1977) and 0.50
mg/L NH_3-N and 0.09 mg/L o-PO_4 (Site 3, 14 February
1977) were recorded. Even the larger volume flowing
streams like Muskeg River, Site 1, 0.57 mg/L NH_3-N and
0.02 mg/L o-PO_4 (11 February 1977), and Hartley Creek,
Site 2, 0.25 mg/L NH_3-N and 0.06 mg/L o-PO_4 (26 January
1977), showed little effect of dilution, utilization,
and increased aeration on the nutrient supply.
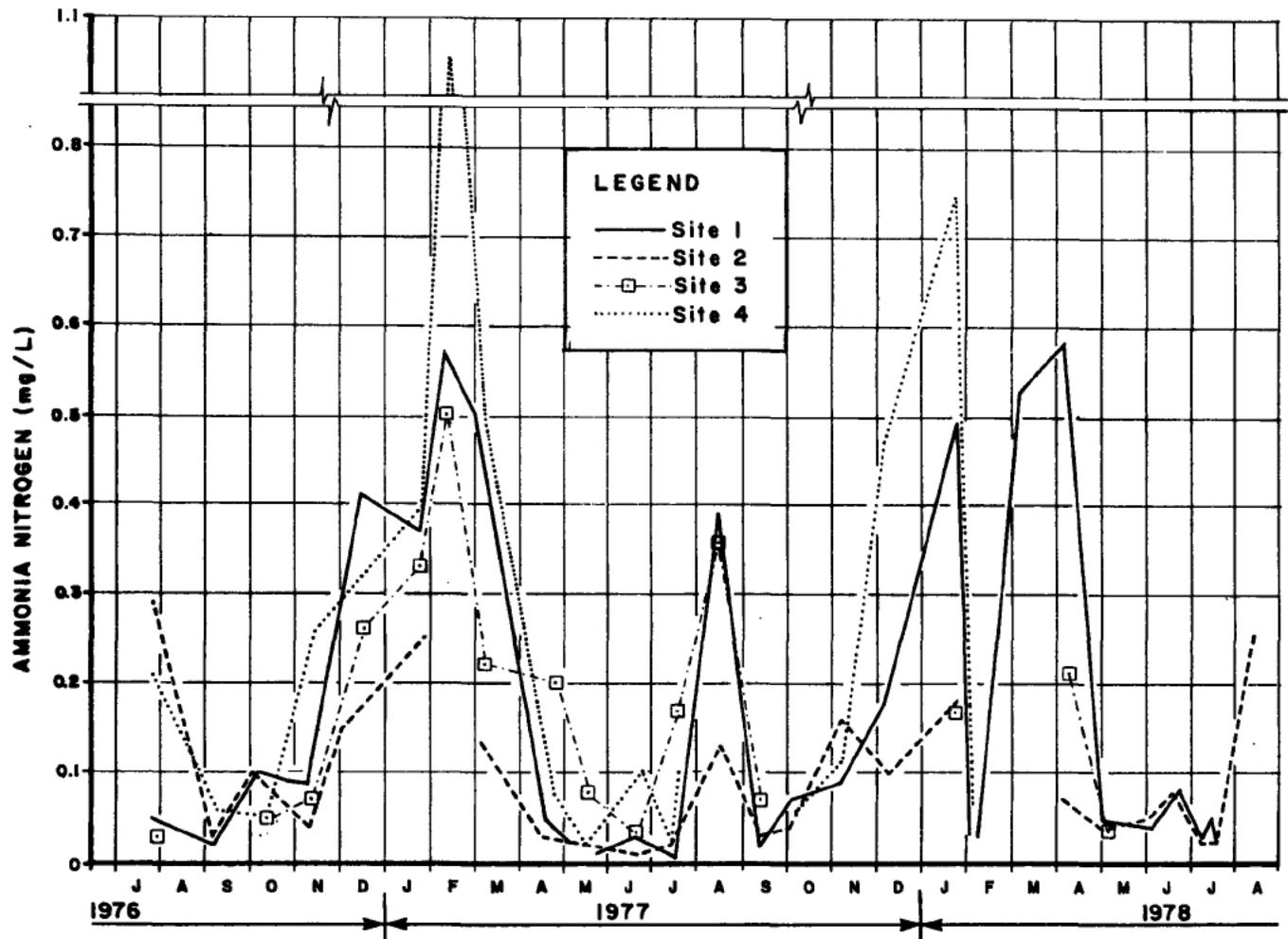
FIGURE 45. Variations in ammonia-nitrogen concentrations (Sites 1,2,3,and 4).
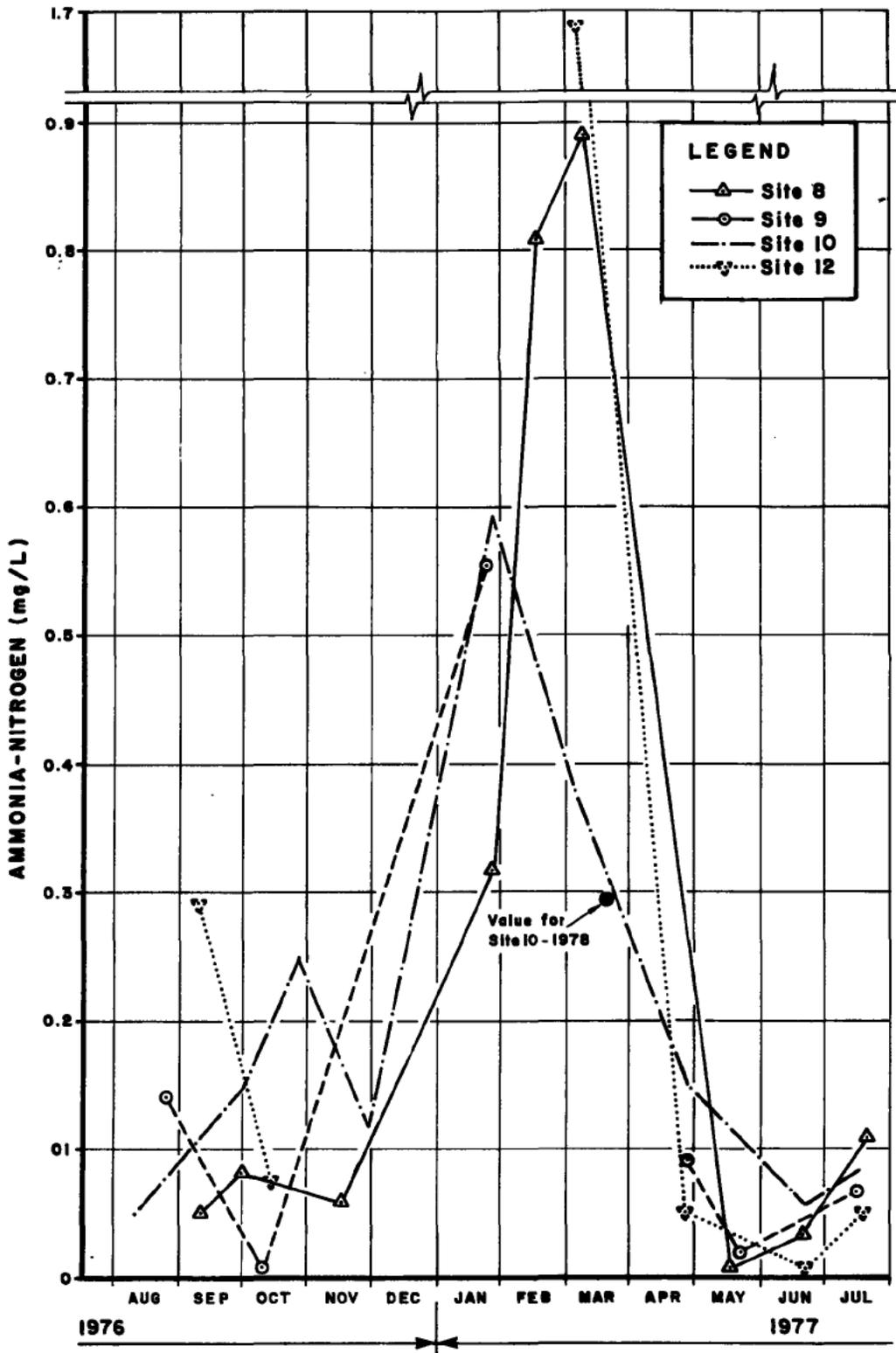
FIGURE 46. Variations in ammonia-nitrogen concentrations (Sites 8,9,10,and 12).

14-29 OCTOBER 1976

24-26 JANUARY 1977

18-28 APRIL 1977

18-20 JULY 1977
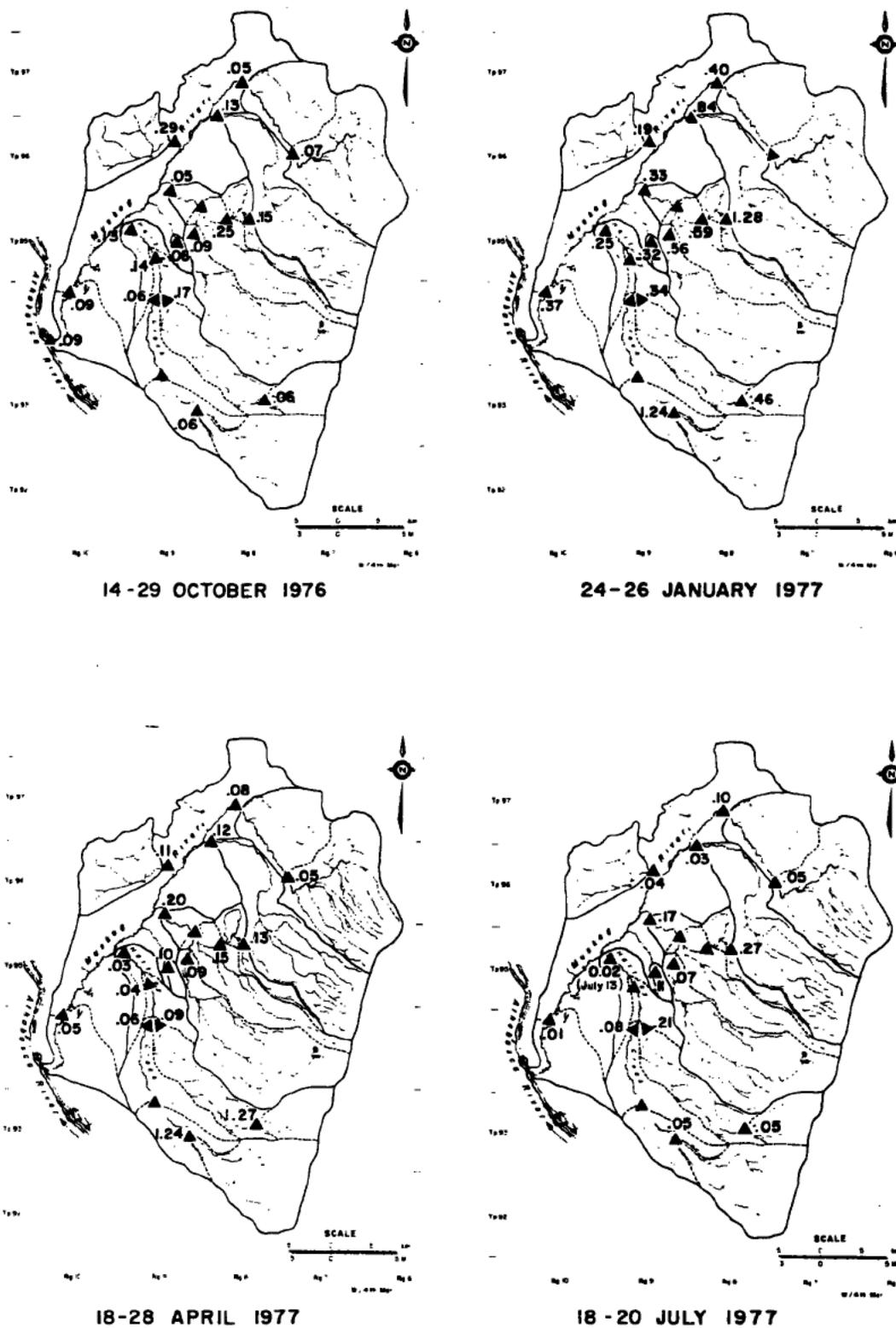
FIGURE 47. Areal variations in ammonia—nitrogen concentrations.

The toxicity of these mid-winter
concentrations of ammonia to aquatic organisms is
probably low since the amount of CO_2 is high and the pH
is only slightly alkaline. Generally, pH's higher than
pH 9 increase the concentrations of non-ionized ammonia
and low concentrations of dissolved oxygen increase the
toxicity of ammonia. McKee and Wolf (1963) have,
however, reported that concentrations of non-ionized
ammonia equivalent to 0.2 mg/L (as NH_3-N) decreased the
survival time of trout at a level of dissolved oxygen
that otherwise had no lethal effects.

Nitrite- + Nitrate-Nitrogen and
Orthophosphate Phosphorus Levels. Nitrite is extremely
unstable in the presence of oxygen and is generally
oxidized to nitrate immediately. But data collected in
this study show that on many occasions NO_2^--N
concentrations higher than backgrounds and NO_3^--N
exist even when the DO levels are high; for instance,
at Site 1 on 13 September 1977, 4 October 1977, 3 May
1978; Site 2 on 4 October 1977; and at Site 3 on 14
September 1977.

Data from analyses for NO_3^--N were sparse and
not amenable to trend analyses. But, assuming that
NO_2^--N concentrations are generally very low relative
to NO_3^--N (an assumption which is obviously not
completely valid under the anoxic conditions), then the
maximum values for NO_2^--N + NO_3^--N and o-PO_4 tabulated
(Table 13) below (for late fall, winter, and early
spring) are indicative of the level of soluble nutrient
supply available for the ice-free season ahead.

The winter maximum concentrations of nitrate-
nitrogen at most sites, except Sites 1, 2, 3, and 4
(Figure 48), were just above the detectable limit
(0.01 mg/L before May 1977 and 0.003 mg/L after)

Table 13. Dates of maximum concentrations of
nitrate- + nitrite-nitrogen and
orthophosphate phosphorus.

Site Number	$NO_2^- + NO_3^-$ (mg/L)	$o-PO_4$ (mg/L)	Dates
1	0.07	0.02	11 Feb 1977
	0.31	0.01	3 Mar 1977
	0.05	0.004	8 Nov 1977
	0.04	0.006	6 Dec 1977
2/A	0.06	<0.01	16 Dec 1976
2	0.05	0.02	2 Dec 1976
	0.02	0.06	26 Jan 1977 [a]
	0.20	0.008	6 Apr 1978 [a]
3	0.07	0.08	16 Dec 1976
	0.09	0.09	14 Feb 1977
	0.11	0.05	8 Mar 1977 [a]
3/A	0.01	0.09	7 Mar 1977 [a]
4	0.14	0.02	18 Feb 1977 [a]
5	0.04	0.02	15 Nov 1976 [a]
6	0.02	<0.01	15 Nov 1976 [a]
7	0.02	0.01	15 Nov 1976
7/A	<0.05	0.02	25 Feb 1977 [a]
8	0.02	0.04	18 Feb 1977
	0.01	0.06	7 Mar 1977 [a]
9	0.02	0.01	25 Jan 1977
10	0.01	0.07	1 Dec 1976
	0.02	0.03	25 Jan 1977
11	0.02	0.04	25 Jan 1977
12	0.01	0.06	4 Mar 1977 [a]
13/A	0.01	0.04	1 Dec 1976 [a]
14	0.12	0.01	4 Mar 1977

[a] indicates a spring, or with a spring, maximum.
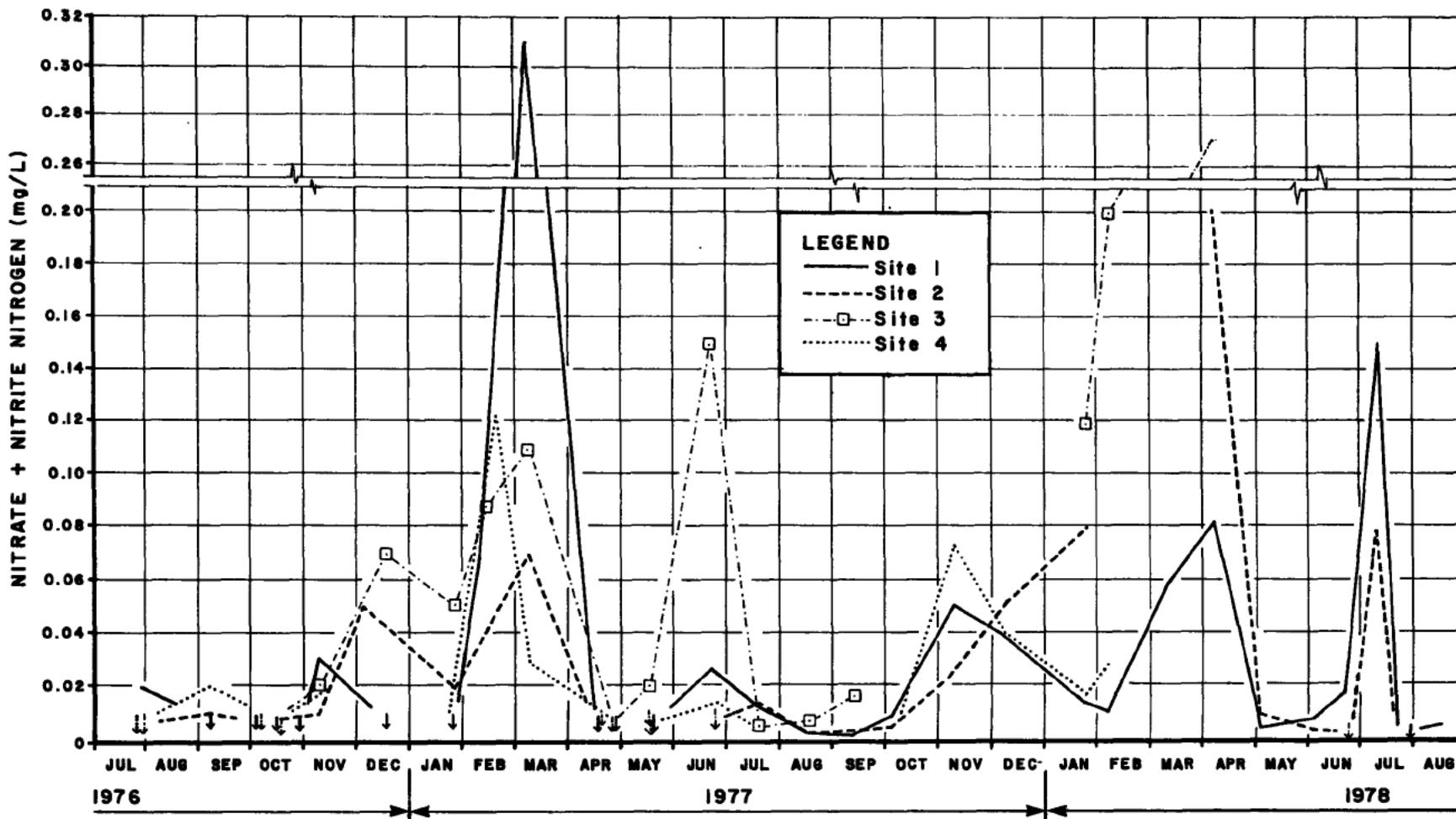
Figure 48. Variations in nitrate − + nitrite − nitrogen concentration (Sites 1,2,3, and 4).

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(Figure 49 and 50). Since nitrate- + nitrite-nitrogen levels during the ice-free periods are generally less than 0.01 mg/L, these detectable levels were probably possible because of minimum uptake of the nutrients by algae and possible input from muskeg and shallow groundwaters. The possibility of groundwater input is indicated by observations of maximum $NO_2^--N + NO_3^--N$ concentrations of 0.31 mg/L and 0.082 mg/L observed at Site 1 on 3 March 1977 and 6 April 1978, respectively; and at the same time, the specific conductances were 480 μS/cm (3 March 1977) and 430 μS/cm (6 April 1978). The values observed at Site 2 on 7 March 1977 were 0.07 mg/L and 660 μS/cm, and on 6 April 1978 were 0.200 mg/L and 545 μS/cm. These high values of specific conductance are clearly indicative of baseflows containing some muskeg drainage or groundwater.

The data from Site 4, located in the middle of a muskeg, show a sharp mid-winter (18 February 1977) peak for $NO_2^--N + NO_3^--N$ of 0.14 mg/L and for total phosphate phosphorus of 0.25 mg/L (o-PO_4, 0.02 mg/L). The specific conductance for the same date was 530 μS/cm. The following month (8 March 1977) the $NO_2^--N + NO_3^--N$ and total phosphate phosphorus values dropped to 0.03 mg/L and 0.09 mg/L, respectively, but the o-PO_4 remained practically the same (0.03 mg/L) and specific conductance rose to 610 μS/cm. It is possible that the non-filterable residue in the sample, which was exceptionally high (78.4 mg/L) on 18 February 1977, was the cause. The non-filterable residue for 8 March 1977 was only 7.6 mg/L. The sampling technique and sample storage used would tend to give high nutrient concentrations on samples containing high non-filterable residues.

From Table 13, it appears that, for most sites, the maxima for $NO_2^--N + NO_3^--N$ appear to lag
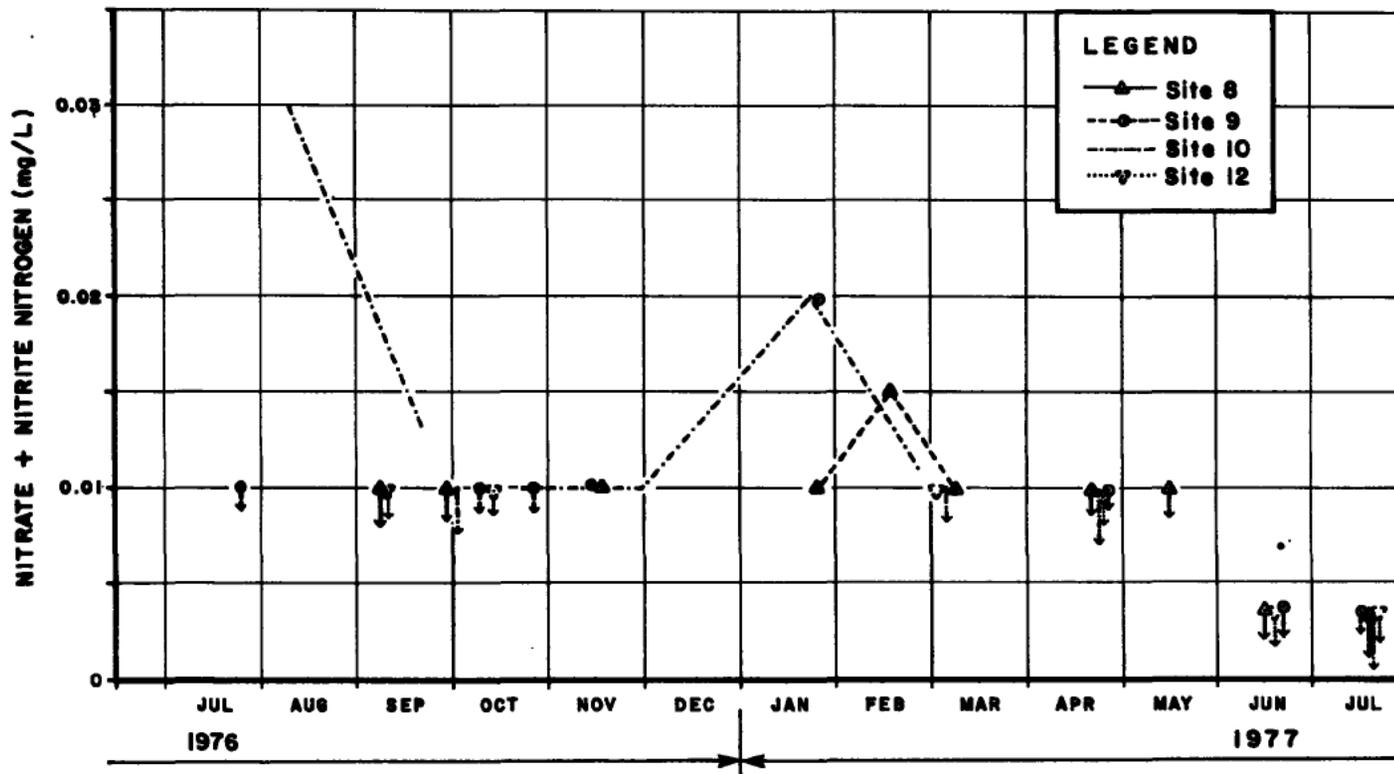
Figure 49. Variations in nitrate − + nitrite −nitrogen concentration
(Sites 8,9,10, and 12).
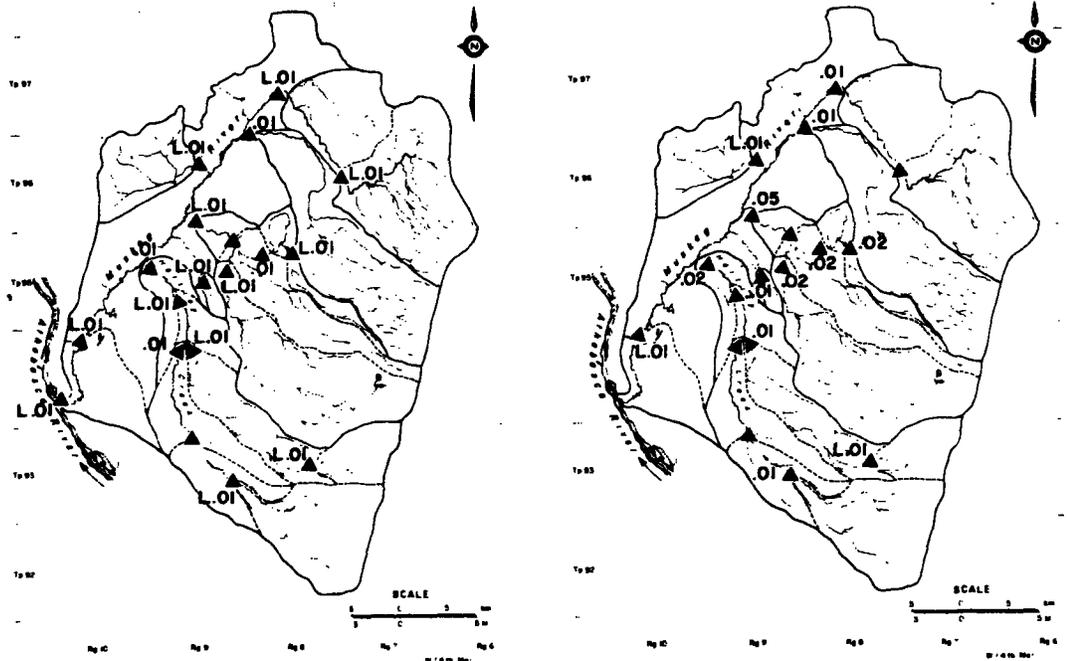
14-29 OCTOBER 1976

24-26 JANUARY 1977
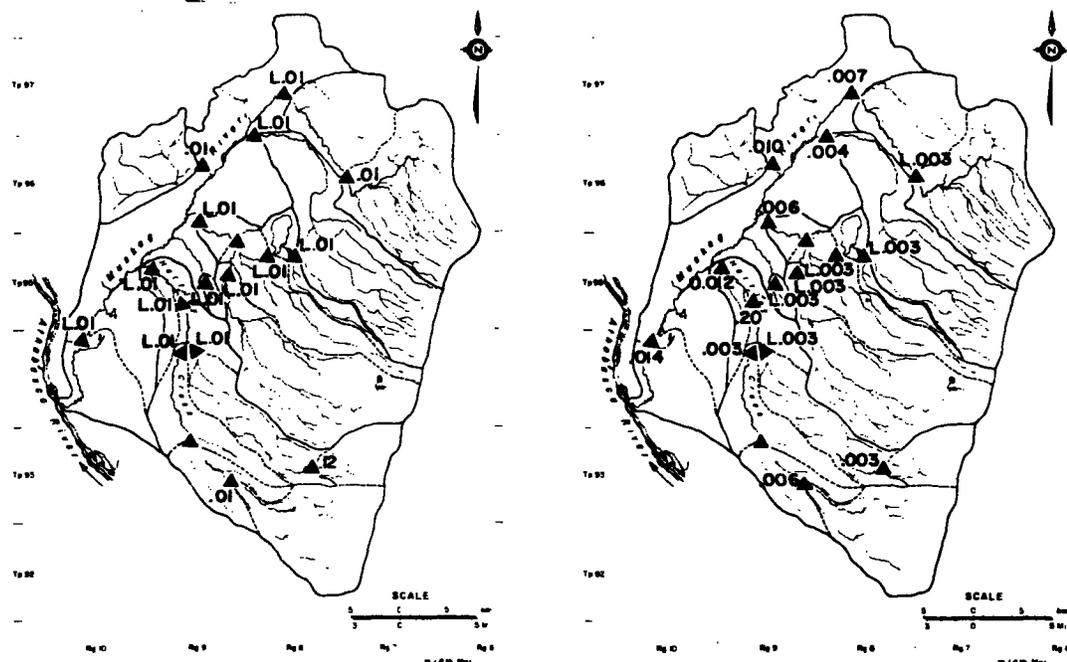
18-28 APRIL 1977

18-20 JULY 1977

Figure 50. Areal variations in nitrate- +nitrate-nitrogen concentration.

behind the orthophosphate ones by about one month;
except for the Kearl Lake outlet (Site 10) where the
order is reversed.

Dissolved Organic Nitrogen and Ammonia-
Nitrogen. Unlike dissolved organic carbon which
remains in solution at relatively uniform levels,
seasonal variations of dissolved organic nitrogen (DON)
(Figure 51) resemble those of NH_3-N; except for the
fact that DON peaks earlier than NH_3-N. It appears
that the autumn leaf-fall and algal die-off result in
massive releases of organic materials. As a result,
most sites in the basin show sharp increases in NH_3-N
and DON starting in early winter.

The slight lag of NH_3-N peaks relative to DON
in some sites (e.g., Sites 1, 2, 10) suggests that the
release of ammonia occurs as a result of mineralization
of the DON and particulate organic nitrogen. And,
although the relationship between nitrification and
organic matter is not clear, Praskasam and Loehr (1972)
have shown that, with other parameters (DO,
temperature, and pH) held constant, the degree of
nitrification decreases significantly with increases in
organic loading. The inhibiting effect of organic
loading on nitrification may be due to dissolved oxygen
limitations. This may explain the fact that DOC and
ammonia-nitrogen peaks occur at approximately the same
time and during the collapse of summer algal blooms.

The ratios (or percents) of NH_3-N to total
Kjeldahl nitrogen also generally increased in the
winter time. For instance, at Muskeg River Sites 1
(Figure 52) and 4 (Figure 53), the ratio of NH_3-N to
total Kjeldahl nitrogen increased from an early fall
value of 1 to 5% (September) up to 15 to 57% in winter
(November to early April). Occasionally, mid-winter
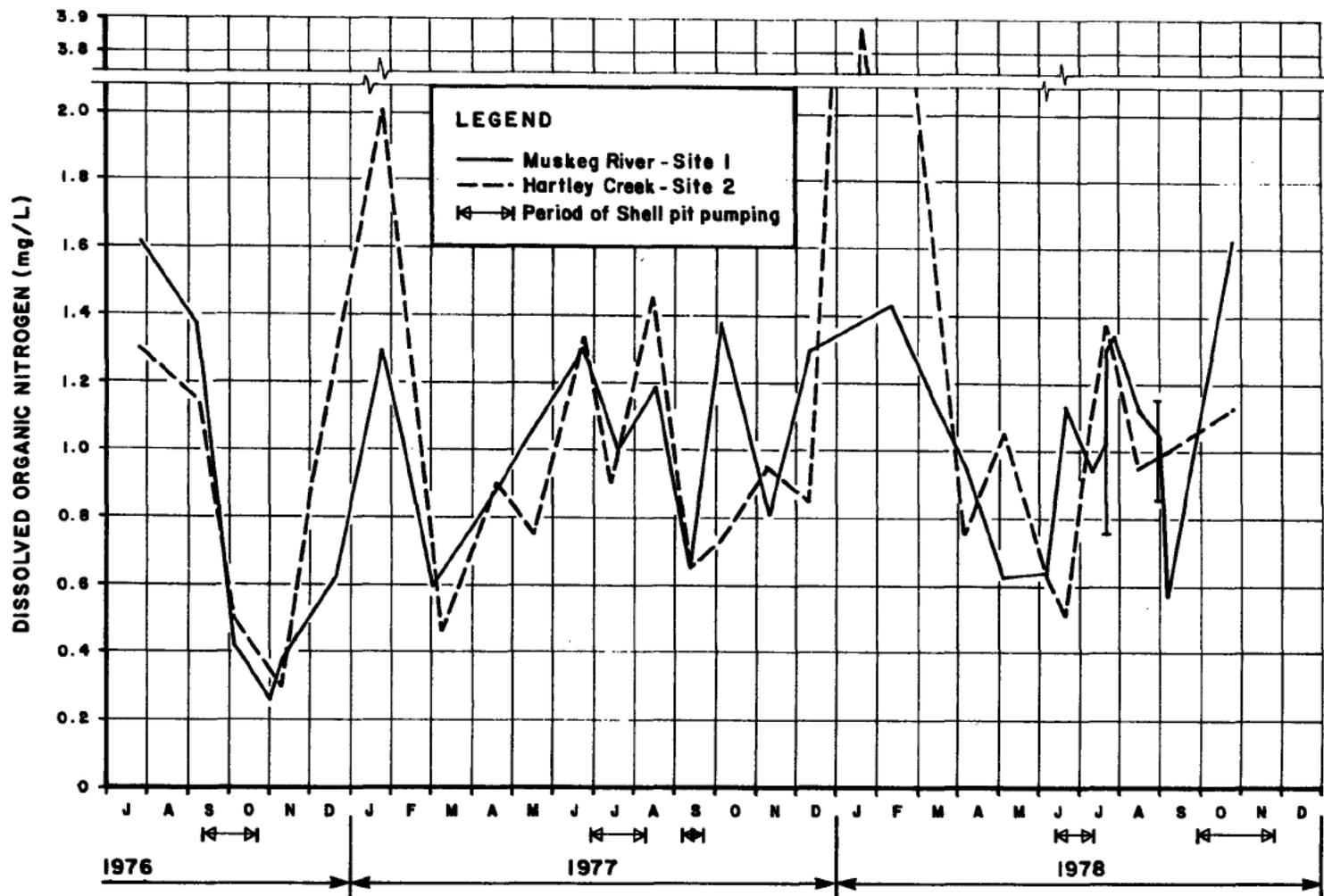
FIGURE 51. Variations of dissolved organic nitrogen concentrations (Sites 1 and 2).
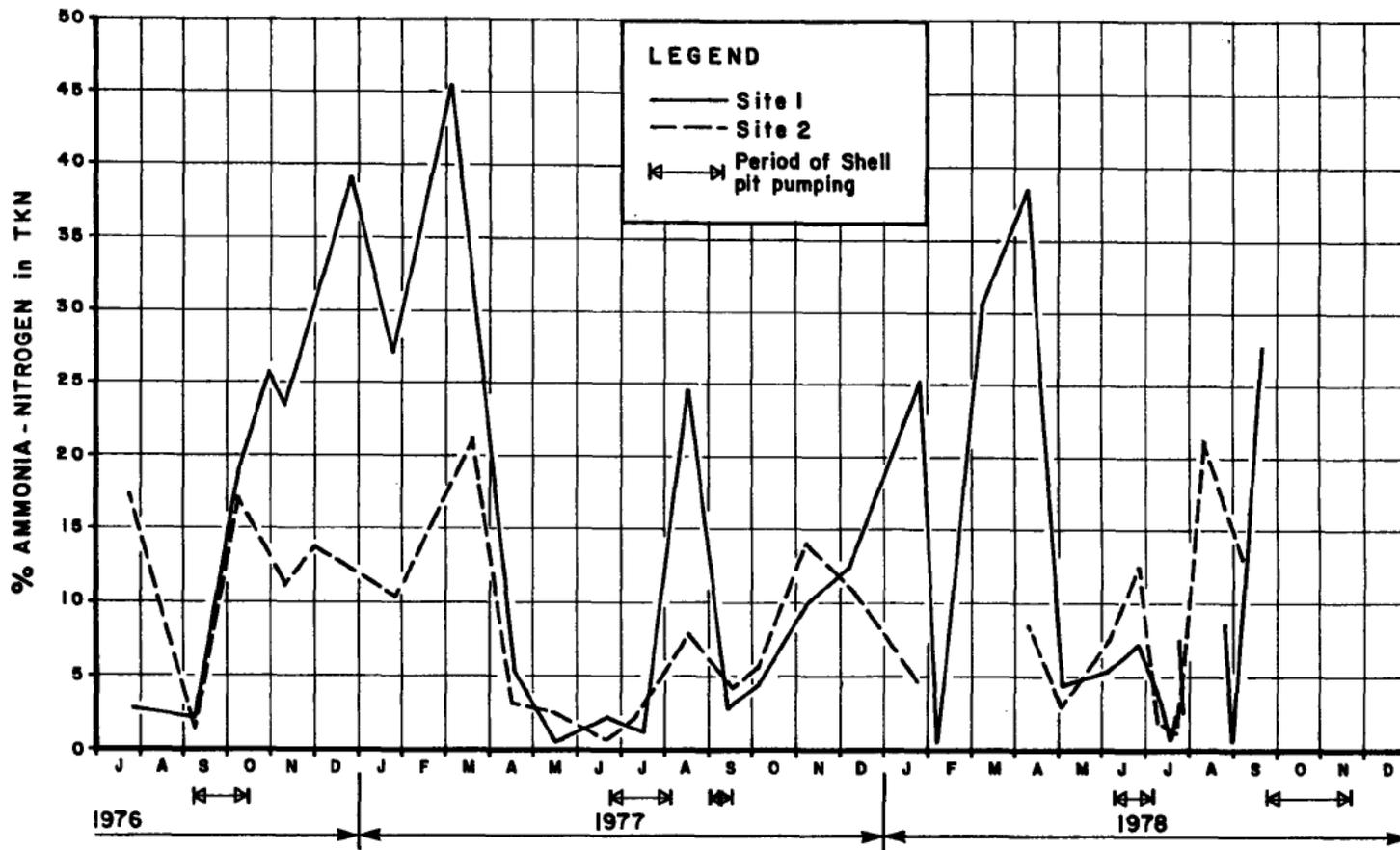
Figure 52. Variations in percent ammonia - nitrogen in total Kjeldahl nitrogen (Sites 1 and 2).
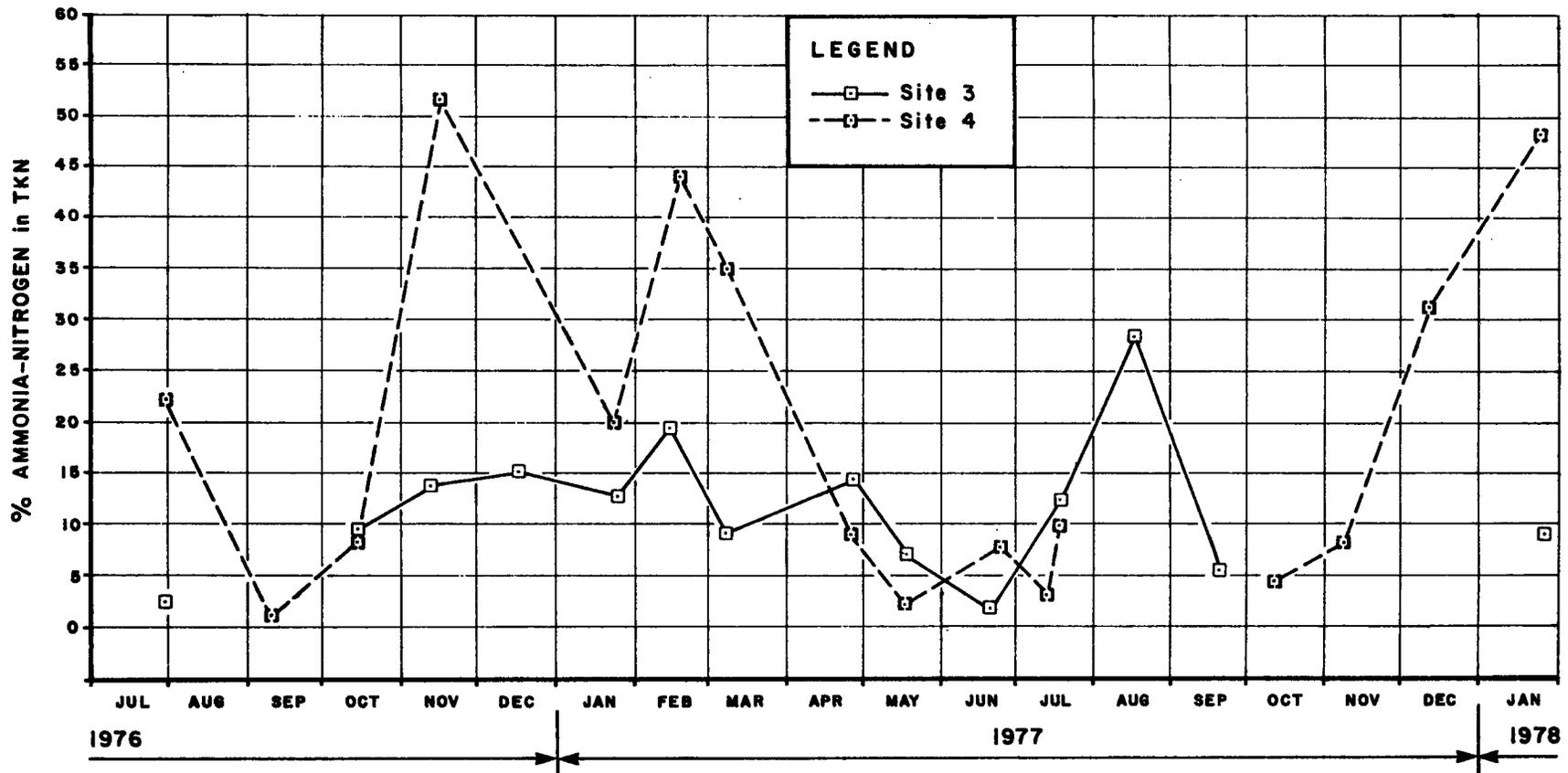
Figure 53. Variations in percent ammonia – nitrogen in total Kjeldahl nitrogen (Sites 3 and 4).

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declines in NH_3-N concentrations were observed. While
the exact causes are not known, the possibility of
microbial oxidation to NO_2^- or NO_3^- appears unlikely
since the concentrations of NO_2^--N + NO_3^--N actually
showed declines at that time. Sampling or analytical
factors could be responsible.

3.4.2.5.4 <u>Nutrient Levels During Ice-Free Periods</u>

   <u>Ammonia-Nitrogen</u>. In early spring, ammonia-
nitrogen concentrations appear to drop sharply in
response to biological activities, warm temperatures,
re-aeration, and the dilution effects of spring
runoffs. During late April, May, or June, the NH_3-N
concentrations dropped to less than 0.1 mg/L at all
sites. These decreased NH_3-N levels and the depressed
dissolved oxygen concentrations (and percents
saturation) reflect the accelerated oxygen depletion
due to utilization, oxidation reactions, and
respiration.

   <u>Nitrite and Nitrate</u>. Nitrate is a sensitive
indicator of biological activity and the end product of
the biochemical oxidation of ammonia:

$$NH_3 \longrightarrow [NH_2OH] \longrightarrow [H_2N_2O_2] \longrightarrow HNO_2 \longrightarrow NO_3^-$$
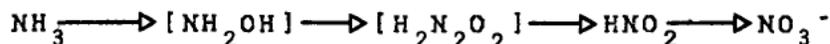
   Examples of mid-summer NO_3^- accumulation were
observed at Site 3 (20 June 1977) where the NO_3^--N and
NO_2^--N + NO_3^--N concentrations were found to be
0.03 mg/L and 0.15 mg/L, respectively. At Sites 2/A,
6, and 7, the concentrations of NO_2^--N + NO_3^--N, during
the productive period (most of spring and summer) of
1976 and 1977, were below or just above the detection
limit. But on 20 June 1977 (0.24 mg/L) and 18 July
1977 (0.20 mg/L) at Site 2/A (Figure 50), located
approximately 2 km upstream from Site 2, high

concentrations of $NO_2^- - N$ + $NO_3^- - N$ were observed.
The $NH_3 - N$ data for Sites 2/A, 6, and 7 indicate that
these are products of nitrification processes. From
the data collected at Site 2, it also appears that
these nutrients were rapidly utilized or converted
within the 2 km reach. The total phosphate phosphorus
(and o-PO_4) data for Site 2/A showed a very slight
decline in June and July compared to May values; while
Site 2 experienced a temporary increase in June (0.043
mg/L) over May (0.02 mg/L) total phosphate phosphorus
values.

Because the concentrations of $NO_2^- - N$ + $NO_3^- - N$
(Figure 50) and PO_4^{3-} at most sites were not
appreciable (in some cases below detectable limit)
during the ice-free period, it is possible to conclude
that intensive development of benthic algae was
occurring.

Dissolved Organic Nitrogen. The concentra-
tion of dissolved organic nitrogen during ice-free
periods is moderately variable but appears to gradually
increase from early spring through to August,
presumably because of an accumulation of extracellular
metabolic products (e.g., secretion) of algae. Studies
by Horne et al. (1977) have shown that increases in
dissolved organic carbon correlate positively with
nitrogen fixation, so that the rise in DON could
reflect the growth of photosynthetic bacteria, blue-
green algal population, and concurrent nitrogen
fixation. Wetzel (1975) has indicated that the numbers
of these bacteria are low where dissolved organic
concentrations are low, and increase, for instance, in
bog lakes (Azotobacter most dominant) where dissolved
humic organic matter concentrations are high. It is
therefore not surprising that the highest mid-summer

DON are observed at Sites 3 (1.69 mg/L), 8 (1.73 mg/L), and 12 (4.90 mg/L). Unfortunately, no humic acid analyses were performed on those samples.

Late Summer Nutrient Concentrations. All sites showed sharp NH_3-N peaks during August (or July) 1976 and August 1977 (where applicable). The peaks in NH_3-N concentration occurred soon after or coincided with the dying off (see Figures 30, 32, and 54) of aquatic organisms (most probably benthic algae), slight increases in DON, DOC, and PO_4^{3-}, and, in some cases, a minimum in dissolved oxygen concentration (and percent saturation).

Around mid-August 1977, at most sites (especially Sites 1 and 2), the standard plate count dropped but the dissolved oxygen concentration went up (to 110% of saturation at Site 2) simultaneously with NH_3-N and DON. The release of nutrients during decomposition processes would be expected. But the lack of response in PO_4^{3-}, TOC, DOC, and COD and a sharp increase in the dissolved oxygen was unexpected. This event was observed by others (Lock and Wallace in prep.) working on the Muskeg River and also in the Athabasca River (Costerton and Geesey 1979). Costerton and Geesey have attributed this to a "washout" effect caused by violent July 1977 rainstorm events. Whatever the effect, it was noticeable in the concentrations of various parameters analysed for in the sample collected from Site 1 but not most of the parameters analysed for at Hartley Creek, Site 2.

The Site 2 data of 16 August 1977 showed sharp increases in the concentrations of NH -N (0.13 mg/L), Cu (0.014 mg/l), Se (0.0007 mg/L), Ag (0.002 mg/L), and SO_4^{2-} (6.1 mg/L) but a decline in Zn (0.008 mg/L) compared to the concentrations of NH_3-N
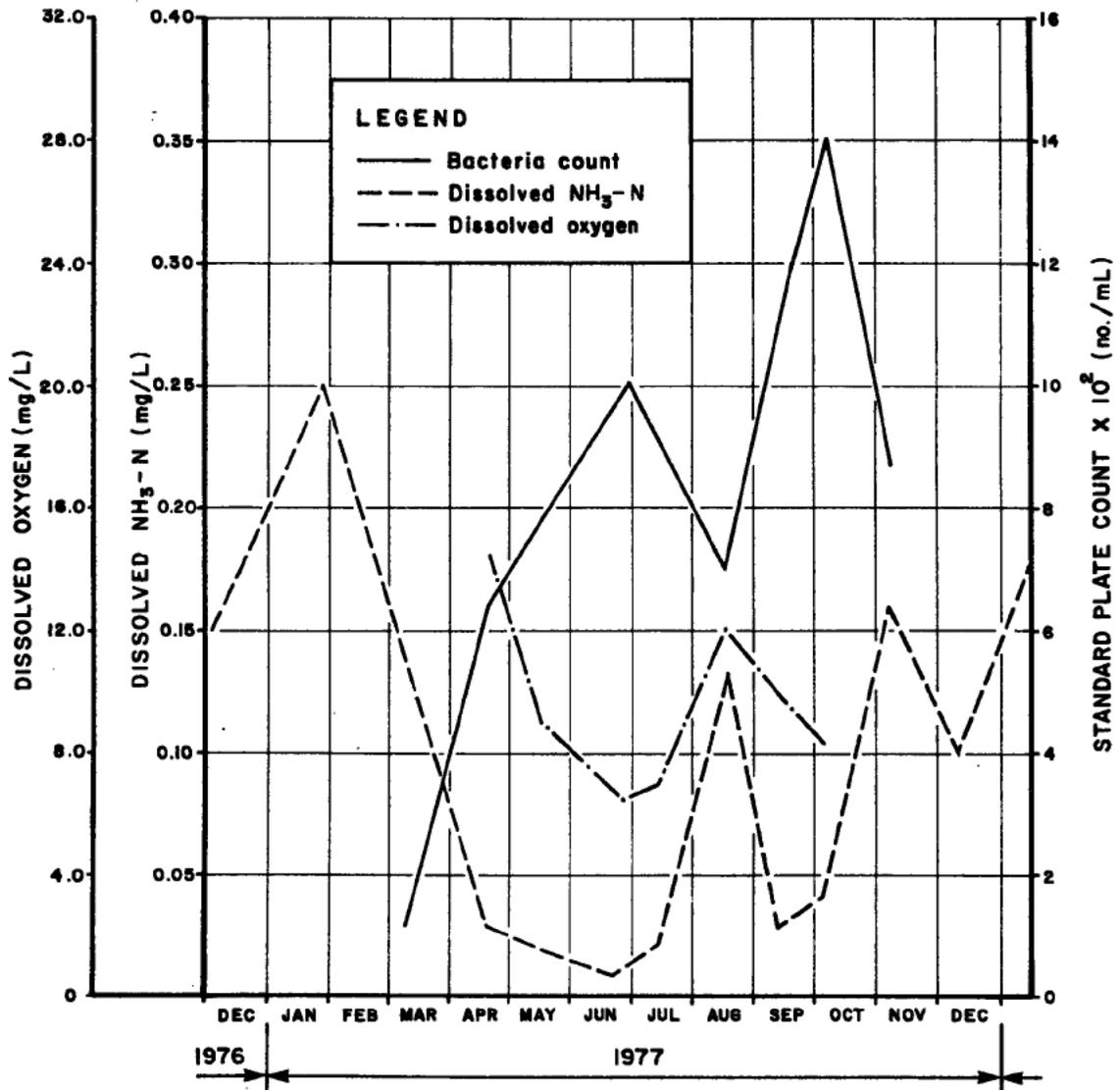
FIGURE 54. Variations of dissolved oxygen and ammonia-nitrogen concentrations and standard plate count (Site 2).

(0.02 mg/L), Cu (0.002 mg/l), Se (<0.0002 mg/L), Ag
(<0.001 mg/L), SO_4^{2-} (4.2 mg/L), and Zn (0.035 mg/L)
observed on 13 July 1977. Because sharp drops in
bacterial populations were also reported by workers in
other watersheds, the possibility of sample
contamination appears less likely.

The data for Site 1 (16 August 1977) showed
slight increases in the concentrations of NH_3-N
(0.39 mg/L) and Ni (0.002 mg/L) but decreases in the
concentrations of Zn (0.005 mg/L) and Al (<0.01 mg/L)
as compared to the 18 July 1977 values of NH_3-N
(0.01 mg/l), Ni (<0.002 mg/L), Zn (0.048 mg/L) and Al
(0.03 mg/L).

Lock and Wallace (in prep.) have suggested
that increased levels of illumination reaching the
epilithon inhibited photosynthesis and resulted in the
observed declines in epilithic biomass. It is also
possible that the lack of oxygen and essential
micronutrients (e.g., Zn) or the availability of a
toxic component (e.g., Cu or Se) contributed to the
collapse in algal and bacterial populations. Synergism
reportedly exists between the sulphates of copper and
zinc and copper and cadmium in their toxic effects to
fish. It also exists between copper and mercury. It
has been noted (Water Survey of Canada 1978) that
copper concentrations as low as 0.01 mg/L have
interfered with the self-purification of streams by
killing the stream bacteria.

Bacterial respiration, which occurs at the
sediment-water interface and where bacterial metabolism
is greatest, is a major consumer of dissolved oxygen.
It is conceivable that the interface regions became
anaerobic, and, because diffusion of oxygen into this
zone from overlying layers occurs slowly (especially in
bogs, eg., Site 3), it caused bacterial kill and/or a

change from aerobic to anaerobic bacterial metabolism, with a marked reduction in overall efficiency of decomposition (Wetzel 1975).

The effect would be what was observed, a drop in algal and (nitrifying) bacterial (especially attached) populations (Figure 32), increase in NH_3-N concentrations, and, because of concurring reaeration processes (except in bogs, eg., Site 3) (Figure 31), no depletion of disolved oxygen in overlying waters.

It is also possible that loadings of certain dissolved organic compounds, especially humic compounds, tannins, and tannin decompositional derivatives, inhibited (Rice and Pancholy 1972) nitrification reactions (after the rainstorm or Shell Pit pumpages) without negatively affecting the dissolved oxygen levels in flowing streams.

3.5   BIOLOGICAL ACTIVITY AND THE ASSIMILATIVE CAPACITY OF THE MUSKEG RIVER

3.5.1   Ammonia-Nitrogen Seasonal Variations

It has been noted that NH_3-N concentrations increase when aquatic organisms die off and decrease when biochemical oxidation reactions convert NH_3-N to NO_2^--N or NO_3^--N. The large amplitude of the seasonal fluctuations of NH_3-N observed in the present study is indicative of a stream capable of converting these natural levels of nitrogenous organic substances to nutrients for aquatic organisms inhabiting the streams

3.5.2   Ammonia-Nitrogen to Nitrate-Nitrogen Ratios

Because of the lack of simultaneous sampling, attempts to correlate trends in the ratio of ammonia to nitrate- and nitrite-nitrogen along a stream were limited to only a few dates. What little data could be correlated showed (Table 14) a definite downward trend

Table 14. Ratio of $NH_3-N/NO_2^--N + NO_3^--N$.

	1 Aug 1976	7 Sep 1976	10 Sep 1976	15 Nov 1976	15 Feb 1977	3 Mar 1977	1 Apr 1977	17 May 1977
Site 12	-	>29	>29	-	-	169	>50	>3
Site 4	>20	3	3	13	9.44	20	15	>2
Site 1	2.5	>2	2	5.38	4.40	1.61	2.3	0.1
Site 2	>30	3	4	2.5	-	2.38	2.33	-

	20 Jun 1977	18 Jul 1977	15 Aug 1977	15 Oct 1977	1 Nov 1977	8 Nov 1977	6 Dec 1977	1 Jan 1978
Site 12	>3	>17	-	-	-	-	-	-
Site 4	6	1.43	-	3.04	1.8	1.53	11.75	20
Site 1	1.07	0.71	13	3.04	2.5	1.80	4.50	13
Site 2	-	2.86	4.33	3.41	8.0	7.27	2.19	2.22

going downstream. Except for the ratios at Sites 1 and
4 on 8 November 1977, when there appeared to be no
definite trends, the decreasing ratios suggest that
ammonia is being oxidized to nitrate or utilized along
the Muskeg River system, and that the process
contributes to continued undersaturation of DO at the
Muskeg River, Site 1.

Detailed information on the changes in the
concentrations of nitrogen forms would be useful in
determining the rate of the process and the self-
purification capacity of these streams.

3.5.3   Dissolved Organic Carbon to Dissolved Organic
         Nitrogen Ratios

Another indication of the ability of the
Muskeg River basin to assimilate carbon compounds is
reflected in the DOC to DON ratio (Table 15). As
organic materials (particulate and dissolved) are
decomposed by fungi and bacteria, proportionately more
carbon than nitrogen is removed; the result is
decreasing C:N ratios. This process proceeds until it
starts to slow down because of the resistance to
decomposition of residual organic compounds. In
muskeg, marsh, and bog areas, the percentage of humic
compounds, low in nitrogen content, are high, while
organic materials produced by decomposition of plankton
contain crude protein with a C:N ratio of about 12:1.
Therefore, the plots of C:N ratios versus time could be
used to identify the sources and/or efficiency of
biological degradation of these organic compounds.

Table 2 gave summaries of soil types, pH,
percent concentrations of organic carbon and total
nitrogen, and the C:N ratios. It appears that the C:N
ratios are higher (31 to 54) where (Sites M77-11 and
M77-28) soil materials contain humic compounds derived

Table 15. DOC/DON ratios.

Date	DOC/DON Site 1	DOC/DON Site 2	DOC/DON Site 3	DOC/DON Site 4
27 Jul 76	10.9	—	—	—
7 Sep 76	15.6	—	—	—
4 OcT 76	—	55.1	—	—
6 Oct 76	54.8	—	—	—
14 Oct 76	—	—	58.3	42.6
29 Oct 76	26.9	—	—	—
10 Oct 76	74.2	74.2	—	—
12 Nov 76	—	—	95.4	—
15 Nov 76	—	—	—	112.5
2 Dec 76	—	37.8	—	—
16 Dec 76	35.9	—	24.8	—
24 Jan 77	—	—	—	16.4
25 Jan 77	23.7	—	15.6	—
26 Jan 77	—	14.5	—	—
11 Feb 77	26.2	—	—	—
14 Feb 77	—	—	17.4	—
18 Feb 77	—	—	—	32.2
3 Mar 77	28.3	—	—	—
7 Mar 77	—	24.5	—	—
8 Mar 77	—	—	13.2	10.9
18 Apr 77	9.2	9.0	—	—
26 Apr 77	—	—	10.3	14.1
16 May 77	31.8	37.3	—	—
17 May 77	—	—	37.1	33.75
20 Jun 77	17.4	—	16.9	—
22 Jun 77	—	16.5	—	—
24 Jun 77	—	—	—	18.6
13 Jul 77	—	27.7	—	22.4
18 Jul 77	24.7	—	27.1	26.1
16 Jul 77	16.8	16.0	31.1	—
13 Sep 77	29.5	33.9	—	—
14 Sep 7	—	—	22.5	—
4 Oct 77	21.0	39.0	—	—
11 Oct 77	—	—	—	19.3
8 Nov 77	22.8	21.3	—	28.8
6 Dec 77	15.7	—	—	—
7 Dec 77	—	—	—	20.9
9 Dec 77	—	27.7	—	—
24 Jan 78	25.5	23.0	23.3	53.7
7 Feb 78	15.0	—	20.0	11.4
9 Mar 78	11.1	—	—	—
6 Apr 78	19.1	15.3	—	—
10 Apr 78	—	—	18.0	—
3 May 78	34.1	18.75	—	—
4 May 78	—	—	—	3.7
5 Jun 78	80.3	79.2	—	—
21 Jun 78	32.0	56.6	—	—
10 Jul 78	6.5	25.5	—	—
20 Jul 78	—	21.0	—	—
15 Aug 78	—	25.0	—	—

from slightly to moderately decomposed leaves, needles
and lichens; and low (∿15) where (Site M77-15) the soil
materials contain organic materials produced by the
decomposition of crude protein; predominantly spongy
matt, mainly of moss composition, and some needles and
leaves permeated with fungal hyphae. Unfortunately,
total nitrogen concentrations were reported in the soil
analyses and not dissolved organic nitrogen (DON).
Thus, the C:N ratios could have limited use.

These general categories established above
are, however, supported by the seasonal patterns in
DOC:DON ratios at Sites 1, 2, 3, and 4 (Table 15).
Table 15 shows significantly higher DOC:DON ratios in
autumn 1976, when rainstorm events were probably
washing into the streams humic compounds derived from
the decomposition of fallen leaves, than in the late
winter-early spring (of 1977 and 1978) when, both the
contribution due to planktonic materials and the
resistance to decomposition of residual organic
compounds, are higher. The sharp initial drops in
these ratios, occurring within the period of a month,
suggest significant rates of decomposition.

3.5.4   Potential Effects of Synthetic Fuel Effluents
         on Freshwater Biota

The development of large scale synthetic
crude oil production from the Athabasca Oil Sands
creates the potential for release of substantial
organic wastes to the aquatic ecosystems. Crude
petroleum and/or refined petroleum and the process
waste waters consist of complex mixtures of organic
compounds. Most recently, Petriconi and Papee (1978)
showed that under sunlight illumination N-heptane,
benzene, and terpin hydrate photoreduce NO_2^- and NO_3^-
to ammonia. This photoreductivity of aqueous NO_2^- and

NO_3^- by organics, likely to be present in the oil
sands, arouses interest on the environmental importance
of the reaction and products; especially those of
polycyclic aromatic hydrocarbons.

In addition to aliphatic and aromatic
hydrocarbons, process products and wastes generally
also contain some nitrogenous polynuclear heterocyclic
bases. Other industrial processes, such as coking (Bark
et al. 1972), currently release these polycyclic bases
in their effluents. Southworth et al. (1978)
investigated the potential for accumulation in aquatic
biota of this class of compounds (specifically
isoquinoline, acridine, and benz(a)acridine) ranging
from two to four aromatic rings.

Certain members of this class of compounds
are known mutagens (Lehninger 1972) and/or carcinogens
(Arcos et al. 1968). The zooplankton, _Daphnia pulex_, a
food source for other aquatic organisms, has been used
in biomonitoring studies, in part, because of its
ability to rapidly accumulate lipophilic organics from
water (Herbes and Risi 1978).

Because aquatic organisms may accumulate
contaminants directly from water or through ingestion
of contaminated food, a program to identify such
products and monitor their uptake ratios and
concentrations along the food chain appears necessary.

3.6   SUMMARY

Temporal variations of a large number of
physicochemical parameters and general trends in
individual parameters and groups of parameters were
described in an effort to establish significant site
characteristics and factors influencing correlations.

Anomalies and seasonal patterns exhibited by
these parameters were also discussed in relationship to

biological components of the watershed streams. The discussion emphasized dissolved oxygen concentrations because dissolved oxygen and macronutrients support the growth of aquatic biota and, in turn, the assimilative capacity of waters of the Muskeg River watershed.

4.   A SURVEY OF HEAVY METALS, TRACE METALS, AND
          INTERACTIONS INFLUENCING THEIR TRANSPORT

4.1   INTRODUCTION
          The speciation and concentrations of heavy
metals and related trace elements in the natural
environment of the Muskeg River watershed are greatly
influenced by surficial geology, anthropogenic inputs,
weathering, and biochemical degradation processes.

          A significant fraction of the metals in the
water and sediment phases is often associated with
complexes. Consequently, the fate and/or versatility
of a particular metal ion depends on the relative
stability (numerically expressed by the stability
constants) of the complexes that the metal ion forms.
The complexing interactions and their effects on the
ecological conditions of the water are further
complicated by the influence of important water quality
variables such as hardness, temperature, dissolved
oxygen, and pH.

          The concentrations of heavy metals in rivers
and lakes of the AOSERP study area have the potential
of being affected by waterborne and airborne emissions
resulting from the extraction and processing of the oil
sands.

4.2   CURRENT STATE OF KNOWLEDGE

4.2.1   Metal Forms and Transportation Processes
          River bank and bottom sediments play a key
role in influencing the concentrations of heavy metals
in fluvial systems. Numerous studies (Vuceta and Morgan
1978; Leland et al. 1978 and references therein) have
shown that many heavy metals are concentrated in
sedimentary materials and transported by association

with suspended particulates. The metal-particulate
association may include:

1. Adsorption of metal ions to oxide
   surfaces;
2. Ion exchange with clay minerals;
3. Binding to organically coated particulate
   matter or organic colloidal material; and
4. Adsorption of metal-ligand complexes to
   particulate materials.

These reactions and transportation paths are
schematically represented (Davis and Leckie 1978) in
Figure 55 and discussed in greater detail in Section
4.4.3.

A recent AOSERP study by Allan and Jackson
(1978) found that Athabasca River bottom sediments
contained heavy minerals as well as quartz, feldspar,
carbonate, and layer silicates. The authors reported
that the heavy mineral particles are coated with
amorphorus inorganic oxides, hydroxides, and organic
material (mostly humic compounds).

Another AOSERP study (Korchinski in prep.)
has examined metal-humic (and fulvic) acid interactions
in rivers and sediments of the AOSERP study area. The
study found higher concentrations of most metals in
bank materials than in river bottom sediments; the
observation appears to indicate that transfers of
metals from overburden to surface water could be more
significant than similar transfers from bottom
sediments.

These AOSERP studies (Korchinski in prep.;
Lutz and Hendzel 1977) analyzed water and sediment
samples at the mouth of the Muskeg River (near Site
7/A) and found the levels of metals presented in Table
16.
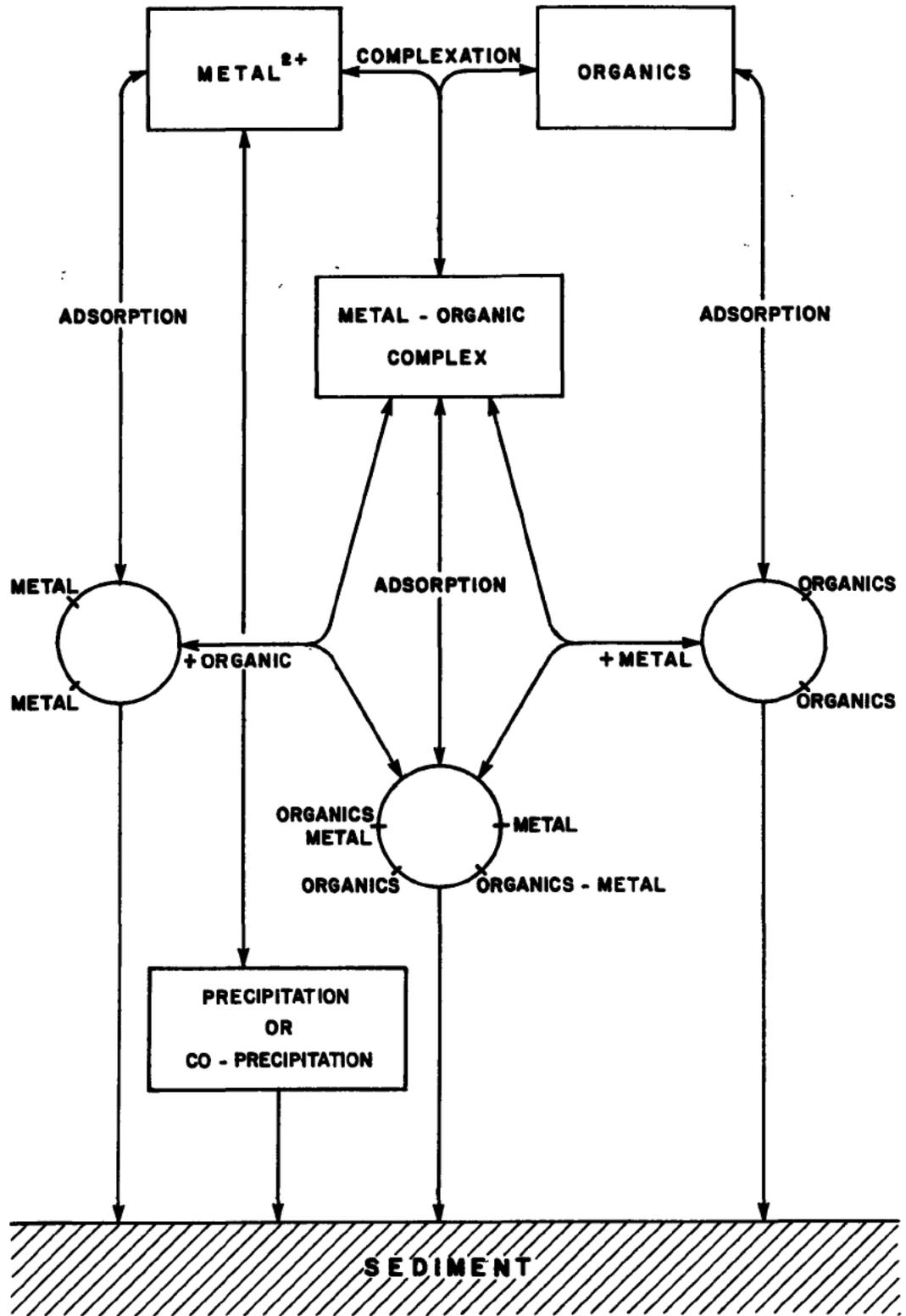
Figure 55. Major reaction pathways for trace metal transport and deposition in sediments in natural aquatic systems.

Table 16. Analyses of water and sediment materials collected from the Muskeg River at the mouth.

A) Sediment Samples 18 November 1976[a]	Concentration of Total Trace Metals (mg/kg)									
	Hg	Cu	Pb	Zn	Mn	Fe	Cd	Co	Ni	V
Bottom Sediment Materials	0.002	<10	<80	<10	350	13 000	<10	<50	20	<80
Bank Sediment Materials	0.032	20	<80	40	420	19 000	<10	60	60	110

B) Sediment Samples September 1976[a]	Concentration of Non-Residual Metals (0.5M HCl Extractable) mg/kg									
	Hg	Cu	Pb	Zn	Mn	Fe	Cd	Co	Ni	V
Bottom Sediment Materials	0.002	1.9	<5.0	6.5	109	4 800	1.0	<5.0	<5.0	<10.0
Bank Sediment Materials	0.032	8.7	5.0	30.0	380	10 000	<1.0	8.0	9.0	17.0

Water and Sediment Samples[b] (1977)	Metal Concentrations											
	Hg	Cu	Pb	Zn	Mn	Fe	Cd	Cr	Ni	V	As	Se
Unfiltered Water (mg/L)	-	0.1	-	30.0	44	756	0.04	1.2	1.7	5.7	<0.4	-
Filtered Water (mg/L)	-	1.3	-	25.0	31	718	0.03	0.9	3.1	4.3	-	-
Sediments (dry wt.) (mg/L)	0.04	26.2	9.9	57.2	327	22 400	0.10	59.0	20.5	86.0	3.5	0.65

[a] Korchinski (in prep.)
[b] Lutz and Hendzel (1977)

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4.3   METHODS AND SOURCES OF DATA

The data collected from the Muskeg River
basin, under AOSERP Project HY 2.5, identifies the
"total" concentrations of trace metals and extractable
heavy metals (Cd, Cu, Fe, V, Mn, Zn, Al, Pb, Ag, Co, B,
Ni, Se, As, Ca, and Hg) in surface waters. These
concentrations were obtained, using the standard
analytical methods listed in Appendix 7.3 (Table 18),
without determining the oxidation states, metal forms,
or the nature of the carrying compounds. The project
also determined the concentrations of a few inorganic
ligands (S^{2-}, CO_3^{2-}, HCO_3^-, SO_4^{2-}, Cl^-, F^-, NH_3, and
PO_4^{3-}) and certain potential complexing organic ligands
(tannin and lignin, humic acid, fulvic acid, phenolic
compounds, and organic carbon), since these parameters
have major influences on heavy metal transport.

Although the procedures used for extractable
heavy metals are designed to remove most humic acids
prior to the metal extraction steps, the possibility of
incomplete extraction still exists. A report by
Schnitzer and Khan (1972) indicated that metal-humic
acid interactions are so strong that it is generally
difficult to obtain humic substances free of complexed
metals.

4.4   RESULTS AND DISCUSSIONS

4.4.1   Colour and Causes

Streams of the Muskeg River watershed are
generally yellowish-brown to dark brown except during
or immediately following the spring runoff period. The
colouration is no doubt caused by a variety of coloured
organic, organo-mineral, and/or mineral compounds.

Despite the cause-effect relationship, the
measured colour is the combined effects of all

dissolved coloured substances and has quantitative
relationship only with each isolated pure substance.

The "apparent" colour readings for streams in
this watershed are generally (Figure 56) lower during
late winter and spring runoff periods than during the
summer, fall, and early winter. The effect of spring
runoffs is sometimes not noticeable at sites located in
bogs and muskeg. For instance, Kearl Lake outlet (Site
10) shows lower values in summer (20 to 60) and higher
values in fall (115) and early spring (140). This,
probably, is caused by the timing of lake drainage as
opposed to channeled flows originating from the inlet
(Site 11) and emptying at the outlet (Site 10) with
little mixing.

Generally, Sites 3, 8, 9, and 11 tend to have
high colour while Sites 3/A and 14 have very low colour
readings.

Natural waters of this watershed contain a
mixture of high (2000 to 300 000) molecular weight
organic substances whose exact structures have not been
determined, but are operationally defined as "the acid-
insoluble organic fraction" (or humic acid) and "the
acid-soluble organic fraction" (or fulvic acid). The
structures and complexing interactions of humic acids
have recently been reviewed by Jellinek (1974).

The range of concentrations of humic acid
reported for all sites in this study varies between
lows of <1.0 and 2.0 mg/L to highs between 2.5 and
13.5 mg/L. Most of the high values were recorded at
the beginning of the study period (prior to November
1976) and were never observed after that. It appears
that the analytical method used at the time might have
determined total humic compounds (both humic and fulvic
acids) and not humic acid, or determined with
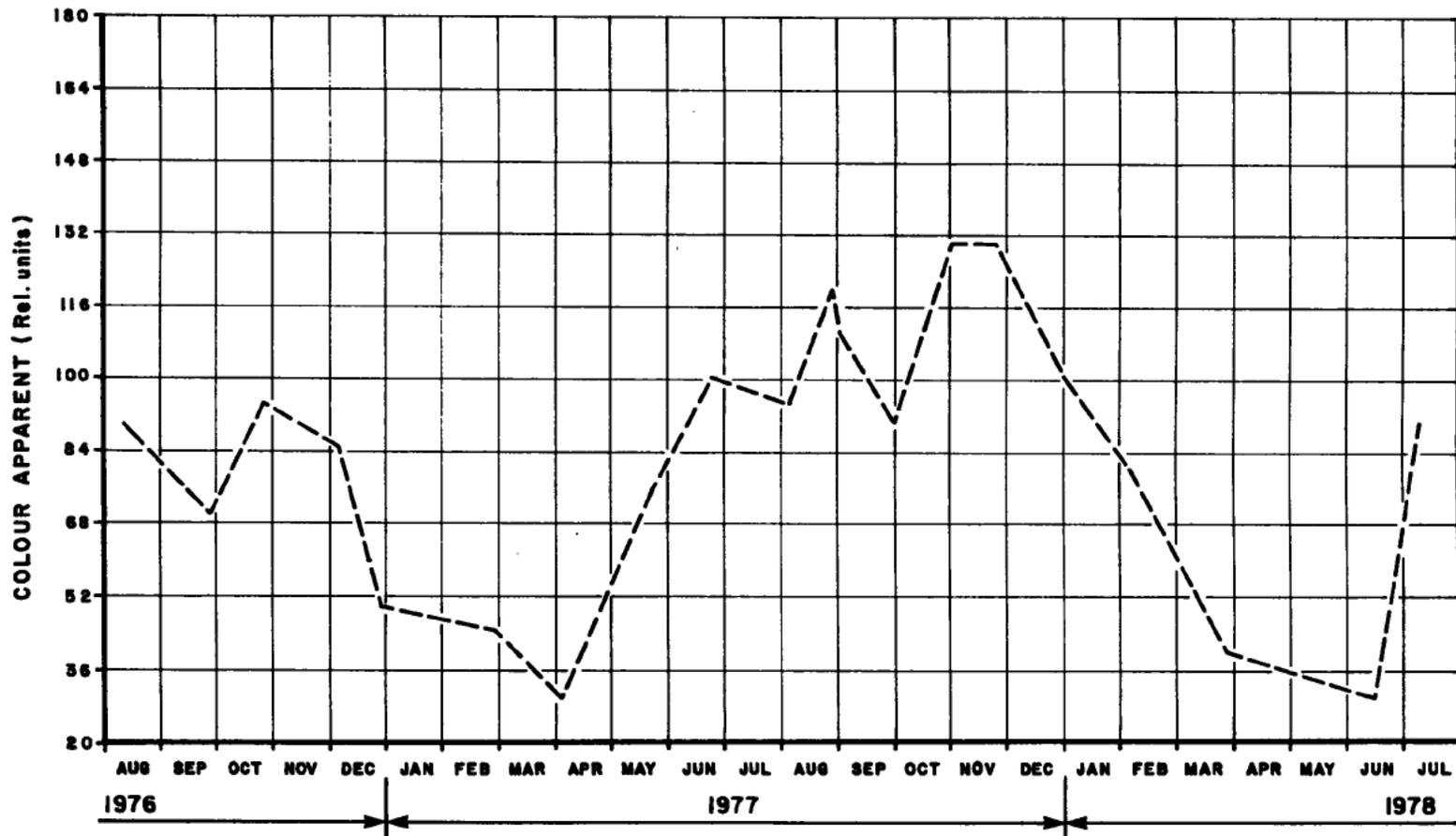
Figure 56. Variations of colour apparent (Site 2).

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accuracies that are too low to permit the use of the
data.

Another important factor is the fact that Fe
(and possibly Mn) concentrations greater than 1.0 mg/L
interfere in the analysis for humic acid. Because Fe
concentrations greater than 1.0 mg/L were more the rule
than the exception, humic acid levels reported in this
study have to be considered preliminary.

4.4.2   Trace Metals

4.4.2.1   Selenium. The dissolved selenium
concentrations at all sites were far below the Alberta
Surface Water Quality objective of 0.01 mg/L. In most
cases, they were less than 0.0005 mg/L. The only times
dissolved selenium concentrations significantly
exceeded this value were at Site 12 on 14 October 1976
(0.0009 mg/L); Site 11 on 29 October 1976 (0.0016 mg/L)
and 26 April 1977 (0.0009 mg/L); Site 9 on 26 October
1976 (0.0012 mg/L); Site 7 on 24 January 1977
(0.0014 mg/L); Site 4 on 26 April 1977 (0.0009 mg/L)
and Site 3/A on 12 November 1977 (0.0013 mg/L). At
Site 1, the concentration of dissolved selenium
generally ranged between less than 0.0002 mg/L to
0.0005 mg/L, except on 16 December 1976 and 25 January
1977, when the observed values reached 0.0008 and
0.0009 mg/L, respectively.

Lutz and Hendzel (1977) reported finding
0.65 mg of selenium per gram of bottom sediment at the
mouth of Muskeg River.

4.4.2.2   Arsenic. The general variation in the
concentration of dissolved arsenic was slightly more
diverse than that of selenium. Most sites had
concentrations equal to or less than 0.001 mg/L. The
Alberta Surface Water Quality Objective is 0.01 mg/L.

Site 1 recorded particularly high values (e.g. 0.012 mg/L, 29 October 1976 and 0.020 mg/L, 16 December 1976). Similar values have been observed at Site 2/A (0.020 mg/L) on 30 September and 16 December 1976; Site 6 on 25 April 77 (0.0136 mg/L); Site 8 on 9 September 1976 (0.012 mg/L); Site 10 on 10 August 1976 (0.025 mg/L); and Site 14 on 11 August 1976 (0.015 mg/L). There appears to be no seasonality to these maxima.

Lutz and Hendzel (1977) found only 3.5 mg of arsenic per gram of dry sediment in sediments collected from the mouth of the Muskeg River.

4.4.2.3 Boron. In this relatively undisturbed watershed, boron probably enters the natural waters by dissolution of boron-containing mineral deposits like sodium or calcium borate.

Area-wide, dissolved boron concentrations ranged from 0.01 to 0.48 mg/L. The highest values recorded during the study period were only slightly less than the 0.5 mg/L required by Alberta Surface Water Quality Objective.

Although no areal pattern in dissolved boron concentrations seems to emerge from the present study, there appear to be some site-specific seasonal patterns (Figure 57). The most obvious involve an April (early spring) maximum and, possibly, a late summer peak. These two peaks are separated by a major low in mid-winter and minor lows occurring in early summer and/or fall. The highest concentrations of dissolved boron were recorded at Site 2 on 7 September 1976 (0.48 mg/L); Site 1 on 3 March 1977 (0.26 mg/L); and at Site 3 on 8 March 1977 (0.32 mg/L). The maxima at the other sites were lower than 0.33 mg/L.

The seasonal trend (Figure 57) in boron concentrations throughout the watershed resembles that
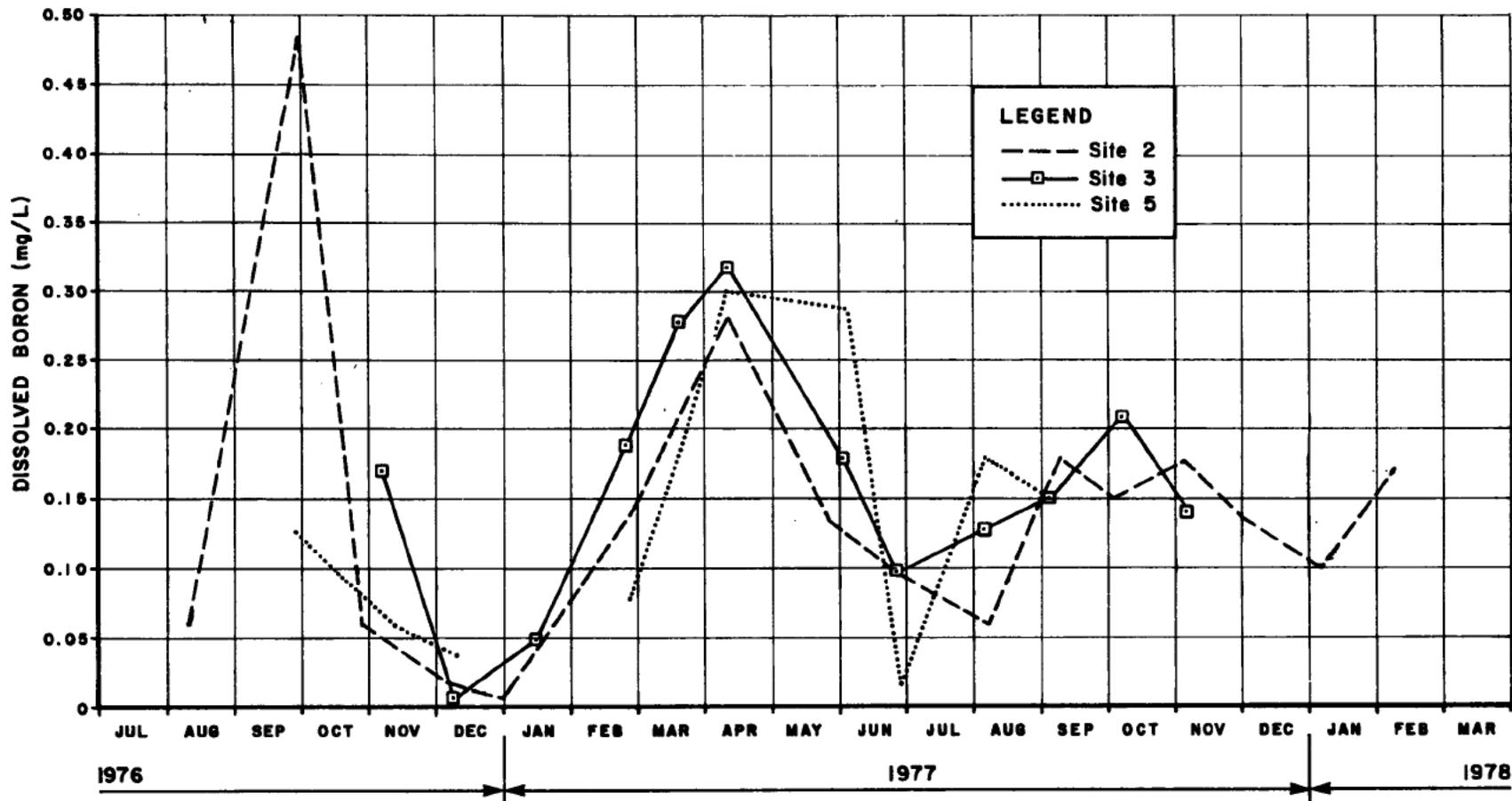
Figure 57.   Variations in the concentrations of dissolved boron (Sites 2, 3, and 5).

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of potassium and suggests some biological influence on
the boron cycle. This would be expected since boron is
an essential element in the nutrition of plants.

The possibility of high boron concentrations
being caused only by groundwater input appear unlikely
since most sites reported high boron concentrations in
waters of low-to-moderate specific conductances. For
example, at Site 2 boron concentrations of 0.48 mg/L
(7 September 1977), 0.01 mg/L (2 December 1977), and
0.18 mg/L (10 July 1977) where found in samples of
specific conductances of 190, 540, and 206 μS/cm,
respectively.

4.4.2.4   Mercury. The concentration of total mercury
is a very important health factor. Unfortunately,
however, analytical methods, including sample
preservation and storage, have only recently been
improved to allow the detection of lower
concentrations.

The total mercury values at a few sites
(e.g., Sites 3, 6, 7, and 11) were equal to or less
than 0.0001 mg/L, the Alberta Surface Water Quality
Objective. At most of the other sites, the total
mercury concentrations fell between 0.0002 and
0.0004 mg/L. There were, however, some unusually high
values; for instance, at Site 3/A on 10 September 1976
(0.0036 mg/L), Site 4 on 10 September 1976 (0.0043
mg/L), Site 8 on 30 September 1977 (0.0012 mg/L), Site
10 on 1 October 1976 (0.0013 mg/L), and at Site 12 on
10 September 1976 (0.0036 mg/L). The fact that most of
these high total mercury values occurred generally in
the autumn of 1976 is worth noting.

Korchinski (in prep.) found total mercury
level of 0.002 mg/kg in the bottom sediment materials
at the mouth of the Muskeg River. If this sediment

value (exceeded by stream samples collected on   10
September 1976 at Sites 3/A, 4, and 12) is genuine,
then microbial release of mercury compounds from the
sediments into the stream water would be suspected.

4.4.2.5. Silver. Except for two occasions involving
Site 5 (22 October 1976) and Site 12 (26 April 1977),
when the extractable silver concentrations were
0.010 mg/L at both sites, all other analyses showed
that extractable silver concentrations were equal to or
less than 0.005 mg/L at all sampling times throughout
the watershed. This is significantly less than the
0.05 mg/L set for the Alberta Surface Water Quality
Objective.

4.4.3   Heavy Metals: Variations, Adsorption, and
           Complexation

4.4.3.1   Variations

4.4.3.1.1 Cadmium. Almost every water sample collected
at Sites 1, 2, 4, 5, 6, 7, 8, 10, 11, 13, and 14 for
the analyses of extractable cadmium was less than or
equal to 0.001 mg/L. Cadmium concentrations of
0.002 mg/L were recorded at Sites 2/A, 3, 3/A, 7/A, 9,
and 12; and 0.003 mg/L recorded at Sites 3 and 3/A.
The highest value recorded in the study was for Site
7/A (0.006 mg/L) on 25 February 1977. These low
results are consistent with other reports (Finest et
al. 1975) which observed that cadmium undergoes no
labile and relatively little nonlabile complexation.
Furthermore, the sediment cadmium concentrations
reported by Lutz and Hendzel (1977) and Korchinski (in
prep.) show that cadmium values are very low even in
river bottom and river bank sediment materials
collected from the mouth of the Muskeg River. These
results suggest that adsorption by hydrous metal

oxides, clay particles, and colloidal organic matter is probably relatively small as well. Davis and Leckie (1978) have recently shown that the adsorption of trace metals on hydrous oxide surfaces was influenced by, among others, the ionic strength and the total trace metal concentration. It is therefore not too surprising that low cadmium concentrations were also observed in the sediments.

4.4.3.1.2 Cobalt. The levels of extractable cobalt concentrations appear very low but uniform; with higher values occurring in spring and summer. Sites 2/A, 4, 6, 10, 11, and 14 never reported values higher than 0.002 mg/L; Sites 2, 3/A, 5, 8, 9, and 13 reported values between 0.002 and 0.005 mg/L. Sites 1, 3, 7, 12, and 13/A reported values between 0.006 and 0.009 mg/L in July 1976. The only higher reading was recorded at Site 9 (0.011 mg/L) on 25 January 1977.

The concentrations of cobalt in bottom and bank sediments, reported by Lutz and Hendzel (1977) and Korchinski (in prep.), show that cobalt exists at very low concentrations even at the mouth of the Muskeg River.

4.4.3.1.3 Chromium(+6). Hexavalent chromium shows similar low levels and uniformity to that observed for cobalt. Higher chromium(+6) values tended to occur more frequently in the winter.

Sites 2/A, 4, 6, 8, 9, and 11, never reported values higher than 0.002 mg/L. Sites 1, 2, 3, 3/A, 5, 7, 10, 13/A, and 14 reported values between 0.002 and 0.009 mg/L. The only higher readings occurred at Site 12 (0.012 mg/L) on 4 March 1977; Site 1 (0.016 mg/L) on 27 July 1976; and Site 14 (0.190 mg/L) on 11 August 1976. The last figure is the only one that exceeds the

Alberta Surface Water Quality Objective for
chromium(+6) of 0.05 mg/L.

Sediment studies (Lutz and Hendzel 1977) did
not analyse for hexavalent chromium but indicated that
total chromium concentrations in sediments are
significant and comparable to Zn and V and higher than
Ni; but the dissolved forms are much lower than those
of Zn, V, and Ni.

4.4.3.1.4 Lead. The concentrations of extractable lead
in the watershed were generally very low. At Sites 6,
7, 8, 9, and 11, all values were equal to or less than
0.003 mg/L. At sites 2, 3, 3/A, 4, 10, 12, and 14,
concentrations up to, and including, 0.009 mg/L were
observed. Relatively higher autumn and winter values
were observed at Site 1 (0.021 mg/L) on 6 October 1977;
Site 2/A (0.018 mg/L) on 30 September 1976; Site 3
(0.015 mg/L) on 8 March 1977; and at Site 13/A
(0.032 mg/L) on 25 October 1976.

The concentrations of lead reported in
studies (Lutz and Hendzel 1977; Korchinski in prep.) of
bottom and bank sediments gave little indication of the
significance of lead in sediments, but results of the
Lutz and Hendzel study clearly showed significant
levels (with respect to bio-accumulation) of lead in
invertebrates of the Muskeg River (28 μg/g of dry
weight) and invertebrates and plankton of other
watersheds within the AOSERP study area.

4.4.3.1.5 Vanadium. Although concentrations of
vanadium are significant in bank sediments (Korchinski
in prep.) and bottom sediments (Lutz and Hendzel 1977)
at the mouth of the Muskeg River, ranking third behind
Fe and Mn, there appears to be very little total or
extractable vanadium in the flowing streams.

This study found the concentrations of total vanadium at Sites 3, 3/A, 6, 7, 7/A, 8, 10, 11, and 12 to be equal to or less than 0.001 mg/L; concentrations at Sites 1, 2, 2/A, and 5 occasionally rose to 0.002 or 0.003 mg/L. The only sites where total vanadium concentrations exceeded 0.003 mg/L were Site 4 (0.006 mg/L on 10 September 1976), Site 9 (0.004 mg/L on 24 August 1976), Site 13 (0.004 mg/L on 24 January 1977 and 0.006 mg/L on 4 March 1977), and Site 14 (0.005 mg/L on 4 March 1977).

Vanadium and nickel are two of the major heavy metal constituents of the Athabasca Oil Sands (Hodgson 1954); and a vanadium to nickel ratio of 2.4:1 is reportedly characteristic of these Cretaceous oils.

4.4.3.1.6 Nickel. Although nickel is supposed to hold a relatively constant ratio against vanadium in the oil sands, because of their similar origin, the amount of extractable nickel in streams of the Muskeg River drainage basin seems more variable than that of vanadium.

Sites 2, 2/A, 3/A, 4, 11, and 14 reported nickel concentrations of 0.004 mg/L or less; while Sites 1, 3, 5, 6, 7, 8, 9, 10, 12, and 13/A reported values up to and including 0.010 mg/L. The highest values were recorded at Site 5 (0.012 mg/L on 7 March 1977), Site 8 (0.013 mg/L on 18 February 1977), Site 10 (0.015 mg/L on 3 March 1977 and 0.024 mg/L on 19 July 1977), Site 12 (0.012 mg/L on 4 March 1977), and Site 13/A (0.022 mg/L on 20 July 1977). The last set of high nickel values exceeds the Alberta Surface Water Quality Objective value of 0.010 mg/L. It appears that values of 0.01 to 0.015 mg/L tended to occur in late winter or early spring, while the higher figures (0.02 and 0.024 mg/L) occurred in the summer.

Although the ratio of the concentration of vanadium to nickel is 1.83:1 in river bank sediments, the ratio in river bottom sediments is 4.2:1. This probably explains why vanadium appears lower and nickel higher in the stream water at the mouth of the Muskeg River.

4.4.3.1.7 Copper. Copper is found in trace amounts in all plants and animal life, and it is believed to be essential for nutrition.

The concentrations of extractable copper in stream waters of the Muskeg River watershed vary from lows of less than 0.02 mg/L, observed at Sites 4, 6, 7, 7/A, 9, 11, and 12, and recommended by the Alberta Surface Water Quality Objective, to moderate levels between 0.02 and 0.10 mg/L, observed during late fall, winter, and early spring at Sites 1, 2, 2/A, 3, 3/A, 5, 8, 10, 13/A, and 14. Significantly higher values of extractable copper were observed at Site 10 (0.102 mg/L on 25 April 1977), Site 5 (0.120 mg/L on 14 February 1977), and Site 14 (0.250 mg/L on 24 January 1977).

It is probable that the low concentrations of copper are a result of solubility controls by basic $CuCO_3$ (or CuS during anoxic conditions). The instances of higher concentrations cited above may be attributed to formation of soluble organic complexes of copper and/or to lower pH's (e.g., Site 5, pH 6.9, and Site 14, pH 7.1) which make basic copper carbonate more soluble.

In addition to the relatively higher concentrations observed during baseflow periods, certain sites recorded moderately high mid-summer copper values; for instance, Site 1 (0.026 mg/L on 27 July 1976), Site 2/A (0.016 mg/L on 20 June 1977), Site 2 (0.014 mg/L on 16 August 1977), Site 3 (0.016 mg/L on

16 August 1977), and Site 14 (0.013 mg/L on 22 June
1977). The possible effects of these high midsummer
concentrations on aquatic organisms and nutrient levels
have been discussed in Section 3.

Although dissolved, extractable, and sediment
copper concentrations are relatively low (Lutz and
Hendzel 1977) at the mouth of the Muskeg River, the
levels in invertebrates and plankton are reportedly
significant.

4.4.3.1.8.   Zinc. The concentrations of zinc in
bottom and bank sediments are surpassed only by Fe, Mn,
and V (and possibily Ni), but the dissolved
concentrations rank third, behind Fe and Mn. It
appears that the chemical versatility and biological
significance of zinc, compared to nickel, plays a role
in its relative abundance in streams. The reported
(Lutz and Hendzel 1977) concentrations of zinc in the
AOSERP study area are at least four times higher in
invertebrates and three times higher in plankton than
nickel.

The concentrations of extractable zinc in the
Muskeg River drainage basin are significantly variable
(Figure 58). Concentrations less than 0.05 mg/L (the
Alberta Surface Water Quality Objective) were observed
at Sites 2, 2/A, 3/A, 4, 5, 6, 7, 7/A, 8, 9, 10, 11,
12, 13, and 14. But, at Sites 1 and 3, higher values
were observed; for instance, at Site 1 on 13 September
1977 (0.091 mg/L) and Site 3 on 16 August 1977
(0.062 mg/L). On both of these occasions the
corresponding nickel concentrations were less than
0.002 mg/L.

The possible effect of zinc during productive
seasons have been discussed in Section 3.
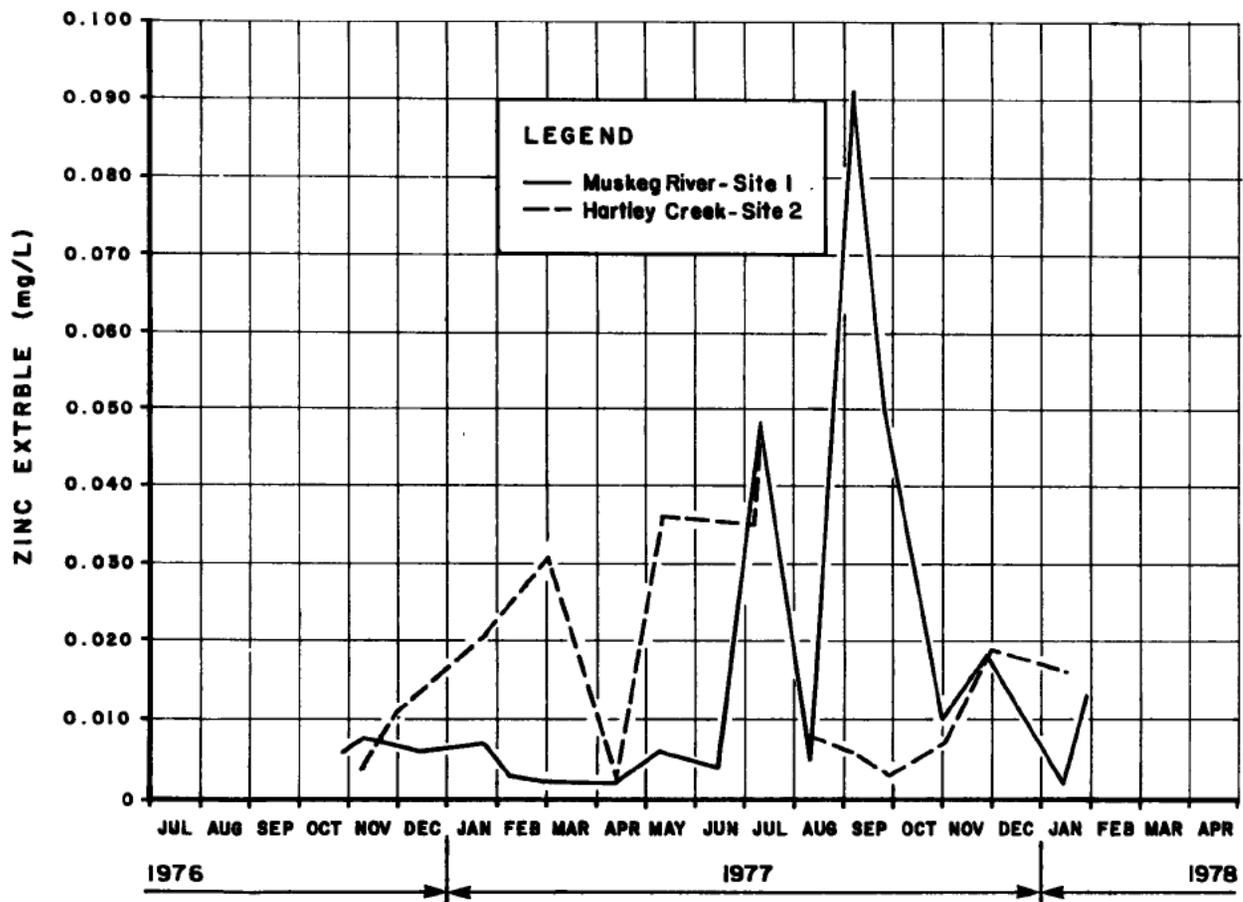
Figure 58. Variations in the concentrations of zinc (Sites 1 and 2).

4.4.3.1.9 _Aluminum_. Aluminum is a major constituent of
the alumino-silicates, which include feldspars, micas,
and clays, and various oxide and hydroxide mineral
forms (e.g., garnet and turquoise).

The abundance of aluminum is not, however,
reflected in the levels of extractable alumium
concentration observed in the present study because
most of the aluminum is held in relatively stable
lattices. These particulate forms of aluminum still
participate in very significant adsorption-desorption
processes relevant to water quality. So that, while
the absolute values of extractable aluminum in these
streams may not be very important, the role played by
aluminum hydrous oxides is invaluable.

Generally, streams of the watershed showed
high winter concentrations of extractable aluminum, a
sharp decline during spring runoff, and only a slight
recovery during summer and fall. Because of the higher
concentrations in sediments compared to the dissolved
form, slight variations in concentrations, which could
be caused by lack of duplication in sampling, will not
be emphasized. The concentrations of extractable
aluminum at Sites 1, 2/A, 3, 3/A, 4, 5, 6, 9, 10, 11,
12, and 14 ranged from <0.01 mg/L to 0.40 mg/L.
Concentrations up to 0.51 and 0.60 mg/L were observed
at Site 2 (24 January 1978) (Figure 59) and Site 7
(24 January 1977), respectively. The highest values
were recorded at Site 8 (1.44 mg/L on 7 March 1977) and
Site 13/A (0.90 mg/L on 28 April 1977). It is,
however, possible that sediments were collected with
these last two water samples.

4.4.3.1.10 _Iron and Manganese_. Iron and manganese are
both essential nutrients for human, animal, and plant-
metabolisms. Furthermore, iron and manganese hydrous
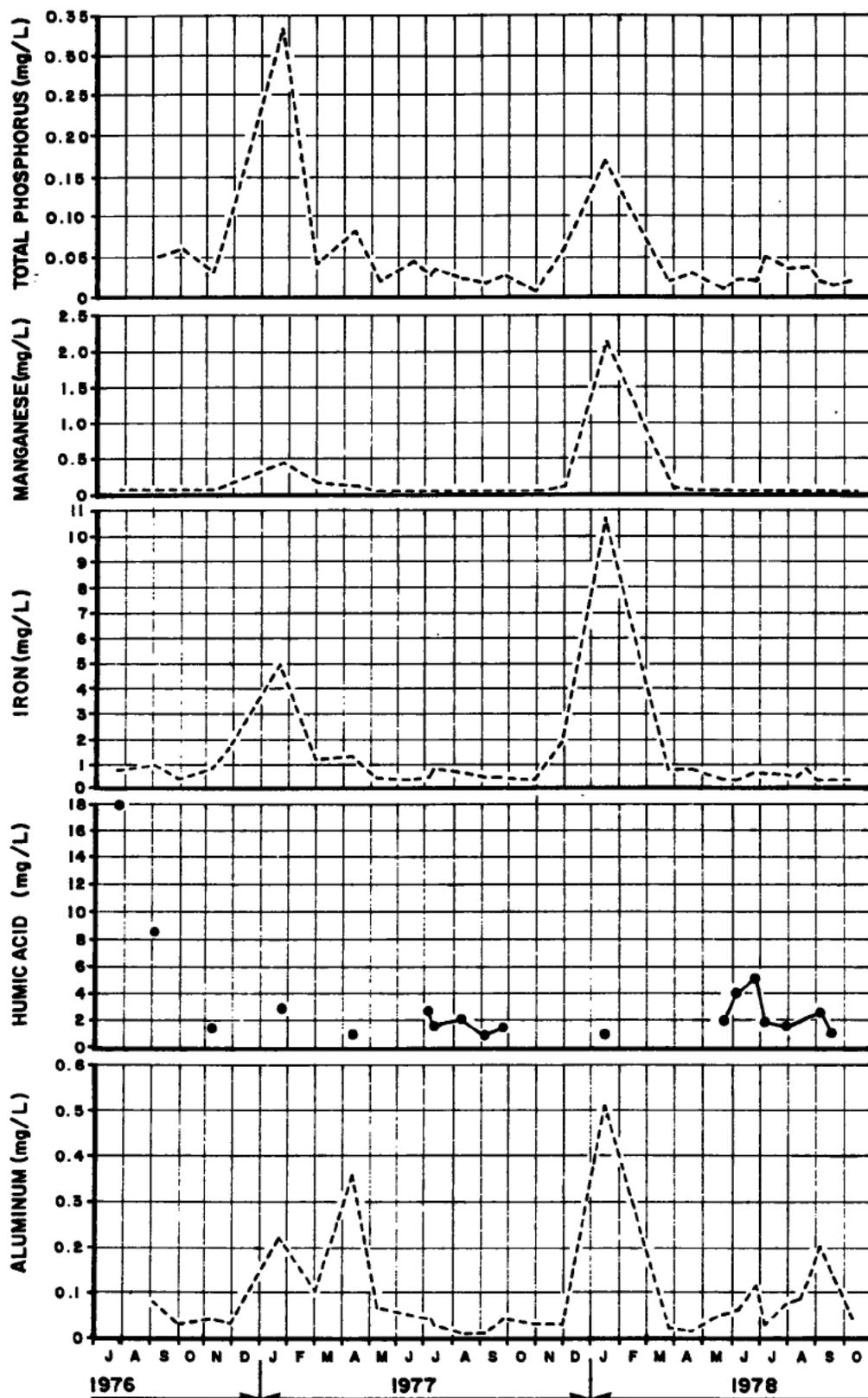
Fig. 59. Variations in the concentrations of water quality parameters (Fe, Mn, Al, Total phosphate phosphorus, and Humic acid), Site 2.

oxides participate in the adsorption reactions
described for aluminum.

The concentrations of extractable manganese
vary from lows of 0.003 mg/L to highs of 1.0 mg/L at
Sites 1, 2/A, 3, 3/A, 4, 5, 6, 7, and 10; the higher
values being observed at Sites 1 and 3/A.

A few significantly higher manganese
concentrations were recorded at Site 2 (2.15 mg/L on
24 January 1978) (Figure 59); Site 8 (2.10 mg/L on
7 March 1977); Site 9 (1.50 mg/L on 24 August 1976 and
3.50 mg/L on 25 January 1977); Site 11 (1.55 mg/L on
25 January 1977); Site 12 (6.10 mg/L on 4 March 1977);
Site 13/A (7.95 mg/L on 24 January 1977 and 1.48 mg/L
on 4 March 1977); and at Site 14 (5.15 mg/L on
24 January 1977 and 7.00 mg/L on 4 March 1977). These
high values could easily be caused by sediments in the
sample. Lutz and Hendzel (1977) reported dissolved
manganese concentrations of only 0.031 mg/L at the
mouth to the Muskeg River; Korchinski (in prep.)
reported manganese concentrations of 350 mg/kg in
bottom sediments and 420 mg/kg in bank sediments.
Thus, it would not take much sediment to increase the
concentration of extractable manganese.

Except for the much-elevated levels, the
concentrations of extractable iron follow (Figure 59)
patterns parallel to those of manganese for each
station; generally high in the winter and relatively
constant from spring to fall.

It appears that the 0.3 mg/L level,
established for iron as the Alberta Surface Water
Quality Objective, was exceeded at least once at each
site in the watershed. The highest values were
recorded at Site 8 (12.2 mg/L on 7 March 1977); Site 9
(13.0 mg/L on 25 January 1977); Site 13/A (28.0 mg/L on

24 January 1977 and 43.5 mg/L on 4 March 1977); and at
Site 14 (15.0 mg/L on 4 March 1977).

It is probable that complexing interactions
involving humic compounds and other donor species in
these streams would add to the level of dissolved iron
and manganese. Unfortunately, trends in humic acid
concentrations (Figure 59) showed no correlations with
those of extractable iron or manganese.

Lutz and Hendzel (1977) reported that the
weight of iron in filtered water sample from the Muskeg
River at the mouth was only 0.718 mg/L while the
unfiltered sample contained 0.756 mg/L. These results
are consistent with the median value of 0.77 mg/L
reported in the Korchinski (in prep.) study. It is
most probable, therefore, that the very high values
reported in this study are due to particulates in the
samples.

As indicated in Section 3, iron, phosphorus,
and (to a lesser extent) aluminum are transported into
streams in the form of particulate matter. Figure 59
suggests similar trends in the concentrations of iron
and total phosphate phosphorus.

The relationship between the concentrations
of iron and stream discharge (Figure 60) was checked
and found to be very poor, although the data seem to
suggest that the concentrations of iron are generally
higher during low streamflow and lower during high
flow. The occurrence of high iron concentrations during
high flow and storm runoff events can be attributed to
sediments carried in suspension.

4.4.3.2 Adsorption

4.4.3.2.1 Peat Moss. Coupal and Lalancette (1976)
recently studied the treatment of waste waters
containing heavy metals, (Hg, Cd, Zn, Cu, Fe, Ni,
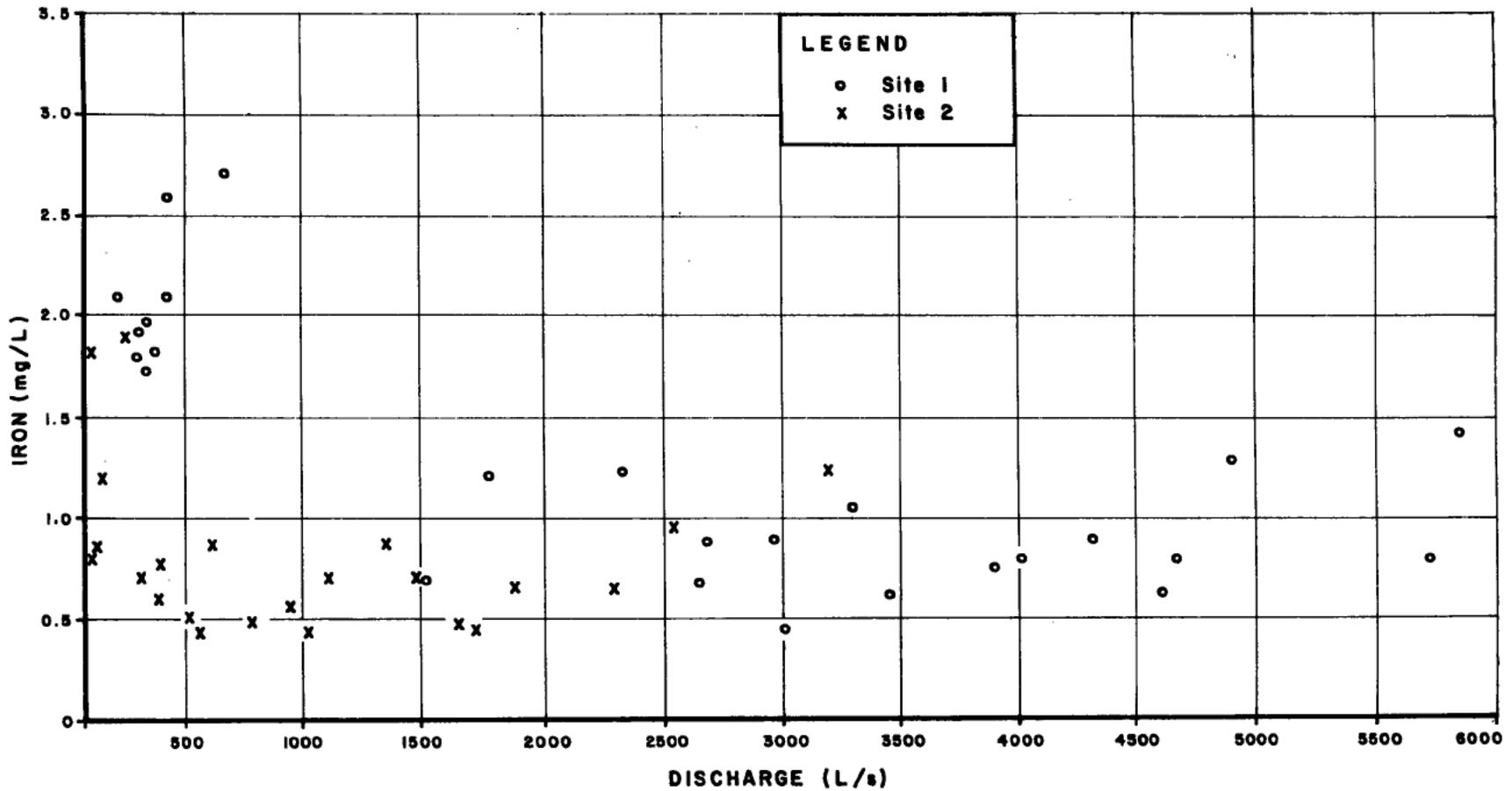
Figure 60. Relationship between the concentrations of iron and stream discharge (Sites 1 and 2).

Cr(+6), Cr(+3), Ag, and Pb), cyanide, phosphate, organic matters (e.g., oils), detergents, and dyes, by contact with peat moss. The above study is particularly relevant to the Muskeg River basin because of the predominance of muskeg. Peat moss contains lignin and cellulose as major constituents. These constituents, especially lignin, have polar organic functional groups (alcohol, aldehyde, ketone, carboxylic acid, phenolic hydroxide, and ether) that can be involved in bonding interactions with metals and polar organic molecules.

The range of concentrations of tannin and lignin reported for all sites in the Muskeg River basin was very narrow. The concentrations varied from lows of between 0.08 to 2.2 mg/L to highs of 1.3 to 3.05 mg/L; the lowest values occurred at Site 3/A (0.2 to 1.3 mg/L), and the highest values at Site 11 (2.2 to 3.05 mg/L).

The study by Coupal and Lalancette (1976) also noted that the capacity of peat to retain cations is related to the pH of the solution. At pH's above 8.5, peat itself is not stable; while at pH's below 3.0, most metals will be leached from peat. But, between these values, peat is very efficient at adsorbing most metals. Thus, the adsorption or release of heavy metals in muskegs could be greatly influenced by pH controlled conditions of peat moss.

As indicated in the discussions of certain metals, variations in concentrations could therefore result from microbial degradation processes which lower the soil pH to around pH 3, thus allowing metals to be leached out of peat moss.

Analyses of soils (mostly organic materials) collected from three sites in the Muskeg River basin gave total cation exchange capacities (TEC) (Table 2)

ranging from 0.4 to 18.8, and soil pH values (4.0 to
5.9) which clearly indicate that heavy metal
concentrations could be influenced by the adsorption
and release from peat moss.

4.4.3.2.2 Particulates and Sediments. Evidence for the
movement of trace metals from dissolved to particulate
phase, due to sorption by Fe and Mn hydrous oxides and
clay particles and uptake by phytoplankton, has been
reported in the literature (Grieve and Fletcher 1977;
Gilbert et al. 1976) and cited in this report.
Generally, low dissolved trace metal concentrations are
associated with sorption, while resuspension of
sediments by currents and wind is considered the major
influence on the distribution. Precipitates of Fe and
other metals (Mn and Al) also influence the
distribution of nutrients, for instance, by scavenging
$o-PO_4$ from solution leaving little available for
algae. Although side-by-side plots of Fe, Mn, and total
phosphate phosphorus (Figure 59) in the present study
appeared to suggest correlations between these metals
and total phosphate phosphorus, efforts to find direct
correlations proved abortive.

Davis and Leckie (1978) found that, in the
presence of complexing inorganic ligands (e.g., Cl^-,
CN^-, $S_2O_3^{2-}$, etc.), adsorption of heavy metals and
trace metals (Cu, Pb, Hg, Cd, Zn, and Ag) on amorphous
iron oxide was decreased and desorption increased where
formation in solution of stable complexes is possible.
These authors also considered the role of natural
organic matter (e.g., humic compounds) in affecting the
distribution of trace metals, since a significant
fraction of the metals in the water and sediment phases
is often associated with organic matter. Although
little is known about the adsorptive characteristics of

oxide surfaces modified by adsorbed organic compounds,
recent studies (Green and Manahan 1977; Guy et al.
1975) have shown that most metal ions are more strongly
absorbed on colloidal humic and fulvic acids than on
oxide surface sites. The study of the effects of
organic complexing ligands with chemical structures and
functional groups similar to naturally occurring
organic compounds (especially humic materials) found
that complexation, surface bonding, and the orientation
of an absorbed ligand(s) are also important factors in
determining the overall effect on metal uptake by
hydrous oxides.

Unfortunately, the present study did not
collect enough relevant data to allow definitive
statements to be made regarding particulate metal
forms, levels, and transport processes.

4.4.3.4 <u>Complexation</u>. O'Shea and Mancy (1978)
studied the competitive interactions between the
hardness metal ions (Ca^{+2} and Mg^{+2}) and five trace
metals [Bi(III), Cd(II), Cu(II), Pb(II), and Tl(I)] for
hydroxo- and carbonato-ligands at pH 6, 7, and 8 and
under conditions simulating natural aquatic
environment. In the absence of calcium ions, these
metal ions interacted (extent increased with pH) with
the ligands, mainly CO_3^{2-} ion, to produce predominantly
non-labile complexes. Specifically, for copper and
lead, the effect of non-labile complexation
predominated at pH 6 and 7 while the significance of
labile complexes increased between pH 7 and 8. The
overall result (pH 6 to 8) indicates that, of the five
trace metals, copper was the most extensively
complexed; Cd(II) and Tl(II) are the least complexed.

The significance of labile complexation (at
pH between 7 and 8) for Zn, Pb, and Cu, in a

predominantly bicarbonate medium, such as exists in the
Muskeg River watershed, suggests that the concentration
of these, and other ions that behave similarily, should
show some relationship with specific conductance, since
both are high during baseflow and low during surface
runoff. Correlations were attempted at a selected
number of sites. The results appeared to suggest that
some relationships probably exist. The correlations
also implied that best fits probably occur for metals
that exist in predominantly ionic metal (or metal
complex) forms (e.g., M^{+2}, $M(HCO_3)^+$, $M(OH)^+$, etc.) and
that deviations would occur when complexation,
adsorption, or precipitation predominates.

Thus, in a predominantly inorganic system, at
pH's above pH 7, Cu, Zn, and Pb would be expected to
stay in solution in the ionic form or as labile
complexes.

The major fraction of dissolved organic
matter in muskeg waters is composed of humic compounds
and products of their decomposition (Gjessing 1976;
Shuman and Woodward 1977). Metalo-fulvic acid
complexes were demonstrated by Schnitzer and Hansen
(1970) to exist in soils. These authors found "3:1
molar Fe(III)- and Al(III)-fulvic acid complexes" in
their soil sample. Schnitzer and Khan (1972) also
found that orthophosphate ions could be linked to the
metal that is complexed to the fulvic acid because the
metal content of these complexes increased with the
phosphate content. They noted that these interactions
are generally so strong that it is generally difficult
to obtain humic substances free of salts, clays and
complexed metals.

Attempts (Figure 61) to correlate dissolved
or extractable metal (Fe, Al, Mn, Zn, and Cu) ion
concentrations with humic acid, fulvic acid, total
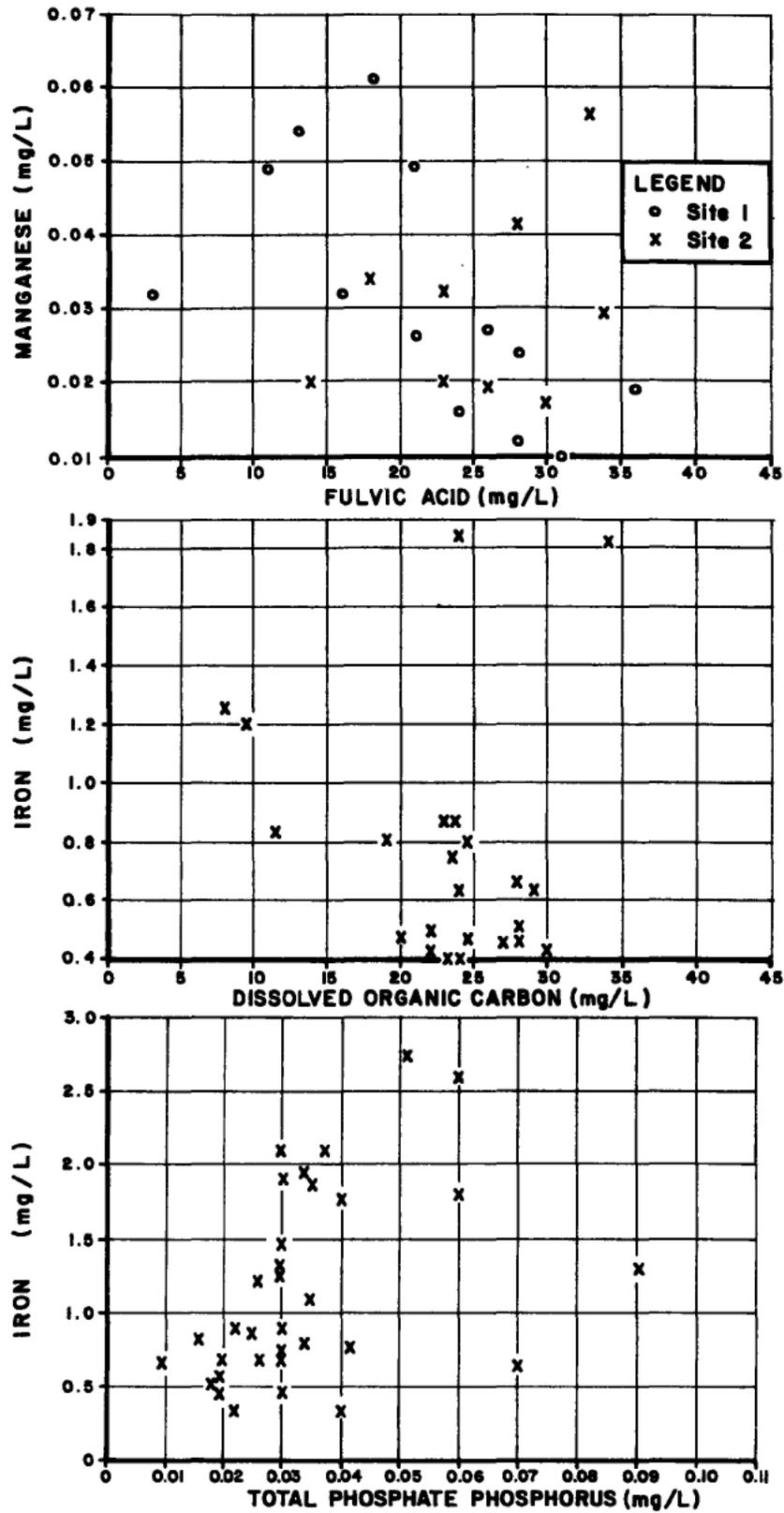
Figure 61. Interparameter relationships and possible transport association.

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phosphate phosphorus, or dissolved (and total) organic
carbon concentrations at all sites failed to give any
definite correlation. Sources of this problem have
already been identified as being: firstly, the presence
of sediments in samples; secondly, the poor humic acid
analysis results obtainable from samples containing
iron in concentrations greater than 1.0 mg/L; and
thirdly, the fact that humic compounds, and their
decomposition products, have varying complexing
capacities and molecular weights, so that correlations
may not occur in the presence of varying concentrations
and formulations.

Schnitzer and Skinner (1966, 1967)
investigated the interactions between fulvic acid and
metals [Cu(II), Fe(II), Zn(II), Pb(II), Ni(II), Mn(II),
Co(II), Ca(II), and Mg(II)] which are known to occur in
soils. They found that the overall order of
stabilities of complexes formed between fulvic acid and
the nine divalent metal ions, at pH 3.5 and pH 5.0,
deviated significantly from the Irving-Williams series:

$$Pb>Cu>Ni>Co>Zn>Cd>Fe>Mn>Mg.$$
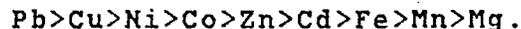
(Irving and Williams 1948). Another study (O'Shea and
Mancy 1978) found that the interaction between trace
metal ions and humic acid in a carbonate medium behaved
individualistically and that there appeared to be no
correlation between the oxidation state of the metals
and their behavior toward complexing organic matter.
Furthermore, they observed that calcium associated to a
relatively higher degree with humic substances at or
above pH 3; and indicated that when trace metals are
introduced to a natural carbonate water containing both
humic substances and calcium, most metal ions [except
ions like Cd(II)] bind to the non-labile sites (and

might release calcium from these sites) but are unable
to complex with the labile sites.

The findings of these studies appear to
indicate that in natural carbonate water, especially
between pH 6 and 7, containing humic substances,
calcium, and most metal ions, the metal ions would bind
to non-labile sites. Thus, attempts to remove humic
compounds from samples during analysis could also have
removed large amounts of metals. This possibility calls
for more detailed investigations of methods used in
studying metal speciation and distribution processes.

4.5   SUMMARY

This report has documented sources,
concentrations, and probable significance of heavy
metals in streams of the Muskeg River watershed. In
addition to identifying seasonal patterns and extremes,
it attempted to give qualitative evaluations of
significant interactions (adsorption, complexation,
etc.) involving heavy metals. Unfortunately,
information on ionic, adsorbed, or complexed (with
organic ligands) metal forms cannot be extracted from
the analyses of total or extractable metals.

While the original objectives for the study
were adequately met, the sampling, sample preservation,
and analysis methods employed limit the usefulness of
the data. Extensive studies designed to identify metal
speciation and distribution processes and to understand
the adsorptive characteristics of adsorbed organic
compounds would have been more revealing.

5.   RECOMMENDATIONS

          The findings of this study indicate the
following areas of recommended research:

          1.   Investigate possible improvement of
sample preservation and analyses for sulphate
and sulphide;

          2.   Identify sources and seasonal hydrologic
interactions between surface and groundwater
flows in sub-basins within the AOSERP study
area, since proposed oil sands developments
could cause dewatering operations and natural
groundwater flows to drastically affect fresh
water aquifer zones;

          3.   Work toward a longer history of baseline
water quality data to help identify
significant time dependent effects (e.g.,
degradation or improvement in chemical
quality) on streamflow related relationships,
and from which to draw meaningful
conclusions. Project HY 2.5 was reduced from
a 24 to a 12 month study;

          4.   Investigate the physical and chemical
mobility of inorganic phosphorus in sediments
to facilitate the evaluation of the impact of
study area bottom sediments on the phosphorus
status;

          5.   Investigate and develop a suitable model
to describe all decomposition processes. A
model that would accommodate the varying
contributions of the major processes of
decomposition; such as leaching and microbial
and invertebrate processes. The development
of such a model might require:

(a) determining the rate of breakdown (as measured by the dry weight loss) of leaves;

(b) determining the role of stream invertebrates in the decomposition; and

(c) determining the nutrient changes in the decomposing litter;

6. Identify lipophilic organics present in AOSERP study area waters, and biomonitor and document the uptake ratios and concentrations of these compounds and of toxic metals along the food chain;

7. Identify the biological species and mechanisms controlling metal speciation, especially where potentially toxic metals are involved, since seasonal trends in certain metals have identified possible biological controls on their seasonal patterns;

8. Describe metal speciation and distribution in an attempt to categorize the roles of certain types of complexing ligands and their probable significance in controlling the distribution of trace metals; and

9. Design (by use of most appropriate analytical techniques, including extracting agents) studies to identify metal forms (e.g., absorbed metals versus metals associated with the crystalling structure of particles), oxidation states, and the nature of the carrying compounds (or transport association).

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7.   APPENDICES

7.1   HYDRAULIC CHARACTERISTICS OF CHANNEL

Site 1.   Gentle slope upstream from site, irregular
                bottom profile, moderate velocity, water
                surface usually below banks.

Site 2.   Gentle to moderate flow through a meadering
                reach, beaver dams (log jam), deep narrow
                channel during low flow (rapids downstream
                of site).

Site 2/A.   Moderate slope, moderately high stream
                velocity, turbulence caused by rapids.

Site 3.   Poorly defined muskeg channels, back-ups,
                very, very gentle flow, downstream and
                upstream beaver dam causing overflow into
                diversions.

Site 3/A.   Narrow channel, regular spillages, very
                gentle flow, very flat channel slope, flow
                orginating from flat bog.

Site 4.   Very flat, low channel slope, frequent
                overbank spillages, bog, deep beaver dams.

Site 5.   Channel cuts through sedge/moss bog,
                numerous beaver dams and logs, very mild
                channel slope, frequent overflows.

Site 6.   Very low slopes, shallow channel (slight
                possibility of back-ups), moderate flow
                velocity.

Site 7.   Rough and steep channel, minor rapids, low
                sloping upstream reach.

Site 8.   Low to moderate flow, narrow creek, erosion
            evident.

Site 9.   Very gently slopes, beaver dams, active
            erosion evident.

Site 10.   Very shallow channel, very slow moving
            (through a gentle sloping channel in a
            muskeg). Generally ice-free in winter.

Site 11.   One of two shallow channels located on a
            muskeg covered alluvial fan, gentle flow,
            occasional back-ups from the lake.

Site 12.   Shallow channel, steep gradient, channel
            boulders cause rapids. Beaver dams
            downstream from site cause occasional back-
            ups.

Site 13/A. Shallow channel, moderate-to-high flow
            velocity controlled by a beaver dam
            upstream, with frequent back-ups and
            diversions.

Site 14.   Shallow (log straddled) channel, very steep
            gradient, active sand movement in channel.

            For more detailed descriptions of sub-
basins and hydraulic characteristics, including
photographs, the reader is referred to the report by
Froelich (in prep.).

7.2   DESCRIPTION OF SOIL TYPES

1.   Moss Bog forms on peat in locations where
the water table is at or near the surface in the spring
and slightly below the remainder of the year.

2.   Fen Bog forms on relatively open peatlands
where mineral rich water tables is at or near the
surface frequently.

3.   Peaty Gleysol forms on water-logged
(poorly drained) areas and generally have organic
surface layers.

4.   Orthic Grey Luvisol develops, in the lower
horizons of well-to-imperfectly drained areas, where
clays (and other associated medium-to-fine-textured
colloidal materials) and base saturated parent
materials under forest cover have interacted with the
product of the leaching of the soluble decomposition
products of forest litter.

5.   Brunisolic soils have a high degree of
base saturation and a lack of well developed mineral-
organic surface horizon.
                (a) Eluviated Eutric Brunisol develops on
                    rapidly-to-moderatley well-drained coarse-
                    textured glaciofluvial deposits.
                (b) Gleyed Eluviated Eutric Brunisol
                    develops in imperfectly drained areas.

6.   Gleyed Rogosol are mineral soils formed in
the lower horizons (c horizon) in well-to-imperfectly
drained areas and have characteristics of the parent
materials.

Table 17.   Bed material size distribution (%).

Site #	Gravel	Sand	Silt	Clay	Organic
1	90(coarse)	10	-	-	-
2	-	99	1	-	-
2/A	100(large)	-	-	-	-
3	-	38(fine)	58	4	-
3/A	-	-	-	-	100
4	-	-	-	-	100
5	-	40(fine)	60	-	-
6	6(fine)	94	-	-	-
7	45	55(coarse to medium)	-	-	-
8	-	94(fine)	3	3	-
9	-	35	27	35	-
10	-	-	-	-	100(loose)
11	-	35(fine)	65	-	-
12	large boulders	60(fine)	35	5	-
13/A	-	42(fine)	34	14	-
14	3(fine)	95	2	-	-

7.3   METHODS AND SOURCES OF DATA

7.3.1   Field Sampling

        Field data collection and analyses included
measurements of water quality parameters (pH, dissolved
oxygen, temperature, and specific conductance) carried
out by project personnel at the sampling site.

        The collection, preservation, and shipping
of water samples collected for this project followed
procedures outlined in Water Survey of Canada (1978)
sampling manual, except as noted in the preservation
procedures (Appendix 7.4).

        Preservative chemicals used to avoid change
in one or more constituents during shipment from
sampling site to laboratory; and sample containers
(glass, plastic, or other bottles) were supplied by
Chemex Laboratories (Alberta) Ltd., Calgary.

7.3.2   Analytical Methods and Detection Limits
        Since immediate analysis of some
constituents was required, samples were air freighted
to Chemex Laboratory as soon as possible. The
analytical methods and detection limits used for the
set of water quality parameters used in this study are
given on Table 18. The NAQUADAT code numbers refer to
standard analytical procedures (refer to Methods Manual
for Chemical Analysis of Water and Wastes, Alberta
Environment, for further detail).

Table 18. Methodology and detection limits.

Parameter	Naquadat Code	Detection Limit
Calcium	20103 L	0.001 mg/L as Ca
Magnesium	12102 L	0.05 mg/L as Mg
Sodium	11102 L	0.05 mg/L as Na
Potassium	19102 L	0.05 mg/L as K
Chloride	17203 L	0.1 mg/L as Cl
Sulphate	16306 L	1.0 mg/L as SO_4
Total Alkalinity	10101 L	0.5 mg/L as $CaCO_3$
pH	10301 L	0.01 pH Units
Carbonate	06301 L	0.5 mg/L as CO_3
Bicarbonate	06201 L	0.5 mg/L as HCO_3
Total Hardness	10603 L	0.5 mg/L as $CaCO_3$
Silica	14101 L	0.2 mg/L as SiO_2
Conductance	02041 L	0.2 µS/cm
Colour	02021 L	5 Pt Co color units
Tannin & Lignin	06551 L	0.1 mg/L
Total Filt. Residue	10451 L	1.0 mg/L
Total Filt. Residue Fixed	10551 L	1.0 mg/L
Total Non Filt. Res.	10401 L	0.4 mg/L
Total Non Filt. Res. Fixed	10501 L	0.4 mg/L
Turbidity	02073 L	0.1 JTU
Humic Acids	06581 L	1 mg/l
Total Organic C	06001 L	0.5 mg/l as C
Total Inorganic C	06051 L	0.5 mg/l as C
Total Diss. Org. C	06101 L	0.5 mg/L as C
$NO_2^- + NO_3^-$ Nitrogen	07110 L	0.003 mg/L as N
Ammonia Nitrogen	07555 L	0.01 mg/L as N

Continued....

Table 18. Concluded.

Parameter	Naquadat Code	Detection Limit
Total Kjeldahl Nitrogen	07013 L	0.01 mg/L as N
Total Phosphorous	15406 L	0.003 mg/L as P
Ortho-Phosphorous	15256 L	0.003 mg/L as P
Phenol	06532 L	0.001 mg/L as phenol
Oil & Grease	06521 L	0.1 mg/L
Sulphide	16101 L	0.05 mg/L as S$^-$
Cyanide	06603 L	0.01 mg/L as CN$^-$
Chlorophyll A	06771 L	0.001 mg/L
Chem. Oxy. Demand	08301 L	1 mg/L as O_2
Cadmium	48302 L	0.001 mg/L as Cd
Hexavalent Chromium	24101 L	0.003 mg/L as Cr^{+6}
Copper	29304 L	0.001 mg/L as Cu
Iron	26304 L	0.01 mg/L as Fe
Lead	82302 L	0.002 mg/L as Pb
Manganese	25304 L	0.001 mg/L as Mn
Titanium	N.A.	0.05 mg/L as Ti
Zinc	30305 L	0.001 mg/L as Zn
Vanadium	23002 L	0.001 mg/L as V
Selenium	34102 L	0.0002 mg/L as Se
Mercury	80011 L	0.0001 mg/L as Hg
Arsenic	33014 L	0.0002 mg/L as As
Nickel	28302 L	0.002 mg/L as Ni
Aluminum	13302 L	0.1 mg/L as Al
Cobalt	27302 L	0.002 mg/L as Co
Boron	05105 L	0.01 mg/L as B
Silver	47302 L	0.001 mg/L as Ag
Ion Balance	00102 L	---

7.4   REGIONAL WATER QUALITY SAMPLING SHEET

A.O.S.E.R.P. REGIONAL WATER QUALITY SAMPLING SHEET: PROJECT _____

SAMPLED BY: _____

STATION DESCRIPTION: _____

STATION -SAMPLE CODE: 0,5,A,0, ,A,T,0,7, , , , , , , ,¼¼¼, , , , , , , ,M S T

                                 D D M M Y Y h h m m .
                                  (date)   (time)

SAMPLING SITE: _____

Access:

                             _____ meters upstream from gauge.

_____ wading   _____ meters downstream from gauge.

_____ cableway   97251F meters from surface.

_____ boat   97206F meters from right bank facing downstream.

_____ ice cover   97202F meters from left bank facing downstream.

Suspended Sediment Sample? _____   Discharge (flow rate) instant. _____ 97161F.
          Stage (lake level). _____   cfs.

FIELD PARAMETERS: _____   02061F temperature (^{o}C) _____   10301F pH

                _____ 02041F specific conductance _____ 08102F dissolved oxygen.

WEATHER CONDITIONS: Air temp. ___^{o}C   Barometric Pressure. _____cm Hg.

    Cloud cover _____%   Precipitation _____   Wind (speed//direction)_____

NUMBER	SYMBOL	TYPE	PRESERVATION	PARAMETERS TO BE ANALYZED
	R	1 litre plastic	None	[ ] All ___Ca, ___Na, ___K, ___Se, ___As ___Mg, ___Cl ___F, ___Silica, ___Sulphate, ___Conductance, ___Alkalinity, ___pH.
	G 1	32 oz glass	None	[ ] All ___odor, ___color, ___Turbidity ___Tannin & Lignin, ___Sulfactants ___Dissolved solids*, ___Cr (+6), ___Susp. solids*, ___Humic Acids, ___Fulvic acids. (* total & volatile)
	G 2	1 litre plastic	2.5 ml Conc H_2SO_4	[ ] All ___COD, ___Total Kjeldahl, ___NH_3-N, ___Total Phosphorous,
	O G	32 oz glass	2.5 ml Conc H_2SO_4	_____ Oil and Greases
	P	32 oz glass	1 gm $CuSO_4$ and 2 ml 85% H_3PO_4	_____ Phenols.
	N C	5 oz plastic	None	[ ] All ___O-PO_4, ___NO_3-N ___NO_2-N ___Total inorg. C, ___Total org. C, ___Total dissolved org. C,
	M	1 litre plastic	10 ml Conc. HNO_3 (add after sampling)	[ ] All ___Cd, ___Cu, ___Fe, ___V, ___Mn, ___Zn, ___Al, ___Pb, ___Ag, ___Co, ___B, ___ ___Ti, ___Ni, ___Be, ___,
	H G	2 oz Pyrex bottle	2 ml sol. of 0.5% HNO_3 & 0.5% $K_2Cr_2O_7$ (add after sampling)	_____ Mercury
	C Y	250 ml plastic	1 ml 6N NaOH	_____ Cyanide
	S	5 oz plastic	2 ml 1M ZnAc	_____ Sulphide
	C H	32 oz plastic	1 ml 10% $MgCO_3$	_____ Chlorophyll "A"
	P H H	40 oz wine bottle	None, (keep cool & out of sun)	_____ Total Hydrocarbon

NOTE: FILL BOTTLE TO 90% CAPACITY.   Telex Lab prior to or soon after shipping samples
(enclose a duplicate copy of each sampling sheet.)

REMARKS - PROBLEMS IN SAMPLING ---- etc. _____

7.5   1976 AND 1977 FLOWS FOR MUSKEG RIVER BASIN STUDY
SITES

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Figure 62. 1976 Flows — Muskeg River basin study sites.

Figure 63. 1977 Flows - Muskeg River basin study sites.

AOSERP RESEARCH REPORTS

1.		AOSERP First Annual Report, 1975
2.	AF 4.1.1	Walleye and Goldeye Fisheries Investigations in the Peace-Athabasca Delta--1975
3.	HE 1.1.1	Structure of a Traditional Baseline Data System
4.	VE 2.2	A Preliminary Vegetation Survey of the Alberta Oil Sands Environmental Research Program Study Area
5.	HY 3.1	The Evaluation of Wastewaters from an Oil Sand Extraction Plant
6.		Housing for the North--The Stackwall System
7.	AF 3.1.1	A Synopsis of the Physical and Biological Limnology and Fisheries Programs whithin the Alberta Oil Sands Area
8.	AF 1.2.1	The Impact of Saline Waters upon Freshwater Biota (A Literature Review and Bibliography)
9.	ME 3.3	Preliminary Investigations into the Magnitude of Fog Occurrence and Associated Problems in the Oil Sands Area
10.	HE 2.1	Development of a Research Design Related to Archaeological Studies in the Athabasca Oil Sands Area
11.	AF 2.2.1	Life Cycles of Some Common Aquatic Insects of the Athabasca River, Alberta
12.	ME 1.7	Very High Resolution Meteorological Satellite Study of Oil Sands Weather: "A Feasibility Study"
13.	ME 2.3.1	Plume Dispersion Measurements from an Oil Sands Extraction Plant, March 1976
14.		
15.	ME 3.4	A Climatology of Low Level Air Trajectories in the Alberta Oil Sands Area
16.	ME 1.6	The Feasibility of a Weather Radar near Fort McMurray, Alberta
17.	AF 2.1.1	A Survey of Baseline Levels of Contaminants in Aquatic Biota of the AOSERP Study Area
18.	HY 1.1	Interim Compilation of Stream Gauging Data to December 1976 for the Alberta Oil Sands Environmental Research Program
19.	ME 4.1	Calculations of Annual Averaged Sulphur Dioxide Concentrations at Ground Level in the AOSERP Study Area
20.	HY 3.1.1	Characterization of Organic Constituents in Waters and Wastewaters of the Athabasca Oil Sands Mining Area
21.		AOSERP Second Annual Report, 1976-77
22.		Alberta Oil Sands Environmental Research Program Interim Report to 1978 covering the period April 1975 to November 1978
23.	AF 1.1.2	Acute Lethality of Mine Depressurization Water on Trout Perch and Rainbow Trout
24.	ME 1.5.2	Air System Winter Field Study in the AOSERP Study Area, February 1977.
25.	ME 3.5.1	Review of Pollutant Transformation Processes Relevant to the Alberta Oil Sands Area

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53.	HY 3.1.2	Baseline States of Organic Constituents in the Athabasca River System Upstream of Fort McMurray
54.	WS 2.3	A Preliminary Study of Chemical and Microbial Characteristics of the Athabasca River in the Athabasca Oil Sands Area of Northeastern Alberta
55.	HY 2.6	Microbial Populations in the Athabasca River
56.	AF 3.2.1	The Acute Toxicity of Saline Groundwater and of Vanadium to Fish and Aquatic Invertebrates
57.	LS 2.3.1	Ecological Habitat Mapping of the AOSERP Study Area (Supplement): Phase I
58.	AF 2.0.2	Interim Report on Ecological Studies on the Lower Trophic Levels of Muskeg Rivers Within the Alberta Oil Sands Environmental Research Program Study Area
59.	TF 3.1	Semi-Aquatic Mammals: Annotated Bibliography
60.	WS 1.1.1	Synthesis of Surface Water Hydrology
61.	AF 4.5.2	An Intensive Study of the Fish Fauna of the Steepbank River Watershed of Northeastern Alberta
62.	TF 5.1	Amphibians and Reptiles in the AOSERP Study Area
63.	ME 3.8.3	Analysis of AOSERP Plume Sigma Data
64.	LS 21.6.1	A Review of the Baseline Data Relevant to the Impacts of Oil Sands Development on Large Mammals in the AOSERP Study Area
65.	LS 21.6.2	A Review of the Baseline Data Relevant to the Impacts of Oil Sands Development on Black Bears in the AOSERP Study Area
66.	AS 4.3.2	An Assessment of the Models LIRAQ and ADPIC for Application to the Athabasca Oil Sands Area
67.	WS 1.3.2	Aquatic Biological Investigations of the Muskeg River Watershed
68.	AS 1.5.3 AS 3.5.2	Air System Summer Field Study in the AOSERP Study Area, June 1977
69.	HS 40.1	Native Employment Patterns in Alberta's Athabasca Oil Sands Region
70.	LS 28.1.2	An Interim Report on the Insectivorous Animals in the AOSERP Study Area
71.	HY 2.2	Lake Acidification Potential in the Alberta Oil Sands Environmental Research Program Study Area
72.	LS 7.1.2	The Ecology of Five Major Species of Small Mammals in the AOSERP Study Area: A Review
73.	LS 23.2	Distribution, Abundance and Habitat Associations of Beavers, Muskrats, Mink and River Otters in the AOSERP Study Area, Northeastern Alberta
-	--	Interim Report to 1978
74.	AS 4.5	Air Quality Modelling and User Needs
75.	WS 1.3.4	Interim report on a comparative study of benthic algal primary productivity in the AOSERP study area

76.	AF 4.5.1	An Intensive Study of the Fish Fauna of the Muskeg River Watershed of Northeastern Alberta
77.	HS 20.1	Overview of Local Economic Development in the Athabasca Oil Sands Region Since 1961.
78.	LS 22.1.1	Habitat Relationships and Management of Terrestrial Birds in Northeastern Alberta.
79.	AF 3.6.1	The Multiple Toxicity of Vanadium, Nickel, and Phenol to Fish.
80.	LS 22.3.1	Biology and Management of Peregrin Falcons (*Falco peregrinus anatum*) in Northeastern Alberta.
81.	LS 22.1.2	Species Distribution and Habitat Relationships of Waterfowl in Northeastern Alberta.
82.	LS 22.2	Breeding Distribution and Behaviour of the White Pelican in the Athabasca Oil Sands Area.
83.	LS 22.2	The Distribution, Foraging Behaviour, and Allied Activities of the White Pelican in the Athabasca Oil Sands Area.

These reports are not available upon request. For further information about availability and location of depositories, please contact:

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