A.F.Penn

The Composition of Waters in a Sub-Arctic Lake System.

THE COMPOSITION OF WATERS IN A SUB-ARCTIC LAKE SYSTEM: KNOB LAKE DRAINAGE BASIN, SCHEFFERVILLE, P.Q.

by

Alan F. Penn

ABSTRACT

In order to evaluate local geological and hydrological controls of ionic concentration, water samples were collected from lakes in Knob Lake drainage basin (38 km^2), Schefferville, P. Quebec, in March-April and August-September, 1969. The dominant ions were HCO_3^{-1}, Ca^{+2} and Mg^{+2}, derived from a dolomite formation traversing the basin and from carbonate minerals in shales. Lakes on dolomite approached equilibrium with dolomite and calcite in summer. Within lakes, ion concentrations reflected thermal stratification and mixing of surface waters and groundwater from shale and dolomite. Other constituents of lake waters described reflected weathering of shales, contributions from atmospheric precipitation and biological activity. Pearce Lake, which receives waste-water from Schefferville, had abnormal concentrations of sulfate, suspended iron and orthophosphate. Proportions of SO_4^{-2}, Cl^{-1}, Na^{+1} and K^{+1} in the lake fluctuated seasonally, and water circulation favoured late winter stagnation and settling of suspended iron and probably phosphorus.

M.Sc. Thesis
Department of Geography
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March, 1971

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A thesis submitted to the Faculty of Graduate Studies
and Research in partial fulfilment of the requirements
for the degree of Master of Science.

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ACKNOWLEDGEMENTS

This study is a contribution to the Hydrology Research Programme in Knob Lake drainage basin, Schefferville, P. Quebec, as part of the International Hydrological Decade. The basin has been designated as a representative of Central Labrador-Ungava region of Canada. The research described here developed from three main points of interest: the nature of chemical weathering in the basin, the role played by lakes in the local hydrology and in the transport of solutes, and the suspected polluted condition of Pearce Lake, downstream from Schefferville townsite. The decision to draw these topics together for this study was dictated primarily by the initial need for a general view of the hydrology and water chemistry of the drainage basin, rather than for detailed work in one small area of the basin. It is hoped that this study at a drainage basin scale will provide the basis for more detailed work on water chemistry.

The field work for this study was carried out between July, 1968, and September, 1969, while I was employed as a meteorological observer at the McGill University Sub-Arctic Research Laboratory at Schefferville. I take pleasure in thanking Dr. Bruce Thom, who as my supervisor at Schefferville provided me with the support and encouragement to explore the subject of water chemistry which was then new to me. I also thank Lee Nichols, geologist with the Iron Ore Company at Schefferville, who told me that it was possible to analyse water samples at Schefferville using Hach reagents and minimum laboratory equipment, and also for the loan of a pH meter. In many entertaining and productive discussions, Lee provided me with the basic understanding necessary for interpreting water analyses. I thank the Ministère des Richesses Naturelles de Québec for supplying me with water level recorders and analyses of water quality and suspended sediment. I am also grateful to Dr. R.C. Zimmermann who accepted the task of supervising me when Dr. Thom left McGill and who steered this thesis through the final stages of preparation. His comments on style and organisation are much appreciated. I thank Mr. Bryan Cook for giving me moral support when my interest flagged and for reading sections of the manuscript. Dr. D'Anglejan, of the Marine Sciences Centre at McGill, and Dr. Kalff, limnologist in the Department of Zoology, offered constructive advice on the carbonate chemistry section of this study, for which I am grateful.

The programme would not have been possible without patient assistance in the field work. For this I extend thanks to Peeter Altosaar, Francois LeMaitre, Hardy Grandberg, Kenn Back, Andy Williams, Dale Bairstow and Tony Price. Jim Franks, who continued the hydrology programme after my departure, supplied me with hydrological data for the remainder of 1969, for which I am grateful. Financial support for the completion of this thesis was provided by the Department of Geography at McGill, while office space and drafting facilities were kindly provided by Dr. Fritz Müller and Phyllis Kelsey. Lastly, I thank Lee Carter, who typed this thesis.

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INTRODUCTION

1. Controls of Lake Water Chemistry.

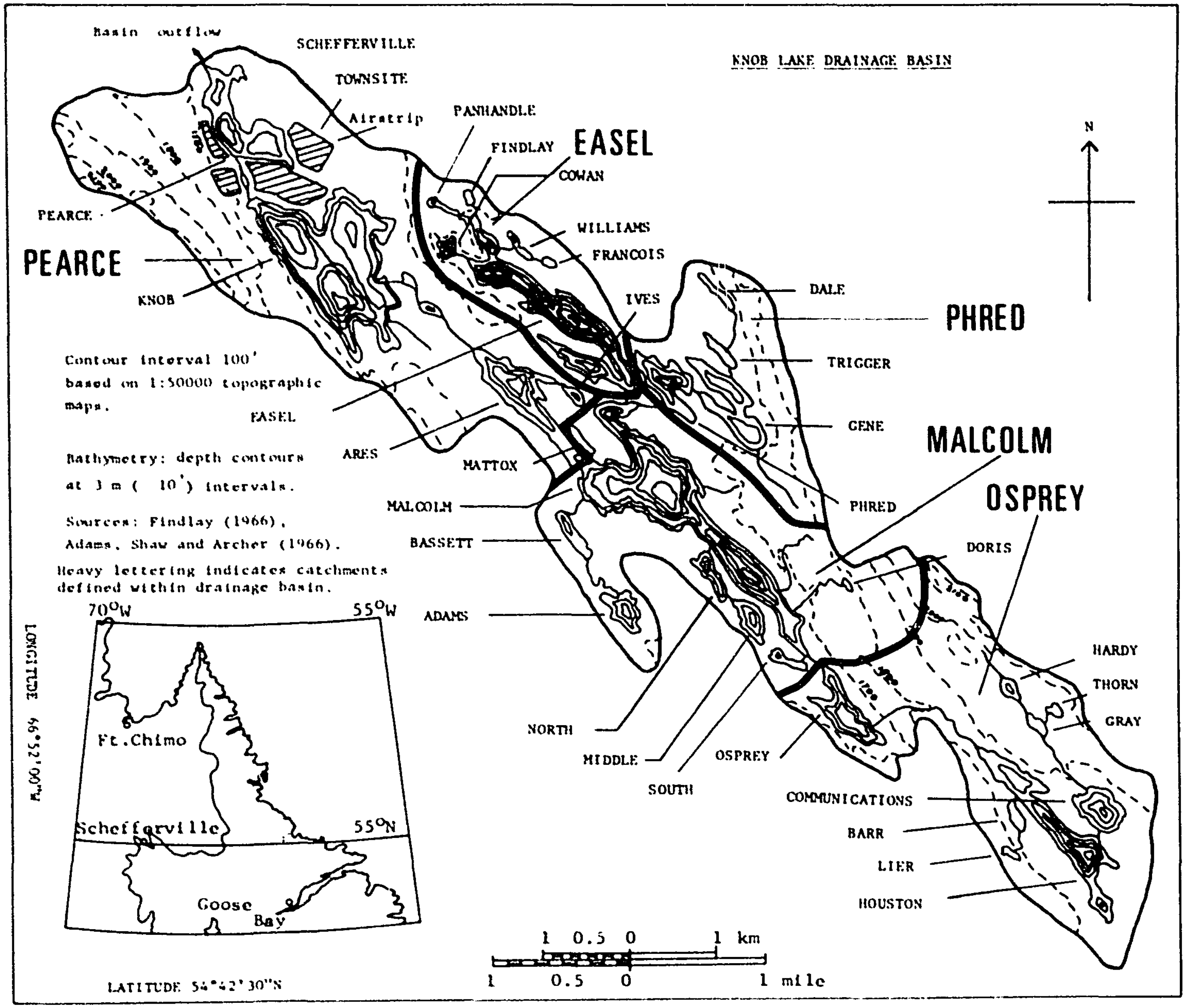
The study of lake water chemistry has as its general objective the identification of chemical and physical processes operating within lakes and their tributary catchments. Chemical analyses of lake water are usually based on samples taken at different depths at intervals throughout the year. Analyses typically include the more abundant cations and anions, nutrient elements and trace quantities of metals of possible toxicity or of geochemical interest. Interpretations of such analyses frequently emphasise vertical distributions of individual constituents in lake water as related to thermal stratification and lake circulation (Hutchinson, 1957) and to chemical exchanges between lake water and bottom sediments (Mortimer, 1941).

Since a lake forms part of a drainage basin, its water chemistry is controlled partly by the geology of the lake floor and the mineralogy of bottom sediments, and partly by the drainage basin geology as it determines the composition of groundwater and surface run-off discharged into the lake. The extension of the study of lake water chemistry to include relationships between water composition and the geology and hydrology of the lake catchment is the main concern of this study. The primary objective is to explain lake water composition in terms of the possible chemical equilibria attained by surface run-off and groundwater in contact with rock-forming minerals in the lake catchment, and in terms of the rates of replacement of lake water and the influence of groundwater discharge into lake basins. In the field situation that was encountered in this study, an explanation of water composition of this nature also required an assessment of nutrient uptake from lake water, the influence of ions present in atmospheric precipitation and the possible effects of human settlement on lake water composition.

2. Location of Research: Knob Lake Drainage Basin.

The Knob Lake drainage basin (Fig. 1) is located south of Schefferville in northern Quebec (54° 45'N 66° 45' W). This small catchment (37.8 km^2) has been selected as a research basin for the International Hydrological Decade (I.H.D.). The chemical composition of the thirty lakes in this catchment forms the subject matter of this study. Run-off in the basin, draining shales, dolomite and iron formation, provides the water supply for the iron-ore mining town of Schefferville. Waste water from this settlement is discharged into Pearce Lake, the outlet of which defines the northern boundary of the drainage basin. A secondary aim of this study is to evaluate changes that have taken place in the chemistry of this lake as a consequence of waste water discharge.

The most important characteristics of the drainage basin which concern this study are the role played by lakes in the transfer of water through the basin, and the existence of two distinctive geological formations (shale and dolomite) as the main controls of water chemistry. Run-off in the basin passes through a sequence of lakes occupying over 20 per cent of the basin area. Very few streams flow overland to the lakes, and the channels between lakes are generally short. Although shale is, by area, the dominant geological formation in the basin, the dolomite, running in a band diagonally across the basin from north to south, influences the



Contour interval 100'
based on 1:50000 topographic
maps.

Bathymetry: depth contours
at 3 m (10') intervals.

Sources: Findlay (1966),
Adams, Shaw and Archer (1966).

Heavy lettering indicates catchments
defined within drainage basin.

Fig. 1 Lake and catchment identification, lake bathymetry and surface topography, Knob Lake Basin.

composition of more than 90 per cent of the lake water in the basin. This is a consequence of the mixing of water draining from shale with water draining from dolomite.

To summarise, the study area is distinguished by drainage through a series of lakes in which water chemistry is related to contact with carbonate minerals. The main problem, therefore, is to describe lake water chemistry in terms of what is understood about local hydrology and the solution of carbonate minerals.

Water samples were collected from each of the lakes in the basin in March-April and August-September, 1969. Between these two major sampling periods, samples were also collected from Pearce Lake and from Cowan Lake, a small lake lying on dolomite. The sampling programme was designed to describe variations in chemistry between lakes in addition to vertical and horizontal variations within lakes. The sampling programme also gave information on seasonal changes in water chemistry, dilution during spring snowmelt, effects on water chemistry of thermal stratification in winter and in summer, and on the effects of waste-water discharge on the chemistry of Pearce Lake.

All water samples collected were analysed for pH, bicarbonate, calcium and magnesium, since these constituents are required in the analysis of carbonate equilibria in lake water. Dissolved silica, sulfate and (suspended) iron were also determined in the majority of samples. Also analysed, but less intensively, were the following: dissolved oxygen, aluminium, manganese, chloride, nitrate and orthophosphate. Sodium and potassium concentrations in samples taken at lake outflows were determined at the water quality laboratory of the Ministère des Richesses Naturelles de Québec.

The hydrological programme concurrent with the lake sampling involved stream gauging and stage observations at the Pearce Lake outflow, stream gauging at other lake outflows in the basin, lake ice surveys, snow course observations and rainfall sampling in representative topographic sites. Meteorological data for the study period were taken from records maintained at the McGill Sub-Arctic Research Laboratory in Schefferville, from which this research was conducted. Geological information pertaining to the mineralogy and the aquifer properties of the formations present in the basin were obtained from published sources, especially Gross (1968), and from unpublished material in the files of the Iron Ore Company of Canada at Schefferville.

3. Literature Relevant to the Interpretation of Lake Water Chemistry.

The chemical equilibria applicable to this study involve the reaction of water with carbonate minerals, different forms of naturally occurring silica and the aluminosilicate minerals present in shales. The discussion of carbonate equilibria is based on a review article on the solubility of dolomite by Hsu (1967), a survey of literature on the effects of variations in composition on the solution of carbonate minerals by Bricker and Garrels (1967), and the treatment of carbonate equilibria in Garrels and Christ (1965). The discussion of the relative saturation of lake waters with respect to dolomite and calcite is based in part on Kramer's analysis of the carbonate chemistry of Lake Erie (Kramer, 1967). The review of silica solubility is based primarily on studies by Krauskopf (1956) and by Stober (1967).

The data on sodium and potassium in lakes of the drainage basin are inadequate to suggest more than general consistency between lake water analyses and the chemical composition of shales. Such inferences as have been made concerning the solution of aluminosilicate minerals were drawn from Feth, Roberson and Polzer's paper on chemical weathering in the Sierra Nevada range (Feth. et. al., 1964) and from papers by Garrels and Mackenzie (1967), Bricker et. al. (1968) and by Helgeson et. al. (1969). These papers describe the stability fields of feldspars and their decomposition products in the presence of water, and the use of water analyses to reconstruct weathering rates of selected minerals.

The literature of limnology has been referred to frequently in connection with observations on the movement of dissolved substances within lakes and between lake water and bottom sediments. Particular emphasis is placed on Hutchinson (1941, 1957) and on Mortimer (1941). Hutchinson's (1941) study is concerned mainly with the relationships between turbulent transfer and the migration of the bicarbonate ion. Mortimer's (1941) studies of chemical exchanges at mud-water interfaces were based on experimental work and on direct observation in Lake Windermere in England. Lastly, to place the waters of this study in perspective, some reference has been made to large-scale compilations of data on water chemistry. The main sources in this connection are Rodhe's analysis of the compositions of Swedish lake waters (Rodhe, 1949), Gorham's work on ions in atmospheric precipitation (Gorham, 1961), and compilations of chemical analyses by the U.S. Geological Survey (Livingstone, 1963; White et. al., 1963).

4. Organisation.

The thesis is divided into three main sections. The first (Chapters I - III) is concerned with the description of lake morphometry and the relation of the lakes to basin geology and vegetation cover, the hydrology of the drainage basin, and the methods employed in the collection and analysis of water samples. The second section (Chapters IV and V) consists of a chapter on the solution of carbonate minerals and their influence on lake water composition, and a chapter on the distribtuion of other dissolved constituents of lake waters not directly related to carbonate equilibria. The third section (Chapter VI) is a detailed description of the chemistry of Pearce Lake in 1969 and its modification by waste-water discharge from Schefferville.

In the final chapter (Chapter VII) an assessment of the results obtained in this study and the methods of analysis is followed by a list of conclusions. Five appendices are included, giving details of sampling programmes, chemical analyses, lake water temperatures, names of plant species referred to in the text, and an extended discussion of carbonate equilibria in lake waters.

CHAPTER I

LAKES OF THE KNOB LAKE BASIN AND THEIR SETTING

1. General Description.

The Knob Lake drainage basin lies in the headwaters of the Kaniapiskau river system which flows northward towards Ungava Bay. South and east of the drainage basin, surface water drains to the east, towards Churchill Falls and the Hamilton River. The drainage basin is elongated north-west to south-east along the strike of the Proterozoic sediments of the Labrador Trough. The maximum length of the basin is 16 km and the average width rather more than 2 km. The sequence of lakes (Fig. 1) from Houston through Osprey, Malcolm, Ares and Knob to Pearce Lake occupies most of the length of the drainage basin. In this sequence, there is a fall in elevation of less than 2 metres between Osprey and Knob Lakes, although the stream flowing from Houston to Osprey Lake falls 60 m over a distance of 2 km. Two groups of lakes within the basin, tributary to Easel and Communications Lakes, drain south-east before flowing north.

The lake plateau (Hare, 1959), on which the Knob Lake basin lies at an altitude of 500 - 650 m, is believed to have been a centre of deglaciation in Labrador - Ungava (Ives, 1960). Glacial meltwaters flowed north-west and south-east along the axis of the Labrador Trough. Schefferville lies close to the drainage divide, and examples of reversal of drainage have been described within the basin (Barr, 1964). The lake basins in this study probably developed when glacial ice and meltwater scoured depressions within pre-existing valleys. Accumulations of glacial drift, which is usually present as a thin veneer on bed-rock, rarely determine lake morphology, although the moraine hill separating Knob from Pearce Lake, on which Schefferville was built, is a notable exception. Both rock-type and structure influence lake form, particularly near the junction of shale and dolomite. Malcolm Lake is an example of a lake in which the shoreline follows in part a shale-dolomite contact. Generally, the deeper and more irregular lake basins, such as in Easel Lake, lie on dolomite.

The Knob Lake drainage basin has been divided into five smaller catchments (Fig. 1) for the purpose of describing groups of lakes with broadly similar lithological and hydrological backgrounds. These catchments, which are defined by the outlets of Pearce, Malcolm, Easel, Phred and Osprey Lakes, are described in Table 1.

2. Lake Morphometry.

Morphometric data for the thirty lakes in the drainage basin, which are summarised in Table 2, were obtained from geological maps of the Iron Ore Company of Canada at a scale of 1:12000 and from topographic maps at a scale of 1:50000. Lake bathymetry was assessed from depth sounding traverses in August, 1964 (Adams, Shaw and Archer, 1966). Estimates of the volumes of small lakes are based on depths sounded below ice in 1965 and again in March and April, 1969. The error involved in the estimates of small lake volumes is believed to be in the range ± 15 per cent. The area of the drainage basin and of the geological formations within the basin were determined by planimetry from the same

TABLE I

Catchments within Knob Lake Drainage Basin:

Distribution of lakes and catchment geology.

Lakes occupy an area of 7.97 km^2 in the Knob Lake basin. This represents 21.1 per cent of the total basin area of 37.8 km^2. The total volume of water in the lakes is equivalent to a layer of water over the drainage basin 1 m thick.

For convenience in referring to groups of lakes with similar geological backgrounds, the basin has been sub-divided into smaller catchments defined by the outlets of Phred, Easel, Osprey, Malcolm and Pearce Lakes (Fig. 1). The Phred, Easel and Osprey catchments drain into Malcolm Lake, the catchment of which is defined as that part of the Malcolm Lake watershed which does not include the Phred, Easel and Osprey catchments. Similarly, the Pearce catchment includes that part of the drainage basin outside the boundaries of the other catchments.

Proportion of total lake volume and area in each catchment:

Catchment	Area (km^2)	% of total	No. of lakes	Area of lakes (km^2)	% of total	% of catchment area	Volume of lake water (m^3 x 10^6)	% of total
Phred	3.94	10.4	4	0.631	7.9	16.0	1.672	4.4
Easel	3.57	9.5	7	0.980	12.3	27.5	6.176	16.3
Osprey	8.81	23.3	8	1.260	15.8	14.3	4.433	11.7
Malcolm	9.18	24.2	8	2.189	27.5	23.9	12.142	32.1
Pearce	12.30	32.6	3	2.913	36.5	23.7	13.420	35.5
	37.80	100.0	30	7.973	100.0		37.843	100.0

TABLE 1 - continued

Catchment Geology

Percentage area of geological formations referred to in the text for each catchment: (the two dominant formations in each catchment are underlined).

Catchment	Attikamagen	Denault	Menihek	Sokoman	Ruth	Wishart
Phred	90.0	3.8	1.2	0.2	2.6	2.2
Easel	14.25	85.75	-	-	-	-
Osprey	54.7	8.0	13.1	10.0	7.7	6.5
Malcolm	53.4	24.8	6.1	5.7	4.6	5.4
Pearce	64.2	3.0	16.7	14.0	1.3	0.8

TABLE 2

Morphometry of Lakes in Knob Lake Drainage Basin.

	Area (ha)	Volume (x 10^6 m^3)	Mean Depth (m)	Max. Depth (m)	Max. Depth / Mean Depth
Main sequence of lakes, from Communications to Pearce Lake:					
Communications	20.0	0.820	4.1	11.0	3.7
Houston	59.0	2.164	3.7	14.0	3.8
Osprey	29.3	1.079	3.7	8.0	2.2
Malcolm	170.7	10.401	6.1	16.5	3.7
Phred	22.8	0.820	3.6	9.5	3.4
Gene	32.9	0.760	2.3	5.5	2.4
Easel	83.9	5.769	6.9	19.5	2.8
Ares	48.3	1.370	2.8	7.5	2.7
Knob	187.4	10.826	5.8	14.5	2.5
Pearce	55.6	1.224	2.3	7.0	3.0
Other lakes in the basin (tributary to Easel, Malcolm, Gene and Houston Lakes)					
North	9.5	0.370	3.9	8.0	2.1
Middle	10.2	0.470	4.6	9.5	2.1
South	5.1	0.081	1.6	3.0	1.9
Bassett	6.0	0.125	2.1	3.5	1.7
Adams	12.3	0.603	4.9	10.5	2.1
Cowan	4.2	0.189	4.5	11.0	2.4
Panhandle	2.5	0.050	2.0	3.5	1.8
Findlay	1.8	0.045	2.5	4.0	1.6
Williams	1.1	0.020	1.8	3.0	1.7
Francois	1.5	0.019	1.3	2.5	1.9
Ives	3.0	0.084	2.7	4.0	1.5
Mattox	4.5	0.086	1.9	2.5	1.3
Gray	5.3	0.133	2.5	3.5	1.4
Hardy	4.0	0.080	2.0	3.0	1.5
Thorn	2.3	0.035	1.5	2.5	1.7
Barr	4.4	0.088	2.0	3.0	1.5
Lier	1.7	0.034	2.0	3.0	1.5
Trigger	4.4	0.062	1.4	2.8	2.0
Dale	3.0	0.030	1.0	2.0	2.0
Doris	0.6	0.006	1.0	1.5	1.5

Table 2 - continued

Lake:	Lmax. (m)	Wmean (m)	Lmax. / Wmean	Azimuth of Lmax.(°)	Perimeter (km)	Shoreline Development
Main sequence of lakes, from Communications to Pearce Lake:						
Communications	625	320	2.0	291	1.77	1.12
Houston	2440	242	10.1	323	6.64	2.44
Osprey	1068	274	3.9	327	3.47	1.81
Malcolm	3700	461	8.0	322	11.67	2.52
Phred	960	238	4.0	321	3.14	1.86
Gene	1370	240	5.7	322	4.72	2.32
Easel	1740	482	3.6	311	10.63	3.27
Ares	1860	260	7.2	321	5.52	2.24
Knob	2285	820	2.8	329	9.63	1.98
Pearce	1220	456	2.7	336	5.39	2.04
Other lakes in the basin (tributary to Easel, Malcolm, Gene and Houston);						
North	610	155	3.9	326	1.58	1.45
Middle	610	168	3.6	327	1.58	1.39
South	457	111	4.1	290	1.16	1.45
Bassett	686	87	7.9	333	1.46	1.69
Adams	610	202	3.0	319	1.62	1.30
Cowan	328	128	2.6	022	0.85	1.17
Panhandle	494	51	9.7	295	1.13	2.02
Findlay	229	79	2.9	331	0.52	1.09
Williams	228	48	4.8	336	1.10	2.96
Francois	228	66	3.5	290	0.49	1.13
Ives	128	91	3.6	324	0.64	1.10
Mattox	457	98	4.5	329	1.07	1.42
Gray	396	134	3.0	326	1.01	1.24
Hardy	396	101	3.9	327	0.88	1.24
Thorn	189	122	1.5	298	0.62	1.15
Barr	380	116	3.3	340	0.85	1.14
Lier	228	75	3.0	314	0.58	1.25
Trigger	534	82	6.5	315	1.10	1.48
Dale	519	58	8.9	317	1.34	2.18
Doris	153	39	3.9	346	0.24	1.50

Key: Lmax. refers to the greatest straight line distance between any two points on a lake shore line without any intervening headland or island. Wmean refers to the area (ha) divided by Lmax.(m).

The shoreline development index (S.D.) is the ratio of the lake perimeter to the length of the circumference of a circle with the same area as the lake. It provides a measure of both the indentation of the shoreline and the circularity of the lake. The index approaches unity for a circular lake, and has the dimension L^{-1} (Hutchinson, 1957, p.166). Lake perimeter here refers to the lake shoreline as defined by lake outlines on maps of the Iron Ore Company of Canada at a scale of 1:12000.

geological and topographic maps. Since the boundary of the basin is not well-defined, the given area for the basin of 37.8 km^2 must be viewed as an approximation. It has been suggested that the boundary shifts seasonally with the amount of surface water storage on divides with little relief (Findlay, 1966, p. 19). It is also probable that topographic divides do not coincide with groundwater catchment boundaries, particularly along the eastern boundary of the basin.

The lakes in the drainage basin are almost all distinguished by high ratios of surface area to depth and pronounced elongation in a northwest - southeast direction along the regional geological strike (Table 2). These two characteristics of lake morphology together promote wind-driven circulation during the ice-free period of the year. The axis of elongation coincides with the prevailing and dominant wind direction at Schefferville (average wind speed from the northwest c. 4.4 m sec^{-1} (10 m.p.h.)). The average depth of most of these exposed lakes is less than 7 m, and only two depressions deeper than 15 m are known to the writer. These depressions were found in Easel and Malcolm Lakes.

Because the lakes are elongated and irregular in form, the total length of lake shore-line is high (over 80 km). In some cases (e.g. lakes on dolomite with deep bottom sediments) this characteristic may result in a high surface area of bedrock in contact with lake water. However, an appreciable part of the shore does not consist of bedrock. Sheltered lakes with a surface area less than 10 ha (especially the small lakes tributary to Easel, Gene and Communications Lakes) support communities of Carex and Salix spp. along their shores (Wassen, 1969).

Although most lakes are similar in terms of length/width and maximum depth/mean depth ratios and the shore-line development index, some of the lakes are anomalous. Cowan Lake is deep (11 m) in relation to its surface area (4.2 ha) and has a shore-line development index of 1.17, indicating that the lake is nearly circular. Cowan Lake is also exceptional in that its greatest length is in a northeast - southwest direction. Communications Lake is another example of a small, deep lake (depth 11 m, area 20 ha) which is nearly circular (shore-line development of 1.12). Finally, some larger lakes consist of two or more basins, which may be separated by an underwater ridge (Knob Lake) or a peninsula (Gene, Phred and Easel Lakes).

3. Heating and Cooling of Lake Waters.

Temperature profiles (Appendix III) were recorded at all sites where water samples were collected for chemical analysis. Additional profiles were recorded before the break-up of the winter ice cover on the lakes, and a record of outflow temperatures was maintained for Knob and Pearce Lakes between May 16 and September 7, 1969. These records have been compared elsewhere with data obtained from thermistor profiles mounted in Knob Lake (Grey, 1966; Mattox, 1964) by Penn (in press) in an analysis of the heat balance of selected lakes in the drainage basin.

Formation of ice on lakes near Schefferville took place in early November in 1968, the usual time of first ice formation. Ice formed first on small, sheltered lakes, and last on the largest and most open lakes such as Knob and Malcolm. Water temperatures at the time of freeze-up were 1 - 1.5°C. The ice cover persisted until mid-June, 1969. The larger lakes then broke up 4 - 6 days later than the smaller lakes such as those tributary to Easel and Malcolm Lakes.

When the lakes were sampled in March and April, 1969, they were all found to be thermally stratified and to have gained heat since ice formation. Differences in the form of thermal stratification, illustrated in Fig. 2, reflect contrasting sources of heat available to lakes with a cover of ice and snow. Lake water under a clear ice cover warms rapidly in response to solar radiation, because clear ice is transparent to visible radiation to about the same degree as distilled water. However, a snow cover or snow ice greatly reduces the amount of radiation reaching the top of the water column. For example, 20 cm of old, dry snow reduces radiation penetration to less than 1 per cent (Ruttner, 1963, p. 23).

The lakes near Schefferville support a snow cover between 30 and 100 cm thick, except in the period immediately after ice formation and after the snow has melted from the ice surface in spring. As long as the snow cover persists, the main heat source to the lakes is the gradual release of heat stored in rock bottoms and bottom sediments during the ice-free period (Bilello, 1968; Brewer, 1958). Outside this period, solar radiation may heat the water through clear ice. The importance of such radiative heating after ice formation is not known, but it is probably highly variable from year to year. However, in spring, after snow has melted from the ice cover, a secondary temperature maximum of 4.0 - 5.0°C just under the ice of Knob Lake persisted for two weeks in late May and early June, 1969.

For most of the winter, heat flow from bottom sediments is the main supply for the lakes. As a result, late winter water temperatures

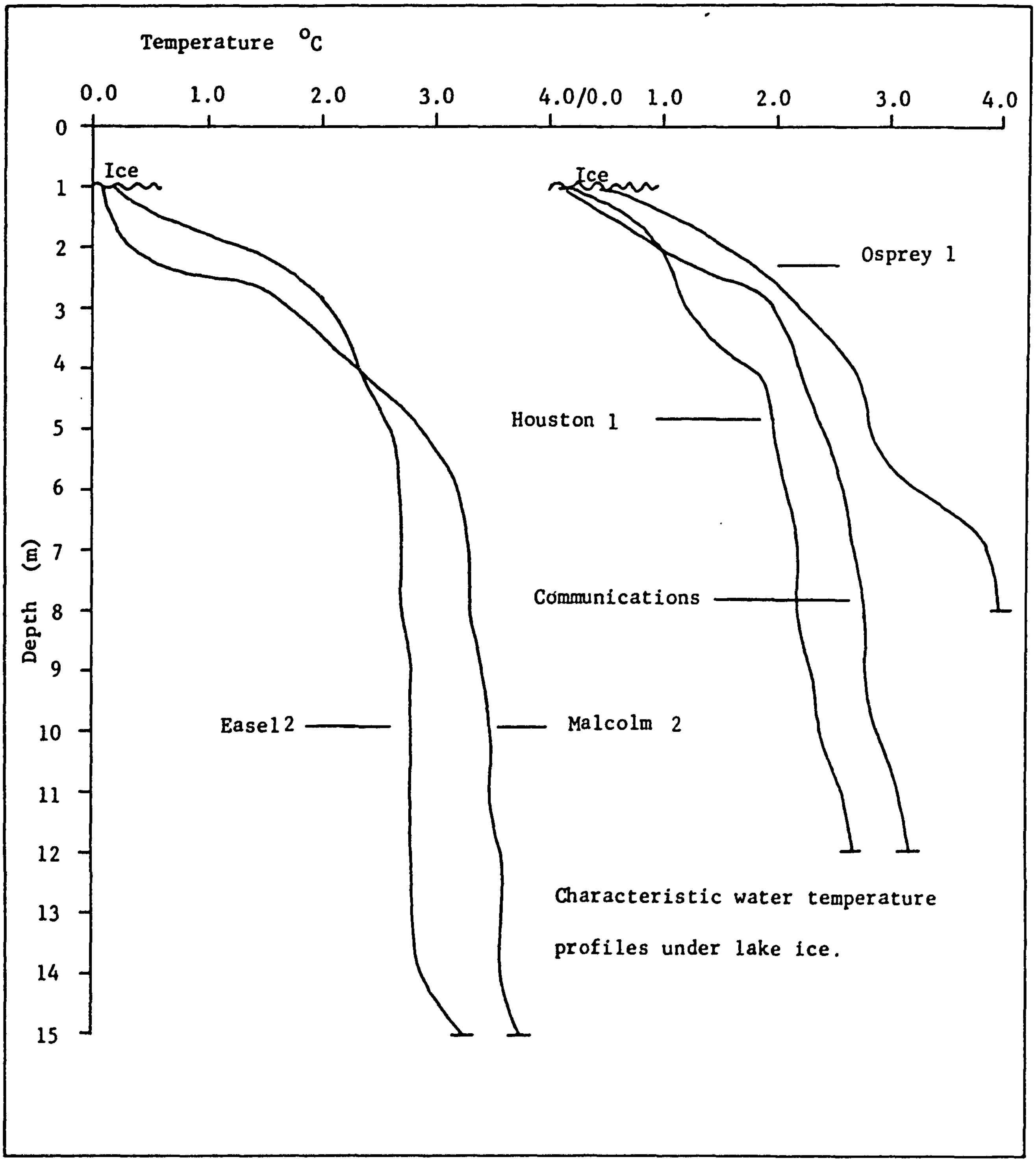


Fig. 2 Examples of thermal stratification under lake ice, winter 1969.

appear to reflect the thickness and thermal conductivity of lake floor sediments. Shallow lakes on dolomite, with soft and deep detrital muds (estimated c. 2m thick), were the warmest lakes at the time of the late winter survey, with temperatures up to 4.5°C near bottom sediments. Lakes on shales of comparable size had water temperatures of 3.0 - 3.5°C near bottom. Other heat sources to the lakes during winter are terrestrial heat flow (about 0.13 cal cm^{-2} day^{-1}: Lee and MacDonald, 1963) and biological oxidation of organic matter (about 0.1 cal cm^{-2} day^{-1}: Likens and Ragotzkie, 1965). These are minor heat sources compared with solar radiation and conduction of heat from bottom sediments, but they contribute to the warming of the water layer close to the lake bottom.

The development of thermal stratification in lakes under an ice cover follows the accumulation of water of relatively high density (max. density is at 3.94°C) at the bottom of the lake and the formation of a sharp temperature gradient at the ice-water interface. Inflowing stream water or groundwater discharge tends to mix the water under the ice, resulting in a more even distribution of temperature with depth. Slight irregularities in temperatures at depth, such as were noted in Easel Lake, may indicated zones of groundwater discharge, while a thick layer of cold and nearly isothermal water near the surface is an indicator of stream flow.

The overall effect of thermal stratification in winter is to limit the vertical circulation of water and therefore the vertical transport of dissolved substances. It is suggested that the movement of water between lakes during the period of ice cover involves the displacement of the water layer near the ice cover, and therefore that longitudinal and lateral dispersion of water and solutes generally dominates over vertical transport during winter.

After break-up, lake water temperatures ranged between 3 and 5°C. Locally, as in the case of Cowan Lake, lenses of cold and dilute snow meltwater create an irregular distribution of temperature down to the lake bottom. Between mid-June and late July, the lakes warm to an average temperature near 12 - 13°C. Some shallow lakes may warm temporarily to 18 - 20°C. The record of surface water temperature for Knob and Pearce Lakes indicates that surface water temperatures may persist above the daily mean air temperature through much of August and September. For the period July - August, 1969, the mean air temperature at Schefferville was 0.5°C below the outflow temperature of Knob Lake, and 4.0°C below the outflow temperature of Pearce Lake. Pearce Lake, being smaller, responded to changes in atmospheric temperature more rapidly than Knob Lake. In both lakes, shallow 'epilimnia' with temperatures up to 20°C form for periods of a few days, but are quickly displaced by rising winds.

The wind affects the heat balance of lakes by exerting a shear stress at the water surface which initiates wave movement and horizontal currents which mix the lake water and redistribute any temperature anomalies. According to Hutchinson (1957), wave amplitude on lakes is usually independent of water depth and proportional to wind speed and the square root to the fetch of the wind generating the waves. On large lakes in the basin, such as Knob and Malcolm, winds in the order of 12 m sec^{-1} (27 m.p.h.) generate waves with an amplitude of about 1 m. This is in approximate agreement with values predicted from the Molitor equation given in Bruce and Clark (1966, p. 121). Wind-driven horizontal currents have an upper velocity of 1 km hr^{-1} in winds of 13 - 15 m sec^{-1} (29 - 34 m.p.h.) (Hutchinson, 1957, p. 277). The uniform distribution of temperature with depth in lakes near Schefferville in late August and early September, 1969, indicates that northwesterly winds were effective in maintaining continuous turbulent diffusion to a depth of at least 17 m.

The temperature data collected for the lakes in this study suggest that stable thermal stratification in summer is infrequent and local. Cowan Lake, which is relatively deep and sheltered by tall spruce stands on surrounding dolomite ridges, did stratify in the summer of 1969 (Fig. 3). In this lake, stratification was collapsing at the time of the August survey, but earlier there is some evidence for thermoclines at depths of 2-3 m and at 8-9 m. Cowan Lake was exceptional in the summer of 1969, but it is possible that in other years, without the strong northwesterly winds and cold weather that dominated the end of July and much of August in 1969, thermal stratification might be more extensive. Those lakes in which stratification is believed possible in relatively calm and warm summers are: Communications, Middle, North, Adams, Easel and Phred. To summarise, the lakes in the drainage basin might be classified as 'cold monomictic' (Hutchinson, 1957, p. 438) with the reservation that, because of the exposure of the lakes to wind, circulation continues well above 4°C. Some lakes, in favourable summers, may be dimictic.

Finally, Pearce Lake, the chemical composition of which is the subject of Chapter VI, has several unusual thermal characteristics which distinguish it from the lakes described above. Its rapid rate of cooling and warming has already been mentioned. In winter, Pearce Lake

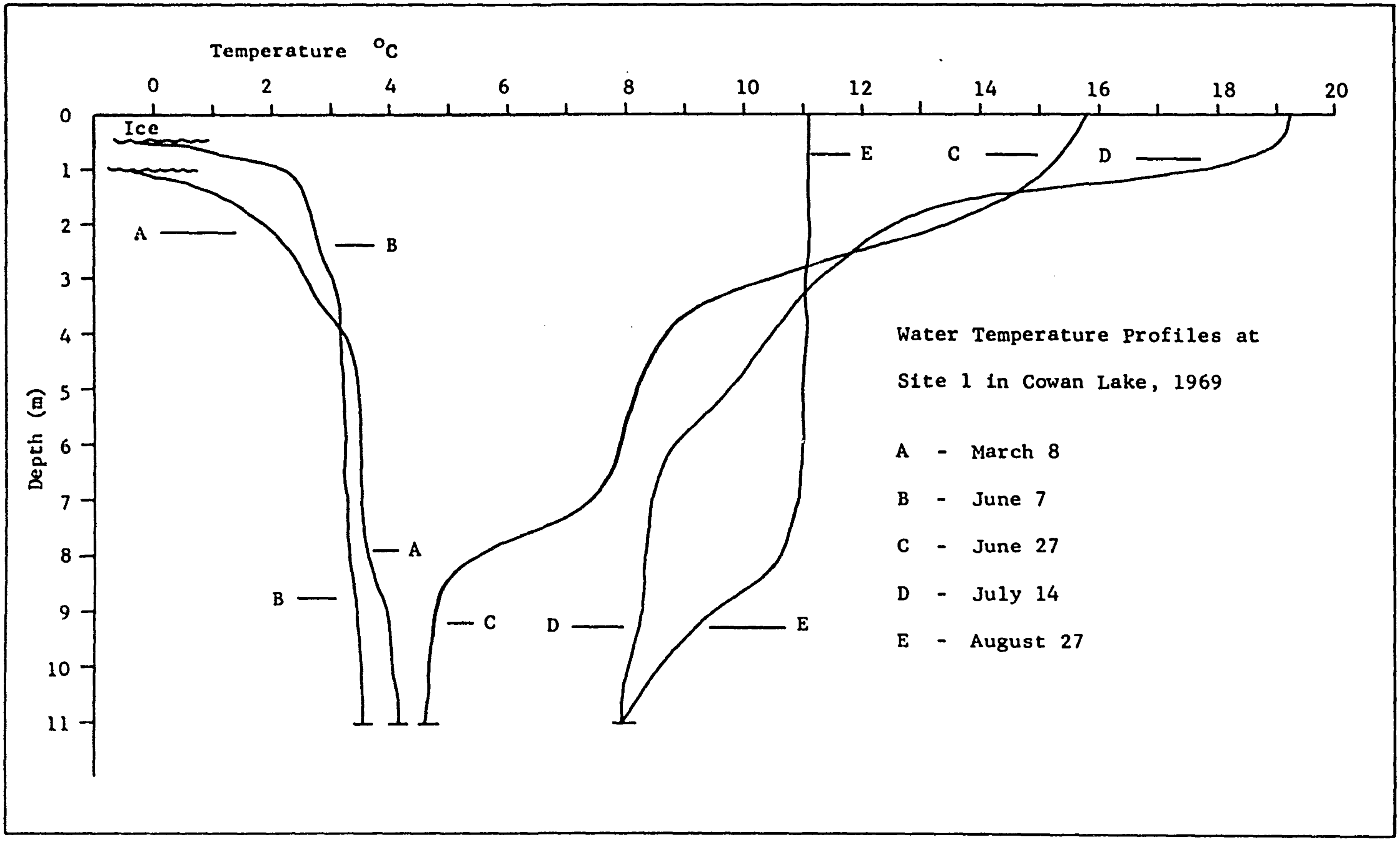


Fig. 3 Temperature profiles at the centre site of Cowan Lake, 1969.

froze a week late and broke up a week earlier than other lakes in the basin. The later freeze-up is attributed to the short residence time of lake water at the time (15 days) and to the discharge of warm water (c. 8°C) from the water treatment plant and Iron Ore Company buildings. This discharge of warm water was sufficient to maintain an open lead opposite the outfalls throughout the winter. The early break-up is attributed to the short residence time during the spring flood (3 - 5 days). Oil, dust and other impurities incorporated into the Pearce Lake ice cover also contributed to the early disintegration of the ice cover.

4. Geology of Knob Lake Drainage Basin.

The Knob Lake basin (Fig. 4) lies in a tightly folded and faulted belt of sediments, volcanics and intrusives known as the Labrador geosyncline or Trough (Gross, 1968; Dimroth, 1970). The geosyncline extends 1100 km south-southeast from Payne River on Ungava Bay to Labrador City, and is 90 km wide at the latitude of Schefferville, which lies 25 km from the western boundary of the geosyncline. At the time of formation, 2,550 to 2,400 million years B.P., the geosyncline was 500 km wide and the entire sequence of sediments deposited within it may have been 6 km thick.

The first event in the evolution of the geosyncline was the deposition of the Kaniapiskau sedimentary series near the western margin of the trough upon an older gneissic and granitic terrain. This terrain is believed to have had east-west trending valleys, within one of which the sediments of the Knob Lake basin were laid down (Gross, 1968). The

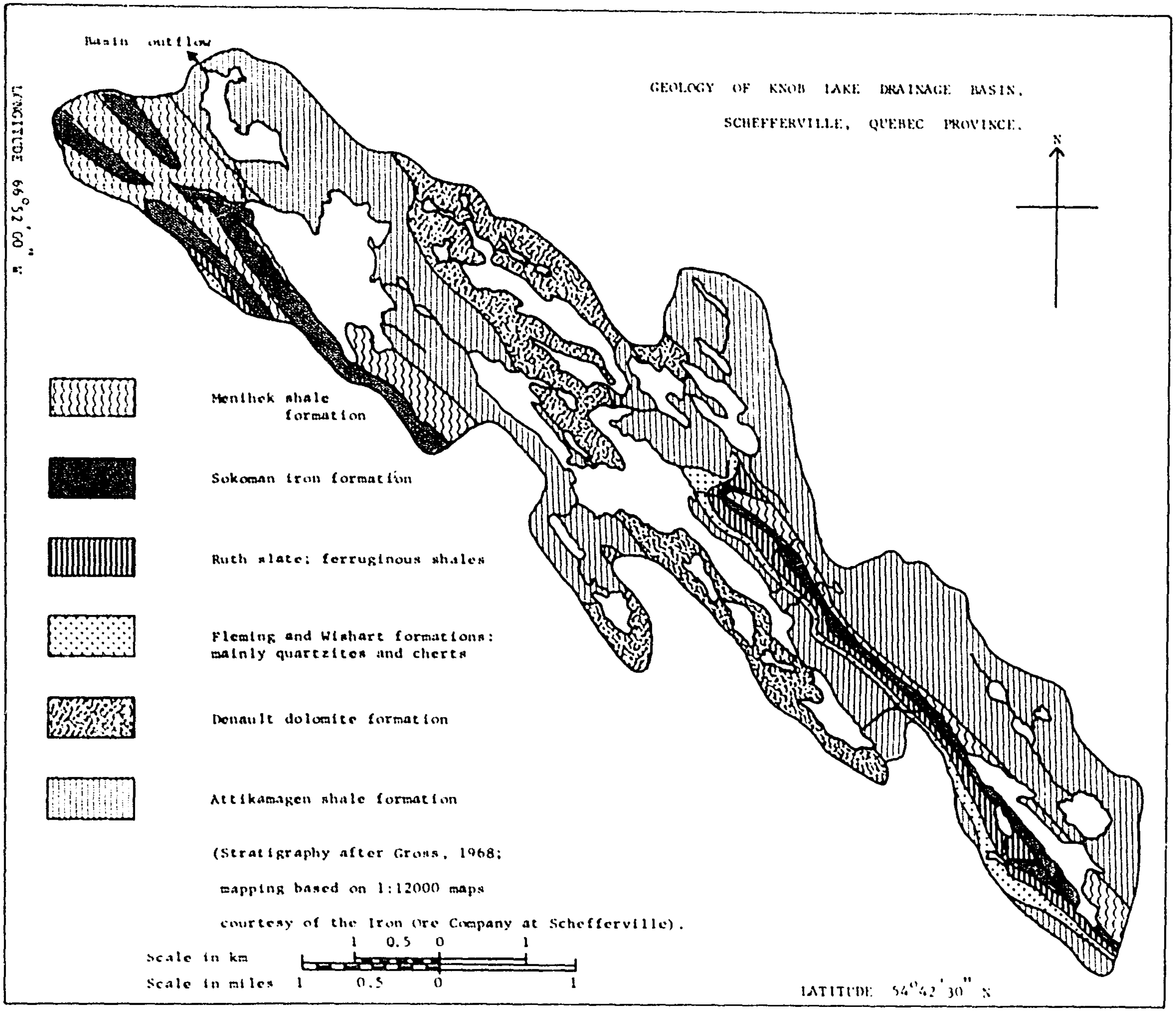


Fig. 4 Geology of Knob Lake Drainage Basin.

Kaniapiskau sedimentary series includes all the formations exposed in the basin. The principal characteristics of these formations are summarised in Table 3, which includes the available information on mineralogy and aquifer properties for each formation. Data on the relationships between basin geology and the distribution of lake waters are presented in Table 3 a, and on the chemical composition of the main formations in Table 4.

The stratigraphic relationships of the Kaniapiskau series exposed near Schefferville may be summarised as follows. Sedimentation began to the west of Schefferville with the deposition of coarse sandstones and arkose which graded into a calcareous and arenaceous shale becoming less calcic and finer grained near Schefferville away from the shelf environment at the edge of the geosyncline. This is the Attikamagen formation, which occupies 58 per cent of the area of the Knob Lake basin. Some vulcanism accompanied the deposition of this formation and is represented in the basin by a few hectares of andesitic lavas on the drainage divide near Communications Lake.

Following the deposition of the shales, carbonate sediments of the Denault formation were laid down in shallow water. This formation is dolomitic in the Knob Lake basin, although limestones have been described 10 km north of Schefferville. The dolomite is locally arenaceous with thick quartz veins, and cross-bedding is sometimes revealed by weathered specimens. The Denault formation runs diagonally across the basin from the lakes tributary to Easel Lake, across Malcolm Lake, to Osprey Lake, and occupies and area of 6.58 km^2, 17.4 per cent of the basin area.

After a period of reduced sedimentation and possible emergence,

TABLE 3 Geological Formations of Knob Lake Group in Knob Lake Drainage Basin (after Gross, 1968).

FORMATION	LITHOLOGY	MINERALOGY	PROBABLE AQUIFER PROPERTIES
MENIHEK >350m	Thinly laminated, fissile, grey-black shales and slate. Some chert and dolomite lenses. Cleavage well-developed: some brecciation.	Similar to Attikamagen shale. Quartz fragments in matrix of K-mica, albitic plagioclase and chlorite. Some horizons rich in carbon. Pyrite and Fe - oxides present.	Generally an aquiclude, but believed to be aquifer in faulted or shattered zones. If so, water movement is NW-SE along strike of steeply-dipping strata nr. Houston and Knob Lks.
SOKOMAN ~170m	Iron formation: chert with iron silicate and carbonate facies. Bands of chert and jasper separate beds of haematite and magnetite. Basal slates occur nr. Ruth slates.	Chert, jasper and quartz are main forms of silica. Iron minerals: minnesotaite, siderite, haematite, goethite and limonite.	Leached Sokoman (nr. Malcolm, Houston and Knob Lakes) is soft and porous through removal of carbonate. Resistant chert and quartzite bands are probably impervious.
RUTH ~20 - 30m	Black, green and maroon ferruginous slate, highly fissile with some chert lenses. Weathered exposures nr. Malcolm Lake appear as red, crumbly, paper slate.	Angular quartz with K-feldspar in matrix of chlorite, mica, iron oxide and granular carbon. Often 20% iron. Minnesotaite and siderite present.	Probably an aquifer in drainage basin, because of highly fissile character. Little surface vegetation on Ruth slate. Water movement preferably SE - NW along strike.
WISHART and FLEMING 80 - 100m	Fleming: coarse quartz and chert breccia: only locally present. Breccia has 2.5-4 cm diameter fragments. Wishart: quartzite and arkose, 0.5-1 mm diam., but some grit-stone. Haematite gives formation red appearance. Current bedding present.	Fleming: quartz, chert and a little interstial dolomite. Wishart: quartz with Na,K - feldspars; some Fe - oxide.	Both formations: massive quartzite bands are resistant and probably impermeable. Removal of of silica and carbonate matrix in chert horizons leaves soft, porous rock -a potential aquifer.

TABLE 3 Continued. Geological Formations in Knob Lake Drainage Basin.

FORMATION	LITHOLOGY	MINERALOGY	PROBABLE AQUIFER PROPERTIES
DENAULT ~200m	Variable thickness; sometimes missing. Locally interbedded with Attikamagen shale and with chert breccia of Fleming/ Wishart formations. A dolomite rock with lenses and veins of chert, quartz and possibly calcite. Dolomite is arenaceous near base of Denault and exhibits current bedding. Leaching at surface has locally left nearly pure sandstone.	Massive, blue-grey dolomite, weathering buff-grey-brown. Dolomite is fine-grained mixture of ferroan dolomite with some ankerite in variable amounts. Ankerite more abundant in weathered sections. Leached rock is highly siliceous, stained with Fe-oxides and deficient in Mg. Fissures have Mn dendrites, and apatite crystals are reported nr. junction with Attikamagen shales.	Massive, unweathered dolomite has bulk porosity nr. zero. Fissures, howver, carry water and Mn dendrites may indicate direction of water movement. Leached or brecciated dolomite is often porous. In general, Denault dolomite is aquiclude in most massive sections, but an effective aquifer in relation to nearby shales where fissures are numerous, or where formation is heavily leached.
ATTIKAMAGEN >350m	Laminated shales and slate, grey-green, black and red. Intricately drag-folded and cleavage well-developed. Often fissile. Strike SE-NW. Shales are usually steeply dipping, both E and W. Some sandstone and dolomite beds, chert near base.	Angular - acicular quartz grains (0.02-0.05 mm), some albite in secondary intergrowth of K-mica and chlorite. Some beds showed marked enrichment with carbon, giving shales black and crumbly form. Carbonate minerals accessory or present as distinct lenses. Fe-oxides and pyrites present.	An aquiclude in more massive and less disturbed sections. Shale is fissile and has shattered appearance near Houston and Malcolm Lakes, where shale supports little vegetation. Probably an aquifer here and therefore a zone of groundwater recharge. Over drainage basin as a whole, the Attikamagen is probably to be regarded as a moderate aquifer, although the manner of water movement is not understood.

Geology of the Knob Lake Drainage Basin.

TABLE 3.a

Distribution of lakes in relation to basic geology

1. Area of geological formations referred to in the text.

Formation	Area (km^2)	Percentage of total area
Attikamagen shale	21.75	57.8
Denault dolomite	6.58	17.4
Menihek shale	3.81	10.1
Sokoman iron formation	3.13	8.0
Ruth slate	1.29	3.4
Wishart quartzite	1.24	3.3
	37.80	100.0

2. Lake shore lithology

The total length of lake shoreline in the drainage basin is 82.07 km, and consists of the following rock types:

Formation	Length of lake shore (km)	Percentage of total length of shoreline
Attikamagen shale	41.20	50.1
Denault dolomite	28.90	35.2
Menihek shale	5.02	6.1
Sokoman iron formation	4.85	5.9
Ruth slate	1.48	1.9
Wishart quartzite	0.62	0.8
	82.07	100.0

Table 3 a - continued

Lake Waters in relation to Drainage Basin Geology.

3. Groups of lakes lying on similar geological formations:

1. Lakes lying entirely on Attikamagen shale. (nine)

Pearce
Communications
Gray
Hardy
Thorn
Bassett
Trigger
Dale
Doris

2. Lakes lying entirely on Denault dolomite:

Cowan
Panhandle
Findlay
Williams
Francois
Ives
North
Middle
South

3. Lakes lying on Sokoman iron formation (mainly cherts and quartzite):

Barr
Lier

4. Lakes lying mainly on dolomite, with Attikamagen shale secondary:

Mattox
Adams
Osprey
Easel

5. Lakes lying mainly on Attikamagen shale, with secondary dolomite:

Ares
Gene
Phred
Malcolm

6. Lakes lying on Menihek shale, Attikamagen shale and Sokoman iron formation:

Knob
Houston

Table 3 a - continued

4. Lake areas and volumes by groups as defined in section 3.

Group	Total area of lakes (ha)	Percentage of total lake area in drainage basin	Total volume of lake water ($m^3 \times 10^6$)	Percentage of total volume of lake water in drainage basin
1.	101.2	12.69	2.515	6.65
2.	38.9	4.87	1.328	3.50
3.	6.1	0.76	0.122	0.32
4.	130.0	16.31	7.537	19.92
5.	274.7	34.46	13.351	35.28
6.	246.4	30.91	12.990	34.33
	797.3	100.0	37.843	100.0

TABLE 4

CHEMICAL ANALYSES OF FORMATIONS REPRESENTED IN KNOB LAKE DRAINAGE BASIN (Sources overleaf)

Constituent (Dry weight %)	1 Attikamagen Shale	2 Denault fresh	3 Dolomite weathered	4 Ruth Slate	5 Sokoman iron formation	6 Menihek shales
SiO_2	66.79	17.01	91.28	53.69	49.97	69.64
TiO_2	0.60	?	?	1.14	?	0.65
Al_2O_3	16.58	0.94	1.70	11.11	0.92	13.68
Fe_2O_3	2.78	0.92	1.83	13.26	10.45	1.68
FeO	2.13	1.50	0.01	5.75	28.57	2.27
MnO	nil	0.19	1.64	?	0.64	?
MgO	1.56	15.53	0.04	0.89	3.12	1.96
CaO	nil	24.78	0.23	0.43	0.18	0.47
Na_2O	1.41	0.16	?	0.72	0.01	0.97
K_2O	4.65	1.24	?	3.81	0.11	3.51
H_2O	3.68	?	?	5.92	-	2.41
CO_2	nil	37.19	1.93	nil	2.62	nil
P_2O_5	tr	0.03	0.04	0.18	0.02	0.11
C	nil	?	?	1.98	?	2.57
S	-	tr	tr	?	0.001	?
Total	100.18	98.58	98.70	99.88	96.61	99.92

KEY TO TABLE 4

(Chemical Analyses of Characteristic
Rock-types in the Knob Lake Basin)

1. Average analysis of 2 samples of Attikamagen shale (Gross, 1951).
2. Average analysis of 6 samples of unaltered Denault dolomite formation, from various parts of the Knob Lake mining area (Stubbins et. al. 1961)
3. Average analysis of 5 samples of highly leached Denault dolomite, from operating mines (Stubbins et al., 1961)
4. Average analysis of 2 samples of unaltered Ruth slate (Gross, 1951)
5. Unaltered silicate - carbonate iron formation, from Ferriman area (Stubbins et. al., 1961)
6. Average analysis of 2 samples of unaltered Menihek shale (Gross, 1951)

The above analyses were taken from Gross (1968).

cherts and quartzites of the Fleming and Wishart formations were laid down in deepening water. Brecciation and cross-bedding are common and indicative of shallow water and vigorous circulation. The quartzites grade into dark graphitic and pyritic shales and slates of the Ruth formation, which were laid down in stagnant water deficient in dissolved oxygen. In places, this formation is sufficiently enriched in iron to rank as ore-grade rock.

The Ruth slate is overlain by the Sokoman iron formation, which is the source of the iron ore mined at Schefferville. Initial dark slates grade into ferruginous shales which give way to an iron silicate-carbonate facies. This facies was deposited in an oxygen-free environment in the presence of high concentrations of dissolved carbonates and silica. The subsequent appearance of iron oxide facies with goethite, limonite and haematite indicates a complete change from a strongly reducing to an oxidising environment, a change which may have taken place up to three times (Stubbins et. al., 1961).

There are two main exposures of the Fleming, Wishart, Ruth and Sokoman formations in the basin. The first takes the form of a faulted syncline which runs from the shore of Gene Lake across the higher ground of the Malcolm catchment to Houston Lake where the Sokoman formation forms the western shore of Houston Lake and part of Houston mountain. There are two small iron-ore bodies within the Sokoman formation in this belt. The first is opposite the southern arm of Malcolm Lake, and the second is near the drainage divide at the extreme southern end of the basin. The second major exposure of the iron bearing formations is on the ridges forming the drainage divide west of Knob Lake, and it contains an ore body which was mined between 1954 and 1956. In the basin as a whole, the Fleming, Wishart, Ruth and Sokoman formations together occupy 5.7 km^2, or 14.7 per cent of the total basin area.

The sediments above the Sokoman formation represent a change to deep and stagnant water conditions in the Schefferville area. Graphitic and pyritic shales of the Menihek formation were laid down on a basal pebble bed. Deposition continued until upwarping and orogeny terminated the Kaniapiskau series. At some time during this period, gabbroic and doleritic sills penetrated the shales and dolomites near Schefferville, and one such dolerite dyke runs across Knob Lake. The Menihek formation occupies an area of 3.81 km^2, 10.1 per cent of the basin area.

The only sediments in the basin younger than the Menihek shales are Quaternary glacial deposits which are represented by a discontinuous layer of drift, generally less than 2 m thick, which is present around Ares Lake and the north end of Malcolm Lake. The channels draining from Malcolm to Ares, and from Ares to Knob Lake also lie partly on glacial drift. Some gneiss and granite boulders are found in these deposits, but the bulk of the material is derived from shale, dolomite and quartzite characteristic of the sediments in the drainage basin. The 30 m high moraine - like hill on which Schefferville was built appears to be the only instance where glacial drift has formed substantial relief in the vicinity of Schefferville.

Soils are generally poorly developed in the basin. Removal of the surface vegetation and decaying litter often reveals a few centimetres of sand and some organic matter resting on bedrock. Podsols may be found on glacial drift, where they show a zone of leaching (A_2 horizon) 2 - 10 cm deep and a darker B_2 horizon 20 - 40 cm deep. Although the clay mineral composition of such soils as do exist is not known, the results of lake water analyses suggest that kaolinite is the stable aluminosilicate phase (Garrels and Christ, 1965, p. 361).

Finally, lake bottom sediments might be considered as a contemporary geological formation. Samples of bottom sediment were collected with an Ekman dredge from depths of 12 - 15 m in Knob, Malcolm and Easel Lakes. The sediment consisted of very dark brown to black gelatinous ooze, composed mainly of particulate organic matter and diatom frustules. Very few grains of sand or silt were found, suggesting that transport of suspended sediment within lakes is extremely small. Bottom sediment from shallow water on dolomite was found to be a light grey colour, and was very easily dispersed in the lake water. This material has the consistency of gyttja, and might contain precipitated calcite (Ruttner, 1953). No mineralogical or chemical analyses of lake sediments were made, and therefore inferred chemical exchanges between water and sediment as controls of chemical composition are based on lake water analyses and literature on mud-water chemical exchanges, and not on direct observation.

5. Vegetation of the Drainage Basin.

Schefferville lies in the zone of transition between boreal spruce forest and tundra (Hare, 1959). The upper limit of tree growth in the area is near 730 m, but the tree line is effectively limited to 600 - 700 m, probably by wind damage (Frazer, 1956). The higher shale and quartzite ridges of the Malcolm and Osprey catchments are sparsely vegetated and probably near the tree line. These relatively bare areas on steeply dipping shales are probably important in the basin hydrology as zones of groundwater recharge.

Much of the remainder of the basin would support spruce forest of varying density were it not for the forest fires and clearing which have affected nearly 60 per cent of the basin area over the last 30 years. Much of the present vegetation is a consequence of human disturbance, and this is especially true of the Malcolm and Osprey catchments and the area around Schefferville townsite. Forest fires are observed several times each year in the vicinity of Schefferville during dry weather. On June 24, 1969, a fire 20 ha in extent killed the spruce and removed the surface lichen cover in the forest around Panhandle and Findlay Lakes. The leaching of soil nutrients from such burnt-over ground may have increased the productivity of some lake waters near Schefferville in recent years. Accelerated leaching of nutrients has recently been demonstrated in cleared forest on schists in New England (Likens and Borman, 1970).

A dwarf birch and alder scrub, with a ground cover of lichens, Labrador tea and Vaccinium spp. characteristically develops on burnt-over ground. Frequently the height of this scrub is about the same as the depth of the winter snow cover. On completely cleared ground this form of regeneration is taking place very slowly, and extensive bare areas of loose shale and chert remain near the Schefferville townsite.

The existing spruce forest, which is best represented in the Easel catchment, consists of black and white spruce with smaller amounts of tamarack, paper birch, balsam fir and juniper. Although all gradations exist between dense spruce forest and open woodland, the forest as viewed from the air is seen to consist of distinctive open lichen woodland on relatively dry interfluves and of close forest on low ground and near water courses.

The forest floor consists mainly of lichens (especially *Cladonia alpestris*), various species of *Vaccinium* and Labrador tea. Feather mosses and sphagnum are abundant in dense forest and poorly drained areas. Spruce reaches a height of 20 m and a d.b.h. of 80 - 90 cm in close forest (3 - 4 m between boles) as at the end of Easel Lake (Hustich, 1954). Hustich (op. cit.) also noted that white spruce is more abundant on dolomite and occurs in more exposed sites than does black spruce. Although tamarack is usually associated with wet ground (e.g. near Easel Lake and in depressions on dolomite ridges), occasional specimens are found on presumably dry upland sites. Paper birch, balsam fir and juniper occur locally on south-facing slopes in spruce forest on dolomite.

An important aspect of the vegetation from a hydrological point of view is the widespread lichen cover. Frazer (1956) found that the lichen ground cover near Schefferville can hold up to 400 times its own weight of water. Although the active branches of lichen dry rapidly, the litter remains wet through much of the summer. Because the lichen litter accumulates water, it reduces the amount of direct surface run-off, and limits the rate at which surface water may enter the ground. The water stored within the litter may be returned to the atmosphere through evapotranspiration, contribute to a gradual downslope surface flow of water within the vegetation cover, or it may contribute to ground water recharge beneath the lichen cover. Unfortunately, there is very little information to show the relative importance of these processes. The absence of this information represents a serious gap in the understanding of precipitation / run-off relationships within the drainage basin, and therefore in the understanding of rates of solution of bedrock by rain and snow meltwater. Outside the basin, it is known that overland flow takes place near the mines during snow melt, over ground with a birch, alder and lichen vegetation cover (L.C. Nichols, I.O.C. geologist, pers. comm., 1969).

The subject of lakeshore vegetation has been treated by Wassen (1969) who found the degree of exposure of the shore to wave action and ice damage during break-up to be an important control of littoral vegetation. On the exposed shores of lakes with surface areas greater than c. 10 ha, a dense fringe of alder with some willow and dwarf birch is commonly found. Smaller lakes may have sub-littoral communities of Mitella, Isoetes and Eleocharis which grade first into sedge and feather moss and then into tamarack or spruce forest.

Aquatic and littoral plants affect water chemistry through the diurnal and seasonal uptake and release of carbon dioxide in photosynthesis. Fluctuations in the carbon dioxide content of lake waters result in seasonal shifts in pH over a range of up to 2 pH units (Appendix V, Section E). The change in hydrogen ion concentration may be sufficient to initiate local precipitation of calcite in sheltered spots during summer. These processes will be described in Chapter IV on the carbonate chemistry of the lake waters.

Littoral vegetation may also affect lake water chemistry by taking part in base exchange reactions. Sphagnum in particular is known to accumulate calcium in its tissue and depress the pH of surrounding water (Ruttner, 1953, citing Baumann and Gully, 1909 to 1913). Oxidised organic muds (possibly a ferro-organic complex: Mortimer, 1941) apparently have the ability to bind calcium ions, which, under reducing conditions, are returned to the aqueous phase. There are some lakes in the drainage basin, notably Williams (south end) and Francois lakes which lie on dolomite, in which such base exchange may explain relatively low calcium and high hydrogen ion concentrations.

6. Direct Effects of Human Settlement.

The town of Schefferville was built to house employees of the Iron Ore Company of Canada (I.O.C.C.) which mines iron ore from open cast pits north and south of Schefferville. The site chosen for the town was a ridge of glacial drift separating Knob from Pearce Lake. A drift site was necessary for laying foundations and service lines to carry the municipal water supply (Humphrys, 1958). Construction of the town began in 1953 and was largely complete by 1955. In the course of construction, the drift was levelled and it now forms the north shore of Knob Lake and the south shore of Pearce Lake. Trees have been planted in the Knob Lake shore, but the artificial shores of Pearce Lake remain largely devoid of vegetation. A series of fires have removed forest vegetation from the ridges west of Schefferville, and there are extensive areas of shale debris between the townsite and the airstrip (Fig. 1) and around the Iron Ore Company buildings. Throughout the basin, dead spruce trunks bear witness to the fires which accompanied the growth of Schefferville.

The snow removed in road clearing operations in winter is dumped into Pearce Lake beside the townsite along with the oil, dust and grit which it contains. The absence of vegetation around the townsite has resulted in accelerated sediment erosion which is especially noticeable during the spring when turbid, red, streams flow into Pearce Lake from railway sidings and Iron Ore Company property. In addition, there is an unsurfaced road which runs the length of the drainage basin to Houston Lake. Although this road is well removed from any of the larger lakes, the streams that cross it carry, as a result, high suspended sediment loads during spring floods and summer rains.

CHAPTER II

HYDROLOGY OF KNOB LAKE DRAINAGE BASIN

1. Previous Research.

In December, 1964, the Canadian National Committee of the International Hydrological Decade (I.H.D.) designated the Knob Lake basin as a hydrological basin representative of central Labrador - Ungava. Before that time, the McGill Sub-Arctic Research Laboratory at Schefferville maintained a first-order weather station under a contract from the Department of Transport which terminated in April, 1970. The observation programme (Tout, 1967) included precipitation measurement, snow course observations, lake ice surveys, and evaporation measurements.

The first objective of the hydrological programme was to evaluate the water balance of the drainage basin. This was undertaken by Findlay who identified his main research problem as the interpretation of the effect of evaporation and transpiration on precipitation/run-off relationships (Findlay, 1966). Findlay based his approach on Hare's (1966) observation that reported precipitation/run-off ratios in northern Quebec and Labrador were higher than would be expected from the amount of radiative energy available for evaporation and transpiration during the summer months.

Findlay, who studied the water year commencing September 1st, 1964, concentrated on measuring precipitation over the basin and run-off, and on estimating rates of evaporation and transpiration. He concluded that precipitation had been markedly underestimated in official climate records for the area; that evapotranspiration (from lichen) does not take place at a potential rate, at least during the middle of the summer; and that 'large groundwater storage facilities ensure that streams have strong base flows well into winter' (Findlay, 1966, p. 81).

Findlay experienced a number of practical difficulties in estimating run-off from the drainage basin, which was originally defined by the outlet of Knob Lake. Run-off leaves the basin, as defined by the Knob Lake outflow, in a number of ways which are not always easy to gauge: through two culverts on Knob Lake (main outflow), the municipal water supply and sewage disposal system for Schefferville, the drift underlying the townsite, and the former outlet of Knob Lake before the construction of Schefferville (Findlay, 1966). Furthermore, the level of Knob Lake, which is the municipal water supply, is regulated to maintain a steady head of water over the pump intakes. The insertion of stop-logs across the two main culverts for this purpose periodically creates changes in the Knob Lake hydrograph which are purely artificial.

In July, 1968, the outlet of Knob Lake drainage basin was redefined as the outlet of Pearce Lake, thereby including Schefferville within the basin boundaries and providing a more suitable gauging site for the basin in the channel draining Pearce Lake. In this way, hydrological studies within the basin can still emphasise problems that are characteristic of central Labrador-Ungava (e.g. groundwater, water movement in a lichen cover, precipitation/run-off ratios) and at the same time evaluate disturbances to the environment created by a mining town.

The following hydrological summary for the basin in 1969 (the water year commencing January 1) is divided into four sections. First, precipitation inputs to the basin as rain and snow are described. Second, run-off from the basin is discussed in conjunction with the run-off record from Menihek power dam, 40 km south of Schefferville. The third section deals with the residence times of lake water in individual lake basins and with the distribution of run-off within the drainage basin. The last section describes water use and waste-water treatment at Schefferville.

2. Precipitation over the drainage basin and its measurement.

Absolute amounts of precipitation over the basin are needed to determine the total amount of water available for chemical weathering at the surface, and, through the study of precipitation / run-off ratios, the proportion of that amount which eventually becomes involved in the transfer of solutes between lakes. Spatial variation in precipitation with the basin requires some attention, since, if it can be shown that precipitation is consistently higher over one part of the basin, it may also follow that rates of chemical weathering are higher and that residence times of lake water in that area are shorter.

Total precipitation officially recorded at Schefferville in 1969 amounted to 76.3 cm (40.4 cm snow, 35.9 cm rain), slightly above the 14-year mean for the McGill station at Schefferville. The corresponding mean annual air temperature (-4.3°C) was slightly above the mean (-4.6°C). The winter was warmer and wetter than usual, with nearly one third of the annual snowfall being recorded in three December blizzards.

The precipitation total given above was obtained from readings at 6 hour intervals from an M.S.C. rain gauge and a Nipher snow gauge (Bruce and Clark, 1966, p. 71). These gauges are located close to the Schefferville air strip, which, being oriented northwest-southeast, is particularly windy. Precipitation gauges always underestimate precipitation, and this is particularly true at the air strip site at Schefferville. Findlay, who was fully aware of this situation, attempted to adjust the station precipitation record to a more realistic value. From snow course observations, he determined that the catch deficiency for the Nipher gauge was about 27 per cent (Findlay, 1966; 1969). The corresponding catch error for the rain gauge was estimated at 16 per cent, 6 per cent of which was attributed to orographically induced precipitation higher up the basin, and 10 per cent to losses resulting from turbulent air flow characteristic of any gauge (McKay, 1965).

It is possible to apply similar corrections for the 1969 precipitation record. On the basis of a 27 per cent Nipher gauge error, the annual snowfall becomes 55.4 cm. The rain gauges maintained in the basin in the summer of 1969 indicated that the catch at Schefferville was consistently 21 per cent below catches elsewhere in the basin. The underestimate of total rainfall may be as high as 30 per cent (assuming a 9 per cent error for turbulent air flow, as above). On this basis the rainfall total becomes 46.6 cm, giving an annual total of 102 cm. The problem of assessing basin precipitation is considered further by Penn (in press). The annual total given in this thesis is, of course, an estimate, and is intended to convey the probable order of magnitude of the measurement error at Schefferville.

Knowledge of the distribution of snowfall within the basin is based on a survey of snow pack water equivalent (excluding snow lying on lakes) made by H. Grandberg between March 28 and April 2, 1969, when snow depth was near the maximum for the year. The mean snow water equivalent in each of the catchments, together with the variability in its distribution, are summarised in Table 5.

The greatest snow water equivalent, and the greatest variability in its distribution, is associated with the higher relief of the shale and quartzite ridges in the Osprey and Phred catchments. Conversely, the dense forest bordering Easel and Ares Lakes has the smallest snow water equivalent, and the least variability in its distribution. These results presumably mean that less snow is trapped by spruce forest than by burnt-over ground, perhaps because snow intercepted by spruce crowns is redistributed outside the forested areas. This conclusion is inconsistent with observations on the snow course near the Schefferville air strip, but is possible in the light of previous basin snow surveys (Adams and Findlay, 1966).

In order to assess the variability of summer rainfall, rain gauges were placed in the Phred, Malcolm and Osprey catchments. The gauges were read at weekly intervals from June 14 to September 7. The sites chosen represent characteristic topographic sites, rather than equal areas of the basin. The reason for this was that the application of a Thiessen polygon or isohyetal method for estimating basin precipitation was not considered justified without knowing either the effect of the air strip location on gauge totals at Schefferville, or the effects of topography and vegetation on rainfall catch within the drainage basin.

One gauge (Phred) was located on a west-facing ridge among

TABLE 5

Distribution of precipitation within Knob Lake drainage basin.

A. Water equivalent of late winter snow pack, March, 1969.

Catchment	Area (km^2)	No. in sample		mean water equivalent (cm)	standard diviation of w.e. data* (cm)
Phred	3.94	35		39.7	10.2
Easel	3.57	41		37.3	9.6
Osprey	8.81	126		43.0	19.7
Malcolm	9.18	91		41.1	12.2
Pearce	12.30	51		40.5	8.8
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	37.80	344	(mean)	40.3	

*data not adjusted for normality.

B. Rain guage catches within Knob Lake drainage basin, summer, 1969.

Week ending	Houston (Osprey	Forest (Malcolm)	Gene Ridge (Phred)	Doris (Malcolm)	Schefferville (Pearce)
	(all values in cm)				
June 21	1.83	1.83	1.63		1.27
June 28	1.04	1.17	1.09		0.79
July 5	4.83	5.09	5.29		4.21
July 12	1.96	2.11	1.80		1.47
July 19	1.04	1.07	1.02		0.81
July 26	0.61	0.47	0.53	0.71	1.58
August 2	3.07	2.84	2.77	2.77	2.16
August 9	2.59	3.00	2.09	3.00	1.09
August 16	2.84	2.63	2.59	4.65	1.68
August 24	5.00	4.72	4.80	2.46	4.06
August 30	1.22	1.25	1.63	1.19	1.02
September 7	2.62	2.57	2.33	2.54	1.60
Totals	28.6	28.8	27.6	(17.2)	21.7

dwarf birch and lichen. A second gauge (Osprey) was placed on an east-facing slope overlooking Houston Lake in birch-alder scrub 1.5 m high. The third gauge (Malcolm) was placed in close spruce forest near Malcolm Lake, away from the direct influence of dripping from trees. Finally, a gauge was placed during the summer on a 40° west-facing slope below Doris ridge near the basin divide to register precipitation in a site that was assumed to be abnormally windy.

The average catch in the Phred, Osprey and Malcolm gauges over the 12-week monitoring period was 6.6 cm, or 30 per cent more than the corresponding rainfall total at Schefferville (Table 5). This discrepancy is conspicuously higher than the 6 per cent described by Findlay for 1965 (Findlay, 1966). It may be that in the summer of 1969 not only did the rain gauge at Schefferville underestimate the rainfall total, but also that the actual precipitation over the townsite was relatively low.

Within the basin, the variations between the gauge catches are small, and those that occur can reasonably be interpreted in terms of the type and direction of arrival of precipitation. Although rain over Schefferville is characteristically of low intensity and long duration (Tout, 1967), afternoon convective showers occur, particularly in July and August, and rain from these showers may be heavy and very local. This is illustrated by the week ending July 26 (Table 5) when precipitation at Schefferville exceeded the precipitation over the rest of the basin as a result of a heavy morning shower, only 2 - 3 km wide, which occurred directly over Schefferville. In contrast with this, rain from stratiform clouds appears to be uniformly distributed throughout the basin. Inspection of the Schefferville wind record and the basin gauge catches suggests that light to moderate winds from the west tend to increase precipitation on west facing slopes, but that stronger winds, over 10 - 12 m sec^{-1}, create an updraft which reduces the catch on the windward slope, and increases the catch on the lee side. This suggestion is tentative, and considerably more gauging would be needed to verify it.

To summarise, the annual total precipitation is about 100 cm. This amount is approximately equivalent to the amount of water stored in the lakes of the drainage basin (37.8×10^6 m^3). Spatial variation in rainfall and snowfall within the basin (excluding Schefferville) is small and generally explicable in terms of relief and cover type. On balance, there is no reason to expect abnormally high rates of exchange of water as a result of locally excessive precipitation, except perhaps to a small extent in the higher areas of the Phred, Osprey and Malcolm catchments.

3. Measurement of discharge from Pearce Lake.

Reliable estimates of run-off from the basin were needed for two main purposes; first, to estimate that part of the basin precipitation which becomes run-off as a basis for outlining the basin water balance, and second, to determine the average residence time of lake waters in the basin during 1969 and during the spring food to assess the effectiveness of snowmelt run-off in 'flushing-out' the water lying in the lakes during late winter.

Run-off determinations during the period of study of lake water chemistry included daily stream gauging at the Pearce Lake outlet in the summer of 1969, estimation of run-off at other times of the year from stage-discharge observations, and periodic stream gauging at the outflows of other lakes in the drainage basin.

The Pearce Lake outflow was gauged daily from the beginning of the spring flood, May 14, until August 31, the end of the period of summer flow. Records of water temperature at the time of gauging were maintained for the Pearce and Knob Lake outflows, and records of relevant synoptic weather were kept for use in the interpretation of the summer hydrograph and for the evaluation of short term thermal stratification in the lakes. The measured discharges and accompanying stage observations were used to prepare a rating curve for a manometer installed beside the Pearce Lake outflow by the Ministère des Richesses Naturelles de Québec. The record from the manometer has been used to construct the annual hydrograph for the Knob Lake drainage basin.

Details of discharge measurement and of the application of stage-discharge observations to the Pearce Lake outflow are contained in a report by Penn (in press) which is summarised below. The selected cross-section is 8 m wide, with a width of flow between 6.7 and 9.5 m, depending on discharge. The channel is bordered on one side by sedges, and on the other by an alder thicket. The channel bed, which consists of shale with a red coating of particulate iron oxide originating from surface drainage and ore testing effluent discharged into Pearce Lake, was stable during the period of study.

Measurements of water depth and flow velocity at 0.6 of the water depth were made at 1 foot intervals across the channel. The discharge (in c.f.s.) was calculated from the mean channel depth and the mean flow velocity, on the grounds that channel depth was nearly uniform and that flow velocity was evenly distributed across the channel. To check this assumption, discharges were also calculated using the 'mid-section' method of the U.S. Geological Survey (Buchanan and Somers, 1969). Agreement between the two methods of calculation was found to be close (within 3 per cent of the discharge) until the stream overflows the channel at about 2.4 m^3 sec^{-1} (90 c.f.s.). Thereafter, calculations involving channel means consistently underestimated mid-section discharges by about 8 per cent. Since the mid-section method is the more accurate, this method should be used whenever the discharge at Pearce Lake exceeds 2.2 m^3 sec^{-1} (77 c.f.s.), which occurred on about 30 days in 1969 during the spring flood.

The establishment of a stage-discharge rating curve for the Pearce Lake outflow proved to be a problem since there was not a one-to-one correspondence between observations on the rising and falling stages of the spring hydrograph, which formed the basis for the rating curve. Therefore, four separate rating curves for different phases of the hydrograph were prepared for the Pearce Lake manometer by the Ministere des Richesses Naturelles de Quebec using a computer programme described by Theoret (1968). The curves were prepared for (a) all observations of stage and discharge; (b) observations during the rising stage of the spring flood; (c) observations during the falling stage of the spring flood; and (d) observations during the falling stage of the spring flood and the summer period.

The difference between these rating curves is sufficient to affect estimates of water yield from the drainage basin by as much as 5 per cent. In particular, the curve for the rising stage of the spring flood differs substantially from other curves in the range 0.57 - 3.4 m^3 sec^{-1} (20 - 120 c.f.s.). The difference suggests that the Pearce outflow channel carries water more efficiently (i.e. through a smaller cross-sectional area) during the spring flood than at any other time of the year. This is believed to be physically reasonable, since in winter there is some obstruction to flow by ice on the banks, and in summer there is a proliferation of filamentous algae and sedges along the banks and across part of the channel upstream. Observations of the water slope at the cross section at high and low stages of the spring flood revealed no change in gradient that would lead to marked deviations in stage - discharge relationships.

The computation of annual run-off from the drainage basin (Table 6), with which the residence times of lake water have been calculated, are based on measured discharges during the spring and summer of 1969, and on the curve for falling stage and summer observations for the remainder of the year. This approach, which assumes that some obstruction to flow, whether from ice, sedges or algae, is characteristic for the channel, is consistent with the available stage-discharge observations for September, October and November, 1969.

4. The Annual Hydrograph for Knob Lake Basin, 1969.

The annual hydrograph, a plot of discharge against time, for a point in a drainage system is the product of precipitation inputs to the system and of the processes which determine the amount of water released as run-off and the rate at which it is released. Depending on the supporting evidence from within the drainage basin, the annual hydrograph can be a valuable source of information on basin hydrology.

In the case of the Knob Lake basin, the hydrograph for the Pearce Lake outflow (Fig. 5; monthly yields given in Table 6) is complicated by the regulation by Schefferville of the level of Knob Lake. This hydrograph will therefore be compared with that obtained from the Menihek power dam (Fig. 6; Table 6), located 40 km south of Schefferville (courtesy of H. Conrad, Menihek dam). The catchment area (19,070 km^2; 7,363 sq. miles) tributary to the Menihek dam is geologically similar to the Knob Lake basin, and is less affected by forest fires. According to Findlay (1969), precipitation over the Menihek basin is about 8 per cent higher than over the Knob Lake basin. Findlay (1966) used the run-off record from Menihek dam to check the water balance for the year 1964 - 1965, and to reconstruct water balances for previous years.

The correspondence between the hydrographs is close, and the differences that exist can be attributed to known changes in the level of Knob Lake. Two particularly sharp surges on the rising limb of the spring flood at Knob Lake coincide with the removal of stoplogs from the outlet culverts on Knob Lake, and the sharp drop in discharge on July 4 follows the replacement of these stoplogs. Additional logs were placed across the channel in mid-October.

Run-off from the Knob Lake basin in 1969 totalled 75.5 cm, compared with 81 cm at Menihek (Table 6). The run-off from the Pearce Lake outflow is only slightly less than the officially recorded precipitation total of 76.3 cm for Schefferville. However, it is 26.5 cm

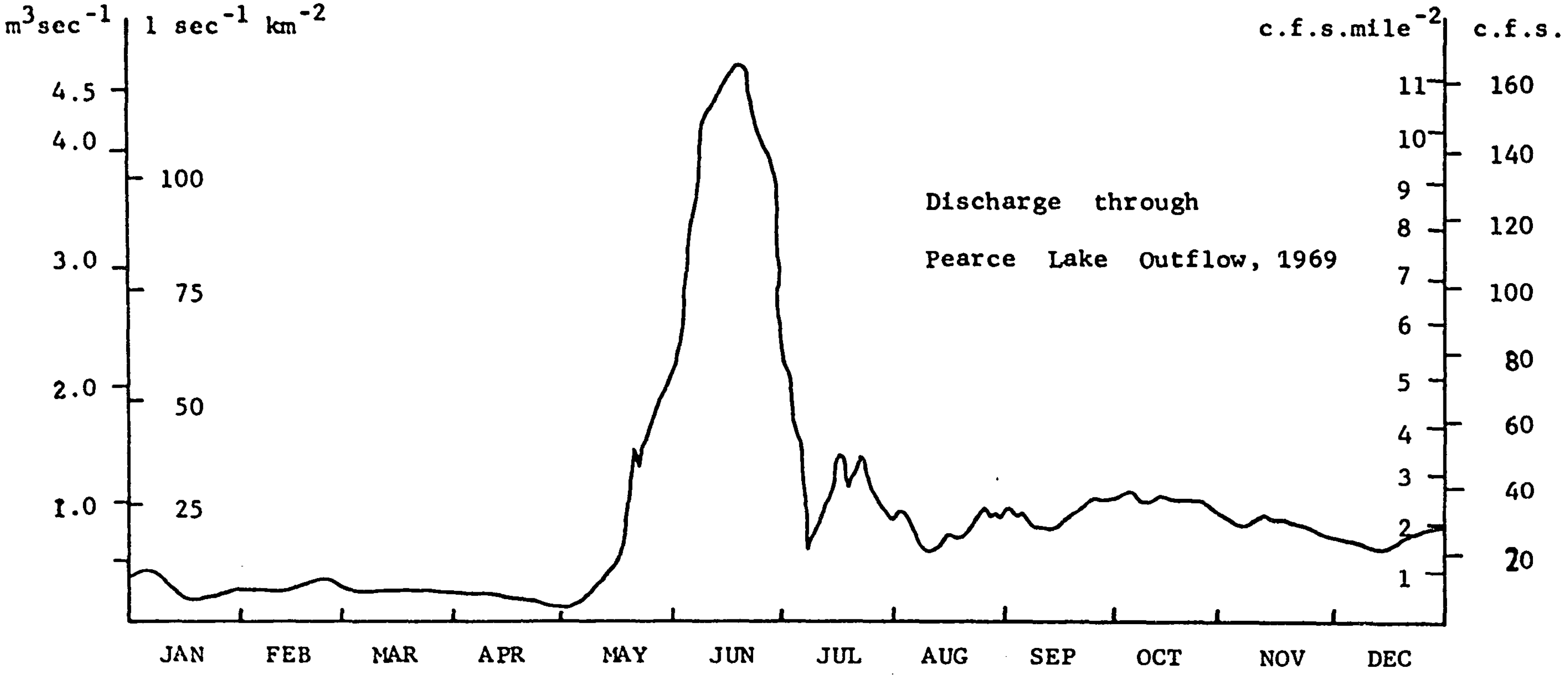


Fig. 5 Annual hydrograph for Pearce Lake outflow, 1969.

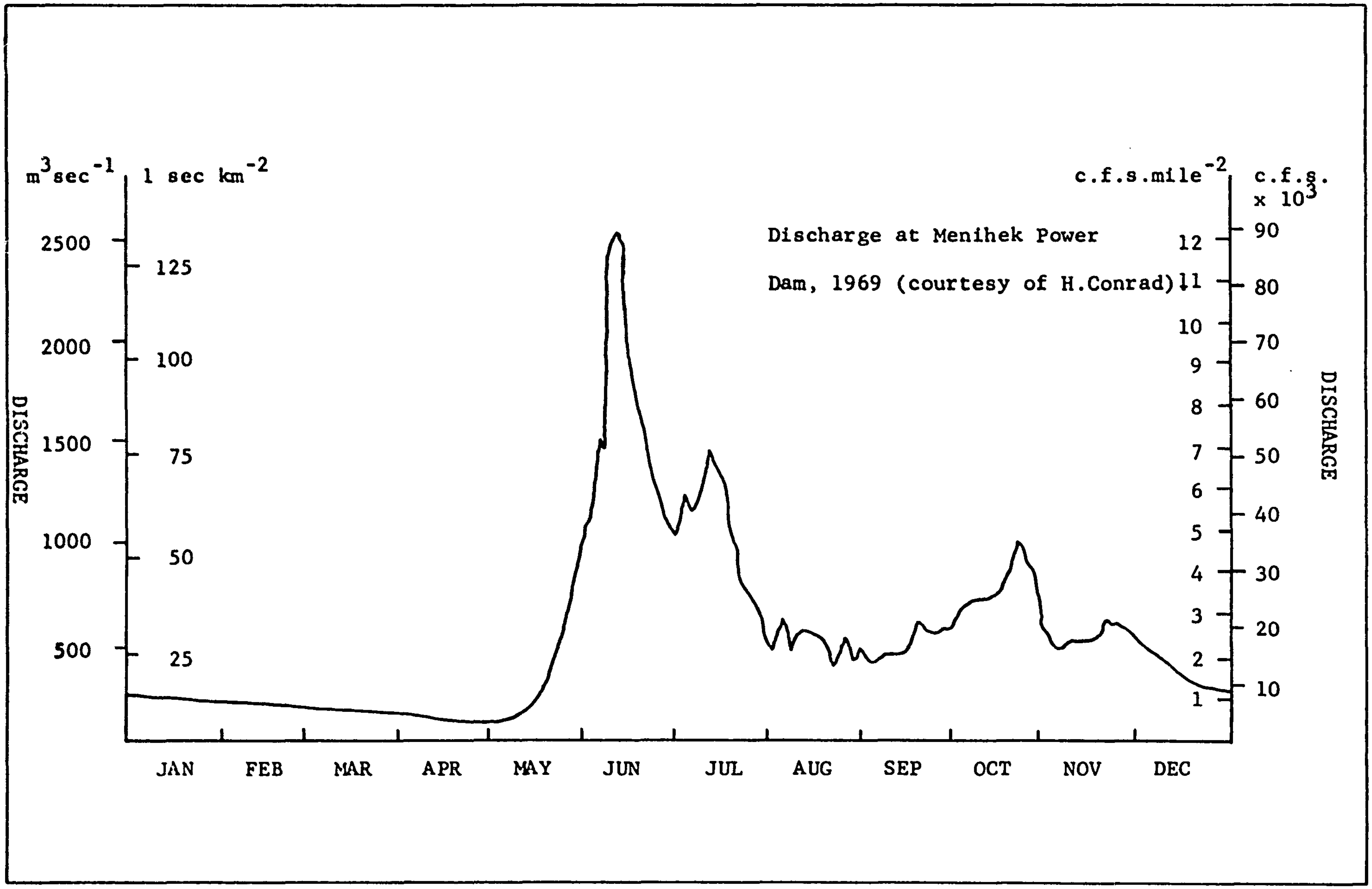


Fig. 6 Annual hydrograph for Menihek Power Dam, 1969

TABLE 6

Run-off from the Knob Lake and Menihek Drainage Basin, 1969

	Knob Lake			Menihek		
	Area: 37.8 km^2; 14.6 $miles^2$			Area: 19,070 km^2; 7363 $miles^2$		
Month	Run-off (cm)	Mean daily yield ($l\ km^{-2} sec^{-1}$)	(Cusecs $mile^{-2}$)	Run-off (cm)	Mean daily yield ($l\ km^{-2} sec^{-1}$)	(Cusecs $mile^{-2}$)
January	1.80	6.7	0.62	2.70	10.0	0.92
February	1.61	6.7	0.61	2.02	8.3	0.76
March	1.78	6.7	0.61	1.79	6.7	0.61
April	1.20	4.7	0.43	1.23	4.8	0.44
May	7.53	28.2	2.57	5.10	19.0	1.74
June	24.20	93.4	8.53	22.30	85.9	7.85
July	7.91	29.6	2.70	13.25	49.5	4.53
August	5.44	20.3	1.86	6.28	23.4	2.14
September	6.65	25.7	2.35	6.60	25.5	2.33
October	7.08	26.5	2.42	9.51	35.4	3.24
November	5.65	21.8	2.00	6.26	24.2	2.21
December	6.65	17.4	1.59	3.27	14.8	1.35
Annual Total:	75.50			81.01		
Monthly Mean:	6.30	24.1	2.18	6.75	25.5	2.34

less than the estimated average basin precipitation of 102 cm, and this amount, if it is correct, represents the order of magnitude of water losses to the basin through evaporation and transpiration, and of the amount of water involved in changes in ground and surface water storage. The value of 26.5 cm is 78 per cent of the 34.3 cm of water evaporated from the class 'A' pan at Schefferville. If 26.5 cm did represent evaporation from the lakes and evapotranspiration from the land surface, a coefficient of 0.75 - 0.8 cm would apply to the Schefferville evaporation pan. The relationships between open pan evaporation and basin water losses to the atmosphere are far more complex than suggested by this simplistic view, and it is certainly true for the Knob Lake basin that changes in water storage have to be taken into consideration. For example, the discharge at the close of 1969 (c. 0.8 m^3 sec^{-1}) was twice that on January 1 of the same year. This difference can be traced partly to heavy snowfall on the lakes at the end of December. However, differences in early winter have been more extreme in other years. On December 4, 1964, the discharge from Knob Lake reached 2 m^3 sec^{-1} (71 c.f.s.), and this peak could not be readily attributed to the removal of stop logs from Knob Lake (Findlay, 1966, p. 60). In contrast, unusually dry and warm weather in October and November of 1970 resulted in discharge below 0.25 m^3 sec^{-1} (c. 9 c.f.s.) from the Knob Lake outflow (J. Franks, pers. comm., Jan., 1970). This extreme variation occurred outside the period when rainfall could plausibly affect the discharge.

These results suggest that run-off from the basin during the second half of the calendar year may vary considerably from year to year, and therefore that changes in water storage within the basin can become an important component of the annual water balance. In 1969, the ratio of precipitation to run-off is believed to be near 0.75 for both the Knob Lake and Menihek basins. In this particular year, there may have been a positive change in water storage resulting from above normal precipitation between October and December.

The lakes in both drainage basins tend to smooth and extenuate the short-term changes in discharge which characteristically accompany high intensities of precipitation in river basins. This has been illustrated for the Knob Lake basin by Penn (in press). Summer rainstorms over Knob Lake basin in 1969 produce hydrograph peaks at the Knob Lake outflow approximately equivalent to the amount of precipitation falling directly on Pearce Lake and the Schefferville townsite. The remainder of the rainfall either contributes directly to lake-water storage or travels slowly towards the lakes as surface or sub-surface flow. In this way, summer rainfall accumulates in the basin as surface or sub-surface water storage, causing smoothed run-off peaks and ultimately the relatively high and steady rate of discharge during October and November. In this way, discharge from Pearce Lake may well reflect the precipitation of previous months. It is this time lag which may lead to changes in water storage from year to year.

One feature of the hydrographs for the Knob Lake and Menihek basins provides indirect evidence of the influence of groundwater movement on the transfer of water. In both hydrographs, a discharge minimum in late July and early August is followed by a gradual but steady increase in flow to a plateau level which persists until November. The yield corresponding to this plateau is about 20 l km^{-2} sec^{-1} for both drainage basins. It is suggested that this steady yield represents the net rate of groundwater discharge during the ice-free period of the year, and that the mid-summer minimum discharge is an indicator of the combined effect of evaporation and transpiration from the lake and land surfaces in the drainage basins. The similarity between the basins also suggests that the Knob Lake basin is representative of a wide area of the Labrador Trough.

5. Snowmelt Run-off, 1969.

The spring flood is the dominant feature of the hydrographs of both the Knob Lake and Menihek basins. The water discharged through the lakes at this time is sufficient to effect complete mixing of lake waters, and in the majority of lakes in the Knob Lake basin this results in complete replacement of the water in individual lakes. Thus, from the point of view of chemical limnology, snowmelt is the critical hydrological event of the year. The number of times of renewal of the water in the lakes of the drainage basin during the spring flood (the ratio of the volume of run-off in the snowmelt period to lake volume) is expressed in Table 8.

Run-off associated with snowmelt began in both drainage basins on May 8, when a low pressure system displaced a cold and stable air mass over northern Quebec which had dominated weather in April. In both basins, the flood peaked on June 10, reaching 4.65 m^3 sec^{-1} (164 c.f.s.) at Schefferville and 2.43×10^3 m^3 sec^{-1} (8.57×10^4 c.f.s.) at Menihek dam. Expressed as yields per square kilometer of drainage basin per second, these discharges are equivalent to 125 litres at Schefferville, and 130 litres at Menihek. The peak discharge at Menihek was the highest in 15 years of record, while at Schefferville a causeway was opened to allow water to drain from Knob Lake through the original outflow. The extension of the flood peak at Schefferville over several days before the causeway was opened indicates that the outlet culverts for Knob Lake cannot discharge more than about 4 m^3 sec^{-1}.

Allowing for baseflow based on discharges in early May and late July, the amount of snowmelt run-off at the Pearce Lake outflow is calculated as 23 cm, 30.5 per cent of the annual run-off. The corresponding snowmelt run-off production at Menihek was 30.4 cm, 37.6 per cent of the annual run-off. In the Knob Lake basin, the average water equivalent of the basin snow pack before snowmelt was about 41 cm. On this basis, about 56 per cent (the value of 23 cm quoted above) of the snow pack contributed directly to run-off. That part of the remaining 18 cm not lost to the atmosphere contributed to groundwater recharge into the dolomite and fissured zones of the shales.

As with the annual hydrograph, the timing of the floods at Schefferville and Menihek is very similar. One important difference is that the proportion of snowmelt run-off in May is greater at Schefferville than at Menihek. This difference probably results from the greater size of the Menihek basin, and from the greater distance of travel of snow meltwater. The peak superimposed on the falling stage of the flood in both basins does not result from snowmelt but from a long period of heavy rain on saturated ground (5 cm over Knob Lake basin in the week ending July 5; Table 5).

6. Residence times of lake waters, and run-off within Knob Lake basin.

The run-off recorded at the Pearce Lake outflow reaches Pearce Lake partly as surface run-off and partly as groundwater flow. The lakes in the basin represent stages in the transfer of both surface and sub-surface flow through the drainage basin. The rate of passage of water through lakes is a reflection of the relatively rapid release of surface flow through lake outflows and of the more gradual release and recharge of groundwater associated with the geological formations comprising the lake basins. In the Knob Lake basin, stream flow is of limited importance and is mainly confined to the channels connecting lakes. Consequently, there are upland areas in the basin where there is little evidence of stream flow. Some of these areas may be zones of groundwater recharge, and some of this water may subsequently be discharged into lakes lower in the drainage system.

For any portion of water passing through a particular lake in the drainage sequence, there is an average 'residence time' during which that portion of water will remain in the lake. This residence time is a function of the area of the lake catchment, the volume of water passing through the lake, and of the lake volume itself. It represents both surface and sub-surface transfer of water between lakes. Residence times, as applied to lake water chemistry, provide one measure of the relative stability of lake water over time and of the magnitude of transfer of water and dissolved substances between lakes. In lake catchments where direct surface run-off dominates the water supply to lakes, those lakes with long residence times are more likely to achieve chemical equilibrium with the rock-type forming the lake basins. In other lake catchments, most of the water reaching a lake may arrive as groundwater flow and this water will be relatively close to chemical equilibrium with the catchment geology. In this case, little further solution will take place in the lake basin and variation in the residence time will, of itself, have little effect on the stability of the chemical composition of the lake water. It is important to note here that the concept of the average 'residence time' involves the assumption that the lake is in full circulation and that all parts of the lake water are being transferred towards the lake outlet at a uniform rate ('steady turbulent flow'). This is a realistic assumption during most of the ice-free period of the year, but the evidence for thermal stratification (Chapter I) and chemical stratification (Chapter IV and V) shows that this assumption is not tenable under an ice cover.

Lake water residence times have been calculated for the year 1969 and for the period of snowmelt for each lake in the basin (Table 7). These residence times are based on the run-off from Pearce Lake, the estimated area of the lake catchment and the lake volume. These estimates assume that the yield of water forming the run-off from Pearce Lake is uniformly distributed throughout the drainage basin. A diagram showing residence time as a function of discharge has been drawn for Pearce Lake (Fig. 28) to show how residence times can be expected to vary during the year.

On the basis of 1969 run-off data, all but five lakes in the drainage basin have residence times less than one year. Residence times for the largest lakes, such as Malcolm, Knob and Houston Lakes, are about 6 months, and near 3 months for many of the smaller lakes in

TABLE 7

RESIDENCE TIMES FOR LAKES IN KNOB LAKE DRAINAGE BASIN
(for annual run-off 75.5 cm uniformly distributed through the basin)

Lake	Catchment area km^2	Volume m^{3}x10^6	Volume/ area cm	No. times of renewal in 1969	No. times of renewal during sp.flood (39.1 cm run-off)	Mean residence time (days)
Houston	6.55	2.164	33.1	2.28	0.85	160
Communications	2.77	0.820	29.6	2.55	0.76	143
Osprey	8.81	1.079	12.3	6.15	3.15	59
Malcolm	25.45	10.401	40.9	1.85	0.96	198
Phred	3.94	0.820	20.8	3.63	1.88	101
Gene	3.31	0.760	23.0	3.29	1.70	111
Easel	3.57	5.769	162.0	0.466	0.24	783
Ares	27.05	1.370	5.1	14.8	7.65	24.7
Knob	34.56	10.826	31.4	2.4	1.25	152
Pearce	37.78	1.224	2.71	27.9	14.40	13.1
North	0.618	0.370	60.0	1.26	0.65	290
Middle	0.289	0.470	163	0.464	0.24	788
South	0.227	0.081	35.7	2.12	1.10	172
Bassett	1.095	0.125	11.4	6.63	3.43	55
Adams	0.490	0.603	123	0.614	0.32	595
Trigger	1.020	0.062	6.1	12.4	6.40	29.5
Dale	0.274	0.030	11.0	6.88	5.70	53
Doris	0.475	0.006	12.6	6.0	6.50	61
Cowan	0.237	0.189	80	0.945	0.49	386
Panhandle	0.163	0.050	30.5	2.48	1.28	147
Findlay	0.213	0.045	21.1	3.58	1.85	102
Williams	0.540	0.020	37.1	2.04	1.05	179
Francois	0.140	0.019	13.6	5.55	2.88	66
Ives	0.100	0.084	8.4	0.90	0.47	406
Mattox	0.119	0.086	72.2	1.05	0.54	350
Gray	0.902	0.133	14.7	5.14	2.66	71
Hardy	0.237	0.080	33.7	2.24	1.16	163
Thorn	0.203	0.035	17.3	4.36	2.26	84
Barr	0.215	0.088	41.0	1.84	0.95	199
Lier	0.104	0.034	32.7	2.31	1.20	158

the basin. Those lakes with residence times above one year are: Easel, Cowan, Middle, Ives and Adams. All these lakes lie on dolomite, have relatively small catchment areas in relation to lake volume, and are deep in relation to surface area. With the exception of the water in these lakes, complete turnover of lake water took place between the times of the two lake sampling surveys. This means,simply, that the water in individual lakes was not sampled twice during the two surveys, except in those dolomite lakes referred to above in which water residence times exceed one year.

The volume of water passing through the basin during the spring flood, between early May and mid-July, is sufficient to replace the water in most lakes of the drainage basin. There are eleven lakes in the basin in which the water is not completely replaced: the five lakes on dolomite mentioned above, and Houston, Communications, Barr, Mattox, North and Malcolm. The spring flood, which is accompanied by the break-down of winter thermal stratification, may be thought of as effective in 'flushing-out' many of the lakes at the end of the winter. This 'flushing-out' involves the addition of fresh snow meltwater to headwater lakes in the basin, and the 'shunting' of water between lakes lower down the drainage basin.

In an attempt to assess the amount of surface run-off occurring within the basin, and from this the amount of water transferred between lakes as surface and sub-surface flow, the outlets of Houston, Osprey, Malcolm, Easel and Ares Lakes were gauged periodically between the falling stage of the spring flood and early September (Table 8). Using the area of the catchment at each lake outflow and the corresponding discharge from

TABLE 8

RUN-OFF DISTRIBUTION WITHIN KNOB LAKE DRAINAGE BASIN, 1969

Date	Lake outflow	Lake catchment area (A) km^2	Discharge (l/sec^{-1}) (Q)	Discharge from Pearce Lake (Q_p)	Q/Q_p	Catchment area/ basin area (A/A_p)	$\frac{Q/Q_p}{A/A_p}$
Jun 15	Houston	6.55	350	4,500	0.078	0.174	0.45
21	"	"	204	3,460	0.059	"	0.44
Jul 5	"	"	222	770[1]	0.290	"	1.67
12	"	"	193	1,250	0.154	"	0.89
19	"	"	148	1,310	0.113	"	0.65
26	"	"	84	925	0.091	"	0.53
Aug 2	"	"	100	815	0.123	"	0.71
9	"	"	104	660	0.158	"	0.91
18	"	"	127	835	0.153	"	0.88
24	"	"	191	842	0.227	"	1.31
30	"	"	118	880	0.134	"	0.77
Sep 7	"	"	114	820	0.140	"	0.81
21	"	"	130	965	0.135	"	0.78
Mar 27	Osprey	8.79	31	250	0.125	0.233	0.54
Jun 21	"	"	850	3,460	0.245	"	1.05
Jul 5	"	"	365	770	0.471	"	2.02
Jul 19	"	"	220	1,310	0.168	"	0.72
Sep 7	"	"	182	780	0.234	"	1.01
Mar 11	Malcolm	25.44	1,450	248	0.583	0.673	0.66
Jun 23	"	"	1,380	3,100	0.444	"	0.66
Sep 5	"	"	480	800	0.606	"	0.90
Mar 11	Easel	3.57	34	250	0.136	0.094	1.46
Jun 23	"	"	122	3,100	0.039	"	0.42
Sep 5	"	"	55	800	0.069	"	0.73
Mar 11	Ares	27.05	142	250	0.57	0.655	0.87
Jun 23	"	"	1,410	3,100	0.46	"	0.71

[1] stop-logs inserted in Knob Lake outflow culverts.

the Pearce Lake outflow, each measured discharge is also expressed as a ratio of that predicted assuming uniform yield of surface run-off throughout the drainage basin.

The stream gauging results indicate that the catchments defined by the outlets of Houston, Osprey, Malcolm, Easel and Ares Lakes did not contribute surface run-off proportional to their surface area. Generally, the ratio of observed run-off to the run-off predicted assuming uniform yield of surface run-off is near 0.9 during the falling stage of the spring flood, and 0.8 in early September. In late July and early August, these ratios fall to 0.4 to 0.5, presumably partly in response to evaporation and transpiration losses from the upland catchments. There are marked deviations from these ratios, some of which (as on July 5) can be explained in terms of the regulation of the level of Knob Lake, and subsequently in terms of summer rainstorms, but others remain unexplained. Run-off contributions from the Houston and Easel catchments are particularly low on the falling stage of the flood. In the case of Houston Lake, this may reflect rapid release of snowmelt run-off from shale ridges, while in the case of the Easel catchment, a large part of the snowmelt may have contributed directly to groundwater reservoirs in dolomite aquifers.

The prevalence of ratios of observed to predicted run-off less than unity suggests that groundwater movement is important in the transfer of water through the basin and between lakes. The ratios would indicate that between 10 and 60 per cent of the flow can take place as groundwater movement. There are unfortunately no direct observations of groundwater flow to support this argument, which must rest as speculative. However, if the speculation is continued a stage further, the conclusion is reached that the topographic lake catchments (used in Table 7 and 8) may not be groundwater catchment boundaries, and appreciable flow of water may take place along the geological strike and across the drainage divides that have been used throughout this report on the basin hydrology. Furthermore, in order to explain the observed run-off from Pearce Lake, there most be a considerable amount of groundwater discharge into Ares and Knob Lakes throughout the summer - a groundwater flow that would explain the sustained yield put forward in section 4 of this chapter. This conclusion could be confirmed or disproved by systematic gauging at a larger number of points within the basin, if possible in conjunction with direct observations of groundwater flow.

If it is true, as suggested above, that groundwater flow is an important control of the rate of passage of water between lakes, it follows that chemical equilibria attained by groundwater are likely to be one determinant of the ionic composition of lake waters (see especially section 9 of Chapter IV). Another important consequence is that the residence times of small lakes near drainage divides may be appreciably longer than indicated by the discharge at Pearce Lake outflow. This argument applies particularly to the small lakes in the headwaters of the Easel catchment and to the small lakes on Attikamagen shale (Gray, Hardy and Thorn) which drain into Communications Lake. It is not possible to say what the effect of groundwater recharge from lakes near drainage divides may be, but residence times in some instances could be raised by a factor of two.

7. Water Use in Schefferville.

The water supply for the Iron Ore Company and for the 3,500 residents of Schefferville is taken from Knob Lake. Reference has already been made to the regulation of the level of Knob Lake for this purpose. The average pumping rate from Knob Lake in 1969 was 7.5 x 10^5 U.S. gallons per day (2.84 x 10^3 m^3 day $^{-1}$); this rate falls to 6.0 x 10^5 in late winter, and rises to 1.0 x 10^6 U.S. gallons per day in midsummer (R. Poitras, municipal engineer, pers. comm., January, 1970). The increased summer consumption results from the watering of lawns and roads. The daily per capita consumption of water by Schefferville residents is 230 gals per day (870 liters), of which more than half is used by the Iron Ore Company of Canada. The domestic consumption is closer to 100 gals day^{-1} (380 l), comparable with domestic water used in American cities (Fair and Geyer, 1958, p. 24). A further 725 Naskaupi and Montagnais Indians living outside the town on a reserve are supplied daily with water from Schefferville by a truck carrying c. 1500 gals.

The sewage treatment plant for the town is located beside Pearce Lake (Fig. 25). The design of the plant has found application in American cities of moderate size (Fair and Geyer, 1958, p. 301). Activated-sludge treatment of raw sewage is preceded and followed by plain sedimentation. The sludge is passed to an anaerobic digester, and the liquor from the digester is recycled through the activated sludge tanks as a nutrient base for the bacteria stock. The effluent is normally chlorinated by passage through a buffer zone maintained at 25 mg/l residual chlorine, but this unit was not in operation at the time of this study.

If a treatment plant of this design is to be operated efficiently, the bacterial population in the activated sludge tanks has to be maintained at a steady rate of growth commensurate with the nutrient supply from municipal sewage. If the sewage quality varies with the amount of dilution by industrial waste-water, the bacterial population fluctuates and the plant efficiency drops sharply. The normal operating efficiency, in terms of the removal of 5-day, 20°C BOD, is placed at 65 - 95 per cent by Fair and Geyer (1958, p. 301). At Schefferville, the bulk of the industrial waste-water, from ore-testing operations, by-passes the treatment plant and is discharged directly into Pearce Lake.

Efficiency may fall if the supply of sewage to the plant falls below the design capacity. The Schefferville plant was designed to treat 5.0×10^5 U.S. gals day^{-1} (1.9×10^3 m^3), but in 1969 it received on average 4.0×10^5 gals day^{-1} (1.5×10^3 m^3) (R. Poitras, pers. comm., 1970). Consequently, it may periodically operate inefficiently and discharge a high BOD load into Pearce Lake in addition to a high coliform bacteria density. Some of the observed and possible effects of effluent discharge from the treatment plant and from the ore testing plant outfall are considered further in Chapter VI on the chemistry of Pearce Lake.

To place water consumption by Schefferville in perspective, the total consumption of 1.135×10^6 m^3 (3.0×10^8 gallons) in 1969 was equivalent to 3 cm run-off from the drainage basin. This is a small portion of the annual run-off (less than 4 per cent) but in late winter, when the discharge from Pearce Lake falls below 170 l sec^{-1}, the water passing through the town amounts to more than 20 per cent of the discharge from Knob Lake. At this time of year, the amount of waste-water entering Pearce Lake is sufficiently large in relation to natural throughflow to cause appreciable accumulation of waste substances in Pearce Lake by the end of winter (Chapter VI).

CHAPTER III

COLLECTION AND ANALYSIS OF CHEMICAL DATA

1. Objectives of the Sampling Programme.

The aim of the sampling programme for the lakes was to describe, for the year 1969, the variation in ionic composition between lakes, and variations within lakes associated with thermal stratification and incomplete horizontal mixing. The programme aimed to describe, as far as possible, all of the thirty lakes in the basin in order to provide comprehensive coverage of the basin within the terms of reference of the International Hydrological Decade programme. Since it was not possible to sample all of the lakes systematically throughout the year, it was decided to sample at the end of winter (before snowmelt) and in late summer (before the breakdown of summer thermal stratification, should it occur). Sampling between these times was directed towards the description of the breakdown of winter stratification during snowmelt and of the chemistry of Pearce Lake. For both the late winter and late summer surveys, the adequate number of samples needed to satisfy the general objectives of the sampling programme proved to be a problem, since there were no previous chemical data available for the lakes. Consequently, the necessary sampling coverage has to be judged in the light of accumulated field data as the surveys progressed.

Three general guidelines were followed throughout the two main surveys:

a) Sample all lakes in the drainage basin.

b) Anticipate some degree of chemical stratification, even in the absence of thermal stratification..

c) Sample for horizontal concentration gradients within lakes wherever waters draining contrasting rock-types enter a lake, and wherever more than one rock type forms the lake shore.

2. Winter Sampling Programme.

An initial series of ten daily samples was collected from the outlets of Knob and Pearce Lakes in November, 1968. These samples were used to find the range of ionic concentration to be expected from these lakes, to gain experience with water analysis and to assess the reproducibility of results. In early January, 1969, vertical profiles were sampled in Easel, Knob and Pearce Lake to determine whether marked vertical gradients in ionic concentration could be expected in the larger lakes. The sites investigated on Easel and Knob Lakes showed very little variation in composition with depth.

The full-scale winter survey was begun in early March and ended on May 1. The survey fell into two phases separated by a three-week period of cold weather (mean air temp. -23°C) which restricted field work. The selection of sample sites (Appendix I) was based on bathymetric maps prepared by Bryan (1964); Adams, Shaw and Archer (1966) and Findlay (1966).

The first lake sampled was Cowan Lake. Samples from this lake indicated that horizontal concentration gradients over distances of about 100 m were probably too small to be analytically reliable, but that pronounced vertical chemical stratification could be expected, at least in dolomite lakes. The next lake sampled, Knob Lake, showed slight but consistent horizontal concentration changes over distances of 1.5 - 2 km, in addition to a widespread but weakly defined vertical concentration gradient. The programme for the other lakes in the basin was based on the results obtained from Cowan and Knob Lake, although the difficulty of access to some of the smaller lakes limited the number of samples that could be collected, and there were three small lakes (Dale, Thorn and Lier) which were not sampled at all in the winter survey.

The field procedure on the lakes was as follows: at each site a hole 10 cm diameter was drilled and the thickness of clear ice, white ice (snow ice) and snow was recorded. The depth of water below the hydrostatic water level was then determined with a plumb line to the nearest 0.5 m.

A temperature profile, with readings at 0.5 m intervals, was than taken to the depth indicated by the plumb line. The thermistor used to register temperature (a Telethermometer marketed by the Yellow Springs Company) could be read to 0.1°C and was considered accurate to 0.2°C (comparable with a D.O.T. meteorological thermometer) after calibration. Because of the displacement of water near the hole in the ice and near the bottom sediments beneath, realistic temperature gradients within these zones could not be obtained.

After allowing time for the settling of sediment disturbed by the plumb line, water samples were collected with a 1 litre Kemmerer sampler (Welch, 1948). The number of levels sampled depended on the depth of the water column and the amount of information required from the particular site. Usually, where the depth of water was less than 3 m, a sample was taken from the mid-point between the lake bottom and the lower surface of the ice cover. If the water depth was between 3 and 6 m, two samples were usually taken from 1/4 and 3/4 of the depth of the total water column. Where the water depth exceeded 6 m, three samples were taken, 1 m below the ice, 1 m above bottom, and mid-way between. In cases of special interest, up to 6 samples were taken, in order to sample water just below the ice and just above the bottom. Although concentration gradients near the mud surface are very important in describing the exchanges of dissolved substances between lake water and bottom sediments, it is normally not feasible to sample this zone with the Kemmerer sampler, and therefore the conditions at the mud-water interface in the lakes of this study have to be inferred.

Samples for dissolved oxygen were transferred to glass-stoppered bottles from the Kemmerer sampler with as little aeration as possible. When air temperatures were close to freezing, reagents for the Winkler method for the determination of dissolved oxygen were added in the field.

A portable Beckman conductivity probe (loaned by I.O.C.) was used on Cowan and Knob Lakes at the beginning of the survey. The instrument was useful in that it indicated increases in conductivity in the water near the ice and near the lake bottom. However, instrument response was poor in air temperatures below -5°C and the probe therefore could not be used during the remainder of the survey.

3. Summer Sampling Programme.

The summer lake survey was scheduled for August and early September in 1969, when it was believed, on the basis of previous climatic records, that any thermal stratification present in the lakes would be best developed. Sampling took place between August 20 and September 7. Any thermal stratification that had developed before this period was broken down (except in the case of Cowan Lake - Chapter I) by the cool northwesterly airstream during the sampling period. Air temperatures by day ranged from 2°C to 11°C, and wind speeds of 11 - 15 m sec^{-1} (15 - 34 m.p.h.) were recorded at Schefferville on most days. Since the outflow temperature record for Knob and Pearce Lakes during the summer did not indicate the development of any stable thermal gradient, it is believed that the conditions encountered during the sampling period were representative of the summer of 1969.

Sampling sites (Appendix I) were similar to those of the winter sampling programme. Less emphasis was placed on the detection of vertical and horizontal concentration gradients since internal variations in fully circulating lakes in summer were likely to be much less marked than in the thermally stratified waters under the winter ice cover. Vertical profiles were sampled on the larger lakes, and samples were also taken to describe the mixing of water of contrasting geological backgrounds.

The equipment used for depth sounding, measurement of temperature profiles and the collection of water samples were collected on the larger lakes from a canoe equipped with an outboard motor. The canoe drifted in strong winds, making the precise location of sampling sites difficult. Portaging the canoe to the smaller lakes proved to be impracticable for the more remote lakes, and samples were collected from these lakes on foot. In these cases, care had to be taken not to contaminate the samples with bottom sediment. When samples were collected on foot, a meteorological thermometer was used to record water temperature.

4. Intermediate Surveys.

Pearce and Cowan Lakes were also sampled during the spring flood (June 1 - 7), after the spring flood had subsided (June 30) and in a period of calm, anticyclonic weather (July 14). On Cowan Lake, the same sites were sampled as in the winter survey, but the location of sampling sites on Pearce Lake was modified because of ice conditions and in order to obtain water samples close to effluent outfalls.

The object of the surveys of Pearce Lake was to describe changes in the chemistry of this polluted lake during the passage of the spring flood, and to assess the conditions under which soluble wastes can accumulate within the lake during the summer. The surveys of Cowan Lake were intended to describe mixing of snow meltwaters in the lake, and to investigate the possibility that this lake would become thermally stratified during the summer. Cowan Lake was chosen for this purpose because it is accessible, and appears to be the lake most likely to stratify in summer of all the lakes in the drainage basin. The lake is nearly circular and is sheltered by spruce on surrounding dolomite ridges 15 - 25 m above the lake. The 11 m deep depression in the centre of the lake lies in the middle of a dolomite shelf 2 - 4 m below the surface.

5. Chemical Analyses of Water Samples.

Chemical analyses of water samples used in this study

(Appendix II) were carried out at Schefferville using glassware and reagents supplied by the Hach Chemical Company of Ames, Iowa. The procedures used follow, wherever possible, recommendations set out in 'Standard Methods for the Examination of Water and Waste-Water' (A.P.H.A., 1965). The Hach procedures were developed for the rapid testing of domestic and industrial supply and waste-waters by sanitary engineers, and the sensitivities of the tests conform to engineers' requirements. The methods are believed to be applicable to geochemical problems where a high order of accuracy is not essential (within 1 mg/l for common cations, and within 2 mg/l for common anions at concentrations of 10 - 15 mg/l), and provided that accurate knowledge of trace quantities is not necessary.

The loss in accuracy of the simplified Hach procedures compared with analyses performed in a fully equipped laboratory was offset by certain practical advantages. Samples could be analysed within 48 hours of sample collection, and a number of determinations could be run simultaneously. Probable sources of error could be identified, which is important in the interpretation of results. The procedures followed for each constituent are summarised in Table 9, together with information on the source of the method and the limitations of the results. Of the tests listed, an attempt was made to determine pH, bicarbonate, calcium, magnesium, silica, sulfate and iron in all samples collected. Other constituents were analysed to determine the range of concentrations to be expected in the lake waters. Sodium and potassium values are based on determinations by flame photometry by the Ministère des Richesses Naturelles de Québec on samples collected at lake outflows.

TABLE 9 Procedures followed in Chemical Analysis of Water Samples

(mainly based on 'Standard Methods for Examination of Water and Wastewater' 12th. ed. (1965))

Constituent	Method	Limitations	Source of method
Aluminium	'Aluminon' method. At pH 4.0, aluminium reacts with ammonium salt of aurin tricarboxylic acid ('aluminon') to give a pink lake with maximum absorbance at 525 mmu.	Method useful in range 0.02 - 1.0 mg/l Al, but success depends on quality of aluminon and control of operating conditions.	"Standard Methods" p.53
Bicarbonate	Obtained from alkalinity, the sum of bicarbonate, carbonate and hydroxyl ions. Sample is titrated with 0.02N sulfuric acid to an endpoint at pH 5.1 - 4.5 given by mixed cresol green-methyl red indicator. Exact pH at endpoint depends on total alkalinity.	Accuracy depends on endpoint recognition at correct pH, and is affected by lighting conditions. Titrations are reproducible within + 1.0 mg/l HCO_3^- down to c.5 mg/l.	"Standard Methods" p.48
Calcium	Sample is buffered to pH 12-13 and titrated with EDTA (0.01M) which combines with calcium in sample. Endpoint is given by Eriochrome Blue Black indicator which is pink in presence of ionic calcium.	Prompt titration is needed to avoid calcium carbonate precipitation after buffering. Alkalinity 35 mg/l HCO_3^- affects endpoint. Titration reproducible to + 1.0 mg/l down to 2 mg/l Ca.	"Standard Methods" p.74
Chloride	Chloride is titrated with mercuric nitrate to form soluble mercuric chloride. At pH 2.3 - 2.8, endpoint is given by diphenylcarbazone which turns purple from orange in presence of excess murcury.	Lacks sensitivity below 5 mg/l Cl, because of indistinct endpoint. Variations of c.0.3 mg/l at conc. of Cl 0.5 - 2.5 mg/l were detectable using 100 ml sample volumes.	"Standard Methods" p.87

Constituents	Method	Limitations	Source
Iron	Phenanthroline and tripyridine methods. Iron is brought to ferrous state at pH 3.3 and reacts with phenanthroline to give an orange complex (510 mmu) which is measured colorimetrically. Tripyridine method is similar, but gives blue complex (550 mmu).	Tripyridine has greater sensitivity at low concentrations than phenanthroline. Minimum iron detectable is 0.01 mg/l. Samples should be filtered to remove interference from particulate iron.	"Standard Methods" p.156
Magnesium	Magnesium is computed from the difference between total hardness and calcium hardness. Total hardness is obtained by titrating a sample buffered to pH 10 with EDTA titrant using Eriochrome Black as a colour indicator sensitive to both calcium and magnesium ions. The colour change is from red to dark blue.	As for calcium, prompt titration is required. Provided other ions contributing to hardness (Ba, Sr) are absent or very small, magnesium can be estimated to within 1 mg/l if Ca plus Mg are greater than 3 mg/l.	"Standard Methods" p.147
Manganese	Periodate method. Manganese is brought into divalent state in acid solution with sodium periodate to give purple permanganate colour, which is measured at 525 mmu.	Method has low sensitivity below 2 mg/l Mn, and is qualitative below 1 mg/l Mn.	"Standard Methods" p.175
Nitrate	Nitrate is reduced to nitrite in the presence of cadmium metal; the nitrite is then determined by forming a red azo dye by coupling diazotised sulfanilic acid with naphthylamine HCl at pH 2.0 - 2.5. The dye is measured 520 mmu.	High reagent blanks and poor colour development limited application of this method in this study, using Hach reagents. Values below 0.5 mg/l $N\text{-}NO_3$ were erratic.	p.77 Strickland & Parsons

Constituent	Method	Limitations	Source
Oxygen, dissolved	Azide modification of iodometric method. Manganese sulfate and strong alkali are added to sample forming Mn(OH)$_2$ precipitate, which is oxidised by dissolved O_2. On acidification in the presence of iodide, oxidised Mn reverts to divalent state, and iodine equivalent to O_2 present is liberated and titrated with phenylarsene oxide.	Quality of results depends on exclusion of air during sampling and avoiding changes in water temperature before addion of $MnSO_4$ and alkali to sample, which may be done in field at time of sampling. Using Hach materials, the iodine titration was sensitive to 0.5 mg/l O_2.	p.21 Strickland & Parsons
Phosphate (Ortho)	Stannous chloride method. Ammonium molybdate is used to form molybdophosphoric acid, which is reduced using $SnCl_4$ to give a deep molybdenum blue, which is determined colorimetrically at 690 mmu.	The method is sensitive to 0.01 mg/l P-PO_4. Analyses of unfiltered samples include some phosphorus absorbed on particulate matter.	p.234 "Standard Methods"
Silica	Molybdosilicate method. Ammonium molybdate at pH 1.2 forms silicomolybdic acid. Molybdophosphoric acid is destroyed with oxalic acid. Aminonaphsulfonic acid is used to reduce molybdic acid to molybdenum blue which is measured at 410 mmu.	Ammonium molybdate reacts promptly in the presence of silicic acid, but more slowly to polymer, colloidal or particulate forms of SiO_2 in lake water. This results in slow colour development without a clear threshold. In duplicate samples, results are reproducible to ± 0.1 mg/l at 2 mg/l SiO_2; the minimum concentration detectable is about 0.03 mg/l.	p.261 "Standard Methods"

Constituent	Method	Limitations	Source
Sulfate	Turbidimetric method. Sulfate is precipitated in acid solution with barium chloride to form a barium sulfate suspension, the absorbance of which is determined as measure of sulfate ion concentration, at wavelength of 420 mmu.	Results are reproducible within 1 mg/l with duplicate samples. Sensitivity is low with concentrations below 5 mg/l SO_4; minimum concentration detectable with reliability about 1.0 - 1.5 mg/l. Turbidity and colour in sample interfere with results.	p.291 "Standard Methods"

A Hach spectrophotometer was used for colorimetric determinations. When possible, concentrations were read in the absorbancy range 0.1 - 0.7, using sample dilution with deionised water if necessary (Rainwater and Thatcher, 1966, p. 44). Blank determinations were run on sample water of low turbidity. A potential source of error in colorimetry is the breakdown of Beer's law on which the majority of tests are based. Beer's law states that a linear relationship exists between the absorbancy of the sample and the concentration of the light absorbing constituent. Deviations from Beer's law result from a change in temperature or a shift in ionic equilibria involving a pH sensitive colour indicator. Most tests were run at 20 ± 2°C to minimise error resulting from temperature variation. This is particularly important in determinations of dissolved silica and soluble orthophosphate.

Titrations were carried out using a plunger operated burette which could be read to 0.01 ml. In the titrations for alkalinity (i.e. bicarbonate ion), calcium and magnesium, this amount of titrant was equivalent to 1 mg/l of the constituent expressed as $CaCO_3$. Fluorescent lighting was used to standardise colour changes near the endpoint.

The pH (hydrogen ion activity) of water samples was recorded in the laboratory with a Beckman 'Electromate' pH meter within a few hours of sample collection. Appropriate pH buffers, in increments of 0.5 pH units, were used with all samples, and the combination glass - saturated calomel electrode was rinsed with deionised water before each determination. Values of pH were read to 0.01 pH units, and rounded to one decimal place in cases where a lake was represented by one sample.

Although the general limitations of the analytical techniques are contained in Table 9, there are certain additional uncertainties which arise in the interpretation of results and which require separate consideration. Firstly, the value of pH recorded in the laboratory may not be the same as the pH of the lake water from which the sample was taken. Inaccuracies can result from changes in the carbon dioxide balance between sample collection and analysis, and from changes in water temperature. Ideally, pH should be recorded in the field immediately after sample collection. The magnitude of the errors involved in the pH determinations in this study is not known. However, it is known that water samples taken in winter were markedly super-saturated with respect to atmospheric CO_2, and that samples collected in summer were also somewhat super-saturated with respect to atmospheric CO_2 (Fig. 11; Appendix V, Section D). These results indicate that the samples did not equilibrate with the atmosphere before analysis, and probably that the observed pH values (except in particularly poorly buffered samples; e.g. Barr Lake) are reasonable approximations of the pH of the lake waters.

Bicarbonate ion concentration is ordinarily determined from total alkalinity titrations which include carbonate and hydroxyl ions present in the sample. In the pH range 6 - 8, carbonate and hydroxyl ion concentrations are much smaller than the bicarbonate ion concentration. The endpoint of the alkalinity titrations was taken as the colour change corresponding to pH $\sim$ 4.5, although for precise work the endpoint pH should be calculated for each analysis from an estimated bicarbonate ion concentration (Barnes, 1964). The colour change at the endpoint depends upon lighting conditions and is difficult to locate precisely.

In view of these uncertainties, values of bicarbonate ion concentration are believed to be approximate within ± 2 mg/l HCO_3^{-1}, although the reproducibility of results under the same lighting conditions is within 1 mg/l HCO_3^{-1}.

Chloride values obtained during the winter survey are believed to be unreasonably high, because of the lack of sensitivity of the technique used below 10 mg/l Cl^{-1}. In summer, larger sample volumes were used, and the results obtained then have been accepted. The winter determinations of chloride are omitted from this study. Nitrate and phosphate were present in the lakes in concentrations near or below the limit of detection with the methods provided by the Hach Chemical Company, and the reported concentrations are not reliable.

Finally, the ammonium molybdate method for the determination of silica not only records silicic acid (H_4SiO_4), but also any colloidal or particulate silica in the sample. Because colour development in samples took place gradually and without a clear limit to colour intensity, all samples were read after a period of 20 - 25 minutes. It is possible that the reported values either overestimate the amount of silica in solution (because of the decomposition and reaction of particulate silica) or underestimate the silica in solution because of a slow rate of reaction.

CHAPTER IV

INFLUENCE OF CARBONATE MINERALS ON LAKE WATER COMPOSITION

1. Introduction.

Bicarbonate, calcium and magnesium are by far the most abundant ions in lake waters of the Knob Lake drainage basin (Figs. 12 - 14; Appendices II and V, section C). These ions are derived mainly from the solution of carbonate minerals (particularly the dolomite of the Denault formation) by surface water and groundwater in the presence of carbon dioxide. Lake waters lying on, or associated with, dolomite have ionic compositions which reflect rates of solution of dolomite, and rates of transfer of water between lakes.

In this chapter, the conditions under which dolomite goes into solution in the drainage basin are discussed first in relation to ideal chemical equilibria attained by water in contact with carbonate minerals under controlled laboratory conditions. Ion activity product diagrams are then used to refer observed water compositions to the ideal laboratory situation and so summarise the carbonate chemistry of the lakes forming the drainage network of the basin. Secondly, distributions of bicarbonate, calcium and magnesium in the lakes are described, and some relations between these ions are discussed. An attempt is then made to evaluate the compositions of lakes receiving drainage from both dolomite and shale in terms of the relative importance of surface and sub-surface flow between lakes.

Carbonate equilibria are discussed further in Appendix V, which deals with such problems as the prediction of calcium and magnesium concentrations in water at equilibrium with dolomite as a function of the partial pressure of carbon dioxide, and relationships between carbonic acid, carbonate ion and pH in the lake waters of this study.

2. Distribution of Carbonate Minerals in Knob Lake Drainage Basin as Sources of Ca^{+2}, Mg^{+2} and HCO_3^{-1} in Lake Waters.

The Denault dolomite formation (Tables 3 and 4) is the main carbonate rock-type in the basin, occupying an area of 6.58 km^2, 17.4 per cent of the basin area. Over 90 per cent of the volume of lake water in the drainage basin either lies directly on dolomite or is mixed with water draining from dolomite. This situation exists not so much because lake basins are preferentially developed on dolomite, but because the Denault formation forms a belt running diagonally across the basin from the headwaters of Easel Lake to Osprey Lake (Fig. 4). Consequently, water draining shales and quartzite in the Osprey and Phred catchments meets and mixes with water from dolomite in the Easel catchment in Malcolm Lake, which itself lies partly on dolomite. Lake water flowing from Malcolm Lake subsequently passes through shales as it flows through Ares and Knob Lake to Pearce Lake. Nine small lakes lie directly on dolomite; they have a total area of 38.9 ha and a volume of 1.33×10^6 m^3. Five of these lakes drain to Easel Lake, one to Ares Lake and three to Malcolm Lake. Three large lakes, Easel, Malcolm and Osprey, lie predominantly on dolomite, and a number os smaller lakes are partly bordered by the same formation.

Shales in the basin also yield variable quantities of calcium and magnesium ions. These are derived partly from the calcite and dolomite which have been reported as accessory minerals in both the Attikamagen and Menihek shales (Gross, 1968). Smaller amounts of calcium and magnesium result from the decomposition of plagioclase feldspar and chlorite. In addition, atmospheric precipitation over the basin can be expected to contain Ca^{+2} in the range 0.4 - 0.8 mg/l, and Mg^{+2} in the range 0.1 - 0.3 mg/l, depending on the source of the air mass bringing the precipitation (figures based on data in Gorham, 1961).

3. The Denault Dolomite Formation.

The composition of the Denault dolomite formation varies from place to place within the basin, depending on the original composition of the formation and the amount of leaching that has taken place. The published data on the mineralogy of the formation have been summarised in Table 3, and two chemical analyses, of weathered and unweathered specimens of dolomite, are given in Table 4. In addition, there are a number of other observations bearing on the spatial variation in the composition of the dolomite within the drainage basin.

Some exposures of dolomite in the basin are markedly arenaceous and exhibit current bedding. Near the contact with the Attikamagen shale, argillaceous horizons occur within the dolomite which reportedly contain finely dispersed crystals of apatite (Gross, 1968). In most exposures, stringers of quartz and chert are abundant. In the vicinity of Easel Lake, the formation is particularly massive, and in the fissures separating blocks of dolomite, manganese dendrites may be found. The orientation of these dendrites could be used to indicate the direction of water movement in fissures (Nichols, 1968).

Fresh Denault dolomite is a mixture of crystalline dolomite ($CaMg(CO_3)_2$) and ankerite, with little if any calcite (Gross, 1968, citing Howells, 1954). Ankerite is a carbonate mineral structurally similar to dolomite, with the general formula Ca (Mg,Fe,Mn) $(CO_3)_2$, with the Fe and Mn substituting for Mg in the crystal lattice. It is apparently more abundant in deeply weathered than in fresh dolomite. The chemical analysis for unweathered dolomite in Table 4 suggests that the whole rock has the approximate composition:

$$Ca_{1.0}\,(Mg_{0.8}\,Fe_{0.15}\,Mn_{0.05})\,(CO_3)_2$$

with the Mg:Ca ratio approaching unity in pure dolomite samples. It is possible that in unweathered samples the iron and manganese is dispersed uniformly through the dolomite, so giving the whole rock the composition of ferroan dolomite (Mg/Fe + Mn greater than 4), and that during the diagenesis which accompanies weathering the dolomite becomes sufficiently enriched in iron and maganese to take on the composition of ankerite (Deer, Howie and Zussman, 1962). If the Denault dolomite dissolves congruently, ratios of magnesium to calcium in the water should reflect the original composition of the rock. However, no information is available to the writer to indicate whether or not congruent solution of ankerite can be expected, or whether the substitution of iron and manganese enhances or limits the solution of dolomite.

Dolomite near the surface may be heavily leached. The leached dolomite is very high in silica (over 90 per cent in the analysis on Table 4) and sometimes has a pumice-like appearance. The residual carbonate is low in magnesium. Some of the ferrous iron originally present in the rock may be conserved during weathering as ferric iron oxides which give the rock its buff appearance in exposures.

4. The Solution of Dolomite.

Rain and snow falling on the Denault formation is intercepted by a vegetation cover which is predominantly spruce and lichen. That part of the precipitation which is not returned to the atmosphere through evapotranspiration comes into contact with dolomite as groundwater or as water in the lichen litter overlying the dolomite. Initially, atmospheric precipitation is in equilibrium with carbon dioxide of the atmosphere (partial pressure $10^{-3.5}$ atm), but within decaying vegetation, the equilibrium pressure of carbon dioxide may be as high as 10^{-1} atm, (Livingstone, 1963).

Percolating water therefore has a highly variable content of free carbon dioxide, and it follows a complicated path between the time it reaches the surface as precipitation and the time it reaches lake water. The carbon dioxide content of the water determines the extent to which solution of carbonate minerals can take place (Appendix V, section C) and the path taken by the water determines whether the water is in contact with carbonate minerals sufficiently long to reach equilibrium. In any practical situation, such as that represented by the Denault dolomite, there are a multitude of possible equilibria which can be reached by percolating waters, just as there are multitude of possible paths of flow of water which may or may not permit equilibrium to be reached for any given carbon dioxide content. Some of the consequences of this situation are considered from a theoretical point of view in Appendix V.

To simplify the problem as far as possible, the situation is considered here in which chemically pure dolomite reacts with chemically pure water in the presence of atmospheric carbon dioxide ($P_{CO_2} = 10^{-3.5}$ atm.), at a fixed temperature of 25°C, and 1 atm. total pressure.

In the presence of water, dolomite dissociates congruently to yield calcium, magnesium and carbonate ions, according to equation (1)

$$Ca\,Mg\,(CO_3)_2 = Ca^{+2} + Mg^{+2} + 2CO_3^{-2} \qquad (1)$$

for which the equilibrium constant (Garrels and Christ, 1965 p. 6), Keq: dolomite, is in the range 10^{-16} to 10^{-20}, and probably near 10^{-17} (see below). In this case, the equilibrium constant is equal to the product of the activities[1] of the aqueous ions resulting from the dissociation of dolomite, since, by definition, the activity of pure, crystalline dolomite is unity.

The carbonate ion formed from the dissociation reacts with water to form bicarbonate ions;

$$\frac{a_{H^{+1}} \cdot a_{CO_3^{-2}}}{a_{HCO_3^{-1}}} = K_{HCO_3^{-1}} = 10^{-10.3} \qquad (2)$$

---

[1] Ion activities, denoted by a small 'a', are used rather than molar concentrations obtained by analysis. The activity of an ion may be thought of as its 'effective concentration' (Krauskopf, 1967); that part of the analysed concentration which determines the behaviour of the ion towards other ions with which it may react. The activity of an ion is decreased by the presence of other electrolytes in solution, but it is otherwise proportional to the concentration of the particular ion. The activity of a pure mineral phase, or of the solvent, is by convention assumed to be unity. The ratio of the ion activity to the analysed concentration is termed the activity coefficient, usually written γ . Activity coefficients, for the range of ionic concentration encountered in this study, have been calculated using the Debye-Hückel formula (Klotz, 1950). An example of the application of this formula is given in Appendix V, section B).

The bicarbonate ions so formed further react with water to form carbonic acid, H_2CO_3, which consists mainly of free molecules of carbon dioxide but is conventionally written as H_2CO_3.

$$\frac{a_{H^{+1}} \cdot a_{HCO_3^{-1}}}{m_{H_2CO_3}} = K_{H_2CO_3} = 10^{-6.4} \qquad (3)$$

The concentration of carbonic acid is related to the external partial pressure of carbon dioxide by the expression

$$\frac{m_{H_2CO_3}}{P_{CO_2}} = K_{CO_2} = 10^{-1.47} \qquad (4)$$

Two additional equations are required to complete the description of the system: dolomite - water - carbon dioxide. The first is the expression for the dissociation of water

$$\frac{a_{H^{+1}} \cdot a_{OH^{-1}}}{a_{H_2O}} = K_{H_2O} = 10^{-14.0} \qquad (5)$$

and the second is the expression for calcite at equilibrium with water, since water in equilibrium with dolomite may also be close to equilibrium with calcite

$$\frac{a_{Ca^{+2}} \cdot a_{CO_3^{-2}}}{a_{CaCO_{3c}}} = K_{CaCO_3} = 10^{-8.3} \qquad (6)$$

The appropriate equilibrium constants, which were obtained from Garrels and Christ, (1965), p. 89, are temperature dependent and are given in Appendix V, section B.

There are several points to note in connection with equations (1) to (6). The variable which determines the concentrations of calcium and magnesium in water at equilibrium with dolomite is the carbonate ion activity, $^{a}CO_3{}^{-2}$. The equations set out above show the dependence of the carbonate ion activity on pH (i.e. - log $_H{}^{+1}$) and the external pressure of carbon dioxide. They also describe the 'buffering' properties of carbonate waters - the ability to resist changes in pH through the formation of hydrogen or hydroxyl ions. To illustrate this point, a change in P_{CO_2} will, following equations (4) and (3) result in an increase in hydrogen ion and bicarbonate ion activities, and a decrease in carbonate ion activity. The change in pH is limited here by the formation of the bicarbonate ion. In natural waters, fluctuations in P_{CO_2} result from the uptake and release of carbon dioxide in plankton photosynthesis and respiration, and the system which comprises carbonate minerals - water - carbon dioxide provides an effective buffering system against extreme changes in pH.

The next problem to consider is the equilibrium constant for dolomite, Keq:dolomite, for equation (1). It must be remembered that, ideally, there are two equilibrium constants to be considered; one for pure dolomite and one for a dolomite rock with the composition of the Denault formation. These equilibrium expressions are:

$$\frac{a_{Ca^{+2}} \cdot a_{Mg^{+2}} \cdot a^{2}_{CO_3{}^{-2}}}{a_{CaMg(CO_3)_2} \quad (a = 1)} = \text{Keq:dolomite} \qquad (7)$$

and

$$\frac{a^{1.0}_{Ca^{+2}} \cdot a^{0.8}_{mg^{+2}} \cdot a^{0.15}_{Fe^{+2}} \cdot a^{0.05}_{Mn^{+2}} \cdot a^{2}_{CO_3{}^{-2}}}{a_{Ca_{1.0}\,Mg_{0.8}\,Fe_{0.15}\,Fn_{0.05}\,(CO_3)_2} \quad (\text{a not necessarily } 1)} = \begin{array}{l}\text{Keq:Denault}\\ \text{dolomite}\end{array} \qquad (8)$$

The argument can be simplified here by dismissing equation (8) because the equilibrium constant is not known and cannot be established within the scope of this study. It is assumed, therefore, that the presence of iron and manganese in solid solution in dolomite does not materially affect its solubility in water, and also that the activity of mineral dolomite can be assumed to be unity.

The difficulties raised by the value for Keq:dolomite in equation (7) have been thoroughly reviewed by Hsu (1967). Estimates of the equilibrium constant in the literature in this review range between extremes of 10^{-15} and 10^{-20}, and these estimates are based on a wide variety of experimental conditions. No single value can be verified experimentally because dolomite, being structurally highly ordered, forms slowly at atmospheric temperatures and pressures and cannot be precipitated in the laboratory. Garrels and his co-workers (1960) regard 10^{-19} as the physically most reasonable value consistent with free energy data for the dissociation products in their aqueous form. Garrels (op.cit.) argued that higher experimental values had been reached when samples had been finely ground, so disordering crystal faces. It could also be argued that in geological problems it is the effect of the disordering of crystal faces that is important in describing the solubility of dolomite.

An alternative method of estimating dolomite solubility may be mentioned briefly. This method relies upon chemical analyses of groundwater in dolomite, and assumes the water in question to be in equilibrium with calcite. Hsu (1966), using analyses of groundwater in Florida, argued that changes in P_{CO_2} over samples, and consequent changes in pH and carbonate ion activity, invalidated many attempts to infer dolomite solubility using methods which involve the calculation of carbonate ion activity (to obtain the ion activity product at equilibrium). However, the carbonate ion activity is still needed to justify the assumption of equilibrium with respect to calcite.

Hsu showed that the molar ratio of calcium to magnesium could be used to estimate the equilibrium constant for dolomite, and his argument is reproduced here in Appendix V, section A,1. He concluded that calculated ion activity products and estimates based on the Mg:Ca ratio gave estimates two orders of magnitude apart, although his data suggest close correspondence between the two approaches, and an equilibrium constant in the order of 10^{-17}. Hsu's argument is useful, not because it yields a precise value for dolomite solubility, but because it provides additional evidence that the solubility of dolomite in the field may not be dictated by the same controls that operate under controlled laboratory conditions.

Several additional topics in dolomite solution which are more peripheral to observed lake water chemistry have been included in Appendix V. Appendix V includes remarks on the solubility of dolomite; the results of an attempt to predict calcium and magnesium activities in equilibrium with dolomite as a function of temperature and carbonic acid concentration, and graphs showing relationships between hydrogen ion and carbonate ion activities and concentrations of carbonic acid.

In the preceding discussion of the solution of dolomite, emphasis was placed not on the complex problem posed by the solution of dolomite by rain and snow meltwater, but on the understanding of the course of solution of dolomite under laboratory conditions in terms of the activities of the aqueous ions in equilibrium with dolomite. This treatment makes it possible in the following section to consider the compositions of lakes in the drainage basin as end-products of the local weathering of dolomite by showing graphically how water compositions are related to equilibrium with respect to dolomite and also with respect to calcite. The problem of the many possible variations in possible equilibria with respect to carbonate minerals in the Denault formation, and the associated problem of the kinetics of the solution of dolomite remain outside the scope of this study, but are nevertheless important in the understanding of the relationships between rock weathering and water composition.

5. Ion Activity Product Diagrams for Dolomite and Calcite Equilibria in Lake Waters.

Ion activity product diagrams (abbreviated IAP) provide a method of relating analysed water compositions to chemical equilibria attained by water in contact with pure minerals under controlled experimental conditions (Figs. 7 - 10). Examples of the application of IAP diagrams to lake waters with compositions determined by equilibria with respect to carbonate minerals are to be found in Kramer's model of Lake Erie (Kramer, 1968) and in Brunskill's study of calcite precipitation in Fayetteville Green Lake (Brunskill, 1969).

Ion activity products for dolomite and for calcite refer to the ion products which form the numerators in the equilibrium expressions for the reaction of water with dolomite (equation 1) and with calcite (equation 6); i.e.

$$a_{Ca^{+2}} \cdot a_{Mg^{+2}} \cdot a^2_{CO_3^{-2}} \quad \text{- IAP dolomite}$$

and

$$a_{Ca^{+2}} \cdot a_{CO_3^{-2}} \quad \text{- IAP calcite}$$

Analysed concentrations and calculated activity coefficients are substituted for each ion activity to obtain an expression for the degree of equilibration of the water sample with respect to dolomite or calcite. An index of relative saturation can then be obtained by dividing the appropriate IAP by the equilibrium constant (i.e. 'solubility product') for the mineral at the temperature and pressure of the sample. An illustration of the calculation of an ion activity product is given in Appendix V, section B.

Calculations of IAP's are no more accurate than the original analyses or estimates of individual ions present in the water. The main source of error in calculating IAP's for dolomite and calcite lies in estimating $a_{CO_3^{-2}}$ from pH (i.e. - log $a_{H^{+1}}$) and the bicarbonate ion concentration ($^{m}HCO_3^{-1}$) obtained from the titration for total alkalinity. The errors result from inaccurate identification of the endpoint in the alkalinity titration, and, more important, the possibility of changes in pH (over a range of 0.2 pH unit) resulting from changes in P_{CO_2} between sample collection and analysis. Within practical limits dictated by field conditions, these errors can be reduced by reading pH and titrating for alkalinity at the time of sampling. Individual ion activity products were calculated to the second decimal place in the exponent, and then rounded to one decimal place for the distribution diagrams (Figs. 8,10).

Ion activity product diagrams for the products $a_{Ca^{+2}} \cdot a_{Mg^{+2}} \cdot a^2_{CO_3^{-2}}$ (dolomite) and $a_{Ca^{+2}} \cdot a_{CO_3^{-2}}$ (calcite) have been drawn for the lakes in Knob Lake drainage basin (Figs. 7 and 9). The distribution of IAP's for individual lakes is shown in Figs. 8a, 8b, 10a, 10b. The analyses used represent surface waters in the centres of the lakes wherever that is possible. Constant temperatures of 2.5°C for winter samples and 10°C for summer samples have been used to simplify the diagrams. The data used in the calculations are given in Appendix V, section D. Lines have been drawn showing the equilibrium constant for calcite and for the range of possible equilibrium constants for dolomite. Lines are also included to connect winter and summer analyses for indivdual lakes and to show the sequence of drainage between lakes. The boundaries describing the fields of shale, dolomite and mixed shale-dolomite waters are also shown. Three lakes appear in the summer column (Dale, Thorn and Lier) which were not sampled during the winter survey.

The two IAP diagrams and the associated distribution maps summarise the carbonate chemistry of all the lake waters described in this study. Figs. 7, 8a and 8b show that in summer (T = 10°C), those lakes lying directly on dolomite are close to equilibrium or somewhat undersaturated with respect to ideal dolomite, given Keq:dolomite between 10^{-16} and 10^{-18}. In winter (T = 2.5°C) the same lake waters are more undersaturated with respect to dolomite, with IAP's about one order of magnitude smaller. If the summer IAP's are extrapolated to 20°C, near the maximum temperature that can be expected for surface waters in the drainage basin, most lake waters lying on dolomite approach equilibrium with dolomite if there is a small (about 0.3 pH unit) further increase in pH induced by photosynthesis. This means that however ions are transported into lake basins, the changes that

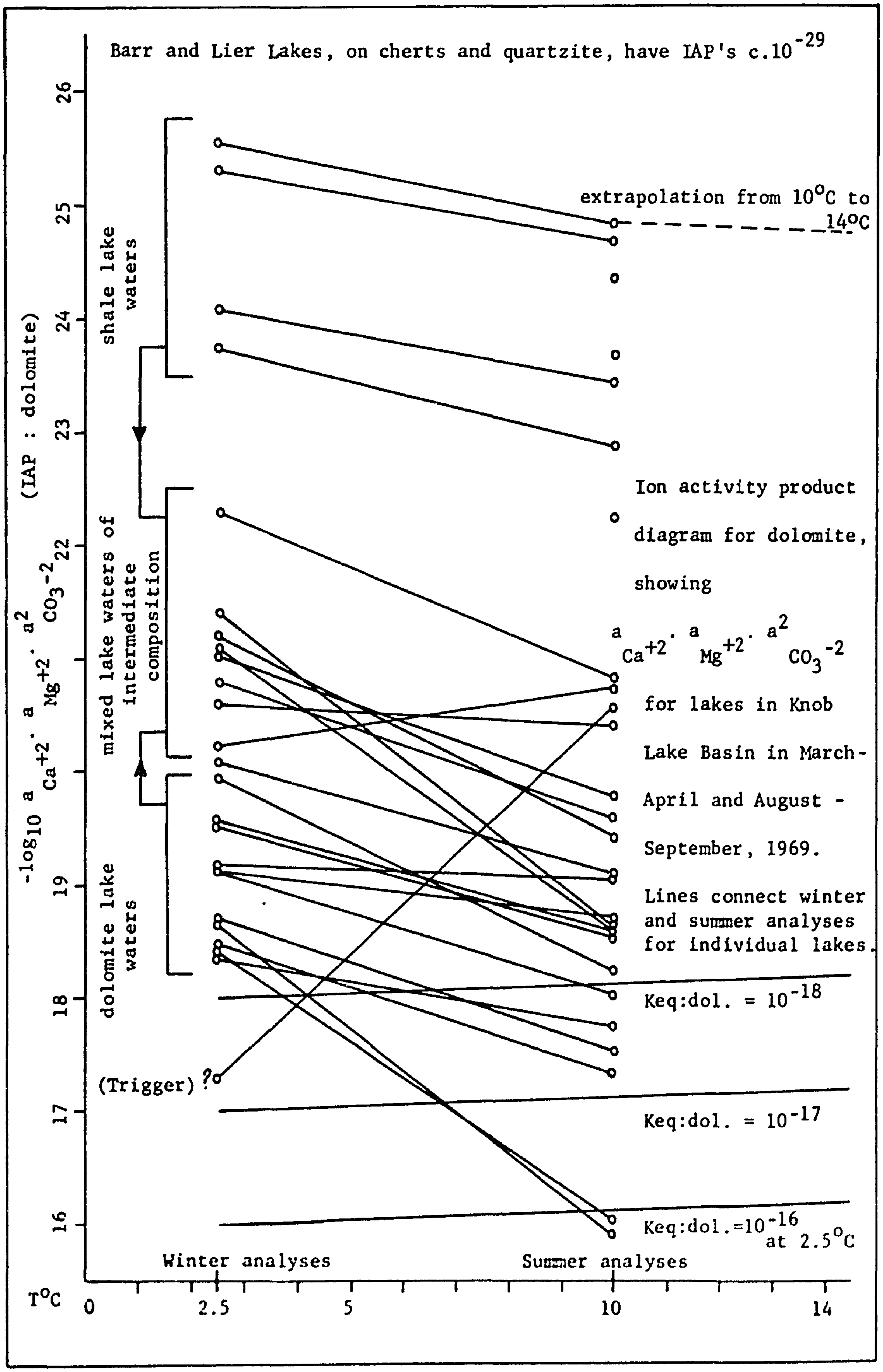
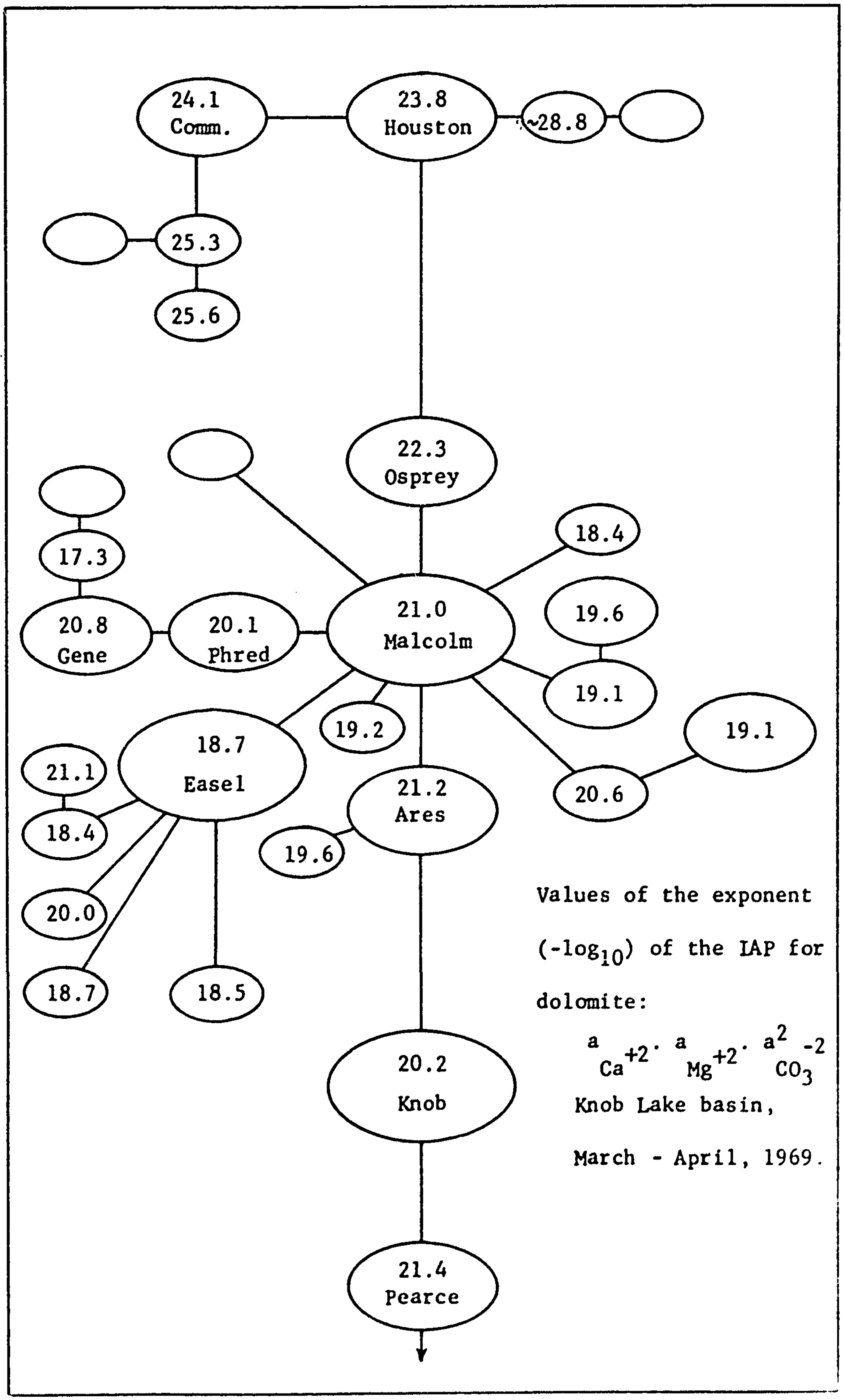


Fig. 7 Ion Activity Product (IAP) diagram for dolomite, Knob Lake basin, 1969.



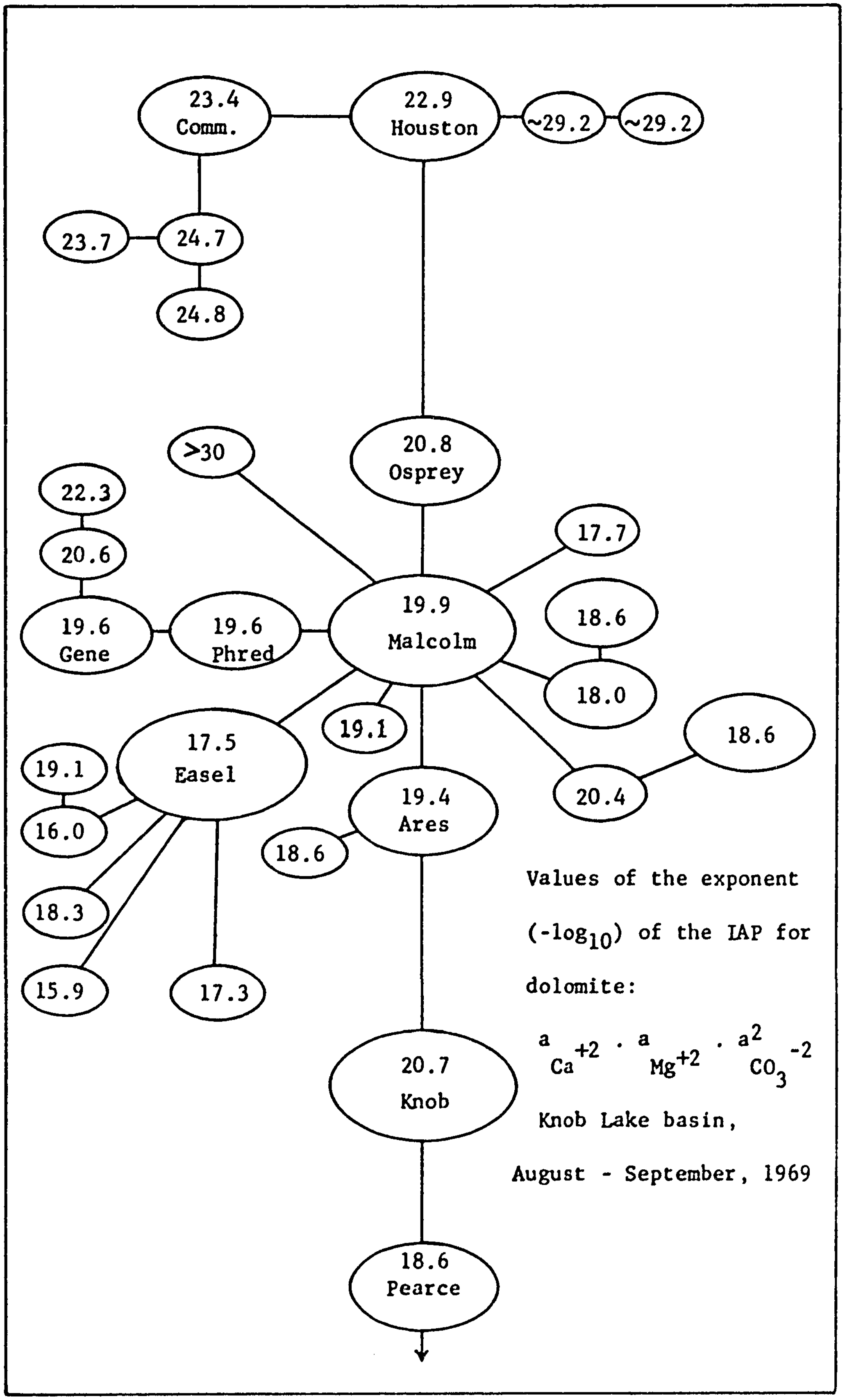
Values of the exponent ($-\log_{10}$) of the IAP for dolomite:

$a_{Ca^{+2}} \cdot a_{Mg^{+2}} \cdot a^2_{CO_3^{-2}}$

Knob Lake basin,

March - April, 1969.

Fig. 8 a IAP's for dolomite for individual lakes - winter, 1969.



Values of the exponent ($-\log_{10}$) of the IAP for dolomite:

$$a_{Ca^{+2}} \cdot a_{Mg^{+2}} \cdot a^2_{CO_3^{-2}}$$

Knob Lake basin,

August - September, 1969

Fig. 8 b IAP's for dolomite for individual lakes - summer, 1969.

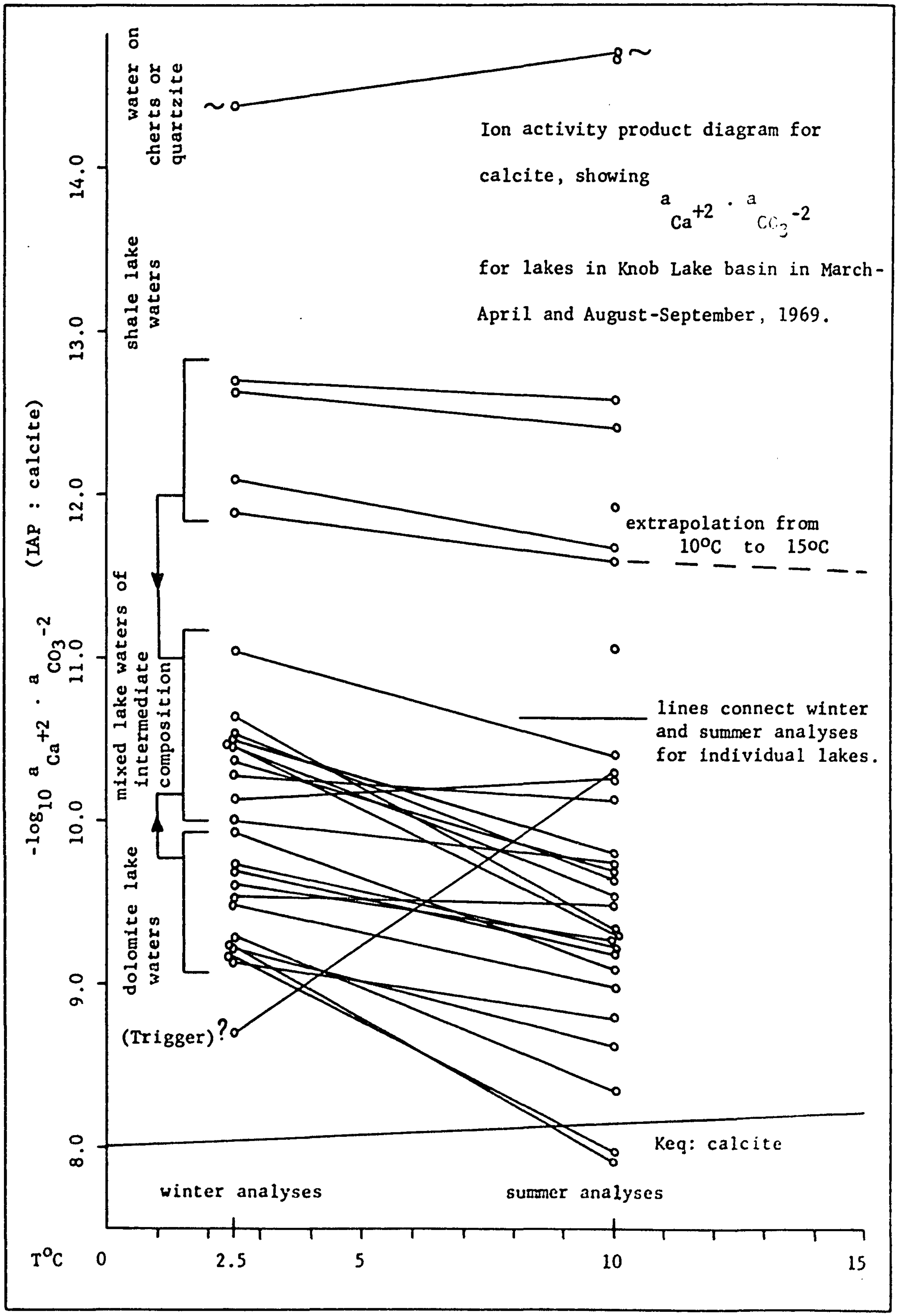
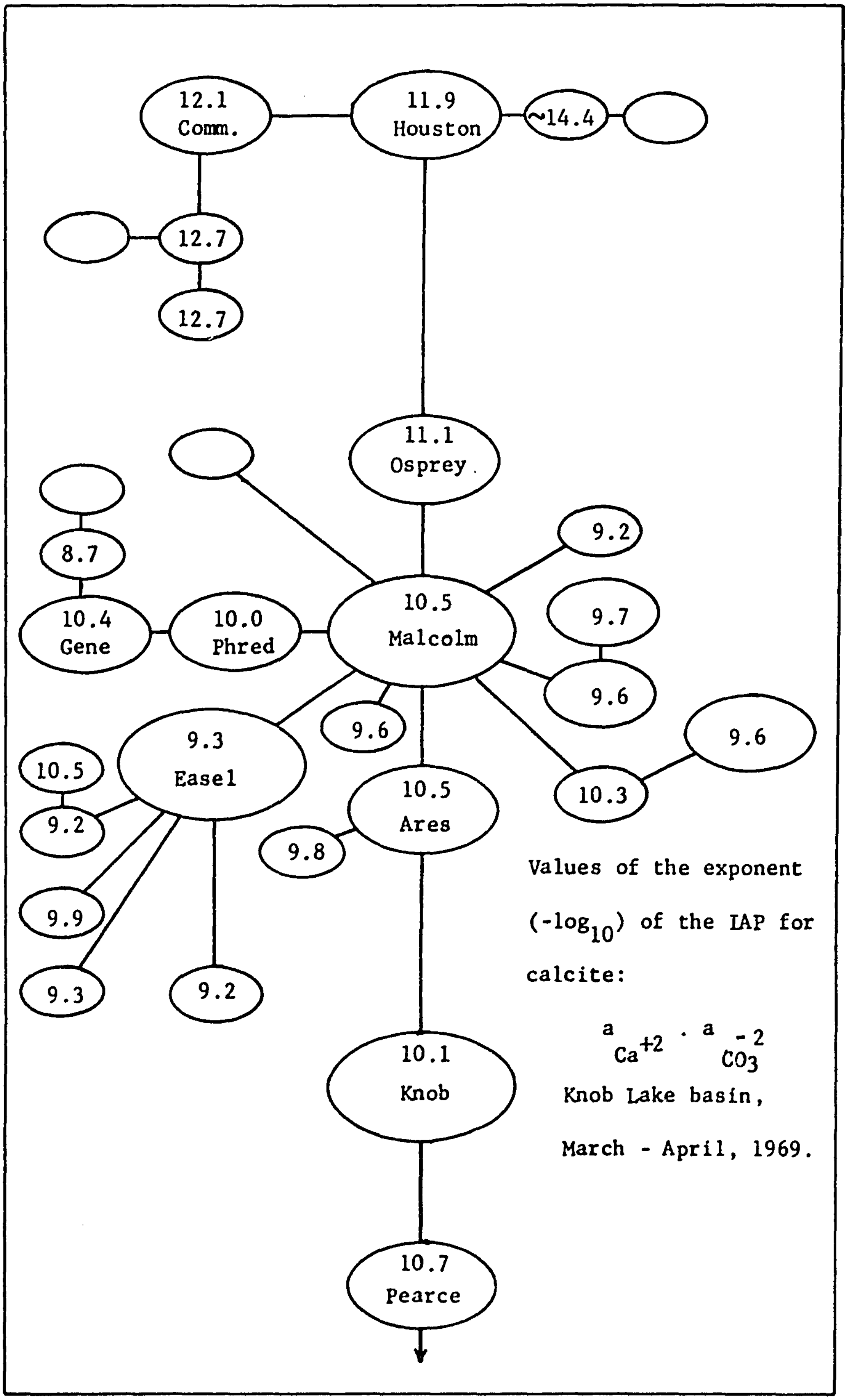


Fig. 9 Ion Activity Product (IAP) diagram for calcite, Knob Lake basin, 1969.



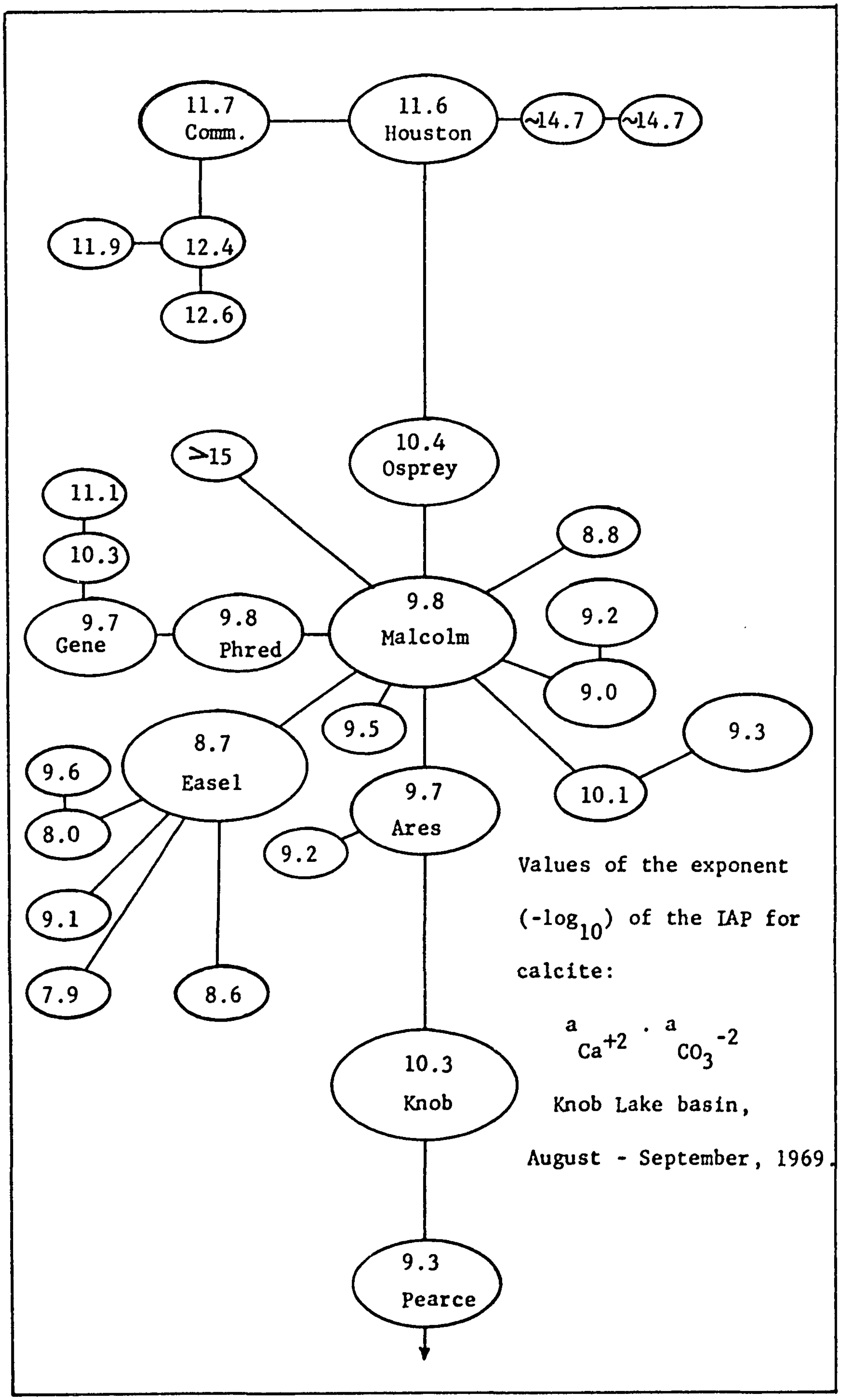
Values of the exponent $(-\log_{10})$ of the IAP for calcite:

$$a_{Ca^{+2}} \cdot a_{CO_3^{-2}}$$

Knob Lake basin,

March - April, 1969.

Fig. 10 a IAP's for calcite for individual lakes - winter, 1969.



Values of the exponent ($-\log_{10}$) of the IAP for calcite:

$a_{Ca^{+2}} \cdot a_{CO_3^{-2}}$

Knob Lake basin,

August - September, 1969.

Fig. 10 b IAP's for calcite for individual lakes - summer, 1969.

occur within lakes (equilibration with atmospheric CO_2; photosynthetic removal of CO_2) are such that surface waters on dolomite are brought into a state of near equilibrium with dolomite in summer from an unsaturated state in winter. This may also mean that, within lake basins, active solution of dolomite may take place in winter, but is less likely in summer.

The IAP diagrams for calcite (Figs. 9, 10a, 10b) describe a situation very similar to that for dolomite. In winter, lakes on dolomite are markedly undersaturated with respect to calcite. In summer, two lakes, Panhandle and Williams, were near equilibrium with respect to calcite, and a number of other surface water samples were sufficiently close to be brought near equilibrium by a further change in temperature of 10°C. From this it can be concluded that under favourable conditions (calm weather, warm surface water, active photosynthesis) the surface waters of lakes on dolomite may become saturated with respect to calcite, and it is possible that some precipitation of calcite would then take place. If this were so, the ratio of magnesium to calcium would change locally in proportion to the amount of calcite formed.

The diagrams also illustrate the markedly different character of water from dolomite, shale and from both dolomite and shale. This is represented in both diagrams by a convergence of IAP values in a central range which is characteristic for the lakes in the sequence Malcolm - Ares - Knob. This central range is in the order of 10^{-20} for dolomite and 10^{-10} for calcite. Lake waters from shales have IAP's about two orders of magnitude smaller than this central range, while lake waters from dolomite have IAP's about two orders of magnitude larger. Seasonal changes in composition in most lakes appear to involve an increase in the IAP of one order of magnitude between winter and summer. The one lake which does not fit this pattern is Trigger Lake. The shallow water under the ice of this lake had high concentrations of bicarbonate and sulfate, presumably an effect of concentration by freezing, and was near equilibrium with both dolomite and calcite in winter, although this lake lies on shale. By summer, the lake had reverted to a composition typical of other shale lakes in the basin. To summarise, IAP values for lake waters provide a concise description of each lake's carbonate chemistry, and a suitable method for relating waters of contrasting compositions from different origins and describing their mixing.

Ion activity products can also be used to describe variations in composition within lakes, both vertical and horizontal. This can be illustrated using the IAP's for surface water samples on Malcolm, Easel and Knob Lakes (Appendix V, section D). In Easel and Knob Lakes, IAP values decline towards the lake outlet, while in Malcolm Lake IAP's increase towards the outlet as shale water mixes with dolomite water. The nature of vertical changes in IAP's for dolomite and calcite is illustrated for Cowan Lake by five vertical profiles from the centre of the lake (Fig. 21). These profiles show that in this case there was no consistent change with depth, except for the June 27 survey. This is partly because changes in temperature in a thermally stratified lake tend to balance changes in composition with depth. Generally, the highest value is found at the lake bottom, and is a reflection of the release of CO_2 in respiration.

The calculation of IAP's was extended to include the partial pressure of carbon dioxide in equilibrium with the water samples. These P_{CO_2} values are presented in Fig. 11. Again, waters of contrasting lithological origins can be identified on this diagram, presumably because they have primary productivities in different ranges. In winter, the larger lakes and the small lakes on shale have equilibrium P_{CO_2} values in the range $10^{-2.5}$ to $10^{-3.0}$ atm., while small lakes on dolomite have values near $10^{-2.0}$ atm. This is a measure of the greater release of CO_2 in biological respiration in lakes on dolomite. In summer, most lake waters appear to have equilibrium P_{CO_2} values between $10^{-3.0}$ and $10^{-3.2}$ atm., although there are some conspicuous departures both above and below this range. These values are somewhat higher than would be expected for water in equilibrium with the atmosphere ($P_{CO_2} = 10^{-3.5}$atm.). This deviation may result from plankton respiration at the time of sampling, or it may reflect consistent error in the determination of pH and total alkalinity.

6. Distribution of Bicarbonate, Calcium and Magnesium and pH in Lake Waters of the Knob Lake Drainage Basin.

An average concentration (mg/l) and a total quantity (metric tons) of bicarbonate, calcium and magnesium in each of the lakes of the drainage basin have been estimated for the times of the late winter and late summer lake surveys in 1969. An average value of the pH of surface water has also been estimated. These figures are presented in Table 10, which also shows the differences between the winter and summer

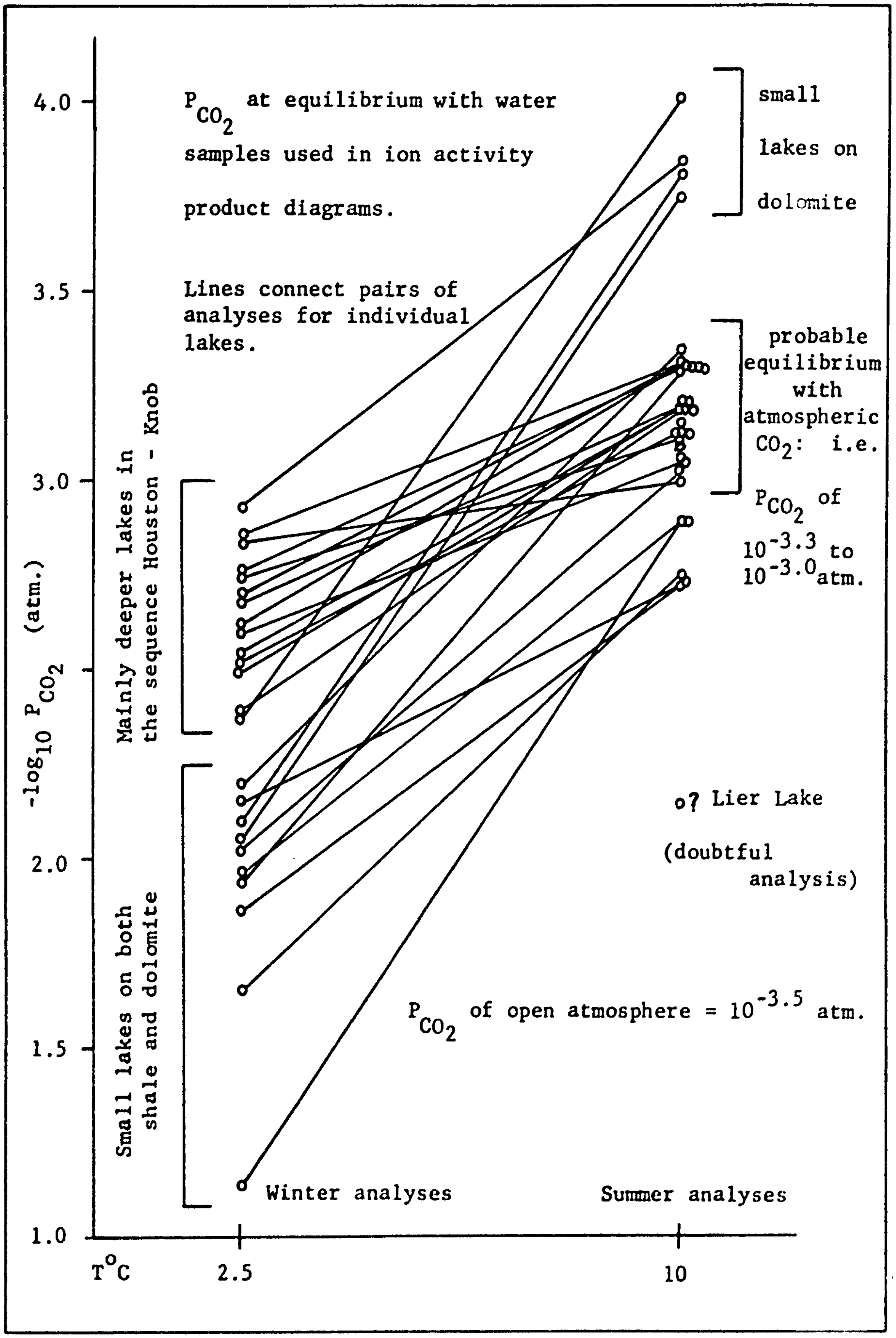


Fig. 11 P_{CO_2} at equilibrium with water samples used in IAP diagrams.

surveys. Most analyses used for these tables represent open water in the central parts of lakes, and an arithmetic mean of the available analyses for each lake (disregarding high values obtained near bottom sediments) is assumed to be a reasonable estimate of the concentration for the lake as a whole. Total quantities are based on average concentrations.

Distributions of HCO_3^{-1}, Ca^{+2} and Mg^{+2} concentrations in the lakes are illustrated in a series of chloropleth maps for the drainage basin (Figs. 12 - 14 and Table 10) for each constituent in winter and summer of 1969. To make each of the maps directly comparable, concentrations of each constituent are expressed in terms of equivalents x 10^{-4}. A similar pair of maps has also been prepared to show the pH of surface waters in the lakes (Fig. 15). Also shown on the maps are the distribution of the Denault dolomite formation and the location of the Schefferville townsite.

Each of the distribution maps shows that the highest ion concentrations are associated with the Denault dolomite, and that the lowest concentrations are associated with lakes on shale and quartzite or chert at the southern end of the basin. Water draining from the shales and from the Denault formation meets in the sequence of lakes from Osprey to Knob, and these lakes have ionic concentrations which reflect the proportion of shale and dolomite in the lake catchment (Chapter IV, section 9). In this respect the pattern of ion concentrations closely follows that described by the ion activity product diagrams, although it does not reflect to the same extent processes operating within lakes that are revealed by ion activity products. Instead, these distribution

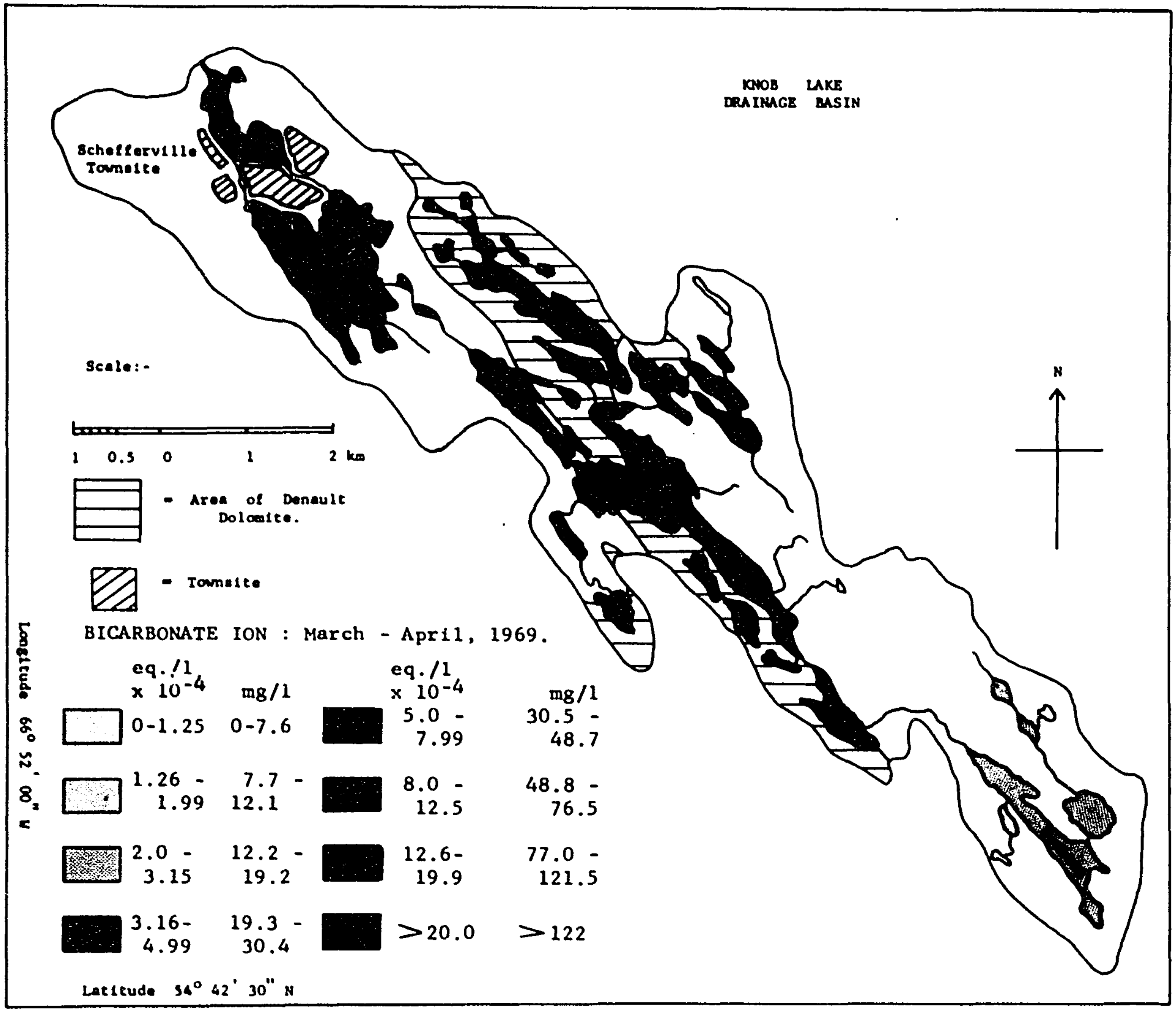


Fig. 12 a Distribution of bicarbonate in lake waters - winter, 1969.

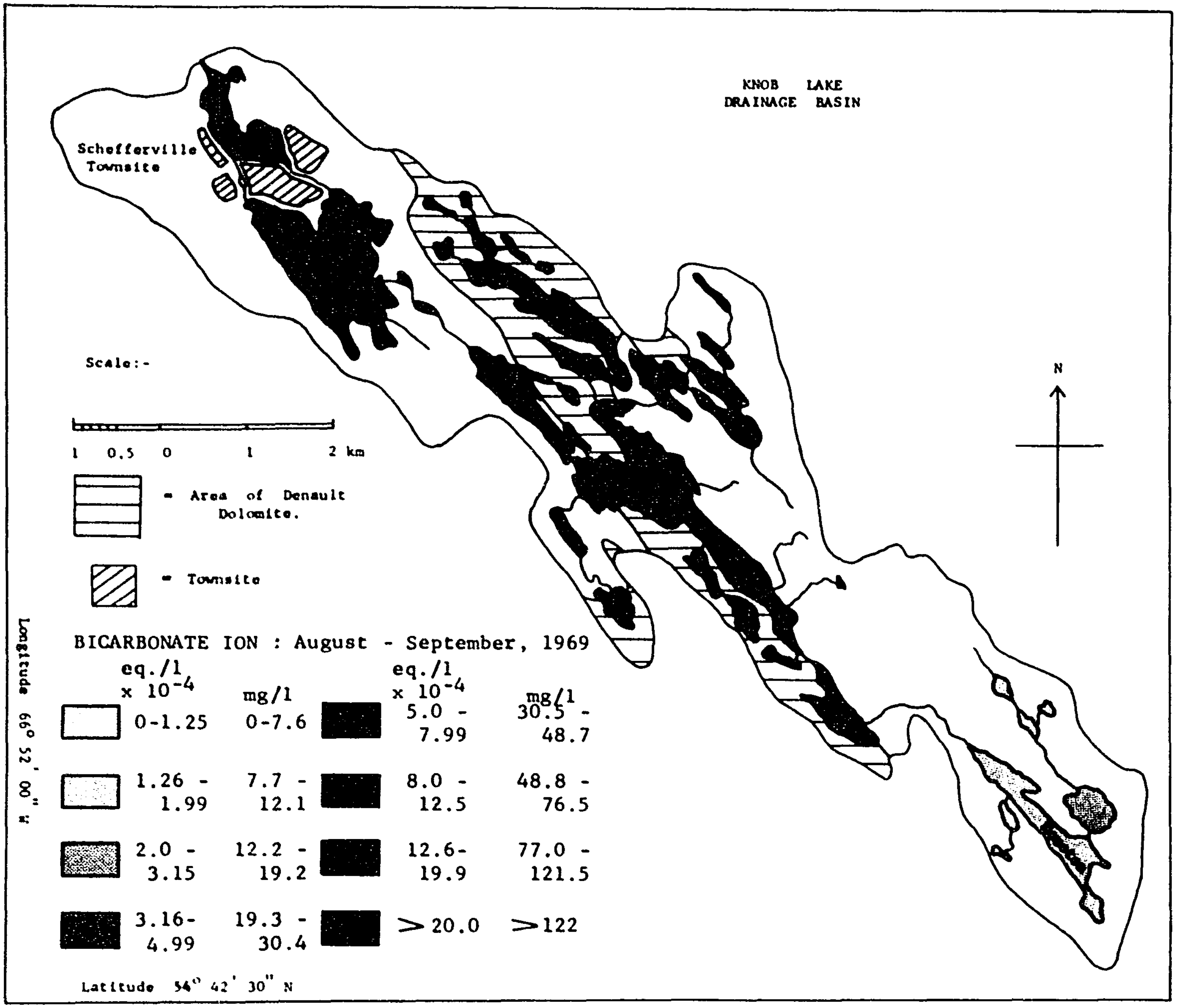


Fig. 12 b Distribution of bicarbonate in lake waters - summer, 1969.

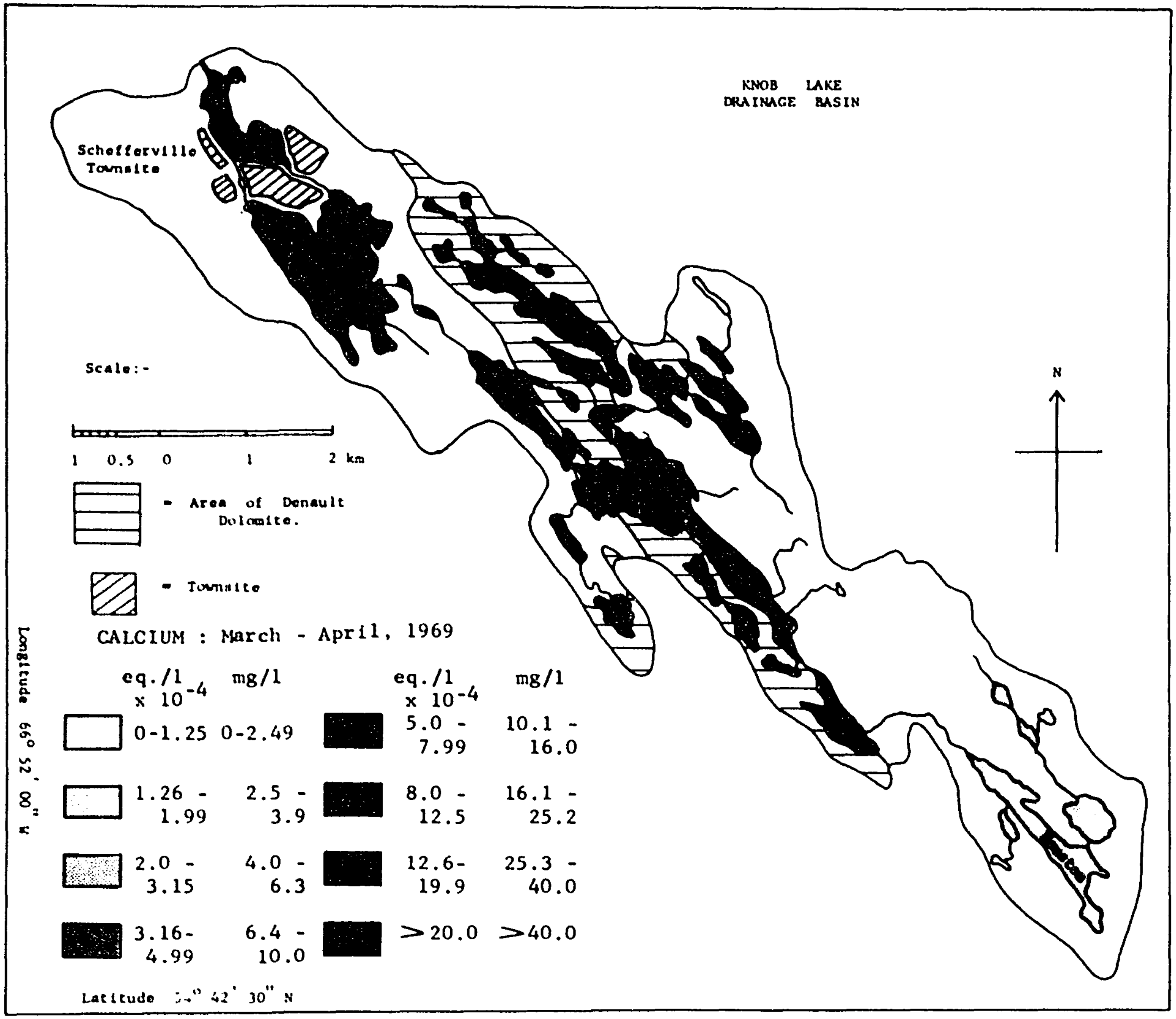


Fig. 13 a Distribution of calcium in lake waters - winter, 1969.

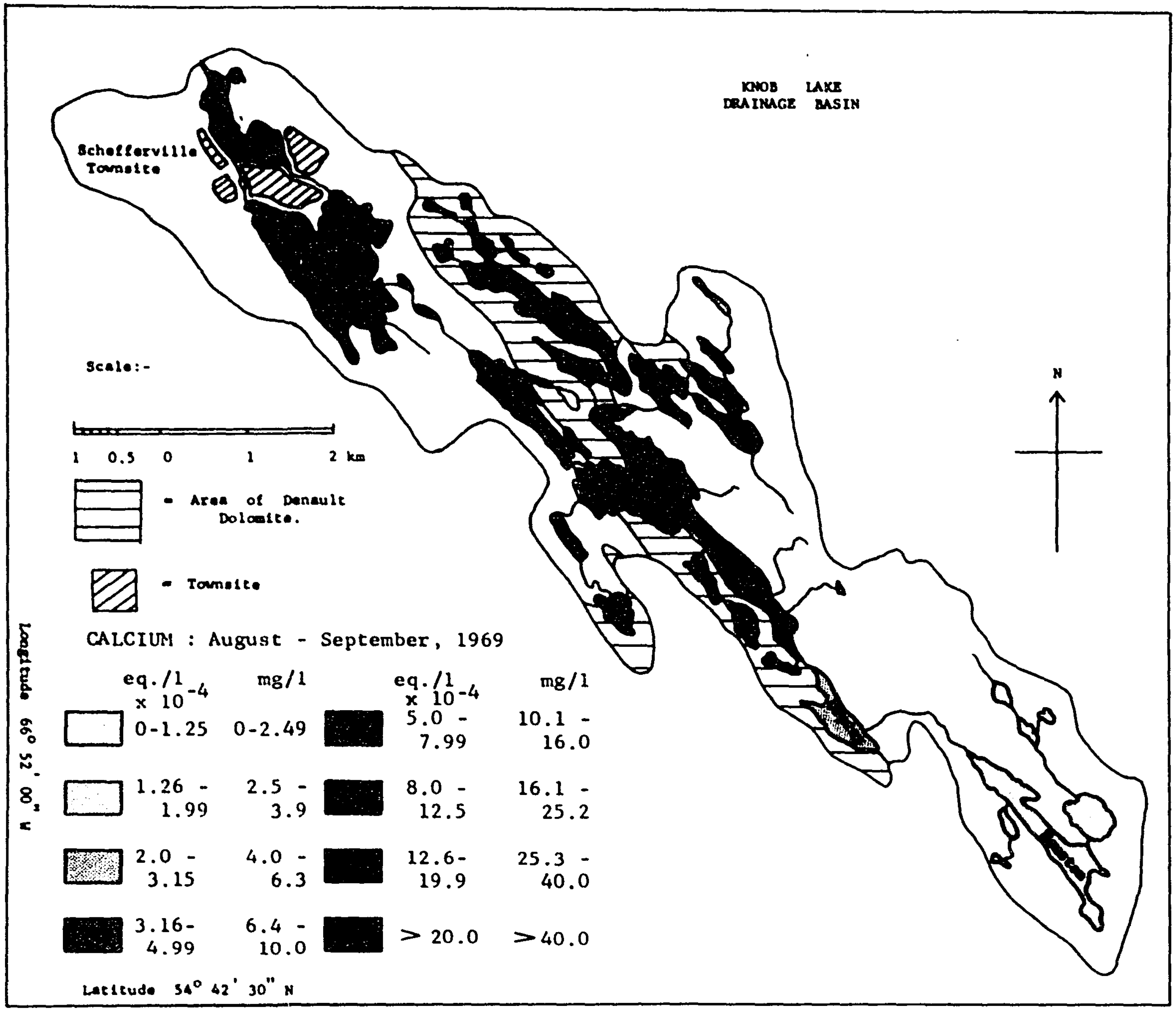


Fig. 13 b Distribution of calcium in lake waters - summer, 1969.

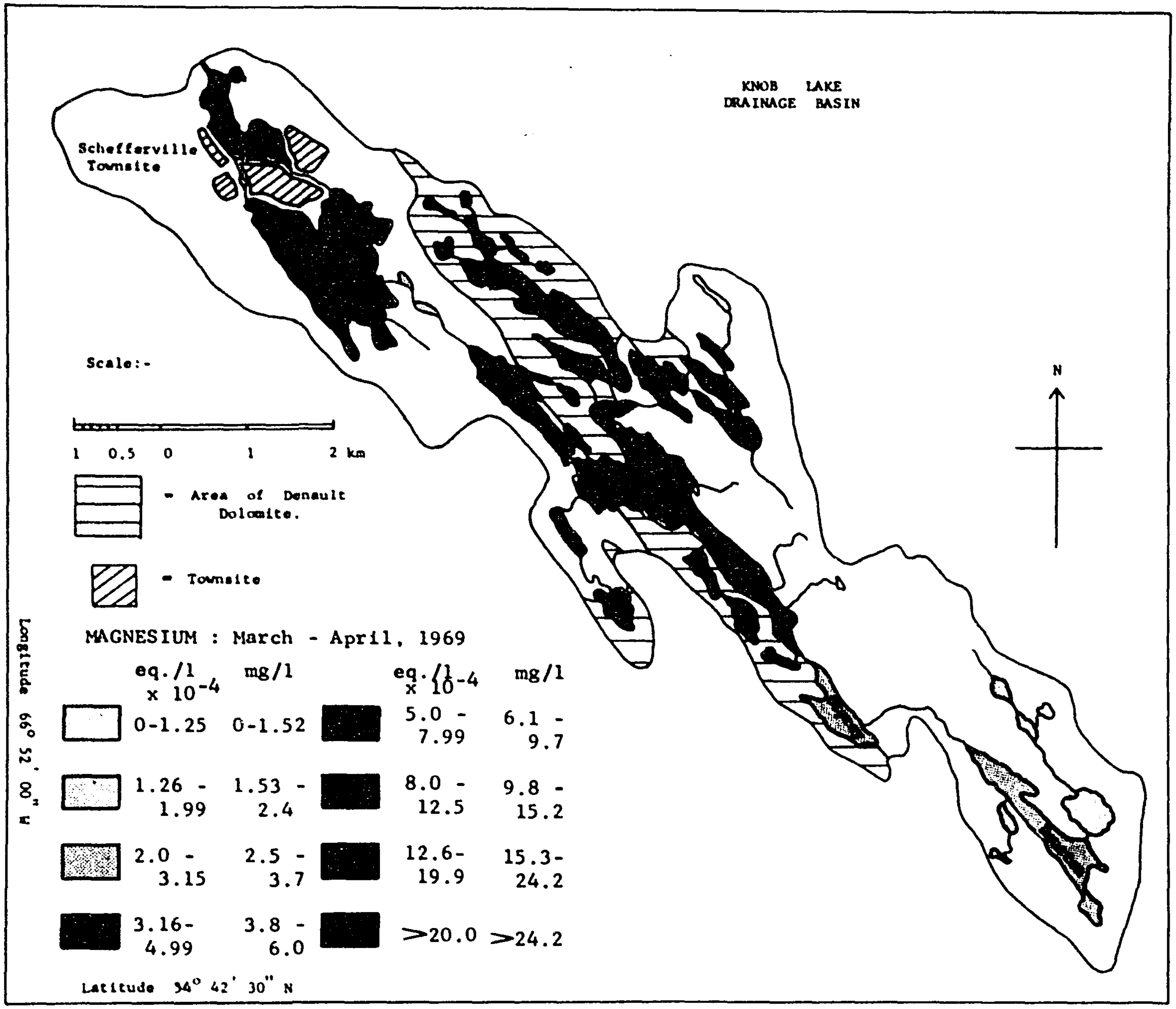


Fig. 14 a Distribution of magnesium in lake waters - winter, 1969.

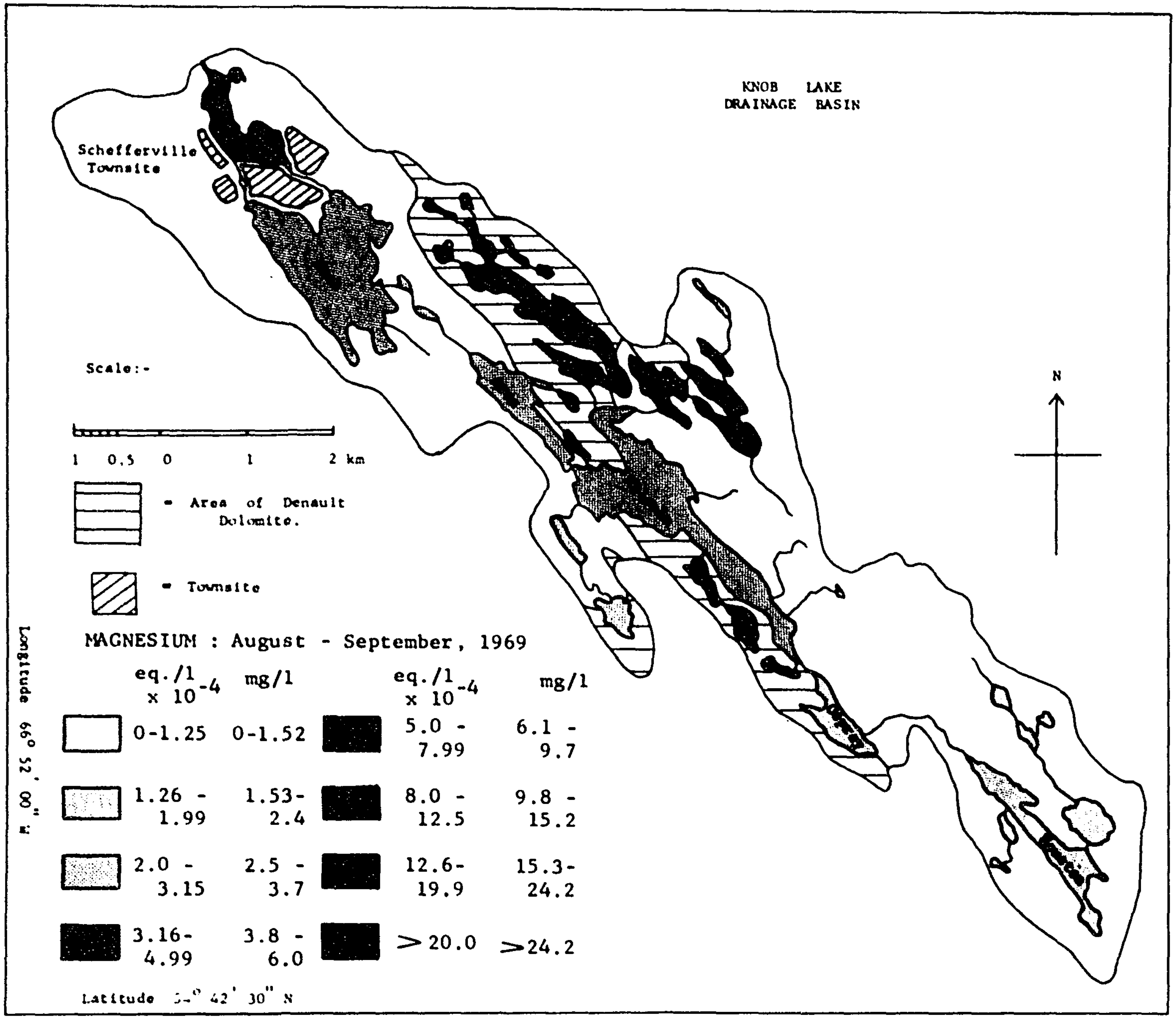


Fig. 14 b Distribution of magnesium in lake waters - summer, 1969.

TABLE 10

Bicarbonate, calcium and magnesium concentrations in lake waters and values of pH of surface waters.

		1. Bicarbonate					2. Calcium				
	Volume ($m^3 x 10^6$)	mean (mg/l)	total ($kg x 10^3$)	Mean (mg/l)	total ($kg x 10^3$)	Seasonal change ($kg x 10^3$)	mean (mg/l)	total ($kg x 10^3$)	mean (mg/l)	total ($kg x 10^3$)	Seasonal change ($kg x 10^3$)
Communications	0.820	14.5	12.0	10.8	8.9	- 3.1	2.0	1.65	1.60	1.31	- 0.34
Houston	2.164	15.0	32.4	11.4	24.6	- 7.8	2.4	5.20	1.4	2.95	- 2.25
Osprey	1.079	36.2	39.0	24.1	26.0	-11.0	6.8	7.35	4.4	4.76	- 2.59
Malcolm	10.401	47.7	497.0	39.1	386	-111	8.9	3.45	7.5	78.0	- 5.5
Phred	0.820	50.4	41.3	42.8	35.2	- 6.1	9.2	7.56	9.2	7.57	- 0.0
Gene	0.760	48.2	36.6	39.4	30.0	- 6.6	9.8	7.46	9.2	7.02	- 0.44
Easel	5.769	90.0	518.0	85.6	494	-24.0	16.6	96.0	16.4	94.4	- 1.6
Ares	1.370	45.0	61.6	38.0	52.0	- 9.6	7.4	10.15	7.5	10.28	0.13
Knob	10.826	39.2	424.0	34.3	372	-53.0	7.4	80.0	7.2	77.7	- 2.30
Pearce	1.224	57.5	70.2	31.5	38.6	-31.6	10.3	12.63	7.9	9.71	- 2.92
North	0.370	78.2	28.9	68.8	25.4	- 3.5	13.7	5.05	9.9	4.55	- 0.50
Middle	0.470	62.0	29.2	56.2	26.4	- 2.8	11.1	5.22	12.3	5.40	0.18
South	0.081	123.0	10.0	84.4	6.8	- 3.2	11.5	1.89	11.5	1.37	- 0.52
Bassett	0.125	81.8	10.2	38.6	4.8	- 5.4	23.3	1.61	16.9	0.91	- 0.70
Adams	0.603	70.8	42.7	66.4	40.0	- 2.7	12.9	7.01	7.2	7.30	0.29
Cowan	0.189	114.8	21.7	95.0	17.9	- 3.8	19.9	3.77	18.0	3.39	- 0.38
Panhandle	0.050	132.4	6.6	91.2	4.5	- 2.1	23.7	1.19	16.5	0.83	- 0.36
Findlay	0.045	86.0	3.9	59.2	2.7	- 1.2	15.5	0.70	11.7	0.53	- 0.17
Williams	0.020	182.4	3.7	101.8	2.1	- 1.6	30.9	0.62	19.9	0.40	- 0.22
Francois	0.019	72.6	1.4	46.0	0.9	- 0.5	11.2	0.21	7.2	0.14	- 0.07
Ives	0.084	86.0	7.2	59.2	5.0	- 2.2	15.3	1.29	11.7	0.98	- 0.31
Mattox	0.086	c310	?	60.4	5.2	?	c54	?	12.5	1.07	
Gray	0.133	10.8	1.4	8.5	1.1	- 0.3	1.6	0.21	0.4	0.05	- 0.16
Hardy	0.080	13.3	1.1	6.1	0.4	- 0.7	1.6	0.13	0.6	0.05	- 0.08
Thorn	0.035	?	?	12.1	0.5	?	?	?	1.6	0.05	
Barr	0.088	7.2	0.1	0.9	0.1	0.0	0.1	0.04	0.1	?	
Lier	0.034	?	?	1.8	0.1	?	?	?	0.1	?	
Trigger	0.062	c350	?	37.4	2.3	?	c78	?	7.2	0.45	
Dale	0.030	?	?	25.0	0.8	?	?	?	5.8	0.17	
Doris	0.006	?	?	0.0	?	?	?	?	0.8	0.01	

TABLE 10 Magnesium concentrations in lake waters and values of pH for lake surface waters. (Continued)

	Magnesium						pH		
		March-April		Aug. - Sept.		Seasonal			
Lake	Volume ($m^3 x 10^6$)	mean (mg/l)	total ($kg x 10^3$)	Mean (mg/l)	total ($kg x 10^3$)	change ($kg x 10^3$)	March-April	Aug. - Sept.	Difference (positive)
Communications	0.820	1.3	1.03	1.0	0.80	-0.23	6.6	7.0	0.4
Houston	2.164	1.8	3.80	2.0	4.31	0.51	6.8	7.1	0.3
Osprey	1.079	3.4	3.66	2.2	2.36	-1.07	6.9	7.5	0.6
Malcolm	10.401	4.7	48.9	3.6	37.9	-11.0	7.1	7.7	0.6
Phred	0.820	5.9	4.85	5.4	4.39	-0.46	7.4	7.6	0.2
Gene	0.760	5.8	4.43	4.6	3.50	-0.93	7.3	7.7	0.4
Easel	5.769	8.5	48.9	8.0	46.1	-2.80	7.6	8.2	0.6
Ares	1.370	4.3	5.89	3.5	4.8	-1.09	7.1	7.8	0.7
Knob	10.826	3.9	42.6	2.8	29.8	-12.8	7.3	7.6	0.3
Pearce	1.224	5.5	6.77	4.6	5.69	-1.08	6.8	8.1	1.3
North	0.370	8.0	2.97	6.6	2.42	-0.55	7.5	8.1	0.6
Middle	0.470	5.6	2.63	4.5	2.28	-0.35	7.6	8.0	0.4
South	0.081	12.2	0.98	7.3	0.59	-0.39	7.5	8.1	0.6
Bassett	0.125	7.8	0.97	3.2	0.40	-0.57	6.8	7.4	0.6
Adams	0.603	8.8	5.28	3.4	3.68	-1.60	7.6	7.8	0.2
Cowan	0.189	10.5	1.99	9.0	1.70	-0.29	7.6	8.2	0.6
Panhandle	0.050	10.9	0.55	8.4	0.42	-0.13	7.4	8.9	1.5
Findlay	0.045	7.9	0.36	6.1	0.27	-0.09	7.1	8.1	1.0
Williams	0.020	17.3	0.35	9.9	0.20	-0.15	7.2	8.7	1.5
François	0.019	5.6	0.11	4.4	0.08	-0.03	6.7	7.9	1.2
Ives	0.084	7.8	0.66	5.4	0.45	-0.21	7.2	7.9	0.5
Mattox	0.086	28	0.1	6.3	0.54		6.5	7.6	1.1
Gray	0.133	0.7	0.1	1.2	0.16	0.06	6.1	6.6	0.5
Hardy	0.080	1.0	0.08	0.9	0.07	-0.01	6.1	6.8	0.7
Thorn	0.035			1.5	0.05			6.7	
Barr	0.088	0.1	0.02	0.2	0.02	0.0	5.4	5.8	0.4
Lier	0.034			0.2	0.01			5.4	
Trigger	0.062			5.1	0.32		7.1	7.3	0.2
Dale	0.030			2.8	0.08			7.2	
Doris	0.006			1.2	0.01			4.2	

maps emphasise the quantities of solutes in transport at different points in the drainage network of the basin.

The distribution maps, taken in conjunction with Table 10, also show that ionic concentrations in summer are without exception lower than in late winter. This is generally a consequence of the marked reduction in the residence time of lake water during the summer, compared with late winter. Extreme changes in ionic concentration occurred in Trigger, Mattox and Bassett Lakes. In these cases, the change in composition results not so much from changes in residence time but from the large volumes of ice and bottom sediments in relation to lake water, which may be reduced to a layer a few tens of centimetres deep sandwiched between ice and mud. Taking the basin as a whole, the relative change in ion concentration is in the order of -20 to -30 per cent, and appears to be independent of both lake volume (except where mentioned above) and lake basin geology. There are a few exceptions to this statement in cases where the geological control of composition shifts as a result of the seasonal change in residence time. Osprey Lake illustrates this point. This lake lies on dolomite (see also section 7 of this chapter) and in winter, the deeper parts of the lake have a composition characteristic of lake water on dolomite. However, in summer there is a volume of water from shale and quartzite flowing through the lake which is large in relation to the lake volume, as a result of which the lake is markedly more dilute in summer than in winter.

The distribution maps make it possible to identify ranges of ion concentration characteristic for lake waters on the different rock-types in the drainage basin. The analyses available for lake waters on the shales and Sokoman iron formation (cherts and quartzite) at the southern end of the drainage basin give bicarbonate concentrations less than 20 mg/l (less than 2.0 x 10^{-4} eq.l.$^{-1}$) and corresponding concentrations of rather less than 2 mg/l (less than 1.0 x 10^{-4} eq.l.$^{-1}$). Lake waters on shale in the Phred catchment have appreciably higher ion concentrations, partly because the shales contain lenses of carbonate minerals, and partly because Denault dolomite outcrops locally within the catchment. Bicarbonate concentrations here reach 50 mg/l, with equivalent or slightly higher concentrations of calcium and magnesium. Perhaps because the shales here are pyritiferous, the waters contain higher sulfate concentrations, with corresponding additional amounts of calcium and magnesium. Carbonate minerals and sulfides are sufficiently abundant to creat the winter situation in Trigger Lake, when, apparently, the water between the ice and the bottom contained about 350 mg/l HCO_3^{-1} and 240 mg/l SO_4^{-2}.

In contrast with the shales, lake water on dolomite had bicarbonate concentrations in the range 50 - 200 mg/l (8 - 32 x 10^{-4} eq.l.$^{-1}$), and corresponding concentration of calcium from 10 - 20 mg/l and magnesium from 5 - 17 mg/l. The highest concentrations occur on small and shallow lakes near drainage divides (e.g. Panhandle, Williams and South) and the lowest in lakes bordering muskeg (notably François). Williams and Francois Lakes are close together and Francois drains into Williams. In view of the fact that other pairs of lakes on dolomite with catchments of similar size and topography have similar ionic compositions (e.g. Middle and North: Cowan and Panhandle), it is of some interest to consider why Williams and François are unlike. The difference here seems to reflect the lake catchment and lake water residence time. Williams Lake receives drainage from a 54 ha catchment which, although it contains some muskeg, consists predominantly of well-drained dolomite ridges. The water in Williams Lake, which has an average residence time of about 18 days, is in much closer contact with the carbonate mineral source provided by the Denault formation than is Francois Lake. This lake has a smaller catchment (14 ha) which is mainly muskeg and low lying tamarack woodland. Surface water within this catchment has less opportunity to come into contact with the Denault dolomite, and there is an abundance of sphagnum mosses and decomposing organic litter which could be involved in cation exchange reactions which would selectively remove calcium from the water and increase the pH (Ruttner, 1953, p. 224).

It remains now to consider briefly the total amount of carbonate minerals being transported through the basin. Lake water in the drainage basin in late winter contained an estimated 1900 metric tons of bicarbonate, 340 tons of calcium and 188 tons of magnesium in solution. About three-quarters of this quantity was stored in Malcolm, Easel and Knob Lakes. The corresponding totals in late summer are 1600 tons of bicarbonate, 320 tons of calcium and 152 tons of magnesium. The relative decrease in bicarbonate in summer is greater than that of either calcium or magnesium - a reflection of the greater abundance of sulfate (and probably chloride) in lake waters during winter.

If it is assumed that the magnesium is derived primarily from dolomite, the total quantity of dolomite in solution in the lakes of the basin was about 1400 tons in winter and 1150 tons in summer. The amount of dolomite lost from the drainage basin in solution through the outflow of Knob Lake in 1969 was about 600 tons (based on an average value of 3 mg/l Mg^{+2} in Knob Lake). This represents a net yield of 90 tons of dolomite per square kilometre of Denault dolomite in the drainage basin. About 60 per cent of this total (54 tons km^{-2}) was lost between the late winter and late summer sampling periods.

The two maps illustrating the distribution of pH values at the surface of the lakes in the drainage basin (Figs. 15a and 15b) describe a pattern similar to that shown by the ion activity product diagrams and the maps of distributions of ion concentrations. In winter, the highest pH values (over 7.5) occur in the lakes on dolomite in the Easel catchment and bordering Malcolm Lake. The lowest values (less than 7) occur in waters on shales and quartzites at the southern end of the drainage basin. The large lakes which receive water from shale and dolomite (Knob and Malcolm Lakes) have intermediate pH values between 7 and 7.5. Pearce Lake has a value below 7 which reflects the excessive productivity of this polluted lake (see Chapter VI). Similarly, in summer the lakes on dolomite and Pearce Lake have pH values over 8, while lakes on shales have values close to or below pH 7. Knob and Malcolm Lake, with waters of mixed origins, have pH values between 7.5 and 8.0.

The amount of seasonal change in pH within the drainage basin varies in proportion to the buffering capacity of lake waters and rates of plankton photosynthesis. The nature of the association between seasonal change in pH and oxygen depletion in in winter (Fig. 23) suggests that those lakes with high buffering capacities are also those with high rates of primary productivity. Most lakes experience surface changes in pH in the order of 0.5 pH unit, but changes in the small lakes on dolomite may

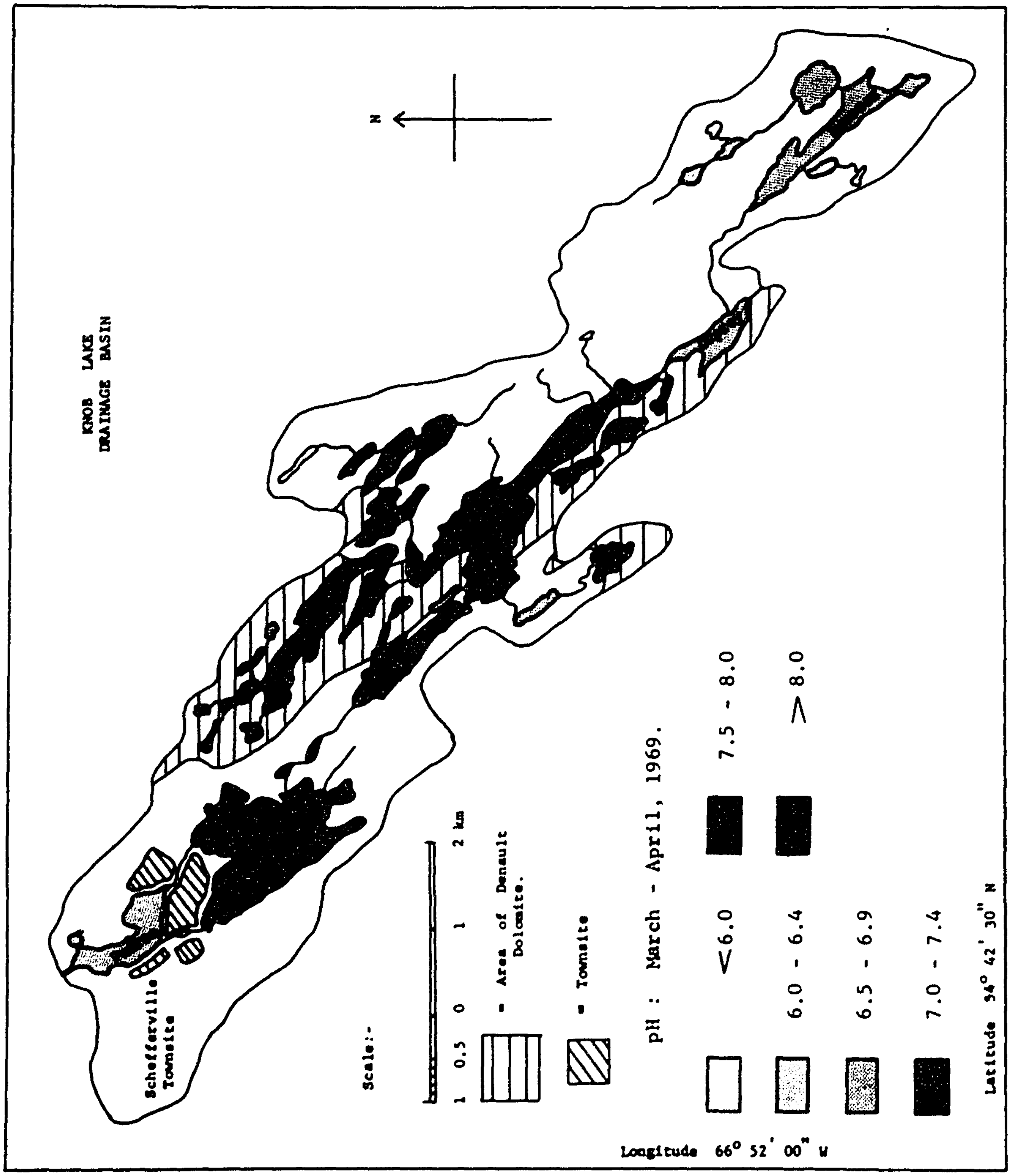


Fig. 15a Values of pH for surface waters of lakes - winter, 1969.

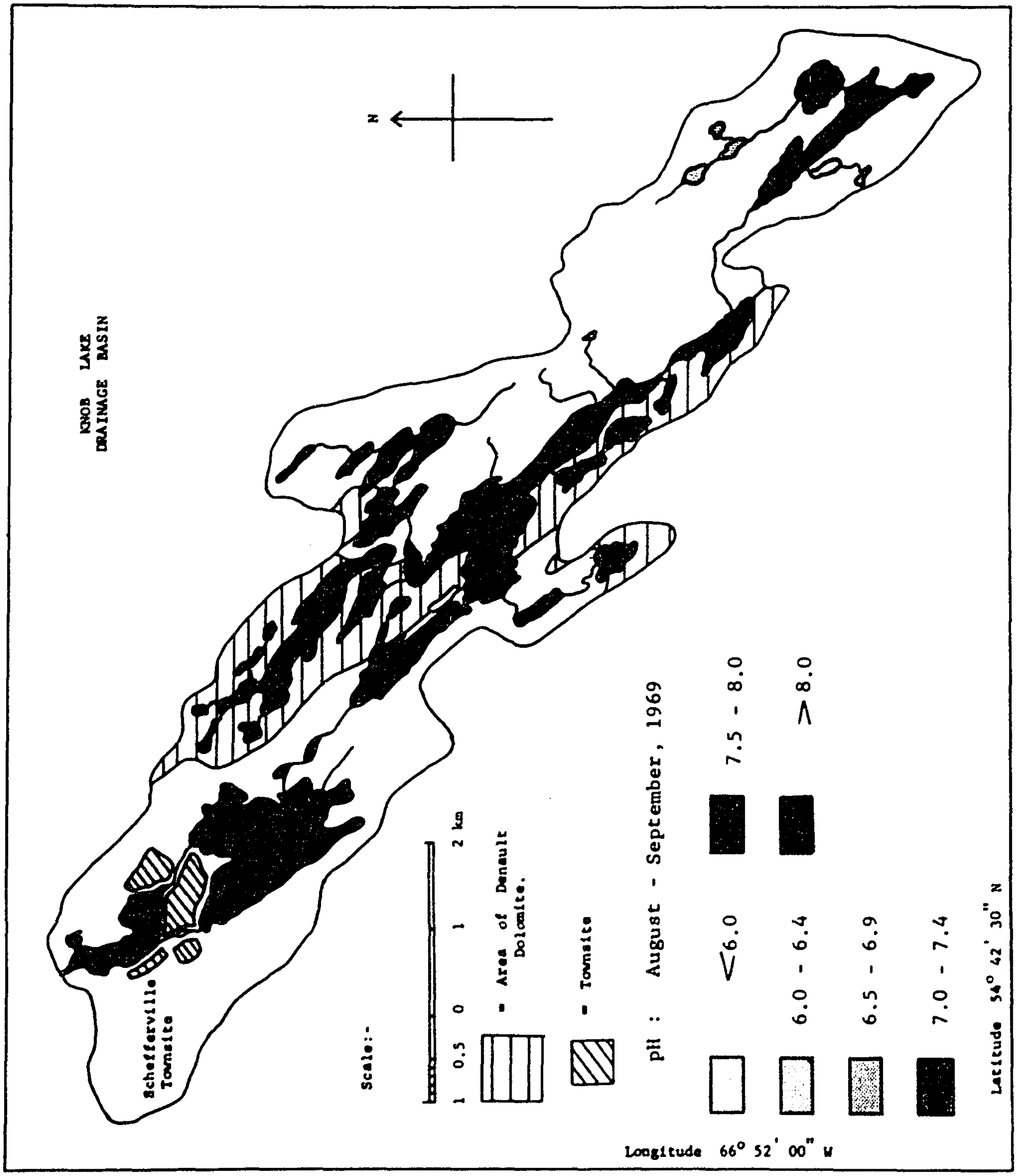


Fig. 15 b Values of pH for surface waters of lakes - summer, 1969.

be as much as 1.5 pH unit. Although the evidence is indirect, dolomite waters appear to be more productive and have high pH values in summer, while shale waters are less productive and have the lowest pH values, both in winter and in summer.

7. The Ratios: $\frac{HCO_3^{-1}}{Ca^{+2}+Mg^{+2}}$; $\frac{HCO_3^{-1}}{Ca^{+2}}$; $\frac{HCO_3^{-1}}{Mg^{+2}}$; $\frac{Mg^{+2}}{Ca^{+2}}$

From the stoichiometry of equations (1) to (6) in the preceding section on the solution of dolomite, it follows that if the solution of dolomite is the main control of ionic composition in lake waters, the ionic ratios set out above for the lakes in this study should fall within certain well defined ranges consistent with the solution of dolomite. Congruent solution of dolomite should yield equivalent ratios of bicarbonate to calcium and magnesium near unity, magnesium-calcium ratios near unity, and bicarbonate-calcium and bicarbonate-magnesium ratios near 2.0. These ratios are ideal, and in the case of lake waters in Knob Lake basin, can be expected to vary because of the irregular composition of the dolomite and the presence of other cations and anions derived from atmospheric precipitation and minerals other than dolomite.

Four diagrams (Figs. 16 - 19) have been drawn to show the equivalent ratios $\frac{HCO_3^{-1}}{Ca^{+2}+Mg^{+2}}$; $\frac{HCO_3^{-1}}{Ca^{+2}}$; $\frac{HCO_3^{-1}}{Mg^{+2}}$ and $\frac{Mg^{+2}}{Ca^{+2}}$ in each of the lakes of the basin. One representative value has been taken for each lake, and where possible from the centre of the lake. Separate symbols are used to indicate winter and summer analyses and lines have been drawn connecting the analyses for individual lakes. These diagrams

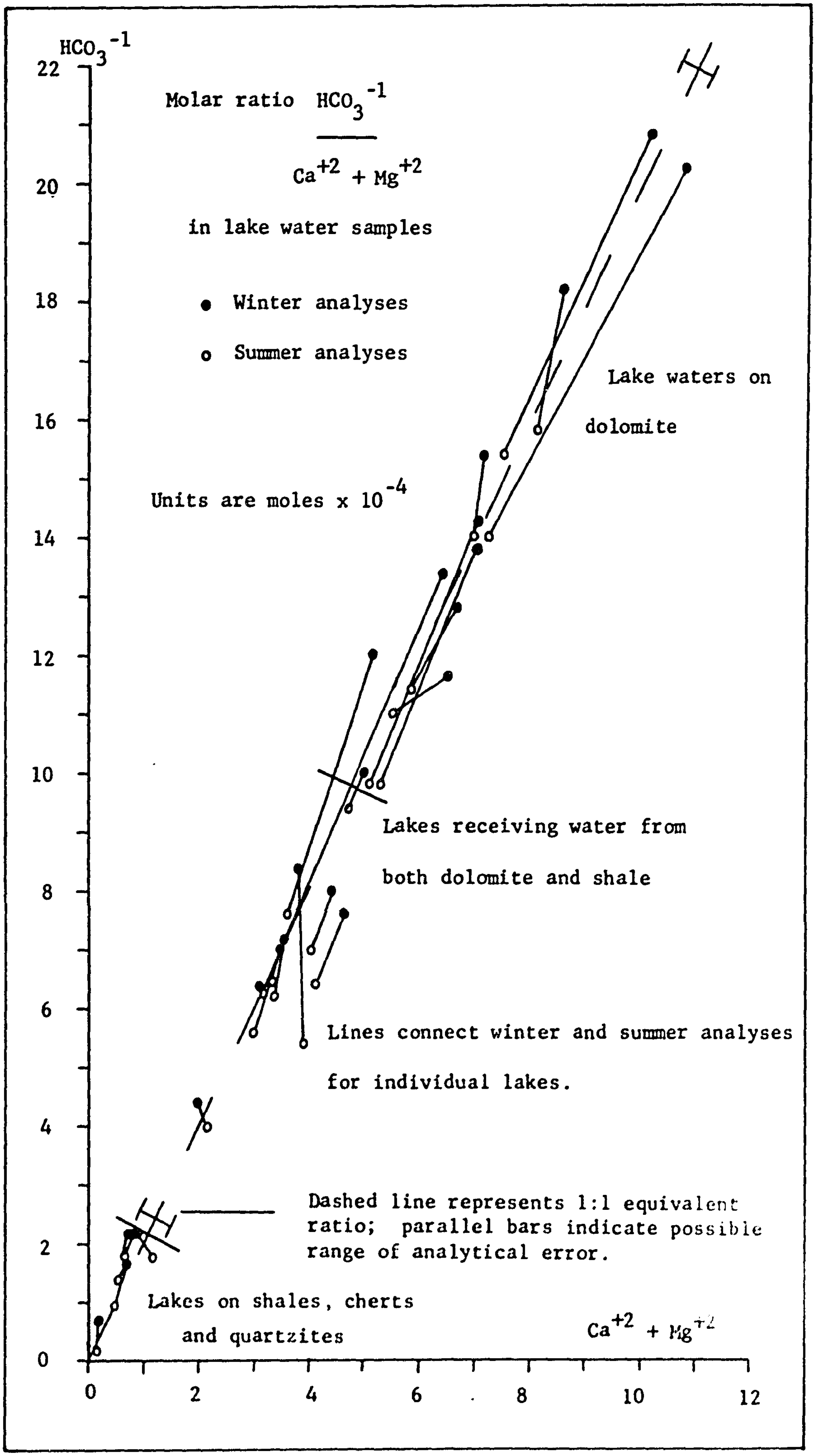


Fig. 16 Molar ratio $\frac{HCO_3^{-1}}{Ca^{+2} + Mg^{+2}}$ in lake samples from Knob drainage basin.

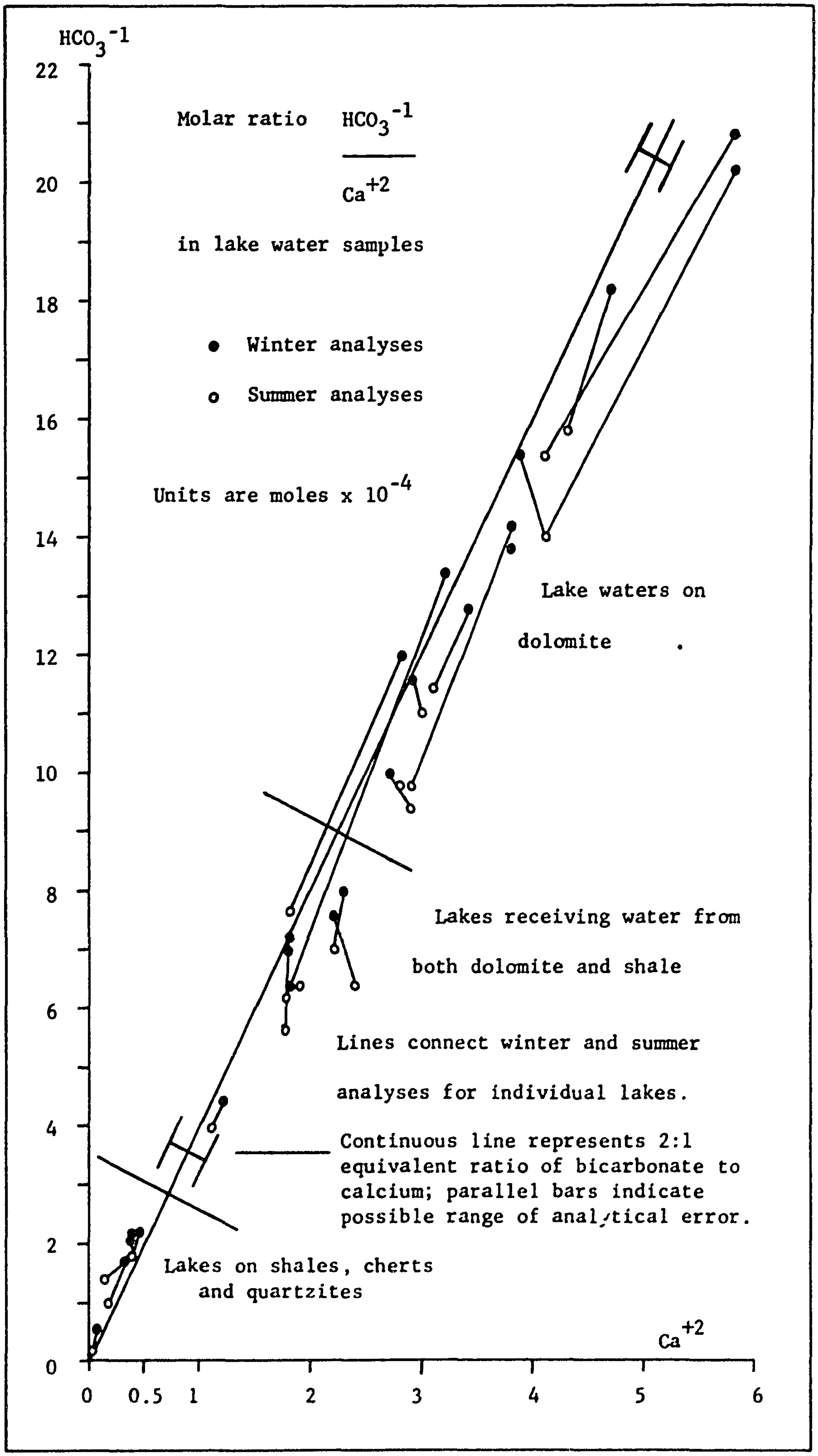


Fig. 17 Molar ratio $\frac{HCO_3^{-1}}{Ca^{+2}}$ in lake samples from Knob drainage basin.

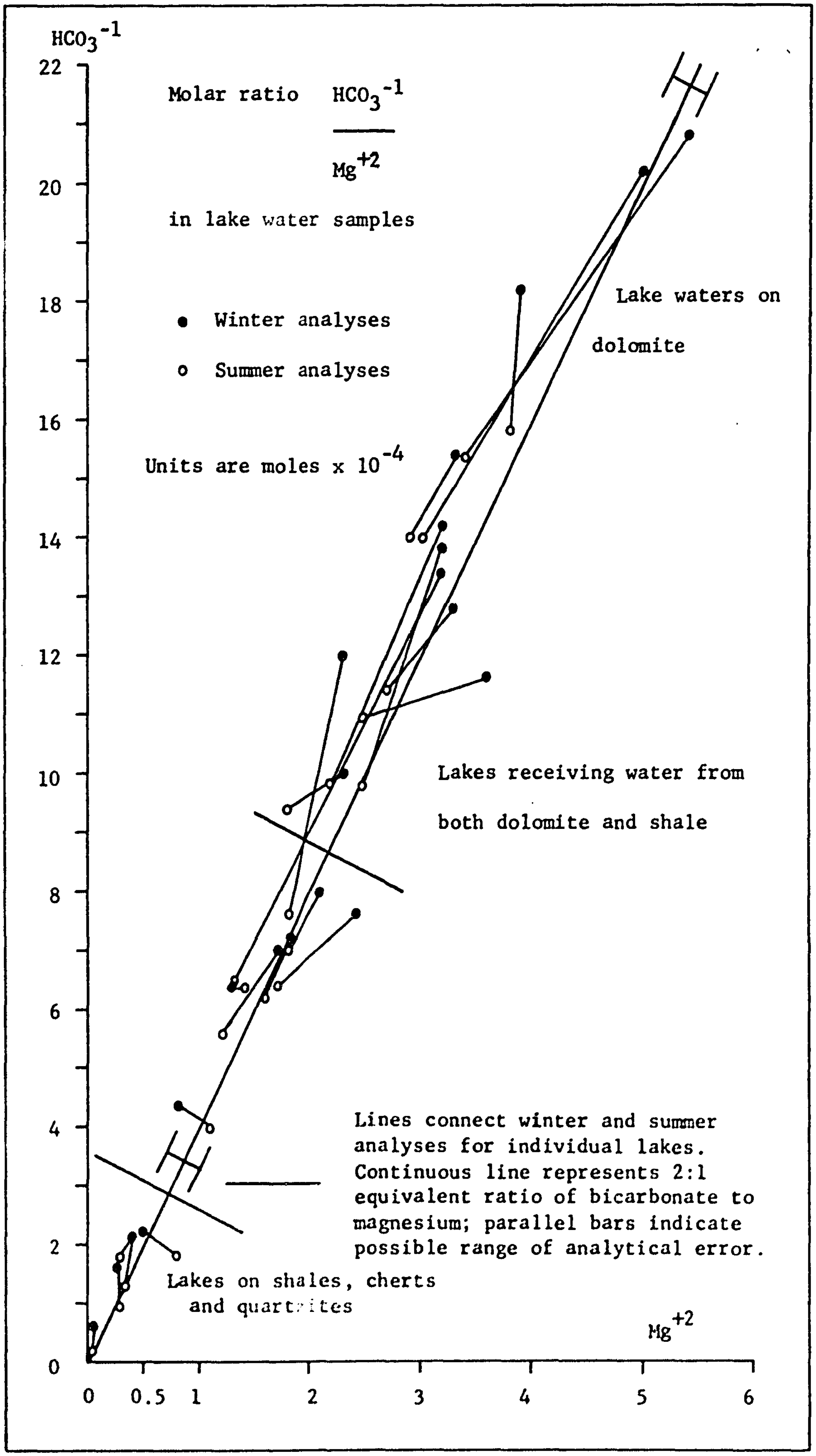


Fig. 18 Molar ratio $\frac{HCO_3^{-1}}{Mg^{+2}}$ in lake samples from Knob drainage basin.

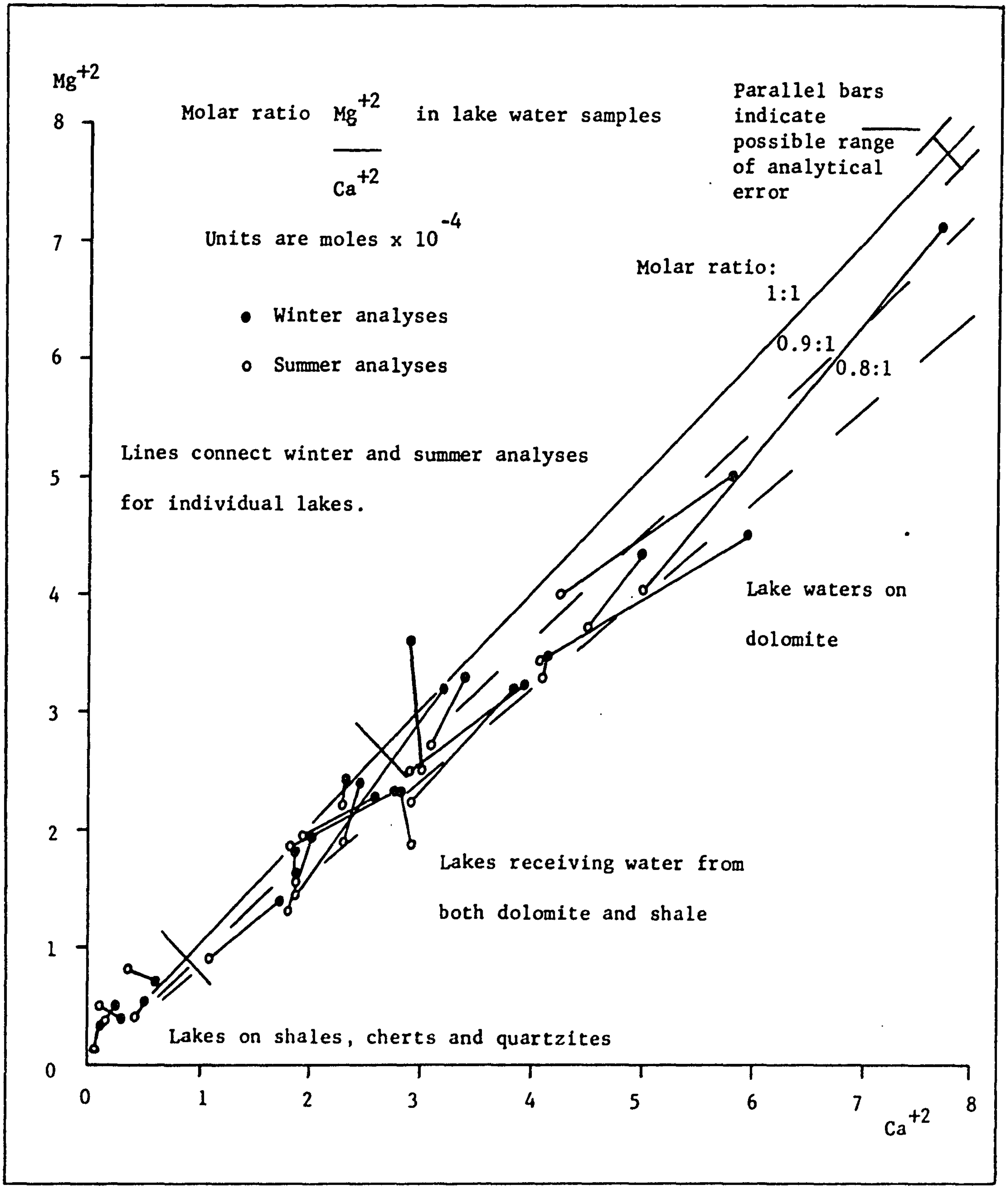


Fig. 19 Molar ratio $\frac{Mg^{+2}}{Ca^{+2}}$ in lake samples from Knob drainage basin.

describe the relation between analysed equivalent ratios and ideal ratios corresponding to the solution of dolomite in pure water. They also show the direction and magnitude of seasonal shifts in ionic ratios for individual lakes and the error that could reasonably be expected to arise from an analytical error range of ± 1.5 mg/l for each constituent.

Values for the equivalent ratio $\frac{HCO_3^{-1}}{Ca^{+2}+Mg^{+2}}$ are near unity, as predicted above (Fig. 16). Winter analyses tend to have slightly smaller values for the ratio than summer analyses. This is consistent with the observation (see Chapter V) that sulfate concentrations, particularly in smaller lakes, are higher in winter than in summer, and indicates that some of the calcium and magnesium in lake waters is electrically balanced by sulfate, partly of atmospheric origin. The ionic ratio is nearly constant or slightly lower in summer in lakes of the main sequence (Osprey - Knob) and superficially suggests that in summer sulfate is flushed out of small lakes into larger lakes further down the drainage basin. The ratio is also near unity in lake waters on shales, suggesting that even in these waters the solution of carbonate minerals is an important determinant of ionic composition.

The values of the equivalent ratio $\frac{HCO_3^{-1}}{Ca^{+2}}$ fall in the range 1.5 to 2.0 in waters on dolomite, and 1.5 to 1.0 in waters on shale. The ratio $\frac{HCO_3^{-1}}{Mg^{+2}}$, which is complementary to the bicarbonate-calcium ratio, falls between 2.0 and 2.5 in waters on dolomite and 1.0 to 1.5 in waters on shale. The differences in these ratios for waters from dolomite and shale is a reflection of the fact that magnesium-calcium ratios tend to be rather less than unity in dolomite waters, and greater than unity in waters on shale. Both ratios tend to be higher in summer than in winter, but seasonal change in the bicarbonate-magnesium ratio is noticeably more erratic. Perhaps calcium is more stable in these lake waters than magnesium.

Magnesium-calcium ratios are near unity, as would be expected from the paragraph above. On dolomite, ratios are less than unity, and on shale the ratios are above unity. This is attributed to an estimated Mg:Ca ratio in the Denault dolomite around 0.8 - 0.9, and to the presence in the shales of chlorite as an additional source of magnesium. There is some evidence that lakes in the intermediate concentration range have smaller $Mg^{+2}:Ca^{+2}$ ratios in summer than in winter. This also suggests that there may be some unexplained selective removal of magnesium from the lakes in summer.

To summarise, the analysis of ionic ratios provides an additional method of describing seasonal changes in composition, and a basis for inferring ionic sources and the processes which affect ion distributions in lakes.

8. Variations in Bicarbonate, Calcium and Magnesium Concentrations within Lakes.

All the lakes in Knob Lake basin from which more than one sample was collected showed some degree of internal variation in ionic composition. Most of the variation found took the form of vertical chemical stratification, but in some cases horizontal variations were found where waters of unlike composition meet in a lake and are imperfectly mixed. The results obtained from Cowan, Osprey, Malcolm, Easel and Knob Lakes indicate the nature of internal variation that can be expected, and these lakes form the basis for the following discussion. Horizontal variation will be discussed first, then variations with depth.

Malcolm and Knob Lake are examples of lakes in which horizontal variations in composition occur. In the case of Malcolm Lake, waters derived primarily from shales, quartzites and cherts in the Osprey catchment enter Malcolm Lake at the southern end, while water draining the Denault dolomite and Attikamagen shales in the Easel and Phred catchments enter Malcolm Lake near the head of the north-eastern arm. By comparison, Knob Lake has one major inflow, the channel flowing from Ares Lake which supplies water to Knob Lake from both shale and dolomite formations. Knob Lake itself is bordered by shales and iron formation, and the water flowing in from Ares Lake becomes slightly more dilute as it moves across the lake towards the outflow at the north-western end.

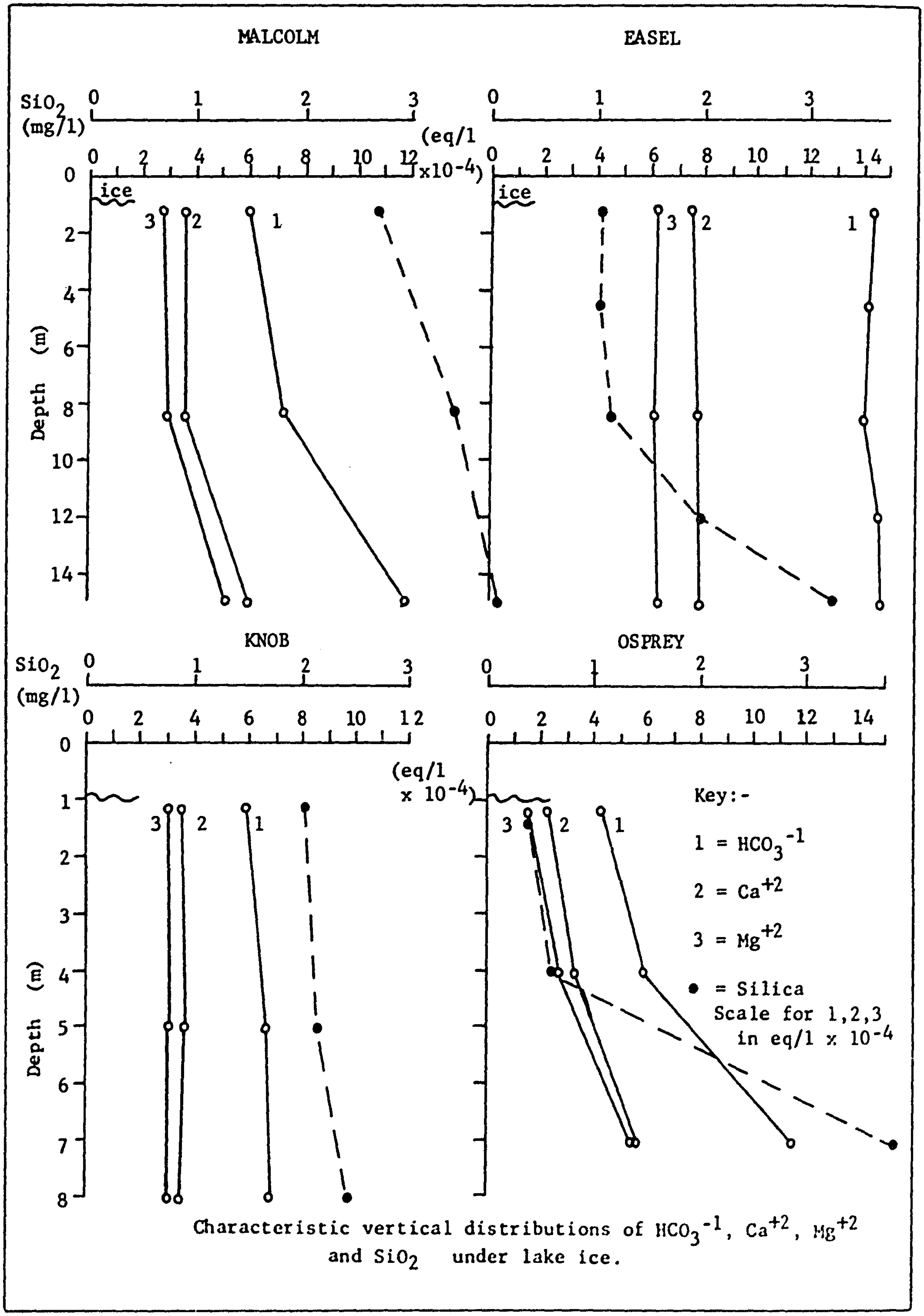
In Malcolm Lake in winter, surface water bicarbonate concentrations ranged from 51 mg/l near the inflow from Easel Lake to 36.6 mg/l in the centre, to 39 mg/l in the southern arm. In other words, a concentration gradient in the order of 12 mg/l existed over a distance of 500 m separating the sampling sites at the centre of the lake and the north-eastern arm. Calcium and magnesium concentrations within the lake varied correspondingly.

During the late summer survey, the bicarbonate ion concentration near the inflow from Osprey Lake was 34 mg/l, rising to 39 mg/l in the centre of the lake, and 38 mg/l near the inflow from Easel Lake. In this case, there was an apparent gradient of 5 mg/l over a distance of about 1 km separating the centre site from the inflow from Osprey Lake. These variations are potentially large enough to justify detailed mapping with a view to estimating rates of mixing, although the number of sites sampled in this study is sufficient only to show the order of magnitude of internal variation that can be expected. Malcolm Lake could provide a suitable situation for describing mixing of waters in an unstratified lake, and for predicting the dispersion of solutes such as the bicarbonate ion.

In Knob Lake, late winter concentrations of bicarbonate ranged from 42 mg/l in the northeastern arm, to 45 mg/l opposite the inflow from Ares Lake, 36.6 mg/l near the western shore and 42.7 mg/l near the outflow. The total range is in the order of 8 mg/l, and further study of the lake would probably point to a pattern of dilution towards the western margin of the lake near the outcrop of Menihek shales and Sokoman iron formation. In contrast, summer bicarbonate concentrations were almost uniform at 35.3 mg/l, with some evidence for a slight decrease towards the outflow. The absence of any marked concentration gradient suggests that the lake was in full circulation at the time of the summer survey.

The five sites sampled in the much smaller Cowan Lake (4.2 ha) revealed negligible horizontal variation, both in the winter and summer surveys. However, during the spring melt period (June 7), the release of snowmelt water into the lake created horizontal differences in bicarbonate concentration up to 30 mg/l. At this time, a band of dilute water extended across the lake on a north-south line, following the local topographic trike and surface drainage.

Vertical distributions of bicarbonate, calcium and magnesium in lakes at the time of the winter survey are illustrated by a series of profiles (Fig. 20) describing conditions in Osprey, Malcolm, Easel and



Characteristic vertical distributions of HCO_3^{-1}, Ca^{+2}, Mg^{+2} and SiO_2 under lake ice.

Fig 20 Characteristic distributions of HCO_3^{-1}, Ca^{+2}, Mg^{+2} and SiO_2 under lake ice.

Knob lakes. A further set of more detailed profiles has been drawn for Cowan Lake to show the results of intermediate surveys and vertical distributions of pH, dissolved oxygen and ion activity products for dolomite and calcite (Fig. 21).

The profiles for Osprey Lake, which are taken opposite the inflow from Houston Lake, describe the over-riding of deep water in contact with dolomite and with relatively high ion concentrations by colder and more dilute water originating from shales and quartzites in the Houston Lake catchment. The profiles for Malcolm Lake describe a similar pattern. In this case, the chemical stratification appears to result from the accumulation of water in the deeper basins of the lake which may have been derived partly from Easel Lake and is in contact with the Denault dolomite forming the lake basin. This water is overlain by relatively dilute water from the southern end of the lake.

In contrast, the profiles for Easel and Knob Lakes show little variation with depth. Slight increases in bicarbonate concentration occur under the lake ice and near bottom sediments. Increases near the ice probably result from the segregation of dissolved substances during ice formation (Mortimer, 1941), although such segregation depends upon the mode of ice formation. Ice formed by the flooding of an existing ice cover after a snowfall probably retains its original ionic composition. The increase in bicarbonate, calcium and magnesium near bottom sediments is problematic, but is believed to be related to the oxidation state of the mud surface, even though the mechanism of release of bicarbonate ion is not clearly understood (Hutchinson, 1941; Mortimer, 1941). Hutchinson also considered that cation exchange at

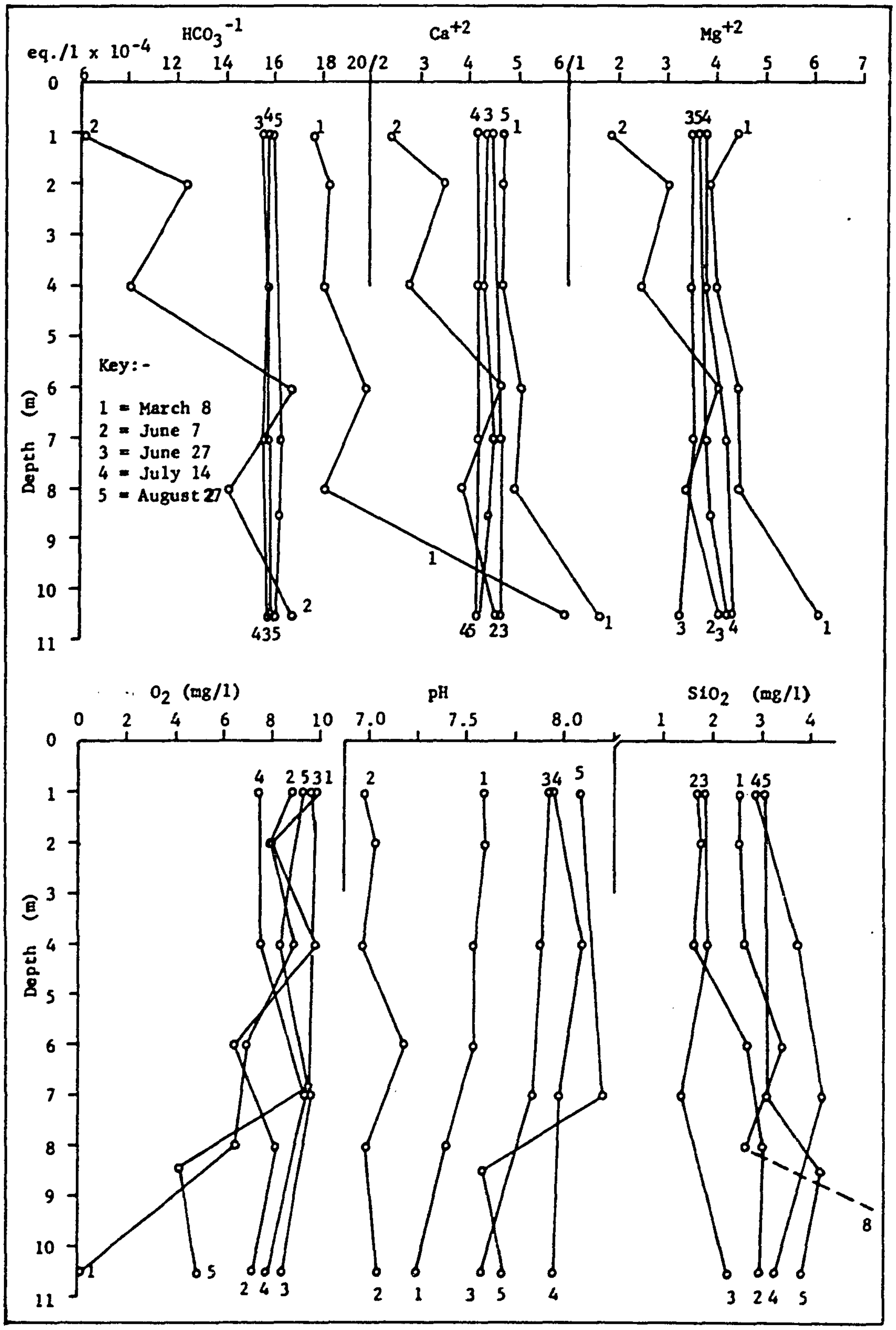


Fig. 21 Variations in the composition of Cowan Lake with depth and time of year, 1969.

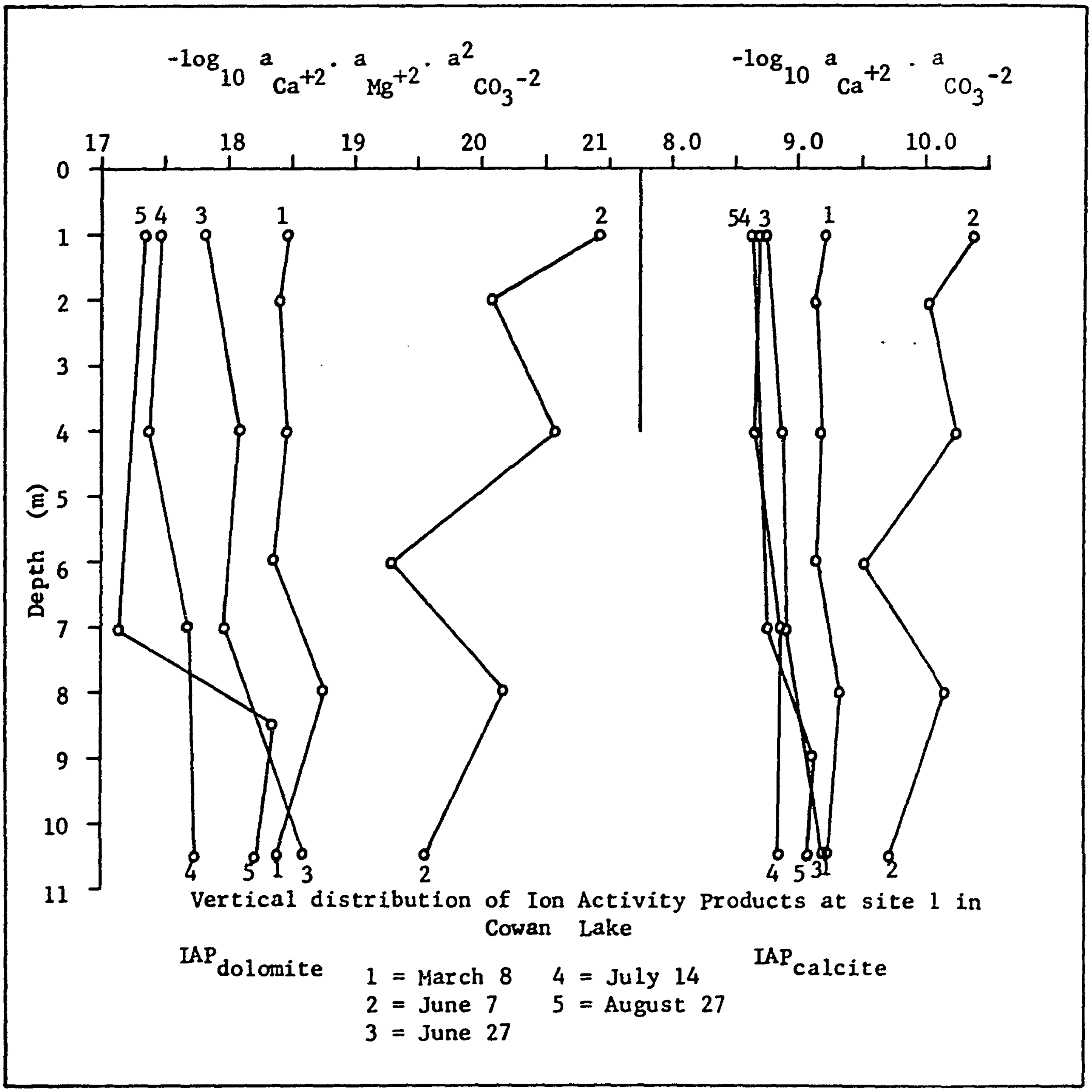


Fig. 21 a Vertical distributions of Ion Activity Products for dolomite and for calcite at the centre of Cowan Lake, 1969.

the mud surface, in conjunction with the solution of particulate carbonate minerals, may have been underestimated in this connection (Hutchinson, 1957, p. 674).

The sequence of profiles for Cowan Lake follow the formation and breakdown of winter chemical stratification, and the development of slight summer chemical stratification accompanying thermal stratification. The irregular profile obtained during the spring flood (June 7) reveals alternate fluctuations in pH and dissolved oxygen which reflect the passage of dilute and well oxygenated snow meltwater into the deeper parts of the lake. A curious feature of the water composition during both the winter and summer surveys is an increase in the ratio of magnesium to calcium with depth. A similar, though smaller, change was noted in Easel Lake. It is difficult to explain this shift in ratio without establishing some mechanisms for the selective removal of magnesium near the surface or for the removal of calcium from the deeper part of the lake.

9. Composition of Lake Waters Derived from Shale and Dolomite.

Concentrations of bicarbonate, calcium and magnesium in the lake sequence Osprey - Malcolm - Ares - Knob - Pearce, and in the tributary lakes Gene and Phred, are determined by the mixing of waters draining the dolomite and shale formations in the drainage basin. The purpose of this section is to attempt an explanation for the composition of these mixed lake waters. A direct explanation in terms of chemical equilibria is not possible since the precise composition of the source of waters is not known. Therefore, an explanation must be sought in terms of the composition of lake waters lying directly on dolomite and on shale, and in terms of the areas of dolomite and shale in the catchments of the main lakes in the Knob Lake drainage basin.

Two extreme points of view are possible concerning overall controls of lake water composition operating in the Knob Lake drainage basin. The first is that the transfer of groundwater through the basin has little, if any effect on the lakes, and that lake water composition reflects the composition of surface drainage (i.e. the composition of tributary lake waters) and some degree of equilibrium with minerals present in individual lake basins. The alternative point of view is that groundwater transfer in the basin is the dominant control of water composition, and that individual lake waters reflect equilibria attained by groundwater rather than by surface drainage or chemical changes within lake basins.

The truth probably lies somewhere between these two points of view. In Chapter II, in the section on the exchange of water between lakes, some suggestions were made about the transfer of water within the basin. The results of stream-gauging at the outflows of larger lakes in the basin indicated that surface run-off was not directly proportional to catchment area, and that between 10 and 60 per cent of the transfer of water through the basin took place as groundwater movement, depending on the time of year and the location within the drainage basin. Groundwater discharge appeared to be especially important in the catchments of Easel and Houston Lakes. It was suggested that groundwater transfer along the regional strike within the drainage basin may increase residence times of water in small lakes near catchment divides by a factor of two or three. It is reasonable, in view of these features of the drainage basin hydrology, to expect groundwater flow to be an important, if not dominant, control of the chemical composition of lake waters.

The interpretation of the composition of lakes receiving water from both dolomite and shale has been approached in two ways, reflecting the two points of view expressed above. In the first approach (Tables 11a, 11b) concentrations of bicarbonate, calcium and magnesium in Communications and Houston Lakes (representative of lake waters on shale) and in Easel Lake (representative of lake water on dolomite) were used in an attempt to predict ion concentrations in the lake sequence Osprey - Malcolm - Ares - Knob - Pearce, and in Gene and Phred Lakes. The predictions were based on the proportion of shale and dolomite in the respective lake catchments. The predicted concentrations of bicarbonate, calcium and magnesium, for winter and summer, were then expressed as ratios of analysed concentrations.

In the second approach, each lake in the above-mentioned sequence is considered to contain a portion of water derived from the Denault formation and a portion derived from shale formations. These portions are in a ratio determined by the areas of Denault dolomite and of shale in the respective lake catchments. Analysed concentrations of bicarbonate, calcium and magnesium obtained from the winter and summer lake surveys are then used to estimate the original compositions of the dolomite and shale contributions to total lake water composition. These contributions reflect both surface and sub-surface transfer of water between lakes. This is achieved by writing simultaneous equations for successive pairs

TABLE 11. A

Predicted Compositions of Mixed Lake Waters based on compositions of dolomite and shale lake waters, and the geology of lake catchments.

Lake	dolomite shale ratio in catchment	Winter						Summer					
		HCO_3^{-1}		Ca^{+2}		Mg^{+2}		HCO_3^{-1}		Ca^{+2}		Mg^{+2}	
		P	A	P	A	P	A	P	A	P	A	A	P
Osprey	1:11.5	21.0	36.2	3.1	6.8	2.1	3.4	17.2	24.1	2.7	4.4	2.0	2.2
Malcolm	1:4.12	29.7	47.7	5.0	8.1	2.9	4.7	25.7	39.1	4.4	7.5	2.8	3.6
Ares	1:5.25	29.7	45.0	5.0	7.4	2.9	4.3	25.7	38.0	4.4	7.5	2.8	3.5
Knob	1:5.75	27.0	39.2	4.5	7.4	2.6	3.9	23.2	34.3	3.9	7.3	2.6	2.8
Pearce	1:41.2	26.1	57.5	4.4	10.3	2.5	5.5	22.3	31.5	3.7	7.9	2.5	4.6
Gene	1:25.3	16.8	48.2	2.5	9.8	1.7	5.8	13.0	39.4	1.9	9.2	1.7	4.6
Phred	1:25.3	17.9	50.4	2.8	9.2	1.8	5.9	14.0	42.8	2.1	9.2	1.8	5.4

Based on winter compositions:	dolomite	HCO_3^{-1}	Ca^{+2}	Mg^{+2}	(Easel Lake)
(mg/l)		90.0	16.6	8.5	
	shale	15.0	2.2	1.5	
summer compositions:	dolomite	85.6	16.4	8.0	(Houston Lake)
(mg/l)	shale	11.2	1.5	1.5	

P = predicted compositions (mg/l)
A - analysed compositions (mg/l)

TABLE 11 B. Ratios of Predicted to Analysed Ionic Concentrations in Table 11.A

	Winter			Summer		
	bicarbonate	calcium	magnesium	bicarbonate	calcium	magnesium
Osprey	0.58	0.45	0.61	0.71	0.61	0.92
Malcolm	0.62	0.63	0.60	0.66	0.59	0.76
Ares	0.66	0.68	0.67	0.68	0.59	0.79
Knob	0.69	0.61	0.67	0.68	0.54	0.93
Pearce	0.45	0.42	0.46	0.71	0.47	0.53
Gene	0.35	0.26	0.29	0.33	0.20	0.36
Phred	0.36	0.30	0.30	0.33	0.22	0.33

TABLE 11.C
Estimated Compositions of Dolomite and Shale Contributions to Mixed Lake Waters.

Lake pair	Winter						Summer					
	Bicarbonate		Calcium		Magnesium		Bicarbonate		Calcium		Magnesium	
	dol.	shale	dol.	shale	dol.	shale	dol.	shale	dol.	shale	dol.	shale
Osprey Malcolm	128	28.1	16.6	6.0	13.9	2.5	144	13.7	30.5	2.2	13.7	1.2
Malcolm Ares	no solution because proportions of dolomite and shale are the same in each catchment											
Ares Knob	180	12.4	8.4	7.2	12.5	2.3	126	16.8	15.2	5.7	N.S.	
Knob Pearce	no solution because of strong sulfate component in ion balance of Pearce Lake											
Gene Phred	185	45	N.S.		11.0	5.7	270	33.6	10.0	9.3	18.0	3.3

Explanation: Let X be concentration of constituent (HCO_3^{-1}, Ca^{+2}, Mg^{+2}) contributed from dolomite, and Y be the corresponding concentration of the contribution from shale. Then, for each of the above lakes, the observed concentration (HCO_3^{-1}, Ca^{+2}, Mg^{+2}) is made up of a dolomite and shale contribution in proportion to the areas of these formations in the lake catchment. This can be expressed for each lake in the form of an equation in X and Y. e.g. (Malcolm - bicarbonate - winter) $X + 4.12Y = 39 \times 5.12 = 200$. The values for X and Y in the table are obtained by solving successive equations for pairs of lakes in the main sequence.

N.S. = no solution.

of lakes in the sequence, in which the two unknowns are the concentrations of bicarbonate, calcium or magnesium attributable to dolomite and shale water in proportion to the area of dolomite and shale in each lake catchment. The results of these calculations are summarised in Table 11c, which also illustrates the development of the simultaneous equations.

Both of these methods of estimating dolomite and shale controls of lake water composition involve simplifying assumptions. Both approaches presuppose that all areas of the basin generate equal amounts of flow through the lakes, whether this flow originates as surface run-off, or as groundwater. The first approach assumes that this flow is predominantly surface run-off. The other assumptions involved are that geological formations other than dolomite and shale are insignificant as controls of lake composition; that chemical exchanges within lake basins are relatively small; and that analysed concentrations of bicarbonate, calcium and magnesium represent the entire volume of each lake.

The first method (Table 11a), based on observed compositions of dolomite and shale lake waters, gave predicted concentrations well below analysed concentrations in each of the lakes studied. For the winter survey of the sequence of lakes Osprey - Malcolm - Ares - Knob, ratios of predicted to analysed concentrations of bicarbonate, calcium and magnesium are between 0.6 and 0.7 (slightly less in Osprey Lake), and the correspondence between the ratios for individual ions is close. Ratios are lower in Pearce Lake (0.45) and in Phred and Gene Lakes (about 0.3).

Ratios of predicted to analysed concentrations based on summer survey results are in the same general range, but reveal differences between the ratios for bicarbonate, calcium and magnesium ions. For bicarbonate, the ratio is close to 0.7 for the lakes from Osprey through to Knob, and 0.33 in Gene and Phred Lakes. The ratio for calcium decreases from 0.6 in Osprey Lake to 0.54 in Knob Lake and 0.47 in Pearce Lake, while in Gene and Phred Lakes the ratio is only 0.3. The ratio for magnesium, which is generally more variable, ranges from 0.75 - 0.93 between Osprey and Knob Lakes, while in Pearce Lake it is 0.53, and 0.33 - 0.36 in Gene and Phred Lakes. Analysed concentrations of bicarbonate, calcium and magnesium are therefore between 30 and 300 per cent higher than concentrations predicted on the assumption that lake water compositions are determined by the mixing of dolomite and shale lake waters.

The second approach, the purpose of which was to estimate dolomite and shale contributions to lake water composition, gave results which also indicated that water flowing into lake from dolomite and shale has appreciably higher concentrations of HCO_3^{-1}, Ca^{+2} and Mg^{+2} than are found in lake waters on these formations. However, the solutions that were obtained for the equations gave results of questionable reliability. Some equations, as in the case of the lake-pair Knob-Pearce, did not yield a solution with positive values for ionic concentration. In the case of Pearce Lake, this is probably a reflection of the influence of sulfate ion on the composition of this lake water (see Chapter VI). Equations could not be solved for Malcolm and Ares Lakes, because the proportion of dolomite and shale in each catchment is the same.

On the basis of analysed winter concentrations, water from dolomite appeared to have a bicarbonate content in the range 130 - 185 mg/l, 8.5 - 17 mg/l calcium and 11 - 14 mg/l magnesium. The corresponding shale water composition was in the range 12 - 45 mg/l HCO_3^{-1}, 6 - 7 mg/l Ca^{+2} and 2.3 - 5.7 mg/lMg^{+2}. The highest concentrations were obtained for both dolomite and shale water from Gene and Phred Lakes. Summer analyses indicated dolomite water composition of 125 - 145 mg/l HCO_3^{-1} (although a value of 270 mg/l was obtained for Gene and Phred Lakes), 10 - 30 mg/l Ca^{+2} and 14 - 18 mg/l Mg^{+2}. The corresponding shale water composition was in the range 14 - 34 mg/l HCO_3^{-1}, 2 - 9 mg/l Ca^{+2} and 1.2 - 3.3 mg/l Mg^{+2}. These synthetic water compositions have ionic concentrations about half as high again as the lake waters on dolomite and shale. Molar ratios of bicarbonate to calcium and magnesium are consistent with the dissolution of carbonate minerals.

The results of these two attempts at interpreting the composition of lake waters of mixed origin do not give specific answers concerning the nature of groundwater composition, or the control on water composition exerted by groundwater flow. However, they do make it possible to offer a series of suggestions regarding the effective controls on lake composition. In the first place, dolomite appears to have a markedly greater influence on water composition than is indicated by the analyses of lake waters on dolomite. Second, it seems that only one-quarter to three-quarters of the concentration of the ions HCO_3^{-1}, Ca^{+2} and Mg^{+2} can be attributed to surface water flow between lakes. This implies that other major sources of ions must be present. The most reasonable hydrological explanation for this is that the transfer of groundwater through the drainage basin via individual lake basins provides the additional source of ions. A further source of ions may be the solution of carbonate minerals within the larger lake basins.

10. Summary

Bicarbonate, calcium and magnesium were found to be most abundant ions in lake waters of the Knob Lake drainage basin. These ions are derived primarily from the solution of carbonate minerals, the principal source of which is the Denault dolomite formation which runs diagonally across the basin from north to south in a band 2 km wide. Smaller quantities of these ions are derived from carbonate minerals and aluminosilicates in the Attikamagen and Menihek shale formations, and from atmospheric precipitation.

The literature on the solubility of pure dolomite and calcite in water suggests that, at equilibrium, water in contact with dolomite should have values for the ion activity product ($a_{Ca^{+2}} \cdot a_{Mg^{+2}} \cdot a_{CO_3^{-2}}$) in the range 10^{-17} to 10^{-19}. For water in equilibrium with calcite, the product ($a_{Ca^{+2}} \cdot a_{CO_3^{-1}}$) should be in the range $10^{-8.0}$ to $10^{-8.3}$ in the temperature range 0 - 20°C. In lake waters such as are found near Schefferville, the carbonate ion activity, and therefore the activities of calcium and magnesium, are related to the hydrogen ion activity, which is dependent on the formation of carbonic acid in water in the presence of gaseous carbon dioxide. The account given here of the solution of carbonate minerals serves to indicate the general order of magnitude of concentrations of bicarbonate, calcium and magnesium that can be expected in waters in contact with dolomite. However, the argument as presented does not indicate the rate at which equilibration of surface waters proceeds, and, in the absence of information on the movement of water near the surface of the Denault dolomite, cannot be used, except in very general terms, to state the necessary conditions for equilibrium with dolomite to be reached.

Ion activity product diagrams for dolomite and calcite have been drawn for lakes in the drainage basin which conveniently summarise what is known about the carbonate chemistry of these lake waters. The main features of these diagrams are the contrasting compositions of shale and dolomite lake waters, and the merging of these waters in the lakes from Osprey through to Knob Lake. Individual ion activity products are consistently higher in summer than in winter, a consequence of higher carbonate ion activities. Lakes lying on dolomite tend to be undersaturated with respect to dolomite and calcite in winter, and to approach equilibrium in warm summer weather. Undersaturation under lake ice in winter probably results from the release of carbon dioxide in biological respiration. The analyses used in the IAP diagrams effected supersaturation with respect to atmospheric carbon dioxide both in winter and summer. The supersaturation in summer (by a factor of ~ 2) may reflect systematic analytical error.

Maps have been presented illustrating distributions of bicarbonate, calcium and magnesium in the lake waters studied. The highest concentrations of these ions occur on and near dolomite, and the lowest on quartzite and shales. The main sequence of lakes (Malcolm, Ares and Knob) have intermediate concentrations, reflecting the mixing of drainage from dolomite and from shale. Molar rations of bicarbonate to calcium and magnesium are close to 2:1 (equivalent ratio 1:1), and of magnesium to calcium close to or somewhat less than 1:1. These ratios are consistent with the hypothesis that these ions are primarily derived from the solution of a rock with the composition of a ferroan dolomite, or a mixture of dolomite and ankerite. Within lakes, the distributions of these ions reflect thermal stratification, exchanges at the mud-water interface, and the mixing of lake waters of contrasting compositions. Except in the case of Cowan Lake, summer thermal stratification appears to be unusual in the lakes studied, and ion distributions in the lakes in summer are correspondingly almost uniform.

An attempt was made to interpret the compositions of lakes receiving drainage from dolomite and from shale in terms of the proportions of these formations in the catchments of individual lakes. Although the interpretation is necessarily speculative, it is suggested that observed compositions are best explained if groundwater movement is regarded as a major control of ion abundance in lake waters. Groundwaters from both dolomite and shale would appear to have ionic concentrations about half as high again as those observed in surface waters on these formations. These findings are consistent with the conclusion, based on stream gauging at lake outlets within the basin, that up to 60 per cent of the transfer of water between lakes takes place as groundwater flow.

CHAPTER V

OTHER CONSTITUENTS OF LAKE WATERS NEAR SCHEFFERVILLE

1. Introduction.

In Chapter IV, the concentrations of calcium, magnesium and bicarbonate ions in lake waters near Schefferville were interpreted in terms of the solution of carbonate minerals and the mixing of waters of differing geological origins. The present chapter deals with the other constituents of lake waters that were analysed in this study; namely, silica, dissolved oxygen, iron, aluminium and manganese, sodium and potassium, sulfate and chloride and nitrate and phosphate. For each of these constituents, a short account of the nature and source of the constituent in lake water is followed by a description of its occurrence in lakes near Schefferville. The chapter closes with a brief section on the ionic composition of lake waters in the drainage basin.

2. Silica.

Silica is commonly present in North American lake waters in concentrations of 1 - 4 mg/l (Hutchinson, 1957, p. 791) compared with the figure of 13 mg/l quoted for major rivers of the world (Bricker and Garrels, 1968). While concentrations of silica in river waters rarely fall below 2 mg/l, the silica of lake waters may fall to a few tenths of a milligram per litre. Not all the silica represented by these values is in true solution. Amorphous silica dissolves yielding weakly dissociated silicic acid monomers, H_4SiO_4, but silicate polymers, and aluminosilicate complex ions, together with particulate and colloidal silica are also present in lake waters (Krauskopf, 1956; Hutchinson, 1957, p. 789). The molybdate method used for the analysis of silica in this study not only determines silicic acid present, but also some of the silica in polymer or particulate form (Strickland and Parsons, 1968). Consequently, silica determinations at low concentrations are not closely reproducible.

Laboratory and field studies (Krauskopf, 1956; Davis, 1964; Feth et. al., 1964) indicate that the mineral source of silica is important in determining the amount of silica present in solution. Water in equilibrium with quartz after several months may have 4 - 12 mg/l dissolved silica in contrast to 100 - 140 mg/l in equilibrium with amorphous silica. The amount of silica in solution is largely independent of pH below pH 10 (Krauskopf, 1956). However, the silica of most rivers and lakes appears to be derived not from chemically pure silica, but from aluminosilicate minerals. Studies of the solution of igneous rock by snow meltwater have suggested that surface waters may come into equilibrium with feldspars within a few metres of travel and over a period of a few hours, (Feth et. al., 1964).

Some of the silica in lakes near Schefferville is derived from surface streams and groundwater flow, and some is derived from the bottom sediments of the lakes themselves. Although the process is not well understood, it appears that silica is involved in the same exchanges which release iron and phosphorous to lake waters from bottom muds at times of oxygen depletion and low redox potential (Hutchinson, 1957; Mortimer, 1941). Other potential sources of dissolved silica within lakes are the solution of diatom skeletons, and the action of benthic diatoms on aluminosilicate minerals. For example *Nitzchia palaea* and *Navicula minuscula* are known to release silica from synthetic clay minerals (Vinogradov and Boichenko, 1942 - cited in Hutchinson, 1957).

Silica may be lost from lakes in the course of diatom production. Seasonal changes in dissolved silica in Lake Windermere in England have been correlated with blooms of *Asterionella*, *Fragilaria* and *Tabellaria* (Lund, 1964). These diatoms have been identified in the plankton of the lakes of the Knob Lake basin (J. Moore, pers. com., 1968 and personal observation). Silica may also be lost through the absorption of a layer of silicic acid on solid silicate particles (Stober, 1967). The distribution of dissolved silica in the lakes of the Knob drainage basin in winter and summer, 1969, is shown in Figs. 22a, 22b and Table 13. The modal values and total silica content for individual lakes are estimates which do not take into account the possibility of higher silica concentrations near bottom sediments or in littoral zones. The apparent change in storage of dissolved silica in the lakes between late winter (115 metric tons) and late summer (83.5 metric tons) is 31.5 metric tons. Corresponding losses in run-off during the period amounted to c. 38.5 tons, so that the replenishment of silica by inflowing stream and by release from bottom sediments exceeded losses presumably due to diatom production by seven metric tons.

Lakes on Attikamagen shales generally have higher silica concentrations (3.0 - 29 mg/l) than lakes on dolomite (0.4 - 6.7 mg/l) or on chert (Barr, 2.0 mg/l; Lier, 1.6 mg/l). This is true in winter and in summer. The majority of lakes lose silica in summer, although concentrations in shale lakes (e.g. Gray, Hardy and Communications)

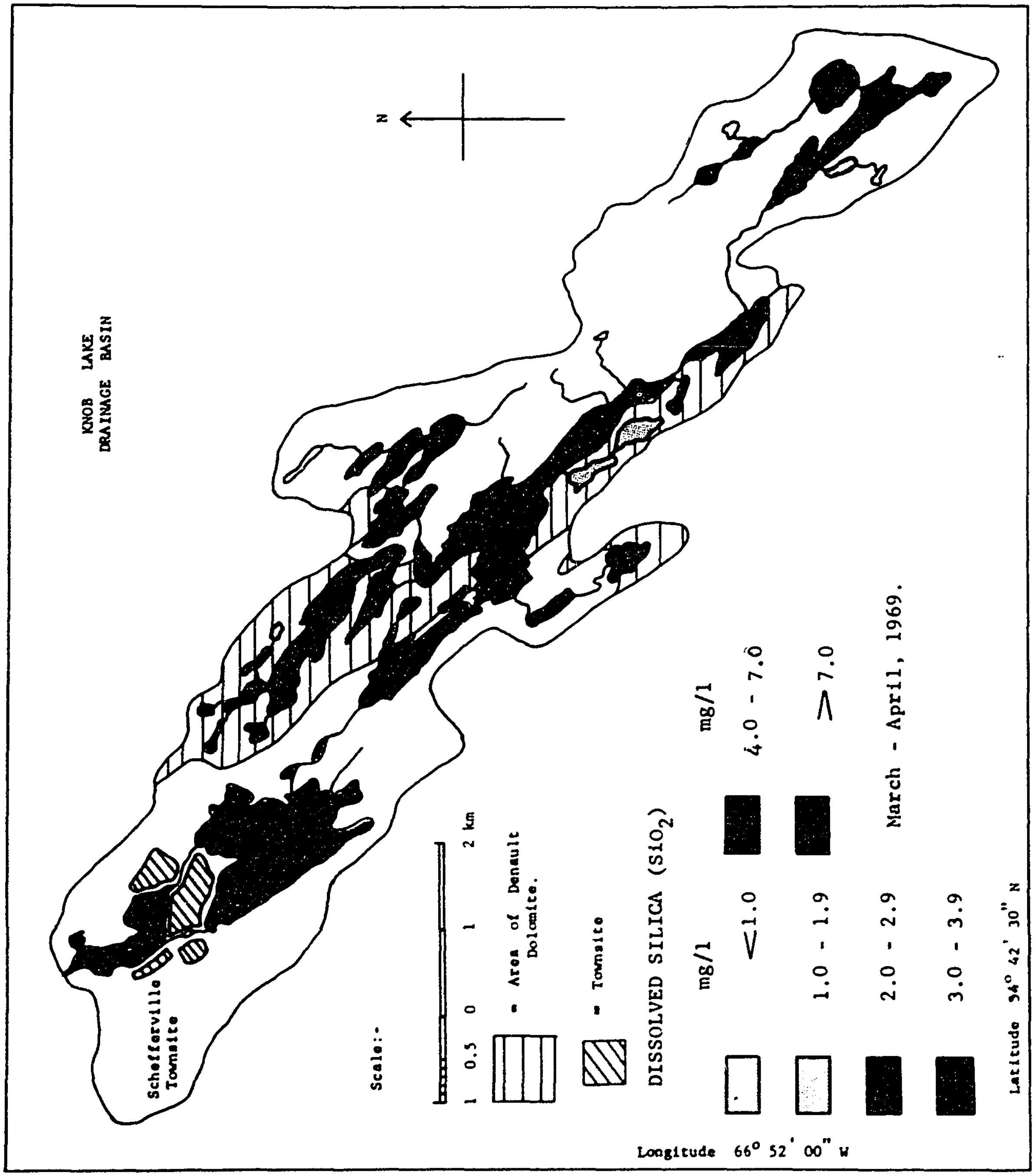


Fig. 22 a Distribution of soluble silica in lake waters - winter,1969.

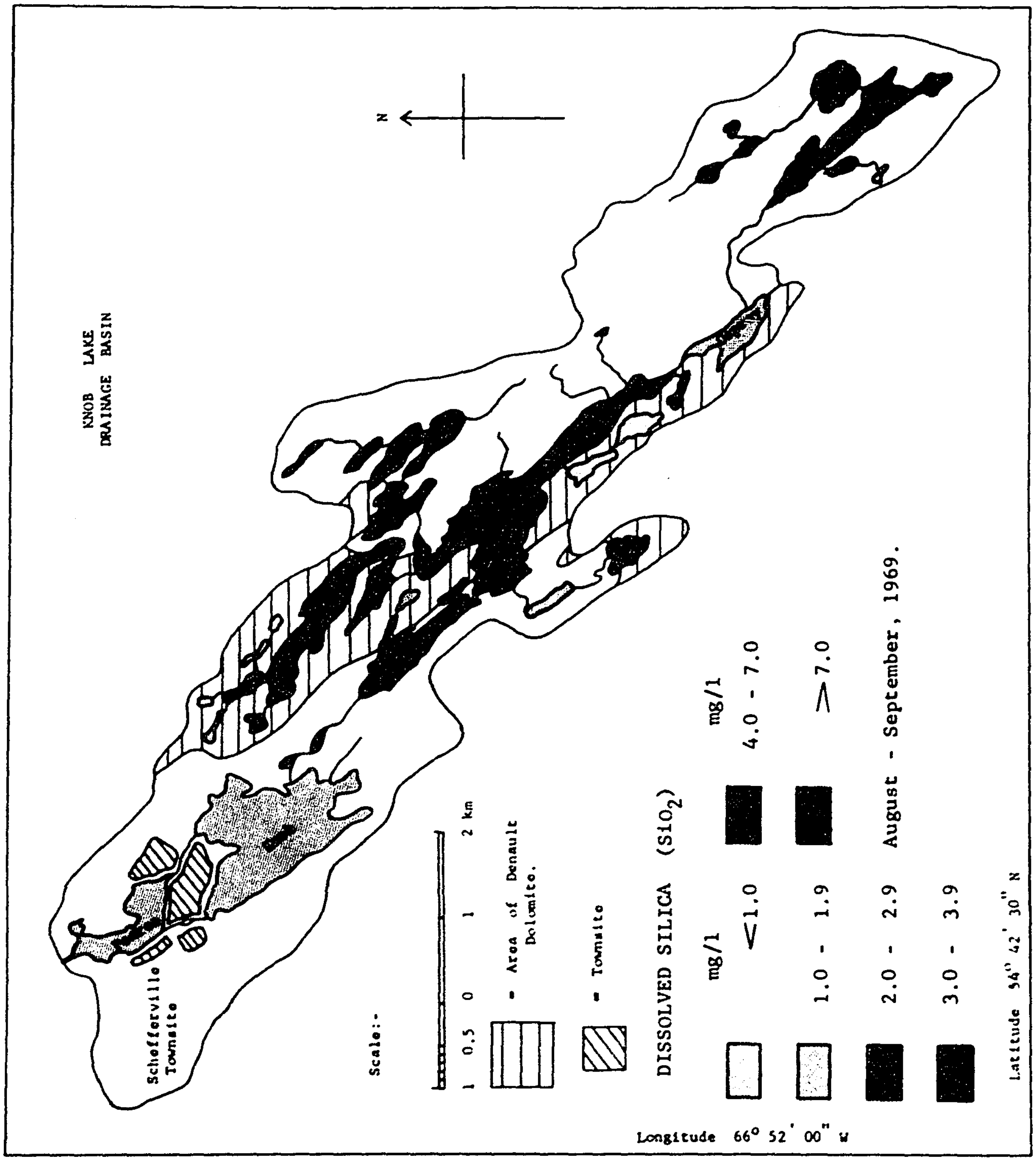


Fig. 22 b Distribution of soluble silica in lake waters - summer,1969.

Distribution of silica in lakes of Knob Lake Basin, 1969.

	Winter		Summer		Seasonal change in storage (kg x 10^3)
	mean (mg/l)	total (kg x 10^3)	mean (mg/l)	total (kg x 10^3)	
Communications	4.3	3.50	4.4	3.6	0.1
Houston	2.7	5.85	3.0	6.5	0.65
Osprey	5.1	5.50	1.5	1.6	- 3.90
Malcolm	3.8	39.5	2.6	26.5	-13.00
Phred	3.9	3.20	2.6	2.13	- 1.07
Gene	5.0	3.75	2.6	1.98	- 1.77
Easel	2.2	12.8	2.3	13.3	0.50
Ares	3.6	4.9	2.6	3.6	- 1.30
Knob	2.4	26.0	1.7	18.6	- 7.4
Pearce	3.6	4.35	1.2	1.50	- 2.85
North	1.3	0.49	0.9	0.34	- 0.15
Middle	1.5	0.71	0.5	0.25	- 0.46
South	3.7	0.30	2.1	0.17	- 0.13
Bassett	3.4	0.42	1.0	0.13	- 0.29
Adams	2.3	1.35	2.1	1.25	- 0.10
Cowan	3.1	0.59	3.2	0.61	0.02
Panhandle	3.5	0.18	1.8	0.09	- 0.09
Findlay	2.6	0.12	0.6	0.03	- 0.09
Williams	6.5	0.13	1.8	0.04	- 0.09
Francois	1.7	0.03	0.4	0.01	- 0.02
Ives	2.5	0.21	1.2	0.10	- 0.11
Mattox	14	?1.20	2.3	0.22	
Gray	4.2	0.34	4.7	0.63	0.31
Hardy	3.9	0.52	3.5	0.28	- 0.34
Thorn			4.3	0.15	
Barr	1.8	0.16	1.6	0.14	- 0.02
Lier			2.0	0.07	
Trigger	29	?	4.3	0.27	
Dale			2.7	0.08	
Doris			8.3	0.05	

Total winter storage: 114.9 tons

Total summer storage: 83.5 tons

Difference: 31.3 tons

remain essentially unchanged. The summer loss of dissolved silica is particularly noticeable in the small lakes on the dolomite around Easel Lake and the west side of Malcolm Lake. In two cases concentrations were reduced to 0.5 mg/l, a value which may be limiting for the diatoms *Asterionella* and *Tabellaria* (Lund, 1964). The magnitude of the seasonal change in concentration in the dolomite lakes appears inversely proportional to the lake catchment area. A few lakes, of which Easel and Houston Lakes are the most conspicuous, appeared to gain silica in summer, implying that the supply of silica to these lakes exceeds the silica removed in run-off and diatom production. Both these lakes have relatively long residence times and may act as silica reservoirs. A decline in silica concentration between Malcolm and Knob Lakes probably reflects a limited supply of silica to these lakes from their immediate catchments in relation to an increasing volume of water passing through the lakes.

Shallow water under the ice of Trigger and Mattox lakes in winter gave unusually high values of dissolved silica of 29 and 14 mg/l respectively. These high concentrations probably result from the concentrating effect of ice formation, or possibly from redox changes in the muds under the lakes.

There is no clear lithological control of silica concentrations in lake waters in the drainage basin, even though higher concentrations are associated with shale waters. This is probably because the rate of removal of silica from lake water is greater on dolomite than on shale, rather than because of intrinsically higher concentrations in shale waters. Dolomite lake waters have a variable silica content, and this variability may well be due to the high sand and chert proportions in some dolomite horizons, and to the leaching which has affected exposed areas of the formation.

3. Dissolved Oxygen.

The concentration of dissolved oxygen in water in equilibrium with the atmosphere is a function of water temperature and of the partial pressure of oxygen in the atmosphere. Since the Knob Lake basin lies at 500 m, saturation values for dissolved oxygen are about 0.94 of corresponding values at sea level (Hutchinson, 1957, p. 576).

Supersaturation with respect to oxygen in lake waters may result either from a sharp increase in water temperature or from the release of oxygen in photosynthesis. Conversely, undersaturation results from sharp decreases in water temperature, biological respiration, and the oxidation of organic matter. If water temperatures are stable, marked departures from saturation are indicative of high biological productivity. Similarly, the depletion of oxygen under lake ice in winter is greater in lakes with high productivity, or a large surface area of organic mud in relation to lake volume.

At the time of the winter survey, all lakes sampled were found to be undersaturated with respect to oxygen. Relative saturation values ranged from 4 to 90 per cent (0.5 - 12 mg/l), with a modal value of 75 per cent (9.5 mg/l). Most lakes investigated showed a decrease in oxygen with increasing depth, with the greatest rate of change occurring near the lake sediments. In some instances (Cowan, Easel and Middle Lakes), minimum oxygen values were found at mid-depth. The greatest oxygen depletion (2 - 4 mg/l) was found in shallow dolomite lakes, and the least depletion (10 - 12 mg/l) in large, open lakes (Knob and Malcolm Lakes). Dissolved oxygen less than 1 mg/l only occurred in very shallow water under ice, and near the bottom of Cowan Lake.

In summer, lake waters in the drainage basin were 80 - 100 per cent saturated with oxygen (9 - 10 mg/l). The large lakes (Knob and Malcolm), and the smaller lakes on shales are closer to saturation than the lakes on dolomite. Deep waters in Knob and Malcolm Lakes were saturated or slightly supersaturated with oxygen. The hypolimnion of Cowan Lake contained 4 - 5 mg/l O_2. Although the implied differences in saturation between lakes on dolomite and lakes on shale suggest the greater productivity of dolomite waters, the general undersaturation throughout the basin may be a consequence of the cooling and circulation of lake waters rather than biological activity.

Changes in saturation with respect to dissolved oxygen, if they result from photosynthesis or respiration, are related to the uptake and release of carbon dioxide. If the flow of water through a lake is small in relation to lake volume, and the lake may be treated conveniently as a closed system, changes in dissolved oxygen may be related empirically to the utilisation of carbon dioxide using a respiration or photosynthesis coefficient (see Hutchinson, 1941 and 1957 p. 675 concerning Linsley Pond). In the Knob Lake basin, lake residence times are short, and the analyses too few to attempt such a calculation. However, in Fig. 23, the seasonal change in pH of surface water in the lakes has been plotted against the relative saturation value for the surface water under lake ice in winter. This diagram serves to describe the relation between oxygen deficit and

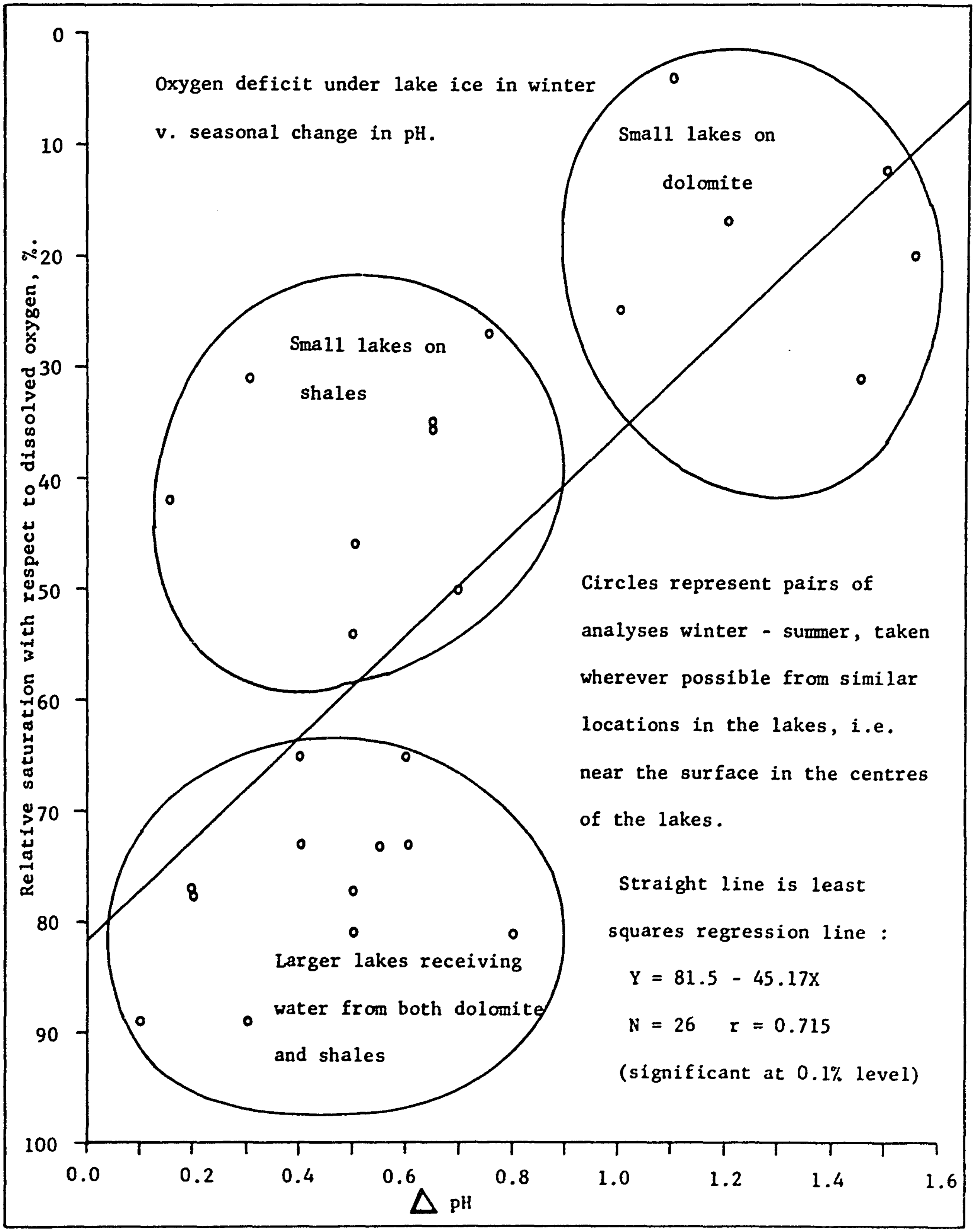


Fig. 23 Winter oxygen deficit in lakes v. seasonal change in pH at lake surfaces.

the photosynthetic removal of carbon dioxide, which is the main control of pH in these lake waters (see also Appendix V, section E, for relationships between pH and carbonic acid concentrations in lake waters).

Lakes with similar geological backgrounds or similar positions in the basin drainage network are grouped in the plot of oxygen deficit against photosynthetic removal of CO_2 (Fig. 21). In this way the sequence of lakes from Houston to Knob Lake appear to have similar productivities, and the small lakes on shale and dolomite apparently fall in two groups indicating that shale waters are generally less productive (i.e. less extreme changes in pH) than dolomite waters. There is also some evidence in this diagram that the winter oxygen deficit is greater on small lakes than large lakes.

4. Iron.

The concentration of ferric iron in true solution in waters in the pH range 6 - 9 encountered in this study is well below the limit of analytical detection with the phenanthroline or tripyridine methods used (Garrels and Christ, 1965; Hem, 1967). The iron appearing in analyses of lake waters in the Knob Lake drainage basin is primarily particulate and highly insoluble ferric hydroxide, although some ferrous iron may be present as soil or sediment particles. In the more acid shale waters, some iron may be in solution with yellow organic acids (Shapiro, 1957). Ferric hydroxide in suspension in lakes may originate as ferrous carbonate formed by the contact of carbon dioxide with ferrous iron, which would be a product, for example, of the weathering of ankerite in the Denault dolomite formation. Ferrous bicarbonate is only stable if dissolved oxygen is less than 0.5 mg/l, a condition which may be attained at the mud-water interface. Ferrous iron in solution would be transported upwards into oxygenated water by turbulent exchange, and then be oxidised to insoluble ferric hydroxide.

The total quantity of analysed iron in the lake waters of the drainage basin amounted to 3.0 metric tons in winter, and 2.1 tons in summer, with run-off losses between the sampling periods amounting to about 0.5 tons. Pearce Lake contributed more than one-third of the iron in the winter survey, and one-sixth in the summer survey, but this is a reflection of the polluted state of this lake. Apart from the disturbed area around Pearce Lake, annual losses of iron from the basin are small, with an estimated yield of 0.23 kg ha^{-1} yr^{-1}.

The main mineral sources of iron are the Sokoman iron formation in the vicinity of Malcolm, Houston and Knob Lakes, ankerite in the Denault formation and iron oxides and sulfides in the Attikamagen and Menihek shales. Distributions of iron in lake waters (Figs. 24a, 24b and Table 13) appear to be related more to the ionic form of iron present in bottom sediments and lake basins than to absolute quantities of iron present in geological formations. For example, the lakes tributary to Easel Lake all contain appreciable quantities of iron (presumably as ferric hydroxide) which are best explained by the passage into water of ferrous iron released from crystalline dolomite or ankerite.

The modal value for iron in lake waters of the drainage basin, excluding Pearce Lake, ranges from 0.03 to 0.07 mg/l. Iron was not detectable, or near 0.01 mg/l, in the surface waters of large lakes (Knob and Malcolm) and in some lakes lying on shales. Higher concentrations (0.10 - 1.0 mg/l Fe) were associated with the smaller lakes on dolomite.

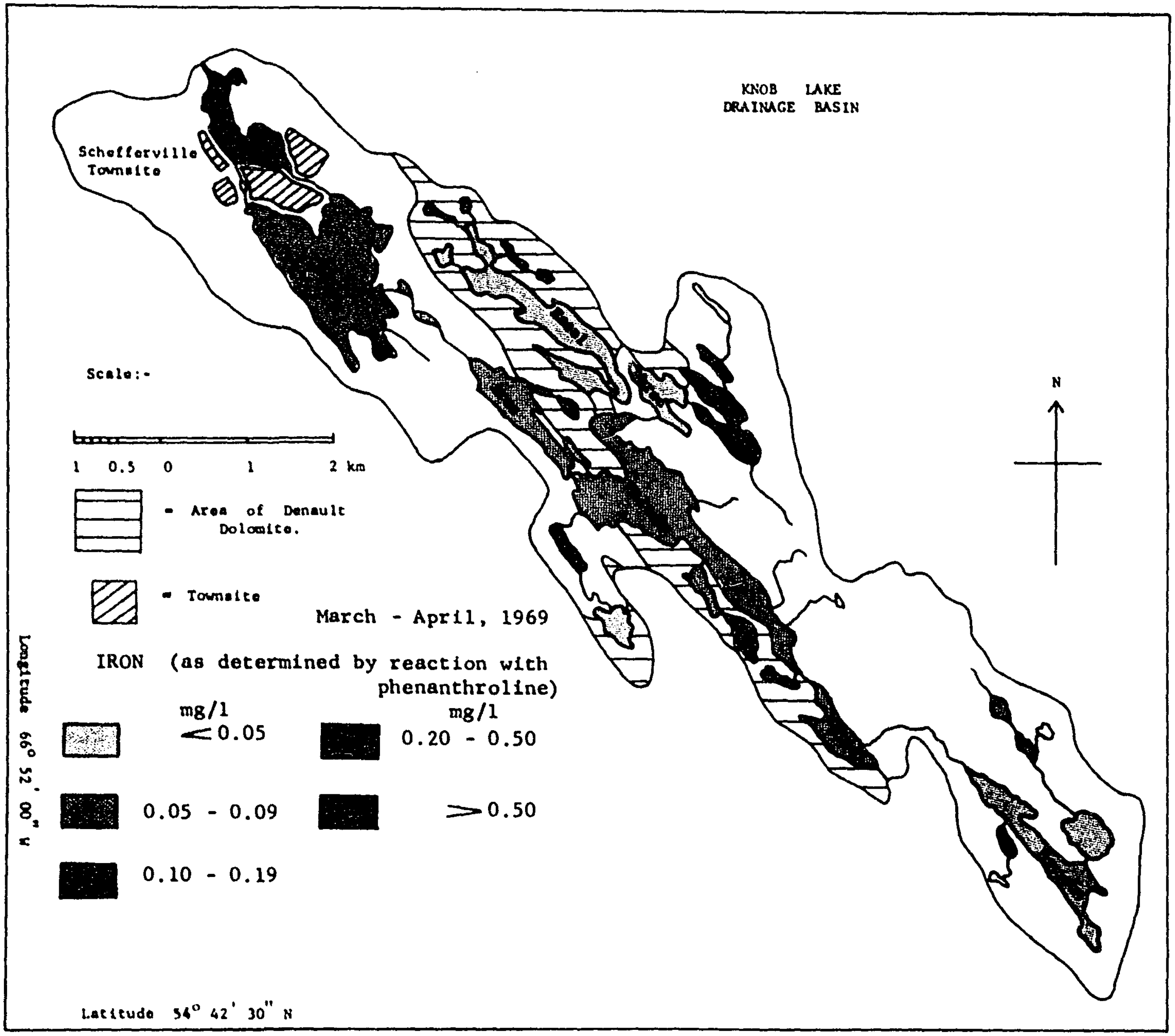


Fig. 24 a Distribution of iron in lake waters - winter, 1969.

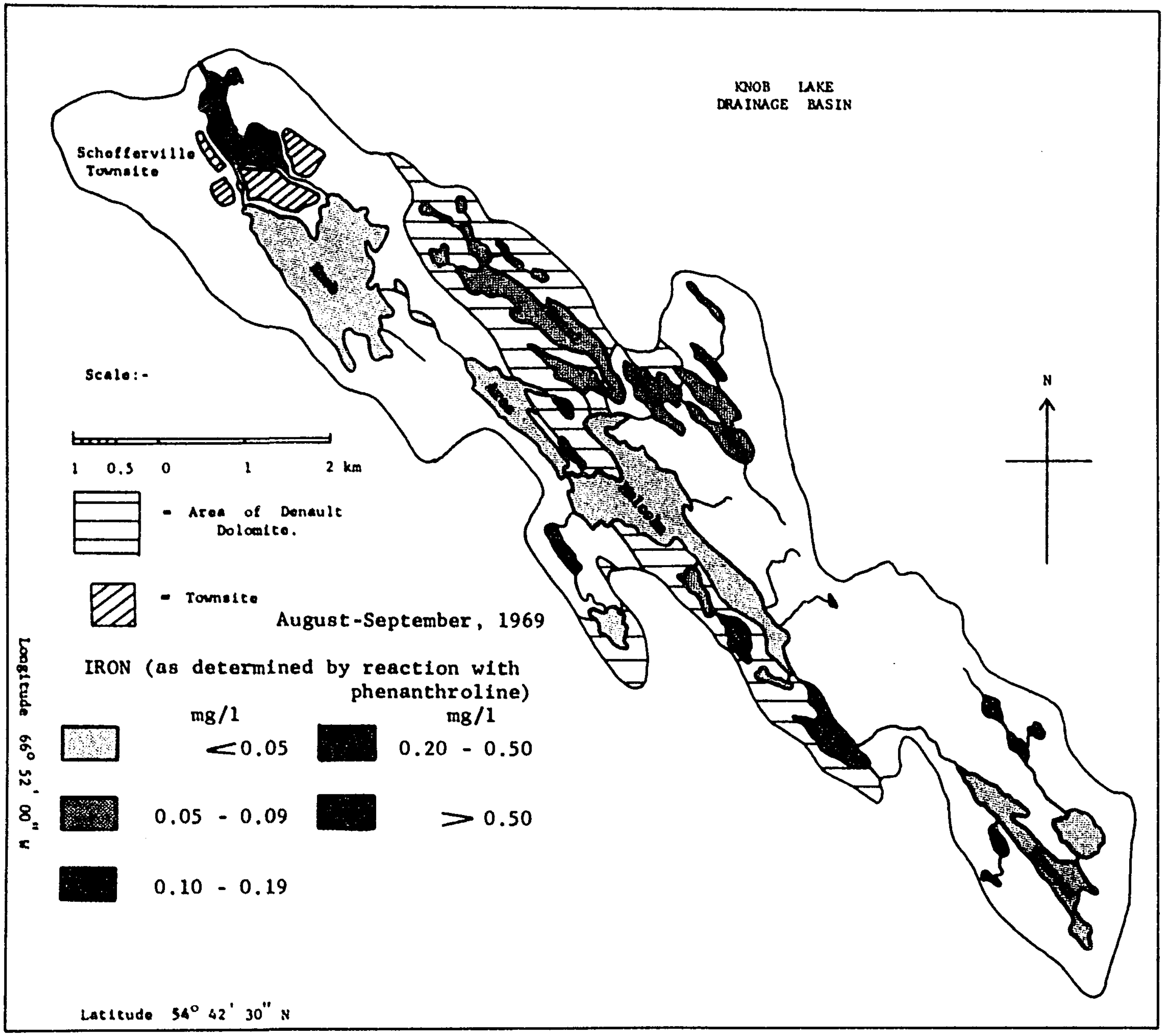


Fig. 24 b Distribution of iron in lake waters - summer, 1969.

Distribution in lakes of Knob Lake drainage basin
of iron reactive with phenanthroline
March-April and August-September, 1969

	Winter		Summer		Seasonal
	mean	Total (kg)	mean	Total (kg)	Change in storage (kg)
Communications	0.01	8	0.01	8	0
Houston	0.01	22	0.02	44	22
Osprey	0.05	54	0.12	130	76
Malcolm	0.05	520	0.03	310	-210
Phred	0.02	16	0.06	49	33
Gene	0.12	91	0.09	68	-23
Easel	0.01	57	0.05	290	233
Ares	0.05	69	0.04	55	- 14
Knob	0.05	540	0.03	320	-220
Pearce	0.80	980	0.30	370	-610
North	0.06	16	0.07	26	10
Middle	0.13	61	0.11	52	- 9
South	0.25	20	0.02	2	- 18
Bassett	0.66	83	0.17	21	- 61
Adams	0.04	24	0.01	6	- 18
Cowan	0.02	4	0.06	12	8
Panhandle	0.30	15	0.05	3	- 12
Findlay	1.00	45	0.05	2	- 43
Williams	0.75	15	0.06	1	- 14
Francois	0.18	4	0.08	2	- 2
Ives	0.30	25	0.10	8	- 17
Mattox	0.00	0	0.10	8	9
Gray	0.08	11	0.11	15	4
Hardy	0.50	39	0.12	9	- 30
Thorn			0.11	4	
Barr	1.60	140	0.18	16	-124
Lier			0.07	2	
Trigger	2.20	140	0.90	56	- 84
Dale			0.07	2	
Doris			0.37	2	

The total storage in winter amounts to c. 3 metric tons, compared with with 2.1 metric tons in summer. Pearce Lake accounts for 33 per cent of the total in winter, and 18 per cent in summer. The other large lakes, Knob, Malcolm and Easel contain much of the remainder.

The two acid lakes (pH below 6), Barr and Lier, also had iron concentrations in this range.

Although iron in true solution in ionic form would not be found in the lakes in concentrations much greater than 10^{-14} M, it is clear from the analyses reported above that transport of iron - as ferric hydroxide - does take place, and that, at a drainage basin scale, the release of iron from bottom sediments is quantitatively important. Although iron plays a negligible part in the ionic balance of the lake waters of this study, iron is not conserved within the basin as might be expected from its very low solubility.

5. Aluminium and Manganese.

Aluminium exists in solution as a cation (Al^{+3}) or anion ($Al_2O_4^{-2}$) (Hem, 1959). Cationic aluminium hydrolyses to form aluminium hydroxide, soluble to the extent of 500 mg/m^{-3} in pure water, while anionic aluminium, on hydrolysis, forms aluminic acid. Detectable quantities ($>$ 10 mg/m^{-3}) of Al^{+3} only exist below pH 5, and of $Al_2O_4^{-2}$ above pH 9. Lake waters near Schefferville are usually buffered between pH 6 and pH 8, so that aluminium is mainly present as the hydroxide, in solution and in particulate or colloidal form.

Aluminium was only determined in lake waters during the summer survey. Most lakes contained less than 100 mg/m^{-3} Al, although Doris Lake, lying below and exposure of Attikamagen shales in a road cutting, contained 530 mg/m^{-3}. The modal value for lake waters was about 20 mg/m^{-3}, concentrations being lower (c. 10 mg/m^{-3}) in larger lakes, and higher (40 - 70 mg/m^{-3}) in lakes on shale. A slight increase in concentration with depth was noted in

Cowan and Malcolm Lakes, and a decrease with depth in Easel and Knob Lakes, but changes in concentration are very small and could well have arisen from analytical error. The range of concentrations found in this study is comparable with the aluminium found in Wisconsin lake waters, which contained between a trace and 70 mg/m^{-3} Al, with a mean value of 16 mg/m^{-3} (Hutchinson, 1957, p. 822).

Manganese may occur in solid solution in dolomite and ankerite, and manganese dendrites have been described in fissures of the Denault dolomite (Nichols, 1968). The solution of manganese through the formation of manganous bicarbonate is analogous to the formation of ferrous bicarbonate (Ruttner, 1953, p. 87), and manganese was therefore sought in dolomite lake waters which contained appreciable quantities of iron. As is the case with iron, any manganese present was probably in particulate or colloidal forms. Manganese was found in winter in deep waters of Cowan Lake, the north arm of Easel Lake, and in Osprey Lake. Concentrations appeared to be in the range 0.1 - 0.3 mg/l Mn. Other dolomite waters examined showed no trace of manganese, nor did waters on shale or chert. Manganese was not found in the lakes in summer.

6. Sulfate and Chloride.

Sulfate in lake waters is derived from atmospheric precipitation, oxidation of sulfide minerals and the weathering of evaporate sediments (Hutchinson, 1957; Gorham, 1961). In the Knob Lake basin, precipitation is the primary source of sulfate, although pyritiferous bands in shales may yield locally higher sulfate concentrations. Chloride in lake waters near Schefferville is almost exclusively derived from precipitation.

When no mineral source of sulfate or chloride is present, the concentrations of these ions in surface waters decreases in proportion to distance from oceanic waters. According to Conway's study (1942 - cited in Hutchinson, 1957, p. 545) on chloride in American surface waters, lakes near Schefferville, 600 km from Hudson Bay or the Atlantic, should contain 0.1 - 0.4 mg/l chloride, and about 1 - 2 mg/l sulfate.

The distribution of sulfate in the lakes of the drainage basin in winter and summer, 1969, are summarised in Figs. 25a and 25b. The source data for the distribution maps are presented in Table 14. Sulfate concentrations are near the limit of detection with the technique used, and the relative accuracy of the results is not high. No comparable diagrams for chloride have been prepared, because winter analyses are believed to be incorrect, and because summer concentrations are too low to permit reliable comparison between lakes.

The estimated amount of sulfate in the lakes in summer (183 metric tons) is slightly less than the amount found in winter (193 metric tons). Losses in run-off between the surveys, based on concentrations in Knob Lake, were about 43 metric tons. In the lakes where there is no obvious mineral source of sulfate, concentrations were found in the range 1.0 - 4.0 mg/l, the range of concentration in atmospheric precipitation. Some shale lakes, particularly those in the Phred subbasin, contained higher concentrations of sulfate which probably resulted from the oxidation of sulfide minerals in Attikamagen and Menihek shales. The lowest sulfate values were found in dolomite lake waters, although lakes tributary to Easel Lake contained 4.0 - 9.0 mg/l SO_4^{-2}, and an exceptional value of 40 mg/l was found at the bottom of Cowan Lake. Generally, changes between winter and summer involved decreases in con-

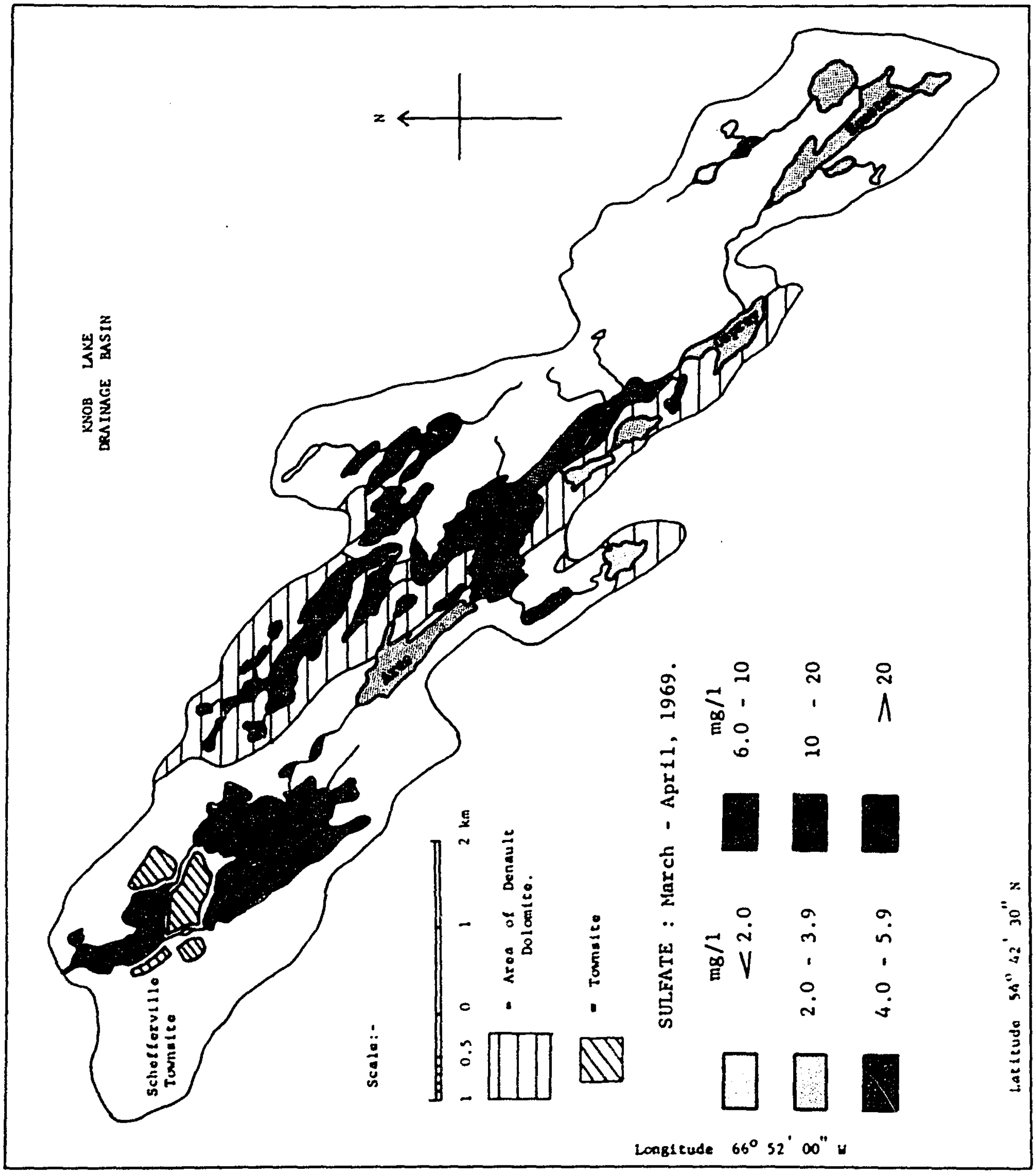


Fig. 25 a Distribution of sulfate in lake waters - winter, 1969.

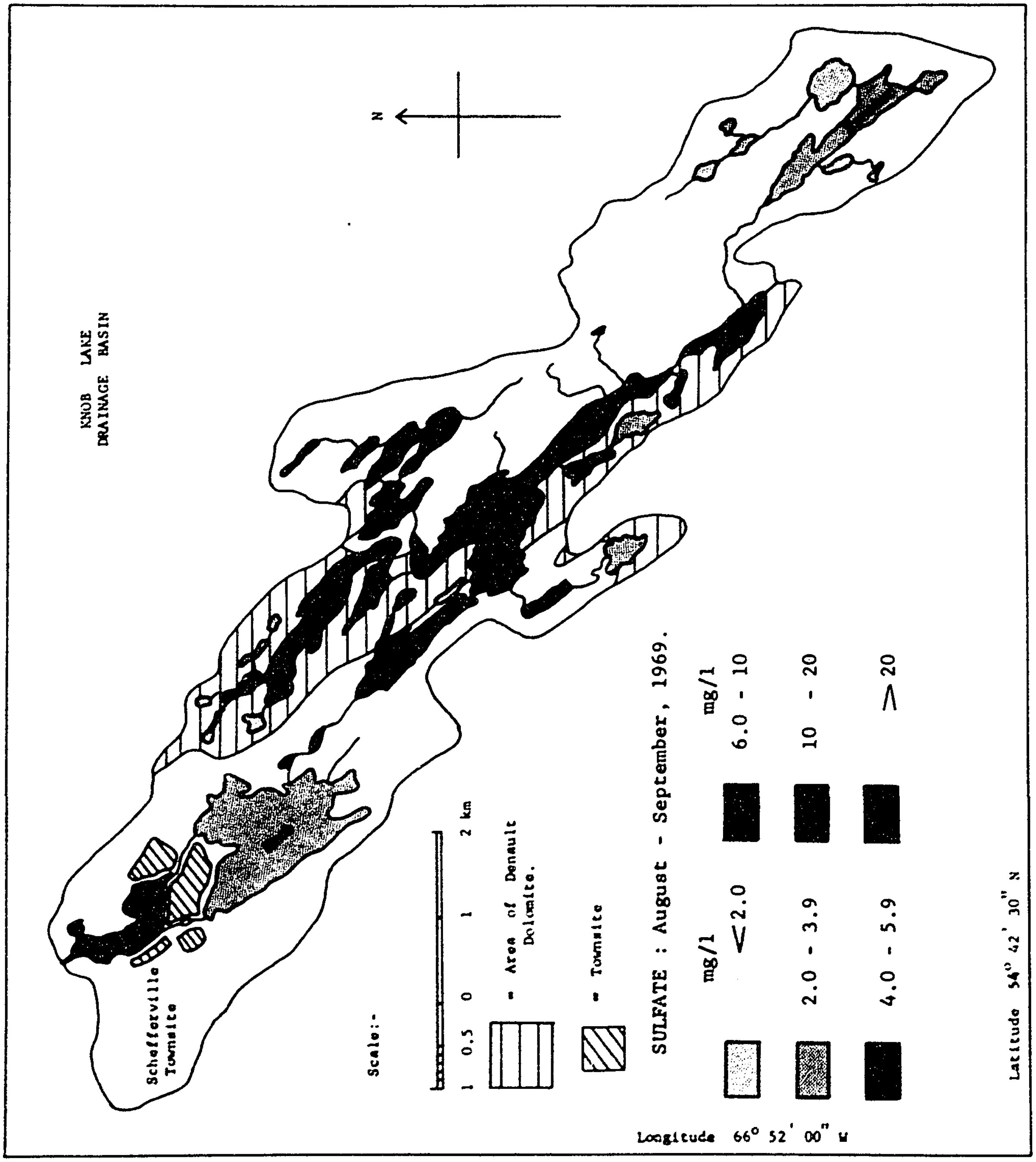


Fig. 25 b Distribution of sulfate in lake waters - summer, 1969.

Distribution of Sulfate in Lakes of Knob Lake Drainage Basin

	Winter		Summer		Seasonal change in storage
	mean (mg/l)	total (kg x 10^3)	mean (mg/l)	total (kg x 10^3)	(kg x 10^3)
Communications	2.0	1.6	0.5	0.4	- 1.2
Houston	2.7	5.8	2.2	4.8	- 1.1
Osprey	3.0	3.2	6.2	6.7	3.5
Malcolm	4.3	44.7	6.0	62.5	17.8
Phred	7.7	6.3	6.5	5.3	- 1.0
Gene	10.5	8.0	8.3	6.3	- 1.7
Easel	5.0	28.8	5.7	32.6	3.8
Ares	3.5	4.8	5.3	7.3	2.5
Knob	5.2	55.5	2.5	27.1	-28.0
Pearce	22	27.0	19	22.8	- 4.2
North	1.0	0.4	4.0	1.5	1.1
Middle	2.3	1.1	3.0	1.4	0.3
South	7.0	0.5	4.0	0.3	- 0.2
Bassett	4.5	0.6	5.0	0.6	0.1
Adams	1.5	0.9	2.0	1.2	0.3
Cowan	4.0	0.8	1.1	0.2	0.6
Panhandle	9.0	0.5	2.0	0.1	- 0.4
Findlay	6.0	0.3	1.0	0.05	- 0.22
Williams	8.5	0.2	2.0	0.04	- 0.13
Francois	9.0	0.2	2.0	0.04	- 0.13
Ives	4.5	0.4	4.5	0.4	0.0
Mattox	15	1.3	1.0	0.1	- 1.2
Gray	1.0	0.1	3.0	0.4	0.3
Hardy	4.0	0.3	2.5	0.2	- 0.1
Thorn			2.5	0.1	
Barr	3.0	0.3	1.0	0.1	- 0.2
Lier			1.0	0.03	
Trigger	c240	?	12.0	0.8	
Dale			5.0	0.15	
Doris			13.5	0.08	

Total winter storage 193 metric tons

Total summer storage 183 metric tons

Difference 10 metric tons

centration in small lakes, and increases in large lakes, with the exception of Knob Lake. The high sulfate values reported for Pearce Lake are abnormal and result from industrial waste water.

Chloride concentrations in the lakes in summer were in the range 0.3 - 1.0 mg/l. In those lakes where sulfate is no higher than 3.0 mg/l, the molecular ratio of sulfate to chloride is near 1:1, which is consistent with reported ratios in atmospheric precipitation (Gorham, 1961).

7. Sodium and Potassium.

Sodium and potassium are commonly present in natural waters as products of the weathering of feldspars and clay minerals. Sodium and potassium are also present in atmospheric precipitation in concentrations of a few tenths of a milligram per litre. Sodium is usually more abundant than potassium, though the ratio in which they occur depends on their mineral sources. For this study, sodium and potassium in lake outflow samples were determined using flame photometry by the Ministere des Richesses Naturelles de Quebec. The most frequently observed concentrations in Knob, Ares and Malcolm Lakes were 0.4 mg/l Na^{+1} and 0.3 mg/l K^{+1}, a molecular ratio of sodium to potassium of 2.2:1. Concentrations appeared to be lower on dolomite (0.2 mg/l Na^{+1} and 0.2 mg/l K^{+1} in Easel Lake) than on shales (0.5 - 0.6 mg/l Na^{+1} and 0.2 - 0.3 mg/l K^{+1} in Houston and Communications Lakes). Although these concentrations are low, the increase in the molecular ratio Na^{+1}:K^{+1} from 1.6:1 in Easel Lake to 3.5:1 in Houston and Communications Lakes is consistent with the weathering of albitic plagioclase which has been described in the Attikamagen and Menihek shale formations (Gross, 1968).

8. Nitrogen and Phosphorus.

Most of the soluble nitrogen in combined form in lake waters (amino-acids, ammonia, nitrite and nitrate) is derived from atmospheric nitrogen, either directly or from decaying vegetation, through the action of nitrifying bacteria in soils and lake water. Some algae, of which the Nostocaceae are an example (De, 1939), are able to fix atmospheric nitrogen directly. Nitrate nitrogen concentrations in unpolluted lake waters are rarely above 1 mg/l N and often below 0.1 mg/l N (Hutchinson, 1957, p. 836 ff.). Nitrogen present as ammonia may equal or exceed nitrate nitrogen concentrations in some lake waters. In this study, water samples were analysed for nitrate using a method which lacked sensitivity below 0.1 mg/l N. Generally, concentrations appeared to be in the order of 0.05 mg/l, both in winter and in summer. Concentrations were somewhat higher (c. 0.1 mg/l N) in small lakes with large catchment areas. The highest value found was at the level of the thermocline in Cowan Lake in late summer (0.17 mg/l N).

Phosphorus in lake waters is derived ultimately from the decomposition of phosphorus bearing minerals such as apatite, minute amounts in atmospheric precipitation, the decomposition of proteins in water and by diffusion from bottom sediments (Hutchinson, 1957). Apatite has been described as an accessory mineral in argillaceous horizons of the Denault dolomite formation and in the Attikamagen shales. Phosphorus is generally much less abundant than nitrogen in lake waters, and an appreciable part of the total phosphorus present (up to 90 per cent) may be in particulate form. Soluble orthophosphate, the form of phosphorus referred to in this study, consists mainly of the phosphate ion HPO_4^{-2}. Concentrations of soluble orthophosphate in the lakes in the drainage basin were near or below the limit of detection (i.e. concentrations of about 5 mg/m^{-3}). The maximum values, about four times this amount, were found in lakes bordered by shale and dolomite in the Phred catchment where some apatite may be present.

9. Ionic Ratios of Lake Waters in the Knob Lake Drainage Basin.

The sum of the equivalent or combining weights of common cations in natural waters approximately balances the sum of the corresponding cations (Hem, 1959). If all the major ions present in the water are included in the balance, and if all the ions are determined with comparable precision, the proportion of different ions contributing to the ionic balance may be used as a means of describing the overall composition of a water sample and of relating that sample to waters from different geological origins.

The ionic composition of the waters is summarised in the form of a Piper trilinear diagram (Piper, 1944), which shows the approximate range of ionic composition of all the lake waters in the basin (Fig. 26). Some data on relationships between specific conductance of water samples and total ionic composition are given in Appendix V, section F.

In this study, most water compositions are determined by weathering of carbonate minerals, and, in terms of ionic ratios, are essentially similar (see Chapter IV). Generally, the sums of calcium and magnesium, expressed as equivalent weights, balance the equivalent

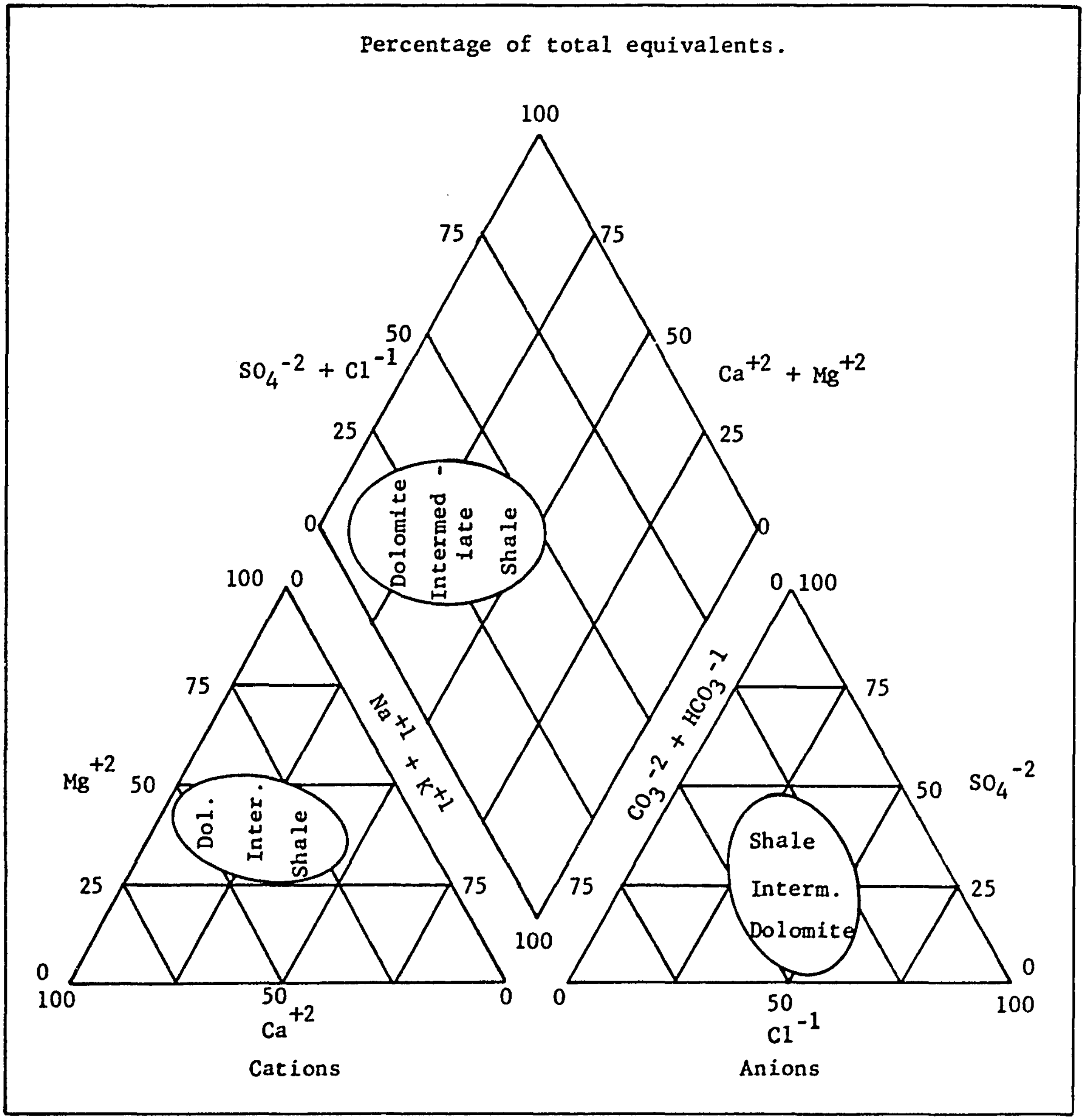


Fig. 26 Trilinear diagram illustrating range of ionic compositions encountered in the lakes of Knob Lake drainage basin (after Piper, 1944).

weight of the bicarbonate ion, the main exceptions occurring where weathering of sulfide minerals results in higher sulfate ion concentrations in lake waters. Because sodium and potassium are missing from most water analyses, and sulfate and chloride ions could not be determined with the same precision as the bicarbonate ion, it is not possible to present a detailed discussion of ionic balances of lake waters in this study. However, it is possible to present a brief outline of the order of abundance of common cations and anions encountered in the waters of the Knob Lake drainage basin.

The order of abundance of cations follows the sequence $Ca \geqslant Mg > Na > K \gg Fe \geqslant Al > H$ in all the lake waters examined. Because of the influence of the weathering of dolomite, many waters exhibit Ca:Mg ratios near unity. An impression of the relative importance of the cations may be gained from the Ca:Mg:Na:K ratios in characteristic lakes: in Knob Lake in winter (water of mixed dolomite and shale origin), 100:88:18:8 (molecular); in Easel Lake, on dolomite, 100:82:3:1.3 ; and in Houston Lake, on shale, 100:110:49:17. The proportion of Na^{+1} and K^{+1} in the cation balance is predictably greatest in shale waters where the influence of carbonate minerals is least. The sequence $Ca > Mg > Na > K > Fe \geqslant Al$ is characteristic of surface waters on old sedimentary or igneous rocks (Gorham, 1961; Hutchinson, 1957; Rodhe, 1949: Livingstone, 1963). Sodium and potassium dominate the ionic balance only in waters associated with recent marine sediments, evaporate deposits, or with igneous rocks deficient in calcium and magnesium.

The ratios of the common anions follows the sequence $HCO_3^{-1} > SO_4^{-2} > Cl^{-1}$. Since the bicarbonate ion concentration is generally determined by the solution of carbonate minerals in the presence of carbon dioxide, whereas sulfate and chloride are mainly of atmospheric origin, the anion ratios in individual lakes are a direct reflection of the influence of carbonate weathering. For example, the ratio HCO_3^{-1}: SO_4^{-2}:Cl^{-1} was 100:1.3:2.5 in Cowan Lake, on dolomite, in contrast with 100:12:8 in Houston Lake, on shale. The molecular ratio of sulfate to chloride is near unity in waters where no mineral source of sulfate is present. The order of anion abundance $HCO_3^{-1} > SO_4^{-2} \geqslant Cl^{-1}$ is again characteristic of inland waters on old sedimentary or igneous rocks. Sulfate and chloride are usually closely associated with sodium and potassium, and therefore also with marine and evaporate sediments.

CHAPTER VI

PEARCE LAKE: A CASE STUDY OF SETTLEMENT INFLUENCE

1. Introduction.

Pearce Lake (Fig. 27) receives municipal and industrial waste waters from Schefferville in addition to the normal throughflow from Knob Lake. Consequently, this lake is turbid, sometimes unsanitary, and has a chemical composition unlike the other lakes studied in the drainage basin. The present chapter is concerned with describing and evaluating some of the more conspicuous changes in the chemistry of Pearce Lake resulting from the discharge of waste waters. First, the sources of pollutants present in Pearce Lake will be reviewed, and the effect of lake bathymetry on water circulation will be considered. The chemistry of the lake water will then be described, and an attempt will be made to assess the circulation of waste waters within the lake, and the processes through which soluble wastes are removed from circulation.

2. Pollutant Sources.

Sewage treatment at Schefferville has been described in the section "Water Use in Schefferville' in Chapter II. There it was explained that the quality of the effluent from the plant depends on operating efficiency, which in turn depends on the volume of water passing through the system and the constancy of composition of raw municipal sewage. At Schefferville, plant efficiency may fluctuate between 60 and 90 per cent, in terms of removal of B.O.D. This means that Pearce Lake

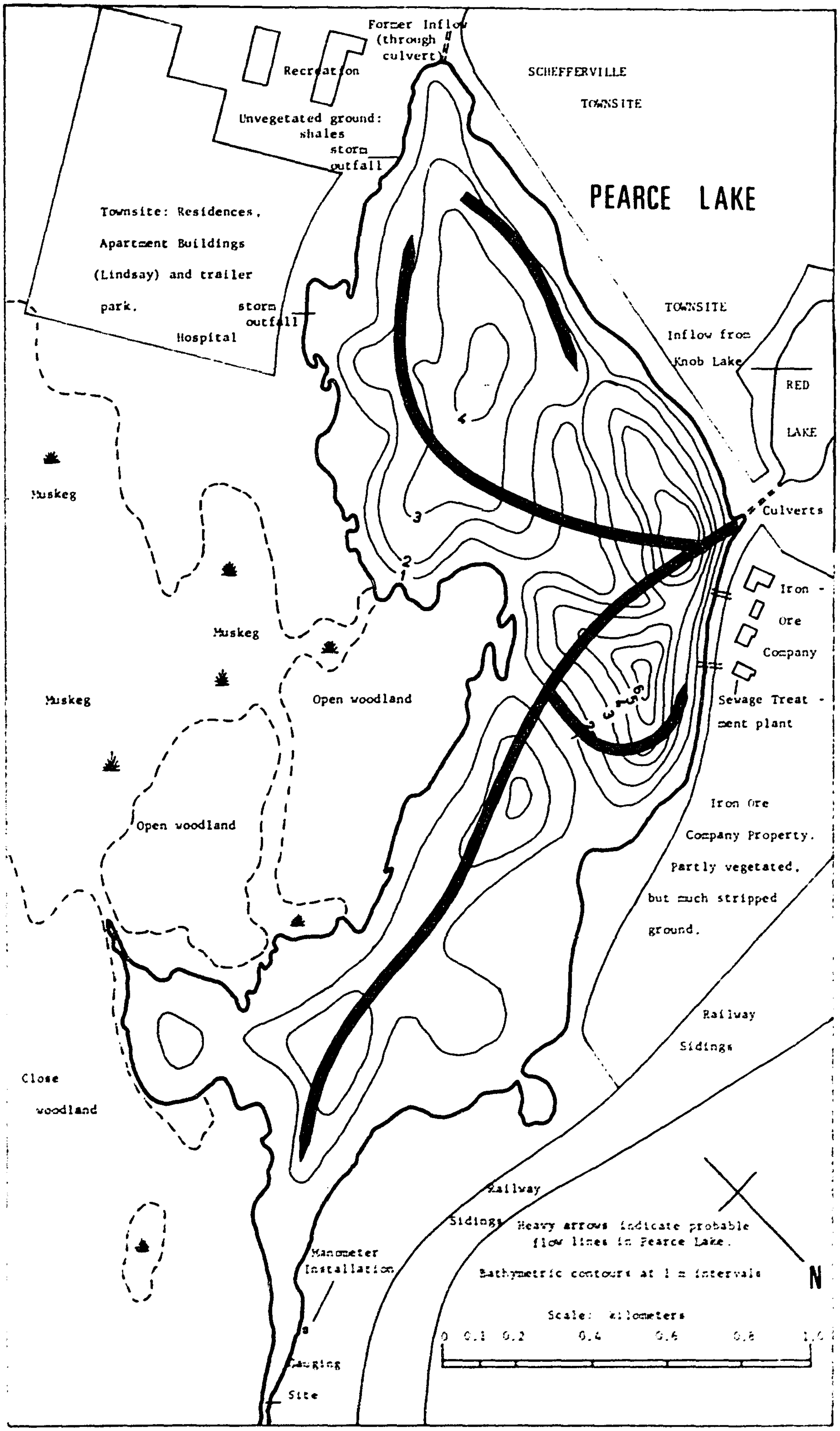


Fig. 27 Pearce lake, showing lake sourroundings, bathymetry and

daily receives between 50 and 100 kg of suspended and dissolved organic matter with a nitrogen content of 3.5 to 14 kg (based on sewage composition data in Fair and Geyer, 1958, p. 298). This is sufficient to maintain nitrate-nitrogen levels in Pearce Lake of 0.1 - 0.5 mg/l, which is in the range of observed concentrations. Similar estimates for phosphorus are more difficult, but extensive use of synthetic detergents with phosphate builders not readily degraded in activated sludge tanks may raise the phosphorus content of treated effluent above that of nitrogen. Water leaving sewage treatment plants also contains traces of metals dissolved from piping and hardware, and tends to have a higher sulfate and bicarbonate content than the original water supply. The domestic use of common salt also raises the sodium and chloride contents of receiving waters. There are two storm outfalls for the sewerage system located on the east side of Pearce Lake. Raw sewage is discharged into the lake through these outfalls during spring snowmelt and summer rains, adding to the lake's nutrient supply and contributing a measure of bacterial pollution.

The outfall from the iron ore testing plant at Schefferville is 100 m away from the sewage treatment plant outfall and close to the inflow from Knob Lake. The deposition of mineral particles opposite the outfall has created a delta which appears to deflect water entering Pearce Lake from Knob Lake. The water from this plant contains high concentrations of iron, particulate and in solution, sulfate, detergents and amine compounds. These are used in the flotation process used to separate iron ore. Sulfuric acid, the sulfate source, is buffered with strong alkali before discharge into Pearce Lake. It is unfortunate for the purposes of the present study that a strike of Iron Ore Company personnel closed this plant during the summer of 1969. Consequently the effect of mining operation on summer conditions in Pearce Lake was much less than in previous years. The lake was said to be far less turbid than usual. The analyses obtained from the late winter survey, before the commencement of the strike, give some indication of the chemical effects of ore testing effluent during winter.

Surface and sub-surface waters draining Schefferville townsite and the land bordering the northern arm of Pearce Lake also contribute to changes in water chemistry. Water seeps into Pearce Lake from the crushed shale underlying the townsite. Although no analyses were made of these seeps, an analysis of standing water on these shales gave a pH below 5, sulfate over 100 mg/l, and iron over 4 mg/l. If, as in this case, water composition is determined by the reaction of iron sulfide with water, seepage from the townsite would affect Pearce Lake water by depressing the pH and increasing concentrations of iron and sulfate. This would have about the same effect as the effluent from ore testing.

North of the townsite, a stream drains into Pearce Lake from the area of railway sidings west of the lake. During snowmelt and summer rain, this stream becomes a red-coloured suspension of iron oxide minerals which can be traced in Pearce Lake some distance away from the point of inflow. A similar stream, channelled through a culvert, enters Pearce Lake at the north-eastern corner, near the former inflow from Knob Lake. A bright orange precipitate coats the lakeshore in the vicinity of this outflow. Another stream enters the northern arm of Pearce Lake from the west side. This stream at the time of this study drained an area of muskeg and was unaffected by earth removal. A further source of suspended iron and the heavy oils and greases which line the lakeshore at the end of winter is the snow cleared from the roads which is dumped into Pearce Lake beside the townsite.

3. Effect of Bathymetry on Water Circulation in Pearce Lake.

Bathymetric data for the map of Pearce Lake (Fig. 27) were obtained from a survey by J. Moore and P. Grevatt in August, 1967, using a Heathkit echo sounder. The annual range of water level is about 40 cm, so depths are about 10 cm less than indicated in winter, and 30 cm greater in spring. That part of the lake opposite Schefferville townsite consists of two basins separated by a ridge 2 m below the surface which runs across the lake from beside the Knob Lake inflow to the headland opposite. One basin, oval-shaped and with a maximum depth of 7 m, lies in front of the sewage treatment plant. The other depression, 5.5 m deep, lies 150 m offshore from the Lindsay apartments on the east side of the lake. The elongated northern arm of Pearce Lake consists of a series of shallow basins 1 - 2 m deep.

The rate of transfer of water through Pearce Lake as a function of time is shown in Fig. 28. The residence times for lake water corresponding to the discharge from Pearce Lake outlet have been adjusted for the growth of the winter ice cover. This diagram shows that if the water in Pearce Lake were in continuous circulation and uniformly mixed, it would be replaced every 15 - 20 days from August to December, every 30 - 55 days in late winter, and every 3 - 10 days during the period of snowmelt run-off. In reality, the lake does not circulate continuously and is not uniformly mixed, and this diagram shows relative rather than absolute rates of transfer of water through Pearce Lake.

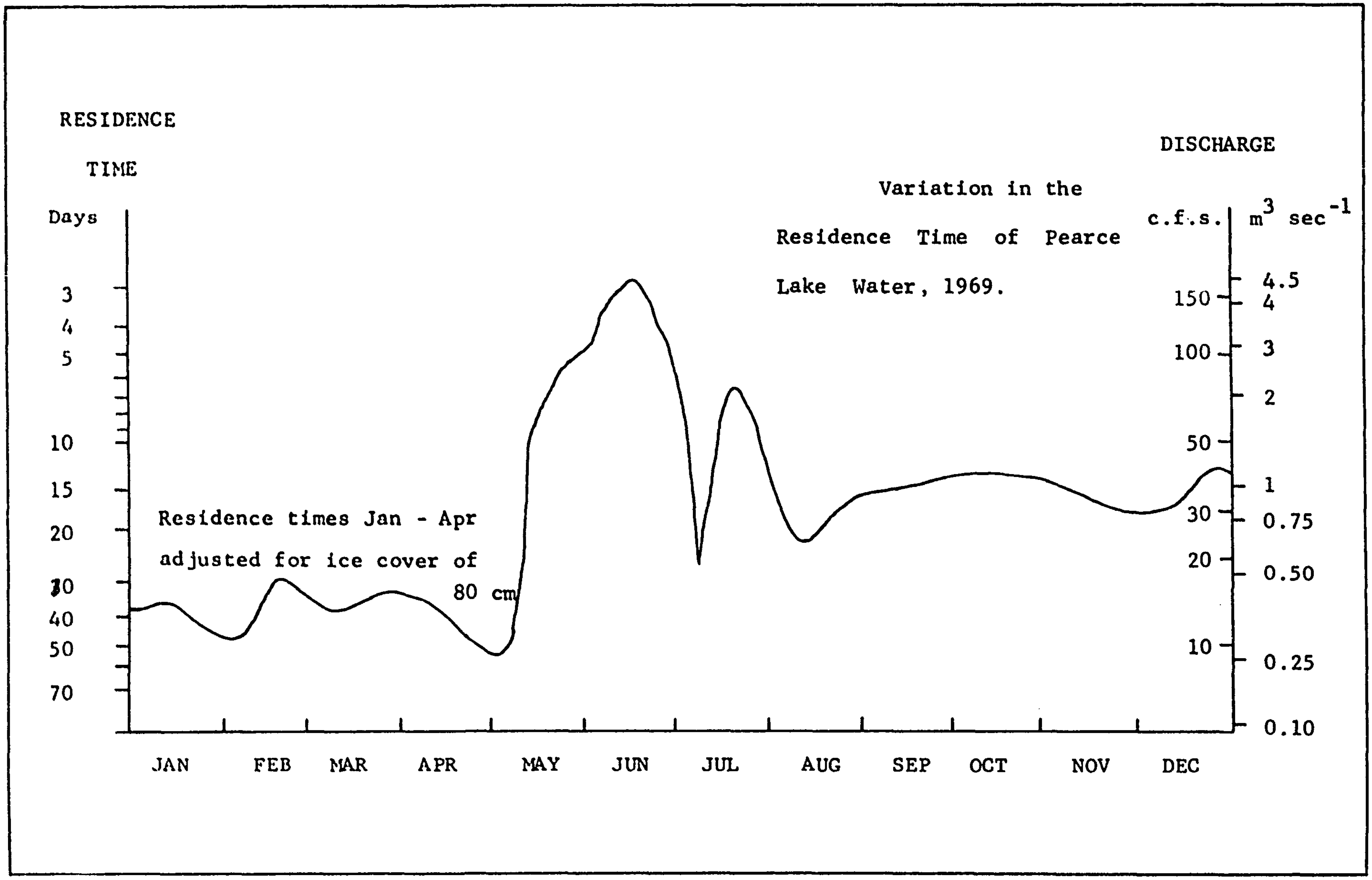


Fig. 28 Variation in residence time of Pearce Lake water as function of discharge and time of year.

A circulation pattern in Pearce Lake consistent with the bathymetry of the lake and direct observations of surface currents is indicated by arrows in Fig. 27. It is suggested that a major flow line runs from the Knob Lake inflow in an approximately straight line to the Pearce Lake outflow. Alongside this flow, there are two main vortices centred over the two larger depressions in the lake, opposite the water treatment plant and offshore from the Lindsay apartments. The suggested centres of these vortices are the areas of maximum turbidity during spring snow melt run-off (as seen from the air) and the areas where oil slicks and foam patches tend to persist.

Lake water in the main depressions and the associated vortices remains in Pearce Lake appreciably longer than water in the flow path from Knob Lake inflow to Pearce Lake outlet. Dissolved waste substances therefore tend to accumulate in these areas, particularly in the relatively deep water immediately opposite the sewage treatment plant. In this way, residence times of lake water and dissolved wastes vary considerably within the lake for a specified discharge at a particular time of year. However, without detailed knowledge of current distribution and turbulent exchange within the lake, it is not possible to attach any figures to the variation in residence time, beyond the statement that water near the bottom of the two depressions mentioned above may not be displaced during the winter period of ice cover.

4. Distributions of Dissolved Substances in Pearce Lake.

The chemistry of Pearce Lake water will be discussed under the four following headings:

a) Iron and sulfate; the major constituents added to Pearce Lake in effluent from ore testing operations, seepage from Schefferville townsite and in surface streams draining Iron Ore Company property.

b) Ions present in treated water leaving the sewage treatment plant (mainly Na^{+1}, K^{+1}, SO_4^{-2}, Cl^{-1}, NO_3^{-1}, PO_4^{-3}).

c) Reductions in dissolved oxygen resulting from the degradation of organic solids and high biological productivity, and variations in pH resulting from photosynthesis and possibly from the discharge of acid waste water.

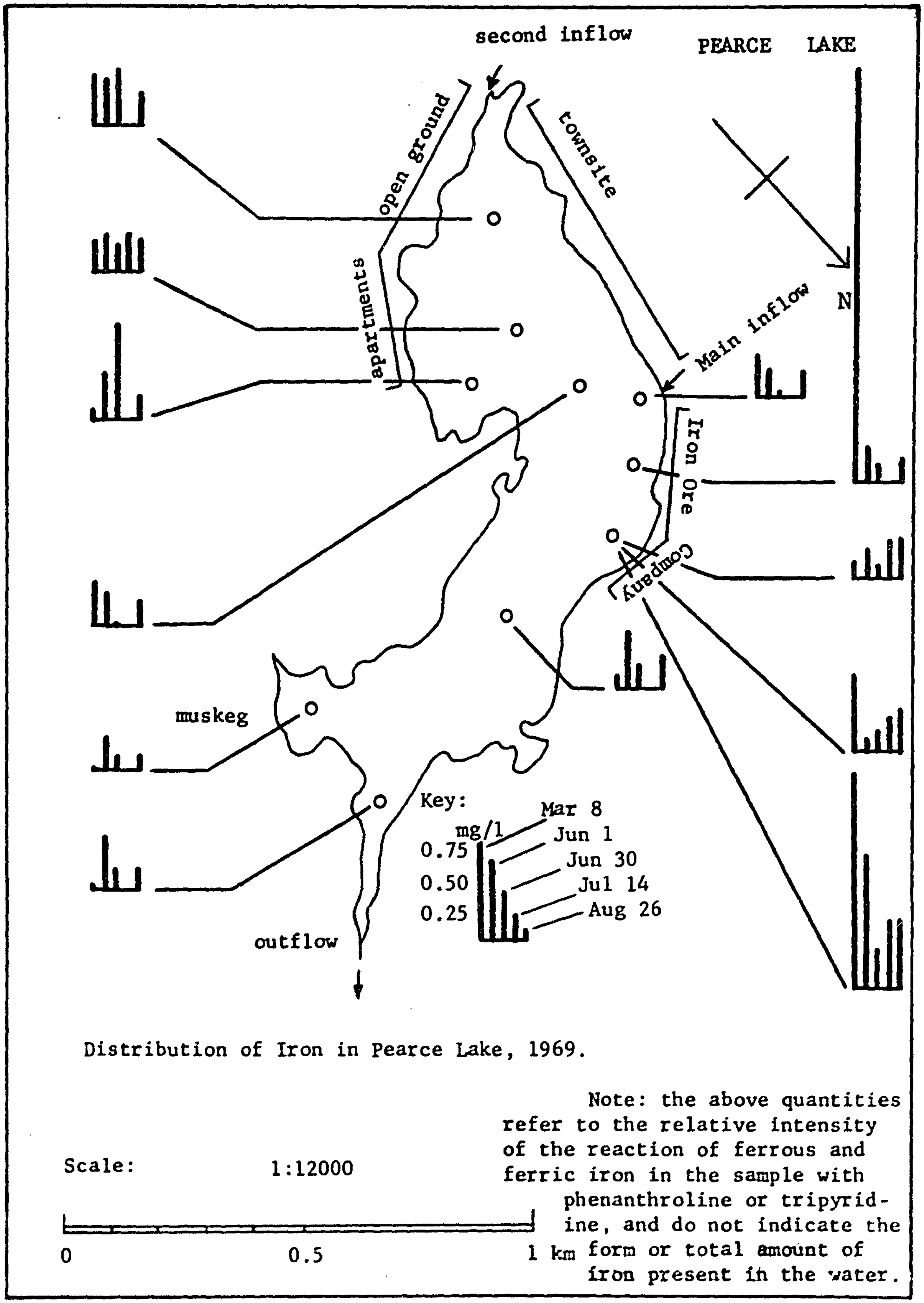
d) Dissolved silica, concentrations of which are controlled by chemical weathering around the townsite, and by uptake by diatoms.

e) Total ionic composition of Pearce Lake water. Bicarbonate, calcium and magnesium; ions of which the concentrations are primarily determined by throughflow from Knob Lake. The proportions of these ions are affected by waste water discharge into Pearce Lake, particularly by Na^{+1}, K^{+1}, SO_4^{-2} and Cl^{-1} present in waste water. The ionic balance of Pearce Lake water is described and used to estimate sodium and potassium concentrations in lake water.

The analyses on which the following discussions are based were obtained from samples collected from Pearce Lake in winter, 1969 (March 28), during and after the spring flood (June 1 and 30), in a period of warm, calm weather (July 17) and in late summer (August 26). Sampling locations, the approximate positions of which are indicated in Figs. 29 - 35, were chosen to describe changes in water chemistry with increasing distance from known pollutant sources rather than represent equal volumes of lake water. Histograms of concentrations found at different survey times are used to illustrate distributions, because the number of sampling sites was too small to permit mapping using isopleths. Samples were usually collected from the middle of the water column, but different levels (usually 3) were sampled opposite the ore testing outfall, the sewage treatment plant, and in the depression opposite the sewage treatment plant. The sampling on July 17, to find out whether short term vertical chemical gradients developed in calm summer weather, involved sampling at three levels at the two deepest sites in the lake, opposite the Lindsay apartment buildings and the sewage treatment plant.

a) Iron and Sulfate.

Distributions of iron and sulfate in Pearce Lake on sampling dates are illustrated in Figs 29 and 30. These diagrams show that concentrations of these two constituents in Pearce Lake in winter tended to reach a maximum in the relatively deep water offshore from the ore testing plant and the sewage treatment plant outfalls. Concentrations were consistently high in the southern arm of Pearce Lake, near the townsite shore and the apartment buildings, but tended to fall towards the Pearce Lake outflow. Iron concentrations ranged from a maximum of 3.5 mg/l beside the ore testing outfall to 0.01 mg/l in the small bay near the lake outflow. Sulfate ranged from 80 mg/l at a depth of 6 m offshore from the sewage treatment plant to 13 mg/l near the lake outflow.



Note: the above quantities refer to the relative intensity of the reaction of ferrous and ferric iron in the sample with phenanthroline or tripyridine, and do not indicate the form or total amount of iron present in the water.

Fig. 29 Distribution of Iron in Pearce Lake, 1969.

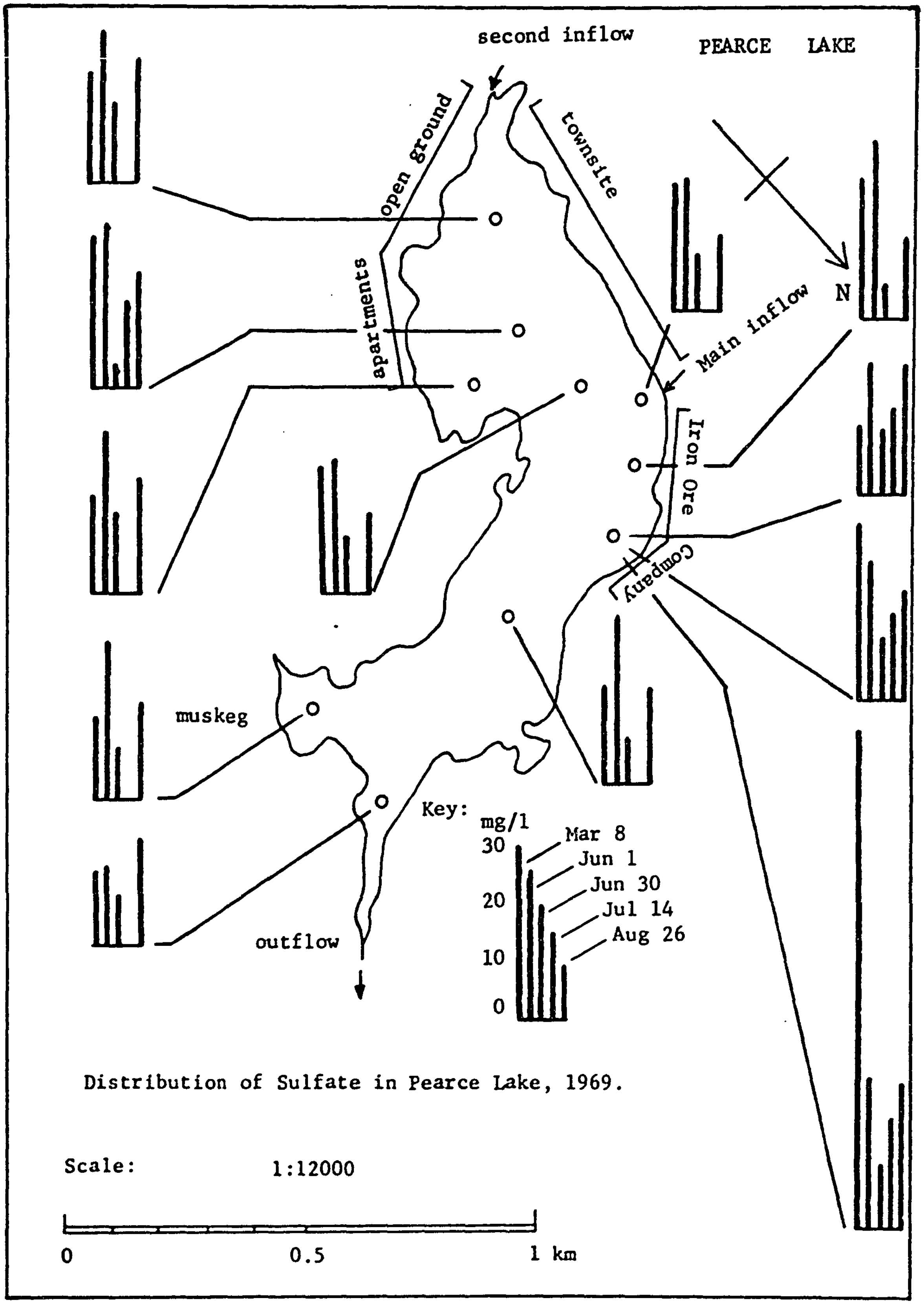


Fig. 30 Distribution of Sulfate in Pearce Lake, 1969.

The average residence time of lake water at this time was of the order of 30 days, but the water in the deeper depressions of the lake seemed to be stagnant at this time.

During the two spring surveys, June 1 and June 30, average lake water residence times were 5 and 10 days respectively, and the volume of water passing through the lake was sufficient to redistribute local concentrations of dissolved solids. Iron concentrations remained high on June 1 (0.3 - 0.5 mg/l being present throughout the lake) but began to fall with distance from the townsite on June 30. These uniformly high iron concentrations suggest vertical transport from iron-rich bottom sediments, or the presence of quantities of suspended iron brought to the lake by surface run-off near the townsite. On June 1, sulfate concentrations were as high or higher than in late winter, but by June 30, these concentrations had fallen to between 3.5 and 12 mg/l, reflecting the throughflow of Knob Lake water with a sulfate content of 3 - 4 mg/l.

Samples taken on July 17 and on August 26 revealed the beginning of a build-up in concentration following the passage of the spring flood. Iron ranged from 0.15 mg/l (near the outflow) to 0.4 mg/l (beside the sewage treatment plant). Higher values were obtained near bottom sediments. Sulfate was again present in concentrations of about 20 mg/l, higher in the south end of the lake, and lower in the north end.

The overall distribution of iron and sulfate in Pearce Lake suggests that the passage of the spring flood through the lake does not 'flush out' excessive concentrations of these substances from the lake, but rather tends to redistribute them. The persistence of higher concentrations in the two main depressions supports the suggestion that vortices exist in these areas which are to some extent independent of wind and wave action. Even though the ore testing plant was not operating during the summer period, concentrations of both iron and sulfate persisted at a high level through most of the period. This may point to the importance of surface and sub-surface drainage around Schefferville in determining the composition of Pearce Lake. Had the ore testing plant been in operation, concentrations of suspended iron would have been much higher, and the transparency of the lake water much lower, as was the case in 1968 and in 1970.

b) <u>Ions present in municipal sewage</u> (primarily Na^{+1}, K^{+1}, SO_4^{-2}, NO_3^{-1}, PO_4^{-3}).

A number of anions and cations are present in municipal sewage which are not removed by conventional treatment processes and which may affect the ionic balance of receiving waters. The more abundant ions are sodium, potassium, calcium, magnesium, chloride, sulfate and bicarbonate (Klein, 1965 p. 90). Calcium, nagnesium and bicarbonate will be treated separately in a subsequent section, since these ions are closely linked to the natural ionic balance of the water flowing into Pearce Lake from Knob Lake. The yield of dissolved minerals in North American sewage amounts to about 80 gms per capita per day (Fair and Geyer, 1958). On this basis, Pearce Lake receives 280 kg per day of dissolved minerals in waste water, sufficient to maintain average concentrations in Pearce Lake of 7.0 mg/l in winter and 3.5 mg/l in summer.

Available analyses of waters discharging from Pearce Lake indicate sodium concentrations of 0.7 - 1.5 mg/l, and potassium concentrations of 0.3 - 1.0 mg/l, in excess of concentrations in natural run-off from Knob Lake (0.3 - 0.4 mg/l Na^{+1}; 0.2 - 0.3 mg/l K^{+1}). Similarly, water discharged into Pearce Lake from Knob Lake in summer contains c. 0.8 mg/l Cl^{-1}, compared with values of 1.8 - 2.8 mg/l obtained within Pearce Lake, suggesting municipal contributions of chloride in Pearce Lake of 1 - 2 mg/l Cl^{-1}. A similar contribution of sulfate would be expected, but the additional sulfate is obscured by the sulfate in ore-testing effluent and surface run-off into Pearce Lake, which raises overall sulfate concentrations in Pearce Lake by 15 - 20 mg/l. Together, the quantity of additional ions in Pearce Lake balance well with the additions indicated by the figures in Fair and Geyer (1958). The contributions of these ions will be considered further in the next section where the problem of changes in the ionic balance of Pearce Lake water will be discussed.

Nitrogen and phosphorus compounds are present in municipal sewage, and also occur in treated effluents in amounts proportional to the efficiency of the treatment plant. Nitrogen and phosphorus compounds in organic matter (mainly proteins) breakdown through bacterial decomposition to yield nitrate and phosphate ions, which are used as indicators of organic pollution. However, in polluted waters, decomposition may be incomplete, and nitrate and phosphate ions, as they are released, may be utilised in plankton production. Analyses of nitrate and phosphate therefore give an incomplete picture of organic pollution.

The case for phosphorus in Pearce Lake is presented in Fig. 31. In winter, very high concentrations of phosphate (PO_4^{-3}), in excess of

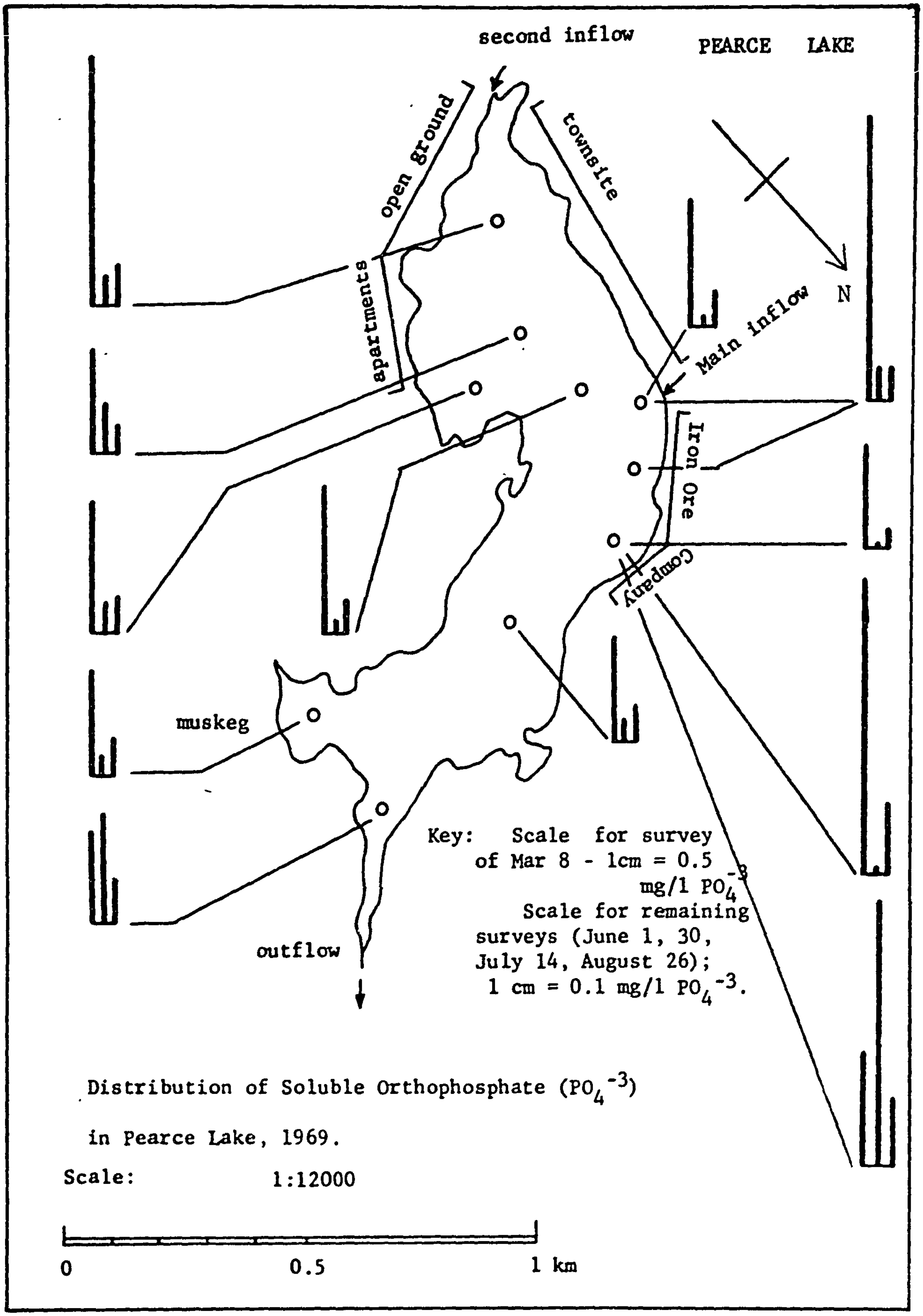


Fig. 31 Distribution of soluble orthophosphate (PO_4^{-3}) in Pearce Lake, 1969.

2mg/l, were present near effluent outfalls and in the southern arm of Pearce Lake. Even at the outflow of Pearce Lake, a value of 0.8 mg/l PO_4^{-3} was obtained. During the spring melt, phosphate concentrations fell sharply to 0.01 - 0.10 mg/l, values which could be expected in moderately eutrophic lakes, rather than polluted waters. Higher concentrations persisted in the deeper depressions in Pearce, where the spring circulation had not penetrated. By August 26, phosphate levels in Pearce Lake ranged between 0.03 and 0.08 mg/l; these values, although quite low, suggest that plankton production[1] does not proceed at such a rate in Pearce Lake as to exhaust the phosphate supply in waste water.

The organic phosphorus content of municipal sewage is related to the protein content of the diet of the population served by the sewage disposal system. In the U.S.A., the daily per capita phosphorus yield is estimated at 1.5 gms, giving concentrations in municipal sewage around 0.5 - 1.0 mg/l P (Sawyer and McCarty, 1967). If half this amount reached Pearce Lake, the lake waters would contain an additonal 0.02 mg/l P in summer and 0.06 mg/l P in winter (0.06 - 0.18 mg/l PO_4^{-3}). These values are considerably smaller than those observed in Pearce Lake in winter, although they are in the same range as those found in the spring and summer surveys. The additional phosphorus in winter is probably inorganic in origin, being derived from synthetic detergents which can raise the phosphorus content of treated sewage ten-fold. In Pearce Lake, the ore testing plant outfall may be a source of such undegraded

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[1] Although no productivity data are available for the period of this study in 1968, primary production in Pearce Lake reached 2,000 mg. C/m^3/day compared with 20 mg. C/m^3/day in Knob Lake, Moore, 1967).

detergents. Because the phosphate builders in detergents are resistant to biological degradation, they tend to persist in receiving waters.

It is possible that in Pearce Lake, where there is considerable ferric iron present in suspension, that ionic phosphorus released from detergents may react with iron to form a highly insoluble ferric phosphate compound, which is precipitated to the lake bottom. Calculations using a suggested equilibrium constant for ferric phosphate (10^{-32} : Cooper, 1948) and theoretically estimated ferric iron activities suggest that a small fraction of the analysed orthophosphate would be lost to the lake in this way. However, where large quantities of iron persist in suspension, ferric phosphate may form continuously in dynamic equilibrium with iron and phosphorus present in the water, and so result in partial removal of phosphorus from the water. A mechanism of this kind has been suggested for sea water (Harvey, 1955). Although Pearce Lake water is in approximate equilibrium with hydroxyapatite (based on data in Kramer, 1967), this compound is slow forming in fresh water, and the formation of ferric phosphate appears to be the most likely chemical process of removal of phosphorus from the water.

Less can be said about nitrate, because of the questionable reliability of the analyses. The nitrogen content of treated waters leaving the sewage treatment plant at Schefferville is sufficient to maintain nitrate-nitrogen levels in Pearce Lake between 0.1 and 1.0 mg/l, depending on the residence time of the lake water and the efficiency of the treatment plant in removing nitrogen from raw sewage (given the N content of sewage to be 10 gm per capita per day; Fair and Geyer, 1958, p. 298). Observed concentrations of nitrogen as nitrate in Pearce Lake were in the range 0.3 - 0.5 mg/l in March and 0.25 - 0.35 mg/l in August. These concentrations would be consistent with sewage plant operating efficiency between 70 and 90 per cent in terms of nitrogen removal, if no allowance were made for nitrogen present as ammonia, nitrate or amino acids, or for the biological utilization of nitrogen. If allowance were made for these factors, the total amount of nitrogen in Pearce Lake would be doubled or trebled.

c. Dissolved Oxygen and pH in Pearce Lake.

Dissolved oxygen concentrations in Pearce Lake are determined by the balance between the supply of oxygen from the atmosphere and through photosynthesis, and the removal of oxygen by zooplankton and the breakdown of organic matter to carbon dioxide and water. In winter, lake ice almost eliminates the contact of lake water with the atmosphere, and in this condition, biological decomposition may dominate and exhaust the supply of dissolved oxygen in the water. In March, 1969, the waters of Pearce Lake, if they had been in equilibrium with atmospheric oxygen, would have contained about 14 mg/l O_2 at 0°C and 12.5 mg/l O_2 at 4.0°C. Instead, lake waters contained about 2 mg/l O_2 (c. 15 per cent of saturation), falling to less than 1.0 mg/l (8 per cent saturation) near the two effluent outfalls, and rising to 5.0 mg/l (40 per cent saturation) near the lake outflow. These figures imply that more than 10 mg/l O_2 had been removed from the lake since ice formation in mid-November. Assuming that oxygen removal continued until break-up, or at least until the arrival of the spring food, lake water in the deeper depressions and in shallow bays probably became almost devoid of oxygen by the end of winter. The occurrence of dead fish in lake ice, high concentrations of ferric hydroxide in suspension, and an odour of H_2S after break-up all suggest that this was the case.

On June 1, when ice still partially covered Pearce Lake, dissolved oxygen levels were 8.0 - 9.5 mg/l (65 - 75 per cent saturation) compared with about 10-12 mg/l O_2 in Knob Lake. Vertical gradients in dissolved oxygen persisted opposite the sewage treatment plant outfall and in the depression opposite the Lindsay apartments - further indications that the passage of snowmelt run-off through Pearce Lake does not result in uniform mixing. The average residence time of Pearce Lake water on June 1 was about 5 days; Pearce Lake, therefore, was probably removing between 1 and 2 mg/l O_2 from the water flowing in from Knob Lake. This implies that the redistribution of unoxidised organic matter in the lake imposes a high short-term oxygen demand on the lake which is met by the reservoir of dissolved oxygen in Knob Lake. The mixing of low oxygen waters in Pearce Lake with throughflowing waters would also tend to reduce dissolved oxygen levels.

The two subsequent surveys, after the spring flood (June 30; July 14) showed that surface waters contained 9.0 - 10.5 mg/l O_2 (10.0 on July 14). The values for June 30 are between 85 and 100 per cent of saturation, and they occur at a time when widespread algal growth was taking place. Surface waters were supersaturated with dissolved oxygen on July 14, a consequence of calm weather, and perhaps of photosynthesis diurnal heating. However, deep water at the two depression sites was undersaturated with oxygen (between 70 and 80 per cent saturation), which suggests that longer periods of calm summer weather at Schefferville could lead to stagnation in bottom waters.

By the end of August, when the oxygen saturation level was 10.5 mg/l, the observed range of concentrations was 8.5 - 11.0 mg/l O_2, between 85 and 110 per cent saturation for a water temperature of 12 - 13°C. Concentrations were lower near waste water outfalls and in the southern arm of the lake, and the maximum value was found near the outflow. A value of 6.2 mg/l O_2 was obtained from the bottom of the depression opposite the Lindsay apartments. To summarise these results, the renewal of Pearce Lake water by throughflow from Knob Lake and contact with atmospheric oxygen is sufficient to maintain lake waters at 75 per cent saturation or over during the ice-free period of the year. However, after ice formation, when residence times of lake water increase, reaeration ceases, and gradual depletion of oxygen follows, probably leading to complete exhaustion of oxygen in waters near bottom sediments.

The distribution of pH in Knob Lake is summarised in Fig. 32. In March, pH values were near or below neutrality (6.65 - 7.1), the lowest values being found near waste water outfalls and near the lake outflow. These values are about 0.5 pH unit below corresponding values in Knob Lake. On June 1, the pH fell in the range 6.4 - 6.8 in Pearce Lake, compared with 7.0 in Knob Lake. This time the lowest values were obtained from bottom waters in depressions. Although the lower pH values obtained from Pearce Lake in comparison with Knob Lake may be a simple reflection of the higher biological productivity of Pearce Lake, and therefore of the greater release of carbon dioxide in winter, it is possible that the reaction of ferrous sulfide in bottom sediments with oxygen and water, forming dilute sulfuric acid, may be an additional

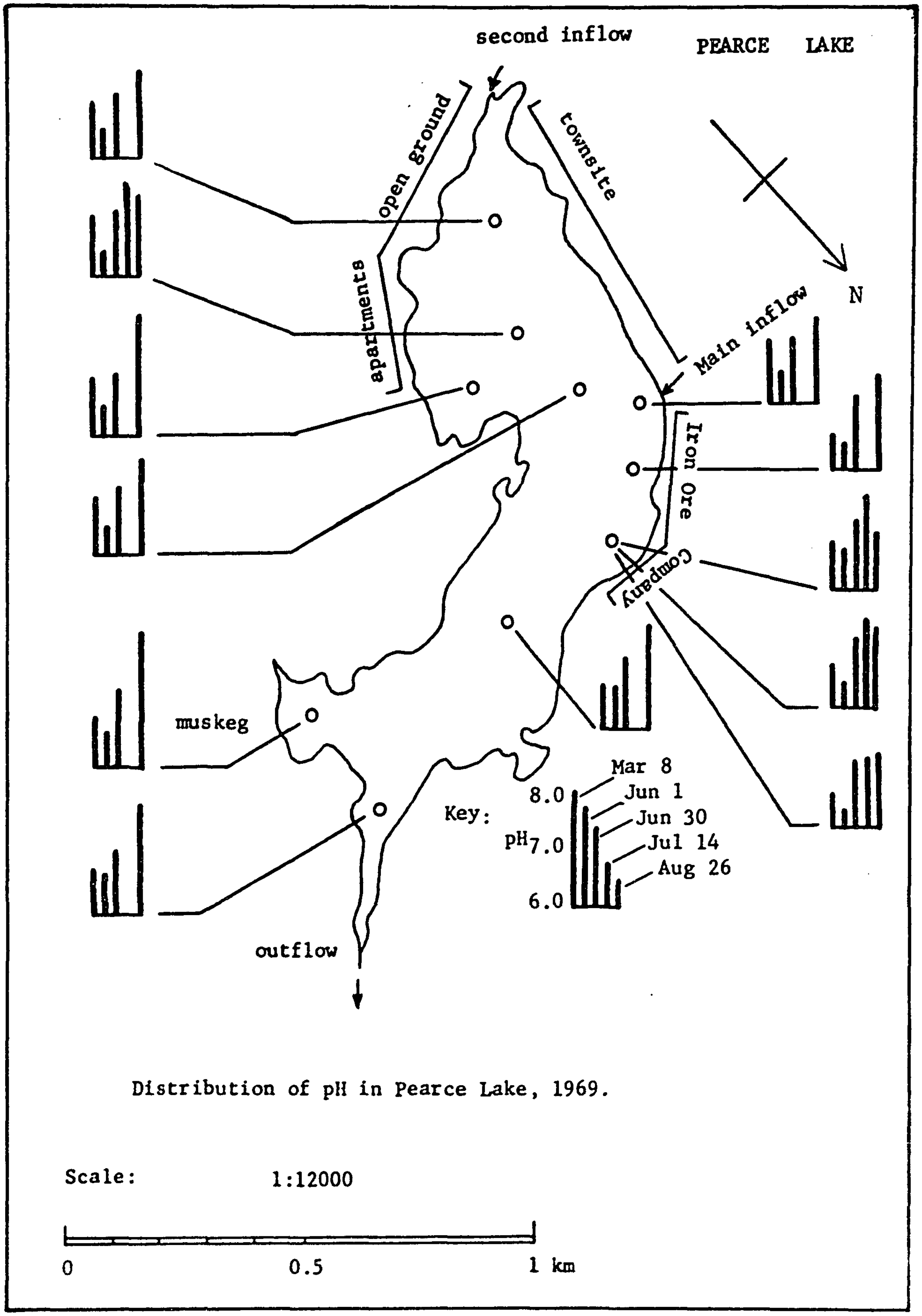


Fig. 32 Distribution of pH in Pearce Lake, 1969.

control of pH. Every 2 moles of FeS_2 oxidised yield 1 mole of hydrogen ions, but since the total iron present in Pearce Lake is not much more than 10^{-6} molar, the size of the change in pH brought about by such oxidation would not be much greater than 0.2 - 0.3 pH unity.

The remaining surveys (June 30, July 14 and August 27) reveal rises in pH in response to the uptake of carbon dioxide in photosynthesis. The uptake reaches a maximum in late August, when pH values greater than 8 were found in the north and south ends of Pearce Lake, although the value of pH of 7.1 near the sewage treatment plant outfall suggests an addition of slightly acid waste-water or surface drainage. In general, the pH range of water in Pearce Lake is comparable with the dolomite lakes tributary to Easel Lake, and is probably related more to rates of plankton photosynthesis than to inorganic controls of pH such as the oxidation of iron pyrites.

d) Dissolved Silica in Pearce Lake.

The major sources of soluble silica in Pearce Lake are throughflow from Knob Lake, the weathering of shales around Schefferville townsite, and silica brought into solution in the ore testing procedure and discharged into Pearce Lake through the ore-testing plant outfall. Silica is removed from Pearce Lake by discharge through the lake outflow and through uptake by diatoms and subsequent sedimentation on the lake floor.

Silica concentrations in March ranged from 2.5 to 5.8 mg/l SiO_2, being highest near the ore-testing and sewage plant outfalls, and lowest near the lake outflow. A noticeable gradient existed opposite the sewage plant outfall; 2.8 mg/l SiO_2 at 1 m, 3.8 mg/l at 3 m, and 5.8 mg/l at 5 m. On June 1, the range was 1.5 - 3.3 mg/l SiO_2, with most samples containing 2.7 - 2.9 mg/l. These concentrations are somewhat higher than in Knob Lake (2.4 mg/l) and imply a local mineral source of soluble silica. On June 30, silica concentrations had fallen to about 2 mg/l (range 1.5 - 2.3 mg/l). This depletion probably reflects silica uptake by diatoms. This trend continued in the next two surveys. On July 14, observed concentrations of silica were in the range 1.1 - 1.35 mg/l in the two sites investigated. On August 27, concentrations fell still further to 0.8 - 2.0 (one value of 2 mg/l SiO_2 was recorded from 4.5 m in the depression offshore from the Lindsay apartments). The lowest value of silica occurred in the southern arm of Pearce Lake. Water flowing in from Knob Lake at the time contained 1.8 mg/l SiO_2. The removal of silica from Pearce Lake is probably a reflection of plankton blooms which occur in this lake (J. Moore, 1968, pers. comm.). The surveys described above suggest that one-third or more of the silica entering the Pearce Lake is taken up. During the months of July and August alone, this would mean that between 2.5 and 3.5 metric tons of silica were removed from the lake. Some of this silica, if it forms the skeletal matter of diatoms, would be sedimented to the lake bottom, some would be redissolved, and some would be lost to the lake through the outflow.

e) Ionic Composition of Pearce Lake Waters.

At the close of Chapter VI, a short section was included on molecular ratios of common anions and cations in lake waters near Schefferville. Calcium, magnesium and bicarbonate, being associated with the weathering of dolomite, generally dominated the ionic balance. In comparison, sodium and potassium, sulfate and chloride were relatively uniformly distributed in surface waters of the drainage basin, in smaller concentrations reflecting atmospheric and local mineral sources of these ions.

In Pearce Lake, sodium, potassium, sulfate and chloride are present in greater concentrations because they occur in the waste waters which enter the lake. In this section, the nature of the resulting changes in ionic balance which took place in 1969 will be described. The changes will be discussed by considering the following ratios as indicators of shifts in ionic ratios in response to waste water discharge:

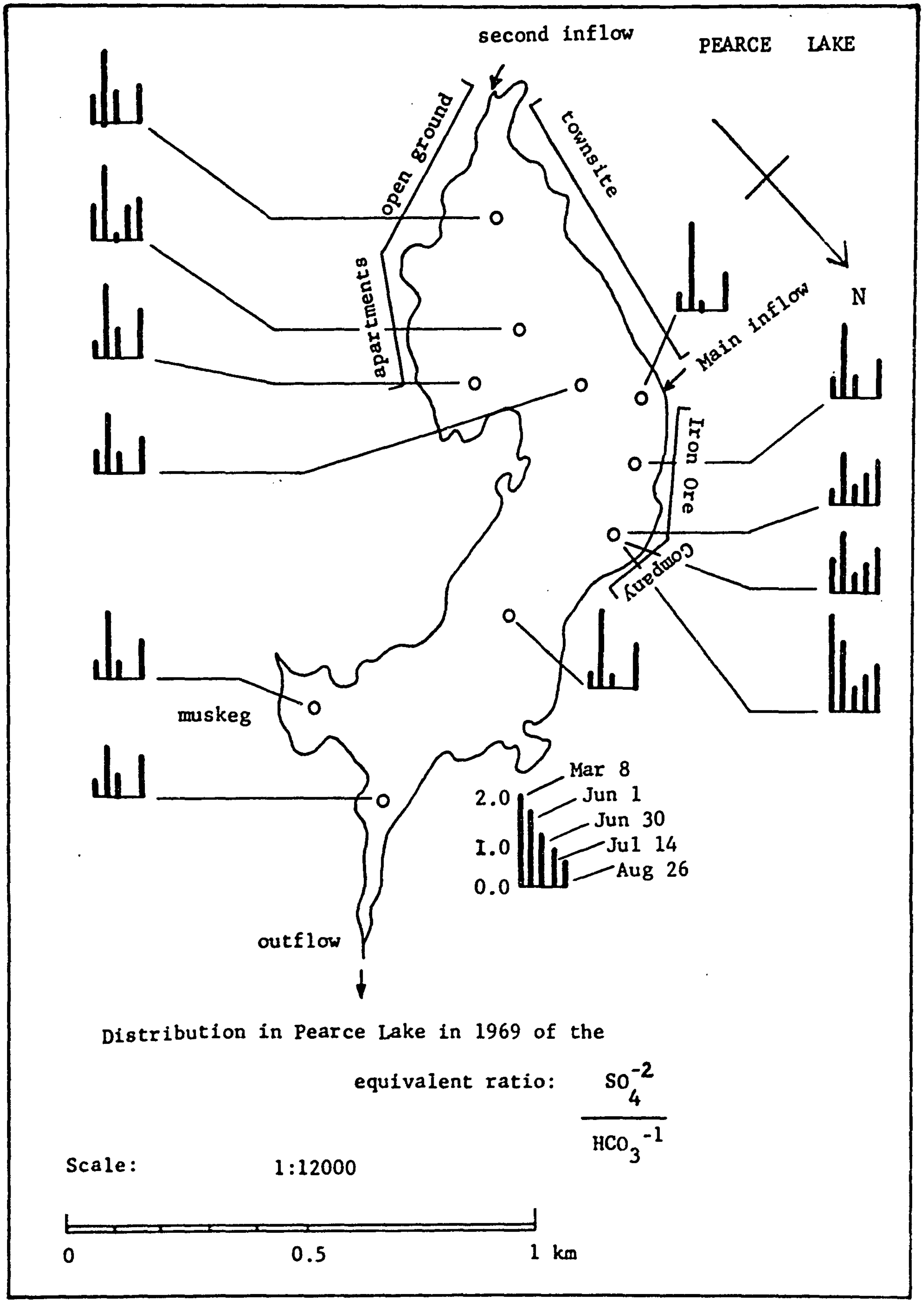
1. $SO_4 + Cl : HCO_3$ (Fig.33, illustrating $SO_4 : HCO_3$)
2. $Ca + Mg : Na + K$
3. $HCO_3 : Ca + Mg$ (Fig.34)
4. $Ca : Mg$ (Fig.35).

1. Ratio of sulfate (and chloride) to bicarbonate. This ratio provides a measure of the combined effect of sulfate from ore testing, surface run-off and domestic sewage, and chloride, mainly from domestic sewage, on the chemical composition of Pearce Lake water. Water flowing into Pearce Lake from Knob Lake has a $SO_4^{+2} + Cl^{-1} : HCO_3^{-1}$ ratio of 0.3 in winter, and of 0.15 in summer, the difference arising primarily from an increase in sulfate ion in Knob Lake in winter. In contrast, the same ratio in Pearce Lake fluctuates widely between extreme values of 4.95 and 0.14, both within surveys and over time. These changes in ratio are presented in Fig. 33. In this diagram, the chloride ion has not been included because of the difficulties experienced in analysis. Chloride concentrations are

probably about 2.0 - 2.5 x 10^{-4} M in winter, and 0.4 - 0.5 x 10^{-4} M in summer, with concentrations uniformly distributed throughout the lake.

The diagram (Fig. 33) shows that in March, 1969, the equivalent ratio of sulfate to bicarbonate ranged from a modal value around 0.3 - 0.4 to 0.7, with one exceptional value of 1.7 occurring in deep water opposite the sewage treatment plant outfall. By the time of arrival of the spring flood (survey of June 1)sulfate had replaced bicarbonate as the dominant anion. At this time, SO_4^{-2}: HCO_3^{-1} ratios were close to or above unity with a modal value of 1.3. An extreme value of 4.95 from the bottom of the depression opposite the Lindsay apartments probably reflects oxidation of sulfides in bottom sediments following spring circulation and reaeration of lake water. On June 30, bicarbonate was again the dominant anion, since sulfate ion concentrations were mainly determined by the throughflow from Knob Lake at this time. The ratio SO_4^{-2}: HCO_3^{-1} had fallen to 0.15 - 0.6, the higher values occurring the the south arm of Pearce Lake and near effluent outfalls. On July 14, the ratios rose to 0.5 - 0.7, and by August 27, the ratio had risen to 0.6 - 1.25, with a modal value around 0.7, reflecting a gradual increase in sulfate during a period of relatively long residence time of lake water (c. 20 days).

In the paragraph above, sulfate has been discussed in relation to bicarbonate on the assumption that bicarbonate concentrations were relatively stable over space and time. This is only partially true. Within individual surveys, bicarbonate concentrations tend to be slightly higher in deep water in the south end of the lake and near the sewage treatment plant outfall. The concentration gradients involved are in the order of a few mg/l. If the March bicarbonate concentrations are used as a baseline



Distribution in Pearce Lake in 1969 of the equivalent ratio: $\frac{SO_4^{-2}}{HCO_3^{-1}}$

Fig. 33 Distribution of equivalent ratio $\frac{SO_4^{-2}}{HCO_3^{-1}}$ in Pearce Lake, 1969.

(modal value of HCO_3^{-1} 9.0×10^{-4} M or 55 mg/l), the ratios of abundance of bicarbonate during successive surveys of Pearce Lake has the general form 100:50:55:55:50. In other words, after the arrival of the spring flood, bicarbonate concentrations in Pearce Lake were relatively stable.

To summarise, the results given above describe an accumulation of sulfate in Pearce Lake during winter, part of which may be reduced and sedimented onto bottom sediments to be released during spring circulation (Hutchinson, 1957, p. 765). This would explain the generally high levels of sulfate found during the survey of June 1. Subsequently, sulfate concentrations fell to levels determined by the composition of Knob Lake; a gradual rise in sulfate then took place as the residence time of lake water increased during July and August.

2. Ratio of Calcium and Magnesium to Sodium and Potassium. Sodium and potassium analyses are not available for lake water samples, and concentrations have therefore been estimated from analyses of lake outflow sample. The limited data available for Na^{+1} and K^{+1} suggest equivalent ratios, in winter, for $Ca^{+2} + Mg^{+2} : Na^{+1} + K^{+1}$ of about 5.5 for Pearce Lake, compared with c. 14 for Knob Lake. The corresponding ratios in summer were 10.7 for Pearce Lake and c. 28 for Knob Lake. Sodium and potassium are together about 2.5 times as abundant in relation to calcium and magnesium in Pearce Lake as in Knob Lake.

3. Ratio of Bicarbonate to Calcium and Magnesium. This ratio, which is illustrated in Fig. 34, is a measure of the extent to which calcium and magnesium carbonates determine bicarbonate concentrations in Pearce Lake. An equivalent ratio $HCO_3^{-1} : Ca^{+2} + Mg^{+2}$ greater than unity

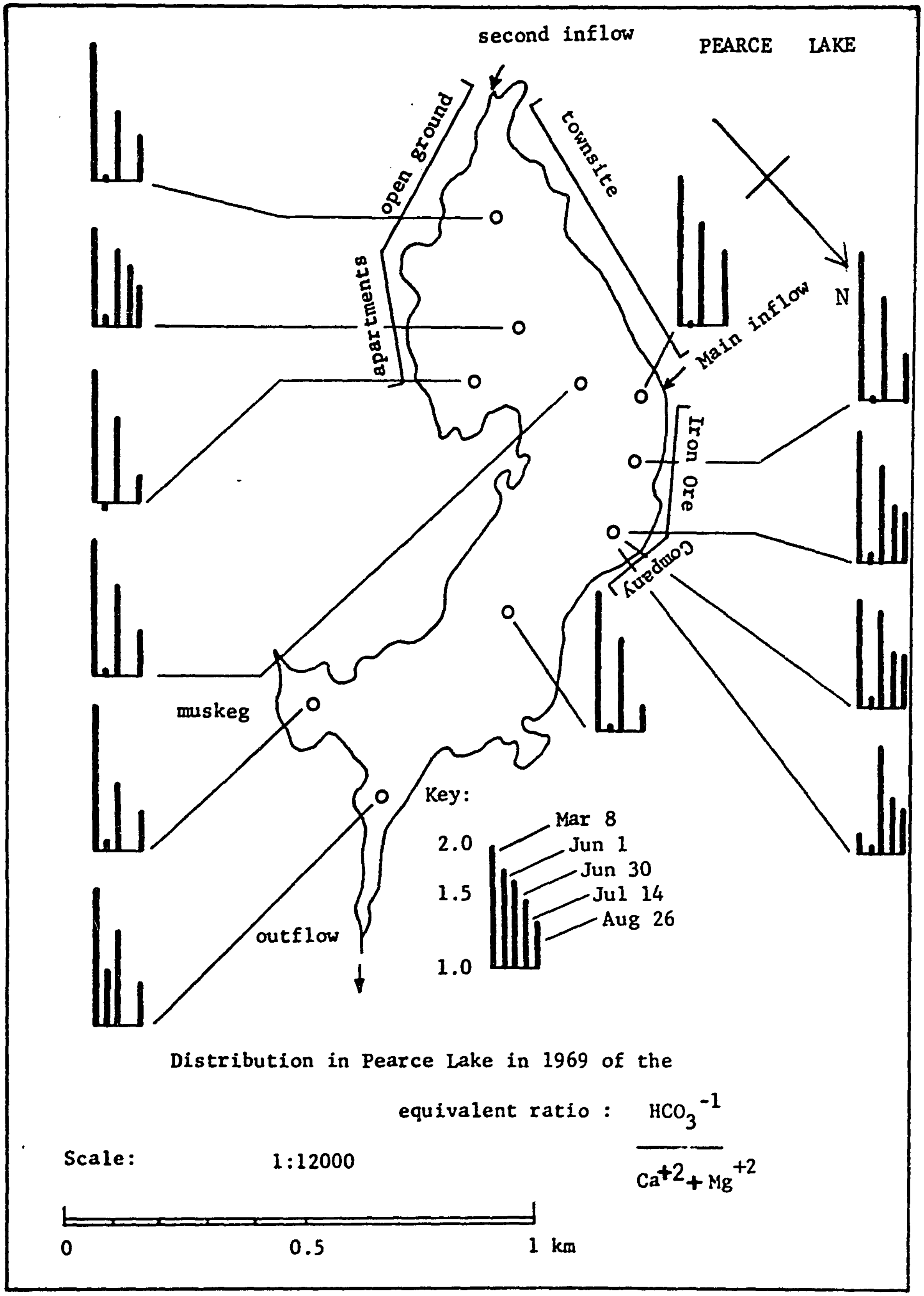


Fig. 34 Distribution of equivalent ratio $\frac{HCO3^{-1}}{Ca^{+2}+Mg^{+2}}$ in Pearce Lake, 1969.

requires that other cations (sodium and potassium) be present to balance the bicarbonate ion in addition to any other anions present. Alternatively, some process might exist which selectively removes calcium and magnesium from the water. Precipitation of calcium as hydroxy-apatite appears to be the only reaction in Pearce Lake which would result in removal of either of these cations (Kramer, 1967). Conversely, an HCO_3^{-1} : Ca^{+2} + Mg^{+2} ratio less than unity indicates that calcium and magnesium, together with any other cations present, are balanced by sulfate, chloride and possibly phosphate anions. This would imply that Ca and Mg were added to the lake as sulfates or chlorides. The difference between the equivalent value of bicarbonate and of calcium and magnesium, in conjunction with equivalent value of sulfate and chloride obtained by analysis, may be used to give a rough estimate of the concentrations of sodium and potassium present, on the assumption that these three anions and four cations comprise the bulk of the ionic balance of Pearce Lake water.

During the March survey of Pearce Lake, ratios of bicarbonate to calcium and magnesium were generally near to or greater than unity. The lowest value (0.6) occurred in the sample taken from 5 m opposite the sewage outfall, which contained 85 mg/l SO_4. The highest values (1.15) occurred near the inflow from Knob Lake and the outflow from Pearce Lake. The ratio was about unity in Knob Lake at the time. Calcium and magnesium concentrations in Pearce Lake were unexpectedly low compared with analysed concentrations of bicarbonate, sulfate and chloride. If the ratio of Na^{+1} to K^{+1} is about 4 : 1 (as at the Pearce outflow) some 12 mg/l of Na^{+1} and about 5 mg/l K^{+1} would be needed to complete the ionic balance of Pearce Lake water at that time. These concentrations are much greater than any results from Pearce Lake outflow, but they may be overestimates if the analysed results of chloride in Pearce Lake (7-9 mg/l Cl^{-1}) are too high.

During the spring flood, on June 1, the situation was reversed and bicarbonate/ calcium plus magnesium ratios fell well below unity to the range 0.5 - 0.6, with extreme values of 0.75 at the Pearce outflow and 0.2 at 4 m in the depression offshore from the Lindsay apartments. At this time, about half the sulfate and chloride in the lake (assuming Cl^{-1} to be 0.4 - 0.5 x 10^{-4} M on the basis of summer analyses) was associated with calcium and magnesium, leaving the remaining 0.2 - 0.3 milliequivalents to be balanced by 1.5 - 2.0 mg/l K^{+1} and 3 - 6 mg/l Na^{+1}. According to individual ionic balances, most of the sodium and potassium was present at the southern end of the lake. The reason for the apparent increase in sulfate in Pearce Lake at the expense of bicarbonate seems to be that bicarbonate concentrations were determined by concentrations in the throughflow from Knob Lake (about 26 mg/l HCO_3^{-1}), whereas sulfate concentrations were determined by surface run-off around Pearce Lake and perhaps by release of sulfate through oxidation from bottom sediments.

On June 30, when the spring flood was subsiding, the HCO_3^{-1} : Ca^{+2} + Mg^{+2} ratio had risen to the range 0.8 - 0.9, the higher values occurring near the inflow from Knob Lake. Sulfate concentrations in Pearce Lake were less than half those found during the June 1 survey. Sodium and potassium concentrations in Pearce Lake, based on considerations of ionic balance, were similar to the June 1 survey, i.e.

3 - 6 mg/l Na^{+1} and 1.5 - 2.0 mg/l K^{+1}. Apparently, the sulfate ion released into the lake during the earlier survey had been largely flushed out, even though concentrations remained two or three times as high as in other lakes in the basin.

During mid-summer (July 14) the ratio HCO_3^{-1} : Ca^{+2} + Mg^{+2} decreased again to the range 0.7 - 0.8 as sulfate concentrations returned to a level of about 13 - 20 mg/l. However, the balance between calcium and magnesium and the anions present was nearly complete, implying the presence of only 0.8 mg/l K^{+1} and 1.8 mg/l Na^{+1} (totalling 0.1 milliequivalent) in the lake, which is in agreement with analyses at the Pearce outflow.

At the time of the final (August 27) survey, when sulfate concentrations had reached 17 - 24 mg/l, the ratio had decreased further to 0.6 - 0.75, with a minimum value of 0.5, occurring in the sample at 4.5 m depth offshore from the Lindsay apartments which had 24 mg/l SO_4^{-2}. With sulfate in the lake 3.5 - 4.5 x 10^{-4} M and chloride 0.45 - 0.8 x 10^{-4} M (1.7 - 2.8 mg/l), 3.5 - 6 mg/l Na^{+1} and 1.5 - 3.0 mg/l K^{+1} would need to be present in Pearce Lake to complete the ionic balance.

Ratios of bicarbonate to calcium and magnesium therefore appear to fluctuate systematically in Pearce Lake, with the value of the ratio depending on the supply of bicarbonate to Pearce Lake from Knob Lake, and on the supply of sulfate ion to Pearce Lake in surface drainage and wastewater. Further sampling of Pearce Lake at regular intervals throughout the year would probably reveal a seasonal variation in the ratio reflecting rates of supply and removal of sulfate ion. Such sampling would also establish the balance of sodium and potassium in the lake water.

4. Ratios of calcium to magnesium. Lake waters elsewhere in the drainage basin (Chapter IV) had Ca:Mg ratios near to or slightly greater than unity which were believed to be determined by the weathering of carbonate minerals, primarily the dolomite of the Denault formation. Consideration of $Ca^{+2}:Mg^{+2}$ ratios in Pearce Lake (Fig. 35) provides a method of assessing whether these alkaline earth elements are added to the lake as carbonates, or in some other form associated with waste water.

In March, the molecular ratio $Ca^{+2}:Mg^{+2}$ in Pearce Lake ranged from 1.0 to 1.4, with some indication of higher ratios near the lake outflow. In that part of Knob Lake nearest Pearce Lake, Ca:Mg ratios were between 1.1 and 1.2; these values are sufficiently close to those in Pearce Lake to suggest that at that stage of the year there were no major sources of Ca^{+2} and Mg^{+2} to Pearce Lake, other than the carbonate waters from Knob Lake.

The situation in March is to be contrasted with that of June 1, when, with one exception (1.05 near the inflow from Knob Lake), $Ca^{+2}:Mg^{+2}$ ratios were in the range 0.77 - 1.0, with a modal value about 0.9. The ratio in Knob Lake at the time was 1.0. This change in ratio implies either removal of calcium or enrichment in magnesium. Widespread removal of calcium is geochemically unlikely, but it is possible that weathering of Attikamagen shales and ore tailings around the townsite, in contact with somewhat acid snow melt water, would yield magnesium and silica in solution from chlorite or Mg-mica (Garrels and Christ, 1965, p. 363). Such a reaction could yield the additional quantity of magnesium (0.25 - 1.4 mg/l Mg^{+2}) required to displace the ionic ration $Ca^{+2}:Mg^{+2}$ in the direction of magnesium.

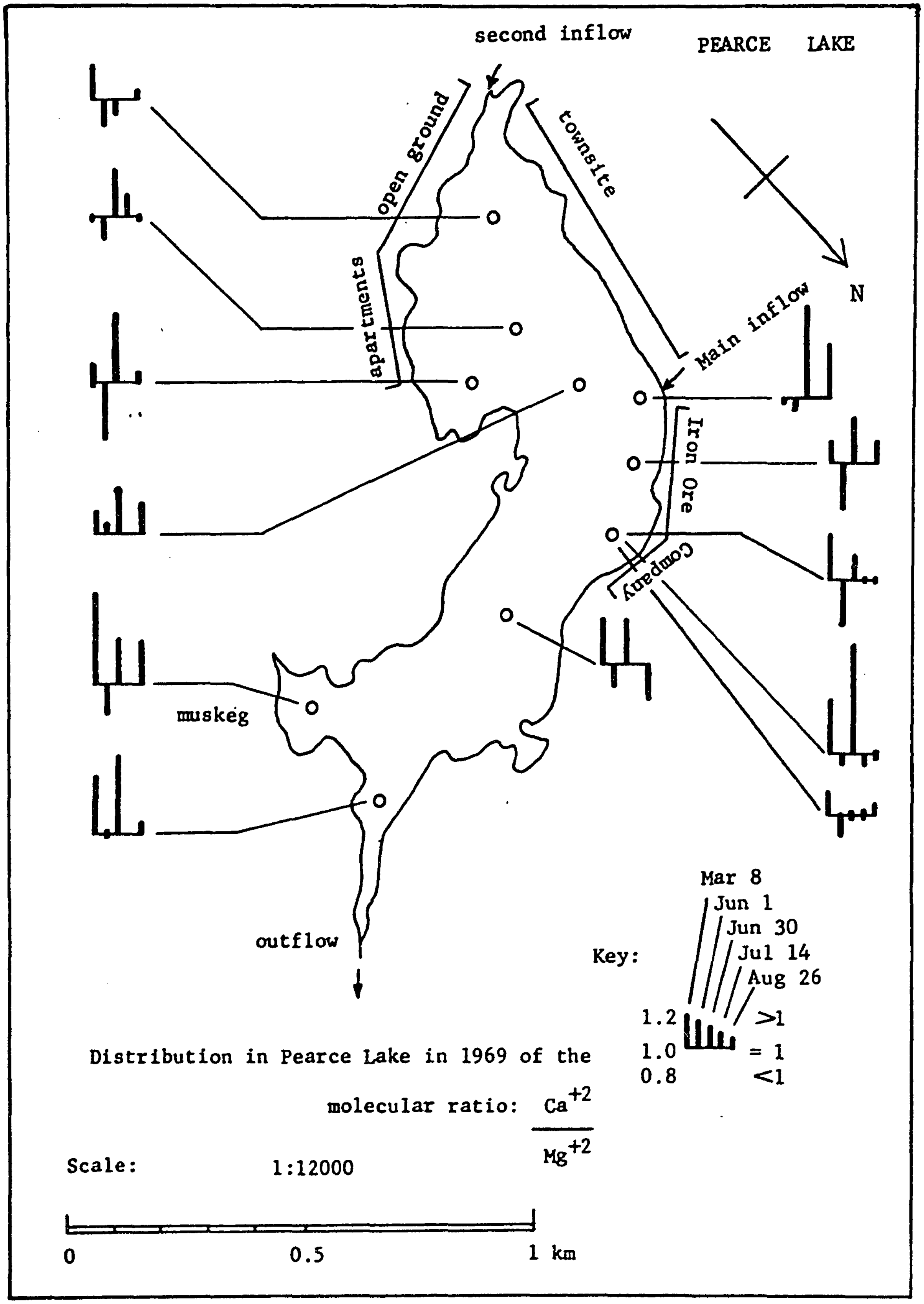


Fig. 35 Distribution of molar ratio $\frac{Ca^{+2}}{Mg^{+2}}$ in Pearce Lake, 1969.

Ratios of calcium to magnesium where equal to or greater than unity during the three remaining surveys (June 30, July 14, August 27). On July 14 and August 27, ratios fell in the range 1.0 - 1.2, comparable with analyses of Knob Lake water, but on June 30, the ratios were more erratic, varying between 0.94 (extreme southern end of the lake) and 1.5 (opposite the sewage treatment plant outfall). The variation during the late June survey, particularly at the latter site (Fig. 35) is not understood, and seems to imply local additions of calcium to the lake. Taking all four surveys together, Ca:Mg ratios in Pearce Lake are not markedly different from other lakes in the basin, which suggest that dolomite solution is the main control of the ratio. However, anomalies do exist in Pearce Lake, particularly during the June 1 survey, which are probably explained by chemical weathering around the townsite, and perhaps also by the discharge of smaller quantities of these cations in waste water.

5. Summary

Pearce Lake has been shown to have a chemical composition unlike that of Knob Lake, from which it receives the greater part of its throughflow. The changes in chemistry result from the discharge into the lake of waste water of domestic and industrial origin, and from surface drainage into the lake from disturbed areas around Schefferville townsite. The major changes involve increases in the concentration of the anions sulfate and chloride and the cations sodium and potassium. High concentrations of suspended iron occur in the lake, imparting red turbidity to the lake water. Addition of nutrients in untreated and partially treated sewage results in a measure of organic pollution. Soluble phosphorus, in particular, is present in very high concentrations, up to 2.4 mg/l PO_4; this phosphorus is probably derived from the use of synthetic detergents in the town. Further studies of phosphorus in Pearce Lake should include phosphorus present in particulate matter, and in soluble forms other than as the orthophosphate ionic form. Part of the phosphate ion may react with ferric iron in the water to form a highly insoluble precipitate of ferric phosphate. During the winter period of ice cover, oxidation of organic matter in the lake water results in widespread depletion of oxygen, resulting in local fish kills. Complete exhaustion of oxygen is likely at the end of winter in deeper parts of the lake and in shallow bays. During the ice-free period of the year, active photosynthesis raises the pH over 8.0 in shallow bays in the lake, and the utilisation of silica by diatoms locally reduces dissolved silica below 1.0 mg/l. Variations in the nature of the ionic balance of the lake water at different survey times reflect rates of supply and removal of sulfate, chloride, sodium and potassium in Pearce Lake. These ions reach maximum concentrations in the lake in late winter and during the early part of the snow melt period. Concentrations then appear to fall off during early summer, and rise again during August. Anomalous Ca:Mg ratios may indicate that weathering of chlorite in shales near the lake yields additional quantities of magnesium to the lake.

Lake bathymetry and lake water residence times are considered to be important controls on the balance of dissolved substances in Pearce Lake. The occurrence of two major depressions in the lake which are separated from the main axis of throughflow results in increased water residence time in these depressions, which is associated with accumulations of dissolved solids and stagnation in late winter. High concentrations of individual constituents of the water persisted even during the summer period of active wind-driven circulation of lake water. The common cations and anions in the lake are stable in the water and are removed from the lake through the outflow. However, an appreciable part of the phosphorus, iron and silica added to the lake may be precipitated or sedimented onto bottom sediments within the lake.

CHAPTER VII

CONCLUSIONS

1. Discussion.

In this study, the main characteristics of the water chemistry of the lakes in Knob Lake drainage basin are described, and an interpretation of the chemistry of individual lakes is offered in terms of probable geological and hydrological controls of ionic concentration. The explanation of the abundance of the ions HCO_3^{-1}, Ca^{+2} and Mg^{+2} is based first on the carbonate minerals (mainly the Denault dolomite formation) in lake catchments, and secondly on observed rates of transfer of surface water between lakes and inferred rates of groundwater movement. These explanations are useful at the scale of Knob Lake drainage basin, but are felt to have less applicability for the understanding of the chemistry of individual lakes. This limited applicability is attributed to the need for the observation or simulation of the details of the processes by which solutes are released from parent minerals and transported into lakes. The explanation of the distribution of other constituents of the lake waters is based on inference from observed vertical distributions in lakes, and on the literature pertaining to each constituent.

The explanation of water chemistry is therefore based on inferred association between ionic concentration and large scale geological and hydrological characteristics of the drainage basin, rather than on the detailed analysis of processes involved in the transport of solutes to lakes, consequently, in order to place the study in perspective, the following section identifies specific research problems in surface water chemistry which arise from the material presented in this study, and evaluates the chemical and hydrological data collected for this study and its suitability for further studies of water chemistry more closelt related to the processes of chemical weatheringé

a) Chemical Analyses.

The chemical analyses used in this study, simplified versions of standard procedures described in 'Standard Methods' (A.P.H.A., 1965), are believed to be closely reproducible but probably lack absolute accuracy. The reagents supplied by the Hach Company are convenient for the rapid assessment of the concentrations of common constituents of lake waters, but the procedures on the whole lack the sensitivity or accuracy that would be required for the detailed study of any one constituent.

In this study, special emphasis was placed on the use of carbonate equilibria to describe the way in which water compositions reflect overall rates of solution of carbonate minerals. The calculation of carbonate equilibria requires that accurate determinations are available for pH, bicarbonate, calcium and magnesium from which the concentrations of carbonate ion (CO_3^{-2}) and carbonic acid (H_2CO_3) can be calculated. The available analyses were suitable for compiling ion activity product diagrams, which were found to be a convenient and consistent method of comparing lake water compositions. However, there was some reason to believe that the values used for pH and possibly for bicarbonate ion concentration were not sufficiently accurate to be used, for example, in experiments to determine the kinetics of the solution of Denault dolomite. For careful work, such as investigating rates of solution, sample pH should be determined in the field as soon as possible after sampling, and if the sample has to be transported, care should be taken to avoid excessive changes in sample temperature of CO_2 balance. For similar reasons, the titration for total alkalinity (preferably potentiometric) should be performed soon after sampling. Since the end-point indicator dyes lack sensitivity at water temperatures found in lakes near Schefferville, tiration has to be performed in the laboratory at room temperatures. The appropriate endpoint for the titration may be determined as a function of ionic strength according to the procedure outlined by Barnes (1964). If there is doubt as to the reliability of determinations of calcium and magnesium using EDTA as a chelating agent, as for example in the analysis of polluted waters, these elements can be checked by atomic absorption or flame emission spectroscopy.

Analyses for iron in water present a problem because it is generally not clear what form of iron is being measured. In this study, samples were not filtered to remove larger iron particles, because the amount of finely divided iron present in suspension was felt to be of some interest. Since it is known that the amount of iron in true solution in ionic form in the samples was negligible, it was concluded that the intensity of the reaction of the sample with phenathroline or tripyridine was proportional to the amount of finely divided and suspended iron in the sample. It could not be concluded, however, that the observed concentrations represented the quantity of particulate iron present. Since it was found that appreciable quantities of iron were being transported through the lake system, it is suggested for further studies of iron in lakes of this kind, that samples be filtered to separate larger iron particles from iron in soluble, colloidal or very fine particulate form. Analyses could then be conducted on filtered and unfiltered samples and would at least provide a crude size separation of the iron present. This argument applies also to determinations of nitrogen and phosphorus.

The accuracy of the analyses of sulfate and chloride reported in this study could be improved, by preliminary concentration of samples by evaporation, to achieve a precision of about 0.1 mg/l. Analyses for sodium and potassium are important for determining ironic strength, descriptions of ionic balance, and for any analysis of the course of shale weathering, and it is unfortunate that analyses for these ions are not available for this study. Sodium and potassium may be determined by atomic absorption or flame emission spectroscopy. Finally, analyses for silica in lake waters must be reported consistently. Although samples may be filtered, it is perhaps best to analyse samples at carefully controlled temperatures for a constant time period, and run duplicate analyses for the same sample where possible. Graphs describing the rate of change of colour intensity with time could be useful for comparing silica determinations in different lakes, or at different depths within the same lake.

b) Sampling.

The lake sampling programme for this study was designed to describe large-scale variations in ionic composition within the larger and deeper lakes at the same time as representing each lake in the basin, both in late winter and late summer, by at least one sample. Consequently, many small lakes are represented by a single sample for each survey, and there were, in addition, four small lakes which were overlooked during the winter survey.

The sampling programme that was adopted emphasised variation between lakes at the expense of providing information which could be used to interpret ion concentrations within lakes. The concentration of some constituents, of which silica is one good example, is known to be regulated by chemical exchanges between lake water and bottom sediment, and since release from bottom sediments is reflected in vertical distributions, emphasis on sampling water very close to and perhaps within bottom sediments would provide the basis for assessing the importance of exchanges within lake basins as controls of lake water chemistry. Further study of distributions in the littoral zone of lakes could be used to infer the effect of bathymetry on the rate of exchange of solutes between water and sediment or bed-rock. Also, the role of lake ice in concentrating the solutes in water during winter was referred to in connection with the abnormally high ionic concentrations in Trigger and Mattox Lakes in winter. Sampling lake ice of various origins (i.e. both columnar clear ice, and granular snow ice) could demonstrate the effect of ice formation on the composition of water bleow an ice cover.

The frequency of sampling in this study was determined mainly by the number of lakes to be sampled. Sampling twice, in late winter and in late summer, revealed lower concentrations in summer than in winter, shifts in concentration within the drainage basin suggesting that the draining of small lakes in summer resulted in increased concentrations (for example, of silica and sulfate) in some of the larger lakes, and general tendencies for a change in ionic ratios corresponding to a seasonal change in the ionic balance of lake waters. It was inferred that the spring food had been effective in 'flushing out' the lakes between the two surveys.

The problems of assessing the effect of thermal stratification in winter on the transfer of solutes between lakes, and the effect on ionic composition of the passage of snow-melt run-off can only be resolved by concentrating on one lake or a small group of lakes and sampling systematically over time using the same sampling sites and depths. The utility of this appraoch was suggested by the surveys that were undertaken in Pearce and Cowan Lakes. Regular sampling over time would also confirm whether there were consistent changes in ionic ratio corresponding to large-scale seasonal changes in ionic balance.

c) Hydrology.

The major unresolved problem in the hydrology of the drainage basin is the importance of groundwater movement along and across the geological strike of the shale and dolomite formations. This general problem is related to more specific questions concerning the movement of water in lichen litter, rates of infiltration of surface water into shales of different degrees of bulk porosity, and the nature of groundwater discharge into lake basins. In Chapter IV, section 9, it was argued that water composition can be used to infer the presence of groundwater discharge into lakes, and in Chapter II, section 6, it was shown that, on the basis of stream gauging at lake outflows, water is transferred between lakes both as surface and sub-surface flow.

Further hydrological studies in the basin, which might be based on experimental run-off plots, should perhaps concentrate on the conditions in which the main geological formations in the basin act as aquicludes or aquifers, on infiltration rates into shales with and without a lichen cover, and, more generally, on the distribution of surface run-off within the drainage basin. Without this information, it is not possible to establish the residence times of water in individual lakes at different times of the year and therefore the relative importance of groundwater equilibria and chemical exchanges within lakes in determining water composition.

d) Physical Limnology.

In Chapter II, section 3, the warming of lakes under the winter ice cover was attributed to the conduction and convection of heat stored in bottom sediments and bedrock. The validity of this explanation might be confirmed by establishing the development of the temperature gradient near the lake bottom, and if possible by obtaining a value for the coefficient of thermal conductivity for characteristic bottom sediments. Temperature profiles after ice formation and before break-up can be used to describe the effect of solar radiation on water temperatures.

The absence of thermal stratification in the lakes in summer suggested that most lakes in the Knob Lake basin circulate continuously under the driving forece of the wind during the ice-free period of the year. However, the absence of stratification could have resulted from the time of sampling and unseasonably cool and windy weather in August and September. A possibility worth considering is that lakes other than Cowan Lake stratify in warmer and calmer summers, and therefore that lakes near Schefferville may be either polymictic or dimictic, depending on the climate for individual years.

e) Lake Water Chemistry.

The problems arising from the treatment of lake water chemistry in this study fall into two classes, the first concerned with processes of chemical weathering, the second with changes in water chemistry which take place within lakes. The discussion of chemical weathering centred on the solution of the Denault dolomite formation, and it was observed that although the composition of lake waters could be treated as the end-product of the solution of dolomite, the theoretical treatment of the solution of ideal dolomite did not bear a close relationship to the solution of an impure dolomite like the Denault formation by soil water and groundwater. This was partly because neither the true composition of the Denault dolomite nor the path taken by water in contact with the dolomite were known. Furthermore, no information was available to the writer on the probable rates of equilibration of water and dolomite.

Some of these problems can be solved, at least in part, by experiment. If the composition of atmospheric precipitation were known, samples of water could be collected from representative situations near the surface of the dolomite (e.g. within lichen, in contact with residual soil, or draining from fissures in the dolomite). At the same time, beaker or water tank experiments could be run in the laboratory to determine rates of solution and equilibrium states in these types of conditions. By comparing the composition of samples obtained in the field with the compositions of synthetic samples in the laboratory, this approach could be used to estimate the rate at which rain or snow melt-water comes into equilibrium with the dolomite in the catchments of, for example, Cowan and Easel Lakes. The carbonate equilibria considered in Chapter IV and Appendix V could then be used to derive the equilibrium P_{CO_2} under which dolomite goes into solution near the surface and in fissures. By suitable experimentation, therefore, it is believed that it is possible to obtain realistic rates for the equilibration of dolomite with atmospheric precipitation before the water reaches the lakes, and therefore to obtain concentrations of calcium and magnesium in water in contact with dolomite under varying values of P_{CO_2}.

Changes in water chemistry within lakes are complex and include other constituents that were analysed in lake water in addition to the ions involved in carbonate equilibria. Interpreting changes within lakes often takes the form of establishing vertical distributions which can then be related to exchanges between water and bottom sediments, turbulent transfer through the water column, and in the case of calcium and possibly magnesium, biogenic removal or precipitation. The analyses reported in this study for constituents such as iron, sulfate and silica, and the method of sampling for dissolved oxygen with a Kemmerer sampler lack the precision necessary for the detailed treatment of vertical and horizontal distributions for any one constituent or group of constituents. Therefore, it is suggested that detailed studies of distributions within lakes require careful analysis of the constituent concerned, and also of the bottom sediment, and that an attempt be made to establish concentration gradients close to the mud and throughout the water column with a view to describing probable rates of turbulent diffusion (c.f. Hutchinson,1941). Finally,for diffusion rates, it would be possible to use the example of Malcolm Lake as a lake with a distinctive horizontal concentration gradient to determine rates of mixing of waters in an elongated lake, both in the stratified condition of late winter, and the unstratified condition of summer.

f) Pearce Lake.

The study of Pearce Lake provided an outline of a somewhat complicated sequence of changes in chemical composition related to rates of natural throughflow and to the types of waste-water and surface run-off entering the lake from Schefferville townsite. The limitations of this part of the study are that the sampling was not sufficiently consistent within the lake or constant over time to reconstruct the details of seasonal changes in composition or the circulation of dissolved substances within the lake. Furthermore, one of the main pollutant sources, the Iron Ore Company plant effluent, was not present during the summer of 1969 owing to a company strike. Also, the analytical techniques that were available were not adequate to describe organic pollution of the lake water by treated and untreated municipal effluent.

Further study of a lake like Pearce requires detailed sampling during the spring flood to establish conditions at maximum stagnation (i.e. the minimum distribution of O_2 in the lake) and then the mixing of stagnant waters with snow melt run-off and the process of the 'flushing out' of the lake during spring. Sampling regularly over the course of a year is also important, and in order to establish the polluted state of the water, samples should be analysed to obtain values for total nitrogen and phosphorus and the approximate composition of the soluble and particulate organic fractions.

2. Results of the Present Study.

a) Morphometric properties of the lakes studied.

Most of the thirty lakes in Knob Lake basin were apparently formed by the scouring action of glacial ice and are elongated in a northwest-southeast direction along the geological strike. Average water depth in the lakes ranges from nearly 7 m (Easel Lake) to 1 - 2 m in small lakes with surface areas below 4 ha. The greatest depth known is about 19 m. The lakes are therefore shallow, have broad littoral zones and long shorelines in relation to surface area.

b) Physical Limnology.

The lakes are stratified (0 - 3.9°C) during the period of winter ice cover. Solar radiation is effective in warming lake water just after freeze-up and before break-up, but while the winter snow cover persists, the main heat source to the lakes is conduction and convection from bottom sediments and bedrock. Small lakes on dolomite tend to be warmer than corresponding lakes of the same size on shale. Winter stratification persists from November to early June, and is followed by a period of more or less continuous circulation until first ice formation in the following year. Cowan Lake, a small and deep lake surrounded by forested ridges, was the only lake known to be stably stratified during the summer. All other lakes were nearly isothermal (10 ± 2°C) during late August and early September. Shallow epilimnia, with temperatures up to 20°C may persist for periods of a few days, but the shallowness of the lakes and their exposure to the prevailing northwesterly winds promotes continuous circulation during the ice-free period of the year.

c) The geological and vegetational setting of the lakes.

Two-thirds of the drainage basin is underlain by tightly folded and faulted Proterozoic shales of the Attikamagen and Menihek formations. A 2 km wide band of dolomite, of the Denault formation, runs diagonally across the basin and occupies a further 6.6 km^2, or 17.4 per cent of the basin area. The remainder of the basin consists of cherts, quartzites, minor shales and iron formation which are all generally remote from lake waters and for the most part have little effect on lake water composition. From the point of view of lake water chemistry, the Denault dolomite is quantitatively the most important formation, since it is the most abundant source of ions and over 90 per cent of all lake water in the basin either lies on dolomite or is mixed with water from dolomite.

Both the Attikamagen and Menihek shales consist of granular quartz, albitic plagiocale, potassium mica and chlorite, with pyrite, dolomite and calcite as accessory minerals. Dolomite sometimes occurs as lenses. The shales, which dip steeply both northeast and southwest and are often fissile, may be important as aquifers in some areas of the basin. The Denault dolomite is a ferroan dolomite or mixture of dolomite and ankerite. It is massive, sometimes arenaceous, and where fissures occur it is an effective aquifer. Local leaching has resulted in replacement of carbonates by silica, and the residual carbonate may be deficient in magnesium.

The natural vegetation bordering the lakes is spruce forest of varying density and a Cladonia lichen ground cover, with a lakeshore scrub of alder and willow. Extensive forest fires have removed much of the spruce, resulting in a low birch-alder scrub which affords little protection to the lakes from wind. The lakes larger than c. 10 ha have rocky shores, but smaller lakes may support sedges and sublittoral communities, primarily of Mitella, Isoetes and Eleocharis. The construction of Schefferville in 1953 has left areas of unvegetated shales around the townsite which result in accelerated yields of suspended sediments and solutes to Pearce Lake.

d) Hydrology.

The average precipitation over Knob Lake basin in 1969 is estimated at 102 cm (55.4 cm snow, 46.6 cm rain). This estimate is based on the official records at Schefferville but takes into account the probable error in measuring snow and rainfall totals. In the year of study, snow accumulation (w.e.) was greatest on high and open ground in the south of the basin, and least in close spruce forest of the Easel catchment. Rainfall, on average, is evenly distributed over the basin, but receipts from individual storms reflect wind speed and direction and surface topography.

The annual hydrograph for the Pearce Lake outflow in 1969 (catchment area 37.8 km^2) is compared with the corresponding hydrograph for Menihek dam (catchment area 19,000 km^2), 40 km south of Schefferville. The general similarity of the two hydrographs suggests that the timing of individual hydrological events is similar and that the Knob Lake drainage basin may be representative of a wide area of the Labrador Trough. There are, however, identifiable anomalies in the hydrograph for Pearce Lake which can be traced to the regulation of the level of Knob Lake for Schefferville water supply. Of the total run-off of 75.5 cm from Knob

Lake, 23 cm is attributed to snow melt run-off from a pack with a w.e. of about 41 cm. Minimum flow occurs in late April, with a secondary minimum in July-August when evapotranspiration losses are at a maximum. A later rise in flow, persisting until November, is believed to reflect groundwater discharge.

Lake water residence times are below 1 year in all but five lakes, which lie on dolomite, have small catchments in relation to lake volume and lie near drainage divides. Easel is the largest of these lakes. The residence times assume uniform discharge of water throughout the basin. The spring flood results in complete turnover or extensive replacement of the water of most lakes in the basin, with the exception of the five mentioned above.

Stream gauging at lake outflows in the basin indicated that surface run-off in the higher parts of the basin is less than indicated by the catchment area. Groundwater flow, therefore, is believed to account for 10 - 60 per cent of the transfer of water between lakes, depending on the time of year and location in the basin. Groundwater recharge near drainage divides may increase the residence time of some smaller dolomite lakes.

Water consumption at Schefferville in 1969 was equivalent to 3 cm of run-off. In the period of minimum flow, domestic and industrial water consumption accounts for up to 20 per cent of the flow between Knob and Pearce Lake and partly accounts for the accumulation of soluble wastes in Pearce Lake.

e) Carbonate chemistry of lake waters.

Bicarbonate, calcium and magnesium, which are derived mainly from the solution of carbonate minerals in the Denault, Attikamagen and Menihek formations, are the most abundant ions in the lakes of the drainage basin. Distribution maps for winter and summer concentrations of these ions show the Denault formation to be the major source of these ions. Smaller quantities of calcium and magnesium are derived from aluminosilicate minerals in shales and from atmospheric precipitation.

Carbonate equilibria applicable to the solution of ideal carbonate minerals under controlled conditions were found to be useful in establishing approximate compositions of water in equilibrium with dolomite or calcite with P_{CO_2} $10^{-3.5}$ atm. These equilibrium conditions were, however, found to be inapplicable to the field situation in which dolomite reacts with percolating soil water and groundwater draining into lake basins. This was attributed to lack of information on groundwater flow, the equilibrium P_{CO_2} in groundwater and soil water, and the kinetics of the solution of dolomite.

Although lake water analyses could not be used to reconstruct the solution of dolomite, they were used to describe the end product of chemical weathering of dolomite. Ion activity product diagrams and maps (Figs. 7 - 10) were found to be useful in describing lake water compositions in relation to equilibrium with dolomite or calcite. The appropriate ion activity products were ($a_{Ca^{+2}} \cdot a_{Mg^{+2}} \cdot a^2_{CO_3^{-2}}$) for dolomite, and ($a_{Ca^{+2}} \cdot a_{CO_3^{-2}}$) for calcite. The equilibrium constant for dolomite was assumed to lie between 10^{-16} and 10^{-18}. These diagrams showed that lake waters on dolomite were somewhat undersaturated with respect to dolomite and calcite in winter, but approached equilibrium in summer. Values of ion activity products illustrate the contrast between the compositions of shale and dolomite water, and when mapped provide a convenient method of describing the mixing of lake waters of contrasting origins. Ion activity products for lakes on the same geological formation were found to vary, some of the variation being attributable to variations in lithology and some to variations in the topography or vegetation of individual lake catchments.

Ion activity products, with a few exceptions, increased between winter and summer. The increase is related to the release of CO_2 in plankton respiration in winter, and the uptake of CO_2 in photosynthesis in summer. Diagrams of seasonal changes in free carbonic acid plotted against seasonal changes in pH and carbonate ion activity (Appendix V, section E) revealed an approximately 1:1 stoichiometric ratio for the seasonal change of these constituents. Calculation of the P_{CO_2} at equilibrium with water samples indicates marked supersaturation (x   10) with respect to atmospheric CO_2 in winter, a consequence of respiration, and slight supersaturation, by a factor of about 2, in summer. The apparent supersaturation in summer may reflect respiration after a period of maximum primary production, or it may reflect consistent error in the calculation of equilibrium P_{CO_2} on the basis of carbonate equilibria.

Equivalent ratios of bicarbonate to calcium and magnesium both together and individually are consistent with the solution of a carbonate mineral with a Mg:Ca ratio between 0.8 and 1.0. This ratio is consistent with the congruent solution of a ferroan dolomite or a mixture of dolomite and ankerite, the composition of Denault dolomite indicated by chemical analyses. Divalent iron and manganese are probably also released into solution in the weathering of dolomite. The Mg:Ca ratio is rather higher in shale waters, implying an additional mineral source of Mg^{+2} which may be chlorite. Seasonal changes in ionic ratio involving bicarbonate ion tend to reflect decreases in summer in the amount of sulfate in small, head-water lakes, and increases in sulfate in lakes lower in the drainage system. Seasonal changes in the ratio Mg:Ca show an unexplained enrichment in calcium in some lakes.

Ion distributions within lakes reflected the development of thermal stratification and the mixing of water of contrasting compositions. Increases in ionic concentration near bottom sediments (particularly in lakes on dolomite) in winter under an ice cover imply the existence of some form of chemical release at the mud surface, as postulated by Mortimer (1941), although the mechanism of release is unknown. Ion distributions are almost uniform within lakes in summer in the absence of thermal stratification.

The compositions of lakes receiving drainage from both dolomite and shale were best explained if groundwater flow is regarded as an important control of ionic concentration in lakes. Concentrations of bicarbonate, calcium and magnesium in lake waters of mixed origins were found to be approximately proportional to the ratio of shale to dolomite in the respective lake catchments, and indicated that the water from dolomite and shale determining ionic compositions had ionic concentrations about half as high again as in lake waters lying on dolomite or shale.

f) Other constituents in lake waters.

Dissolved silica was usually present in the lake waters studied in the concentration range 2 - 4.5 mg/l, irrespective of catchment geology. This silica is derived in part from inflowing surface and groundwaters, but consistent increases in silica concentrations near bottom sediments suggest that release from these sediments is an important source of dissolved silica. Higher silica concentrations occur in winter (up to 29 mg/l) in very shallow lakes, in which the silica is probably concentrated by ice formation. Minimum concentrations were found in summer in lakes lying on dolomite near drainage divides, with large lake volumes in relation to catchment area. These lakes have relatively long residence times ($\sim$ 1 year) and possibly high rates of diatom production. Silica concentrations less than 0.5 mg/l may be limiting for diatoms such as *Asterionella*, which are common in these lake waters.

Relative saturation with dissolved oxygen ranged between 4 and 90 per cent in winter, with a modal value of about 75 per cent saturation, while in summer most lake waters were near saturation. Oxygen depletion under lake ice in winter was greatest in shallow lakes and least in the largest and deepest lakes. The depletion was proportional to the seasonal change in pH of the lake water, and in so far as change in pH is indicative of biological productivity, suggests that productivity was greatest in smaller dolomite lakes, intermediate in smaller shale lakes, and least in the large lakes with waters of mixed origins. Small and shallow lakes, with a relative large surface area of oxidisable organic matter on bottom sediments in relation to lake volume, tend to experience greater oxygen depletion than larger and deeper lakes.

Appreciable amounts of iron are transported through the lakes in the basin as a very fine suspension of particles, yielding apparent concentrations of soluble ferric iron (by reaction with phenanthroline) in the range 0.01 to 0.10 mg/l Fe. Some higher values in small lakes are believed to be associated with suspended organic tissue, and may in part represent a soluble organic iron complex. Changes in the oxidation state of the lake mud surface may account for the passage of iron (possibly as ferrous bicarbonate) into lake waters.

Aluminium, in solution and as colloidal aluminium hydroxide, was found to be present in the lakes in summer in the concentration range 10 - 70 mg/m^{-3} Al. The aluminium is derived from the weathering of aluminosilicate minerals in shales. Manganese was locally present in dectectable amounts in lakes on dolomite, where divalent manganese is released during the weathering of ankerite.

Sulfate and chloride in lakes near Schefferville are derived mainly from atmospheric precipitation, although some sulfate is derived from sulfide minerals in shales. Sulfate concentrations where no mineral source of sulfate is present range from 1 - 6 mg/l, while chloride concentrations lie between 0.8 and 1.0 mg/l. In summer, the molecular ratio of sulfate to chloride was close to unity, which is consistent with analyses of maritime precipitation. Where sulfide minerals are present, as in the Phred catchment, sulfate concentration are near 10 mg/l in lake waters. Sodium and potassium, derived from shale weathering and atmospheric precipitation, are generally present in lake waters in concentrations below 1 mg/l. The molecular ratio Na:K is about 2.2:1 in waters leaving

Knob Lake, but this ratio tends to be higher in lakes on shale (perhaps because of the decomposition of albitic plagioclase) and lower in lakes on dolomite.

Nitrate-nitrogen was less than 0.1 mg/l in most water analyses, and soluble orthophosphate was near or below 0.01 mg/l. These concentrations are below the limit of reliable detection with the methods used, but serve to suggest probable orders of magnitude.

The order of abundance of major cations follows the sequence $Ca^{+2} \geq Mg^{+2} > Na^{+1} > K^{+1}$, and the corresponding order of abundance for anions is $HCO_3^{-1} > SO_4 \geq Cl$. These orders of abundance are typical of inland waters on shale or carbonate sediments. Bicarbonate, calcium and magnesium are associated with the solution of carbonate minerals, and therefore tend to dominate the ionic balance in waters derived from carbonate rocks.

g) Pearce Lake

Pearce Lake was studied in detail because its chemical composition is affected by the discharge of industrial and municipal waste-water from Schefferville and by run-off from unvegetated shales near the townsite. Changes in the composition of Pearce Lake water are related to the volume and composition of throughflow from Knob Lake, and the volume and composition of waste-water and surface run-off entering the lake from Schefferville townsite. The changes involve marked increases in suspended iron, soluble orthophosphate and, probably, total nitrogen, in addition to shifts in the proportion of sulfate, chloride, sodium and potassium in the ionic balance of the lake water. Very high phosphorus concentrations (in excess of 2 mg/l PO_4^{-3}) were attributed to the failure of sewage treatment (activated sludge treatment preceded and followed by plain sedimentation) to remove detergent phosphorus from waste-water. Sulfate and iron enter the lake in effluent from ore-testing operations and in surface run-off from the townsite.

Bicarbonate, calcium and magnesium concentrations in Pearce Lake are determined primarily by concentrations in throughflow from Knob Lake and the residence time of water in Pearce Lake. Generally, the proportion of these ions in the ionic balance is greatest during the spring flood and least during late winter, when sulfate, (and probably chloride), sodium and potassium appear to accumulate in the lake. Ratios of magnesium to calcium were less than unity in winter and summer, but rose above unity during the spring food. The explanation is not clear, but it may involve an increase in magnesium resulting from accelerated chemical weathering of shales near the townsite. In summer, active photosynthesis raises the pH of surface water from less than 7 to over 8, maintains dissolved oxygen levels slightly below saturation (although the lake is in active circulation), and depresses concentrations of soluble silica below 0.5 mg/l.

The bathymetry of Pearce Lake favours the accumulation of soluble wastes during the period of ice cover in two depressions, one opposite the sewage treatment plant, the other in the centre of the southern arm of the lake. Water in these depressions stagnates during winter and may become anoxic by the time of arrival of the spring flood. Part of the iron and phosphorus discharged into Pearce Lake is probably sedimented within the two depressions. Elsewhere in the lake, levels of dissolved oxygen may fall below 1.0 mg/l in shallow bays, near bottom muds and near storm outfalls. The overall effect of waste-water discharge into Pearce Lake is to create a stagnant body of water in late winter with a residence time of about 50 days and with insufficient oxygen at the end of winter to support fish life. The spring flood is effective in 'flushing-out' the lake, but the complete replacement of lake water may take several weeks. The lake is turbid and subject to plankton blooms in summer.

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Abbreviation: M.S.A.R.P. = McGill Sub-Arctic Research Paper

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APPENDIX I

Location of Sampling Sites for Lake Surveys.

Note: Identification of the smaller lakes may be found Fig. 1, p.3.

Names of individual lakes were assigned by members of the McGill Laboratory at Schefferville, and have not necessarily been officially adopted.

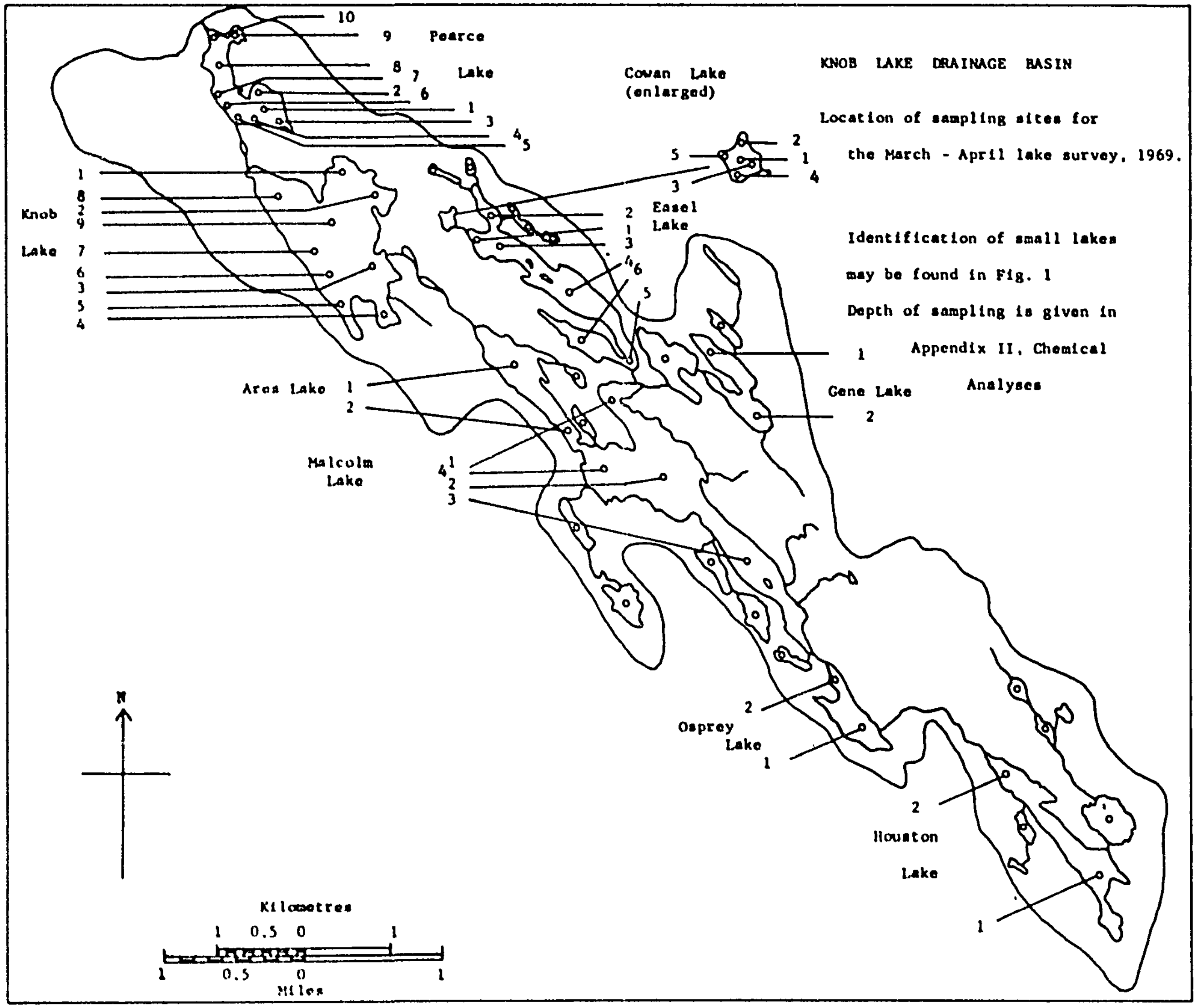
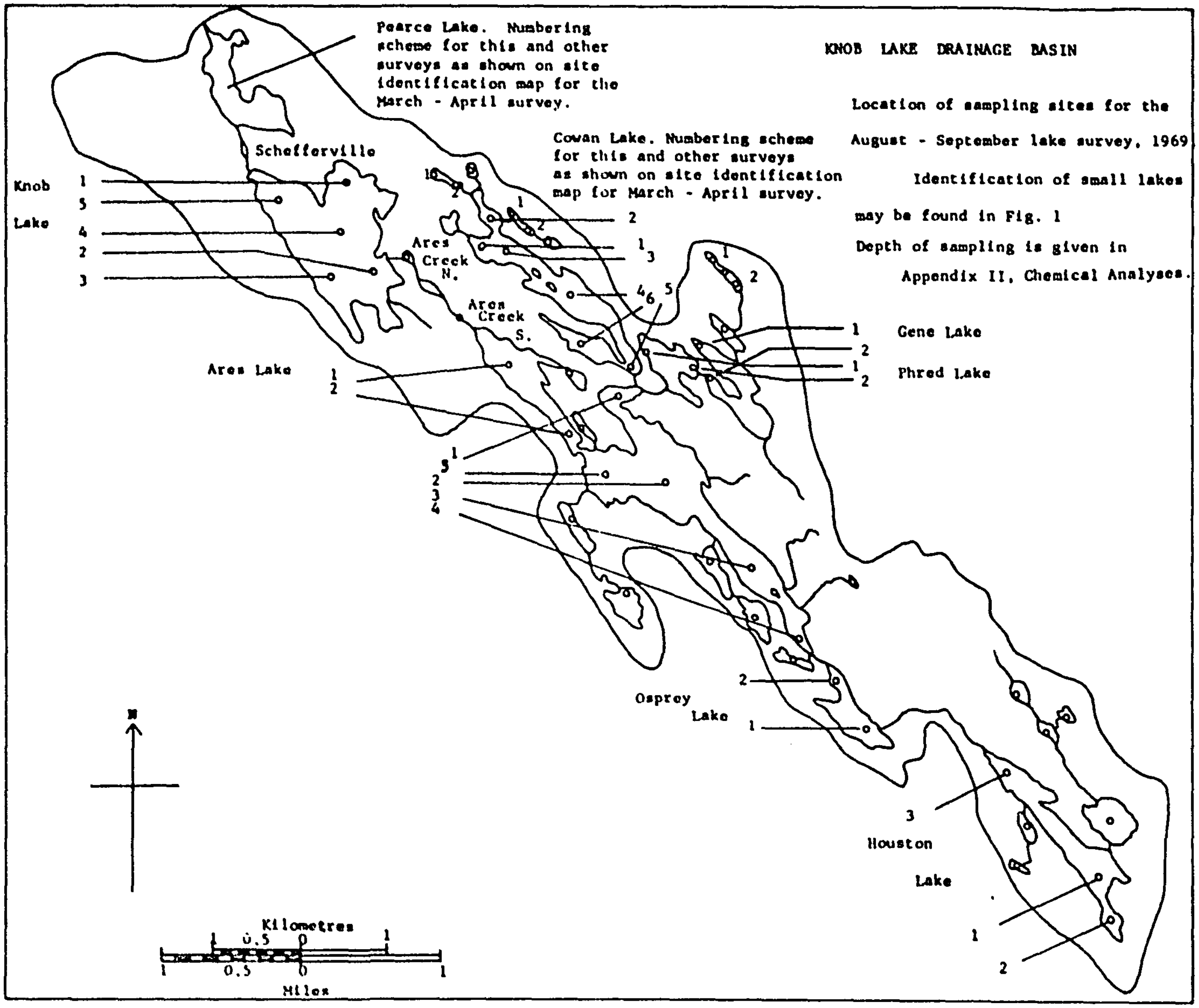


Fig. 36 Location of sampling sites for the March - April lake survey, 1969.



KNOB LAKE DRAINAGE BASIN

Location of sampling sites for the August - September lake survey, 1969

Identification of small lakes may be found in Fig. 1

Depth of sampling is given in Appendix II, Chemical Analyses.

Pearce Lake. Numbering scheme for this and other surveys as shown on site identification map for the March - April survey.

Cowan Lake. Numbering scheme for this and other surveys as shown on site identification map for March - April survey.

Fig. 37 Location of sampling sites for the August - September lake survey, 1969.

APPENDIX II

Chemical Analyses

The following analyses represent the raw data on which this study was based. Apart from the exclusion of the analyses for chloride obtained in the winter survey, the results have not been adjusted. All concentrations are expressed as mg/l, except where specified as moles x 10^{-4} for bicarbonate, calcium and magnesium. Concentrations, as mg/l, for these constituents were obtained by multiplying the molecular weight by appropriate atomic weights, and no attempt has been made to round the figures so obtained, except where bicarbonate ion concentrations exceed 50 mg/l. D.O. refers to dissolved oxygen (mg/l).

Lake and site	T°C	pH	HCO_3^{-1} (mg/l)	(m x 10^{-4})	Ca^{+2} (mg/l)	(m x 10^{-4})	Mg^{+2} (mg/l)	(m x 10^{-4})	SO_4^{-2}	Cl^{-1}	SiO_2	D.O.	Fe	Al	NO_3^{-1}	PO_4^{-3}
KNOB LAKE (March, 1969)																
1 1.5m	2.2	7.25	40.3	6.6	7.6	1.9	4.9	2.0	3	Unreliable: estimated 3 - 6 mg/l	1.9	12.0	.05		.25	
2 2m	1.5	7.15	36.6	6.0	7.6	1.9	3.9	1.6	5		2.6	11.0	.03			
3 1.5m	0.8	7.20	43.9	7.2	6.8	1.7	4.6	1.9	4		2.9	11.5	.02		.4	.02
4 2m	3.0	7.30	45.1	7.4	7.6	1.9	3.4	1.4	7		2.8	11.5	.01			
5 2.5m	2.8	7.40	42.7	7.0	7.6	1.9	3.9	1.6	5		2.7	12.5	nil			
6 2m	1.0	7.35	36.6	6.0	7.2	1.8	3.9	1.6	5		2.1		.01			
5m	2.7	7.25	41.5	6.8	7.6	1.9	3.9	1.6	6		2.2	11.0	.01			
8m	3.4	7.05	42.6	7.0	7.2	1.8	3.9	1.6	6		2.5	10.0	.03			
7 2m	0.8	7.55	39.1	6.4	7.2	1.8	3.9	1.6	3		2.2	11.5	.04			
6m	2.6	7.45	34.2	5.6	6.8	1.7	3.6	1.5	4		2.3	11.0	.03			
10m	3.3	7.35	37.8	6.2	7.6	1.9	3.4	1.4	6		2.4	10.5	.05			
8 4m	2.5	7.45	42.7	7.0	7.2	1.8	4.1	1.7	7		2.5	10.0	.16			
9 2.5m	2.3	7.45	42.7	7.0	7.6	1.9	3.9	1.6	6		2.2	10.5	.08			
KNOB LAKE (Sept., 1969)																
1 2m	11.0	7.67	35.3	5.8	7.6	1.9	3.2	1.3	3	1.0	1.8		.04	.02	.17	
2 2m	11.1	7.70	35.3	5.8	7.2	1.8	2.9	1.2	4	0.9	1.6		.02	.02	.22	
3 2m	11.3	7.58	34.2	5.6	7.2	1.8	3.4	1.4	2	0.9	1.7	9.0	.02	.05	.18	.02
6m	11.2	7.57	35.3	5.8	6.8	1.7	3.4	1.4	1	0.8	1.5	8.5	.02	.01	.26	.02
12m	11.1	7.65	32.9	5.4	6.8	1.7	3.2	1.3	1.5	0.9	1.7	10.5	.03	.005	.31	.01
4 3m	11.3	7.65	35.3	5.8	7.2	1.8	3.2	1.3	4	0.9	1.9		.01	.02	.13	
5 4m	11.3	7.30	34.2	5.6	7.2	1.8	2.9	1.2	1.5	1.2	1.9		.02	.02	.13	

Lake and site	T°C	pH	HCO_3^{-1} (mg/l)	HCO_3^{-1} (m x 10^{-4})	Ca^{+2} (mg/l)	Ca^{+2} (m x 10^{-4})	Mg^{+2} (mg/l)	Mg^{+2} (m x 10^{-4})	SO_4^{-2}	Cl^{-1}	SiO_2	D.O.	Fe	Al	NO_3^{-1}	PO_4^{-3}
MALCOLM LAKE (April)																
1 2m	0.9	7.10	51.1	8.4	9.2	2.3	5.1	2.1	5.5		3.6	9.0	.02			
4.5m	1.9	7.19	54.9	9.0	9.2	2.3	5.1	2.1	6		3.0	8.0	.08		.35	
6.5m	2.2	7.24	52.4	8.6	8.8	2.2	6.1	2.5	5		4.1	7.5	.38			
2 2m	1.3	7.10	36.6	6.0	7.2	1.8	3.4	1.4	4.5		2.7	10.5	.05		.39	.04
8.5m	2.8	7.02	43.9	7.2	7.2	1.8	3.6	1.5	3		3.4	8.0	.06		.57	.03
15m	3.3	7.13	72.0	11.8	12.0	3.0	6.3	2.6	4		3.9	6.0	.09		.35	.03
3 2m	1.3	7.30	39.0	6.4	6.4	1.6	3.9	1.6	3		3.7	9.0	.04			
6.5m	2.7	7.10	46.3	7.6	7.2	1.8	4.4	1.8	4.5		4.2	8.0	.03		.22	
11m	2.9	6.93	47.6	7.8	7.6	1.9	4.6	1.9	6		5.7	5.5	.60			
4 2m	1.0	7.07	43.9	7.2	7.2	1.8	4.4	1.8			3.5		.05			
3.5m	2.1	7.19	43.9	7.2	7.2	1.8	4.6	1.9			3.9		.04			
5m	2.3	7.30	40.3	6.6	7.2	1.8	4.6	1.9			4.0		.04			
MALCOLM LAKE (September)																
1 2.5m	9.7	7.65	37.8	6.2	8.0	2.0	4.1	1.7	6		2.6		.02			
2 1m	9.9	7.60	39.0	6.4	7.6	1.9	3.4	1.4	4	0.9	2.7	9.7	.03	.01	.22	.01
9m	9.9	7.70	37.8	6.2	7.2	1.8	3.4	1.4	6	0.8	2.6	9.3	.06	nil	.09	.03
16m	9.9	7.50	36.6	6.0	8.0	2.0	3.6	1.5	8	0.8	2.7	10.3	.19	.03	.18	.04
3 4m	9.8	7.70	36.6	6.0	7.2	1.8	3.6	1.5	6		2.6		.03			
4 1m	8.9	7.65	34.2	5.6	7.2	1.8	3.4	1.4	8		2.3		.03			
5 2m	10.0	7.65	37.8	6.2	7.2	1.8	3.9	1.6	4		2.5		.01			

Lake and site	T°C	pH	HCO_3^{-1} (mg/l)	HCO_3^{-1} (m x 10^{-4})	Ca^{+2} (mg/l)	Ca^{+2} (m x 10^{-4})	Mg^{+2} (mg/l)	Mg^{+2} (m x 10^{-4})	SO_4^{-2}	Cl^{-1}	SiO_2	D.O.	Fe	Al	NO_3^{-1}	PO_4^{-3}
EASEL LAKE (April)																
1 2m	0.2	7.64	86.5	14.2	15.3	3.8	8.0	3.3	3.5		1.7	11.0				
7m	1.3	7.70	93.0	15.2	15.3	3.8	8.0	3.3	2.5		1.8	10.0				
12m	3.5	7.42	95.0	15.6	16.1	4.0	8.0	3.3	2.5		2.5	10.0	.01			
2 1m	0.2	7.53	88.0	14.4	14.9	3.7	7.5	3.1	4		1.6	9.5			nil	
5m	2.9	7.65	86.5	14.2							1.6	9.6				
8.5m	3.4	7.70	86.5	14.2	15.7	3.9	7.5	3.1	5		1.7	10.5			nil	.01
12m	3.6	7.56	89.0	14.6							2.0	9.0				
15m	3.8	7.35	90.0	14.8	16.1	4.0	7.8	3.2	7		3.3	7.0	.04		.04	
3 2m	1.1	7.90	97.5	16.0	16.1	4.0	9.2	3.8	6		1.9	9.8	nil			
4.5m	3.8	7.48	106	17.4	18.1	4.5	9.0	3.7	4		2.2	9.0				
7m	4.6	7.39	156	25.4	26.9	6.7	12.9	5.3	8		6.9	8.6	.70			
4 2m	0.5	7.74	91.0	15.0	15.3	3.8	7.8	3.2	2		1.8					
12m	3.7	7.66	90.0	14.8	15.3	3.8	7.8	3.2	3		1.5					
5 2m	1.0	7.65	94.0	15.4	15.7	3.9	8.0	3.3	3		1.9					
5m	3.5	7.70	94.0	15.4	15.7	3.9	8.0	3.3	8		1.8					
6 4m	3.0	7.57	?	?	16.1	4.0	9.2	3.8	12		1.8	10.0				
EASEL LAKE (September)																
1 5m	10.6	8.22	83.0	13.6	16.5	4.1	7.5	3.1	4		2.1		.03			
2 1m	10.5	8.07	84.0	13.8	15.6	3.9	7.5	3.1	5	0.9	2.4	8.5	.06	.005	.18	.04
8.5m	10.7	8.09	84.0	13.8	16.1	4.0	7.8	3.2	7	0.9	2.3	8.5	.04	.05	.13	.02
16m	10.4	7.65	84.0	13.8	15.6	3.9	7.5	3.1	5	0.8	2.8	8.0	.03	.03	.22	.05
3 1m	10.1	8.47	94.0	15.4	16.1	4.0	9.2	3.8	7		2.3	9.5	.11			
4m	10.2	8.44	92.5	15.2	17.3	4.3	9.0	3.7	6.5		2.3	9.5	.06			
7m	10.1	8.50	92.5	15.2	18.1	4.5	8.5	3.5	6		2.4	8.5	.10			
4 5m	10.6	8.25	83.0	13.6	16.1	4.0	7.8	3.2	4.5		1.9		.03			
5 2m	10.2	8.15	85.5	14.0	16.5	4.1	7.5	2.9	4	0.8	2.4		.02			
6 2m	9.4	8.50	81.5	13.4	15.6	3.9	8.0	3.3	7.5		2.2		.02			

Lake and site	T°C	pH	HCO_3^{-1} (mg/l)	HCO_3^{-1} (m x 10^{-4})	Ca^{+2} (mg/l)	Ca^{+2} (m x 10^{-4})	Mg^{+2} (mg/l)	Mg^{+2} (m x 10^{-4})	SO_4^{-2}	Cl^{-1}	SiO_2	D.O.	Fe	Al	$NO3^{-1}$	PO_4^{-3}
COMMUNICATIONS (April)																
2m	1.0	6.63	13.4	2.2	1.6	0.4	1.2	0.5	2.5		3.4	8.5	nil			
6.5m	2.7	6.39	14.6	2.4	2.0	0.5	1.2	0.5	2.0		4.1	7.5	nil			
11m	3.1	6.43	19.5	3.2	3.4	0.9	1.8	0.8	1.5		5.4	5.5	.01			
COMMUNICATIONS (August)																
1m	11.0	7.01	11.0	1.8	1.6	0.4	0.7	0.3			4.1	9.0				
4.5m	10.9	7.18	12.2	2.0	1.6	0.4	1.2	0.5	2.0		4.5	9.5	.01	.03		
8m	10.6	7.03	9.8	1.6	1.6	0.4	1.0	0.4			4.6	9.5				
HOUSTON (April)																
1 2m	1.0	6.79	13.4	2.2	1.8	0.45	1.2	0.5			2.5	11.5	nil			
7m	2.2	6.66	14.6	2.4	1.8	0.45	1.2	0.5			2.5	11.0	.01		.18	.01
12m	2.7	6.20	12.2	2.0	1.6	0.4	1.3	0.55			3.1	6.5	.28			
2 1.5m	2.0	6.65	25.6	4.2	4.8	1.2	3.4	1.4			4.6	4.5	.12			
HOUSTON (August)																
1 2m	11.5	7.08	11.0	1.8	1.6	0.4	1.9	0.8			3.1	9.5			.26	.02
7m	11.1	7.18	11.0	1.8	1.6	0.4	1.7	0.7	0.5	0.5	3.0	9.5	.01	.02		
12m	10.7	7.15	12.2	2.0	1.6	0.4	1.7	0.7			3.3					
2 1m	11.0	7.18	12.2	2.0	1.2	0.3	2.1	0.9	2.5		3.0		.03			
3 1m	10.3	7.00	11.0	1.8	1.2	0.3	2.4	1.0	1.0		2.6		.03			
OSPREY (April)																
1 1m	0.5	6.90	26.8	4.4	4.8	1.2	1.9	0.8	2.5		4.4	9.5	.01			
4m	2.7	6.80	36.6	6.0	6.8	1.7	3.4	1.4	2.5		4.6	6.5	.10			
7m	3.9	6.90	64.5	10.6	11.6	2.9	6.8	2.8	4.0		7.9	2.0	.82(Mn=0.4)			
2 1m	1.3	6.83	24.4	4.0	4.8	1.2	2.9	1.2	3.0		3.5	9.0	.10			

Lake and site	T°C	pH	HCO_3^{-1} (mg/l)	(m x 10^{-4})	Ca^{+2} (mg/l)	(m x 10^{-4})	Mg^{+2} (mg/l)	(m x 10^{-4})	SO_4^{-2}	Cl^{-1}	SiO_2	D.O.	Fe	Al	NO_3^{-1}	PO_4^{-3}
OSPREY (September)																
1 2m	9.4	7.50	24.4	4.0	4.4	1.1	2.7	1.1	4		1.4	9.5	.10	.03	.18	.03
8m	9.2	7.40	24.4	4.0	4.4	1.1	2.9	1.2	7.5		1.4	10.0	.19	.03	.13	.04
2 1m	9.5	7.64	25.6	4.2	4.0	1.0	2.9	1.2	7	0.7	1.7		.07			
ARES (April)																
1 1m	0.3	7.10	39.0	6.4	7.2	1.8	3.2	1.3	4.5		2.8	10.5	.01			
3m	2.8	7.07	45.0	7.4	7.2	1.8	4.4	1.8	4.0		3.0		.05			
6m	3.9	6.92	69.5	11.4	10.8	2.7	5.1	2.1	3.5		5.5	1.5	.35			
2 1m	0.7		36.6	6.0	7.2	1.8	4.4	1.8	2.0		3.1		.10			
ARES (September)																
1 1m	10.8	7.84	39.0	6.4	7.6	1.9	3.4	1.4	3	0.9	2.6	7.0	.01	.03	.22	.02
6m	10.8	7.75	37.8	6.2	7.6	1.9	3.4	1.4	7	0.9	2.5	8.3	.03	.03	.31	.01
2 1m	11.3	7.78	37.8	6.2	7.2	1.8	4.6	1.9	6	1.2	2.7		.08	.04	.44	.01
Ares Creek S.	10.5	7.78	36.6	6.0	6.8	1.7	3.2	1.3	7	0.9	2.6		.09	.02	.26	.01
Ares Creek N.	10.5	7.71	35.4	5.8	8.0	2.0	3.4	1.4	6	0.9	2.5		.05	.05	.22	.01
PHRED (April) 2m	1.7	7.42	48.8	8.0	9.2	2.3	5.1	2.1	5.5		3.4	10.0	.02			
4m	3.0	7.23	48.8	8.0	8.8	2.2	6.1	2.5	8.5		3.3	8.0	.02		.35	.01
6m	4.1	6.96	53.6	8.8	9.6	2.4	6.6	2.7	9.0		5.1	3.0	.28			
PHRED (September)																
1 0.5m	9.8	7.60	42.7	7.0	8.8	2.2	4.4	1.8	6	0.8	2.7		.07		.13	.01
2 0.5m	9.4	7.60	44.0	7.2	9.6	2.4	4.4	1.8	7		2.5		.04			

Lake and site	T°C	pH	HCO_3^{-1}		Ca^{+2}		Mg^{+2}		SO_4^{-2}	Cl^{-1}	SiO_2	D.O.	Fe	Al	NO_3^{-1}	PO_4^{-3}
			(mg/l)	(m x 10^{-4})	(mg/l)	(m x 10^{-4})	(mg/l)	(m x 10^{-4})								
LAKES ON SHALES AND CHERTS:																
GENE (April)																
1 2m	3.3	6.98	50.0	8.2	10.8	2.7	5.8	2.4	12		5.7	8.5	.09			
2 1.5m	3.5	7.26	46.4	7.6	8.8	2.2	5.8	2.4	9		4.3		.14			
GENE (September)																
1 0.5m	8.4	7.6	42.7	7.0	8.8	2.2	4.6	1.9	8		2.8		.06			
2 0.5m	9.1	7.7	39.0	6.4	9.6	2.4	4.1	1.7	8.5		2.5		.11	.01	.27	.02
TRIGGER (April) 1m	0.7	7.1	366	58.4	78	19.5	66	27.0	240		29		2.2		.6	.02
TRIGGER (Sept.) 0.5m	7.4	7.25	37.9	6.2	7.2	1.8	4.6	1.9	12		4.3		.90			
DALE (Sept.)																
1 0.5m	6.8	7.2	14.7	2.4	3.2	0.8	1.5	0.6	2		2.2		.05	.03		
2 0.5m	6.8	7.5	36.6	6.0	6.0	1.5	5.3	2.2	7.5		3.2		.09	.02		
DORIS (August) 0.5m	12.5	4.2	nil	nil	0.8	0.2	1.9	0.8	14		8.3		.37	.53		
BASSETT (April) 1m	2.5	6.77	81.5	13.4	12.9	3.2	7.8	3.2	4.5		3.4		.66			
BASSETT (Sept.) 0.5m	8.6	7.4	39.0	6.4	7.2	1.8	3.2	1.3	5		1.0		.17	.04		

Lake and site	T°C	pH	HCO_3^{-1}		Ca^{+2}		Mg^{+2}		SO_4^{-2}	Cl^{-1}	SiO_2	D.O.	Fe	Al	NO_3^{-1}	PO_4^{-3}
			(mg/l)	(m x 10^{-4})	(mg/l)	(m x 10^{-4})	(mg/l)	(m x 10^{-4})								
LAKES ON SHALES AND CHERTS (Continued)																
GRAY (April) 1m	2.1	6.10	11.0	1.8	1.6	0.4	0.7	0.3	1		4.2	.08				
GRAY (August) 0.5m	10.5	6.6	8.5	1.4	0.6	0.15	0.9	0.35	3	0.8	4.7		.11	.03	.26	.02
HARDY (April) 1m	1.8	6.07	13.4	2.2	1.6	0.4	1.0	0.4	4		3.9	3.5	.50			
HARDY (August) 0.5m	10.0	6.8	6.1	1.0	0.8	0.2	0.7	0.3	2.5		3.5		.12	.04		
THORN (August) 0.5m	9.8	6.7	12.2	2.0	1.6	0.4	1.5	0.6	2.5		4.3	9.0	.11	.05		
BARR (April) 1.5m	1.2	5.4	4	0.6	.4	.1	.2	.1	3		1.8	4.0	1.6			
BARR (August) 0.5m	10.8	5.8	1.2	0.2	-	-	.2	.1	1		1.6		.18	.05	.05	.01
LIER (August) 0.5m	10.5	5.4	1.8	0.3	-	-	.2	.1	1		2.0		.07	.04		
RAINWATER:																
DORIS RIDGE		5.8	2.4	0.4					1	1.5			.33			
MALCOLM SHORE		6.0	1.8	0.3					1							
SNOW:																
nr. Airstrip		6.1	1.2	0.2					1	1.1	.25		.37			

Lake and site	T°C	pH	HCO_3^{-1}		Ca^{+2}		Mg^{+2}		SO_4^{-2}	Cl^{-1}	SiO_2	D.O.	Fe	Al	NO_3^{-1}	PO_4^{-3}
			(mg/l)	(m x 10^{-4})	(mg/l)	(m x 10^{-4})	(mg/l)	(m x 10^{-4})								
SMALL LAKES ON DOLOMITE																
PANHANDLE (April)																
1m	1.1	7.37	127	20.8	23.3	5.8	10.7	4.4	5		2.1	2.6	.27			
3m	3.9	7.11	140	23.0	24.1	6.0	11.9	4.9	13		5.0	1.8	.70			
PANHANDLE (August)																
1 0.5m	10.0	8.9	94	15.4	16.5	4.1	8.3	3.4	2	1.1	1.9	9.0	.05	.04	.2	.04
2 0.5m	10.8	8.85	91	14.8	16.5	4.1	8.5	3.5			1.7		.01			
FINDLAY (April)																
1m	1.1	7.05	84	13.8	15.3	3.8	7.8	3.2	3.5		2.4	3.3	.7			
3m	4.3	7.02	89	14.6	15.7	3.9	8.0	3.3	8.5		2.9	4.4	1.2			
FINDLAY (August)																
0.5m	10.6	8.05	60	9.8	11.3	2.8	6.1	2.5	1	1.0	0.6	8.0	.13	.02	.2	.01
Pond nr.Findlay	9.6	7.6	29.3	4.8	4.8	1.2	2.4	1.0	5	1.3	0.3		.27	.06	.4	.02
WILLIAMS (April)																
1m	3.3	7.2	184	30.2	31.0	7.7	17.3	7.1	8.5		6.5	1.6	.75		.4	
WILLIAMS (August)																
1 0.5m	9.6	8.7	112	18.4	20.1	5.0	9.7	4.0	2	1.0	1.9	8.5	.07	.02	.25	.02
2 0.5m	9.6	8.1	100	16.4	19.7	4.9	10.0	4.1			1.7		.05			
FRANCOIS (April)																
1m	3.5	6.7	72	12.0	11.3	2.8	5.6	2.3	9		1.7	2.2	.18			
François-Ice		8.1	76	12.4	12.1	3.0	6.8	2.8	1.5		1.4					
FRANCOIS (August)																
0.5m	9.8	7.9	46.5	7.6	7.2	1.8	4.4	1.8	2	1.1	0.4		.15	.02	.35	.02

Lake and site	T°C	pH	HCO_3^{-1} (mg/l)	(m x 10^{-4})	Ca^{+2} (mg/l)	(m x 10^{-4})	Mg^{+2} (mg/l)	(m x 10^{-4})	SO_4^{-2}	Cl^{-1}	SiO_2	D.O.	Fe	Al	NO_3^{-1}	PO_4^{-3}
SMALL LAKES ON DOLOMITE (cont.)																
IVES (April)																
2m	2.8	7.2	87	14.2	15.3	3.8	7.8	3.2	4.5		2.5	6.5	.29			
IVES (August)																
0.5m	11.0	7.9	60	9.8	11.7	2.9	5.3	2.2	4.5		1.2		.10			
MATTOX (April)																
1m	2.7	6.5	310	50.6	53	13.2	28	11.6	15		14	0.5	nil			
MATTOX (August)																
0.5m	10.5	7.6	61	10.0	12.5	3.1	6.3	2.6	1		2.6		.10		.2	.01
ADAMS (April)																
4.5m	2.7	7.6	71	11.6	11.7	2.9	8.7	3.6	1.5		2.3	10.0	.04			
ADAMS (Sept.)																
0.5m	10.1	7.8	67	11.0	12.0	3.0	6.1	2.5	2		2.1		.01			
SOUTH (April)																
1m	1.7	7.5	123	20.2	23.3	5.8	12.1	5.0	7		3.7	4.5	.25			
SOUTH (Sept.)																
0.5m	8.5	8.05	87	14.0	16.9	4.2	7.3	3.0	4		2.1		.02			
MIDDLE (April)																
1m	0.4	7.55	61	10.0	10.8	2.7	5.6	2.3	2.5		0.7	9.5	.05			
4m	2.6	7.20	62	10.2	11.2	2.8	5.3	2.2	1.5		1.5	5.0	.16			
7m	3.9	7.25	62	10.2	11.2	2.8	5.8	2.4	3.0		2.4	8.0	.17			
MIDDLE (Sept.)																
1m	9.6	7.97	58	9.4	11.7	2.9	4.4	1.8	2		0.5	8.2	.07			
7m	9.6	7.89	56	9.2	11.3	2.8	4.6	1.9	4		0.5	8.5	.14			
NORTH (April)																
2.5m	2.8	7.5	78	12.8	13.7	3.4	8.0	3.3	1		1.3	7.0	.06			
NORTH (Sept.)																
1m	9.6	8.07	70	11.4	12.5	3.1	6.6	2.7	3		0.9	7.8	.04		.18	
6m	9.6	7.95	70	11.4	12.0	3.0	6.6	2.7	5		1.0	7.0	.10			

Lake and site		T°C	pH	HCO$_3^{-1}$ (mg/l)	(m x 10^{-4})	Ca^{+2} (mg/l)	(m x 10^{-4})	Mg^{+2} (mg/l)	(m x 10^{-4})	SO$_4^{-2}$	Cl^{-1}	SiO$_2$	D.O.	Fe	Al	NO$_3^{-1}$	PO$_4^{-3}$
COWAN LAKE (March)																	
1	1m	0.2	7.60	107	17.6	18.9	4.7	10.2	4.2	3		2.6	10.0	nil	0.2		.01
	2m	1.8	7.60	111	18.2	18.9	4.7	9.5	3.9	4		2.6	8.0		1.9		
	4m	3.2	7.55	110	18.0	18.9	4.7	9.7	4.0	3		2.7	9.0		3.2	.75	
	6m	3.5	7.55	121	19.8	20.4	5.1	10.9	4.5	4		3.5	7.0		3.5		
	8m	3.6	7.40	110	18.0	19.7	4.9	10.9	4.5	16		2.7	6.5	.06	3.7		.01
	10m	4.1	7.25	171	28.0	26.9	6.7	15.3	6.3	40		8.0	0.1	3.80	4.1		
2	1m	2.2	7.7	110	18.0	19.3	4.8	9.7	4.0	5		2.4		.03	2.2		
	3m	3.1	7.6	110	18.0	19.7	4.9	10.5	4.3			2.4	7.0		3.1		
3	1m	0.8	7.6	110	18.0	19.7	4.9	10.0	4.1	5		2.5		.34	0.8		
	3m	2.9	7.3	110	18.0	19.7	4.9	10.0	4.1			2.5			2.9		
4	1m	0.8	7.75	110	18.0	19.3	4.8	9.7	4.0	4		2.5			0.8		
	3m	3.1	7.4	113	18.6	18.9	4.7	10.7	4.4			2.9	7.5		3.1		
5	1m	0.6	7.65	112	18.4	18.9	4.7	10.2	4.2	3		2.9		.30	0.6		
	2m	1.2	7.3	118	19.4	19.7	4.9	10.3	4.3			2.9			1.2		
COWAN LAKE (June 7th)																	
1	1m	2.2	6.97	48.8	8.0	9.6	2.4	4.6	1.9	2.5		1.7	9.0	.15			
	2m	2.6	7.05	75.5	12.4	14.1	3.5	7.5	3.1	1.5		1.8	8.0	.07			
	4m	3.2	6.96	61.0	10.0	11.2	2.8	6.1	2.5	2.5		1.7	10.0	.11			
	6m	3.2	7.19	102.5	16.8	18.9	4.7	10.0	4.1	3.5		2.75	6.5	.14			
	8m	3.3	6.98	86.5	14.2	15.7	3.9	8.3	3.4	4.5		3.05	8.3	.45			
	10m	3.5	7.05	104.0	17.0	18.5	4.6	10.0	4.1	6.0		3.0	7.2	.50			
2	1.5m	2.3	7.16	52.5	8.6	9.6	2.4	4.9	2.0	4.0		1.0	10.3	.04			
3	2.5m	2.6	7.10	68.5	11.2	12.0	3.0	6.3	2.6	5.0		1.6	8.5	.06			
4	1.5m	2.0	7.10	47.5	7.8	8.8	2.2	4.6	1.9	5.0		1.1	10.5	.08			
5	1.5m	2.2	7.16	75.5	12.4	13.6	3.4	7.3	3.0	3.0		1.4	8.0	.05			

Lake and site	T°C	pH	HCO_3^{-1} (mg/l)	HCO_3^{-1} (m x 10^{-4})	Ca^{+2} (mg/l)	Ca^{+2} (m x 10^{-4})	Mg^{+2} (mg/l)	Mg^{+2} (m x 10^{-4})	SO_4^{-2}	Cl^{-1}	SiO_2	D.O.	Fe	Al	NO_3^{-1}	PO_4^{-3}
COWAN LAKE																
June 27:																
1 1m	15.2	7.94	97.5	16.0	17.3	4.3	8.5	3.5	2		1.8	9.5	.03			
4m	8.7	7.88	96.5	15.8	17.3	4.3	8.5	3.5			1.9	8.5	.04			
7m	7.5	7.85	100.0	16.4	16.9	4.2	8.8	3.6			1.4	9.5	.05			
10m	4.7	7.58	99.0	16.2	18.5	4.6	8.0	3.3	2.5		2.4	9.3	.07			
2 1m	14.6	7.83	95.0	15.6	18.5	4.6	8.3	3.4			1.9	9.2				
3 2m	12.9	7.87	97.5	16.0	17.7	4.4	8.5	3.5			2.0	9.5				
4 2m	12.2	7.86	97.5	16.0	18.1	4.5	8.3	3.4			1.7	8.5				
5 1m	15.7	7.96	97.5	16.0	17.3	4.3	8.8	3.6			1.8	10.0				
July 14:																
1 0.5m	19.1	7.95	95.0	15.6	16.1	4.2	9.2	3.8			2.9	7.5	.04			
4m	10.4	8.10	96.5	15.8	16.1	4.2	9.0	3.7			3.8	7.7	.05			
7m	8.5	7.97	96.5	15.8	16.1	4.2	9.2	3.8			4.3	9.5	.06			
10.5m	8.0	7.95	97.5	16.0	16.1	4.2	9.2	3.8			3.3	7.9	.10			
August 26:																
1 1m	11.1	8.10	96.5	15.8	18.1	4.5	8.7	3.6	2	1.3	3.1	9.5	.03	.03	.18	.01
7m	11.1	8.20	96.5	15.8	17.3	4.3	9.2	3.8	1.5	1.0	3.1	9.5	.04	.06	.13	.01
8.5m	10.9	7.60	96.5	15.8	17.7	4.4	9.5	3.9	1	1.0	4.3	4.2	.22	.04	.70	.03
10.5m	8.3	7.70	95.0	15.6	16.9	4.2	10.5	4.3	2	0.9	3.9	5.0	.62	.08	.09	.05
2 1m	11.1	8.30	95.0	15.6	19.3	4.8	8.0	3.3	0.5		2.8		.03		.18	.01
3 2m	11.1	8.23	95.0	15.6	18.1	4.5	8.7	3.6	0.5		3.1		.02		.22	.02
4 2m	11.1	8.20	96.5	15.8	18.1	4.5	8.7	3.6	0.5		2.8		.02		.26	.02
5 1m	11.1	8.28	96.5	15.8	18.1	4.5	8.7	3.6	0.5		2.9		.01		.18	.01

Lake and site		T°C	pH	HCO_3^{-1} (mg/l)	HCO_3^{-1} (m x 10^{-4})	Ca^{+2} (mg/l)	Ca^{+2} (m x 10^{-4})	Mg^{+2} (mg/l)	Mg^{+2} (m x 10^{-4})	SO_4^{-2}	Cl^{-1}	SiO_2	D.O.	Fe	Al	NO_3^{-1}	PO_4^{-3}
PEARCE LAKE																	
March:																	
1	1.5m	No temperature data available	7.0	47.5	7.8	8.4	2.1	5.4	2.1	26	9	3.4	3.0	.28(Mn-.3)		.35	0.90
2	1.5m		7.1	60	9.8	9.7	2.4	5.1	2.1	17	7	3.0	2.5	.10		.40	1.10
3	2m		6.95	55	9.0	8.8	2.2	4.6	1.9	19	8	3.3	2.4	.45			2.1
5	3m		6.65	73	13.8	12.0	3.0	7.3	3.0	24	9.5	4.6	1.0	3.5			2.4
7	1m		6.85	49	8.0	8.0	2.0	4.1	1.7	12	6.5	2.8	3.5	.15			0.9
	3m		6.75	61	10.0	10.8	2.7	5.4	2.2	30	8.5	3.8	2.0	.70(Mn-1.7)			2.5
	5m		6.60	65	10.6	18.5	4.6	10.2	4.2	85	8.5	5.8	0.8	1.85			1.0
9	1m		6.8	50	8.2	8.4	2.1	3.6	1.5	14	7	2.9	5.0	.01		.18	0.9
10	1m		6.8	51	8.4	8.4	2.1	4.1	1.7	13	6.5	2.5	4.0	.19		.35	0.8
June 1:																	
1	1m	2.0	6.4	24.4	4.0	6.8	1.7	4.4	1.8	20		2.3	9.0	.33			.07
	2m	3.0	6.45	26.8	4.4	8.0	2.0	5.4	2.2	28		2.7	8.5	.33			.09
	3m	3.7	6.1	14.7	2.4	10.8	2.7	7.3	3.0	57		3.3	7.5	1.1			.18
2		3.5	6.55	26.8	4.4	8.0	2.0	6.3	2.6	28		3.0	8.5	.42			.05
3		3.5	6.5	25.6	4.2	7.6	1.9	5.4	2.2	26		2.8	7.5	.34			.07
4		3.0	6.5	26.8	4.4	8.8	2.2	5.1	2.1	23		2.8	9.0	.29			.02
5		2.7	6.45	24.4	4.0	8.4	2.1	5.4	2.2	30		2.8	8.5	.31			.06
6	1m	2.7	6.76	31.1	5.2	8.0	2.0	5.1	2.1	26		2.7	9.0	.20			.02
	3.5m	2.8	6.73	26.8	4.4	7.6	1.9	5.8	2.4	28		2.8	9.5	.13			.01
	6m	2.8	6.71	26.8	4.4	8.0	2.0	5.4	2.2	31		2.7	9.0	.83			.10

Lake and site	T°C	pH	HCO_3^{-1} (mg/l)	(m x 10^{-4})	Ca^{+2} (mg/l)	(m x 10^{-4})	Mg^{+2} (mg/l)	(m x 10^{-4})	SO_4^{-2}	Cl^{-1}	SiO_2	D.O.	Fe	Al	NO_3^{-1}	PO_4^{-3}
PEARCE LAKE - Continued																
June 1 - continued																
7 1m	2.8	6.72	30.5	5.0	8.0	2.0	6.1	2.5	23		2.9	9.0	.26			.01
3.5m	2.9	6.47	28.1	4.6	8.0	2.0	5.1	2.1	24		2.8	8.5	.13			.01
6m	2.8	6.35	26.8	4.4	7.6	1.9	5.1	2.1	26		2.9	8.0	1.15			.45
8	1.5	6.65	26.8	4.4	8.0	2.0	5.4	2.2	29		3.0	9.5	.44			.04
9	3.0	6.75	29.3	4.8	8.0	2.0	5.6	2.3	27		2.6	9.0	.50			.02
10	1.8	6.55	19.5	3.2	4.4	1.1	2.7	1.1	14		1.5	9.0	.48			.19
KL Outflow	3.0	7.0	25.6	4.2	4.8	1.2	2.9	1.2	3		2.4	10.0	.01			.01
June 30:																
1 1m	10.5	7.13	31.7	5.2	6.8	1.7	3.4	1.4	3.5		2.0	10.0	.02			
4.5m	11.5	7.18	33.0	5.4	7.2	1.8	3.2	1.3	5.0		2.2	10.0	.50			
2 2m	10.0	7.1	31.7	5.2	6.8	1.7	3.2	1.3	14		2.3		.82			
3 2m	9.8	7.07	30.5	5.0	6.0	1.5	3.9	1.6	14	1.3	2.1	9.0	.50			
4 2m	9.7	7.12	34.2	5.6	6.8	1.7	3.4	1.4	10		2.0		.03			
5 2m	9.7	7.34	34.2	5.6	6.8	1.7	2.9	1.2	6		2.3	9.5	.15			
7 1m	9.9	7.21	34.2	5.6	6.4	1.6	3.4	1.4	11	1.5	2.3	9.5	.11			
3.5m	10.0	7.20	34.2	5.6	7.2	1.8	2.9	1.2	11		2.1	10.3	.19			
6m	10.0	7.18	35.4	5.8	6.0	1.5	3.6	1.5	13		2.9	9.5	.35			
8 1.5m	10.8	7.25	34.2	5.6	6.8	1.7	3.4	1.4	8		1.5		.21			
9 1m	9.6	7.15	30.5	5.0	6.8	1.7	3.4	1.4	9		2.1	8.8	.13			
10	11.0	7.25	31.7	5.2	6.4	1.6	2.9	1.2	9		1.6		.17			

Lake and site		T^oC	pH	HCO_3^{-1} (mg/l)	HCO_3^{-1} (m x 10^{-4})	Ca^{+2} (mg/l)	Ca^{+2} (m x 10^{-4})	Mg^{+2} (mg/l)	Mg^{+2} (m x 10^{-4})	SO_4^{-2}	Cl^{-1}	SiO_2	D.O.	Fe	Al	NO_3^{-1}	PO_4^{-3}
PEARCE LAKE - Continued																	
July 14 :																	
1	1m	17.0	7.8	34.2	5.6	7.6	1.9	4.4	1.8	13		1.4	10.0	.25			
	3m	12.4	7.6	31.7	5.2	7.2	1.8	3.9	1.6	16		1.2	9.0	.35			
	5m	9.9	7.45	30.5	5.0	7.6	1.9	4.6	1.9	14		1.1	7.5	1.2			
7	1m	15.7	7.6	33.0	5.4	7.2	1.8	4.4	1.8	15		1.3	10.2	.32			
	3.5m	10.3	7.55	34.2	5.6	7.2	1.8	4.6	1.9	15		1.3	9.2	.34			
	6m	9.7	7.2	35.4	5.8	7.6	1.9	4.6	1.9	19		1.3	8.8	,60			
August 27:																	
1	1m	11.2	7.7	32.9	5.4	8.0	2.0	4.9	2.0	20	1.8	0.8	9.5	.22	.05		
	4m	10.6	7.3	24.4	4.0	8.0	2.0	4.9	2.0	24		2.0	6.2	.50	.06		
2		10.7	8.1	29.3	4.8	8.0	2.0	4.6	1.9	20	2.0	0.8		.23	.04	.18	.06
3		11.6	7.5	35.4	5.8	8.4	2.1	4.9	2.0	21	2.0	0.9		.27	.06	.18	.07
4		10.8	7.65	34.2	5.6	8.4	2.1	4.4	1.8	17	1.7	1.1		.23	.04	.26	.06
5		10.8	7.55	31.7	5.2	8.0	2.0	3.9	1.6	14	1.9	1.9	9.3	.21	.01	.31	.06
7	1m	11.1	7.07	35.4	5.8	8.0	2.0	4.9	2.0	22	2.8	1.1	8.8	.30	.06	.13	.04
	3.5m	10.7	7.42	34.2	5.6	7.6	1.9	4.6	1.9	19	1.8	1.0	9.0	.40	.03	.09	.12
	6m	10.5	7.28	32.9	5.4	8.0	2.0	4.6	1.9	20	2.5	0.8	8.5	.60	.04	nil	.12
8		11.1	8.05	28.0	4.6	6.8	1.7	4.9	2.0	17	1.8	1.9		.32	.03	.18	.07
9		12.0	7.8	30.5	5.0	8.0	2.0	4.2	1.7	17	1.9	1.3		.18	.02	.13	.07
10		10.8	8.25	32.9	5.4	8.0	2.0	4.6	1.9	19	2.0	1.3	11.0	.15	.01	.22	.08

APPENDIX III

LAKE WATER TEMPERATURE DATA

i) Temperatures under ice in March-April, 1969.

For each chemical analysis of lake water in this study, a temperature has been assigned which was taken from a temperature profile at the sample site (Appendix I). Temperature profiles are similar for most sites, being bounded by the freezing point at the ice surface and temperature of maximum density of fresh water, 3.94°C. The following profiles, taken from deeper lakes in the drainage basin, have been chosen as characteristic of the lakes studied. Smaller and shallower lakes have similar, but more compressed profiles. Water temperatures were originally recorded to 0.1°F, and have been converted to °C, and rounded to 1 decimal place.

Depth.	Cowan Lake (1)		Malcolm Lake (2)	Easel Lake(2)
	March 8	June 7	April 28	April 14
0m		0.2		
1m	0.2	2.2	0.2	0.1
2m	1.9	2.6	1.3	0.2
3m	2.5	3.0	2.1	1.7
4m	3.2	3.2	2.3	2.3
5m	3.4	3.2	2.6	2.9
6m	3.5	3.2	2.7	3.2
7m	3.5	3.3	2.7	3.3
8m	3.6	3.3	2.7	3.3
9m	3.9	3.4	2.8	3.4
10m	4.1	3.5	2.8	3.5
11m		3.5	2.8	3.5
12m			2.8	3.6
13m			2.8	3.6
14m			2.9	3.6
15m			3.3	3.8

Depth	Ares (April 20)	Osprey (April 28)	Houston (April 24)	Communications (April 24)
1m	0.1	0.4	0.2	0.6
2m	1.4	1.6	1.0	1.0
3m	2.8	2.2	1.2	2.0
4m	3.3	2.7	1.8	2.2
5m	3.9	2.8	2.0	2.4
6m	4.2	3.3	2.1	2.6
7m		3.9	2.2	2.7
8m		4.0	2.2	2.8
9m			2.3	2.8
10m			2.4	2.9
11m			2.6	3.1
12m			2.7	3.2

ii) Water temperatures in late August-early September, 1969.

Temperatures of individual samples are given in table of chemical analyses (Appendix II). With the exception of a few small lakes on high ground sampled in cold weather, water temperatures throughout the basin fell in the range 9.0 - 12.0°C. For purposes of discussing chemical equilibria in lake waters, 10.0°C has been taken as a standard water temperature during the late summer lake survey.

For larger lakes in the basin which were sampled by boat, the following results may be noted:

Knob Lake.	Observed surface temperature range 11.0 - 11.6°C. Higher temperatures at deep water sites 3, 4, 5, away from inflowing waters. Water at depth 10 m 0.3°C colder than surface water.
Ares Lake.	Temperature 10.8 at northern end of lake; no change with depth. Water flowing into Ares from Malcolm, 11.3°C.
Malcolm Lake.	No change of water temperature with depth; cold water entering lake from south. Temperatures at sampling sites as follows:

Site	1.	9.7
	2.	9.9
	3.	9.8
	4.	8.9
	5.	10.0

Osprey Lake. Water temperature 9.3°C throughout water column opposite inflow from Houston Lake.

Houston Lake. Surfaces temperatures; 10.3 south end, 11.0 north end, and 11.5 at centre, falling to 10.7 at 11m.

Communications Lake. Surface temperature 11.0 falling to 10.6 at 8m.

Easel Lake. Slight temperature variation with depth (0.1 - 0.2°C) Temperatures at sample sites as follows:

Site 1.	10.6		Site 4.	10.6
2.	10.5		5.	10.2
3.	10.1		6.	9.4

Pearce Lake. Air temperature at time of survey c.15°C; light winds. Parts of lake weakly stratified, with temperature gradients of 1 - 2°C.
Surface water temperature range 10.6 - 12.0°C, with major portion of lake at 11.0°C.

The following temperatures were obtained for other lake samples:

Panhandle	1.	10.0	Gene	1.	8.4
	2.	10.8		2.	9.1
Findlay		10.6	Phred	1.	9.4
Williams		9.6		2.	9.4
Francois		9.8	Trigger		7.4
Ives		11.0	Dale		6.8
Mattox		10.5	Gray		10.5
Bassett		8.6	Hardy		10.0
Adams		10.1	Thorn		9.8
North		9.6	Barr		10.8
Middle		9.6	Lier		10.5
South		8.5	Doris		12.5

Cowan Lake was thermally stratified during the summer of 1969. Surface temperatures were uniform at survey times. The temperature record for the centre of the lake is as follows:

Depth	June 27	July 14	August 27
0m	15.8	19.3	11.1
1m	15.2	17.7	11.1
2m	13.3	12.5	11.1
3m	10.5	11.2	11.0
4m	8.7	10.4	11.1
5m	8.2	9.8	11.0
6m	7.9	8.7	11.0
7m	7.5	8.5	10.9
8m	5.2	8.3	10.6
9m	4.8	8.3	9.4
10m	4.7	8.0	8.5
11m			7.9

Although stratification persisted in Cowan Lake, the thermocline became more gradual and diffuse with each survey. The lake may have been close to fall turnover by the end of August.

There is little indication of thermal stratification in any other lake, although there is some evidence of incomplete horizontal mixing in Malcolm, Knob and Easel Lakes. Variations in temperature between lakes result from differing sampling dates rather than site or elevation.

APPENDIX IV

List of Scientific and Common Names of Plant Species Referred to in the Text (after Wassen, 1969).

Vascular Plants

Abies balsamea (L.) Mill.	Balsam fir
Alnus spp. (esp. A. crispa (Ait.) Pursh)	Alder
Betula glandulosa Michx.	Dwarf birch
Betula papyrifera Marsh	White birch
Carex spp. (esp. C. aquatilis Wahlenb.)	Sedges
Eleocharis acicularis (L.) R. & S.	
Isoetes echinospora Dur.	
Larix laricina (Du Roi) K. Koch	Tamarack
Ledum groenlandicum Oedee	Labrador tea
Mitella nuda (L.)	
Picea glauca (Moench) Voss	White spruce
Picea mariana (Mill.) BSP	Black spruce
Salix spp. (esp. S. planifolia Pursh)	Willows
Vaccinium spp. (esp. V. uliginosum L.)	

Mosses

Sphagnum warnstorfianum Du Rietz

Lichens

Cladonia alpestris (L.) Rabenh.

Cladonia rangiferina Wigg.

Cladonia silvatica (L.) Hoffm.

APPENDIX V

Carbonate Chemistry of Lake Waters.

A. Comments on the solubility of dolomite

  1. Estimation of the equilibrium constant for dolomite using Mg:Ca ratios of water in equilibrium with both calcite and dolomite.
  2. Temperature dependence of the equilibrium constant for dolomite in the range 0 - 25°C.

B. Calculation of ion activity products relating to equilibrium of water with respect to dolomite and calcite.

C. Approximate concentration of calcium and magnesium in water at equilibrium with dolomite as a function of temperature and carbonic acid concentration.

D. Results of Carbonate Equilibria Calculations for Knob Lake drainage basin.

E. Relationships between hydrogen ion activity, carbonate ion activity and molar concentration of carbonic acid.

F. Specific conductance of lake water samples in relation to concentration of major ions.

A. Comments on the solubility of dolomite.

1. Estimation of the equilibrium constant for dolomite (Keq: dolomite) from analyses of water in equilibrium with dolomite and with calcite, after Hsu (1964).

According to Hsu:

since $$a_{Ca^{+2}} \cdot a_{CO_3^{-2}} = \text{Keq:calcite} \quad (1)$$

and since $$a_{Ca^{+2}} \cdot a_{Mg^{+2}} \cdot a^2_{CO_3^{-2}} = \text{Keq:dolomite} \quad (2)$$

so that $$a^2\, _{Ca^{+2}} \cdot a^2_{CO_3^{-2}} = K^2\ \text{eq:calcite} \quad (3)$$

dividing (2) by (3):

$$\frac{a_{Mg^{+2}}}{a_{Ca^{+2}}} = \frac{\text{Keq:dolomite}}{K^2\ \text{eq:calcite}}$$

from which,

$$\text{Keq:dolomite} = \frac{a_{Mg^{+2}}}{a_{Ca^{+2}}} \cdot K^2\ \text{eq:calcite}$$

In other words, to obtain an apparent solubility product for dolomite, all that is needed is the appropriate equilibrium constant for dolomite at the required temperature, and the ratios of the activities of calcium and magnesium. In dilute solutions (ionic strength below 10^{-2}) activity coefficients for magnesium and calcium are the same, within experimental error, so that the molar ratio Mg:Ca may be used in place of the activity ratio.

2. Temperature dependence of the equilibrium constant for dolomite in the range 0 - 25°C.

Calculation of Keq:dolomite as a function of temperature over the range 0 - 25°C requires that each component of the equation defining electrical neutrality in the sample of water at equilibrium be expressed in terms of one component, such as pH (as shown in section C of this Appendix). Unfortunately, the new equilibrium constant is needed to express the calcium, magnesium and carbonate ion activities in terms of pH, and the equilibrium constant cannot be obtained until the problem is solved.

To avoid this impasse, the equilibrium constant has been estimated for different temperatures assuming that the temperature dependence of Keq:dolomite is analogous to that of Keq:calcite. This seems reasonable, since the structure of dolomite involves substitution of magnesium for calcium in a calcite crystal lattice, and since there is general agreement in the literature that dolomite dissociates congruently. Experimental data for calcite solubility (Table 13, section C) (Larson and Buswell, 1942) give $^{p}K_{CaCO_3}$ as 8.02 at 0°C and 8.28 at 25°C : $^{p}K_{CaCO_3}$ is a linear function of temperature within this range. By analogy, the temperature dependence of Keq:dolomite is approximated by squaring the values for calcite. Therefore, if Keq:dolomite is $10^{-16.0}$ at 0°C, it is about $10^{-16.5}$ at 25°C. This is the basis for the assumption in Fig. 7 of Chapter V (ion activity product diagram for dolomite) that between 2.5°C and 10.0°C the equilibrium constant varies by a factor of $10^{-0.1}$.

B. Calculation of ion activity products relating to equilibrium of water with respect to dolomite and calcite.

The problem is to obtain values for the ion activity products ($a_{Ca^{+2}} \cdot a_{CO_3^{-2}}$) and ($a_{Ca^{+2}} \cdot a_{Mg^{+2}} \cdot a^2_{CO_3^{-2}}$) which can then be related to appropriate equilibrium constants for calcite and dolomite. As an example, we will consider the analysis of a water sample taken at a depth of 1 m from the centre of Cowan Lake on August 26, 1969. The temperature of the water was 11.1°C. The analysis gave:

pH	8.1	
HCO_3^{-1}	96.5 mg/l	$10^{-2.80}$ M
Ca^{+2}	18.1 "	$10^{-3.35}$ M
Mg^{+2}	8.7 "	$10^{-3.44}$ M

For the purpose of computing ionic strength, as described below, we note also that $SO_4^{-2} \simeq 2$ mg/l and $Cl^{-1} \simeq 1.3$ mg/l. Assuming that sodium and potassium together balance the chloride and half the sulfate, $Na^{+1} \simeq 0.8$ mg/l and $K^{+1} \simeq 0.25$ mg/l. These assumptions are included for the sake of completeness, but in practice they make a negligible difference to the results of the calculation.

The first problem[1] is to compute ion activity coefficients from which ion activities ('effective concentrations') may be computed. The individual ion activity coefficient is computed from the Debye-Hückel formula below:

$$- \log \gamma_i = \frac{A . z_i^2 . \sqrt{I}}{1 + \mathring{a}_i . B . \sqrt{I}} \qquad (\gamma = \text{ activity coefficient})$$

---

[1] The argument that follows is largely based on Garrels and Christ, "Minerals, Solutions and Equilibria", p. 74 (1965).

A and B are constants, given in Table 15 characteristic of the solvent (water) and dependent on temperature and pressure; z_i is the charge on the i_{th} ion in solution, and the quantity $\mathring{a}_i$ has a value dependent on the 'effective diameter' of the i_{th} ion in solution (Table 13, section B). The ionic strength, I, is computed from the expression

$$I = \frac{1}{2} \sum m_i \cdot z_i^2$$

where z_i is previously defined, and m_i is the molar concentration of the i_{th} ion in solution.

In this example for Cowan Lake, $I = 10^{-2.60}$. If values are assigned for the other constants in the Debye-Hückel expression according to Table 15, $\gamma HCO_3^{-1} = 0.95$, $\gamma\, Ca^{+2} = 0.81$ and $\gamma\, Mg^{+2} = 0.81$. Multiplying molar concentrations by appropriate activity coefficients,

$$\begin{array}{lcll} a_{H^{+1}} & = & 10^{-8.10} & \text{(given by pH = 8.1)} \\ a_{HCO_3^{-1}} & = & 10^{-2.82} & \\ a_{Ca^{+2}} & = & 10^{-3.44} & \\ a_{Mg^{+2}} & & 10^{-3.53} & \end{array}$$

In order to obtain $(a_{CO_3^{-2}})$,

from

$$\frac{a_{H^{+1}} \cdot a_{CO_3^{-2}}}{a_{HCO_3^{-1}}} = K_{H_2CO_3} = 10^{-14.47} \qquad \text{(Table 15)}$$

$$a_{CO_3^{-2}} = \frac{10^{-2.82} . 10^{-10.47}}{10^{-8.10}} = 10^{-5.19}$$

Therefore, the ion activity product for calcite, $IAP_c = a_{Ca^{+2}} \cdot a_{CO_3^{-2}}$

$$= 10^{-5.19} \,.\, 10^{-3.44} = 10^{-8.63}$$

At equilibrium with calcite at the water temperature of this example (11°C), $IAP_c = 10^{-8.16}$

TABLE 15

Constants used in carbonate equilibria calculations.

A. Values of A and B in the Debye-Hückel expression, 0 - 25°C.

T°C	A	B (x 10^{-8})	
			Data given in Garrels and Christ (1965).
0	0.4883	0.3241	
5	0.4921	0.3249	Originally in G.G. Manov, Bates, R.G., Hamer, W.J. and Acree, S.F., J.Am.Chem. Soc., 65, 1765 (1943).
10	0.4960	0.3258	
15	0.5000	0.3262	
20	0.5042	0.3273	
25	0.5085	0.3281	

B. Values of $\mathring{a}_i$ for ions involved in carbonate equilibria (Klotz, 1951).

	$\mathring{a}_i \times 10^8$		$\mathring{a}_i \times 10^8$
HCO_3^{-1}	4.0 - 4.5	Ca^{+2}	6
CO_3^{-2}	4.5	Mg^{+2}	8
OH^{-1}	3.5	H^{+1}	9

C. Carbonate Equilibria (from Garrels and Christ, 1965, p. 89).

T°C	pK_1	pK_2	pK_c	pK_{co_2}
0	6.58	10.62	8.02	1.12
5	6.52	10.56	8.09	
10	6.47	10.49	8.15	
15	6.42	10.43	8.22	
20	6.38	10.38	8.28	1.47
25	6.35	10.33	8.34	

Where $pK_1 = -\log K_{H_2CO_3}$ $pK_c = -\log$ Keq:calcite

$pK_2 = -\log K_{HCO_3^{-1}}$ $pK_{co_2} = -\log K_{co_2}$

Similarly, for dolomite, $IAP_d = a_{Ca^{+2}} \cdot a_{Mg^{+2}} \cdot a^2_{CO_3^{-2}}$

$$= 10^{-3.44} . 10^{-3.53} . 10^{-10.34} = \underline{10^{-17.31}}$$

This reasoning may be extended to compute the concentration of free carbonic acid[1] H_2CO_3, and the P_{CO_2} in equilibrium with the water sample.

$$a_{H_2CO_3} = \frac{a_{H^{+1}} \cdot a_{HCO_3^{-1}}}{K_{H_2CO_3}}$$ where $K_{H_2CO_3}$ is $10^{-6.46}$ at 11°C

$$= \frac{10^{-8.10} . 10^{-2.82}}{10^{-6.46}} = \underline{10^{-4.46}}$$ which is related to the external

P_{CO_2} by the expression $$\frac{a_{H_2CO_3}}{P_{CO_2}} = K_{CO_2} = 10^{-1.28}$$ at 11°C

Therefore, $$P_{CO_2} = \frac{10^{-4.46}}{10^{-1.28}} = \underline{10^{-3.18}}$$

These results indicate that the water dample was somewhat undersaturated with respect to calcite, and probably also with respect to dolomite, if Keq: dolomite 10^{-17}. At equilibrium at the carbonate ion activity specified above, $m_{Ca^{+2}}$ would be $10^{-2.88}$ (53 mg/l), compared with the analysed concentration of $10^{-2.35}$ (18 mg/l). Thus, the water sample is approximately 34 per cent saturated with respect to calcium. Since atmospheric P_{CO_2} is close to $10^{-3.5}$ atm., the calculated equilibrium P_{CO_2} for the water sample of $10^{-3.2}$ atm., suggests that the water sample was in equilibrium with a partial pressure of carbon dioxide twice as high as

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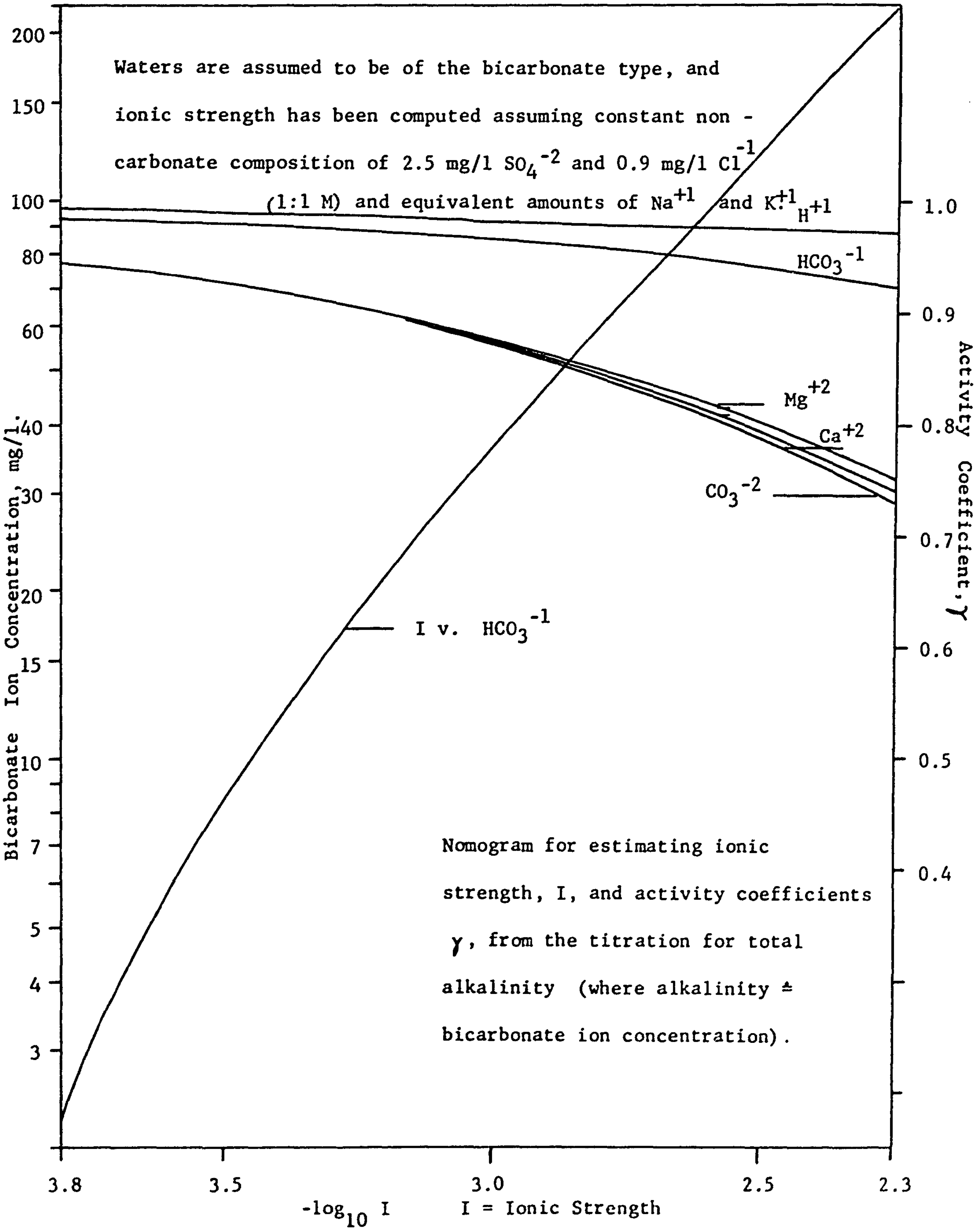
[1] Carbonic acid, H_2CO_3 actually consists of molecules of CO_2 and H_2CO_3 in a ratio of 386:1 (Garrels and Christ, 1965, p. 76, Footnote 1).

that of the atmosphere. Since the sample in question was collected in the evening, the supersaturation might have arisen through the release of CO_2 in the respiration of plankton. This explanation is consistent with concurrent undersaturation with dissolved oxygen by about 1.5 mg/l. An increase in pH of 0.5 unit (from 8.1 to 8.6) would bring the water sample into equilibrium with calcite. An increase of this magnitude might accompany a daily peak in photosynthesis (c.f. analyses for Williams and Panhandle Lakes, taken under similar weather conditions but near the solar noon).

Computing the ionic strength of water samples in the Knob Lake basin is simplified if a plot of activity coefficient v. ionic strength is used. Also, since ionic strength in lake waters is primarily a function of the concentrations of HCO_3^{-1}, Ca^{+2} and Mg^{+2}, and the other ions (SO_4^{-2}, Cl^{-1}, Na^{+1} and K^{+1}) are present in small and relatively constant amounts, it is possible to express ionic strength as a function of one measure of total ion concentration such as HCO_3^{-1}. This is illustrated in Fig 38, a graph of both γ v. I, and of I v. $^{m}HCO_3^{-1}$. Activity coefficients for the ion activity product diagrams were estimated from such a diagram.



Waters are assumed to be of the bicarbonate type, and ionic strength has been computed assuming constant non - carbonate composition of 2.5 mg/l SO_4^{-2} and 0.9 mg/l Cl^{-1} (1:1 M) and equivalent amounts of Na^{+1} and K^{+1}

Nomogram for estimating ionic strength, I, and activity coefficients γ, from the titration for total alkalinity (where alkalinity ≐ bicarbonate ion concentration).

Fig. 38 Nomogram for estimating ionic strength and ion activity coefficients from bicarbonate ion concentration.

C. Approximate concentrations of calcium and magnesium in water at equilibrium with dolomite, as a function of temperature and carbonic acid concentration ($^{m}H_2CO_3$).

Concentrations of free carbonic acid in the lake waters of this study were found to be mainly in the range $10^{-3.0}$ and $10^{-5.0}$M. This variation was in part a consequence of an ice cover sealing off lake waters from the atmosphere in winter, but resulted primarily from the uptake and release of carbon dioxide in photosynthesis. Because the concentration of H_2CO_3 affects the quantity of Ca^{+2} and Mg^{+2} ions passing into solution from dolomite, some data are presented here on the dependence of calcium and magnesium concentrations in water in equilibrium with dolomite on concentrations of H_2CO_3.

The problem has been solved for the temperatures 2.5°C, 10°C and 20°C, representing water temperatures in late winter, late summer, and peak temperatures of surface waters in mid-summer. Values of H_2CO_3 of 10^{-3}, 10^{-4}, 10^{-5} and 10^{-6} M have been used, and different solutions have been obtained for assumed Keq:dolomite at 2.5°C of 10^{-16}, 10^{-17}, 10^{-18} and 10^{-19}. The exponent is assumed to increase by 0.1 (i.e. $10^{-16.1}$ etc.) at 10°C, and by 0.23 at 20°C (i.e. $10^{-16.23}$ etc). This range of values for Keq:dolomite is based on Hsu (1967) and on the fact that Keq:dolomite as computed from free energy data is in the order of $10^{-18.8}$ at 25°C. (A discussion of free energy data for dolomite is to be found in Stout and Robie, 1963). The method of solution below is based on Garrels and Christ, (1965, p.78).

Values of $^{a}Ca^{+2}$ and $^{a}Mg^{+2}$ are required at equilibrium with dolomite. As a first approximation, this can be achieved by writing the equation defining electrical neturality (eq. 1), and by expressing all components in the expression in terms of one component, such as hydrogen ion activity (assuming here that activity = molarity). This yields an expression which can be solved for $a_{H^{+1}}$, and the value so obtained can be used to give the carbonate ion activity, and the activities of calcium and magnesium as a function of $a_{CO_3^{-2}}$. In this first approximation, water, dolomite and CO_2 gas are assumed to be the only phases present, and at a total gas pressure of one atmosphere. As a first approximation, activity coefficients are assumed to be unity, so that $m_i = a_i$. The consequences of this assumption are considered below.

In the following example, we consider the situation in which $T = 10°C$, $H_2CO_3 = 10^{-5.0}$ M (somewhat less than at equilibrium with the atmosphere), and Keq: dolomite = $10^{-17.10}$. Solutions for other temperatures, carbonic acid concentrations and equilibrium constants for dolomite are summarised in Fig. 39.

The equation for electrical neutrality is:

$$2m_{Ca^{+2}} + 2m_{Mg^{+2}} + H^{+1} = 2m_{CO_3^{-2}} + m_{HCO_3^{-1}} + m_{OH^{-1}} \qquad (1)$$

In terms of pH ($a_{H^{+1}}$)

$$a_{HCO_3^{-1}} = \frac{10^{-6.47} \cdot 10^{-5.0}}{a_{H^{+1}}} = \frac{10^{-11.47}}{a_{H^{+1}}} \qquad (2)$$

and $$a_{CO_3^{-2}} = \frac{10^{-10.49}\ a_{HCO_3^{-1}}}{a_{H^{+1}}} = \frac{10^{-21.96}}{a^2_{H^{+1}}} \qquad (3)$$

and $$a_{OH^{-1}} = \frac{10^{-14.53}}{a_{H^{+1}}} \qquad (4)$$

and $$a_{Ca^{+2}} \cdot a_{Mg^{+2}} = \frac{10^{-17.10}}{a^2_{CO_3^{-2}}} = 10^{27.02} \cdot a^4_{H^{+1}} \qquad (5)$$

From which, assuming congruent solution of dolomite,

$$a_{Ca^{+2}} \text{ or } a_{Mg^{+2}} = 10^{13.51} \; a^2_{H^{+1}} \qquad (6)$$

Substituting these terms in equation 1, and noting that activities are substituted for molar concentrations

$$2 \times 10^{13.51} \cdot a^2_{H^{+1}} + 2 \times 10^{13.51} \cdot a^2_{H^{+1}+H^{+1}} = \frac{2 \times 10^{-21.96}}{a^2_{H^{+1}}} + \frac{10^{-11.47}}{a_{H^{+1}}} + \frac{10^{-14.54}}{a_{H^{+1}}} \qquad (7)$$

Multiplying by $a^2_{H^{+1}}$, and collecting terms:

$$10^{14.11} \cdot a^2_{H^{+1}} + a^3_{H^{+1}} - 10^{-11.47} \cdot a_{H^{+1}} - 10^{-21.66} = 0 \qquad (8)$$

This equation was solved using Newton's iteration procedure, giving

$$a_{H^{+1}} = \text{pH equilibrium} = 10^{-8.49}$$

Substituting this value for $a_{H^{+1}}$ into equations (2), (3) and (6);

$$a_{HCO_3^{-1}} = 10^{-2.98}$$

$$a_{CO_3^{-2}} = 10^{-4.98}$$

$$a_{Ca^{+2}} = a_{Mg^{+2}} = 10^{-3.57}$$

and, assuming $a_i = m_i$, Ca^{+2} = 10.8 mg/l and Mg^{+2} = 6.5 mg/l. However, the solution obtained above using the equation of electrical neutrality now permits the calculation of the ionic strength of the solution at equilibrium with dolomite, from which activity coefficients may be determined for each ion. This calculation gives the following results:

$$-\log \gamma\ Ca^{+2} = 0.074 \qquad -\log \gamma\ HCO_3^{-1} = 0.019$$
$$-\log \gamma\ Mg^{+2} = 0.072 \qquad -\log \gamma\ H^{+1} = 0.017$$
$$-\log \gamma\ CO_3^{-2} = 0.075 \qquad -\log \gamma\ OH^{-1} = 0.019$$

Based on an approximate ionic strength of 1.61×10^{-3}, computed from molar concentrations and not activities.

With the above activity coefficients, molar concentrations (as opposed to activities) of HCO_3^{-2}, CO_3^{-2}, Ca^{+2} and Mg^{+2} in terms of $a_{H^{+1}}$ can now be calculated. Substituting these recalculated values in the equation of electrical neutrality (1), a new equation (9) is formed, similar to (8);

$$10^{13.85} \cdot a^4_{H^{+1}} + a^3_{H^{+1}} - 10^{11.45} \cdot a_{H^{+1}} - 10^{-21.57} = 0 \qquad (9)$$

Solving by trial and error,

$$a_{H^{+1}} = \sim 10^{-8.26} = \sim pH = 8.26$$

Substitution of $a_{H^{+1}} = 10^{-8.26}$ into equations (2), (3) and (6) yields the following activities;

$$a_{HCO_3^{-1}} = 10^{-3.21}$$
$$a_{CO_3^{-2}} = 10^{-5.44}$$

$a_{Ca^{+2}} = a_{Mg^{+2}} = 10^{-3.11} = (31.1$ mg/l Ca^{+2} and 18.9 mg/l $Mg^{+2})$

These activities can be divided by the activity coefficients given above, yielding molar concentrations as follows;

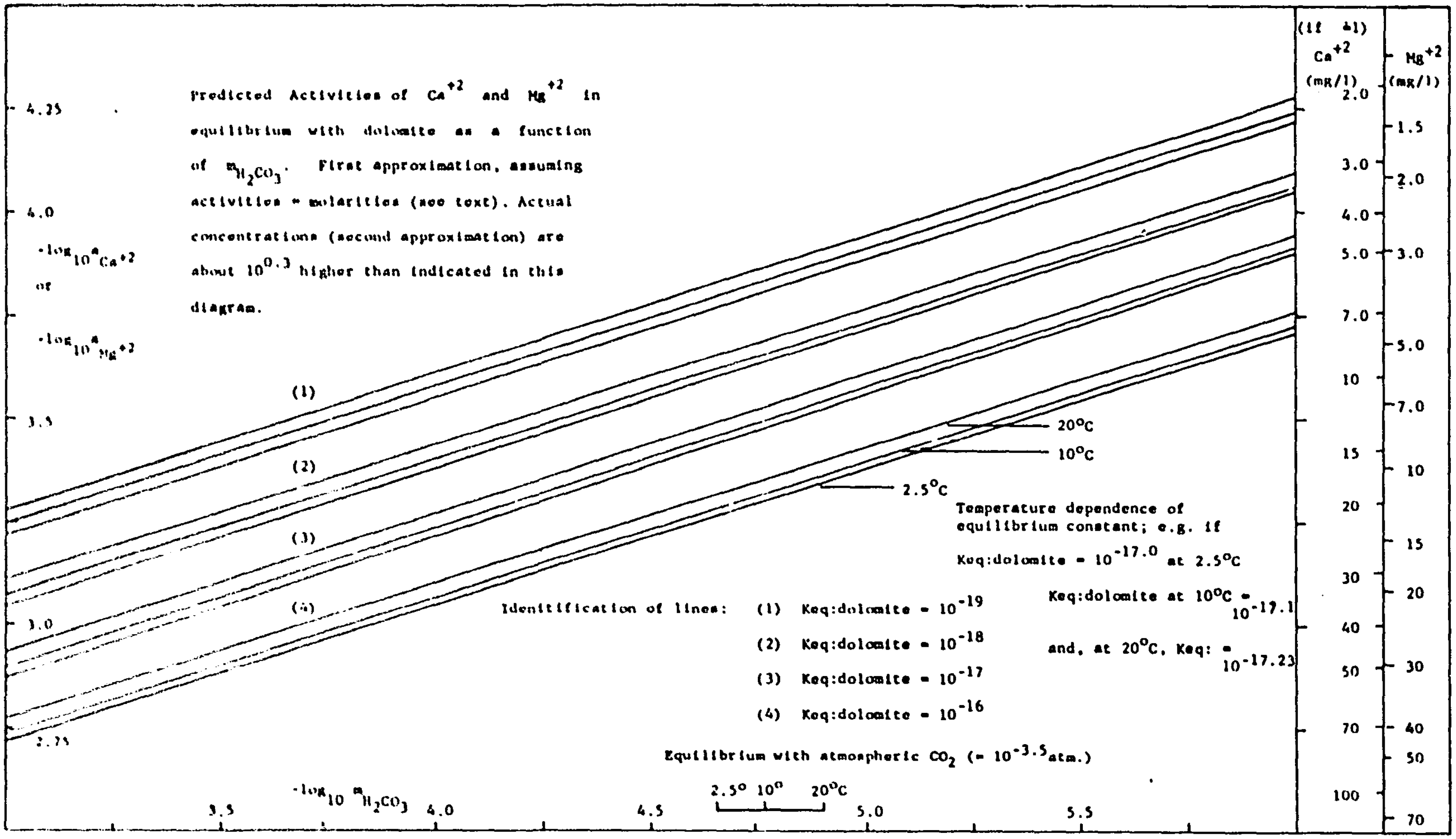
$$m_{HCO_3^{-1}} = 10^{-3.19}$$
$$m_{CO_3^{-1}} = 10^{-5.36}$$

$^{m}Ca^{+2} = {}^{m}Mg^{+2} = 10^{-3.04} = (36.5 \text{ mg/l } Ca^{+2} \text{ and } 22.2 \text{ mg/l } Mg^{+2})$

To summarise this example, the calculations have shown that as a first approximation, about 11 mg/l Ca^{+2} and 6.5 mg/l Mg^{+2} could be expected in a solution in equilibrium with dolomite, given $H_2CO_3 = 10^{-5.0}$, T = 10°C, and Keq:dolomite = $10^{-17.10}$.

However, using the same constants, but taking into account ion activities calculated from data given in the first approximation, recalculation of molar concentrations give Ca^{+2} = 36.5 mg/l and Mg^{+2} = 22.2 mg/l. This represents an increase by a factor of 3.3 in the concentrations of calcium and magnesium at a second approximation. These calculations could be continued by re-calculating ionic strength, finding new activity coefficients and estimating new molar concentrations. However, the new value of ionic strength would differ little from the previous one, and a third approximation would yield calcium and magnesium concentrations close to those reported for the second approximation.

In conclusion, the example used here has demonstrated the necessity for taking into account ion activities when computing concentrations of calcium and magnesium in equilibrium with dolomite. The results of the first approximation are expressed in Fig. 39, which shows activities of calcium and magnesium in equilibrium with dolomite as a function of carbonic acid concentration. The values of pH at equilibrium with dolomite are shown separately in Fig. 40 to show the range of pH that can be expected to occur in water in contact with dolomite on purely chemical grounds. The probable order of magnitude of the concentrations of calcium and magnesium at equilibrium is tentatively shown by the shaded area.



Predicted Activities of Ca^{+2} and Mg^{+2} in equilibrium with dolomite as a function of $m_{H_2CO_3}$. First approximation, assuming activities = molarities (see text). Actual concentrations (second approximation) are about $10^{0.3}$ higher than indicated in this diagram.

Temperature dependence of equilibrium constant; e.g. if Keq:dolomite = $10^{-17.0}$ at 2.5°C

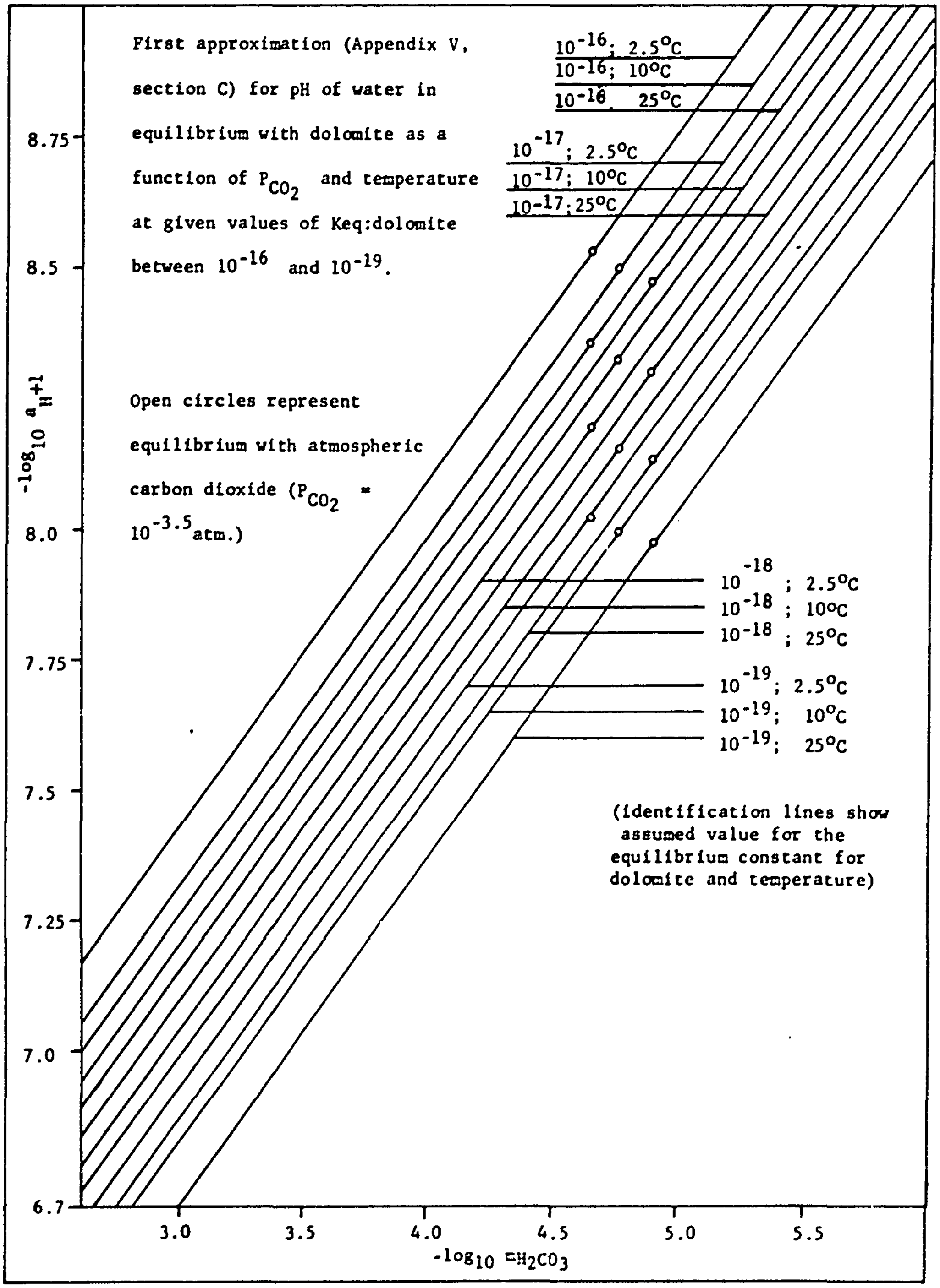
Keq:dolomite at 10°C = $10^{-17.1}$

and, at 20°C, Keq: = $10^{-17.23}$

Identification of lines:
(1) Keq:dolomite = 10^{-19}
(2) Keq:dolomite = 10^{-18}
(3) Keq:dolomite = 10^{-17}
(4) Keq:dolomite = 10^{-16}

Equilibrium with atmospheric CO_2 (= $10^{-3.5}$atm.)

Fig. 39 Calcium and magnesium concentrations in water at equilibrium with dolomite as function of P_{CO_2} and temperature.



First approximation (Appendix V, section C) for pH of water in equilibrium with dolomite as a function of P_{CO_2} and temperature at given values of Keq:dolomite between 10^{-16} and 10^{-19}.

Open circles represent equilibrium with atmospheric carbon dioxide (P_{CO_2} = $10^{-3.5}$ atm.)

(identification lines show assumed value for the equilibrium constant for dolomite and temperature)

Fig. 40 pH of water in equilibrium with dolomite as function of carbonic acid concentration and temperature.

D. Results of Carbonate Equilibria Calculations for Knob Lake Basin.

All terms are expressed as negative logarithms.

WINTER SURVEY

T = 2.5°C, IAP = Ion activity product for dolomite (IAP_d) and calcite (IAP_c)

Lake and Site		IAP_d	IAP_c	$^{a}CO_3^{-2}$	$^{m}H_2CO_3$	P_{co_2}[1]
Communications	2m	24.08	12.10	7.65	3.75	2.60
Houston (1)[2]	2m	23.75	11.90	7.49	3.90	2.75
Osprey (1)	1m	22.30	11.06	7.08	3.72	2.57
Malcolm (1)	2m	20.68	10.32	6.60	3.65	2.50
Malcolm (2)	2m	21.24	10.57	6.74	3.79	2.64
Malcolm (3)	2m	20.78	10.39	6.52	3.96	2.80
Malcolm (4)	2m	21.04	10.52	6.69	3.68	2.53
Ares (1)	1m	21.22	10.54	6.71	3.76	2.61
Knob (2)	2m	21.01	10.46	6.68	3.84	2.69
Knob (7)	2m	20.19	10.07	6.25	4.21	3.06
Knob (8)	5m	20.23	10.14	6.32	4.08	2.93
Pearce (5)	3m	21.08	10.55	6.90	3.06	1.91
Pearce (3)	2m	20.91	10.47	6.71	3.37	2.22
Pearce (10)	1m	21.41	10.66	6.89	3.25	2.10
Easel (2)	1m	19.00	9.46	5.93	3.85	2.70
Easel (3)	2m	18.07	9.02	5.52	4.18	3.03
Easel (5)	2m	18.71	9.32	5.81	3.91	2.76
Phred (1)	2m	20.08	10.02	6.30	3.99	2.84
Gene (1)	2m	20.81	10.38	6.73	3.54	2.39

---

[1] P_{co_2} = P_{co_2} at equilibrium with sample.

[2] Numbers in parentheses refer to sampling sites identified in Appendix I.

Lake and Site		IAP_d	IAP_c	$^{a}CO_3^{-2}$	$^{m}H_2CO_3$	P_{co_2}[1]
Panhandle	1m	18.70	9.29	5.94	3.51	2.36
Findlay	1m	19.95	9.94	6.43	3.36	2.21
Williams	1m	18.42	9.19	5.95	3.18	2.05
Francois	1m	21.07	10.49	6.84	3.09	1.94
Ives	2m	19.59	9.76	6.25	3.52	2.37
Mattox	1m	19.18	9.56	6.54	2.29	1.14
Trigger	1m	17.28	8.71	5.85	2.82	1.67
Bassett	1m	20.60	10.30	6.72	3.11	1.96
Adams	4m	19.14	9.63	6.00	4.01	2.86
North	4m	19.13	9.56	6.00	3.86	2.71
Middle	4m	19.55	9.74	6.08	4.02	2.87
South	1m	18.38	9.16	5.82	3.65	2.50
Gray	1m	25.56	12.72	8.27	3.30	2.15
Hardy	1m	25.32	12.66	8.21	3.18	2.03
Barr	1m	28.75	14.40	9.40	3.10	1.84

---

[1] P_{co_2} = P_{co_2} at equilibrium with sample.

SUMMER SURVEY

T = 10°C

Lake and site		IAP_d	IAP_c	$^aCO_3{}^{-2}$	$^mH_2CO_3$	P_{co_2}[1]
Communications	1m	23.44	11.68	7.24	4.30	3.04
Houston (1)	1m	22.89	11.61	7.17	4.37	3.11
Osprey (1)	2m	20.84	10.42	6.40	4.44	3.18
Malcolm (2)	3m	19.92	9.89	6.10	4.34	3.08
Malcolm (1)	1m	19.75	9.84	6.07	4.41	3.15
Malcolm (4)	1m	19.90	9.90	6.10	4.44	3.18
Malcolm (5)	3m	19.80	9.82	6.06	4.40	3.14
Ares (1)	1m	19.43	9.65	5.85	4.57	3.31
Knob (2)	2m	19.89	9.86	6.04	4.48	3.22
Knob (3)	2m	20.09	9.99	6.18	4.38	3.12
Knob (5)	4m	20.72	10.27	6.46	4.10	3.84
Pearce (5)	2m	20.11	10.01	6.24	4.38	3.12
Pearce (3)	2m	20.07	10.03	6.25	4.29	3.03
Pearce (10)	1m	18.64	9.31	5.53	5.07	3.81
Easel (2)	1m	17.68	8.79	5.30	4.48	3.22
Easel (3)	1m	16.74	8.36	4.86	4.84	3.58
Easel (5)	2m	17.53	8.71	5.22	4.56	3.30
Phred (1)	1m	19.59	9.75	6.01	4.25	2.99
Gene (2)	1m	19.58	9.71	6.01	4.45	3.19

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[1] P_{co_2} = P_{co_2} at equilibrium with sample.

Lake and site.		IAP_d	IAP_c	$a_{CO_3^{-2}}$	$m_{H_2CO_3}$	P_{co_2}[1]
Panhandle (1)	1m	15.93	7.93	4.44	5.28	4.02
Findlay (1)	1m	18.25	9.10	5.47	4.61	3.35
Williams	1m	16.03	7.97	4.56	5.00	3.74
Francois	1m	19.10	9.55	5.73	4.57	3.31
Ives	1m	18.59	9.24	5.62	4.46	3.20
Mattox	1m	19.08	9.50	5.91	4.15	2.89
Trigger	1m	20.56	10.29	6.47	4.01	2.75
Bassett	1m	20.42	10.14	6.31	4.15	2.89
Adams	1m	18.64	9.28	5.67	4.31	3.05
North	1m	18.04	8.99	5.39	4.57	3.31
Middle	1m	18.59	9.19	5.57	4.55	3.29
South	1m	17.74	8.80	5.32	4.46	3.20
Gray	1m	24.84	12.60	7.75	4.00	2.74
Hardy	1m	24.68	12.43	7.70	4.34	3.08
Thorn	1m	23.68	11.93	7.50	3.94	2.68
Dale	1m	22.26	11.07	6.92	4.36	3.10
Barr	1m	29.2	14.7	9.45	4.00	2.74
Lier	1m	29.2	14.7	9.45	3.40	2.14

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[1] P_{co_2} = P_{co_2} at equilibrium with sample.

Carbonate Equilibria in Cowan Lake - Centre Site

Depth	Temp.°C	IAP_d	IAP_c	$a_{CO_3^{-2}}$	$a_{H_2CO_3}$	P_{co_2}[1]
March 8						
1m	0.2	18.48	9.22	5.79	3.80	2.68
2m	1.9	18.40	9.14	5.76	3.81	2.66
4m	3.2	18.47	9.18	5.80	3.78	2.62
6m	3.5	18.35	9.15	5.76	3.74	2.57
8m	3.6	18.74	9.35	5.95	3.63	2.46
10m	4.1	18.38	9.18	5.90	3.30	2.12
June 7						
1m	2.2	20.94	10.42	6.73	3.53	2.38
2m	2.6	20.07	10.01	6.47	3.43	2.28
4m	3.2	20.59	10.27	6.64	3.44	2.28
6m	3.2	19.29	9.62	6.19	3.45	2.29
8m	3.3	20.19	10.17	6.47	3.31	2.15
10m	3.5	19.55	9.75	6.32	3.30	2.14
June 27						
1m	15.2	17.81	8.76	5.31	4.34	3.01
4m	8.7	18.09	8.90	5.45	4.27	2.96
7m	7.5	17.96	8.95	5.48	4.16	2.94
10m	4.7	18.58	9.22	5.79	3.87	2.69

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[1] P_{co_2} = P_{co_2} at equilibrium with sample.

Depth	Temp.°C	IAP_d	IAP_c	$a_{CO_3^{-2}}$	$m_{H_2CO_3}$	P_{co_2}[1]
July 14						
0.5m	19.1	17.51	8.73	5.27	4.40	3.01
4m	10.4	17.38	8.66	5.20	4.45	3.18
7m	8.5	17.69	8.82	5.36	4.30	3.06
10.5m	8.0	17.75	8.85	5.39	4.28	3.05
August 26						
1m	11.1	17.34	8.63	5.19	4.46	3.18
7m	11.1	17.14	8.54	5.09	4.56	3.28
8.5m	10.9	18.34	8.14	5.70	3.96	2.69

P_{co_2} = P_{co_2} at equilibrium with sample.

E. Relationships between hydrogen ion activity, carbonate ion activity and molar concentration of carbonic acid in lake water samples.

In section 4 of Chapter IV, the presentation of the equations describing carbonate equilibria was followed by a brief description of the dependence of pH and carbonate ion activity on the uptake and release of carbon dioxide through photosynthesis by phytoplankton. The data obtained in the ion activity product calculations permit a more precise definition of the association between ${}^{a}H^{+1}$, ${}^{a}CO_3^{-2}$ and ${}^{m}H_2CO_3$. This is illustrated by a series of diagrams utilising water analyses to show the following:

1. ${}^{a}CO_3{}^{-2}$ v. ${}^{m}H_2CO_3$ (Fig. 41)
2. ${}^{a}CO_3{}^{-2}$ v. ${}^{a}H^{+1}$ (Fig. 42)
3. ${}^{m}H_2CO_3$ v. ${}^{a}H^{+1}$ (Fig. 43)
4. $\Delta\ {}^{a}CO_3{}^{-2}$ v. $\Delta\ {}^{m}H_2CO_3$ (Fig. 44)
5. $\Delta\ {}^{a}H^{+1}$ v. $\Delta\ {}^{m}H_2CO_3$ (Fig. 45)

where, in Figs. 44 and 45, Δ refers to seasonal changes (March - April to August - September) at the same point in each lake.

In so far as ${}^{m}H_2CO_3$ represents the concentration of CO_2 molecules in the water (Garrels and Christ, 1965, p. 76, Footnote 1) and free carbon dioxide is the major form of carbon assimilated in photosynthesis, Figs. 44 and 45 describe the dependence of pH and carbonate ion activity on rates of photosynthesis and respiration.

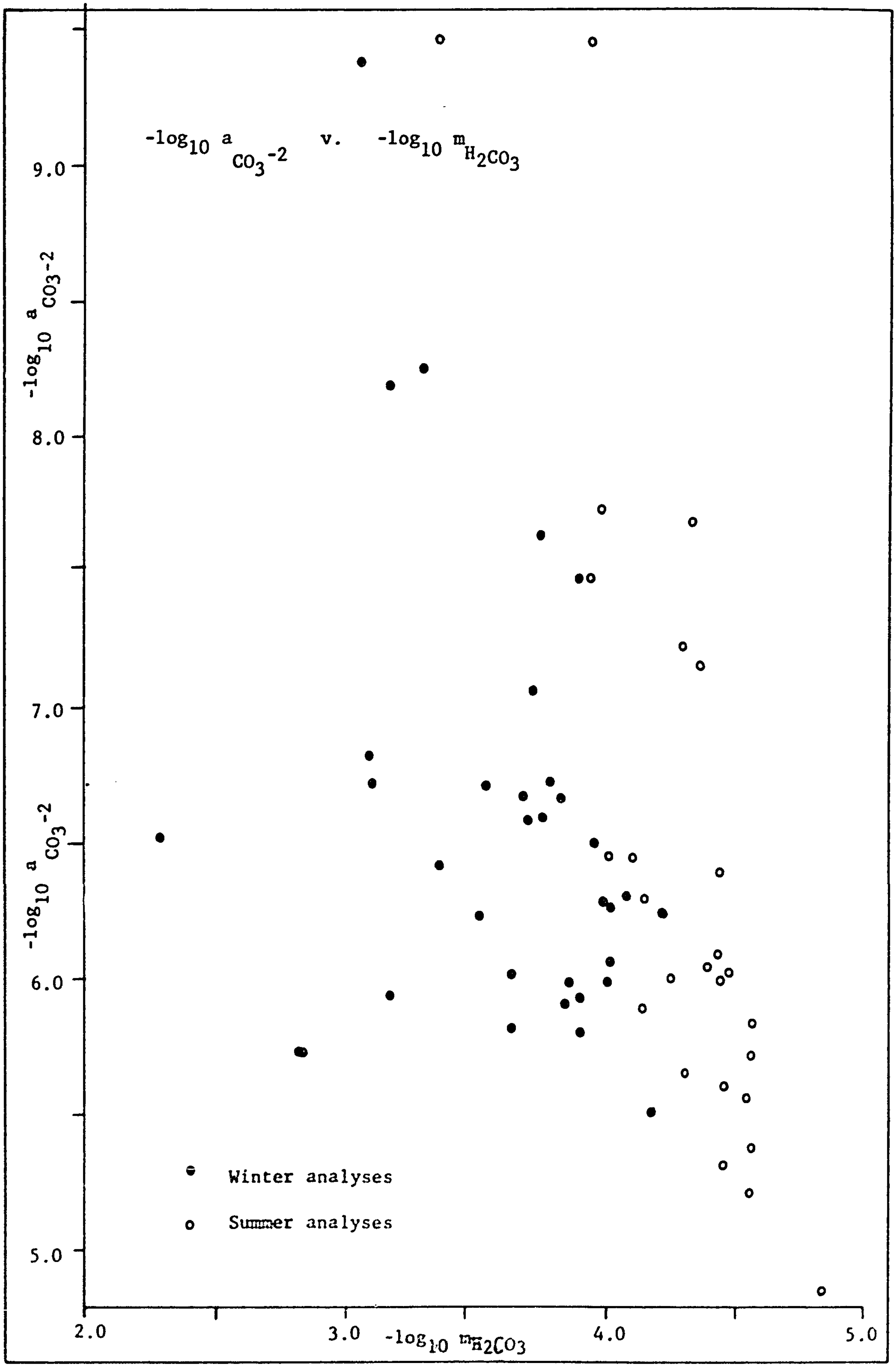

Fig. 41 Carbonate ion activity vs free carbonic acid in lake samples.

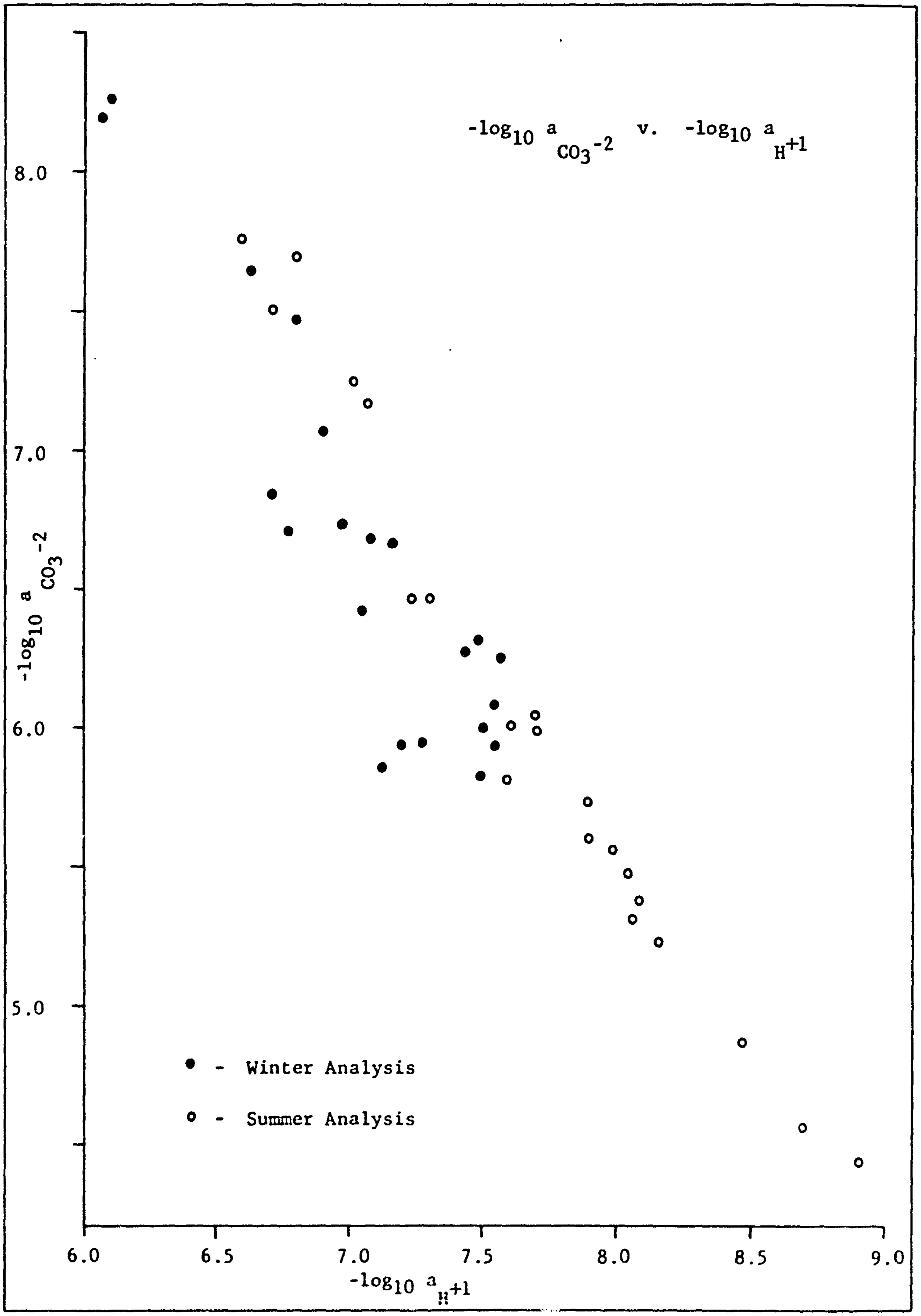

Fig. 42 Carbonate ion activity v. pH in lake water samples.

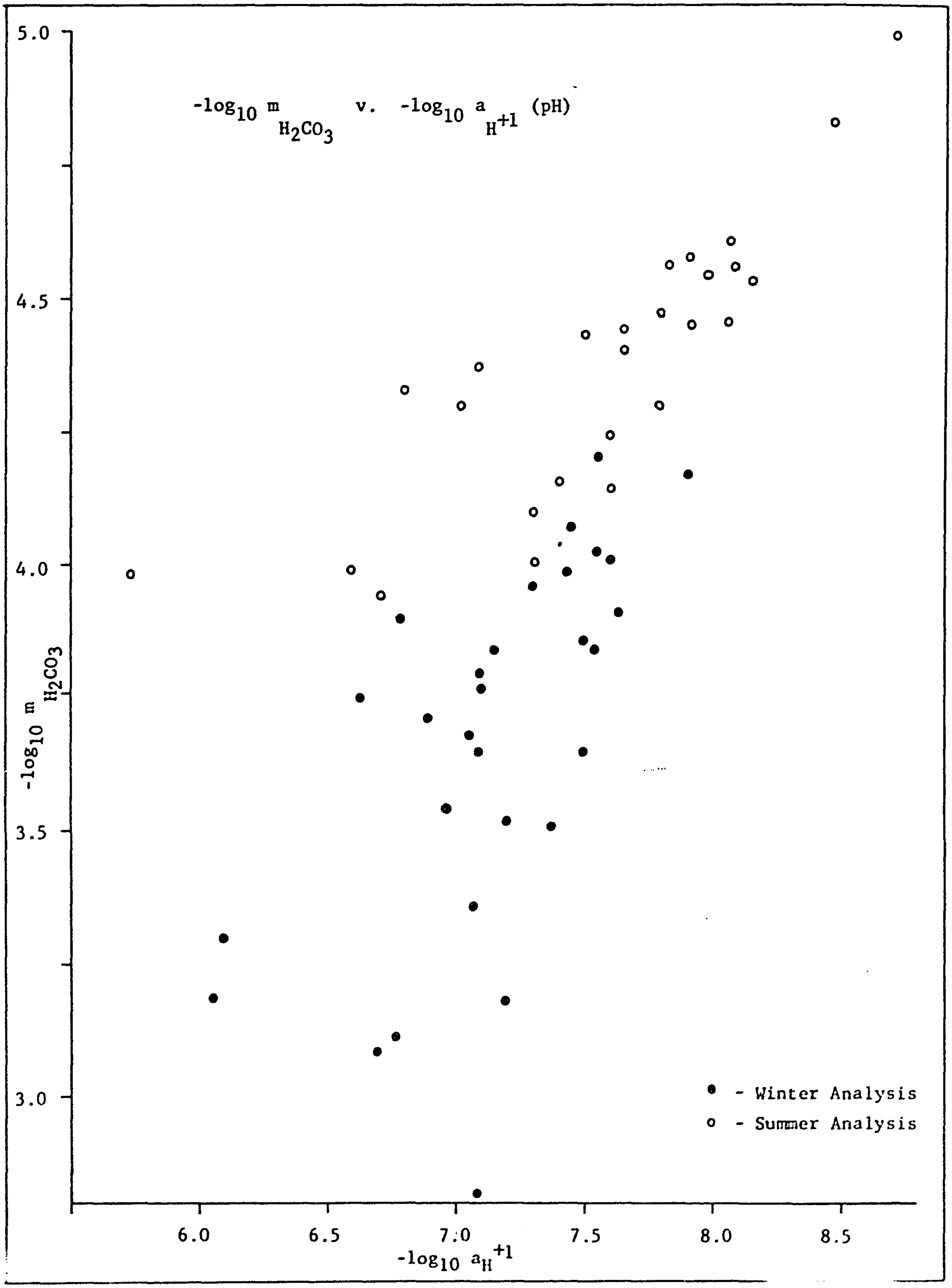

Fig. 43 Free carbonic acid v. pH in lake water samples.

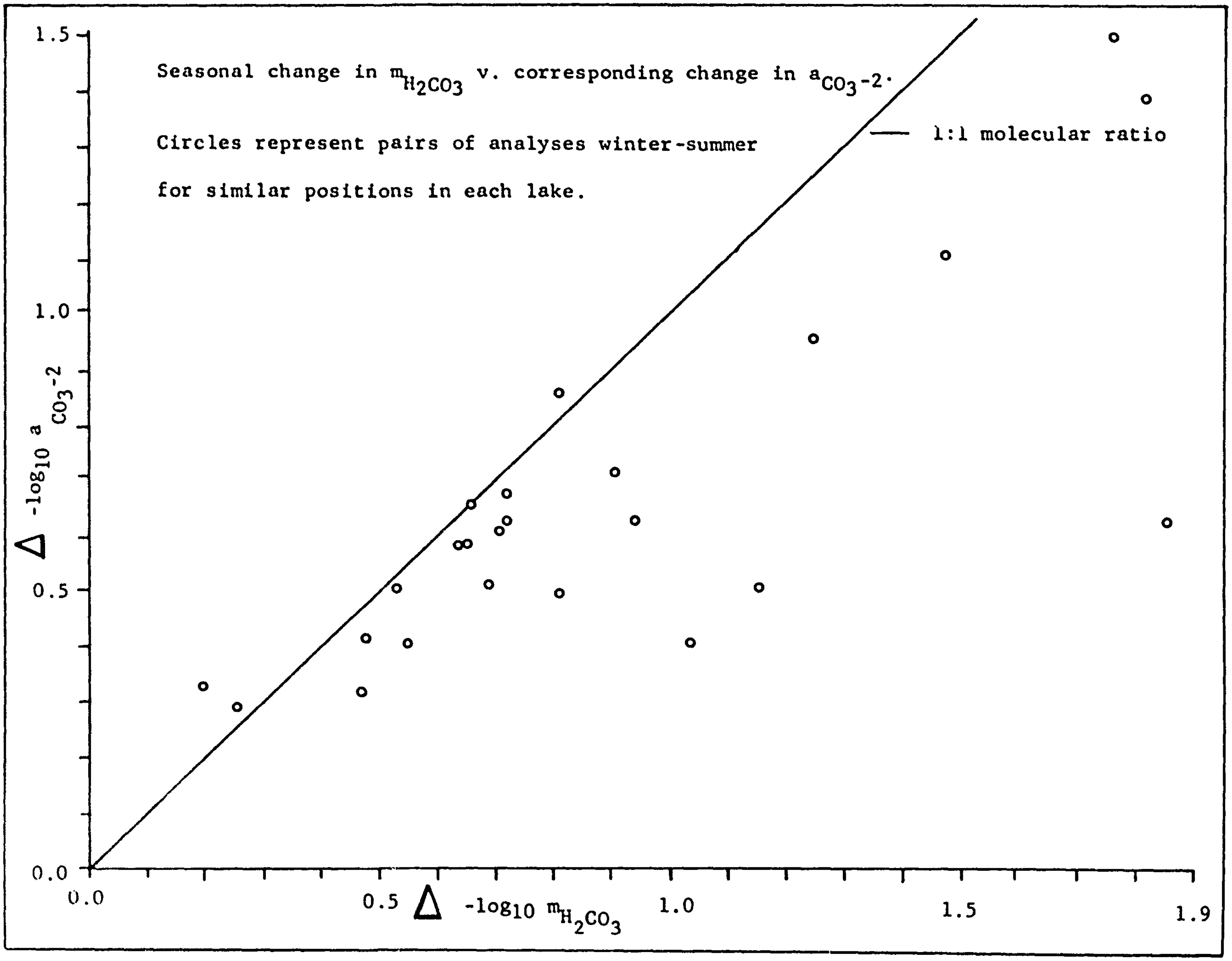

Fig. 44 Seasonal change in carbonate ion activity v. seasonal change in free carbonic acid.

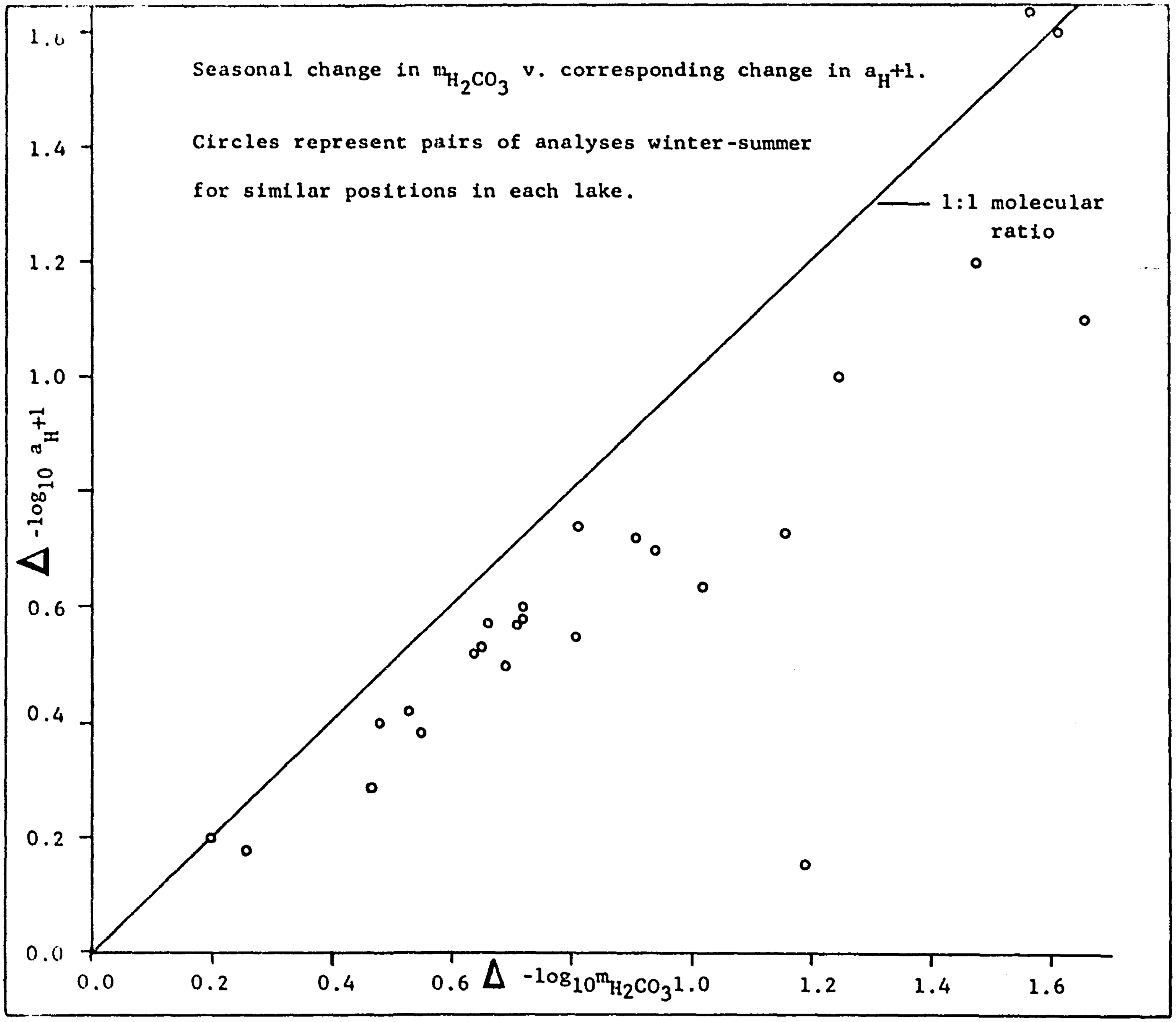

Fig. 45 Seasonal change in pH v. seasonal change in free carbonic acid concentration.

However, Ruttner (1953) reports that submersed phanerogams and many algae are able to assimilate carbon through the decomposition of bicarbonate and the release of hydroxyl ions. This is the explanation why photo - synthesis from leaves of Elodea in a closed chamber will raise the pH to about 11. Therefore, carbonic acid may not be the only available source of carbon and seasonal changes in bicarbonate ion concentration, attributed in the text to annual variation in rates of solution of dolomite and in the transport of solutes, may be partly related to the photosynthetic decomposition of bicarbonate. On the other hand, concentrations of carbonic acid in lake samples may not have reached sufficiently low levels for the decomposition of bicarbonate to become the dominant source of carbon. The writer is unaware of any literature defining limiting concentrations of carbonic acid as a base for photosynthesis, but the lakes in this study were rarely less than 10^{-5}M in H_2CO_3 (equivalent to 0.6 mg/l) and few lakes reached saturation with calcite (which promptly follows the biogenic decomposition of bicarbonate). Perhaps it is only in exceptional cases in lake waters of the Knob Lake basin that free carbonic acid ceases to be the major source of carbon for photosynthesis.

Carbonate ion activity is closely related to pH (Fig. 42) and winter and summer anlyses clearly fall into distinctive fields. The relationship between carbonic acid and pH (Fig. 43) is more diffuse, although winter and summer analyses are readily distinguishable, and the scatter in this case is more closely related to the bicarbonate ion and therefore to the presence of dolomite as a bicarbonate source. The scatter in Fig. 41 (particularly the winter analyses) reflects the effect of lake volume in determining the release of CO2 from sediments under lake ice.

F. Specific conductance of lake water in relation to concentrations of bicarbonate, calcium and magnesium.

The specific conductance of a water sample (expressed here in micromhos cm^{-2} at 25°C) is a function of the equivalent conductance of the ions present in the sample, and, if the solution is dilute, is directly proportional to ion concentration (Barrow, 1966, p. 648 ff.). If a number of water samples are known to have a similar ionic composition (as is the case with the lake waters of Knob Lake drainage basin in which the dominant ions are bicarbonate, calcium and magnesium), specific conductance measurements can be used to give a rapid estimate of ion concentration. This procedure is outlined below for water samples from Knob Lake drainage basin.

Of a total of 125 determinations of conductivity[1], 49 have been chosen to represent the lake waters in summer and winter, 1969. One determination is used to represent each lake. Trigger and Doris lakes have been omitted because they contained relatively large concentrations of sulfate. Barr and Lier lakes were excluded becaused analysed concentrations of bicarbonate, calcium and magnesium in these lakes were below the limit of reliable analysis in this study. Lier Lake is a curiosity because it is extremely dilute (sp. cond. = 5.1 micromhos) with a conductivity which is exceptionally low for natural waters.

Least - squares regression analysis was used to derive equations describing the dependence of specific conductance (K) (mmhos at 25°C) on

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[1] Specific conductance measurements were made with a Fisher Wheatstone bridge in the limnology laboratory of McGill Department of Zoology, by kind permission of Dr. Kalff.

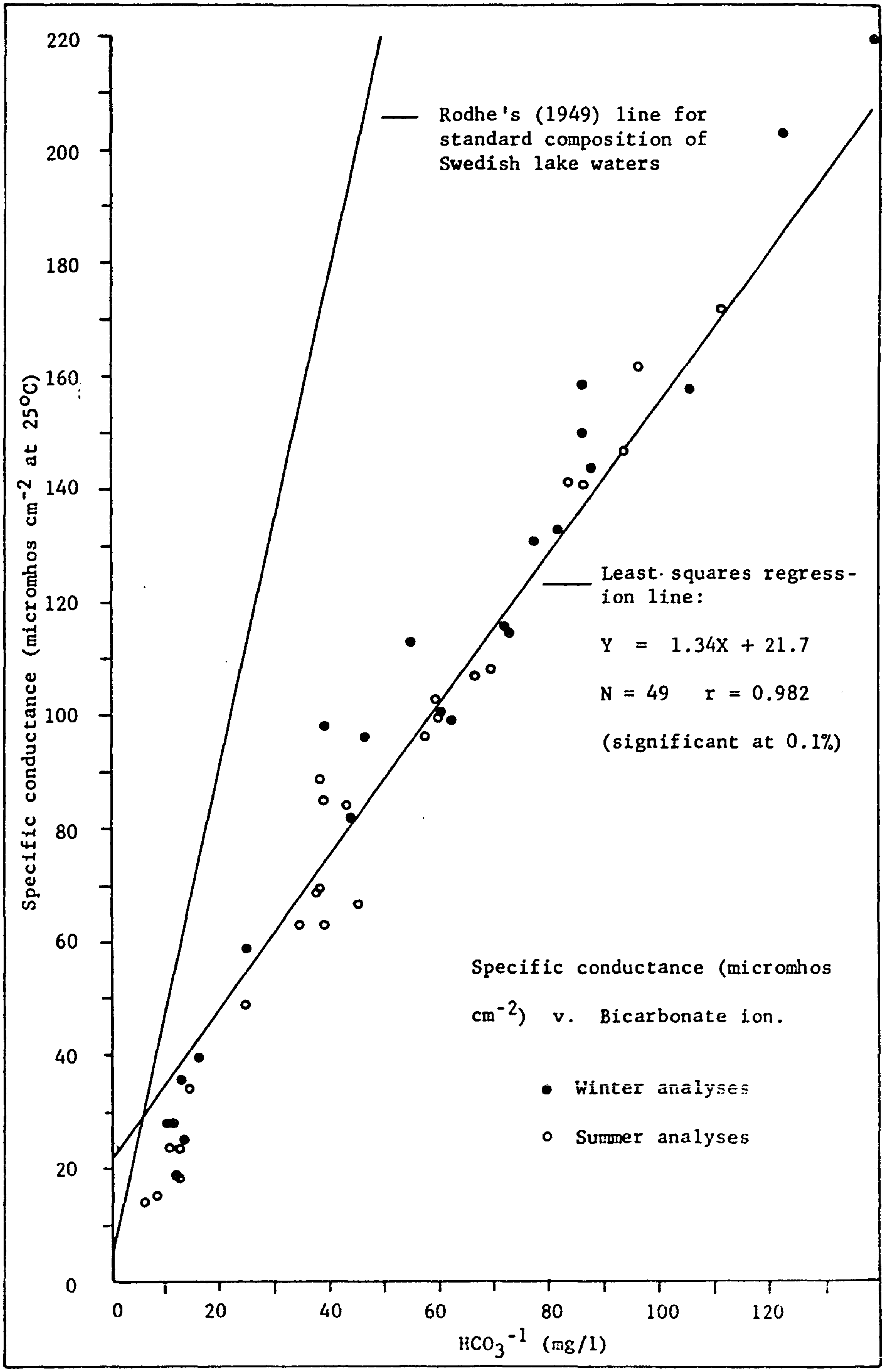

Fig. 46 Specific conductance (micromhos cm^{-2} at 25°C) v. HCO_3^{-1} (mg/l).

concentrations of bicarbonate (B), calcium (C) and magnesium (M) (all in mg/l). The number of observations is 49. The correlation coefficients are all significant at the 0.1% level.

The equations are:

$$K = 1.38\,B + 21.66 \qquad r = 0.98$$

$$K = 7.55\,C + 20.42 \qquad r = 0.98$$

$$K = 14.45\,M + 19.82 \qquad r = 0.98$$

Concentrations of bicarbonate, calcium and magnesium may therefore be estimated as a first approximation from the following simple expressions, where K is the specific conductance in micromhos cm^{-2} at 25°C

$$\text{Bicarbonate (mg/l)} = 0.75\,K$$

$$\text{Calcium (mg/l)} = 0.13\,K$$

$$\text{Magnesium (mg/l)} = 0.07\,K$$

The association between specific conductance and ion concentration is illustrated in Fig. 46 which shows specific conductance of winter and summer lake water samples plotted against bicarbonate ion concentration. Also shown is the line given by Rodhe (1949) describing the specific conductance of synthetic water samples with a composition based on the estimated average composition of a number of Swedish lake waters. The difference between the slope of this line and the slope of the least - squares regression line for the results of this study results from the relatively low and constant concentrations of sulfate and chloride in lake waters of Knob Lake drainage basin.