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THE EFFECTS OF PRECIPITATION CHEMISTRY AND CATCHMENT AREA LITHOLOGY ON THE QUALITY OF RIVER WATER IN SELECTED CATCHMENTS IN EASTERN AUSTRALIA

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Abstract

The results of partial chemical analyses of precipitation and river water samples from north-east Queensland and south-eastern New South Wales are presented. Comparisons of water quality in the two areas are made using ionic ratios. While the sodium and chloride contents of precipitation in the two areas are similar, higher concentrations of calcium, magnesium and potassium occur in precipitation samples collected in New South Wales. Precipitation supplies between 25% and 70% of the total solute loads of the rivers studied. In the Southern Tablelands of New South Wales more chloride is supplied to the catchment areas than is removed by the rivers. River water quality reflects catchment lithology more than the climatic contrasts between the two study areas. Nevertheless, precipitation chemistry exerts an influence on the ionic ratios of these Australian rivers with low total dissolved solids concentrations.

INTRODUCTION

The solutes contained in river waters may be derived from a variety of sources, those of chloride in Japanese rivers including rain, wind-borne salts, human contamination, mineral springs, and the decomposition of rocks (Hanya, 1959). The solute composition of river water varies in time through changes in the relative importance of these different sources, and in the contributions of groundwater and surface runoff to total streamflow. The chemistry of water from different drainage basins varies with contrasts of lithology and through the influence of climate and human activity.

During a study of the rate of denudation of catchment areas in humid tropical north-east Queensland and in the Central and Southern Tablelands and Highlands of New South Wales (Table 1), partial analyses of the solute content of the waters of 39 rivers (Table 2) were made at intervals in the period from 1963 to 1965. The choice of catchments in the two areas (Figures 1, 2 and 3) with similar lithologic characteristics made possible the evaluation of the influence of climate on water quality. Under the humid tropical conditions of the Cairns and Atherton Tableland area of north-east Queensland weathering might remove from the soils elements which would not be subject to chemical erosion in the temperate environment of south-eastern New South Wales. This paper discusses the sources of the solutes, with particular emphasis on precipitation chemistry, and then considers the significance of the contrasts in the water chemistry of rivers draining different rock types, and draining similar rock types under different climatic conditions. While the results of analyses are expressed in parts per million (ppm) (Table 2), ionic ratios based on equivalent-weight units, expressed as equivalents per million (epm) are used to typify waters from different environments.

PRECIPITATION CHEMISTRY

The chemistry of river waters is affected by precipitation chemistry through the direct supply of solutes to rivers and through the influence of the chemical quality of rainfall on weathering processes. In rivers with low quantities of total dissolved solids, such as those listed in Table 2 where the maximum average total

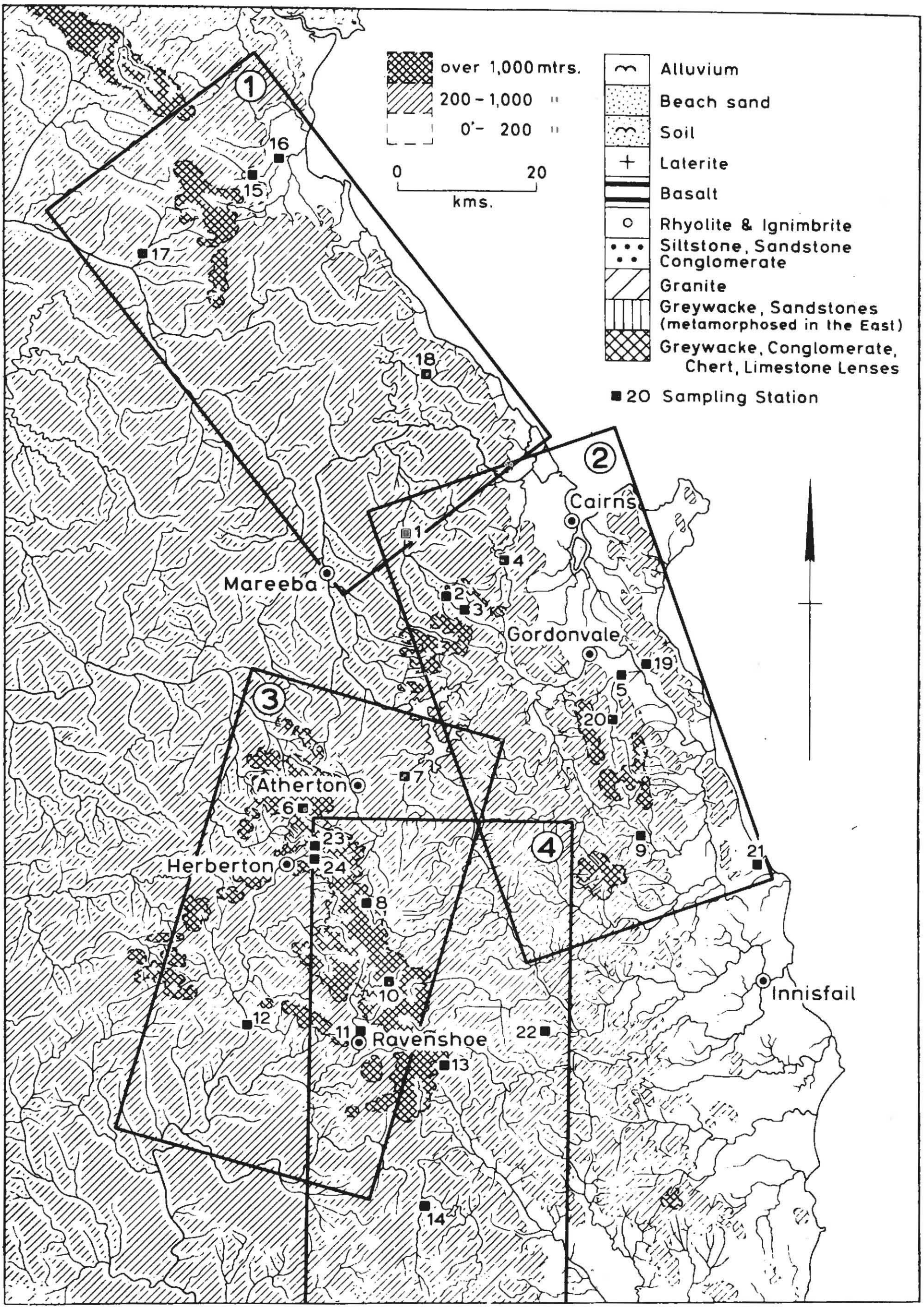

Figure 1. Location of the water-sampling stations in north-east Queensland. The areas indicated by the rectangles numbered 1 to 4 represent the districts shown on the lithological maps in Figures 4 to 7 respectively.

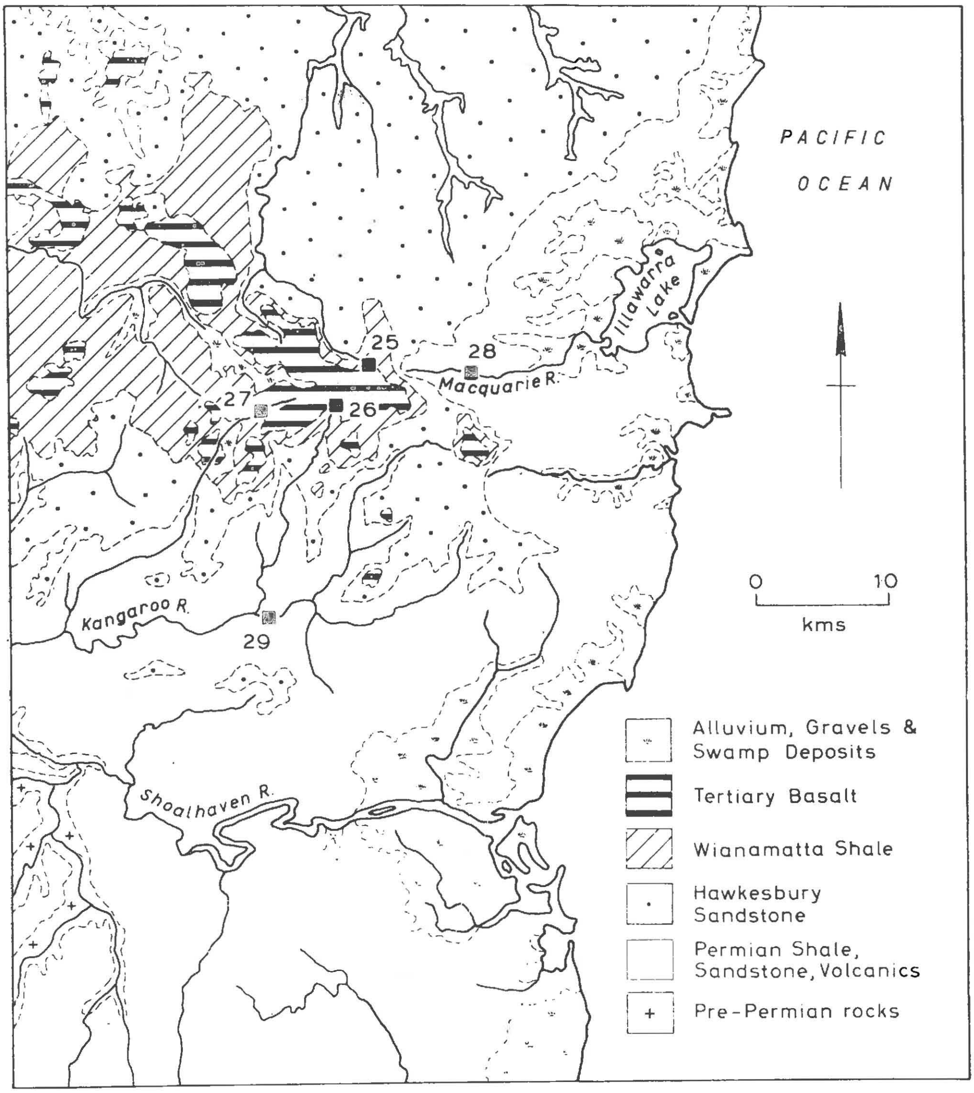

Figure 2. Location of the water sampling stations in the Robertson area of New South Wales, showing main lithological types.

dissolved solids concentration is 101ppm, the solutes supplied from precipitation make up an important proportion of the total load. As analyses of rainfall samples from N.E. Queensland and the Australian Capital Territory on the Southern Tablelands of S.E. Australia (Table 3) show considerable variation in precipitation chemistry in both time and space, this section discusses these variations and then the contribution of solutes from precipitation to rivers.

N.E. Queensland

The maximum number of rainfall samples collected at one point in N.E. Queensland was five, from the Herberton Range near Station 6 (Figure 6), just west of the divide between the Coral Sea and Gulf of Carpentaria drainage areas. Analysis of variance between the results from this point and those from Babinda

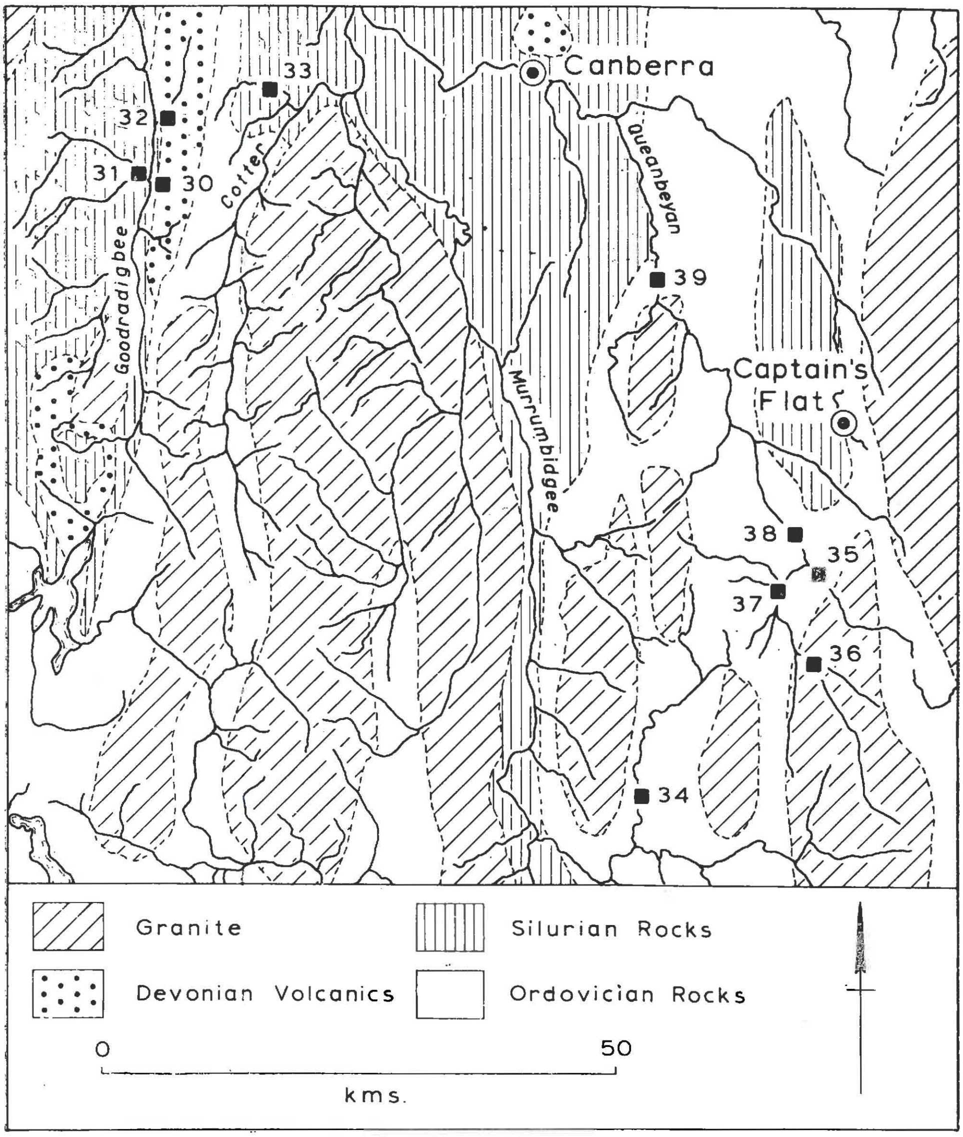

Figure 3. Location of the water sampling stations in the Southern Tableland and Highlands of New South Wales and the Australian Capital Territory, showing main lithological types.

Boulders (Station 9, Figure 5), where three samples were collected, shows only slight differences significant at the 0.1 level in the calcium content and at the 0.2 level in the Na:Mg ratio. These slight differences indicate a decrease in the calcium concentration and in the dominance of the sodium ion away from the coast. The within group variation of the majority of solute concentrations and ionic ratios at Babinda Boulders or on the Herberton Range is greater than the between group variation and thus a real difference between precipitation chemistry near the coast and that further inland cannot be demonstrated with the small number of samples collected.

Table 1. Characteristics of the catchments studied.

Station Number	River	Locality	Catchment Area km²	Mean Annual Rainfall mm	Height of Station m	Relief of Catchment m	Relative Relief *	Major Lithology	Percentage of area under Major Lithology
North-east Queensland									
1.	Davies	Tichum Jct.	105.67	1270	396	924	2.352	G	82.3
2.	Davies	Forestry Rd.	14.17	1397	602	718	3.405	G	100
3.	Davies	Jungle	5.59	1524	716	604	5.208	G	100
4.	Freshwater	Copperlode	44.03	2235	320	1000	3.122	M	43.9
5.	Behana	Aloomba	82.88	4000	9	1576	3.709	G	68.6
6.	Walsh	Herberton Rd.	1.55	1270	1082	168	2.894	G	100
7.	Barron	Picnic Crossing	225.33	1562	678	587	1.559	B	54.0
8.	Barron	Crater	11.91	1778	991	274	1.065	B	100
9.	N. Babinda	Boulders	15.36	4320	85	783	4.056	G	53.4
10.	Millstream	Evelyn Hwy.	19.81	2032	1020	274	1.375	R	85.9
11.	Millstream	Ravenshoe	82.80	1900	884	412	0.838	R	63.3
12.	Wild	Recorder	585.34	1015	640	610	0.537	R	34.0
13.	Canabullen	Forestry Rd.	11.47	2032	950	274	1.873	B	70.0
14.	Nitchaga	Road Bridge	75.11	1900	678	308	0.838	G	64.0
15.	Mossman	Gorge	83.13	1800†	)			G	100
16.	Mossman	Daintree Rd.	113.96	1820†	) No	detailed	Maps	G	76.4
17.	Mary	Crossing	90.65	1145†	343	945	2.067	G	73.8
18.	Flaggy	Black Mtn. Rd.	51.02	2040	404	358	1.075	M	100
19.	Campbell	Tramway Bge.	5.72	3810	8	968	9.858	G	100
20.	Behana	White's Falls	35.48	4200	274	1311	5.154	G	79.0
21.	Joyce	Forestry Rd.	2.28	3300	15	305	4.404	M	100
22.	Douglas	Palmerston Hwy	1.35	2413	518	152	2.630	B	100
23.	Wild N. Branch	Moomin	7.82	1375	920	311	2.473	G	100
24.	Wild S. Branch	Moomin	5.02	1325	920	311	2.876	G	100
South-eastern New South Wales									
25.	Mittagong	Robertson	1.19	1660	635	145	2.239	B	100
26.	Johnston's	Robertson	3.39	1660	615	145	1.648	B	100
27.	Meadow	Wilde's Meadow	7.51	1490	680	130	1.054	B	100
28.	Macquarie	Albion Park	28.49	1450	28	737		S	66.0
29.	Kangaroo	Kangaroo Valley	203.05	1270	73	717		S	57.0
30.	Brindabella	Brindabella	26.13	1016	610	815	3.207	R	56.2
31.	Bramina	Brindabella	68.32	1200	585	845	1.683	S	62.5
32.	Flea	above junction	40.25	950	460	920	3.467	R	100
33.	Condor	Blundell's	21.07	920	480	940		S	100
34.	Strike-a-light	Recorder	215.57	590	716	714	No	S	72.0
35.	Sherlock	Road Crossing	58.09	740	897	568	large	S	51.0
36.	Queanbeyan	Anembo	57.19	710	890	585	scale	G	80.0
37.	Queanbeyan	Boolboolma	172.16	700	880	595	maps	G	71.0
38.	Queanbeyan	Narongo	284.15	720	875	750		G	54.0
46.	Snowy	above Guthega	76.40	2290	1591	639	1.450	G	67.0

Lithology: B — Basalt; G — Granite; M — Metamorphic rocks; R — Rhyolite; S — Sedimentary rocks.

* Calculated according to Melton (1957).

† Probably an underestimate.

Table 2. Arithmetic average chemical quality of rivers in Eastern Australia

Station Number	Number of Samples Analysed	Total Dissolved Solids ppm	SiO_2 ppm	Ca ppm	Mg ppm	Na ppm	K ppm	Cl ppm	$\frac{Ca + Mg}{Na + K}$ Ratio epm	Na : Cl Ratio epm	Ca : Cl Ratio epm
1.	22	69	10	2.83	1.29	8.08	1.69	12.4	0.30	1.00	0.40
2.	14	53	10	1.69	0.55	5.91	1.67	9.2	0.43	0.99	0.32
3.	13	46	7	0.95	0.37	4.52	1.55	8.3	0.33	0.84	0.20
4.	21	52	7	1.71	1.12	5.23	0.93	9.8	0.70	0.83	0.31
5.	23	34	6	0.57	0.43	3.54	0.65	7.1	0.37	0.77	0.14
6.	15	45	6	0.57	0.54	4.72	1.64	11.0	0.29	0.66	0.09
7.	97	65	6	2.69	2.50	5.57	1.01	10.1	1.27	0.85	0.47
8.	27	49	6	1.45	1.41	4.94	1.19	9.8	0.77	0.78	0.26
9.	19	33	5	0.62	0.39	3.68	0.72	7.9	0.35	0.72	0.14
10.	20	39	3	0.53	0.44	3.30	0.93	7.8	0.37	0.65	0.12
11.	24	45	5	1.18	1.09	4.54	1.09	8.3	0.66	0.84	0.25
12.	22	66	9	3.01	2.23	7.05	1.76	11.4	0.95	0.95	0.47
13.	18	39	6	0.71	0.41	3.41	1.08	6.9	0.39	0.76	0.18
14.	5	54	7	0.64	0.64	6.76	1.75	12.1	0.25	0.86	0.09
15.	6	34	7	0.74	0.29	3.77	0.74	8.7	0.33	0.67	0.15
16.	4	43	5	0.95	0.34	3.65	0.64	11.0	0.43	0.51	0.15
17.	7	43	7	0.44	0.40	5.60	1.00	11.5	0.20	0.76	0.07
18.	6	64	6	1.18	1.36	8.53	1.04	16.4	0.43	0.80	0.13
19.	7	49	7	0.71	0.51	5.35	1.14	10.8	0.29	0.77	0.12
20.	8	29	5	0.56	0.30	2.91	0.55	7.5	0.37	0.60	0.13
21.	5	64	4	3.09	1.08	5.74	0.37	15.0	0.94	0.59	0.36
22.	8	51	11	3.13	2.33	4.54	0.82	8.6	1.58	0.81	0.64
23.	6	48	6	0.36	0.50	5.41	1.16	10.4	0.22	0.81	0.06
24.	5	42	9	0.34	0.37	4.80	1.04	8.7	0.20	0.84	0.07
25.	12	42	2	2.62	1.61	5.18	0.46	9.2	0.87	0.51	1.72
26.	12	48	2	2.31	2.01	4.56	0.57	8.9	0.79	0.46	1.72
27.	12	44	2	1.95	1.81	4.82	0.41	9.4	0.79	0.37	2.16
28.	6	96	3	9.34	4.62	13.29	1.28	23.7	0.87	0.70	1.24
29.	4	85	5	5.64	3.18	11.50	1.14	20.4	0.87	0.49	1.78
30.	14	57	6	4.54	1.99	5.02	0.68	4.4	1.76	1.83	1.04
31.	13	55	8	3.49	2.38	4.84	0.66	4.2	1.79	1.47	1.21
32.	7	64	8	4.94	1.84	7.87	0.96	4.1	2.95	2.13	1.38
33.	7	46	4	2.13	1.93	4.08	0.75	4.7	1.33	0.80	1.67
34.	19	101	4	8.21	5.56	10.83	1.39	14.0	1.19	1.04	1.15
35.	17	61	6	4.29	2.59	5.81	0.61	5.9	1.52	1.29	1.18
36.	16	76	7	7.22	2.94	6.29	0.75	5.6	1.73	2.28	0.76
37.	17	87	6	6.80	3.59	7.85	0.86	7.5	1.61	1.59	1.01
38.	15	71	5	5.44	3.19	7.21	0.82	6.9	1.60	1.38	1.16
46.	1	19	2	0.54	0.12	1.43	2.02	1.3	0.33	1.67	0.76

Ca, Mg, Na and K were determined by atomic absorption spectrophotometry by Dr J. David of the Division of Plant Industry, C.S.I.R.O., Canberra.

Table 3. Arithmetic average chemical quality of precipitation at eastern Australian locations

Location	Ca epm	Mg epm	Na epm	K epm	Cl epm	Na:Ca epm	Na:K epm	Na:Mg epm	Na:Cl epm	Ca:Cl epm
N.E. Queensland										
Herberton Range	0.011	0.011	0.027	0.010	0.078	3.18	3.23	3.52	0.35	0.22
Atherton	0.027	0.018	0.052	0.009	0.071	2.69	6.13	2.58	0.73	0.65
Mareeba	0.044	0.006	0.042	0.006	0.064	0.94	8.50	6.80	0.66	0.71
Lamb Range	0.029	0.012	0.056	0.008	0.084	1.91	6.93	6.19	0.67	0.35
Babinda	0.027	0.021	0.046	0.026	0.104	2.27	3.07	9.62	0.45	0.24
S.E. Australia										
A.C.T.	0.054	0.016	0.044	0.022	0.079	0.81	2.00	2.75	0.56	0.68

Ca, Mg, Na and K were determined by atomic absorption spectrophotometry by Dr J. David of the Division of Plant Industry, C.S.I.R.O., Canberra.

The variation of precipitation chemistry at any one place over a period of time may obscure contrasts between localities. In the samples collected on the Herberton Range, the lowest concentrations of solutes were found in a composite sample representing rain that fell between 2nd and 28th December 1964, including the very heavy rain associated with cyclone "Flora" which yielded 1545mm at the Atherton Post Office Gauge 10km north-east of the Herberton Range. The highest solute concentrations at this station were in the period 24th November to 2nd December during which a few thunderstorms produced a total of 580mm at the Atherton Gauge.

Low Na:Ca ratios in rainfall in north-east Queensland occur in thunderstorms and rains at the beginning of the wet season following long periods of dry weather. High Na:Ca ratios occur in heavy cyclonic rains. As the Na:Ca ratio of sea water is 22 (Hutton and Leslie, 1958), these findings suggest that thunderstorm rains tend to collect more solutes of terrestrial origin than cyclonic rain derived largely from the Pacific Ocean. Rains of early in the wet season tend to wash salts out of the atmosphere, particularly those salts which have been blown up from the land surface and which are collected by falling raindrops beneath the level of the cloud-base.

S.E. Australia

All the precipitation samples from south-eastern Australia were collected in and around Canberra, at three points less than 10km apart, Acton, Red Hill and Yarralumla Creek, which may be considered to be representative of the lower part of the A.C.T. The average concentrations (Table 3) show a dominance of sodium chloride but more calcium than sodium. The Na:Ca ratio of 0.81 is typical of inland rainfall, being similar to the Na:Ca ratio of thunderstorm rain in N.E. Queensland. The Na:K ratio of 2.0 is low even in comparison with rain over 500km from the ocean collected at Urbana, Illinois, which has a Na:K ratio of 3.00 (Larson and Hettick, 1956).

Table 4. Precipitation chemistry during the storm of 30 May 1964 at Canberra.

	First Sample at onset of storm epm	Second Sample after three hours epm
Calcium	0.153	0.025
Chloride	0.079	0.048
Magnesium	0.022	0.003
Sodium	0.018	0.004
Potassium	0.010	0.002
Nitrate	<0.001	<0.001

The two samples in Table 4 illustrate how the first storm after a dry period washes solutes out of the lower layers of the atmosphere. Twelve millimetres of rain fell in the month prior to 30 May 1964 and none after 26 May. Rain at the beginning of the storm contained more solutes than that later in the storm, but the decrease in concentration is not uniform, chloride concentrations decreasing least markedly. The Na:Ca ratios of this storm, lower than any others for precipitation in the A.C.T. or N.E. Queensland, suggest that much of the solute content of the rain is of terrestrial origin.

A snow sample collected three hours after snow began falling on 7 August 1965 had the lowest chloride concentration for precipitation sampled. Snow at the beginning of the storm had probably washed higher concentrations of solutes out of the atmosphere. Direction of the rain-bearing wind has some effect on the solute concentration in Canberra, rain from a southerly wind tending to have lower solute concentrations than rain from west or north-west winds.

Comparison of precipitation chemistry in Queensland and New South Wales

While the sodium and chloride contents of precipitation in the two areas are similar, there are higher concentrations of calcium, magnesium and potassium in the samples collected in Canberra. Analysis of variance shows the difference in the Na:Ca ratios of samples from the two areas to be significant at the 1% level.

The difference in the precipitation chemistry of the two areas is probably related to the distance from the sea and the direction of the prevailing wind. Thus while the Cairns and Atherton Tableland area is largely less than 100km from the sea and has the south-easterly prevailing wind blowing off the sea, the A.C.T. is almost 200km from the sea with prevailing westerly winds blowing from the interior of the continent. The few samples from these two areas suggest there is no basic difference in the precipitation chemistry of tropical and extra tropical areas. Evidence from other Australian localities (Tables 5 and 6) suggests that position in relation to marine and continental sources of solutes and to prevailing wind are the important factors affecting precipitation chemistry. Thus high chloride concentrations are found in rain at sites on exposed coasts of Western Australia and Victoria.

Table 5. Published arithmetic average chemical quality of precipitation at Australian localities.

Location	Ca epm	Mg epm	Na epm	K epm	Cl epm	Na:Ca epm	Na:K epm	Na:Mg epm	Na:Cl epm	Ca:Cl epm
*Belka Valley W.A.					0.150				0.90	0.04
†Cape Bridgewater, Victoria ...	0.080	0.130	0.650	0.018	0.730	8.10	36.10	5.00	0.89	0.11
†Coleraine Victoria ...	0.020	0.030	0.120	0.005	0.140	6.00	24.00	4.00	0.86	0.14
†Horsham, Victoria ...	0.020	0.020	0.060	0.005	0.060	3.00	10.00	3.00	1.00	0.33
†Walpeup, Victoria ...	0.030	0.020	0.050	0.004	0.040	1.67	12.50	2.50	1.25	0.75
†Merbein, Victoria ...	0.100	0.030	0.050	0.005	0.050	0.50	10.00	1.67	1.00	2.00
‡Katherine, N.T. ...		0.003	0.005	0.001	0.007		5.00	1.67	0.71	
§Alice Springs, N.T. ...	0.050	0.082	0.131	0.026	0.028	2.63	5.01	1.61	4.70	1.78

Sources: * Bettenay, Blackmore and Hingston, 1964.
† Hutton and Leslie, 1958.
‡ Wetselaar and Hutton, 1963.
§ Williams and Siebert, 1963.

Table 6. Ranked list of chloride concentrations in rainfall in various Australian localities.

No.	*Location*	*Cl. (epm)*	*Source*
1.	Katherine, N.T. (lowest value recorded)	.001	F
2	Canberra, A.C.T. (snow)	.008	A
3	Omeo, Victoria	.010	D
4	Mitta Mitta, Victoria	.010	D
5	Tallangatta, Victoria	.010	D
6	Kyneton, Victoria	.020	D
7	Seymour, Victoria	.020	D
8	Dookie, Victoria	.020	D
9	Upper Murray Catchment, Victoria	.028	B
10	Horsham, Victoria	.030	D
11	Beaufort, Victoria	.030	D
12	Elmore, Victoria	.030	D
13	Charlton, Victoria	.030	D
14	Swifts Creek, Victoria	.030	D
15	Hopetoun, Victoria	.040	D
16	Walpeup, Victoria	.040	D
17	Merbein, Victoria	.040	D
18	Katherine, N.T. (highest value recorded)	.042	F
19	Parwan, Victoria	.050	D
20	Atherton, Queensland	.056	A
21	Mareeba, Queensland	.063	A
22	Herberton Range, Queensland	.067	A
23	Derrinallum, Victoria	.070	D
24	Sale, Victoria	.070	D
25	O'Shannassy Catchment, Victoria	.076	B
26	Canberra, A.C.T.	.079	A
27	Lamb Range, Queensland	.083	A
28	Cressy, Victoria	.090	D
29	Mundiwindi, Western Australia	.098	C
30	Warragul, Victoria	.100	D
31	Babinda, Queensland	.101	A
32	Wiluna, Western Australia	.113	C
33	Merredin, Western Australia	.120	B
34	Cavendish, Victoria	.120	D
35	Yarra Catchment, Victoria	.124	B
36	Coleraine, Victoria	.140	D
37	Belka Valley, Western Australia	.150	E
38	East Camberwell, Victoria	.159	B
39	Salmon Gums, Western Australia	.160	B
40	Rawlinna, Western Australia	.177	C
41	Helena Catchment, Western Australia	.187	B
42	Condon, Western Australia	.231	C
43	Barwon Catchment, Victoria	.236	B
44	Heywood, Victoria	.250	D
45	Cue, Western Australia	.270	C
46	Warrnamboul, Victoria	.320	C
47	Coolgarlie, Western Australia	.338	C
48	Perth, Western Australia	.462	C
49	Esperance, Western Australia	.580	C
50	Yorke Peninsula, South Australia	.609	B
51	Cape Bridgewater, Victoria	.700	D
52	Geraldton, Western Australia	.805	C

Sources. A — Fieldwork and laboratory analyses.

B — Anderson, V.G., 1945.

C — Wilsmore and Wood, 1929.

D — Hutton and Leslie, 1958.

E — Bettenay, Blackmore; Hingston, 1964.

F — Wetselaar and Hutton, 1963.

Table 7. pH of precipitation at tropical and temperate localities

Locality	*Tropical pH Range*	*Source*
Singapore	4.7 - 8.2	Robinson, 1958
Sarawak	4.9 - 6.0	Wilford and Wall, 1965
Selangor	5.1 - 7.2	Douglas, 1968
Ivory Coast	5.1 - 7.4	Rougerie, 1960
N.E. Queensland	5.2 - 6.6	Douglas, 1968
Surinam	5.3 - 6.9	Bakker, 1957
El Salvador (mean)	5.5	Hölting, 1962

Locality	*Temperate pH Range*	*Source*
Plymouth, U.K. (mean)	4.0	Atkins, 1947
Lake District, U.K.	4.0 - 5.8	Gorham, 1955
Ingleborough, U.K.	4.0 - 7.1	Sweeting, 1966
Scandinavia	4.8 - 6.6	Barret & Brodin, 1955
E. Yorkshire, U.K.	5.1 - 6.7	Author
Kentucky, U.S.A.	5.5 - 6.2	Hendrickson and Krieger, 1964
A.C.T.	5.6 - 6.7	Douglas, 1968
Downderry, U.K. (mean)	6.6	Atkins, 1947

These observations in Australia also reinforce the general conclusion that the acidity of tropical rain is not different from that of Temperate zone rainfall (Table 7) low pH values at some United Kingdom localities being associated with dilute sulphuric acid in precipitation caused by sulphur dioxide pollution. Sweeting (1966) has suggested that this pollution of rain affects weathering rates. Highly alkaline pH values were measured in Guinea, a pH of 9 at the beginning of the storm, falling to 8.5 then 6.8 after 30 minutes of rain (Tricart, 1965, p. 37). Such high pH values may result from high concentrations of ammonia (NH_4), the production of which has been associated with electrical activity in thunderstorms. However, apart from this isolated example, there is no evidence that tropical rain is either more acid or more alkaline than precipitation in temperate regions.

Precipitation chemistry in relation to total solute load of rivers

In the Australian study of chemical denudation, insufficient rainfall samples were collected to permit an exact calculation of the input of solutes from rainfall to every catchment studied. Studies of the type conducted by Likens and co-workers (1967), in which the detailed budgets of individual elements are calculated, are needed to evaluate the full migration of elements. In place of a detailed solute balance for each catchment, the average chemical composition of precipitation over an area enables the approximate proportion of the total dissolved load of a river derived from solutes brought down in rain to be calculated. Estimated contributions from precipitation to total dissolved load for Northern Europe are, for Finland, 36% (Viro, 1953) and for Kärkevagge, 26% (Rapp, 1960). The proportions of the solute loads of the Queensland rivers so derived vary from 70% at Station 4 (Figure 5) to 31% at Station 7 on the Barron River (Figure 6). In New South Wales the range was from 62% on Strike-a-light Creek (Station 34) to 25% on the Sherlock River (Station 35, Figure 3). Among the factors causing this wide range of the importance of precipitation are the differing solubilities of rocks in the various catchments and the difficulty of accurately estimating precipitation in ungauged headwater areas. In New South Wales precipitation contributes more of the total load to the catchments with the lowest rates of chemical denudation even though these catchments often have the highest mean solute concentration. These observations confirm Anderson's conclusion (1945) that in areas of comparatively high runoff ratio the composition of river water is influenced more by chemical denudation than in areas of low percentage runoff where the river waters have a composition close to precipitation.

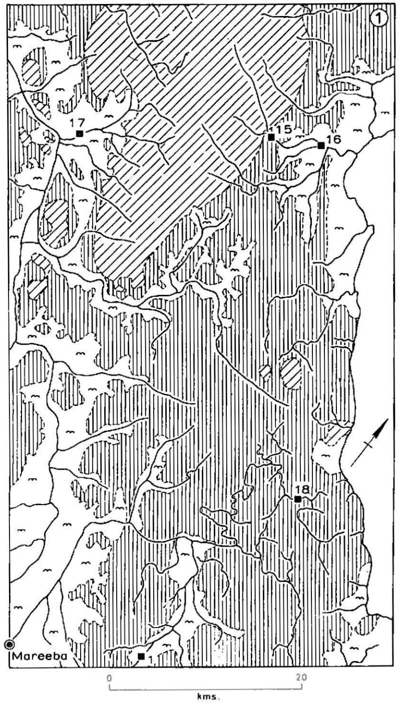

Figure 4. Samping stations and lithology in the Mossman area of Queensland.

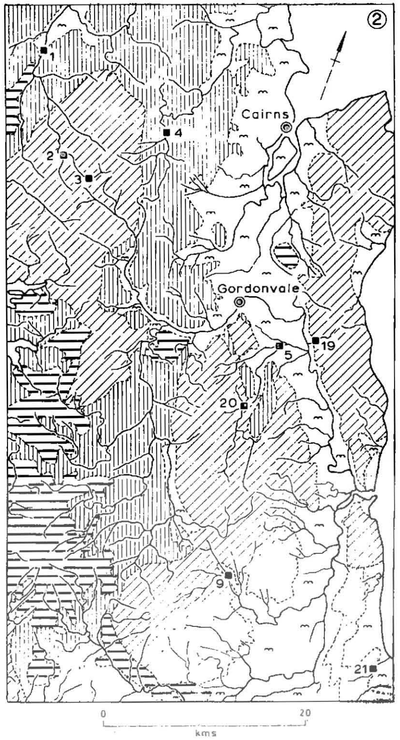

Figure 5. Sampling stations and lithology in the Gordonvale area of Queensland.

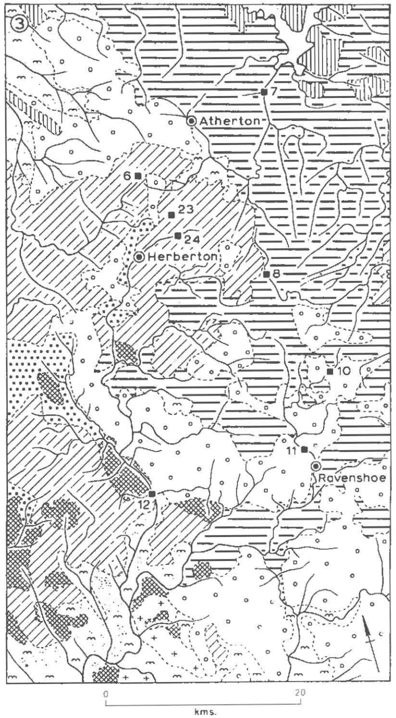

Figure 6. Sampling stations and lithology in the Atherton Tableland area of Queensland.

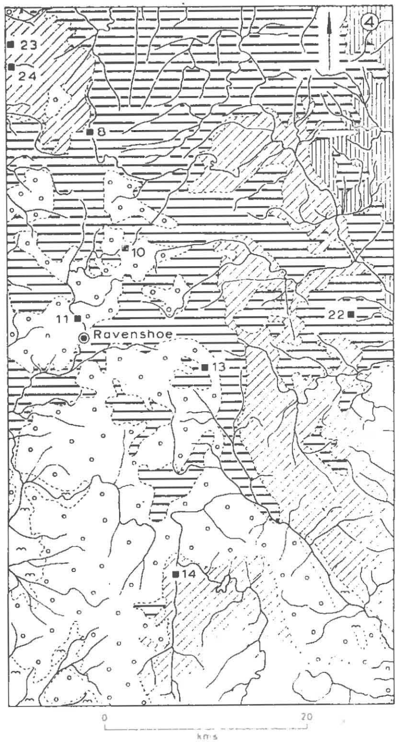

Figure 7. Sampling stations and lithology in the Upper Johnstone and Tully River areas of Queensland.

Similar relationships between solute load and supply of atmospheric salts are reported from the Potomac River Basin (Feltz and Wark, 1962). The North Fork Shenandoah River at Cootes Store, Virginia had 68% of the total solute load derived from precipitation, but also had the lowest rate of solute denudation. The North Branch of the Potomac River at Pinto, Maryland, which has the highest rate of solute denudation, has only 6% of the total solute load supplied by precipitation.

Supply of chloride from precipitation

In the western U.S.A. the supply of chloride to rivers from precipitation is greatest in the wettest catchments close to the north-west coast (Van Denburgh and Feth, 1965). Even in these catchments the chloride supplied by precipitation only amounts to 20% of the total chloride removed by rivers. In Finland on the other hand, chloride supplied to the land surface from precipitation slightly exceeds that removed by rivers (Viro, 1953). In Queensland rainfall supplies 70% of the total chloride removed by the Millstream at Ravenshoe (Station 11) and only 55% of that removed by the Wild further inland (Station 12). On the basis of the rainfall : runoff ratio the estimated average concentration of chloride in waters from Strike-a-light Creek (Station 34) in New South Wales would be 18ppm, but the average measured concentration of only 14ppm suggests a net accumulation of chloride in that catchment area. Problems of salt accumulation are common on the Southern Tablelands (Wagner, 1957) and very high concentrations of salt occur in small catchments, such as Yarralumla Creek where concentrations of over 300ppm occur at low flows. Van Dijk (1965) has described local areas of salt accumulation in the Yarralumla Creek catchment, Basinski (1960) recognising similar effects in the Yass Valley. In the Robertson area on the Central Tableland of New South Wales (Figure 2), on the other hand, only 49% of the total chloride removed by rivers is supplied by precipitation.

Potassium in precipitation and river waters

Similar variations in the atmospheric supply and fluvial transport of solutes are found when other ions are considered. The potassium removed by north-east Queensland rivers approximately equals the amount derived from rainfall, except at Stations 4, 5 and 7 (Figures 5 and 6) where the supply from rainfall exceeds the volume removed and at Station 12 (Figure 6) where only 60% of the potassium removed is derived from precipitation. There appears to be a net accumulation of potassium in all the New South Wales catchments. Similar contrasts are found elsewhere, for while only 55% of the potassium in Finnish rivers is derived from precipitation (Viro, 1953), a net gain to the land surface of 0.7 kg/hectare/year was measured in the Hubbard Brook Experimental Forest (Likens and co-workers, 1967). The latter gain is to be compared with net losses of 50kg/ha of calcium, 1.9kg/ha of magnesium and 4.9kg/ha of sodium. It is possible that in the eastern Australian localities and in New Hampshire the potassium measured in rain is part of the terrestrial cycling of salts described by Jennings (1956).

THE RELATIONSHIP OF WATER QUALITY TO GEOLOGIC CONDITIONS

In general the chemical composition of river water provides some information on soil and rocks through which the river has flowed (Rainwater, 1962). Sioli (1951a, b, 1954, 1964) has recognised close relationships between water types and lithology and soils in the Amazon Basin. General correlations between rocks and water chemistry appear readily on the scale of the conterminous U.S.A. or the Amazon Basin, but in smaller areas, with less diversity of climate and lithology, it is less easy to define distinct water types.

Hack (1960) provides typical analyses for waters draining quartzite, igneous, sandstone-shale and carbonate rocks in the Shenandoah Valley (Figure 8). The lowest concentrations of solutes are found in waters draining the resistant quartzites and the highest in waters from carbonates. The $\frac{Ca + Mg}{Na + K}$ ratio is lowest in waters from igneous rocks and highest in those from carbonate rocks, while silica concentrations are highest in streams draining igneous rocks.

In an attempt to find similar relationships between geologic conditions and water chemistry in Australia the catchments studied were divided into the following broad categories: sedimentary rocks, basalts, granites, metamorphics and rhyolites, the analyses for each category being illustrated in the histograms on Figure 8 which compare the silica content with the concentrations of metal ions.

The ratio of calcium and magnesium to sodium and potassium

The $\frac{Ca + Mg}{Na + K}$ ratios are lowest in waters from granites, with a mean of 0.52, the highest in those from sedimentary rocks with a mean of 1.94. The mean values of the ratio in the three categories are metamorphic rocks 0.69, rhyolite 0.74 and basalts 1.08. The significance of the differences between the ratios of the various categories was tested by calculating Student's *t* for each pair of lithologic groups. The probability of random values falling outside the limits of $\pm t$ in each pair are:

	Sedimentary	*Basalt*	*Granite*	*Metamorphic*	*Rhyolite*
Sedimentary		0.001	0.001	0.05	0.01
Basalt	0.001		0.001	0.3	0.3
Granite	0.001	0.001		0.7	0.5
Metamorphic	0.05	0.3	0.7		0.9
Rhyolite	0.01	0.3	0.5	0.9	

There is a clear distinction between the composition of water from sedimentary rocks and that from other rock types. Waters from basalt differ significantly from those from granite. The small differences between waters from metamorphic rocks and rhyolite and those from other rocks arise from their composition being between that of granite and basalt derived waters (Figure 8).

Part of the difference between waters from sedimentary rocks and those from other rocks might be thought to arise from climatic effects, all the sedimentary rock catchments being in New South Wales where several samples were collected under drought conditions when ionic concentrations in river water had been increased by evaporation. However, comparison of the ratios for all Queensland stations and all New South Wales stations except Station 46 shows that the contrasts in $\frac{Ca + Mg}{Na + K}$ due to lithologic influences are greater than those due to climatic factors. Although the mean values of the ratio were 0.52 and 1.46 respectively, the probability of random values falling outside the limits $\pm t$ is 0.02, a lower level of significance than the differences between waters draining sedimentary rocks and those from igneous terrains.

The sodium : calcium and sodium : chloride ratios

Climatic factors are important in the variation in the Na : Ca ratio, the difference between the mean Na : Ca ratios values of 5.18 and 1.37 for Queensland and New South Wales respectively being highly significant. Comparison of Na : Ca ratio variation between lithologic groups shows smaller, less significant differences than those in values of the $\frac{Ca + Mg}{Na + K}$ ratio. The probability of random values of the Na : Ca ratio falling outside the limits ±*t* in each pair of lithologic groups is:

	Sedimentary	*Basalt*	*Granite*	*Metamorphic*	*Rhyolite*
Sedimentary		0.1	0.02	0.1	0.05
Basalt	0.1		0.05	0.3	0.4
Granite	0.02	0.05		0.4	0.2
Metamorphic	0.1	0.3	0.4		0.8
Rhyolite	0.05	0.4	0.2	0.8	

Differences between waters from sedimentary rocks and other rock types are fairly significant, as is the difference between basalt and granite derived waters.

Another major contrast in water quality between New South Wales and Queensland lies in the Na : Cl ratio. The highest Na :Cl ratio for the catchments of the Southern Tablelands and Highlands of New South Wales (Figure 3) is 1.19. The Na : Cl ratios of the Robertson area streams (Figure 2) range from 0.79 to 0.87 and are similar to those of Queensland rivers. Eriksson's suggestions (1955) that Na : Cl ratios of river and rainwater should be comparable holds for Queensland where rainfall samples all have ratios less than 1.0 (Table 3). But as the Canberra precipitation samples all have Na : Cl ratios less than 1.0 the contrasts in values of the Na : Cl ratio for river waters cannot be explained as a reflection of the precipitation chemistry. The difference may arise in part from the effects of evaporation, individual samples collected at low flows in New South Wales streams having the highest Na : Cl ratios. In Queensland streams variations are more complex, for example at Station 12 the values of the Na : Cl ratio at the lowest and highest discharges sampled are 0.99 and 0.95 respectively, while the extreme values are 0.67 and 1.18. On the Condamine River at Dalby (Simmonds, 1963) the mean Na : Cl ratios for high and low flows being 1.67 and 0.53 respectively, a trend contrary to that noted for New South Wales.

In the discussion on the relationship between precipitation chemistry and river water quality a net accumulation of chloride in the Southern Tablelands was revealed. The accumulation of chloride from precipitation may be greater than that of sodium which is released from the catchment surface while chloride is precipitated, perhaps in conjunction with calcium as gypsum, as is noted by McLaughlin (1966) in a discussion of the salinity of the lakes of the Victorian Mallee. An alternative explanation may be that an ion exchange occurs in the soil zone of the Southern Tablelands, calcium and magnesium being removed from the water and sodium added, so creating an excess of sodium over chloride. Either of these mechanisms could explain a high Na : Cl ratio in river water.

Classification of water types from Queensland and New South Wales

Most of the Queensland waters have a dominance of sodium chloride. The $\frac{Na + Cl}{Ca + Mg + K}$ ratio exceeds 2.0 at all Queensland stations except 7, 12, and 22, at which water partially derived from basalt or soluble sediments has $\frac{Na + Cl}{Ca + Mg + K}$ ratios between 1.0 and 2.0. While the five Robertson streams (Figure 2) have $\frac{Na + Cl}{Ca + Mg + K}$ ratio values of 1.0 to 2.0 comparable to the three Queensland stations just described, only Stations 32 and 33 on the Southern Tablelands (Figure 3) have $\frac{Na + Cl}{Ca + Mg + K}$ ratio values exceeding 1.0, the others, with ratios between 0.70 and 0.96, being less dominated by sodium chloride.

The New South Wales waters fall into the transition zone between sodium chloride and bicarbonate water types. Most Australian surface waters are sodium chloride types, Williams (1967) noting that "The most salient feature concerning ionic proportions in Australian lentic waters is the predominance of Na amongst the cations and Cl amongst the anions. These predominances operate in both fresh and saline waters, although more exceptions occur in freshwaters." While the comment refers to lake waters, river waters tend to show the same characteristics, although they are more influenced by geologic and hydrologic factors and less influenced by evaporation.

One feature of the importance of sodium chloride in the composition of Australian surface waters is that $\frac{Ca + Mg}{Na + K}$ ratios are low compared with those of most other river waters (Table 8). Corbel (1964) compares $\frac{Ca + Mg}{Na + K}$ ratios of Alaskan, humid temperate, semi-arid and tropical rivers draining igneous rocks, concluding that the highest values of the ratio, which occur in Alaska, arise because solution of calcium and magnesium proceeds more rapidly in colder climates through the abundant aggressive CO_2 available when the temperature is just above freezing point. That a similar difference due to climate cannot be clearly demonstrated for the Australian Rivers has already been shown. While the three stations on the Queanbeyan River (Stations 36 to 38) which have a predominance of granite in their catchment areas have values of the ratio ranging from 1.73 to 1.60 which are much higher than those for granite catchments in Queensland, the single sample collected under snow melt conditions at station 46 has a ratio of only 0.33. Furthermore, the ratios of individual samples collected at the coldest time of the year (water temperature 1°C.) at Station 36 are lower than the mean value for samples at that station.

Table 8. Range of the $\frac{Ca + Mg}{Na + K}$ ratio for selected rivers

Locality	*Range (epm)*	*Source*
N.E. Queensland	0.20 - 1.58	Table 2
Trinity R. at Rosser, Texas	0.29 - 3.41	Leifeste and Hughes, 1967
Neches R. at Alto, Texas	0.39 - 0.85	Hughes and Leifest, 1965
Ivory Coast rivers	0.56 - 1.85	Corbel, 1964
Brazos R. at Richmond, Texas	0.92 - 2.66	Hughes and Shelby, 1962
S.E. New South Wales (excl. Station 46)	1.03 - 2.07	Table 2
Adelaide Plains, S. Australia	1.07 - 1.90	Miles, 1952
Ephemeral Central Australian Rivers ...	1.38 - 2.71	Williams and Siebert, 1963
Alaskan rivers	1.44 - 8.73	Corbel, 1964
Hubbard Brook Experimental Forest, New Hampshire	1.65 - 1.78	Likens and co-workers, 1967
Clarion R. at Piney, Pennsylvania	1.77 - 2.71	McCarren, 1967
Delaware R. Basin, New York	1.89 - 11.73	Archer and Shaughnessy, 1963
Shelon' R. at Zapole, Russia	2.95 - 12.36	Skakal'skiy, 1965
Conecuh R. at Brantley, Alabama	6.70 - 17.81	U.S. Geol. Surv. 1965-66
Rudawy R. at Cracow, Poland	7.04 - 9.82	Tlalka, 1967
Shelon' R. at Porkhov, Russia	56.39-183.37	Skakal'skiy, 1965

The north-east Queensland streams have $\frac{Ca + Mg}{Na + K}$ ratios similar to those for the Ivory Coast rivers, but also comparable with those for Texan rivers draining very different environments. The lowest values of the ratio for the Trinity River arise from pollution by oilfield brines which raise the sodium concentration at low flows to between 400 and 500 ppm, but at high flows such effects are minimised. Brine pollution is not so marked on the Neches and Brazos Rivers, but is probably sufficient to cause ratios lower than those which would normally occur on rivers draining sandstones, shales and limestones. The New South Wales rivers have a range of $\frac{Ca + Mg}{Na + K}$ ratios similar to those of other rivers in temperate environments such as the Hubbard Brook and Clarion. However, streams draining areas where limestones predominate, for example the Rudawy River, have much higher ratios. The Shelon' River which also drains limestones and dolomites has exceptionally high ratios of calcium and magnesium to sodium and potassium at low flows because such flows are derived from groundwater containing over 50 ppm calcium and less than 0.5ppm sodium.

The low $\frac{Ca + Mg}{Na + K}$ ratios of the Australian rivers are thus partly a reflection of the lithology of the catchment areas, which yield low concentrations of calcium

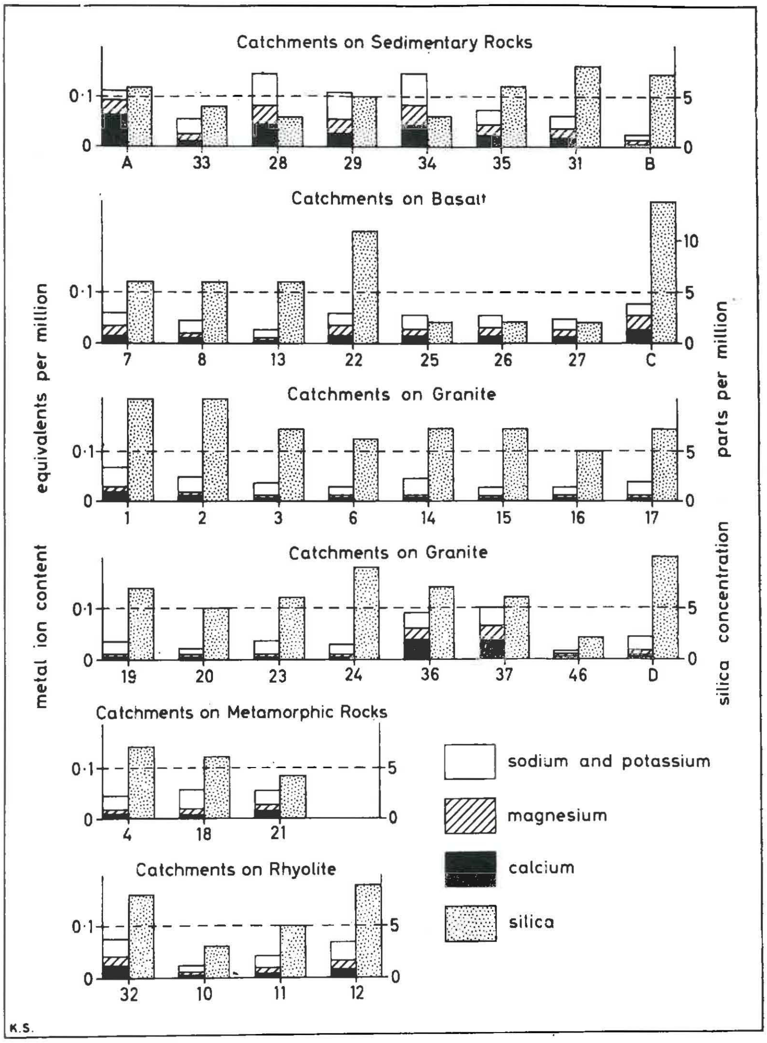

Figure 8. Histograms of ionic composition of arithmetic average chemical quality of eastern Australian river waters. The figures beneath the histograms refer to the numbers of the stations listed in Table 1. Analyses A, B, C and D are from Hack (1960) and are shown for comparative purposes.

and magnesium. The ratios may also reflect the age of the land surfaces, most soils in the Australian areas for which data is presented being heavily leached. However, the powerful supply of sodium chloride from precipitation, particularly of salts of terrestrial origin, may be of more significance in the chemistry of Australian rivers, especially those with low solute concentrations, than in streams in other areas. The $\frac{Ca + Mg}{Na + K}$ ratios and other ionic ratios reflect combinations of many different environmental conditions, but used in conjunction with other parameters they help to advance the understanding of the natural and man-made processes which change catchment areas.

CONCLUSION

While this reconnaissance investigation cannot give details of the geochemical cycle in any one catchment area, through lack of information on the chemical processes in specific plant and soil zones, it provides evidence of the relative importance of geologic and climatic factors in the chemical composition of rivers in two widely separate areas. The solutes derived from precipitation are shown to be an important influence on the total solute content of river waters, particularly in relatively dilute waters such as those of the rivers studied here. Precipitation chemistry however exerts less influence on the composition of river waters, in which catchment lithology is shown to be a more important factor than climate. The contrasts between areas stem from both lithological differences and variations in mean annual runoff per unit area. Regional studies of water chemistry offer a means of supplementing the data available on the processes of landscape change, particularly those of interest to the geomorphologist. Without understanding of the operation of both the hydrologic and geochemical cycles the evaluation of the chemical processes of denudation is incomplete.

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