

## Geochemistry of Lake Waters from the South Island, New Zealand<sup>1</sup>

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**ABSTRACT:** Snow and lake water samples from the New Zealand region have been analyzed for a range of constituents. The results indicate that the lake waters are generally low in ionic constituents and that these constituents are distributed uniformly with depth in the lakes. The concentrations of sodium and potassium in the lake waters indicate that these elements are derived principally by direct atmospheric transport of marine aerosols. Calcium, magnesium, and silica are enriched relative to sodium in the lake waters when compared with rainwater by leaching of the surrounding schist and graywackes in the sequence calcium > magnesium > silicon silica.  $\text{SO}_4^{2-}$  is also enriched relative to sodium in the lake water compared with the precipitation samples.

ALTHOUGH considerable data are available on the interrelation between the chemistry of seawater, marine aerosols, rainfall, and groundwaters in Europe and the United States (e.g., Gorham 1958, 1961; Lodge 1959; Eriksson 1960; Junge 1963; Duce, Seto, and Moyers 1969; Duce, Stumm, and Prospero 1972; Horne 1969; Turekian 1969; Bruyevich and Ivanenkov 1971; Bowers 1972; Deevey 1972; Delany, Pollock, and Shedlovsky 1973; Martens and Harriss 1973), relatively few publications have dealt with the chemistry of either precipitation (Wilson 1959*a, b*; Miller 1961; Dean 1963; Mizutani and Rafter 1969; Rafter 1972) or lake waters (Phillipps and Grigg 1922; Briggs 1962*a, b*; Goldman 1964, 1972; Jolly 1968; Fish and Chapman 1969; Stout 1969*a, b*; Barker 1970; Johnstone 1972; McColl 1972; McColl and Forsyth 1973; Vidal and Maris-McArthur 1973) in the New Zealand region. For this reason, data on the chemistry of snow and lake water samples from New Zealand are presented in an attempt to define the gross patterns of fractionation of the major elements in their passage from the sea to the inland aquifers. It must be emphasized, however, that the data presented in this report are preliminary and no attempt has

been made to be systematic in the collection of samples. No conclusions concerning the regional patterns of groundwater chemistry or the synoptic patterns of rainwater chemistry in the New Zealand region can therefore be inferred from this study.

In order to study the chemistry of precipitation, we collected snow samples during the austral winter from four locations on the central mountain range of New Zealand: two on the North Island and two on the South Island. Lake water samples were also collected at a series of depths from three South Island lakes (Wanaka, Hawea, and Tekapo) with Knudsen metallic sampling bottles. The lakes form part of a lake system known as the Southern Glacial Lakes on the eastern side of the Southern Alps and were formed as basins during the last period of glaciation. Whereas Wanaka and Hawea are situated entirely in the Otago Schists, Tekapo lies mainly in moraine and outwashed gravel overlying principally Torlesse Group graywackes with smaller areas of Otago Schists. The lakes are fed principally by rivers draining the mountain ranges but, whereas Wanaka and Hawea are clear lakes fed by rivers (Secchi Disc readings 12 to 19 meters and 14 to 21 meters respectively), Tekapo is a turbid, glacier-fed lake (Secchi Disc reading 5 to 6 meters). All three lakes occur in regions of rugged topography in either bush (Wanaka and Hawea) or tussock (Tekapo) country which in part has been brought under cultivation. The lakes are oligotrophic

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TABLE 1

SUMMARY OF SAMPLE LOCATIONS TOGETHER WITH HEIGHT ABOVE SEA LEVEL, DISTANCE FROM SEA, AND MEAN ANNUAL RAINFALL

LOCATION	LATITUDE ° S	LONGITUDE ° E	HEIGHT ABOVE SEA LEVEL (m)	DISTANCE FROM SEA IN A WESTERLY DIRECTION (km)	MEAN ANNUAL RAINFALL (cm)	DATE OF COLLECTION	SAMPLE DESCRIPTION
Egmont 1	39° 18.3'	174° 05.0'	1500	25	~ 596	7 Aug. 1971	Fresh snow sample collected on side of steep gully
Egmont 2	39° 18.1'	174° 04.6'	1600	25	~ 596	7 Aug. 1971	Fresh snow sample taken at top of gully
Tararua	40° 53'	175° 25.4'	1110	40	~ 402	5 Sept. 1971	Residual snow sample
Coronet Peak	44° 55.6'	168° 44.3'	1160	115	~ 112	1 Aug. 1971	Fresh snow sample
Lindis Pass	44° 34'	169° 42'	970	140	~ 55	11 Aug. 1971	Residual snow sample
Lake Wanaka	44° 30'	169° 08'	279	90	~ 130	5 Aug. 1971	L290, Stn. 10; water depth 262 m
Lake Hawea	44° 27'	169° 17'	346	100	~ 81	4 Aug. 1971	L298, Stn. 8; water depth 302 m
Lake Tekapo	43° 53.5'	170° 32'	716	110	~ 56	2 May 1971	L265, Stn. 40; water depth 65 m
						3 May 1971	L270, Stn. 45; water depth 109 m

NOTE: The dimensions of the three lakes are: *Lake Wanaka*—max. depth 311 m, max. length 45 km, max. breadth 5 km, area 192 sq km; *Lake Hawea*—max. depth 384 m, max. length 30.5 km, max. breadth 8 km, area 120 sq km; *Lake Tekapo*—max. depth 120 m, max. length 18 km, max. breadth 5.5 km, area 96 sq km.

The lake heights in the above table refer to the maximum height above sea level, and the position of the lake refers to the position at the center of the lake.

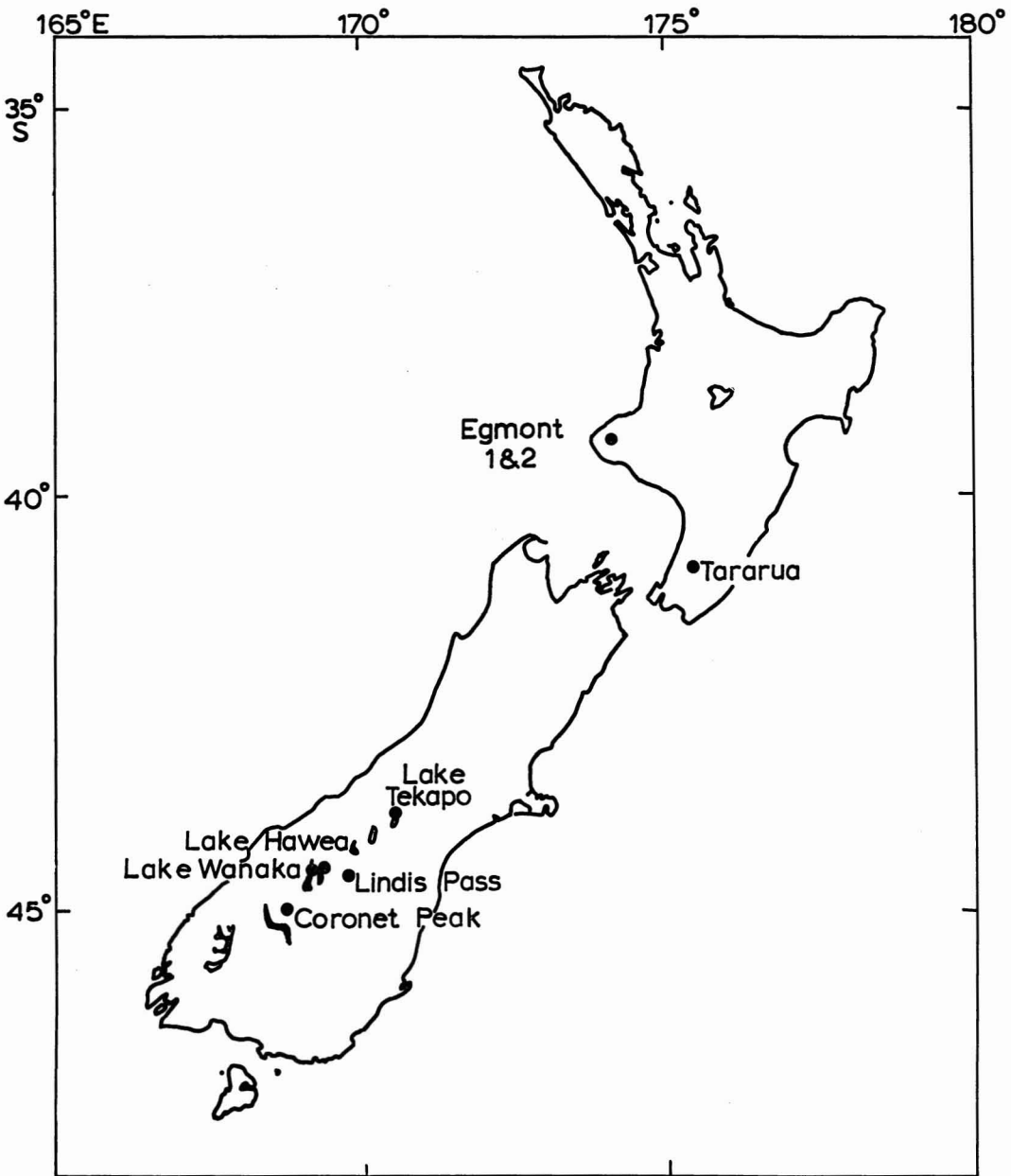


FIG. 1. Schematic diagram showing position of sampling sites in New Zealand.

(Irwin, personal communication) and have been classified as warm monomictic lakes (Jolly 1968) (i.e., thermally stratified in summer but not in winter). Short period internal waves have been recorded in Lake Tekapo (Ridgway 1974). Details of the sampling sites including

mean annual rainfall and distance from the sea are presented in Table 1 and a schematic diagram showing sample location is presented in Fig. 1.

Samples were analyzed for a range of constituents at the Chemistry Division, Department of

TABLE 2

## CHEMICAL ANALYSIS OF SNOW AND LAKE WATER SAMPLES

ITEM	pH	NITRITE NITROGEN	AMMONIACAL NITROGEN	ALBUMINOID NITROGEN	TOTAL			CHLORIDE (Cl <sup>-</sup> )	SULPHATE (SO <sub>4</sub> <sup>2-</sup> )	IRON (TOTAL Fe)	DISSOLVED SILICA (SiO <sub>2</sub> )
					HARDNESS (EDTA)*	TOTAL SOLIDS	SOLUBLE SOLIDS				
PRECIPITATION SAMPLES											
Egmont 1	-	-	-	-	-	-	-	0.5	< 1	< 0.05	3
Egmont 2	-	-	-	-	-	-	-	0.5	< 1	0.05	< 1
Tararua	-	-	-	-	-	-	-	1.5	< 1	< 0.05	< 1
Coronet Peak	-	-	-	-	-	-	-	0.9	< 1	< 0.05	< 1
Lindis Pass	-	-	-	-	-	-	-	0.9	< 1	0.05	< 1
LAKE SAMPLES											
Lake Wanaka											
0 m	-	-	-	-	-	-	-	0.3	4	< 0.05	3
50 m	-	-	-	-	-	-	-	0.5	4	< 0.05	3
100 m	-	-	-	-	-	-	-	< 0.1	4	< 0.05	< 1
150 m	-	-	-	-	-	-	-	0.2	4	< 0.05	3
200 m	-	-	-	-	-	-	-	0.4	4	0.05	< 1
260 m	-	-	-	-	-	-	-	0.4	4	< 0.05	3
Lake Hawea											
0 m	-	-	-	-	-	-	-	< 0.1	2	< 0.05	4
50 m	-	-	-	-	-	-	-	0.8	4	< 0.05	2
100 m	-	-	-	-	-	-	-	0.1	3	< 0.05	2
150 m	-	-	-	-	-	-	-	0.1	2	< 0.05	3
200 m	-	-	-	-	-	-	-	0.2	3	0.05	3
300 m	-	-	-	-	-	-	-	0.2	2	< 0.05	4
Lake Tekapo											
Station 40											
Surface froth	7.0	N.D.	0.05	0.02	32	39	19	< 1	24	0.1	4
15 m	7.1	N.D.	N.D.	N.D.	25	42	22	1	< 1	0.1	6
45 m	7.0	N.D.	Trace	0.02	22	38	24	< 1	< 1	< 0.05	3
Station 45											
Surface froth	7.2	N.D.	N.D.	N.D.	22	174	28	< 1	14	0.1	9
0 m	7.1	N.D.	0.05	0.10	27	45	18	< 1	< 1	0.1	5
WORLD AVERAGE FRESH WATER†	-	-	-	-	-	-	-	7.8	11.2	-	12.8
SEAWATER (salinity 35 ‰)‡	-	-	-	-	-	-	-	19,353	2712	10-100	0.04-8

TABLE 2 (cont.)

ITEM	MANGANESE (Mn)	SODIUM (Na <sup>+</sup> )	POTASSIUM (K <sup>+</sup> )	CALCIUM (Ca <sup>2+</sup> )	MAGNESIUM (Mg <sup>2+</sup> )	SO <sub>4</sub> <sup>2-</sup> :Na <sup>+</sup>	SiO <sub>2</sub> :Na <sup>+</sup>	K <sup>+</sup> :Na <sup>+</sup>	Ca <sup>2+</sup> :Na <sup>+</sup>	Mg <sup>2+</sup> :Na <sup>+</sup>
PRECIPITATION SAMPLES										
Egmont 1	< 0.05	1.1	0.03	0.4	0.04	< 1	2.7	0.03	0.36	0.04
Egmont 2	< 0.05	1.4	0.07	0.2	0.1	< 1	< 1	0.05	0.14	0.07
Tararua	< 0.05	1.3	0.01	0.3	0.2	< 1	< 1	0.01	0.23	0.15
Coronet Peak	< 0.05	1.0	0.02	0.8	0.1	< 1	< 1	0.02	0.80	0.10
Lindis Pass	< 0.05	1.4	0.07	0.2	0.04	< 1	< 1	0.05	0.14	0.03
LAKE SAMPLES										
Lake Wanaka										
0 m	< 0.05	0.9	0.06	11	0.6	4.35	3.33	0.07	12.2	0.67
50 m	< 0.05	0.9	0.06	11	0.6	4.35	3.33	0.07	12.2	0.67
100 m	< 0.05	1.3	0.09	11	0.6	3.08	< 0.77	0.07	8.46	0.46
150 m	< 0.05	0.9	0.06	11	0.6	4.35	3.33	0.07	12.2	0.67
200 m	< 0.05	1.1	0.07	11	0.6	3.63	< 0.91	0.06	10.0	0.55
260 m	< 0.05	1.0	0.07	11	0.6	4.00	3.00	0.07	11.0	0.60
Lake Hawea										
0 m	< 0.05	1.6	0.06	8	0.7	1.25	2.50	0.04	5.00	0.44
50 m	< 0.05	1.7	0.05	8	0.7	2.35	1.18	0.03	4.70	0.41
100 m	< 0.05	1.6	0.06	8	0.7	1.87	1.25	0.04	5.00	0.44
150 m	< 0.05	1.7	0.05	8	0.7	1.18	1.76	0.03	4.70	0.41
200 m	< 0.05	2.0	0.07	8	0.8	1.50	1.50	0.04	4.00	0.40
300 m	< 0.05	1.7	0.05	8	0.7	1.18	2.35	0.03	4.70	0.41
Lake Tekapo										
Station 40										
Surface froth	0.01	0.7	0.5	7.1	—	34.3	5.71	0.7	10.1	—
15 m	0.2	1.1	0.7	7.6	—	< 0.91	5.45	0.6	6.91	—
45 m	< 0.05	0.7	0.6	6.4	—	< 1.43	4.30	0.9	9.14	—
Station 45										
Surface froth	0.2	1.2	0.9	8.2	—	11.7	7.50	0.8	6.83	—
0 m	0.1	0.8	0.6	6.8	—	< 1.25	6.25	0.8	8.50	—
WORLD AVERAGE FRESH WATER†	—	6.3	2.3	15	4.1	1.78	2.03	0.4	2.38	0.65
SEAWATER (salinity 35 ‰)‡	0.5–3	10,760	387	413	1,294	0.25	4–740 × 10 <sup>-6</sup>	0.04	0.04	0.12

NOTE: Dashes indicate that item was not analyzed. All analyses except those for pH are in ppm. N.D., not detected.

\* As calcium carbonate.

† Data from Armstrong and Schindler (1971).

‡ Data from Culkin (1965) and Riley (1965).

Scientific and Industrial Research, with standard methods of analysis (see appendix) and results are presented in Table 2. It is probable that adventitious low level contamination of the samples during collection, or by the sample containers themselves, may have given rise to some of the variability observed between the different precipitation samples, and, to a smaller extent, between the lake waters taken from the same sample positions at different depths. However, with the exception of the chloride results, the enrichments observed are large enough for this possible contamination to be insignificant in the subsequent assessment of the likely origin of the ions found in the lake waters. Chloride results are presented here only as an indication of the order of magnitude of concentrations present in these waters (see appendix).

The data presented in Table 2 indicate a low ionic concentration for both the precipitation and lake water samples and as such the lake waters fall into the category of dilute soft-water lakes (Hutchinson 1957, Armstrong and Schindler 1971). In order to measure the extent of chemical fractionation throughout the complete hydrological cycle, we ratioed elemental concentrations relative to sodium in accordance with the conclusions of the working symposium on sea-air chemistry (Duce, Stumm, and Prospero 1972). The relative constancy of sodium in the lake waters and precipitation samples (Table 2) indicates that leaching of sodium from the schists and graywackes does not occur on any significant scale in the catchments studied here. Sodium is not readily adsorbed onto soils or clay minerals and under the conditions prevalent in New Zealand appears to be a satisfactory reference element for consideration of the relative enrichment of other elements in lake waters. It is used therefore as the reference element throughout this paper.

Comparison of the ratios K:Na and Mg:Na for the precipitation samples with the ratios for these elements in seawater suggests that the sodium, potassium, and magnesium in these samples are derived predominantly from seawater. The corresponding ratios for calcium and possibly silica are greater than those observed for seawater, indicating an enrichment of these elements relative to the proportions in seawater. The reason for this enrichment is not

known, but may possibly be associated with inclusion of wind-eroded materials from land in the precipitation.

In Lakes Wanaka and Hawea, the ratio K:Na is close to that observed for seawater, suggesting that potassium in the lakes is derived predominantly from precipitation with, at most, minor contributions from leaching of the catchments. The ratios Ca:Na, Mg:Na, and  $\text{SiO}_2$ :Na are higher than those for seawater or for the precipitation samples, indicating that these elements are introduced into the lake water principally by low-temperature leaching of the surrounding schists and graywackes. The higher K:Na ratio in Lake Tekapo suggests that K in this lake is also derived by low-temperature leaching. There is also a marked enrichment of  $\text{SO}_4^{2-}$  in the lake waters relative to the precipitation samples, but the source of this enrichment cannot be simply ascertained on the basis of the present data, although oxidation of sulphide minerals may be responsible. The froth samples taken from the surface of Lake Tekapo appear to be enriched in  $\text{SO}_4^{2-}$  and total solids relative to the deeper lake water but the significance of this is not known. Finally, Mn and Fe show no evidence of enrichment even in the deeper regions of the lake. It is concluded therefore that diagenetic remobilization of these elements from the bottom sediments into the lake waters as reported by Mortimer (1941, 1942) for lakes in the English Lake District is not occurring on any significant scale, at least at the time of collection of these samples.

The data indicate the importance of studying further facets of the hydrological cycle in defining the chemistry of natural water systems in New Zealand.

Dr. C. D. Stevenson is thanked for his critical comments on the manuscript.

## APPENDIX

### SUMMARY OF ANALYTICAL TECHNIQUES

**METALS:** All metals were determined by atomic absorption with direct aspiration. An ionization buffer of 0.08-percent CsCl and 1 percent  $\text{HClO}_4$  (v:v concentration in the samples) was used.

<i>Element</i>	<i>Flame</i>	<i>Wavelength</i> ( $\mu\text{m}$ )
Sodium	HAF	589.6
Potassium	HAF	766.5
Calcium	NOAF	422.7
Magnesium	AAF	285.2
Iron	AAF	248.3
Manganese	AAF	279.5
Silicon	NOAF	251.6

Note: AAF, air-acetylene flame; HAF, hydrogen-air flame; NOAF, nitrous oxide-acetylene flame.

A single-slot burner with a thermostat was used in all cases.

**CHLORIDE:** Chloride was determined colorimetrically with mercuric thiocyanate (American Society for Testing and Materials 1965).

**SULPHATE:** Sulphate was determined turbidimetrically with barium chloride crystals as precipitant and glycerol as stabilizer (American Public Health Association 1971).

All analyses were conducted without pre-concentration.

Recent collaborative studies of water analyses carried out in New Zealand (Kingsford, Stevenson, and Edgerley 1973*a, b*; Kingsford and Stevenson 1973) indicated that water laboratories commonly report analytical results distributed with standard deviations between 5 and 15 percent, about a mean value that is not significantly different from the true value for sodium, potassium, calcium, and magnesium analyses at concentrations about an order of magnitude higher than the concentrations found here. The sensitivity of atomic absorption analyses is such that the accuracy and precision of analysis of the samples in this study are likely to be similar. Other collaborative studies (Skougstad, personal communication) indicate a similar situation for silica analyses. The concentrations of iron and manganese found here are at or below the detection limits of the methods used and must be considered only as limits. The accuracy and precision of the method used to analyze for sulphate and chloride have not previously been assessed at the low concentrations encountered in this study. At these low levels,

the risk of sample contamination becomes high and it is likely that it is this factor which causes the low precision of the chloride analyses reported here.

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