Composition of Atmospheric Precipitation

I. Nitrogen compounds

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Introduction

The purpose of this paper is to present a survey of published data on chemical analysis of atmospheric precipitation; to discuss different cycles proposed for inorganic compounds in atmospheric precipitation and, finally, to assess the importance of these compounds from different points of view. Investigations of rainwater with a view to determine atmospheric pollution in industrial areas will be mentioned incidentally but no results will be given in detail as they concern only small areas and abnormal conditions. The literature on this special subject is, furthermore, rather voluminous and should well deserve a separate review.

A. Historic review

The historic review presented below is largely built on existing reviews [see e. g. MILLER (213, 214), RUSSELL & RICHARD (254) and WAY (298)[1]] and will therefore not contribute anything new. The history of the research on chemical compounds in rain and snow is the history of the research on nitrogenous compounds in atmospheric precipitation. For a long time ammonia and nitrate nitrogen were the only compounds of interest while analysis for compounds like sulfate, alkali and alkaline earth metals have been carried out practically only for the last three decades. Chloride takes an intermediate position.

The first discovery of nitrate in rainwater was made by the German chemist MARGGRAF in the winter 1749—50 and in 1780—90 it was rediscovered by a Swede, TORBERN BERGMAN. In the beginning of the 1800's DE SAUSSURE in France showed the presence of ammonia in the atmosphere. Thus the two compounds of greatest interest were known to be present in the atmosphere at a time when the revolution in agricultural chemistry took place.

This revolution was mainly due to two other very important discoveries. In 1799 a Dutch, JOHAN INGENHOUSS, published his studies about the assimilation of CO_2 from air by plants and five years later DE SAUSSURE in France showed that inorganic constituents of plants were taken up by the plant roots from the soil. These two discoveries founded our present concepts of plant nutrition but it took, however, about half a century before they were accepted in the scientific world.

An important man in conveying these ideas

[1] References are listed in a bibliography to be published at the end of the second part of this study.

was no doubt JUSTUS VON LIEBIG although his role to a great extent was that of a propagandist. The actual outline of modern agricultural chemistry was made by another German, CARL SPRENGEL. At about the same time also BOUSSINGAULT in France, although leaning towards the old humus theory of plant nutrition, made a valuable contribution through some classical field experiments. Among other things he observed the difference between legumes and non-legumes with respect to nitrogen; the legumes were able to use atmospheric nitrogen for their nutrition. Despite of many years work he failed to find the reason for this difference.

BOUSSINGAULT was also the first to make analyses of rainwater in order to estimate the yearly contribution of combined nitrogen from rainwater.

In 1840 LIEBIG published his well-known "Die organische Chemie in ihre Anwending auf Agrikultur und Physiologie". In this work he strongly criticizes earlier concepts of plant nutrition and stated the modern concepts. In a later edition he changed his views on the uptake of nitrogen by plants. As he had found ammonia in plant sap he concluded that this compound, which was then known to be present in the atmosphere, was assimilated by the plants directly from the atmosphere in the same way as carbon dioxide. This was, of course, a rather obvious conclusion at that time. It may be of interest to cite him in a letter to "Revue Scientifique et Industrielle" given in English translation in the Farmer's Magazine (182). He states — "if the soil be suitable, if it contains a sufficient quantity of alkalies, phosphates and sulfates, nothing will be wanting; the plants will derive their ammonia from the air as they do carbonic acid. We know well that they are endowed with the faculty of assimilating these two aliments; and I really cannot see why we should search for their presence in the manures we use".—"Ammonia added with the manure may be useful but is certainly not necessary."

His quoted data on the amount of combined nitrogen which was brought down to the soil yearly with precipitation was very high, 27 kg/ha (1 ha = 10^4 m^2), and it was mainly this figure which initiated the many long-termed research projects on combined nitrogen in rainwater which were carried out during the later part of the 19. century. Among these the work carried out at Rothamsted is probably best known. (See LAWES & GILBERT (171), LAWES, GILBERT & WARINGTON (173, 174), MILLER (213), RUSSELL & RICHARD (254), WARINGTON (296), WAY (298, 299, 300). During the discussion which took place LIEBIG's theory about ammonia in plant nutrition was turned down on the basis of data from field experiments at Rothamsted [LAWES & GILBERT (171)], and his estimate of combined nitrogen in rainwater was shown to be too high as the yearly data from Rothamsted showed.

It is very probable that this controversy between LIEBIG and the Rothamsted scientists, combined with the increasing interest in the new concepts of plant nutrition, initiated many of the investigations which were carried out in Europe during this period. As will be shown below, similar investigations in U.S.A. were started much later.

Most of the inorganic compounds present in rainwater were known before 1850, but naturally, they did not arouse the same interests as nitrogen.

B. Nitrogen compounds in rainwater

1. Introduction

Most of the investigations carried out on rainwater concern nitrogen compounds, most frequently ammonia and nitrate, although a few cases also included nitrite and organically bound nitrogen, generally called albuminoid ammonia. Most of these investigations were carried out in the period 1870—1920. Fig. 1 shows the frequency of such investigations during successive 10-year periods, the frequency being given as the total number of years of investigation within each period. It will be seen from this figure that a maximum occurs in 1881—1890. The distribution for Europe is, further, approximatly normal while for other countries it is asymmetrical, starting with a relatively great number of years of investigations in the 1881—1890 period. In the period 1911—1920 there is a minimum in the number of investigations in Europe, probably connected with the occurrence of the first world war.

The contribution from Rothamsted is seen to take a central part in the distribution.

2. Nitrogen as ammonia and nitrate

a. Sampling and analytical errors

Before discussing the results some remarks on the sampling, the analytical methods and their errors will be made.

There are obviously two groups of errors which can be introduced; one group consists of errors due to the sampling technique and the storage of rainwater samples; the second group consists of errors in the analytical procedure used.

The sampling errors can be classified into inevitable errors and non-inevitable errors. Dust carried from the soil to the atmosphere (cyclic dust) and precipitated together with rain is an inevitable source of error as the dust particles may carry with them absorbed ammonia and nitrate or organic nitrogen compounds which are liable to give off their ammonia to the rainwater during the analytical procedure. The magnitude of this source may be considerable but is difficult to estimate. Existing data on yearly income of nitrogen compounds with the atmospheric precipitation may represent the total income but not the net amount, which from an agricultural point of view is of greater interest.

Cyclic dust seems to be the only inevitable error. Sampling errors which can be avoided include

a. Bird droppings.
b. Losses of ammonia from the sampling device due to aeration.
c. Transformation of the nitrogenous compounds in the sampling device by reactions with the sample and the material of the device or by microbiological activities during storage.

Bird droppings can produce errors in two ways, firstly by giving off nitrogen compounds as ammonia or as nitrate during the storage or the analytical procedure, and secondly by giving off substances which interfere with the analytical method used. In the second case it is, however, an error of the analytical method.

Bird droppings certainly can increase the content of nitrogenous compounds in rainwater. JOHNSON (154) compared protected and unprotected gauges and found that the bird droppings in the unprotected gauge raised

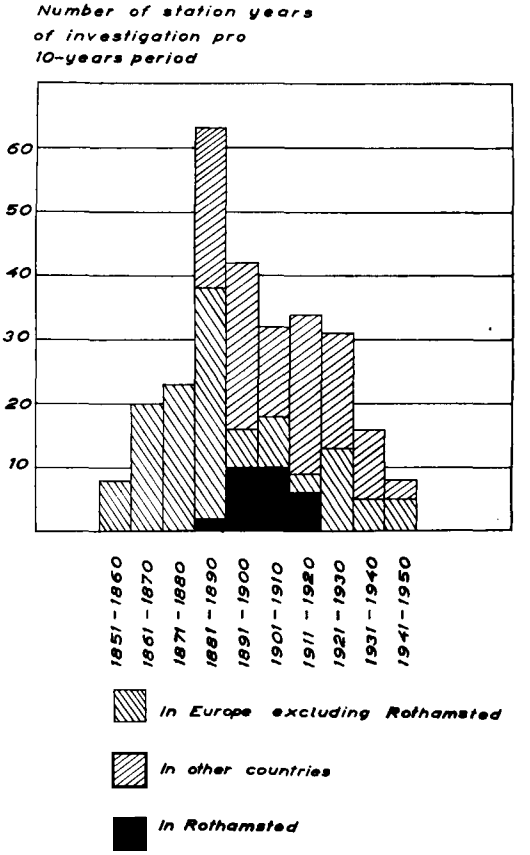

Fig. 1. Number of years of investigation (station-years) on nitrogen compounds in precipitation for successive 10-year periods.

the ammonia content considerably. The nitrate content was not materially affected.

HARRISON & WILLIAMS (133) found definitely higher nitrogen contents when using copper funnels for sampling rainwater than when using glass funnels. They explained this as due to a greater contamination by bird droppings in the copper funnels. The birds found the copper funnels suitable as a resting place while they probably got scared by the light reflections in the glass funnels.

The error produced by bird droppings will, of course, depend upon the population density of birds at the place concerned and further upon the habits of the different species present. At seaside places the errors caused by birds may be very great. In the second paper by MILLER (214) concerning investigations of rainwater from the west coast of Scotland several

samples were contaminated, apparently by bird droppings, to such a degree that the analyses and to be excluded. In inland places the errors due to bird droppings may not be great. A simple and effective device for preventing birds from using sampling gauges as resting places has recently been described.[1]

Losses of ammonia by aeration can be prevented by a suitable design of the collecting gauge. If the rainwater reacts with the material of the gauge the pH of the liquid will generally rise and thus enhance the ammonia losses.

Reactions between the sampling gauge and the rainwater have been studied to some extent. CROWTHER & STUART (82 *cf.* 81) found that copper containers were likely to neutralize rainwater, especially acid rainwater and in the above mentioned Swedish investigation it has been shown that galvanized iron in sampling gauges is liable to cause large errors due to reactions between Zn and water. As $Zn(OH)_2$ is formed, the pH will increase to such values that losses of ammonia can occur; further the hydrogen formed in this reaction is very active and reduces nitrate almost quantitatively to ammonia even when present in such low concentration as in rainwater.

Microbiological activities may occur during storage of rainwater. HANSEN (130) found that toluol was effective in preventing microbiological activity during storage. In many cases lead-lined gauges have been used. The small amounts of lead which go into solution are then sufficient to prevent microbiological activities during storage. This type of container was used in Rothamsted.

The analytical errors are due entirely to unsuitable methods for the analysis of ammonia and nitrate in rainwater. The most common methods for these compounds are colorimetric, using Nessler's reagent for the determination of ammonia, and phenoldisulphonic acid for the nitrate. The Nessler reagent is rather sensitive to the organic compounds always present in rainwater. If the determination is made directly in the rainwater, by adding the reagent, large errors can be produced, the magnitude and sign of which will depend on the special type of reagent which can be made up in a number of ways. ROMELL (251) has recently shown that water contaminated by pollen interferes with the Nessler reagent in the direct determination to a very high degree probably due to formaldehyde given off by the pollen grains. Many investigations have been carried out using this straight forward procedure and their results may be misleading. It is, further, probable that the errors are systematic and positive so that the given data are too high.

An indirect method using the Nessler reagent was used at Rothamsted. The ammonia in the rainwater was distilled off and the ammonia determined in the distilled portion by the reagent. This method, which has also been used in other places, gives quite reliable values. The ammonia in the distilled portion can also be determined by titration provided special care in taken during the distillation. This method has been used by HANSEN (130, 131) in Denmark and must be regarded as highly reliable.

The direct determination of nitrate by the phenol-disulphonic acid has been widely used but is not satisfactory as losses of nitrate may occur during the procedure (130). In older investigations of this type the nitrate figures may therefore be too low. In Rothamsted WARINGTON (296) introduced a new method of determining nitrate by reducing it to ammonia by a copper-zinc couple, followed by distillation and estimation of the ammonia by the Nessler reagent. Later Devarda's alloy was used for the reduction. This process seems to be quite satisfactory and has been used also in other places. The technique of using ion exchange resins in the sampling of atmospheric precipitation was described in the paper by Egnér and coll. cited in footnote on this page.

It is, of course, difficult to divide published rainwater nitrogen data into a reliable and an unreliable group based on the analytical methods used. In many cases no statement concerning the method is given, in other cases the data seem quite normal despite less satisfactory methods. There are so many factors involved (including the sampling factors) that rejection of data on the basis of unsatisfactory analytical methods cannot be done. The best way is to point out the most reliable investigations, basing the discussion mainly on these, leaving the rest as "probable" or in single cases as "quite improbable".

[1] EGNÉR, ERIKSSON and EMANUELSSON, 1949, Ann. Agr. Coll. Sweden *16*, 593—602.

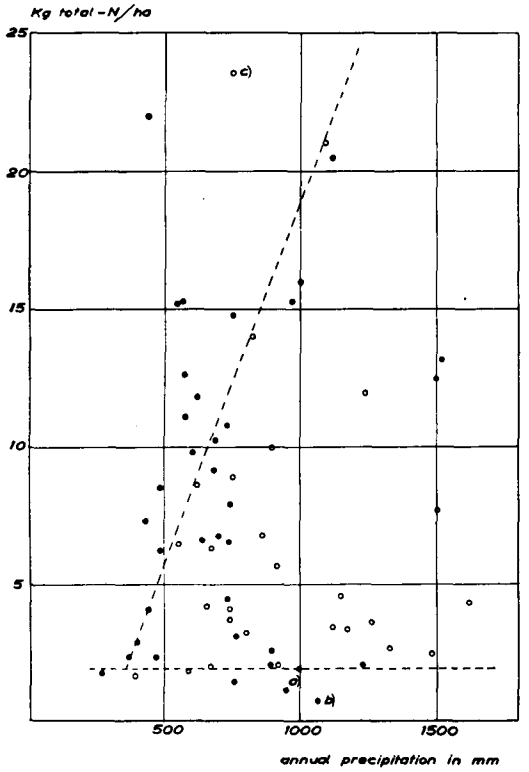

Fig. 2. The average yearly amounts of total nitrogen in precipitation plotted against the yearly precipitation.
Filled circles: European places.
Open » : non-European places.

b. Results

A survey of data up to 1900 has been given by MILLER (213). The investigations published since then do not change the general impression although they are quite numerous. For the sake of completeness existing data have been compiled; the averages for different periods and places being summarized in tables 1—3.

The results in tables 1—3 have been arranged diagrammatically in figs. 2 and 3 to show the distribution of yearly amounts as a function of the rainfall. In these figures a division between European and non-European places has been made.

The total nitrogen as ammonia and nitrate shows a very wide variation (fig. 2). There is a fairly marked minimum level of around 1.9 kg N/ha and year and it may be concluded that this is probably the smallest amount which is brought down by precipitation (except in deserts). The two exceptionally low values marked a) and b) in fig. 2 belong to coastal stations at Vifelstadir, Iceland, and Butt of Lewis in the Hebrides. It appears to be possible to draw another boundary for the distribution (the sloping line) which can be interpreted as the maximum nitrogen amount for a given yearly rainfall outside Europe. It is seen from fig. 2 that this maximum amount is greater in Europe than in other places. The places which lie above the sloping line are with one exception from Europe, namely from Russia, Germany (five from 1860—70 and one from 1928—35) and Denmark. The exceptionally high value c) comes from Buenos Aires. In the Danish investigation (HANSEN 129) the analyses were very accurate so there can be no analytical error involved, further there cannot be any great immediate contamination from industry.

The nitrate-nitrogen distribution is shown in fig. 3 and it will be seen that the minimum amount is not so distinct as in the case of total nitrogen. The sloping line of the maximum amount is, however, much more distinct than in fig. 2. On the other hand there is no marked difference between European and non-European places although there is a slight indication. The exceptionally high value a) is from an old German investigation (PROSKAU 1864).

It should be mentioned that the division of the data into a European and a non-European group has significance only from the point of density of population and industrial activities. Another possible division is tropical and non-tropical places; this is, however, of but little value as the investigations carried out in tropical places are rather few and incomplete. This can be seen in fig. 4, where the amount of total

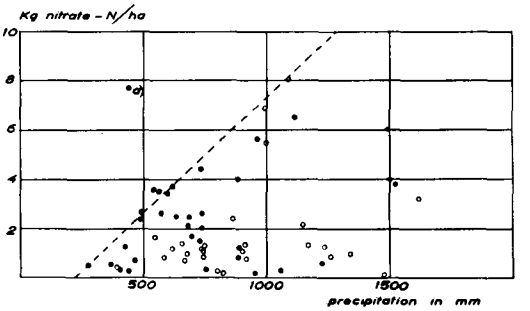

Fig. 3. The same as fig. 2 for nitrate nitrogen.

Table 1. Ammonia and nitrate nitrogen in precipitation in Europe

Ref.	Place	Period	Precip. in mm	mg N/l			kg N/ha		
				as H_3N	as NO_3	as tot. N	as H_3N	as NO_3	as tot. N
	Austria								
103	Feldkirch	1876	—	2.79	1.76	4.55	—	—	—
194	S:t Michael	1885—1887	1,114	1.17	.67	1.84	13.03	7.44	20.47
	Belgium								
235, 236	Gembloux	1889—1893	693	1.14	.35	1.49	7.92	2.39	10.31
146	Bulgaria		—	—	—	—	11.86	.96	12.82
	Denmark								
291	Copenhagen	1880/81—1884/85	577	1.91	.45	2.36	11.00	2.62	12.62
131	Askov	1922/23—1926/27	740	.71	.35	1.06	5.25	2.63	7.88
131	Blangsted	1925/26	600	1.07	.57	1.64	6.44	3.41	9.85
131	Spangsbjerg	1925/26	730	.88	.60	1.48	6.42	4.39	10.81
131	Hornum	1925/26	495	.74	.54	1.28	3.66	2.65	6.31
	Finland								
112	Storkyrö		—	—	—	—	1.8	—	—
	France								
176	Methroy	1877	760	.41	—	—	3.1	—	—
179—181	Montsouris	1876—1900	545	2.13	.66	2.79	11.60	3.60	15.20
	Germany								
213	Liebwerd, Bohemia	1877/78	620	1.3	.61	1.91	8.05	3.78	11.83
213	Peček »	1883/84, 1885/86	490	1.26	.50	1.76	6.17	2.45	8.62
53	Ida-Marienhütte	1865—1870	580	—	—	1.88	—	—	11.10
314	Kushen	1864/65—1865/66	369	.48	.16	.64	1.77	.59	2.34
314	Insterburg	1864/65—1865/66	642	.65	.39	1.04	4.15	2.49	6.64
314	Dahme	1865	427	1.42	.30	1.72	6.07	1.28	7.35
314	Regenwalde	1864/65—1865/66	568	2.08	.62	2.70	11.82	3.52	15.34
314	Proskau	1864/65	445	3.21	1.73	4.94	14.29	7.70	21.99
255	Weihenstephan	1928—1935	750	—	—	1.97	—	—	14.80
	Great Britain								
254	Rothamsted	1888—1916	730	.41	.20	.61	2.98	1.48	4.46
81	Garforth, Leeds	1906—1909	685	1.04	.32	1.36	7.09	2.16	9.25
214	Laudale, Ardgour	1907	2,250	.14	.06	.20	3.12	1.41	4.53
214	Barrahead, Berneray	1910—1913	895	.15	.14	.29	1.30	1.24	2.54
214	Shilay, Mon. Islands	1910—1913	1,230	.12	.05	.17	1.41	.66	2.07
214	Butt of Lewis, Stornoway	1908—1913	1,060	.04	.03	.07	.40	.34	.74
	Holland								
144	Groningen	1910—1912	700	.72	.24	.96	5.05	1.68	6.73
177	Hilversum (aver. of 6 places)	1932—1937	—	—	—	—	3.8	.7	4.5
	Iceland								
214	Vifelstadir	1911—1912	949	.09	.03	.12	.86	.28	1.16
	Italy								
24	Florens	1869—1875	970	1.00	.57	1.57	9.70	5.55	15.25
24	Vallombrosa	1872—1875	1,520	.62	.25	.87	9.40	3.80	13.20
232, 233	Scandicci	1888—1890	740	.61	.27	.88	4.55	2.00	6.55
21	Catania (outside town)	1889/89	466	.33	.16	.49	1.52	.75	2.27
	Norway								
252	Ås	1864/65	670	.31	—	—	2.1	—	—
51	Trondhjem	1928/29	889	.13	.10	.26	1.17	.87	2.04
51	Voll (7km east of Trondhjem)	1928/29	758	.14	.05	.19	1.06	.38	1.44
	Russia								
239	Odessa	1903	275	.49	.18	.67	1.35	.50	1.85
292	Novosil	~ 1905	—	—	—	—	—	—	7.50
164	Taschkent	1945/46—1946/47	~ 400	.6	.1	.7	2.5	.4	2.9
301, 302	Ploty	1900—1903	445	.85	.06	.91	3.88	.27	4.15
	Sweden								
106	Flahult	1909	827	.45	.18	.63	3.72	1.46	5.18
	Switzerland								
120—124	Basel	1870/71	890	—	.46	—	—	4.05	—

Table 2. Ammonia and nitrate nitrogen in precipitation in Asia, Australia, New Zealand and Africa

Ref.	Place	Period	Precip. in mm	mg N/l			kg N/ha		
				as H_3N	as NO_3	as tot. N	as H_3N	as NO_3	as tot. N
	Asia								
	East Indies								
200	Pasoeroean, Java	1891/92	920	.14	.09	.23	1.27	.79	2.06
250	Sumatra, Deli	1925—1940	2,045	—	—	1.5	—	—	30.4
80	Malaya	1941	—	—	—	—	—	.10	—
	India								
243	Allahabad	1932	—	.50	.88	1.38	—	—	—
213	Calcutta	1891	1,170	.17	.12	.29	2.00	1.34	3.34
137, 175	Cawnpore	1904/05	1,260	.22	.06	.28	2.73	.85	3.58
137, 175	Dehra Dun	1904/05	2,220	—	—	.18	—	—	4.02
213	Madras	1888—1893	995	—	—	.19	—	—	1.91
86	Sylhet	1931/32	3,950	.13	.09	.22	5.06	3.74	8.80
17, 60	Hanoi, Tonkin	1902—1909	1,650	.79	2.94	3.73	13.0	48.5	61.5
18	Ceylon,	1898/99	2,090	.20	.07	.27	4.09	1.43	5.52
162	» Peredeniya	1941/42—1942/43	2,850	.27	.18	.45	7.82	5.22	13.04
	Japan								
157	Tokio	1883/84	1,337	.13	.07	.20	1.67	.97	2.64
216	»	1938	—	.58	—	—	—	—	—
216	Kobe	1938	—	.28	—	—	—	—	—
216	Hamamatu	1938	—	.19	—	—	—	—	—
	Australia								
56	Brisbane, Queensland	1908	1,150	.22	.19	.41	2.48	2.14	4.62
56	Roma, »	1908	660	.42	.21	.63	2.77	1.37	4.14
	New Zealand								
125	Lincoln, Canterbury	1884—1887	755	.08	.17	.25	.56	1.27	1.83
	Africa								
156	Bloemfontein, South Africa	1910/11—1911/12	550	.87	.30	1.17	4.76	1.67	6.43
156	Cedera » »	1912	680	.78	.14	.92	5.27	.97	6.24
156	Durban » »	1911—1912	910	.47	.15	.62	4.23	1.39	5.62
156	Grahamstown, » »	1911/12	590	.18	.14	.32	1.05	.82	1.87
156	Kokstad » »	1912	670	.19	.11	.30	1.25	.75	2.00
149	Pretoria » »	1904/05	620	1.19	.20	1.39	7.40	1.21	8.61
44	Mauritius	1895	(1,500)	(.43)	(.40)	(.83)	6.45	6.00	12.45
191	»	1938	1,002	3.38	—	—	3.80	—	—
222	Reunion	1886—1887	(1,000)	—	.69	—	—	(6.9)	—

nitrogen and nitrate nitrogen is plotted against the latitude of the place in question. It will be seen that the tropical zone is so poorly represented that it is difficult to make a fair comparison between this zone and the temperate ones. Fig. 4 is interesting, however, as it shows a very high frequence of large total nitrogen values in the northern hemisphere. The nitrate nitrogen seems to be fairly evenly distributed throughout all the zones.

Returning to figs. 2 and 3 the sloping border lines suggest that the variation in maximum nitrogen amount tends to be proportional to the amount of precipitation, or, expressed in a different way, that the maximum concentration of nitrogen is independent of the annual amount of rainfall. The significant difference between European and non-European places is that the maximum nitrogen concentration in European rainfall is able to reach somewhat higher values than in non-European. For nitrate nitrogen there is no such pronounced difference (fig. 3).

As the nitrate nitrogen does not show any pronounced difference in the distribution between European and non-European places the difference in fig. 2 must be due to the ammonia nitrogen; the ammonia nitrogen

Table 3. Ammonia and nitrate nitrogen in precipitation in America

Ref.	Place	Period	Precip. in mm	mg N/l			kg N/ha		
				as H_3N	as NO_3	as tot. N	as H_3N	as NO_3	as tot. N
	North America								
271—275	Ottawa, Canada	1908—1924	860	.51	.28	.80	4.43	2.39	6.82
310	Alfred, N.Y. U.S.A.	1923/24—1924/25	820	1.67	.03	1.70	13.70	.28	13.98
310	Brockport » »	1923/24—1925/26	800	.36	.03	.39	2.91	.26	3.17
75	Geneva » »	1919—1928	900	.99	.12	1.11	8.91	1.07	9.98
332, 335	Ithaca » »	1915/16—1925/26	750	1.07	.12	1.19	8.00	.91	8.91
110	Goodwell, Oklahoma U.S.A.	1930	390	.28	.12	.40	1.11	.48	1.59
115	Kentucky, six places U.S.A.	1922/23	1,090	1.19	.74	1.93	13.00	8.02	21.02
104	Manhattan, Kansas U.S.A.	1886/87—1889/90	740	.39	.16	.55	2.87	1.16	4.03
15, 115, 117, 160, 161, 234, 246, 269, 290, 305, 306, 313,	Mont Vernon, Iowa U.S.A. (8 years)	1912/13—1931/32	740	.35	.15	.50	2.63	1.08	3.71
102	Salt Lake City, Utah U.S.A.	1891—1893	—	—	—	—	5.65	.40	6.05
289	Missouri, U.S.A.	1894—1895	1,120	.24	.07	.31	2.63	.82	3.45
	West Indies								
133	Barbados	1886—1889	1,620	.07	.20	.27	1.12	3.24	4.36
61	Trinidad	1901—1912	1,480	.16	.01	.17	2.37	.10	2.47
	South America								
134	Georgetown, Br. Guiyana	1890—1909	2,520	.05	.08	.13	1.13	2.06	3.19
196, 222	Caracas, Venezuela	1889/90, 1895	(1,000)	1.55	.55	2.10	(15.5)	(5.5)	(21.0)
268	Montevideo, Uruguay	1912	1,504	.24	.27	.51	3.68	4.03	7.71
58	Buenos Aires, Argentine	1906	750	2.96	.18	3.14	22.2	1.33	23.53

content varies more in Europe than in other places.

The proportions of ammonia to nitrate nitrogen is shown in fig. 5, arranged in the same way as in fig. 4. It has been concluded by MILLER (213), that trophical rains contain a higher percentage nitrate nitrogen than non-tropical. As seen in fig. 5 this seems to be true when comparing zones II and III and is probably due to the earlier mentioned greater concentration of ammonia in European rainfall. Comparing zones III and IV it seems, however, that there is no reason to believe the proportions to be really different. As a matter of fact there are only two places in the tropical zone that show a low ammonia percentage.

In this connection it should be mentioned that some investigations show an abnormally high ammonia percentage, especiellly those carried out in the state of New York, U.S.A. There is probably some error involved, either in the sampling or the analysis which have led to a reduction of nitrate to ammonia, or in the analysis, in which contamination present has affected the ammonia figures. The second explanation is more probable. It has been pointed out earlier by ROMELL (251), that the ammonia figures from these places are abnormally high and he suggested interferences in the direct determination of ammonia by Nessler's reagent, caused by substances given off by pollen grains in the rainwater samples.

It is difficult and probably not justified to work out an average of nitrogen brought to the soil by rainwater in different parts of the world as the variation between different places probably is more significant than an average.

c. Monthly variation

The amount of combined nitrogen brought to the soil with the rain each month will vary not only with the rainfall but also with the general climatic conditions and the habits and occupation of the population. For some of the

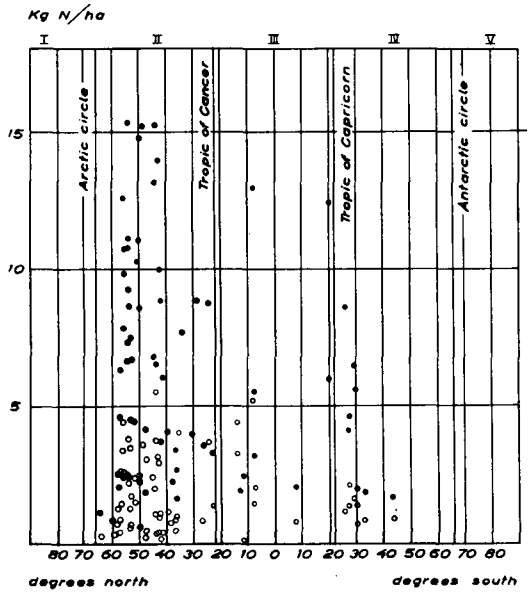

Fig. 4. The average yearly amounts of total nitrogen and nitrate nitrogen for different places plotted against their latitude.
Filled circles: total nitrogen.
Open » : nitrate »

places recorded in tables 1—3 monthly averages are given and a few representative investigations of these are shown in table 4.

In Gembloux, a place where atmospheric pollution is fairly high, the monthly amount of nitrogen is fairly well correlated with the monthly amount of rainfall. The season has, however, also a direct influence on the amounts. This can already be seen from the figures in the table and is clearly shown by statistical analysis. Assuming that the relationship between amount and precipitation is linear and the seasonal influence is a simple periodic one, the relation arrived at reads

$$N = 0.274 \cos 30\,(T + 0.3) + 0.0143\,p - - 0.166 \quad \text{(A)}$$

where N is the amount of ammonia nitrogen in kg/ha/month, T is the number of the month starting with January equal to zero and p is the monthly rainfall in mm. The argument of the cosine function is expressed in degrees. Thus, there is a higher ammonia content in the precipitation in winter than in summer which may be due to an increased coal combustion during the winter.

In Rothamsted there is a maximum in the amount of ammonia nitrogen in August and a minimum in February. The influence of the rainfall is obscured by the fact that it also varies periodically showing a maximum in October. The ammonia concentration during different months (weighed averages, not given in the table) shows, however, two maxima, one in the spring and one in the late summer as a generally somewhat higher level during the warm season than during the cold.

A significant feature for Ottawa is that the rainfall varies very little from month to month. The variation in the amounts of ammonia nitrogen can therefore be ascribed mainly to seasonal influences. An analysis of the data gives a relation which reads

$$N = 0.150 \sin 30\,(T - 4.1) + 0.099 \sin 60\,(T - 1.5) + 0.368 \quad \text{(B)}$$

and is graphically illustrated in fig. 6. The seasonal variation has thus been resolved into two components, the first of which follows the expected yearly temperature of the air at such a place. The second one has two periods within the year with maxima in spring and autumn just as indicated by the figures on the ammonia content in Rothamsted. Both of the

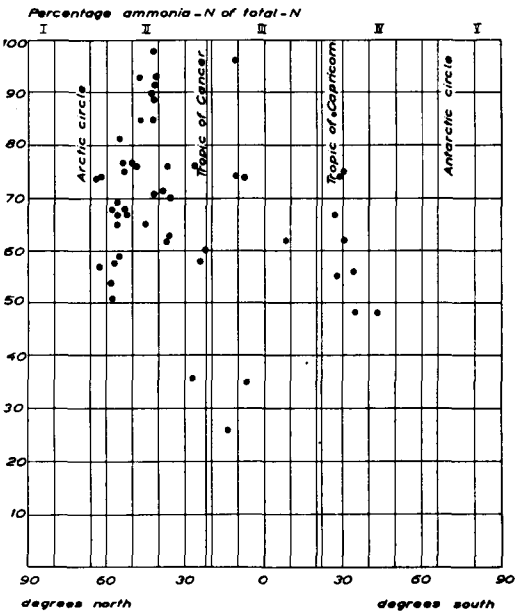

Fig. 5. The percentage ammonia nitrogen of total for different places, plotted against their latitude.

Table 4. Monthly distribution of amounts of nitrogen compounds in precipitation in a few representative places

Ref.	Place and item	Jan.	Febr.	March	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
235	Gembloux												
	H_3N—N, kg/ha...	.54	.23	.79	.57	.53	.81	.81	.97	.42	.89	.76	.61
	NO_3—N, kg/ha...	.19	.03	.15	.18	.32	.26	.29	.33	.17	.23	.15	.11
	rainfall, mm.....	44	13	51	46	59	93	104	85	45	62	52	42
254	Rothamsted												
	H_3N—N, kg/ha...	.21	.19	.23	.23	.26	.27	.28	.31	.24	.26	.25	.25
	NO_3—N, kg/ha...	.10	.10	.11	.11	.13	.13	.12	.15	.12	.18	.12	.13
	rainfall, mm	55	51	61	43	51	64	61	72	48	82	67	78
275	Ottawa												
	H_3N—N, kg/ha...	.21	.15	.22	.43	.43	.40	.33	.53	.51	.61	.35	.25
	NO_3—N, kg/ha...	.14	.17	.17	.26	.19	.22	.28	.31	.17	.20	.14	.13
	rainfall, mm	81	64	72	65	74	72	70	74	68	80	69	71
133	Barbados												
	H_3N—N, kg/ha...	.06	.05	.05	.05	.06	.08	.17	.23	.12	.10	.11	.06
	NO_3—N, kg/ha...	.12	.10	.10	.10	.21	.18	.30	.40	.21	.23	.50	.31
	rainfall, mm	76	52	42	30	93	114	177	257	203	141	208	117
133	British Guiyana												
	H_3N—N, kg/ha...	.10	.16	.18	.19	.20	.11	.11	.19	.01	.07	.17	.09
	NO_3—N, kg/ha...	.33	.26	.12	.18	.27	.34	.32	.15	.08	.06	.17	.19
	rainfall, mm	336	259	184	205	312	328	278	173	64	51	142	380
162	Peredeniya												
	H_3N—N, kg/ha...	.57	.11	.75	.26	.46	.36	.21	.87	1.75	.55	1.23	.70
	NO_3—N, kg/ha...	.16	.34	1.09	.29	.88	.58	.15	.30	.43	.33	.54	.13
	rainfall, mm	64	45	146	279	603	296	112	183	203	349	359	226

sine functions in relation (B) are statistically significant. It would be of interest to see if this distribution of ammonia nitrogen might be related to the occurrence of forest fires.

In the tropical places Barbados, British Guinea and Peredeniya the variation in rainfall is very great and obscures the direct influence of the season. A correlation between the amounts and the rainfall is indicated by the data.

The nitrate nitrogen does, in general, show less influence of the season than ammonia but is fairly well correlated with the rainfall. From the Ottawa figures it can be seen, however, that there is a certain seasonal influence. A relation of type (B) for nitrate nitrogen reads

$$N = 0.070 \sin 30\,(T - 2.6) + 0.022 \sin 60\,(T + 0.3) + 0.199 \quad \text{(C)}$$

both sine functions being statistically significant although the contribution from the second one is rather small. The maximum due to the first component occurs between June and July; it differs from the ammonia relation in that respect by one and a half month. The maxima of the second component occurs in February and August. Its significance from meteorological point of view is doubtful.

d. Yearly variation and trends

The variation of the yearly amounts of nitrogen compounds at a certain place is in general fairly large. This may be due to a number of factors such as yearly rainfall, prevailing winds and the habits and occupation of the population dwelling in or around the place in question. These factors vary periodically but some may have a very long period and give rise to what is called yearly trends. A closer study of these trends necessitates long-termed series of observation, especially when the yearly variation is large.

At two places, namely at Rothamsted and in Ottawa, the yearly amounts of ammonia

and nitrate nitrogen in precipitation have been estimated for relatively long periods. In Ottawa (from 1908 to 1924) the yearly amounts have a tendency to increase with time. This increase is especially noticeable for the last four years. The average amount of ammonia nitrogen for the first ten years is 3.88 kg N/ha while the average for the whole period (17 years) is a high as 4.40 kg N/ha. The increase is probably due to increasing human activities. For nitrate nitrogen no trend at all is detectable.

At Rothamsted (from 1888 to 1916) the amounts of ammonia does not show any clear trend but the nitrate nitrogen, as was also pointed out by RUSSEL and RICHARD (254) increases slowley but steadily with time. The reason for this increase may be difficult to find.

In the period 1908 to 1916 the two series overlap. There is, however, no obvious correlation neither between the amounts of ammonia nor between the amounts of nitrate at the two places. This is also interesting as it shows that the factors reponsible for the yearly variation may be fairly local in extension.

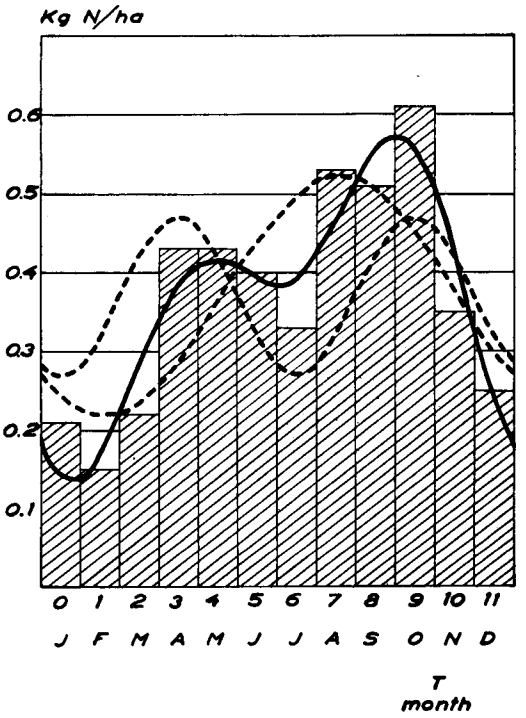

Fig. 6. The monthly amounts of ammonia nitrogen of Ottawa precipitation.
Dashed lines: the two components of the full drawn line mentioned in the text.

3. Albuminoid nitrogen

This name has been assigned to the ammonia released from organic matter in the rainwater when treating it with oxidizing agents, for instance $KMnO_4$, or by Kjeldahl digestion. There are a few data available for albuminoid nitrogen in rainwater. In Mont Vernon, Iowa, (ref. 15, 114, 115, 160, 161, 234, 246, 269, 290, 305, 306, and 313) it is estimated to be 2.7 kg/ha and year as an average for 9 years and at an average rainfall of 755 mm. In Ottawa, Canada, (271—275) the yearly amount was 0.98 kg/ha as an average for 17 years and a rainfall of 860 mm. At Dehra Dun in India (86), the amount for 1931—32 was 6.05 kg/ha at 2,950 mm rainfall. In Rothamsted MILLER (213) has estimated the amount to 1.5 kg/ha/year, the estimate being based on 69 analyses. In New Zealand GRAY (125) found 0,5 kg/ha.

From these scattered data it is seen that the contribution may be considerable in some places. Some of this nitrogen is apparently derived from cyclic dust and, thus, does not contribute anything to the nitrogen economy of the soil.

4. Nitrite nitrogen

The nitrite nitrogen, when reported, is in general very low. In some investigations it is automatically included in the nitrate fraction as the determination of nitrate is made by reducing it to ammonia by a metal alloy. Such a reduction obviously also includes the nitrite.

FAILER and WILLARD (104) tested daily samples of rain in Kansas qualitatively for nitrite. Of 171 samples 75 per cent gave a clear positive reaction, 8 per cent no reaction and the remaining 17 per cent a doubtful reaction for nitrite. The frequency of nitrite present was higher during summer than during winter.

The investigations carried out in Mont Vernon, Iowa, show variations in the daily samples from a trace to 0.051 mg nitrite nitrogen/l or roughly about 10 per cent of the nitrate nitrogen. The same was also esti-

mated at Sylhet, India (86) where the total nitrite nitrogen for a year amounted to 0.46 kg/ha, most of it being delivered during April—June. Analysis of rainfalls near Bombay over a half year period gave nitrite nitrogen contents ranging from traces to 0.002 mg N/l. In Japan (216) the average contents for three places were 0.0027, 0.0040 and 0.0067 mg N/l as nitrite. An old French investigation (69) show comparatively high values, but from the more recent ones quoted here it seems likely that the amounts are relatively low. Some investigations carried out in Australia will be discussed later.

Most of the data quoted here were obtained on samples from single rainfalls, analysed very soon after the precipitation. Hence the figures should be quite reliable.

5. Nitrogen compounds in fog, dew, frost and condensed water from the air

The compositions of these forms of atmospheric precipitation have been investigated to some extent.

a. Fog. In 1853 BOUSSINGAULT (50) found more ammonia and nitrate in fog than in rain. The amount of ammonia ranged from 3—9 mg N/l. This was later confirmed by LEVY (180) who, however, found a low nitrate content in fog. In Belgium PETERMAN and GRAFTIAU (236) made three analyses which gave 2.60, 5.64 and 5.00 mg total-N/l and in Bologna in Italy CASOLI (62) found values ranging from 14—58 mg ammonia nitrogen/l. From Russia it is reported (244) that fog, dew and frost contained two and a half times as much ammonia as did rain and two and a half times less nitrate.

b. Dew. BOUSSINGAULT (50) found as much ammonia in dew as in fog but much less nitrate. In Cawnpore in India (137, 175) the analysis of dew gave 0.85—2.65 mg ammonia nitrogen and 0.51—4.12 mg nitrate nitrogen/l of dew. For the six month period in 1904—05 the amount of ammonia and nitrate nitrogen delivered to the soil by dew amounted to 0.06 kg/ha of each. Also LEVY (180) reported that dew was rich in ammonia.

Recently QUITMANN and CAUER (241) compared the composition of condensation water near the ground with that of rain on the same occasion. They got (two cases)

	H_3N mg/l	NO_2 mg/l
Condensation water .	10.0, 10.0	0.10. 0.05
Rain	1.5, 1.0	0.35, 0.10

which shows a considerable difference in composition between these two forms of precipitation.

c. Frost. The Belgium (236) investigation gives an average of 7.52 mg total nitrogen per litre for five analyses; in Bologna (62) the range of concentration of ammonia in frost was 22.4 to 44.7 mg N/l. Some recent analyses from Germany of MROSE (218) show lower values with a variation ranging from 0—4.8 mg ammonia nitrogen and 0—3.7 mg nitrate notrogen/l.

From all these results it can be concluded that those forms of precipitate which are derived from near the soil surface as a rule are much richer in ammonia than ordinary rainwater.

In this connection some observations on the rate of rainfall and size of raindrops on the ammonia content of rain should be mentioned. As early as 1870 ROSING (252) in Norway observed that a very fine rain (drizzle) had a higher ammonia content than ordinary rain. Later also HANSEN (131) pointed out that a long continous rain falling at a low rate had a higher ammonia content than showers.

6. Origin of ammonia nitrogen in rain

a. *The equilibrium in the air—sea water system*

In connection with his fundamental plant nutrition experiments BOUSSINGAULT suggested that the sea was the source for ammonia in air. His theory was strongly supported by SCHLÖSING who in a series of papers (257—265) discussed this possibility on the basis of his own experimental data. In an introductory paper he outlined the theory as follows: As all plants take up nitrogen only in combined form (nitrogen fixing bacteria were not known that time) and some loss of combined nitrogen occur during the decay processes of plants and animals, the total reserve of combined nitrogen in air must decrease unless there are some processes by which it is brought to the air or converted to combined form. It is known that electric discharges in the air oxidize nitrogen

to nitrate which is carried down in rainwater. This amount can, however, not account for the nitrogen taken up by the plants and lost in drain water; there must exist a big reservoir which can deliver combined nitrogen to the air. This reservoir is the sea which contains relatively large amounts of ammonia. The ammonia cycle is then this: The nitrate in drainage water is carried to the sea where it becomes reduced to ammonia which diffuses into the air and is either absorbed from the air by the soil or even the plants or is washed down by rain. The losses which occur (free nitrogen) during this cycle are compensated by formation of nitrate in electrical discharges.

SCHLÖSING tried to verify his theories experimentally. He determined the equilibrium constant in the air and at different temperatures. Further he analysed air for ammonia and from his results he draw the conclusion that his theory was correct. He also studied the absorption of ammonia by the soil and estimated that about 40 kg ammonia nitrogen was absorbed from air per year and hectare. Further he found that rainfall did not always make the ammonia content of air to decrease. Sometime it even increased after a rainfall all depending on how the equilibrium conditions in the place where the rain was formed differed from the equilibrium conditions near the surface.

His theory was, however, not accepted everywhere. An investigation from Spain (10) indicated that the ammonia content in rain was in general lower when the wind came from the sea and the same was observed also by POSNJAKOV (239) in Russia. In Great Britain MILLER (214) started an investigation on rainwater collected at a number of seaside places and isles on the Scottish west coast and found in general low ammonia contents (see table 1), Similar results have been obtained later by BRAADLIE (51), HANSEN (131), and LEEFLANG (177). Unless the higher inland figures are due to a greater portion of cyclic dust present it is obvious that these observations do not tally with SCHLÖSING's theory about the sea as a source for ammonia in air.

The actual ammonia distribution in the sea is fairly well-known. The concentration at the surface in the temperate and tropical zones has been estimated to 0.03 mg ammonia/l. (WATTENBERG (297) see also BUCH (57). It decreases downwards to around 0.01 mg at 100 m depth and to around 0.005 mg at 200 m depth. Already this gradient could suggest that there is a steady absorption of ammonia from the air by the sea. But the gradient is normally explained in a different way. The nitrate shows an opposite gradient. It is practically zero at the surface but increases downwards to reach a comparatively constant value below 200 m depth. This is due to the content of plankton which is greatest at the surface but which is limited there by the nitrate supply, in this way keeping a relatively high ammonia concentration at the surface. At greater depths the limiting growth factor is light; the nitrate level is therefore greater and that of the ammonia less. This organic life thus acts as a catalyst for the photo-chemical reduction of nitrate to ammonia, the equilibrium being determined by the light intensity. In polar regions and elsewhere where vertical convection takes place no such gradient is observed with the well-known result of an intense plankton production.

From this point of view the concentration gradient of ammonia in the sea does not necessarily indicate a transport of ammonia from the air to the sea.

Calculations by BUCH (57) show on the other hand that at equilibrium with the ammonia content in sea water the concentration of ammonia in air should be only 0.4 $\mu g/m^3$ air. BUCH, however, points outt hat reliable figures on the ammonia pressure at equilibrium have been obtained only at relatively high ammonia concentrations. An investigation at lower concentration would be desirable.

The actual ammonia concentration in air has been determined in a few cases, mostly long time ago. The most reliable results are summarized in table 5. Of these investigations that of LEVY from Montsouris covers a whole year with daily analyses. It is seen that the monthly variation is small and there was no clear trend between different months. In Budapest the values were higher in summer than in winter. The results from Buenos Aires are comparatively high probably due to atmospheric contamination. The figures from Pic du Midi (at 2,900 m altitude) are probably the most realiable ones existing for the ammonia content in uncontaminated air. The average of these is 13.5 $\mu g/m^3$.

Table 5. Ammonia in air

Ref.	Author and year	Place	μg H_3N/m^3	Remarks
179	Levy 1880	Montsouris, France	21—29	
113	Fodor 1881	Budapest, Hungary	39	average
219	Müntz et al, 1882	Pic du Midi, summit, France	7.2—30.3	
58	Buenos Aires 1906	Buenos Aires, Argentine	75—87	monthly averages

The ammonia concentration in air thus appears to be about 30 times higher than the equilibrium concentration calculated by BUCH, and the sea as a source for ammonia in air seems to be out of question, unless it is brought to the air by some other means than pure diffusion. One such possibility is the spray which is known to carry chlorides and other salts from the sea up into the air. If the amounts of different salts brought into the air by spray were in the same proportion as in the sea, however, the amount of ammonia in spray should be very low. If the spray has a different composition from the sea water an enrichment of ammonia in the spray is possible.

As a conclusion it can be stated that all evidence so far is against SCHLÖSING's theory about the sea as the great source for ammonia in air.

b. *The equilibrium in the air—soil system*

In 1872 BRETSCHNEIDER (54) published an account of experiments where he tried to estimate the amount of ammonia absorbed by the soil. These are probably the first experiments of this kind. He relates an earlier discovery by another German, SCHÖNBEIN, who found that H_4NNO_3 was formed on evaporation of water. The conclusions drawn by this discovery was that H_4NNO_3 was synthesized in the plants during their transpiration. BRETSCHNEIDER calculated, however, that a field of red clover would receive only four per cent of its nitrogen in this way. (This was also before the discovery of the nitrogen fixing ability of legumes). He found, further, that water which had been in contact with air contained an excess of ammonia over nitrate and concluded that the excess must have been absorbed from the atmosphere. He then started to investigate the absorption ability of "synthetic" soil and found that a moist mixture of 95 per cent quartz sand and 5 per cent ulmin (a humic acid prepared from sugar) absorbed 46 kg ammonia nitrogen/ha/year. Pure quartz sand absorbed only 1.6 kg and a water surface 0.8 g. His conclusion was that if SCHÖNBEIN's theory was correct the amount of nitrogen fixed in this way was of much less importance than the absorption of ammonia from the air. Very soon it was found, however, that SCHÖNBEIN's theory was incorrect, his results were due to contamination of the air in the laboratory where he made his discovery. But BRETSCHEIDER's results were really important. Similar experiments using acids instead of soil carried out in Rostock (138) in 1879—1891 gave 30.6 kg ammonia nitrogen/ /ha/year and in Tokyo (157) 11.6 kg. SCHLÖSING found, as mentioned before, that the soil absorbed 40 kg.

In 1911 HALL & MILLER (129) in Rothamsted published results of a critical study on the absorption of ammonia from air by acids. They were unable to show that soil could absorb ammonia from the atmosphere in direct experiments. By using two dishes filled with acid, mounted at different heights in the same place, they found, however, that the lower contained generally less ammonia than the upper one which they took as an indication of a steady absorption of ammonia by the soil. To this interpretation it can be objected that the difference in ammonia contents could also be due to differences in the volume of air brought in contact with the dishes. The turbulence of the air is generally increasing with the height above surface. The amount they found absorbed in the dishes were, however, quite low. The results from 1908—09 and 1909—10 for four different fields at Rothamsted are shown below, the amounts are all given in kg per hectare. The dishes were placed at 5 and 105 cm height respectively.

Field	I		II		III		IV	
	Upper	Lower	Upper	Lower	Upper	Lower	Upper	Lower
1908—1909	1.55	0.88	1.25	1.45	1.17	1.29	0.79	0.66
1909—1910	1.77	1.02	1.28	1.98	1.41	2.11	0.95	0.88

The fields II and III are manured with ammonium sulfate in the spring. This manure brought about a greater absorption of ammonia in the lower together with an 10-fold increase which persisted for some time. This explains why the "lower" figures are higher for these fields. Thus a reverse process may take place under certain conditions.

The figures in the table are, however, quite low and they drew the conclusion that the amounts of ammonia absorbed from air by the soil is of no practical importance. They had, however, the dishes covered with fine meshed brass nets to prevent dust particles from entering the dishes. This arrangement, of course, does not allow a free contact with air which they also showed by comparison with uncovered dishes. Uncovered dishes absorbed about four times as much ammonia. Their results are thus not comparable with those related before. Obviously considerable amounts of ammonia can be absorbed from the atmosphere by soils under suitable conditions.

That a reverse process may take place has also been observed by EHRENBERG (96) and SCHNEIDEWIND (266). They showed that lime-rich soils, when receiving ammonia in fertilizers, may lose ammonia to the atmosphere.

Any moist soil, with a pH lower than 7 will, however, absorb ammonia from air, the amount depending upon the ammonia content of the air, and the rate of vertical mixing, i. e. the volume of air brought into contact with unit soil surface. In this connection some recent results given by INGHAM (148) indicate that plant leaves can adsorb ammonia physically, this ammonia then being washed down to the soil by rain.

c. *The source of ammonia in air*

In their summary on the Rothamsted rainwater investigations RUSSELL & RICHARD (254) in 1919 listed the probable sources of ammonia in air as the sea, the soil and fossil deposits in which ammonia is released by combustion. They thought that the soil was probably the most important source, this conclusion being based mainly on the work of HALL & MILLER (loc. cit.) and the fact that, at least at inland places, the ammonia content in rain is higher during summer than during winter. The work by HILL & MILLER has been discussed in the preceding section and if the sea, with a pH of about 8, absorbs ammonia from the air most soils will certainly do the same. The fact that the ammonia contents are higher during summer than during winter at inland places may be due to increased convection in the air during summer, the excess over winter merely reflecting the contribution of cyclic dust during the hot season. Thus the sea and the soil cannot act as a real source for ammonia in air.

The third source, namely ammonia in fossils used as fuel is considerable. Already RUSSELL & RICHARD calculated that in Great Britain the amount of ammonia nitrogen released by combustion of coal was about 5 times higher than that actually received from rain water but they did not think it could be the only source. It is well known that the ammonia in rainwater in industrial centres is high but it generally decreases rapidly going out from the centre. Due to the general turbulence and movement of air masses the ammonia delivered from local spots will be rapidly spread out to cover extensive areas. To this source should be added the role of forest fires, as yet unexplored. As a matter of fact these sources of ammonia are the only ones possible as far as we know. Maybe in future some physico-chemical processes of ammonia formation in nature can be discovered, e. g. photo-chemical reduction of nitrate or even nitrogen to ammonia. So far, however, no processes of that kind seem to be known.

The higher European values in fig. 2 compared to non-European are most probably due to a higher coal consumption in Europe than in other countries.

To summarize, it can be stated that the only net source of ammonia in air seems to be the ammonia released on combustion of fuels. Ammonia in cyclic dust adsorbed on fine particles from the ground does not increase the ammonia pressure of the air and does not contribute anything new to the soil when washed down by rain.

7. The origin of nitrate and nitrite

The formation of nitric oxide from nitrogen and oxygen at high temperatures has been known for a long time. It was therefore quite natural to assume that nitrate in rain was derived entirely from electric discharges in the atmosphere especially as many earlier investigations reported increasing nitrate contents in rainwater during thunderstorms. Later there was, however, some doubt about this point; POSNJAKOV (239) for instance, failed to find any correlation between nitrate content and frequency of lightning; the same was also pointed out by RAM (243). Others (110, 111, 164) found that both ammonia and nitrate increased during thunderstorms. In one place with exceptionally high nitrate content, namely Hanoi, Tonkin (17) there was a positive correlation but these values are so extremely high that they may be classified as "very improbable".

HUTCHINGTON (145) has, on basis of the analyses from Oklahoma (110, 111) estimated the amount of nitrate which could be derived from electric discharges in this place and found around 14 per cent could be accounted for. The rest must be derived from some other source. This low estimate is compatible with the fact that in tropical places with a very high frequency of electric discharges the total amount of nitrate nitrogen is not exceedingly high and not at all in proportion to the frequency of lightning.

Some workers from India, namely RAO, GAPOLO & DHAR (244), DHAR & RAM (89) and RAM (243) have suggested another possible source of nitrate in the atmosphere. On examining the relative amounts of ammonia and nitrate in rainwater in temperate and tropical places it was found (see MILLER [213]) that the relative amount of nitrate nitrogen is higher in tropical places although the total nitrogen is of the same order. This they explained to be due to a photo-chemical oxidation of ammonia to nitrate in tropical places, the intense ultraviolet radiation delivering the necessary activation energy. According to RAM (243) the ammonia molecule should be oxidized by O_2 possibly through the formation of ozone, O_3 from O_2 by the action of ultraviolet radiation, the ozone being a strong oxidant.

Several objections can be raised against this theory. Firstly it is doubtful whether the nitrate fraction is higher in tropical places than in temperate ones. This has been discussed earlier in this paper (see p. 222). Secondly the amount of ultraviolet radiation received near the ground is highest at the poles, and decreases towards the equator.

There seems to be, however, a positive correlation between nitrate in rain and ozone content in air. This has at least been shown qualitively in 1876 by EUGLING (103). This could, of course, be taken as an indication that the nitric oxide formation in air is facilitated by the presense of ozone. But on the other hand the appearance of ozone at lower altitudes indicates great vertical convections in the upper atmosphere as suggested by REGENER (245). If nitrate is formed at high altitudes such great convections will bring fresh reserves of nitrate into the lower atmosphere as well, where it could easily influence the nitrate content of rainwater. So it does not seem necessary to assume that ozone itself takes an active part of the nitrate formation.

In the atmosphere there seems to be a considerable concentration of nitrous oxide. It was first discovered by ADEL (2) in 1939 from its absorption spectra in the infra red. Later it was estimated by the masspectrographic method on samples of air taken near the ground to $5 \cdot 10^{-5}$ per cent by volyme. (SLOBOD and KROGLI [276] in 1950). On the basis of these and some other results ADEL (3, 4) proposes a nitrogen cycle in which nitrous oxide takes part. He suggests that N_2O is formed in the soil by decomposition of H_4NNO_3. As N_2O is a rather inert gas it escapes into the soil air from where it diffuses into the atmosphere. When it reaches high altitudes it is decomposed by the action of ultraviolett light ($\lambda < 2{,}000$ Å) into N_2, O_2 and NO. The nitric oxide thus formed is, however, also photo-chemically decomposed

into N_2 and O_2. The nitrogen formed diffuses into the lower atmosphere where it is recombined with O_2 to NO under influence of electric discharges. The nitric oxide formed in this process is brought to the soil by precipitation where it combines with ammonia to H_4NNO_3 whereby the cycle is closed.

Several objections can be raised against this theory. The decomposition of H_4NNO_3 into N_2O and water is well known. For the pure, dry salt, however, it does not occur below 180° C. The reaction might, of course, still occur in the soils at ordinary temperatures as the result of some now unknown microbiological action, especially as the energy released during the decomposition is considerable. The presence of H_4NNO_3 in the soil is, however, also unlikely. The ammonia content in soils is generally very low, much lower than the nitrate as it is rapidly oxidized to nitrate as soon it is released on decay of organic matter.

It is more probable that the N_2O of the atmosphere is formed from nitrogen compounds in fossils in their combustion.

The decomposition of N_2O under the influence of ultraviolet radiation is known to occur, at least in presence of oxygen, when NO is formed. If the decomposition stopped at that stage the NO thus formed could well account for the nitric oxides present in the atmosphere.

That nitric oxide exists to fairly high altitudes can be inferred from an Australian investigation in 1914, ANDERSON (11, 12), MASON (202, 203) et al. They made daily analyses of nitrate and nitrite in rainwater near Melbourne and found that the content and amount of these compounds was dependent on the origin of the air masses. They grouped the values according to the weather type into the following groups

1. antarctic low pressures
2. antarctic low pressures influenced by tropical low pressures
3. tropical low pressures.

It was found that each individual rainfall of types 2 and 3 carried down an amount of nitrate and nitrite which was independent of the amount of rainfall. The tropical low pressure rains gave the greatest amount of nitric nitrogen.

Further analyses of the air for nitric nitrogen confirmed their assumption that the amount of nitric nitrogen in each rainfall was to a great extent dependent upon the vertical extension of the air masses involved. From their air analyses they calculated the height required to give an amount corresponding to a certain type of rainfall. The calculated height was of the same order of magnitude as that estimated by meteorologists. They also found that the nitric nitrogen content of air was much higher on the forward side of a low pressure system than on the rear side.

From their results it appears that nitric nitrogen should be fairly evenly distributed throughout the troposphere.

8. The geochemistry of nitrogen

Geochemical data on nitrogen gives an interesting picture of its distribution in nature. Some data are given by HUTCHINGTON (loc. cit.). The nitrogen content of igneous rocks is surprisingly constant, roughly 0.005 per cent (by weight). Most of it is present as ammonia while nitrate seems to be absent. Sedimentary rocks contain as an average 0.051 per cent, 0.046 per cent thus being biochemically fixed. The total amount present is thus

Igneous rocks	37,000 g N	per cm²
Sedimentary rocks	87 » »	» »
In the atmosphere	755 » »	» »

Thus it is seen that roughly 10 per cent of the nitrogen content in the atmosphere has been fixed by the biosphere during the time since life appeared. Part of this nitrogen is being released at the present time through combustion of coal but this amount is probably small. The fixation process is, of course, still going on.

9. The biological importance of combined nitrogen in air and precipitation

For most plant species a supply of combined nitrogen is essential for development, and of course, they do not care about the origin of this. The rate of delivery is the only relevant question for the plants.

It may be of some advantage to classify all the combined nitrogen brought to the soil in two groups, namely cyclic and non-cyclic,

the term cyclic taken in a short time sense. To the cyclic group belongs all nitrogen precipitated from the atmosphere as cyclic dust and nothing more. To the non-cyclic group belongs all other forms of combined nitrogen, even that released on combustion of coal.

The cyclic dust does not contribute anything new to the total land surface, on the contrary some of it may be carried out over the sea and precipitated there. This fraction represents a loss. The biological importance of cyclic dust lies in the fact that it will redistribute non-cyclic nitrogen and even out differences in the soil income of non-cyclic nitrogen.

As cyclic dust will be represented in rain-water analyses, these may well represent the total income from atmospheric precipitation but are not a reliable figure for the net income. The possibility of a direct absorption of ammonia from the air by the soil must, however, also be taken into consideration.

(To be continued in the next issue.)