A Note on the Chemical Composition of Rainwater

By W. A. MORDY, Honolulu, T. H.

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Abstract

A limited number of observations of nitrogen, sodium and chloride in rainwater made in Hawaii are presented. Because of frequent and high rainfall, calculations of the annual amounts of nitrogen received in various Island localities are rather large. In one storm nitrogen was brought down by rainfall at a nearly constant rate although rainfall intensity varied considerably.

In general, the concentrations of these elements in Hawaiian rains agree with observations in other oceanic areas.

In view of the current interest in atmospheric nitrogen, Dr C. G. Rossby recently asked me to submit to the readers of Tellus some observations of nitrogen and other chemical constituents in rainwater in Hawaii.

During March and April 1953, several samples of rainwater were collected and analyzed for nitrogen content. Total nitrogen (ammonia and nitrate) was determined by distillation in the presence of alkali and Devarda's alloy, reducing the nitrate to ammonia. Ammonia in the distillate was nesslerized and the color was measured on an Evelyn photo-electric colorimeter.

The results of these determinations are shown in Table 1. It appears that these figures

Table 1

Date	Time[1]	Elapsed Time	Rate of Collection	Rainfall Intensity	Volume of Sample	Total Rain for Day	Total N[2] NH_4-NO_3-N	N/min	Na[3]	Cl[4]
		min	cm³/min	mm/h	cm³	cm	mg/l	g/min	mg/l	mg/l
3/11/53	9: 34—9: 37	3	220	13.2	660		.16	35.2		
	9: 38 3 4									
	9: 43 1/2	4—3/4	97	5.9	460	1.19	.11	10.6		
3/27/53	14: 24—14: 27	3	188	11.3	566	.47	.08	15.1		
4/22/53	14: 45—15: 10	25	38	1.8	740		.51	15.1	2.8	4.8
	15: 12—15: 43	31	23	1.4	715		.39	9.0	1.4	3.0
	15: 44—15: 55	11	65	3.9	720		.10	6,6	.6	.6
	16: 08—16: 25	17	35	2.1	591		.24	8.4		
	16: 28—17: 30	62	11	.7	707	.35	.66	7.5	2.0	2.0
							Av = .28			

[1] Hawaiin Standard Time = 150th Meridian Time.
[2] Nitrogen Determined by Distillation and Colorimetry.
[3] Sodium Determined by Flame Photometer.
[4] Chloride Determined by Titration.

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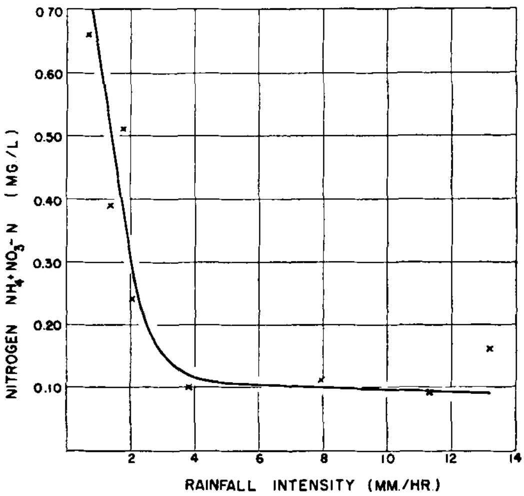

Fig. 1. Relationship of rainfall intensity to rainwater nitrogen content for 8 samples of rainwater collected in Honolulu for March 11 to April 22, 1953.

are in good agreement with the figures found elsewhere in ocean climates, ERIKSSON (1952). They are somewhat lower than the figures that ÅNGSTRÖM (1952) indicated should be found for rainfall from tropical air masses, and the relationship which he suggests concerning the decrease in the rate of collection of nitrogen as the rainfall endures, is not borne out in the one test of it here on April 22 where five consecutive samples were obtained.

An inverse relationship between nitrogen content and rainfall intensity appears to exist in these data. Only one observation, the first on March 11, 1953, lies away from the line sketched in on the scatter diagram, Fig. 1. If the nitrogen is absorbed by the rainwater in a washing action of the rain an inverse relationship might be expected. Such a relationship also might be expected to show better in these data from Hawaii due to the nature of the rainfall. These samples were of orographic rainfall collected at the meteorological observatory on top of the Hawaiian Sugar Planters' Association Experiment Station 4 miles (6 km) leeward from the crest of the Koolau Mountains, Fig. 2. Because the rainfall was orographic it can be considered essentially stationary with new air pouring into the rainy zone with the speed of the wind.

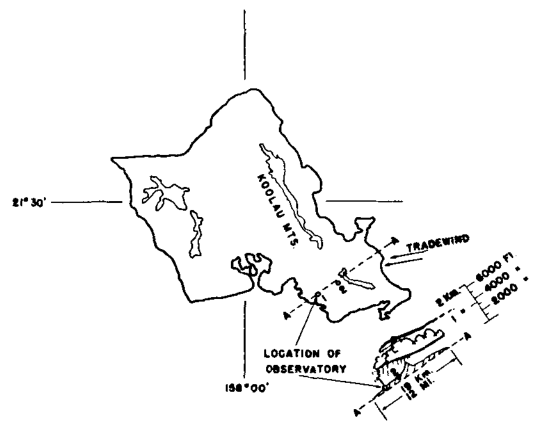

Fig. 2. Location of meteorological observatory Experiment Station of Hawaiian Sugar Planters' Association, where rainwater samples were collected. Rainwater was collected orographic rainfall 4 miles (6 km) leeward from the crest of the Koolau Mountains.

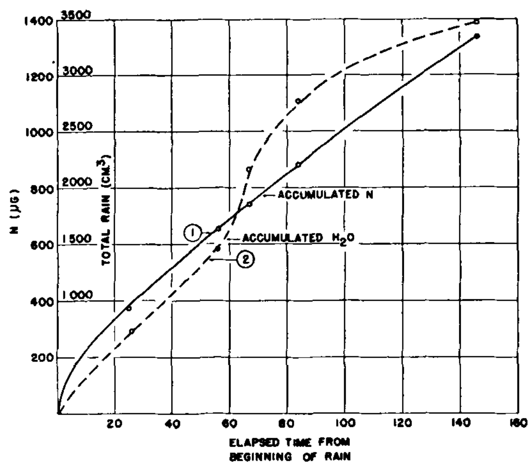

Fig. 3. Rate of accumulation of nitrogen (curve 1) with the accumulation of rainwater (curve 2), on April 22, 1953. The rate of accumulation of nitrogen per unit time appears to be quite constant, while the rate of accumulation of rainwater as a result of changes in rainfall intensity is quite different.

If the air contains only a fixed amount of nitrogen which can be brought down by the rain, then the rainwater from the higher intensity rains will contain less nitrogen per unit volume of water than the lower intensity rain. Such reasoning would also require, of course, that the washing efficiency of high and low intensity rains be nearly the same.

The amount of nitrogen accumulated in the rainwater per unit time has been examined with this reasoning in mind. In Fig. 3 are graphs of the accumulated nitrogen and the accumulated rainfall after a given elapsed time from the beginning of the rainfall. It is interesting to see that the rate of nitrogen accumulation (slope of curve 1) seems fairly steady for a two hour period, while the rate of rainfall (curve 2) accumulation varies significantly. This is interpreted by the author, somewhat intuitively, to mean that the nitrogen exists as a limited supply in a given volume of the atmosphere and is almost completely brought down from the air through which the rain falls.

A further point of interest lies in the relationship between the nitrogen and sodium or chloride determinations. Sodium and chloride determinations have been made on a number of rainfall samples in cloud physics studies during the past year. Variations in the latter elements have been accounted for by postulating the role the sea salt particles in the atmosphere play in the formation of raindrops, (WOODCOCK 1951, BLANCHARD 1952). It is interesting therefore to compare the amounts of nitrogen with the sodium and chloride determinations to determine:

1. If the nitrogen in the rainwater could be directly from the sea as it has been reasoned the salt is;
2. If the nitrogen and salt exist as particles in the air which might be washed down rather than the salt being the nucleus for raindrops.

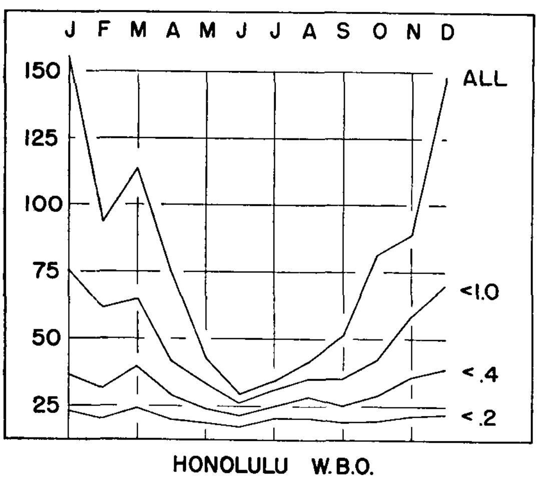

Fig. 4. The amount of rain at the Honolulu Weather Bureau office for the years 1909 to 1949 inclusive, which resulted from rains of 0.2 in. (0.51 cm) or less, 0.4 in. (1.02 cm) or less, 1 in. (2.54 cm) or less per day, and the total rain received for the 39 year period by months. Rains of less than an inch per day account for more than half the total rainfall.

If the nitrogen and sea salt get into the rainwater by the same route from the sea, then the ratio of salt to nitrogen should be relatively the same in rain and sea water or at least the amounts of nitrogen and chlorides should be strongly correlated. This is not the case since the nitrogen to chloride ratios in the rainwater exceeds roughly 1,000 times the nitrogen to chloride ratio in sea water (SVERDRUP 1946).

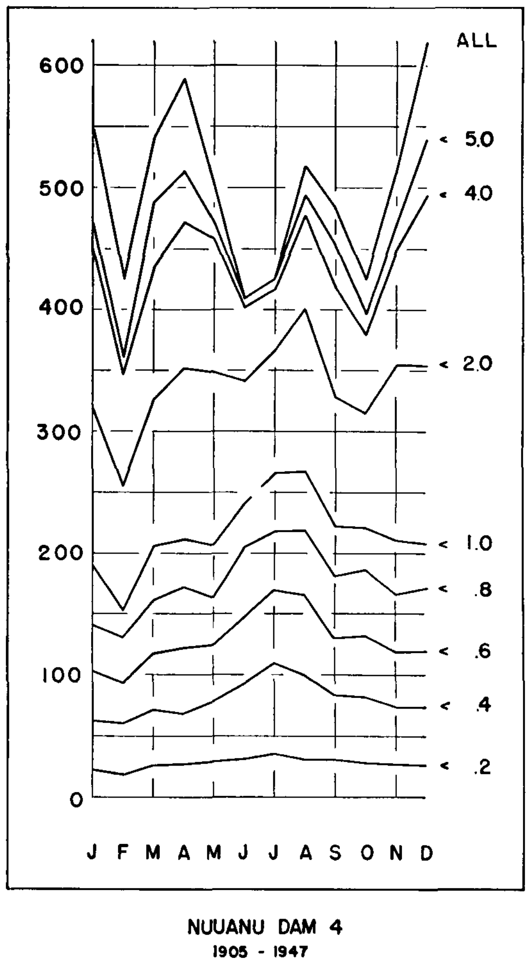

Fig. 5. Rainfall at Nuuanu Dam No. 4 (average rainfall 150 in.) which has resulted from rains of various amounts per day. Rains smaller than 1 in. (2.54 cm) per day count for approximately half of the total rainfall.

Secondly, if the nitrogen and salt were part of the same particles, or separate particles subject to the washing action of the rain the ratio of nitrogen to salt in the different rainfall samples taken within relatively short periods of time should be fairly constant. In the four April 22 cases in Table 2 where this comparison can be made, this is not the case.

The amount of nitrogen which arrives in the soil as a result of rainfall is a main point of interest. In view of the apparent inverse relationship between rainfall intensity and nitrogen content, some rough calculations can be performed which are likely to be conservative, since the rainfall was in each case heavier than the median rainfall and similarly of greater intensity.

To perform these calculations it is helpful to look first at monthly frequency distributions of two rainfall stations, the Honolulu U.S. Weather Bureau office with 30 inches (76 cm) average annual rainfall, and Nuuanu Dam No. 4 with 150 inches (381 cm) average annual rainfall, on the Island of Oahu. These distributions are different from the usual representation of such data in that they show the amount of the total rainwater which is received by each category of rainfall (Figs 5, 6). It can be seen that daily rains which are one inch or less comprise over half the total rainfall for the thirty inch station, and rains of one inch or less similarly comprise over half the total rainfall at the 150 inch station.

In another study the author has examined the rainfall from a number of such stations and found that in general the increase in rainfall in the wetter areas of the island is due to increased frequency of smaller rains particularly, although of course the frequency of all intensities of rain is greater.

These statements are intended to help show that if we calculate nitrogen arriving on the surface of the land by using the figures from the graph in Fig. 1 or by using the average nitrogen figure of .28 from Table 1, we are likely to arrive at a result somewhat less than the actual, the *average* nitrogen/unit vol. figure producing the lower value of the two for nitrogen per unit area.

Using the average value of nitrogen/unit vol. from Table 1, the results obtained were:

Table 2

Average Rainfall		Calculated Kg N/Ha/year
Inches	cm	
30	76.2	2
100	254	7
200	508	14
400	1 016	28
600	1 524	43

Later, more meaningful calculations can be made when more data have been assembled showing the relationship of nitrogen to raindrop size, rainfall intensity, and daily rainfall.

However, in lieu of these calculations it is interesting to examine some unpublished observations of monthly amounts of nitrogen in rain water made here at the HSPA Experiment Station (38 inches annual rainfall) and the HSPA Manoa Arboretum (160 inches annual rainfall), Fig. 2, by L. R. Smith in 1935—36. These data are shown in Table 3.

The methods which Smith used in his determinations are subject to some criticism. 1) The use of zinc in his alkaline distillation was likely to reduce some of the nitrate present to ammonia. The ammonia values therefore may be too high. 2) No provision was made to remove chlorides. In the presence of chlorides and upon the addition of concentrated sulphuric acid in the phenol-disulfonic acid reagent, nitrate may have been lost by reduction to gaseous nitric oxide. Nitrate values may then be too low. The magnitude of the gain in ammonia and the loss in nitrate is of course speculative. Assuming that these errors are compensatory, then the total nitrogen values may not be too greatly in error. It can be seen that the estimates of nitrogen from the average determinations is low for the Makiki case and high for the Manoa station.

As a final point of discussion, one factor stands out in Eriksson's table of values of nitrogen determinations for various parts of the world. This is the near uniformity of the low values which have been obtained in isolated oceanic regions. There appears to be little difference between areas of frequent storms where electrical discharges would not be uncommon and areas such as Hawaii where a thunderstorm or lightning discharge is very

Table 3

1936—1937	Manoa Arboretum		Rainfall	Total N for Month	Makiki Experiment station		Rainfall	Total N for Month
	NH_3N	NO_3N			NH_3N	NO_3N		
	Kg/Ha	Kg/Ha	Cm	Kg/Ha	Kg/Ha	Kg/Ha	Cm	Kg/Ha
September	.14	.27	53.59	.41	.28	.05	7.01	.33
October	.53	.25	52.83	.79	.23	.15	29.26	.37
November	.97	—	19.33	.97	.15	.06	6.99	.20
December	.19	.14	52.02	.33	.89	.09	17.73	.98
Januari	.55	.36	70.28	.92	.21	.21	21.36	.43
February	—	—	41.63	—	.80	.23	18.85	1.03
			Total 5 months	3.42		Total 6 months		3.34

infrequent. Although the proportion of nitrogen in the rainwater is fairly constant from one ocean area to another, the amount and frequency of rainfall, of course, is very different. Hence the distribution of nitrogen brought down by the rainfall over different parts of the world should be very uneven indeed.

A continuing program of nitrogen observations is planned to attempt to relate nitrogen with drop size, rainfall intensity, character, and the general weather synopsis.

Acknowlegment

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