A PRELIMINARY STUDY OF THE COMPOSITION OF PRECIPITATION IN S.E. ONTARIO

G. K. RUTHERFORD

Department of Geography, Queen's University, Kingston, Ontario, Canada

Received April 14, 1967

As a prelude to the study of chemical weathering of rocks and soils in S.E. Ontario, a study of the composition of precipitation waters at 12 sites within the area was initiated. Analyses of bulk precipitation of both rainfall and snowfall are presented and compared with similarly derived results in other areas.

The silica and aluminum contents are regarded as being high, although in snow silica is absent and aluminum is quite high. Areal differences in silica content appear to be connected with local differences in lithology. Iron occurs in the same concentrations as aluminum and is probably derived from atmospheric dusts. The sodium content is high, especially when compared with inland sites in other areas. Potassium is generally somewhat lower than sodium. Although the calcium content may reflect local differences in lithology, the dissolved magnesium is surprisingly uniform. Lithological differences in the area are also reflected in the significantly higher nitrate-nitrogen concentrations in the limestone area. Snowfall is markedly high in sulfates, which is considered to be a function of climatic and industrial causes. The high chloride concentrations in such a 'non-marine' environment are not explained.

INTRODUCTION

There is an increasing awareness of the importance of investigations into the composition of rainwaters throughout the world (Carroll 1962). The importance of such knowledge in the fields of geochemistry can hardly be overemphasized and in latter years, the content of Cs and Sr as fall-out products of atomic explosions in rainfall has been closely followed. Anticipating studies in the geochemistry of soil formation and rock weathering in S.E. Ontario, the author began, in 1965, a long-term appraisal of the quality of precipitation waters in the area. As a preliminary investigation the total rainfall during the autumn was collected as well as samples of snowfall during the winter. This program is to be expanded considerably to include bi-monthly sampling during the summer and to include investigations of the amounts of radioactivity in the precipitation. Such information will be of use not only to agriculturalists and geochemists but also to climatologists, town planners, and other local authorities.

METHOD

An approach was made to the Ontario Water Resources Commission as well as to the Meteorological Branch, Canada Department of Transport, to initiate sampling and analysis of the samples. The latter arranged for weather observers in the Belleville–Brockville area to collect precipitation samples, and the former had the samples analyzed in their laboratories.

A number of weather observer stations were selected in the above area (Fig. 1) and provided with large polyethylene containers into which the rain gauges were emptied after measurement. These containers were collected in late December and the water samples sent for analysis. At those weather stations remaining open during the winter the observers agreed to collect newly fallen

Canadian Journal of Earth Sciences. Volume 4 (1967)
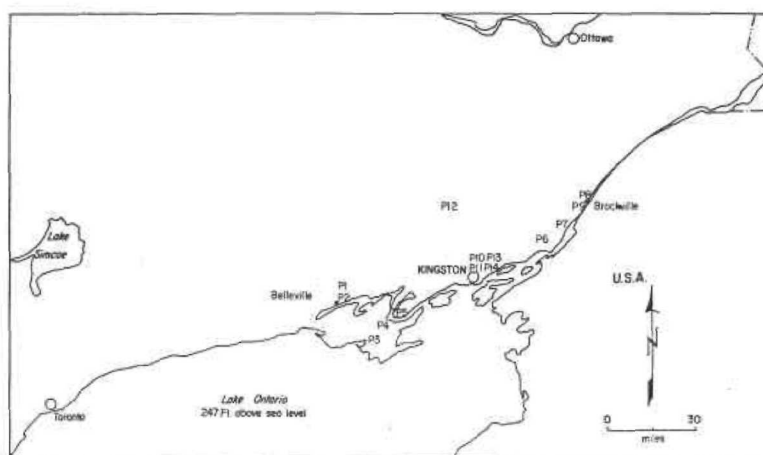
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FIG. 1.   Map showing precipitation sampling localities, S.E. Ontario.

snow at regular intervals and to empty the melt water into the polyethylene containers.

The cation contents were determined by flame spectrophotometry, and nitrate was determined by the phenoldisulfonic acid method. Chloride was determined by the mercuric thiocyanate-ferric ion, and sulfate by a spectro-photometric-titration method. The analytical methods are those recommended for water and waste water by the American Public Health Association (1965).

RESULTS AND DISCUSSIONS

Introduction

The results of the analyses carried out on the autumn rainwater and winter snow in the 1965 to 1966 period are presented in Table I, and summarized in Table II. Table III presents some relevant calculated ratios for rainfall and snow, and similar ratios for river, lake, and sea waters. Table IV summarizes the precipitation data from most of the observation stations in the relevant period.

All of these samples must be considered as bulk precipitation samples. White-head and Feth (1964) have pointed out the need to differentiate between bulk precipitation collected over a long period of time and rain or rainwater col-lected after each shower, and have shown the content of various ions in the former to be 4 to 10 times that in the latter. The difference is assumed to be accounted for by dry fallout in the bulk precipitation samples, and the relative amount of dry fallout would in turn depend on the duration of the collecting period. In this way all bulk precipitation samples are not strictly comparable. A review of the literature indicates that the following sampling techniques have been used:

Egner and Eriksson (1955)   : analyzed monthly
Feth, Rogers, and Robertson (1964): one representative uncontaminated snow
                                     sample
Gambell (1963)   : bulk precipitation

Gambell and Fisher (1964)   : rainfall analyzed after each storm
Gambell and Fisher (1966)   : bulk precipitation
Junge (1958)   : rainfall analyzed monthly, no dry fallout
Laney (1965)   : apparently rainfall
Rankama and Sahama (1949)   : uncertain, original sources not available
Wetselaar and Hutton (1963)   : rainfall analyzed after each storm
Yaalon (1964)   : bulk precipitation
Yaalon and Katz (1962)   : bulk precipitation

It has not been possible to ascertain the method of collection of the precipitation analyses cited by Rankama and Sahama (1949), but it is suspected that they were rainwater samples. Similarly, the data provided by Egner and Eriksson (1955) would be more comparable with the snowfall figures in Table I, as the former were collected in November and December in Scandinavia.

Reliability of the Data

The samples contained dry fall-out and dust settling on the gauges so that they were filtered before examination in order to remove the undissolved particles. The overall accuracy of the data is difficult to assess. Microbial activity in the water samples can alter chemical concentrations of nitrates, but has much less effect on other constituents. Large integrated samples of precipitation can give no more than an average for the period concerned. It is realized that the figures presented give only general indications of ionic levels in precipitation, and a more accurate picture will emerge when sampling is more frequent. For reasons stated above, the comparison of these results with those of other workers must be considered with caution. As far as possible, comparisons will be made with analyses of bulk precipitation where this is known for certain. However, with respect to soil weathering, the analyses of rainwater should be more relevant than those of bulk precipitation, although the difference may be hardly significant.

The literature has an unexpected paucity of analytical results for the contents of Al and Fe rainwater and snow. In fact, no data for Fe could be found and only the results of Feth *et al.* (1964) for Al in snow could be brought to light.

Using similar methods, Gambell and Fisher (1966) showed standard deviations of generally less than 0.1 p.p.m. for standard solutions analyzed concurrently with the monthly precipitation samples. The value of cations minus anions in equivalents per million, divided by cations plus anions, in equivalents per million, was less than 0.05.

Silica

Figures of up to 0.4 p.p.m. in rainfall are surprisingly high and may represent contributions from fine atmospheric dusts. The lack of silica in snow in Table I is interesting, since the amount of suspended materials in the snow was much higher than in the rainwater. Silica contents higher than 0.4 p.p.m. all occur to the west of Kingston, in the area called the limestone plain. The cement manufacture at Picton may have had some effect on these figures. In future

TABLE I

Composition in p.p.m. (A) of rainwaters collected between 8 Oct. 1965 and 27 Dec. 1965 and (B) snow collected between 27 Dec. 1965, and 1 Apr. 1966, at some stations in S.E. Ontario

	P1		P2		P3		P4		P5		P6		P7	
	A	B	A	B	B	B	A	B	A	B	A	B	A	B
SiO_2	0.48	0	0.56	0	0.48	0	0.6	0	0.56	0	0.08	0	0.0	0.0
Al	0.8	0.18	0.8	0.15	1.3	0.9	1.0	0.7	1.0	0.6	0.64	0.07	0.52	0.11
Fe	0.8	0.54	0.76	0.48	1.8	1.8	0.75	0.7	0.96	x	0.72	0.12	0.23	x
Na	6.3	8.9	0.4	3	0.3	1.1	1.4	1.9	tr	5.1	0.1	1.2	0.2	0.9
K	2.7	4.9	0.95	1.1	0.8	0.7	1.7	1.0	0.65	0.9	1.0	0.4	0.9	0.5
Ca	12	9	7	13	4	7	10	8	4	x	1	5	0	3
Mg	1	1	1	1	1	1	2	1	1	x	1	2	1	1
$N-NO_3$	0.5	0.3	0.6	0.5	0.3	0.5	0.5	tr	0.22	x	0.17	0.3	0.10	0.0
SO_4	32	16	14	15	8	11	13	11	8	23	10	5	11	21
Cl	9	15	2	7	2	3	3	3	1	x	2	3	2	2
Alkalinity $CaCO_3$*	14	20	10	27	8	10	·15	15	8	x	5	7	6	6
Hardness $CaCO_3$†	34	26	20	38	12	22	24	22	14	x	6	20	4	12

TABLE I (*concluded*)

	P8		P9		P10		P11		P12		P13		P14	
	A	B	A	B	A	B	A	B	A	B	A	B	A	B
SiO₂	x	0	0.0	0.0	0.16	0	0.0	z	0.0	z	0.0	0.0	0.36	0.0
Al	x	x	0.88	0.11	0.8	1.0	0.4	z	1.0	z	0.85	0.22	1.12	1.0
Fe	x	x	0.13	0.45	0.9	0.8	0.07	z	0.3	z	0.5	0.43	1.07	2.7
Na	tr	14	tr	3.7	0.5	5.4	tr	z	tr	z	tr	1.2	0.6	1.1
K	0.65	0.5	0.7	0.6	1.0	1.4	0.7	z	0.7	z	0.8	0.4	1.5	0.8
Ca	x	5	1.0	2	3	4	2	z	0	z	1	6	2.0	6
Mg	x	1	0.2	1	1	12	2	z	1	z	1	1	6	1
N–NO₃	0.6	0.4	0.6	0.34	0.25	0.3	0.4	z	0.6	z	0.12	0.54	0.25	0.16
SO₄	x	x	9	6	10	10	8	z	6	z	15	10	8	3
Cl	1	x	1	3	3	5	2	z	2	z	2	3	2	4
Alkalinity CaCO₃*	x	17	7	6	4	15	8	z	7	z	4	14	9	18
Hardness CaCO₃†	2	18	2	8	10	58	12	z	2	z	6	18	10	18

NOTE: P1 Belleville water purification   P4 Picton   P7 Mallorytown   P10 Marine radio, Kingston   P13 Ontario Hydro, Frontenac
P2 Belleville sewage plant   P5 Glenora Ferry   P8 Brockville   P11 Ontario Hydro, Cataraqui   P14 Lakeland Nat. Gas, Kingston
P3 Bloomfield   P6 Lansdowne   P9 Brockville sewage plant   P12 Ontario Hydro, Hinchinbrooke

x = not sufficient material for complete analysis
z = snow not collected
*Alkalinity of 14 p.p.m. is the equivalent neutralization power of a strong acid as a solution of 14 p.p.m. CaCO₃ at pH 4.7.
†Hardness 34 p.p.m. is equivalent to the hardness of a solution of 34 p.p.m. CaCO₃.

TABLE II

Summary of chemical analyses of precipitation in part of S.E. Ontario (p.p.m.)

	Rain				Snow			
	M	H	L	No.	M	H	L	No.
SiO_2	0.25	0.56	0.0	13	0.0			12
Al	0.80	1.12	0.52	13	0.46	1.00	0.07	11
Fe	0.69	1.80	0.13	13	0.89	1.80	0.12	9
Na	0.70	6.30	tr	14	3.97	14.00	14.60	12
K	1.05	2.7	0.65	14	1.10	4.90	0.4	12
Ca	3.61	12.0	0.0	13	6.18	13.0	2.0	11
Mg	1.55	2.0	1.0	13	2.09	12.0	1.0	11
$N-NO_3$	0.37	0.6	0.1	13	0.33	0.54	tr	10
SO_4	11.8	32	8	13	11.91	23	3	11
Cl	2.44	9	1	14	4.80	15	2	10
Alkalinity	8.08	14	4	13	14.09	27	6	11
Hardness	11.3	34	2	14	23.6	58	8	11

*M = mean; H = highest; L = lowest; No. = number of analyses.

TABLE III

Some ratios of dissolved solids in rainwater and snow in S.E. Ontario and comparable ratios for lake and river waters and sea water

	Rain				Snow				Lake and river*	Sea water*
	M	H	L	No.	M	H	L	No.		
Na/Cl	0.25	0.5	0.03	8	0.58	1.2	0.1	9	1.02	0.55
Ca/Mg	3.9	12.0	1.0	11	5.6	13.0	0.3	11	6.0	0.31
Na/K	0.65	2.4	0.1	8	3.08	6.15	1.36	11	2.73	27.8

*Rankama and Sahama 1949.
M = mean; H = highest figure; L = lowest figure; No. = number of ratios.

TABLE IV

Total precipitation (in inches) at weather observation stations in S.E. Ontario (1 in. depth of snow = 0.1 in. precipitation)

Station	September–December 1965	January–March 1966
P1	12.40	7.43
P2	13.44	6.06
P3	11.60	6.50
P4	11.35	6.01
P6	11.81	8.13
P7	13.96	6.23
P9	14.88	7.23
P10	13.78	6.16
P11	14.47	7.80
P12	14.82	6.50
P13	14.51	7.56
P14	10.62	3.91
P5/P8	Not available	

analyses the composition of the suspended solids separated from the precipitation waters by centrifuging may give an indication of the origin of this element in these rainwater samples. Feth *et al.* (1964) found no silica in fresh snow in the Sierra Nevada, Utah, and Colorado. Whitehead and Feth (1964) presented 40 rainwater analyses with silica contents ranging from 0.0 to 1.8 p.p.m., most

of which are lower than those from S.E. Ontario, although their figures for bulk precipitation do not appear to be strictly comparable.

Aluminum

As aluminum is geochemically stable, the figures for this element in Table I must be considered high for both snow and rain. The aluminum content of rainfall is similar to silica but significantly higher for snow. The figures are of the same order of magnitude as those recorded for the St. Lawrence River (Clarke 1924), for lake and river water (Rankama and Sahama 1949), and for snow (Feth *et al.* 1964).

Iron

The values for iron are of the same order of magnitude as those for aluminum, but do not show similar trends. Unfortunately comparative figures for iron are lacking. Most of the iron may have been contributed by atmospheric dusts.

Sodium

The sodium content varies from trace amounts to 6.3 p.p.m. in rainfall and from 0.6 to 14 p.p.m. in snow, being thus markedly higher in snow than in rainfall. The figure for sample P8 (Table I) may be suspect, but those of P1 are almost consistently higher than those given by Gambell (1963), Gambell and Fisher (1964), and Laney (1965). However, Gambell and Fisher (1966) gave figures of 1.5 p.p.m. at coastal stations, decreasing to less than 0.5 p.p.m. at 120 miles from the coast. Wetselaar and Hutton (1963) showed variations of 0.0 to 5.7 p.p.m. at Katherine in Northern Australia; MacIntire and Young (*in* Rankama and Sahama 1949) showed contents of 3.6 in the urban center of Knoxville, Tennessee and 1.5 p.p.m. $1\frac{1}{2}$ miles away. These values are considerably higher than those given by Egner and Eriksson (1955) except for coastal stations. At present, no explanation of these seemingly high contents is offered, but as the area is approximately 250 miles from the nearest coastline, other contributing factors than sea water must be sought.

The Na/Cl ratios in snow and in rainwater in the area under discussion are given in Table III, and can be compared with the average Na/Cl ratios of the dissolved solids in lake and river water and sea water (Rankama and Sahama 1949). The Na/Cl ratio for snow is considerably higher than for rainfall, about the same as for sea water, but much lower than for lake and river waters. Such a low ratio was not expected and is contrary to the findings of Junge and Werby (1958).

Potassium

The values for potassium on Table I are considerably higher than those of Gambell (1963), Gambell and Fisher (1966), and Wetselaar and Hutton (1963), but similar to those of MacIntire and Young (*in* Rankama and Sahama 1949) for urban and rural areas near Knoxville, Tennessee. The values are generally somewhat lower than for sodium. Egner and Eriksson (1955) reported somewhat lower potassium values in rainfall in Scandinavia, where coastal stations show markedly higher values than inland. Their potassium values are much

lower than their sodium values. The Na/K ratio in rainwater is considerably lower than in snow and in river and lake waters, and much lower than in sea water. Thus most of the potassium is probably of terrestrial origin.

Calcium

The calcium content (Table I) varies from 0.0 to 13 p.p.m., being higher in the areas underlain by lower Paleozoic limestone than in the areas underlain by acidic rocks of the Canadian Shield. The figures for rainfall and snow are similar to, but in general much higher than, those given for rainfall by Egner and Eriksson (1955), Gambell (1963), Gambell and Fisher (1964), Junge and Werby (1958), and MacIntire and Young (*in* Rankama and Sahama 1949). The high calcium contents may be a function of the lithology of the area, but it should be stressed that this area is generally well covered by vegetation, and dust storms are uncommon, particularly in autumn and winter when the samples were collected, so that the calcium accession from dust should be minimal. The Ca/Mg ratio for rainwater is lower than that for snow and river and lake waters, but much higher than that for sea water, which suggests a terrestrial origin for this element.

Magnesium

There is surprising geographical uniformity for the values of dissolved magnesium shown in Table I. These are slightly higher than, but of the same order of magnitude as those quoted for precipitation by Clarke (1925), Rankama and Sahama (1949), and Wetselaar and Hutton (1963), but significantly higher than those recorded by Gambell and Fisher (1966) for central eastern U.S.A. These values are generally somewhat lower than those recorded by Egner and Eriksson (1955) for Scandinavia, for the Scandinavian coastal stations where the magnesium values are far higher than those recorded for S.E. Ontario. Soil dust may be the principal cause of the observed magnesium concentrations, but the difference between samples from the limestone area and those from the Canadian Shield area is not so obvious as for calcium.

Nitrate-Nitrogen

The nitrate-nitrogen content does not represent the total nitrogen in precipitation waters; the differences between nitrate-nitrogen and ammonium-nitrogen (which occur in rainwater in Israel) have been well documented by Yaalon (1964). The N-NO₃ values shown on Table I are similar to those presented by Junge (1958) and Wetselaar and Hutton (1963) and generally somewhat less than those given by Yaalon (1964) for Israel. Both areal distribution and seasonal patterns tend to discount the influence of lightning in fixing atmospheric nitrogen. Junge (1958) has produced some nitrate-precipitation maps of the United States and concluded that the major amount of nitrate in rainwater comes from the soil rather than from industrial and other human activities. He also suggested that the occurrence of ammonium nitrate may be associated with soil processes, and showed that higher concentrations occur in regions with calcareous soils, a relationship which has been confirmed by Yaalon (1964) in Israel. In the area included in the present investigation the

precipitation over the limestone plains is generally significantly higher in nitrate than that over the Canadian Shield. The values obtained are in close agreement with those provided by Egner and Eriksson (1955), although they do not appear to reflect the lithological differences as well as $N\text{-}NO_3$ values for the Fennoscandian Shield and the Paleozoic limestones in Scandinavia.

Sulfates

Sulfate concentrations shown on Table I are considerably higher than those quoted for rainfall by Gambell (1963), Gambell and Fisher (1964, 1966), and Laney (1965), although they are in line with concentrations presented by Clarke (1925) and Rankama and Sahama (1959) and with concentrations in precipitation collected over the Pacific Ocean (Gambell and Fisher 1964). The SO_4 values for precipitation collected in Scandinavia in November and December are generally lower, although of the same order of magnitude as the ones presented on Table I. Of particular interest is the high concentration of sulfates in snow, a feature recorded for snow in Iowa by Rankama and Sahama (1949), but not confirmed by Feth et al. (1964). In some localities, the sulfate content is higher in snow than in rain. The presence of sulfur in the atmosphere has been attributed to natural causes. Gambell and Fisher (1966) maintained that much sulfate has been derived from SO_2 by oxidation and that long periods of atmospheric stagnation during winter may cause significant concentrations of SO_2 to build up. In S.E. Ontario the high sulfate content in snow may be caused by the increased use of fuel oil in furnaces in winter for heating homes and factories, during a time of year when atmospheric conditions are relatively quiet. The gases from such furnaces are generally more widely dispersed than those from automobile exhausts.

Chlorides

With the exception of sample P1-B, the concentrations of chlorides given on Table I are well within the range of values reported by Rankama and Sahama (1949) and are generally similar to those presented by Gambell and Fisher (1966) for Virginia and North Carolina, Wetselaar and Hutton (1963) for Northern Australia, and Egner and Eriksson (1955) in Scandinavia, but considerably higher than those given by Gambell (1963) and Laney (1965). Gambell and Fisher (1966) contended that previous experience, as well as their own, shows that sea salt is the major and perhaps only source of Cl in rainfall except in arid regions. However, as this area is far from any sea coast and the Cl concentration is generally considerably less than 5 p.p.m. there can be little doubt that other sources must be considered.

CONCLUSIONS

Preliminary investigations of rain and snow in S.E. Ontario show surprisingly high contents of dissolved cations and generally higher concentrations of some anions than previously reported. The contents of SiO_2, Al, and Fe are considerably higher than have been recorded previously.

Future investigations will attempt to take samples more regularly so that

changes in ion content and in particular nitrate-nitrogen and ammonium-nitrogen may be more accurately followed.

ACKNOWLEDGMENTS

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