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THE PROPORTIONS OF CHLORINE AND OF NITROGEN AS NITRIC ACID AND AS AMMONIA IN CERTAIN TROPICAL RAIN-WATERS.

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DURING the years 1880 to 1885 determinations of the quantity of nitrogen present in the forms of nitric acid and ammonia were, from time to time, made by one of us upon samples of rain water which had fallen in the island of Barbados, British West Indies, and in others of the West Indian Islands.

It was noticed that the proportions of combined nitrogen present in the rain waters in the forms of nitric acid and ammonia did not in any way support the received ideas that tropical rain-water contains considerably higher proportions of combined nitrogen than does that of temperate climates.

When a Botanic Station was started in the island of Barbados, at Dodd's Reformatory, steps were taken to systematically collect samples of rain-water, representative of the whole rainfall. The samples were collected by J. R. Bovell, Esq., F.C.S., F.L.S., the superintendent of the Botanic Station, and analyzed as soon as possible after collection by one of us (J. B. H.). This was continued from June, 1885, to February, 1890, soon after the analyst was transferred to British Guiana.

In the latter colony, in January, 1890, steps were taken to carry out a similar investigation and samples representative of the whole rainfall were collected at the Government Laboratory and at the Botanic Gardens in Georgetown. The results reported in this paper are those obtained in Barbados in latitude

13° 4′, north, and longitude 59° 37′ west, during a period of four years and nine months, ended in February, 1890, and in Georgetown, Demerara, in latitude 6° 49′ 24″ north, and longitude 58° 11′ 30″ west, from January, 1890, to June, 1896, a period of six and a half years.

The investigation has therefore extended over a period of eleven years—long enough, we think, to supply a fairly reliable record of the contents in combined nitrogen of the rain-waters in these low latitudes.

Both in Barbados and at the Government Laboratory in British Guiana, the rain has been invariably collected by means of large (eight to ten inch) glass funnels fitted with 100 mesh wire gauze sieves to prevent the entrance, into the collecting vessel, of leaves, insects, etc.

At the Botanic Gardens, British Guiana, at the commencement of the investigation there, the rain was collected in an eight-inch copper rain gauge, later in both this and in a glass funnel, and finally by means of the glass funnel only.

From the commencement of the experiments the methods of analysis used have been but slightly varied. The chlorine has been always determined by direct titration with centinormal silver nitrate solution, standardized in solutions of sodium chloride of approximately the same strength as the rain-waters to be examined, using 100 cc. of the rain-water at each estimation.

During the first four years, the ammoniacal nitrogen was determined directly on the water by means of Nessler's test; a quantity of the water was made very faintly acid with oxalic acid specially purified from all traces of ammonia and nitrates, divided into two portions, one of which was allowed to act for two or three days until reduction of the nitrates was complete, upon zinc copper couples prepared as directed by M. W. Williams,[1] the other being kept for the purpose of diluting the standard ammonia solution used for comparison in nesslerizing the water which had been exposed to the action of zinc copper couples. The errors thus fell on the nitric nitrogen, but as the proportions of this in the rainfall under consideration was, as a rule, much higher than that of the ammoniacal nitrogen, the amount of error introduced would be small.

Since the publication of Warrington's paper[2] the ammoniacal

[1] Trans. Chem. Soc., *1881*, 100.
[2] *J. Chem. Soc.*, **55**, *1889*, 537.

and nitric nitrogen have been invariably determined by the method there given; 500 cc. of the rain-water are boiled rapidly in a Keene's revenue still with a little recently ignited magnesia, or with a very minute amount of chemically pure sodium hydroxide prepared from sodium, until 200 cc. have distilled over. In an aliquot part of the distillate the ammonia is determined by nesslerizing. The residue in the flask of the still is transferred to a wide-mouthed stoppered bottle containing copper zinc couples and kept closely stoppered at the temperature of the laboratory, 25° to 30° C., for four or five days. The water is afterwards distilled and the ammonia in the distillate, representing the nitrogen originally present as nitric acid, determined. Traces only of nitrites in a few instances have been detected in the rain-waters.

During this investigation 306 samples, representing the whole rainfall, have been examined.

Fortnightly and frequently weekly examinations were made of the rainfall during the first eight years of the experiments, but since 1893 monthly examinations only have been made of the mixed rain-water collected during the month.

BARBADOS RAIN.

The average compositions of the yearly rainfalls are shown in the following:

Years.	1885. Seven months.	1886.	1887.	1888.	1889.
Inches of rain	34.65	74.50	59.52	55.77	66.11
No. of samples analyzed	22	36	44	38	53
		Milligrams per liter at 27° C.			
Chlorine	7.755	7.604	8.417	8.473	7.923
Nitrogen as nitric acid.	0.097	0.255	0.173	0.153	0.200
Nitrogen as ammonia..	0.116	0.070	0.076	0.046	0.082
		Pounds per acre.			
Chlorine	60.850	128.300	113.450	107.010	118.611
Nitrogen as nitric acid.	0.761	4.302	2.332	1.932	2.994
Nitrogen as ammonia..	0.910	1.181	1.024	0.581	1.228

The average compositions of the monthly rainfalls and of the wet and dry seasons were as follows:

Months and seasons.	No. of years.	No. of samples analyzed	Average rainfall in inches	Mgms. per liter at 27° C.			Pounds per acre.		
				Chlorine.	Nitrogen as nitric acid.	Nitrogen as ammonia.	Chlorine.	Nitrogen as nitric acid.	Nitrogen as ammonia.
January..	4	14	2.94	14.171	0.160	0.074	9.435	0.106	0.049
February.	4	13	2.03	21.514	0.195	0.093	9.890	0.089	0.043
March ...	4	11	1.66	17.796	0.240	0.124	6.691	0.090	0.046
April	4	10	1.17	16.818	0.346	0.161	4.457	0.092	0.042
May	5	13	3.65	8.706	0.226	0.068	7.181	0.187	0.056
June	5	18	4.49	9.489	0.161	0.069	9.648	0.163	0.070
July	5	21	6.98	7.479	0.170	0.094	11.822	0.268	0.148
August...	5	21	10.12	6.388	0.155	0.091	14.640	0.355	0.208
Sept'mber	5	19	8.00	5.838	0.103	0.061	10.574	0.186	0.110
October ..	5	20	5.56	5.904	0.161	0.073	7.468	0.203	0.092
November	5	20	8.19	5.422	0.233	0.051	10.056	0.442	0.094
December	5	13	4.61	9.977	0.263	0.048	10.416	0.275	0.050
Wet season July to November.		101	38.85	6.197	0.164	0.074	54.520	1.443	0.651
Dry season December to June.		92	20.55	13.422	0.215	0.077	62.461	1.000	0.358

Wide variations occurred in both the chlorine and nitrogen contents of different rainfalls. The samples which were examined during the investigation which had the highest and lowest contents showed as follows:

	Mgms. per liter.	
	Highest.	Lowest.
Chlorine	47.042	2.476
Nitrogen as nitric acid	0.914	0.001
Nitrogen as ammonia	1.812	none

The average annual rainfall during these experiments was at the rate of 59.40 inches, having as average contents in milligrams per liter at 27° C., 8.699 of chlorine, 0.181 of nitrogen as nitric acid, and 0.075 of nitrogen as ammonia, and yielding to the soil 116.98 pounds of chlorine, 2.443 pounds of nitric nitrogen, and 1.009 pounds of ammoniacal nitrogen per acre. Of these approximately two-thirds of the ammoniacal nitrogen and three-fifths of the nitric nitrogen were contained in the rain which fell in the five months comprising the rainy season, during which period electrical atmospheric disturbances are common in Barbados.

In 1886, on August 16, an opportunity occurred for the collection and examination of samples of the rain which fell whilst a hurricane was raging to the north of the island. 9.14 inches were collected and were found to contain

	Mgms. per liter.
Chlorine	42.52
Nitrogen as nitric acid	0.329
Nitrogen as ammonia	0.057

The rain of this storm supplied 0.681 pounds of nitrogen as nitric acid per acre, or equal to twenty-eight per cent. of the average amount present in an ordinary year's rainfall.

BRITISH GUIANA RAIN.

The average compositions of the yearly rainfalls collected in this colony are shown in the following:

Years.	1890.	1891.	1892.	1893.	1894.	1895.	1896. Eight months.
Inches of rain	125.63	109.38	128.03	135.24	76.67	82.56	64.55
No. samples analyzed	39	26	24	12	12	12	8
			Mgms. per liter at 27° C.				
Chlorine	8.293	5.284	3.827	3.155	3.032	4.187	5.179
Nitrogen as nitric acid	0.090	0.128	0.035	0.066	0.036	0.237	0.082
Nitrogen as ammonia	0.075	0.034	0.043	0.068	0.045	0.065	0.078
			Pounds per acre.				
Chlorine	235.780	130.900	110.595	96.600	52.640	78.280	78.710
Nitrogen as nitric acid	2.559	3.171	1.015	2.022	0.625	4.431	1.199
Nitrogen as ammonia	2.135	0.842	1.247	2.083	0.781	1.215	1.141

The average compositions of the monthly rainfalls and of the wet and dry seasons were as follows:

Months and seasons.	No. of years.	No. of samples analyzed	Average rainfall in inches	Mgms. per liter at 27° C.			Pounds per acre.		
				Chlorine.	Nitrogen as nitric acid.	Nitrogen as ammonia.	Chlorine.	Nitrogen as nitric acid.	Nitrogen as ammonia.
January	7	11	13.21	6.174	0.097	0.030	18.469	0.290	0.090
February	7	13	10.19	6.417	0.102	0.060	14.808	0.235	0.138
March	7	13	7.26	5.043	0.063	0.100	8.291	0.103	0.164
April	7	14	8.05	6.197	0.087	0.094	11.297	0.158	0.171
May	7	12	12.29	5.595	0.086	0.062	15.572	0.239	0.173
June	7	13	12.93	3.278	0.104	0.033	9.598	0.304	0.096
July	7	12	10.96	3.076	0.116	0.038	7.634	0.288	0.094
August	7	12	6.81	3.399	0.089	0.111	5.242	0.137	0.171
Sept'mber	6	9	2.50	4.846	0.119	0.014	2.743	0.067	0.008
October	6	8	1.99	7.113	0.120	0.142	3.205	0.054	0.064
November	6	8	5.58	4.001	0.121	0.121	5.056	0.153	0.153
December	6	10	14.94	3.321	0.049	0.023	11.236	0.165	0.078
Wet seasons December to February. May to July.	71		74.52	4.313	0.090	0.039	72.784	1.519	0.658
Dry seasons March and April. August to November.	64		32.19	4.915	0.092	0.091	35.829	0.671	0.663

During the period over which the experiments have been

spread, the rainfall has been at an average rate of 106.71 inches per annum and has contained 4.494 mgms. of chlorine, 0.0915 mgm. of nitric nitrogen and 0.055 mgm. of ammoniacal nitrogen per liter at 27° C. This is equivalent to a yield of 108.613 pounds of chlorine, 2.190 pounds of nitric nitrogen, and 1.351 pounds of ammoniacal nitrogen per acre.

During this part of the investigation the highest recorded contents of chlorine was 16.10, the lowest 0.45 mgm. per liter. The highest contents of nitric nitrogen was 0.823 and of ammoniacal nitrogen 1.376 mgms. per liter; the lowest in both cases was none.

THE INFLUENCE OF THE COLLECTING VESSEL UPON THE APPARENT COMPOSITION OF THE RAIN.

At the commencement of the investigation in British Guiana, samples were collected in the grounds of the Government Laboratory by means of a glass funnel and at the Botanic Gardens by means of an eight-inch rain gauge. It was at once noticed that the rain collected in the metal gauge invariably contained the higher proportions of ammoniacal nitrogen and usually also of nitric nitrogen. In consequence a glass funnel was afterwards used at the Botanic Gardens being placed on the tower of the house some fifty feet above the ground. During the latter half of 1890 determinations were regularly made of the contents of nitric and ammoniacal nitrogen in the rain collected by the two receivers. The following gives in mgms. per liter at 27° C. the results obtained from June to December, 1890:

		Collected by glass funnel. Nitrogen as		Collected by metal gauge. Nitrogen as	
Month.	Inches of rain.	nitric acid.	ammonia.	nitric acid.	ammonia.
June.....	13.17	0.087	0.123	0.352	1.860
July	10.90	0.225	0.046	0.723	3.257
August	5.71	0.075	0.270	0.486	4.000
September.	3.18	0.263	0.026	3.047	1.138
October....	0.16	0.823	0.296	0.626	1.057
November .	2.97	0.214	0.091		
December .	9.47	0.049	0.015	0.330	0.178

The rainfall amounted to 45.56 inches in the six months and whilst the rain collected by the glass funnel contained an average of 0.125 mgm. per liter of nitric nitrogen and 0.092 of ammoniacal nitrogen that collected in the rain gauge contained 0.660

and 2.007 mgms. per liter of nitric and ammoniacal nitrogen respectively. Examinations of the rain collected in the rain gauge showed that it usually contained phosphoric acid and that the high content of nitrogen, which might have been considered as characteristic of tropical rain, was due to contamination of the receiving surface by birds. It was noticed that birds, in which this colony is peculiarly rich, constantly frequented and perched upon the copper gauge whilst they avoided the glass funnel, scared, probably, by the reflected rays of the sun.

To further examine into this matter, in 1892, determinations were made on the rains collected in a small copper rain gauge and by a glass funnel in the grounds of the Government Laboratory. These were placed side by side, about twelve inches apart, at about three feet above the ground so as to avoid splashing from the soil, as it was probably to nitrification induced by such splashing that the high content of nitric nitrogen noticed in the rain collected in the Botanic Garden's rain gauge was due. The following are the results in mgms. per liter, at 27° C., of the comparisons made during the months of July, August, and September, 1892:

		Collected by glass funnel. Nitrogen as		Collected in metal gauge. Nitrogen as	
Month.	Inches of rain.	nitric acid.	ammonia.	nitric acid.	ammonia.
July	11.40	0.051	0.063	0.037	0.229
August	8.05	0.053	0.222	0.049	0.652
September.	5.78	0.060	0.007	0.126	2.751

The rainfall of 25.24 inches contained 0.053 and 0.100 mgm. per liter, respectively, of nitric and ammoniacal nitrogen when collected by the glass funnel and 0.061 and 0.942, respectively, when collected in the copper gauge. Here, where there was but little chance of nitrification being induced by splashings from the earth, it is evident that the excess of nitrogen in the water collected by the copper rain gauge, was almost entirely in the form of ammonia. We are desirous of placing these observations on record, as they may to some extent explain the high nitrogen contents reported at times in the tropical rain-waters by other observers.

In our results, as far as used for the determination of the nitrogen present as nitric acid and ammonia we have, of course, only taken into consideration the figures obtained from the examinations of rain collected by means of glass funnels.

COMPARISON OF THE RESULTS OBTAINED IN BARBADOS AND BRITISH GUIANA WITH THOSE REPORTED FROM ELSEWHERE.

With an average annual rainfall in Barbados of 59.40 inches, the rain contained 0.101 mgm. per liter of nitrogen as nitric acid and 0.075 mgm. per liter of nitrogen as ammonia. The average amount of nitrogen in the two forms was therefore equal to 3.452 pounds per acre per annum.

With an average annual rainfall in British Guiana of 106.71 inches, the rain contained 0.0915 mgm. of nitrogen as nitric acid and 0.055 mgm. of nitrogen as ammonia per liter, at 27° C. Thus, the average amount of nitrogen in these two forms was equal to 3.541 pounds per acre per annum.

We may safely assume, therefore, that during the eleven years over which the investigation has extended, the nitrogen contents of the rainfall present as nitric acid and ammonia was approximately three and a half pounds per acre per annum in these two colonies situated in the tropics and in the direct course of the trade-winds.

The total amount of nitrogen present in the Rothamsted rain-water is given by Warrington,[1] at 3.74 pounds per acre per annum, a figure with which our results obtained by similar methods of analysis closely agree.

The Barbados rain-water contained approximately three-fourths of the nitrogen as nitric nitrogen; the British Guiana rain-water, two-thirds of the nitrogen as nitric nitrogen; while in the Rothamsted rain-water the nitric nitrogen was approximately only one-fourth of the whole.

Results obtained in New Zealand and at Tokio, in Japan, quoted by Warrington in his paper, show decidedly lower contents of nitrogen in these forms; and in both of these places the ammoniacal nitrogen is present in the rain water in far higher proportions to the nitric nitrogen than we have found here in the tropics. It is probable, therefore, that the rain-water of the tropics contains a higher proportion of its nitrogen present as nitric acid than does that of temperate climates.

As regards tropical rain, the only published results we are acquainted with are those of Müntz and Marcano,[2] on rain-waters

1 *Loc. cit.*

2 *Compt. rend.*, 108, 1062.

from Caracas, Venezuela, and from St. Denis, Reunion. In the former the mean proportion of nitric nitrogen was found to be 0.578 part per million, in the latter 0.69 part.

These results are far in excess of the quantities found by us, although, from time to time, instances have occurred to us in which the nitrogen present as nitric acid has approached or even exceeded these amounts.

Possibly, the results obtained by Müntz and Marcano were from rainfalls lower in quantity than those which occurred during our present investigation, whilst probably the composition of rain-water may be materially affected by the prevalence or not of the trade-winds.

Briefly our somewhat extended investigation leads to the conclusion that the rainfalls of certain tropical climates whilst containing a higher relative proportion of the nitrogen as nitric acid, do not supply to the soil a larger quantity of nitrogen as nitric acid and as ammonia than is supplied by the rain-water of temperate climates.

ANALYSIS OF AN IRON RAIL TAKEN FROM A GALLERY OF AN UNUSED COAL MINE.

By H. P. Talbot and A. G. Woodman.

Received November 21, 1896.

THE section of the rail in question was taken from a gallery of the "Hub Mine," at Glace Bay, Cape Breton. The gallery was allowed to fill with water in 1872, and was pumped out by the Dominion Coal Company last year. The rail had, therefore, lain unused in the gallery for over twenty years, most of the time under water which is reported to be "impregnated with acid," and, as indicated by the analysis, had undergone an entire change in composition. The rail was initially, presumably, of cast iron, and it is interesting to record the report which has come to us, that utensils of steel, and articles of wrought iron, did not undergo material change during the same length of exposure to the same conditions. So far, the writers have not had opportunity of examining any of these samples of wrought iron or steel.

After the mine had been pumped out, the rail was found to have lost its initial density and strength, and was easily broken or cut into fragments.