NITROGEN AND PHOSPHORUS ANALYSES OF RAINFALL AT ROTORUA, NEW ZEALAND

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ABSTRACT

Analyses of the dissolved inorganic nitrogen and phosphorus content of rainfall at Ngapuna, Rotorua, were made between 21 July 1972 and 19 March 1974. Dry fallout was excluded from the water samples by exposing collectors only when rain was falling or imminent. The total rainfall sampled was 341 mm and its mean solute concentration expressed in g/ha.mm (=g/m^3×10) was 0.057 PO_4-P, 0.842 NH_4-N and 0.215 NO_3-N. The mean solute concentration of 34 rainstorms (in g/ha.mm) was 0.08 PO_4-P, 1.83 NH_4-N and 0.43 NO_3-N. No seasonal changes in solute concentrations were discovered. Synoptic samples collected in open country (e.g. Tongariro National Park) were similar in composition to those from Ngapuna, Rotorua, but samples collected at city sites (e.g. Christchurch) contained more phosphate.

INTRODUCTION

Nutrients in the rain falling on the surface of Lake Rotorua provided approximately 5 percent of the reactive phosphorus and 15 percent of the inorganic nitrogen entering the lake in the budget cast for all nutrient inflows during 1967–70 (Fish, 1975). The estimate was based on analyses of only 14 samples of rainwater and served mainly to indicate that atmospheric precipitation is an important source of plant nutrients.

More comprehensive data have now been collected from rainfall sampled between 21 July 1972 and 19 March 1974. A subsequent paper (Fish, 1976) will consider the nutrients in dry fallout and in total precipitation.

The concentration of dissolved material found in the rainstorms of varying duration that were sampled here is best expressed according to the data collected in g/ha.mm. This unit is also convenient for comparison with data collected elsewhere because transforma-

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tion into other commonly used units is easy ($=g/m^3 \times 10$) and logical (e.g. g/ha, g/ha.day, g/ha.annum) if standard rainfall records (i.e. mm/day) for other sites are also available.

METHODS

Most samples were collected at the Fisheries Research Laboratory at Ngapuna, Rotorua, using a V-shaped trough of plate glass which was permanently mounted on a roof. The site has no hills or higher buildings nearby and is well away from tall trees. All collecting surfaces were carefully cleaned and rinsed before use, as were the reservoirs. The collecting devices and their associated raingauges were exposed only when rain sampling commenced and were covered again when sampling stopped at the apparent conclusion of the storm. In this way a minimum of dry fallout was included in the samples, but in practice the amount of work involved limited the number of rainstorms that could be sampled, particularly when frequent sampling was made during individual rainstorms. The collected water samples were usually analysed immediately. If analysis was likely to be delayed for more than about six hours, the samples were preserved by freezing soon after collection.

Ammonium concentrations reported here as ammonium nitrogen (NH_4-N) were estimated using the phenol hypochlorite method, and nitrate concentrations reported as nitrate nitrogen (NO_3-N) were found by nitrite estimation following cadmium reduction (Strickland and Parsons, 1968). The absence of nitrite was frequently confirmed in the water samples by omitting the reduction step in duplicate nitrate analyses. Soluble reactive phosphorus concentrations, reported as phosphate phosphorus (PO_4-P), were estimated using a modification of the Murphy and Riley method reported by the N.Z. Department of Scientific and Industrial Research (1970). Other phosphorus and nitrogen compounds were oxidized to phosphate and nitrate by mercury-lamp irradiation in an apparatus similar to that described by Henricksen (1970) and results are reported here as total P or total N concentrations. Analytical accuracy and precision were tested and found satisfactory in two collaborative tests conducted between New Zealand analysts by the DSIR Chemistry Division in 1973 and 1974.

RESULTS

Rain at Ngapuna, Rotorua

Thirty-four rainstorms were analysed at Ngapuna. The results from each storm, expressed in g/ha.mm of inorganic P and N, are presented in Appendix 1 and the means are given in Table 1.

TABLE 1 — The inorganic plant nutrient content in g/ha.mm of the rain that fell over the duration of 34 rainstorms at Ngapuna, Rotorua. The significance of the correlation between parameters is assessed (32 degrees of freedom) as *<0.05 and ***<0.001.

	PO_4-P	NH_4-N	NO_3-N
Mean	0.083	1.825	0.433
Standard error	0.013	0.509	0.105
Standard deviation	0.078	2.967	0.615
Maximum value	0.300	12.500	3.200
Minimum value	0.010	0.050	0.010
Correlation coefficients:			
mm rainfall	−0.341*	−0.325*	−0.368*
PO_4-P		0.535***	0.656***
NH_4-N			0.877***

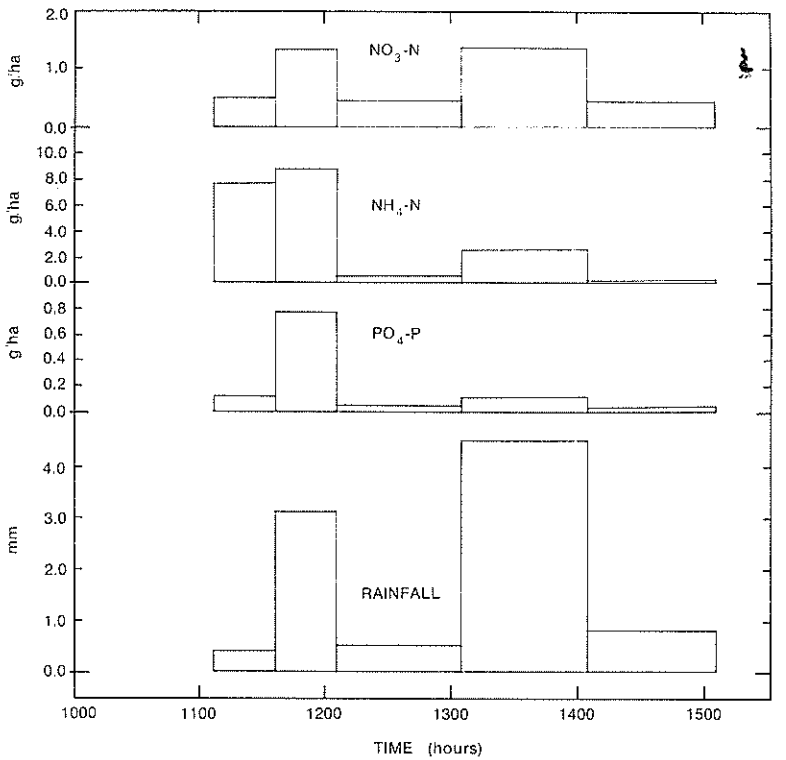

FIG. 1 — Inorganic N and P analysis of a subsampled rainstorm on 5 February 1974. Fallout of NH_4-N was high during the initial low rainfall and of all solutes in the heavy rainfall at midday. Further heavy rainfall at 1400 hours provided a low fallout of NH_4-N and PO_4-P but that of NO_3-N remained more closely proportional to the amount of rainfall.

The negative correlations between rainfall and solute concentrations (Table 1) show that – in most instances – the heavier the rainfall, the lower the nutrient concentrations. This would not be so if the source of solutes was also that of the water vapour providing the raindrops. On the other hand, there is a highly significant, direct relationship between the concentrations of the three solutes measured. It is therefore likely that they originate from the same or similar sources.

These conclusions are supported by an examination of the individual rainstorms, e.g. Fig. 1. A series of 15 such results was collected and examined; this showed that an average of 70 percent of the PO_4-P, 66 percent of the NH_4-N, 63 percent of the NO_3-N, but only 55 percent of the water fell during the first half of these rain periods.

The differences found in water quality between rainstorms are not suitable for estimating rainwater quality over periods of time. Such data are better provided by weighting the concentrations found in the samples with the water volumes of the monitored storms. Over the whole study period, a total of 341 mm of rainfall was sampled, giving a mean concentration of 0.057 PO_4-P, 0.842 NH_4-N and 0.215 NO_3-N as g/ha.mm (Table 2).

TABLE 2 — Mean precipitation of inorganic N and P from 34 rainstorms monitored over the period 1972–74 (total rainfall: 341.3 mm) and the concentration in g/ha per millimetre of rainfall.

Parameter	*Solute precipitation per rainstorm (g/ha)*				*Mean concentration (g/ha.mm)*
	Mean	*Std dev.*	*Std error*	*Range*	
PO_4-P	0.57	0.76	0.13	0.07–4.06	0.057
NH_4-N	8.60	15.32	2.63	0.63–88.07	0.842
NO_3-N	2.09	2.15	0.37	0.11–10.38	0.215

Some of the rainwater samples from Ngapuna were oxidized to determine total P and total N. The resulting estimates of total P ($n=44$) showed that the fraction present of PO_4-P was 78.4 percent (standard error = 3.2, standard deviation = 21.1, range = 33–100 percent) and estimates of total N ($n=23$) showed that the fraction present of inorganic nitrogen was 55.6 percent (s.e. = 3.5, s.d. = 16.6, range = 16–64 percent).

The rainwater samples always had a low pH. Samples were checked as soon as possible after collection, for it was expected that the water would be only lightly buffered. The mean pH of the samples taken ($n=81$) was found to be 5.2 (s.e. = 0.1, s.d. = 0.5) and the observations ranged from pH 4.1 to pH 6.5.

TABLE 3 — The F ratios of a two-way analysis of variance. None of the values is sufficient for significance at the 5-percent level.

	Degrees of freedom	*PO_4-P*	*NH_4-N*	*NO_3-N*
Year:	2	1.33	1.19	1.79
Season:	1	0.21	0.28	0.60

TABLE 4 — The delivery of inorganic N and P by rain at sites near Rotorua. The results of the synoptic rainstorm sampling are expressed as a percentage of that collected at Ngapuna Fisheries Research Laboratory (sites were 3, 13, 37 and 100 km from Ngapuna, respectively).

Place	*Date*	*PO_4-P*	*NH_4-N*	*NO_3-N*
Rotorua City	3 Aug 1973	377	251	128
	13 Aug 1973	320	126	113
	21 Sep 1973	96	52	98
Hamurana Spring	14 Jun 1973	258	187	81
Purukohukohu experimental basin	25 Sep 1973	78	130	4
Turangi trout hatchery	21 Sep 1973	159	105	100

Many of the factors likely to affect rainwater quality vary seasonally (e.g. topdressing, pollen discharge) and the collections were continued until at least one sampling was made in each month of the year. Evidence of seasonal change was sought by dividing the data into those of winter (May, June, July) and non-winter seasons, then using a two-way analysis of variance to detect and measure any difference. The results of the analysis were that the estimated content of inorganic N and P in the rainwater samples showed no significant difference either between years of collection or between the winter and non-winter samples (Table 3).

Comparisons Between Sites

On six occasions, rainstorm samples were collected simultaneously at Ngapuna and elsewhere. All samples were frozen after collection and despatched to Ngapuna for analysis. Table 4 shows the results of synoptic collections in the North Island. Although the data are too few for any firm conclusion, it is interesting that the NO_3-N content of the rainstorm samples was more uniform than the other solutes and that most PO_4-P was collected from the urban site in Rotorua City compared to those in bush (Turangi), pastoral (Purukohukohu) or suburban (Ngapuna) areas.

Collections were made at Turangi for the additional purpose of discovering whether snow, which is likely to fall through the atmosphere relatively slowly, is different in quality compared to rain. Most of the results (Table 5) are within the expected range of concentration for rain precipitation.

TABLE 5 — The concentrations (in mg/m³) of inorganic N and P found in samples of rain at three collection sites and of snow from a site in the Tongariro National Park (eastern slopes of Mount Ruapehu).

Date	*Place*	*Precipitation*	*NH_4-N*	*NO_3-N*	*PO_4-P*
13 Aug 1973	Ngapuna	rain	25	7	1.0
17 Aug 1973	Turangi	rain	<10	4	<1
21 Aug 1973	Turangi	rain	14	15	2.5
18 Aug 1973	Tukino	snow	<10	<1	<1
20 Aug 1973	snowfields	rain	160	16	8.5
21 Aug 1973	snowfields	rain	20	8	1.0
21 Aug 1973	snowfields	snow	10	4	14.0

Through the co-operation of laboratories in Auckland and Christchurch, analytical results from rainfall collections were compared and are presented in Table 6. The NO_3-N content of the rainwater in Auckland was, with one exception, much lower than that found in Ngapuna. In Christchurch the PO_4-P content was consistently greater, sometimes by a factor of 10 or more.

TABLE 6 — The precipitation of inorganic N and P by rainstorms at two sites (174 km and 650 km from Rotorua) expressed as a percentage of the amounts collected from rainstorms monitored at approximately the same time in Ngapuna, Rotorua. The concentrations (in mg/m³) in parentheses are from analyses made by Mr J. H. Leonard, N.Z. Forest Products Ltd, Auckland, and by the Government Analyst, DSIR, Christchurch.

Date of collection	*PO_4-P*	*NH_4-N*	*NO_3-N*	*Date of reference collection, Ngapuna*
Data from Penrose in Auckland:				
19 Sep 1973	52 (7)	130 (200)	2 (<5)	21 Sep 1973
20 Sep 1973	43 (5)	1 (4)	2 (<5)	21 Sep 1973
21 Sep 1973	–	43 (60)	2 (<5)	21 Sep 1973
15 Nov 1973	119 (19)	49 (160)	1 (<5)	21 Nov 1973
9 Mar 1973	582 (17)	1510 (800)	1915 (220)	15 Mar 1974
18 Mar 1974	274 (80)	113 (600)	35 (40)	15 Mar 1974
Data from Ilam in Christchurch:				
15 Mar 1974	353 (12)	–	1821 (193)	17 Mar 1974
18 Mar 1974	819 (18)	–	24 (2)	18 Mar 1974
19 Mar 1974	2057 (72)	–	3 (1)	19 Mar 1974
4 Apr 1974	1667 (25)	–	–	19 Apr 1974
5 Apr 1974	3333 (50)	–	129 (9)	19 Apr 1974
8 Apr 1974	800 (12)	–	86 (6)	19 Apr 1974
20 Apr 1974	5000 (75)	–	27 (2)	19 Apr 1974
21 Apr 1974	8333 (125)	–	100 (7)	19 Apr 1974
26 Apr 1974a	1733 (26)	–	300 (21)	19 Apr 1974
26 Apr 1974b	800 (12)	–	129 (8)	19 Apr 1974
26 Apr 1974c	2467 (37)	–	271 (18)	19 Apr 1974

The collection of results from other countries proved difficult, perhaps because it was considered essential for participants to use the same methods for collection, preservation and analysis. However, Prof. A. Johnson (Nan Yang University, pers. comm.) made 39 samplings of rainfall for reactive phosphorus analysis and 12 for nitrogen salts from a site in the suburbs of Singapore. She sampled from a total measured rainfall of 150.6 mm, and the mean of her results showed that Singapore rain had a content, in g/ha.mm, of 0.07 PO_4-P, 0.57 NH_4-N and 0.13 NO_3-N during the period August–December 1973. Such heavy rainfalls would be expected to be more dilute, as shown by their generally lower nitrogen contents, but it is interesting to find that the PO_4-P contents are so closely similar to those found during this study in New Zealand.

DISCUSSION

One difficulty in comparing data on solutes from rain precipitation is their frequent lack of uniform presentation. For example, the present results are expressed using units of rainfall (i.e. per mm) instead of time (i.e. per annum). Little evidence to favour either expression is likely to be available until much more is known of the origins of the solutes concerned, but the authors of a recent review of solutes in rainwater (Chapin and Uttormark, 1973) show that high-rainfall areas receive greater amounts of dissolved substances from rain than low-rainfall ones in several of the references they examined. It follows that the amount or frequency of rain is a more important parameter than the period over which it precipitated. Therefore the present expression of results in terms of amounts of inorganic N and P falling on a measured area and contained in a known rainwater volume is the more satisfactory.

Data from New Zealand on N and P solutes in rainfall are sparse. Miller (1961) found a mean of 0.16 g/ha.mm of total P and 2.1 g/ha.mm of total N in rain collected over the period 1956–58 at Taita near Wellington. Will (1959) found between 0.02 and 0.07 g/ha.mm of total P in samples of unimpeded rainfall at sites in the Kaingaroa Forest (Central Plateau, North Island). Both authors chose sites some distance from any urban or agricultural developments.

Chapin and Uttormark (1973) recognized several factors that increased the amounts of N and P delivered by precipitation. These included nearby intensive agricultural and forestry development, distance from large water bodies and tropical climates. However, they considered that industrial and urban developments were associated only with an increased precipitation by rainfall of N salts.

These conclusions are only partially supported by the present data. No important difference was found in the quality of rainfall between Ngapuna and Turangi although the latter is much further inland, and the most important difference between results from collections at Ngapuna and those from Rotorua City, Auckland and Christchurch seems only to be in the increased PO_4-P content of the city rainfall.

Although the concentrations of solutes in the Singapore rain were slightly lower than those found at Ngapuna, the amounts of rain that fell over the collection period were much greater. This relatively higher precipitation of N and P salts per unit time may be considered to support the conclusion that enhanced yields are found in tropical climates but, in this instance, the proximity of Singapore City must also be important.

The mean pH of 5.2 in the rainwater at Ngapuna is only slightly lower than would be expected from water equilibriated with the carbon dioxide locally present in the air. Much lower pH values are found elsewhere. Likens *et al.* (1972) have recorded evidence of a long-term trend towards acid values in rainwater collected in the European and American continents. Recent measurements are as low as pH 2.8 and seem to be associated with industrial and urban development. Some non-industrial areas such as the English Lake District have rainfall of an average pH of less than 4.5 owing to wind movement of acidic effluvia. Similarly, gaseous effluents from British and Dutch industry may be responsible for the extremely low pH of rainfall on undeveloped country in Norway and Sweden. The pH of rainfall has proved to be a useful criterion for monitoring air pollution which, as yet, seems to have had little significant effect on rainfall quality at Ngapuna.

It was surprising to find that the annual seasons had no significant effect on rainfall quality at Ngapuna, since pronounced seasonal changes have been found in some overseas surveys. Likens (1972) investigated the chemistry of precipitation at several sites in the State of New York during 1970–71 and found pronounced seasonal fluctuations in rainwater solutes, with N and P concentrations dropping markedly in August and January. Possibly, seasonal changes will become evident when dry fallout is included in precipitation samples, for Likens often collected continuously for periods of up to seven days. However, his results are taken from analyses of clear water samples only with the intention of reducing the complicating factor of dry fallout. At his five sampling sites, the mean solute content of rainfall, expressed as g/ha.mm, was 0.05–0.60 (PO_4-P), 3.1–5.2 (NH_4-N) and 4.4–6.6 (NO_3-N). The values, especially for

N salts, are higher than those found at Ngapuna but, in any case, a proportion of dry fallout material is completely soluble.

Likens' publication is of particular interest in that he was able to make comparisons of rainwater quality at some of his sites from records that extend over very long periods of time (some of the data quoted were collected as early as 1920). The present data collected in New Zealand on N and P concentrations in rainwater are comparatively few. However, as time goes on, these records may serve as base-line data to help measure future changes in the quality of rainfall.

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APPENDIX 1 — The amount of precipitation and its content of inorganic N and P for monitored rainfalls at Ngapuna, Rotorua.

Date	*Rainfall (mm)*	*Solute concentration (g/ha.mm)*		
		PO_4-P	NH_4-N	NO_3-N
21 Jul 1972	0.3	0.230	4.340	0.800
9 Aug 1972	11.3	0.014	0.110	0.010
9 Aug 1972	10.3	0.053	0.089	0.049
16 Aug 1972	4.7	0.259	0.485	0.116
12 Oct 1972	3.5	0.069	1.957	0.071
6 Dec 1972	6.7	0.029	1.419	0.592
17 Jan 1973	7.0	0.230	1.220	1.050
24 Jan 1973	3.0	0.040	0.900	0.450
8 Feb 1973	2.0	0.100	12.500	1.600
6 Mar 1973	17.0	0.026	1.395	0.216
12 Mar 1973	14.5	0.136	6.074	0.716
12 Apr 1973	5.3	0.070	0.400	0.140
18 May 1973	2.9	0.038	0.424	0.072
6 Jun 1973	0.5	0.150	1.260	0.230
14 Jun 1973	12.0	0.019	0.075	0.122
3 Aug 1973	6.0	0.012	0.528	0.175
13 Aug 1973	16.9	0.010	0.412	0.099
21 Sep 1973	2.3	0.115	1.385	0.444
8 Oct 1973	3.2	0.060	1.250	0.350
23 Oct 1973	7.7	0.019	0.213	0.038
27 Nov 1973	5.2	0.160	3.250	0.800
11 Dec 1973	1.0	0.300	12.000	3.200
18 Dec 1973	0.7	0.150	2.800	1.080
19 Dec 1973	4.5	0.060	2.600	0.680
5 Feb 1974	9.2	0.124	2.190	0.424
17 Mar 1974	14.0	0.034	0.913	0.106
18 Mar 1974	18.3	0.022	0.069	0.083
19 Mar 1974	2.0	0.035	0.500	0.300
19 Apr 1974	50.0	0.015	0.100	0.070
3 May 1974	33.8	0.120	0.050	0.060
28 Jun 1974	21.7	0.045	0.100	0.060
18 Jul 1974	10.2	0.025	0.450	0.180
5 Aug 1974	23.7	0.045	0.100	0.040
27 Sep 1974	9.9	0.020	0.500	0.360