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Thunderstorm and fixation of Nitrogen in rain

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ABSTRACT. Recent determinations of the nitrates and ammonia in rain water in Sweden has led to the conclusion that thunder, i.e., electrical spark discharges in the atmosphere, is not the determining factor in the production of Nitrogen compounds formed in rain water. In the light of the above conclusion, available data of combined Nitrogen in rain water in India have been examined. It supports the conclusions reached by Swedish workers.

It is well known that Nitrogen dissolved in rain water is mostly in the form of nitrate, nitrite or ammonia. It has been till now the general belief that nitrates in rain water are produced from Oxides of Nitrogen formed by the electrical discharges in the thunderstorm. The reactions are indicated by the following equations—

$$N_2 + O_2 = 2NO$$

$$2NO + O_2 = 2NO_2$$

$$2NO_2 + H_2O = HNO_3 + HNO_2$$

These reactions suggest that in rain water the amounts of nitrate and nitrite should be the same, a fact which is seldom found. In most cases, the amount of nitrite is much less than that of the nitrate in the same sample. One possible explanation for this may be that nitrites react with ozone formed in the atmosphere during thunderstorm and thus give rise to nitrates.

Hutchinson (1944) in surveying this subject, gives the various processes by which fixation of nitrogen takes place in the atmosphere. They are:

1. Electrical
2. Photo-chemical
3. Trails of Meteorites
4. Industrial contamination

Hutchinson excludes the last named source on some well founded reasons. He also points out that the trails of the meteorites should contribute only a small fraction of the nitrate ordinarily present in the rain water.

Angstrom and Hogberg (1952), from their observations in different parts of Sweden state that there is no indication that an electrical process takes any major part in the production of nitrates in rain. In Sweden, thunder and atmospheric discharges occur mostly in summer and rarely in autumn, winter and spring. But they observed a pronounced maximum of nitrate concentration in spring in that country. Moreover Hutchinson (1944) has shown from the data of Finnel and Houghton (1932) at Goodwell (Oklahoma) that at most 350 gm of N_2 are fixed per hectare in the temperate region through electric discharges, whereas the annual precipitation contains 1 kgm ha^{-1}. These speak certainly against an electrical source for the observations.

In India there has not been any systematic determination of nitrates in rain water. Comparatively recent determinations were made in Sylhet (now in Eastern Pakistan) by Das, Sen and Pal (.933), and in Bombay by Narayanaswamy (1939). A close scrutiny of their data and the meteorological conditions specially the occurrence of thunderstorms, during that period has been made in the present paper with a view to check Angstrom and Hogberg's conclusion.

Narayanaswamy (1939) has briefly indicated the meteorological conditions during the period he collected the sample. Table 1 has been drawn up in the descending order of nitrogen content with a view to check under what conditions the maximum and minimum amount of nitrogen in rain water was observed by him.

TABLE 1

Nitrate (*mg/litre*)	Nitrite (*mg/litre*)	Rainfall (*inches*)	Date	Remarks
0·24	0·0008	3·2	14- 6-1938	Thunderstorm with rain
0·18	0·0008	0·4	11- 8-1938	Thunderstorm with rain
0·18	0·0020	3·5	1-10-1938	Severe thunderstorm with rain
0·14	0·0005	1·1	15- 6-1938 to 22- 6-1938	
0.14	0·0004	0·8	26- 6-1938 to 28- 6-1938	
0·14	0·0004	3·2	7- 8-1938	
0·12	0·0004	2·3	23- 6-1938	
0·12	Very small	1·5	3- 7-1938	
0·12	0·0004	1·1	8- 8-1938	
0·12	0·0004	7·0	14- 9-1938	Mild thunderstorm with rain
0·10	0·0003	2·0	14- 7-1938 to 20- 7-1938	
0·08	0·0004	3·6	2-10-1938 to 4-10-1938	Thunderstorm with rain
0·08	0·0004	6·9	6-10-1938	

From Table 1 it is evident that while the maximum amount of nitrate is obtained in rain associated with thunderstorm, the minimum amount is also associated with the same condition. Moreover, if nitrogen fixation is due to electrical cause we should expect a considerable amount of nitrite in rain water associated with thunderstorm and that the amount should be more or less of the same order as the nitrate concentration in the same sample. But this is not so. These facts show that fixation of nitrogen cannot be attributed primarily to electrical discharges.

The data for Sylhet are also scrutinised below. The data for nitrogen concentration and also the amount of rainfall have been taken from the paper of Das, Sen and Pal (1933). As there was no meteorological observatory in Sylhet, the occurrence of thunderstorm in that place during the period of observation is not known. So, weather in the nearest observatory, Silchar (about 50 miles east of Sylhet) and two other nearby stations, Cherrapunji and Shillong, have been considered instead (Table 2). The data for the occurrence of thunderstorm was obtained from the *Indian Daily Weather Report* published by India Meteorological Department. Further, the normal days of occurrence of thunderstorm have also been considered (Table 3). These normals are taken from the *Climatological Atlas for Airmen.*

From the above tables, it is quite obvious that the amount of nitrates and nitrites in rain water is not dependent upon the occurrence of thunderstorms only.

It appears, therefore, that the fixation of nitrogen is primarily due to some other process, probably photo-chemical in nature. Regarding this point, a suggestion has been made by Angstrom and Hogberg. "The simplest way in which this would occur would be through a photo-chemical process, occurring for instance in small droplets, where

TABLE 2

Date	Rainfall (*inches*)	Nitrates (*parts per million*)	Nitrites (*parts per million*)	Occurrence of thunderstorm		
				Silchar	Cherrapunji	Shillong
8-14 April 1931	1·90	0·237	0·059	..	Thunder-storm	Thunder-storm
15-21 April 1931	7·49	0·050	0·041	..	Do.	Do.
22-28 April 1931	10·73	0·083	0·044	Thunder-storm	Do.	Do.
29 April-5 May 1931	10·38	0·091	0·041	Do.	Do.	Do
6-12 May 1931	10·54	0·082	0·030	Do.	Do.	Do.
13-19 May 1931	4·24	0·115	0·041	Do.	Do.	Do.
20 May-2 June 1931	11·37	0·178	Nil	..	Do.	Do.
3-16 June 1931	9·83	0·091	Do.	..	Do.	Do.
17-30 June 1931	19·50	0·044	Do.	..	Do.	Do.
1-14 July 1931	7·38	0·045	Do.	..	..	Do.
15-27 July 1931	7·08	0·040	Do.	..	..	..
28 July-11 August 1931	11·45	0·091	Do.	..	..	..
12-25 August 1931	5·18	0·040	Do.	..	Thunder-storm	Thunder-storm
26 August-8 September 1931	12·39	0·066	Do.	..	..	Do.
9-22 September 1931	8·29	0·125	Do.	..	..	Do.
23 September-6 October 1931	3·84	0·100	Do.	..	..	Do.
7-20 October 1931	3·19	0·166	Do.	..	..	Do.
21 October-3 November 1931	4·81	0·050	Do.	..	..	Do.
4-17 November 1931	1·92	0·152	Do.	..	..	..
21 January-11 February 1932	1·25	0·352	0·007	..	..	Thunder-storm
12 February-23 March 1932	2·29	0·357	0·015	Thunder-storm	..	Do.
24 March-7 April 1932	0·59	1·000	Nil	Do.	..	Do.

TABLE 3

Normal number of days of thunder in and around Sylhet

January	0 to 1	July	2 to 4
February	1 to 2	August	4 to 8
March	2 to 4	September	4 to 8
April	4 to 8	October	2 to 4
May	4 to 8	November	0
June	2 to 4	December	0

the free nitrogen of the atmosphere, according to the laws of the gaseous absorption of nitrogen in water, must be present to a concentration of about 15 mg/litre. A simple reaction according to the formula given below is possible.

$$12\ N + 18\ H_2O = 4NH_4NO_3 + 4NH_4OH + O_2\ ''$$

Of course they suggest this reaction only after assuming that nitrogen molecule is broken up into nitrogen atoms by some photo-chemical process.

This reaction no doubt explains the result observed by these workers in Sweden, *viz.*, concentration of nitrogen in the form of nitrate is 0·48 times the concentration of nitrogen in the form of ammonia. But it is not known, and does not seem to be possible, that by the photo-chemical process nitrogen molecule will break up into atomic nitrogen, *i.e.*, $N_2 = 2N$, also does not appear as an effect by any radiation received from the sun. When, however, two nitrogen atoms combine they give out an energy corresponding to the wave number 50, 700 cm^{-1}. If at all nitrogen molecule is supposed to be breaking up into atoms by photo-chemical process by a radiation of this wave number, it means that very short ultraviolet waves are required for the process. Such a wave does not reach the troposphere. So that the first assumption of the reaction, that nitrogen molecule breaks up into nitrogen atoms by some photo-chemical reaction does not appear to be correct.

Moreover the concentration of nitrogen as ammonia is also not in any way related to that of nitrogen as nitrate. In Sweden, the proportion of the two was of course constant and the value was 2:1. In Sylhet the value obtained was 1:0·82. It was stated by Dr. E. J. Russel (1915) in a discussion on this subject that ammonia is sometimes not present in rain water collected in light houses remote from land. So we see that this observation goes contrary to the reaction suggested by Angstrom and Hogberg.

In this connection, Virtanen (1952) has checked up all the available data in the literature and has shown diagrammatically that the inter-relationship between the amounts of NO_3—N and NH_4—N is not fixed. So that the common cause of origin of nitrates and ammoniam compounds in rain water cannot be suggested.

In the light of above discussion it is obvious that the mechanism of the formation of nitrates in the atmosphere is quite complicated. Adel and Lampland (1938) have detected spectroscopically the presence of N_2O_5 in the ozonosphere. It seems quite possible that this N_2O_5 is formed by some photo-chemical process. This may be the source of fixed nitrogen in the atmosphere. But it is not known how this N_2O_5 is carried down to the troposphere. In the lower atmosphere, electrical spark discharge may have some effect, but it is not primarily responsible for the formation of nitrates in rain water and we must search for some other mechanism. The author is of the same opinion as Virtanen (1952) that the determination of nitrogen compounds at different altitudes is indispensable for gaining information of the nitrogen fixation in the atmosphere. "This work is difficult in method, but as far as I can see there is no other way."

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