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On the Content of Nitrogen in Atmospheric Precipiation in Sweden. II.

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Abstract

In the present paper an attempt is made to give a general idea of the geographical distribution of fixed nitrogen (NH_4-N) transferred to the soil through precipitation in Sweden. Further a map is given showing the distribution af α, a quantity proportional to the nitrogen concentration in the precipitation at the beginning of a rain and, it is assumed, representative for the content of fixed nitrogen in the atmosphere before the rain is falling.

A discussion of different causes of the concentration of fixed nitrogen in precipitation is presented and a photochemical process is suggested, which would explain the almost constant ratio between NH_4-N and NO_3-N frequently found within the temperate zones. It is evident, however, that other causes also are at work, especially at lower latitudes. The need of laboratory experiments is emphasized.

In our previous paper on this subject (ÅNGSTRÖM, HÖGBERG 1952), we reached the conclusion that the concentration of NH_4-N and NO_3-N in precipitation is dependent upon the amount of precipitation previously fallen. We further found a pronounced dependence of the concentration on the character of the air mass. Thus the tropical air contains between 10 and 30 per cent greater amount of nitrogen than the polar air, and almost double the amount found in the arctic air.

An attempt was made to express mathematically the change of concentration in its dependence of the quantity of precipitation fallen. The following expression was found valid:

$$s = \alpha \log (1 + P) \qquad (1)$$

where s is the quantity of nitrogen transferred through the precipitation P, and α is an arbitrary constant. The equation evidently implies that the concentration at a given moment in the falling precipitation is gradually decreasing. It has its largest value at the beginning of the rain, at which time the concentration has the value α. Referred to a certain given precipitation the quantity of nitrogen transferred is proportional to α.

For a given locality two quantities seem in this connection to be of a general importance, namely (1) the quantity of nitrogen, s, transferred through precipitation during the year and during different parts of it, and (2) the quantity α, denoting the nitrogen concentration at the beginning of precipitation. It seems reasonable to assume that α can be regarded as a measure on the nitrogen content of the atmosphere before the precipitation is beginning to fall.

Now the quantity s of nitrogen transferred in every individual case of precipitation has been measured only at Ultuna D and it is

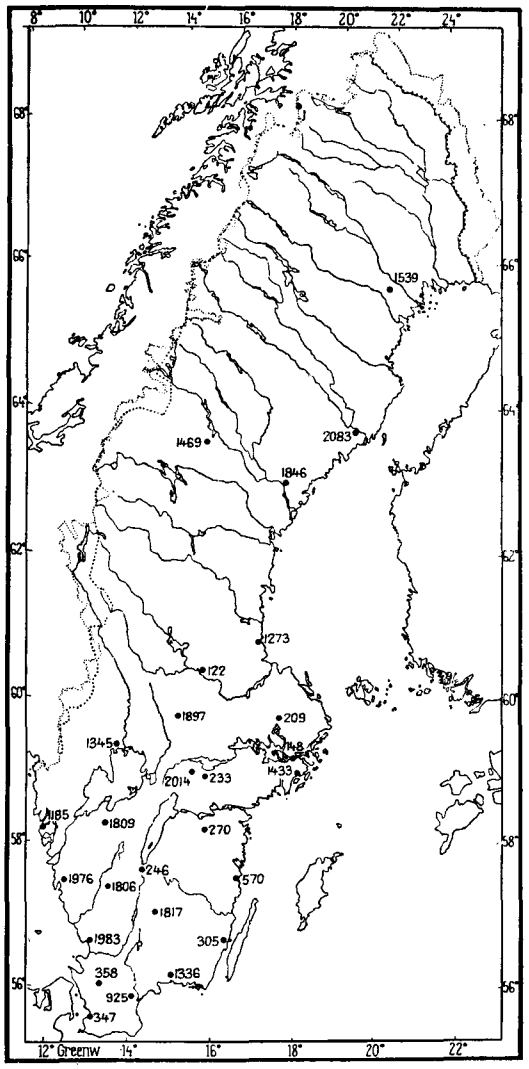

Fig. 1. Station map.

from these measurements that the equation (1) and consequently also the value of α has been computed. At all other stations the quantity s measured refers only to the monthly sums, s_m. If we assume, which seems reasonable, that the transfer of nitrogen at all stations is connected to the precipitation already fallen through an equation of the general form (1) we can on the basis of this assumption and knowing the frequencies of different amounts of rain compute α for the different stations. We have namely then:

$$s_m = \Sigma s = \alpha \Sigma \log (1 + P_i) \qquad (2)$$

At this process of adding up, we have not taken account to the occurrence of different air masses or their trajectories; the coefficient α consequently corresponds to a mean value for cases where α has had rather different values. As the separation of one case of precipitation from another often meets with great difficulties, a simplified procedure has been applied, in the same way as in our previous paper: instead of taking the sum corresponding to all the separate precipitation values the terms have been referred to the separate daily totals. As it is not quite clear, without further, that this simplification does not include considerable differences between the results of the two methods of computation respectively, we have computed α_D for the station Ultuna D according to the more exact procedure — separate occasions of precipitation — and compared it with the α_A computed for the station Ultuna A, situated in the immediate vicinity of Ultuna D. In the former case we got a value: $\alpha_D = 0.0275$, in the latter one: $\alpha_A = 0.029$. For the purposes here in view it therefore seems reasonable to exchange the more cumbersome method, which it is not possible to apply at most stations, against the simplified one.

If we let n_i represent the frequency value for different intervalls within the daily precipitation observations and further P_i the corresponding mean value of the precipitation for the same intervall, we get, using 10logaritms:

$$s_m = \alpha \sum_i n_i \log (1 + P_i) \qquad (3)$$

For daily precipitations above 40 mm the mean P_i has been evaluated to be 50 mm. The total precipitation and the number n_i of precipitation days are given in tables 1—2.

On the basis of these assumptions the table 3 has been computed. For comparison the tables 4—5 also are shown here. They refer to the content of NH_4-N alone. The reasons for not including NO_3-N also, will be given below.

Variation of s and α with the time of the year.

It is evident from the results already obtained that the quantity s is dependent not

only of α, the concentration when precipitation is starting, but also of the quantity of precipitation and of its frequency distribution. If we assume for a given station as well α as also the annual precipitation P to be given, the quantity s is still undetermined as we do not know the way in which P is distributed on more or less heavy rains. The more P is devided up on small quantities of precipitation, the larger we ought to expect s to be. On the other hand α, as it has been defined above, is independent as well of the amount of precipitations as of its frequency distribution. Its value therefore has a more fundamental character than s.

If we consider first the variation of α with the time of the year, we find for all stations a pronounced maximum in the spring and a minimum in the autumn or the winter. Exactly the same annual variation is in fact characteristic at the northern hemisphere for the content of solid or liquid particles in the air which give rise to the scattering of sun radiation. The cause of this variation may not be a single one. That the instability of the atmosphere, which reaches a maximum in the spring on account of the heating from below, must have en effect of permitting dust and pollen to be more freely carried from the earths surface to the atmosphere, seems rather evident. But it seems also probable that the effect of precipitation in washing out particles or molecules from the atmosphere ought to be least pronounced at the time of the year when the amount of precipitation itself has a minimum. The annual variation found to exist, seems on the other hand to speak against the electrical discharges in the atmosphere as producing to considerable extent the nitrogen ions here concerned. The electrical phenomena have on the northern hemisphere in general a pronounced maximum in the summer months July—August, a maximum not at all reflected in the variation neither of α or s. That thunderstorms, and electrical discharges in the atmosphere in general, must produce nitrogen ions, especially nitrogen oxides and related compounds, seems evident from other researches, but it seems on the other hand probable from the material here treated that phenomena must be of a secondary character as regards the causes of the nitrogen content in precipitation.

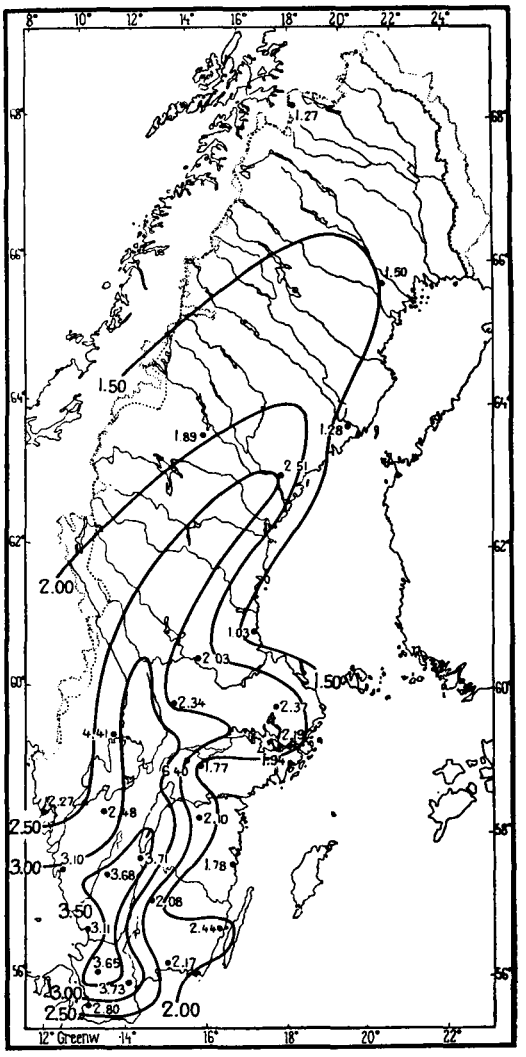

Fig. 2. Geographical distribution of annual amount of NH_4 in precipitation (kg per ha).

The annual variation of s as it appears from table 3 is evidently closely related to the amount of precipitation.

Geographical distribution of NH_4—N in precipitation.

The stations at which measurements have been made of the nitrogen concentration are not numerous enough to give more than a rather superficial idea of the geographical distribution. Yet, in figs. 2—3, an attempt is

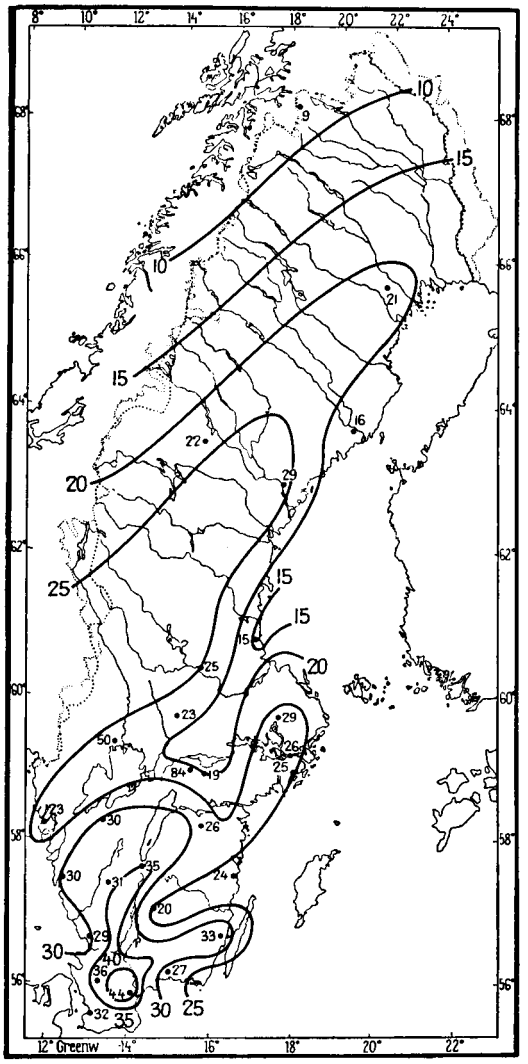

Fig. 3. Geographical distribution of average value of α for the year. The actual values of α are here multiplied by 10^3.

made to draw a map showing lines of equal α and s. If we make an exception for the station Kvarntorp, which will be discussed below, we generally find the quantity s to depend on the amount of precipitation, in the way that low values on the precipitation correspond also to low values for s and vice versa. There is, however, also a decided dependence on latitude, in the way that the nitrogen transfer through precipitation decreases with an increase in latitude. The highest values on s are found in the southwestern parts of Sweden, where its value in general is considerably higher than 3 kg per ha (10^4 m^2). Special attention must be given to the high values at the stations Kvarntorp and Varpnäs. As regards the former station the high value is undoubtedly a consequence of the industrial activity at that place. The same may be the case at Varpnäs.

As regards α there seems to be no decided dependence on the total precipitation. The most apparent characteristics as regards the general distribution seem to be the dependence on latitude, the values decreasing generally from south to north as illustrated in figs. 4—5.

Trying to find an equation satisfying these values in their dependence of latitude within Sweden, we get:

$$\alpha = 0.10 \cos^2\varphi \qquad (4)$$

$$\text{and} \quad s = 9.1 \cos^2\varphi \text{ kg/ha} \qquad (5)$$

As well α as s refer here to the NH_4-N alone. It could perhaps be expected that a similar treatment as that described above would give us the geographical and annual variation of α and s, referred to NO_3-N, which nitrogen element has also been measured in a similar way as NH_4-N. However, in the course of the treatment of the material of observations, it became clear, that only the momentary measurements of NO_3-N, referring to separate days or separate occasions of precipitation could be fully depended upon. The measurements referring to accumulated NO_3-N for the month or longer periods were affected, from causes still not clear, with considerable errors. Only the measurements of NO_3-N at Ultuna could therefore be regarded as reliable. In order to get an idea of the probable transfer of NO_3-N in its geographical and annual variation, we therefore were induced to base our considerations on the intimate correlation found to exist between NH_4-N and NO_3-N at Ultuna *D*. This correlation is clearly demonstrated in table 6. If we compute the correlation coefficient between the quantities of N transferred in the form of NH_4 and NO_3 respectively (in gram per ha), we get:

$$r = 0.777 \pm 0.025$$

The relationship can be well expressed through the linear equation:

$$s_{NO_3} = 0.48 s_{NH_4}$$

which implies that the quantity of nitrogen transferred to the ground in precipitation in the form of NO_3 is just about the half of the quantity transferred as NO_4.

Consequently, in order to get total quantity of nitrogen transferred through precipitation, we have to add 50 per cent to the values for NH_4 alone, viz to the values on the maps fig. 3 and in the table 4.

Remarks and suggestions

A historical survey on the investigations concerned with nitrogen in precipitation has been given by ERIK ERIKSSON (1952). Another very valuable survey has been presented by G. EVELYN HUTCHINSON (1945). Both papers together give a rather clear idea of the present state of the question. We may then limit ourselves to mention here some results of immediate bearing upon our present work.

In the first place some researches of A. H. WOODCOCK (1952) of SUGAWARA (1949), and of Y. MIYAKE and Y. SIGIURA (1950) to which our attention has been drawn after the writing of our first paper ought to be mentioned. These authors have all investigated the chloride concentration in rain, and they have obtained results similar to our own in the respect that the concentration generally decreases with time and with the intensity of rain. In fact the two last named authors in their common paper arrive at a formula for the concentration of chloride as a function of the precipitation previously fallen very similar to our own for combined nitrogen. Woodcock in his very interesting paper enters in detail into the process through which condensation takes place upon small salt particles and upon the way in which larger drops are assimilating smaller ones. Their results seem of great interest for the question concerning rain formation.

As regards chloride there seems to be no doubt that it enters the precipitation either as condensation nuclei or is caught in the form of particles or small drops at the falling of larger drops. In our present case the question is open as regards the way in which combined

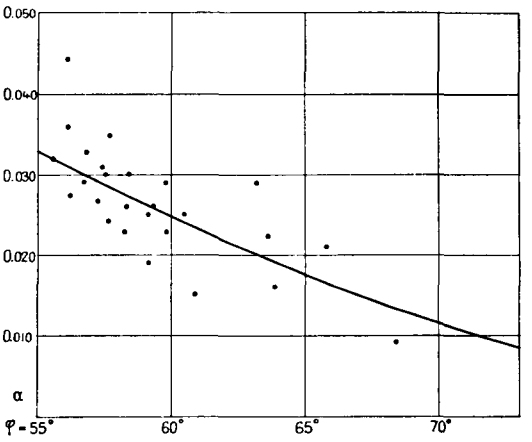

Fig. 4. Variation of α with latitude.

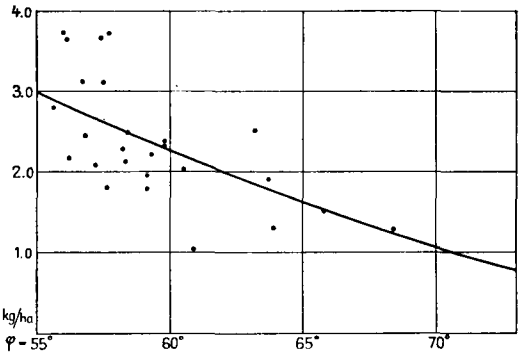

Fig. 5. Variation of annual amount of NH_4 (kg per ha) with latitude.

nitrogen is introduced in precipitation. Does it exist in a gaseous, liquid or solid state before the assimilation into drops of rain or cristals of snow? Perhaps the similarity between our results and those of the authors mentioned above, concerning the rate of decrease of concentration with amount of precipitation or intensity would suggest a similarity also of the form in which the salts are present, viz. we would be inclined to conclude that the nitrogen compounds here investigated are also *chiefly* present in form of particles or dissolved in small drops, in the way that the laws governing their entrance into precipitation will be the same as for the case of the chloride particles. This conclusion, however, must be put forward with great reserve, as it seems probable that nitrogen, especially as ammonia, is transferred to precipitation in several ways among

Table 1

Station Number	Station	Precipitation during the whole period $^{1}/_{10}$1947—$^{30}/_{9}$ 1950. mm				
		Spring	Summer	Autumn	Winter	Year
1	Riksgränsen	547	975	1,047	459	3,029
1539	Brännberg	391	345	401	365	1,502
2083	Norrfors	351	383	524	410	1,669
1469	Gisselås	375	562	326	348	1,610
1846	Offer	333	579	450	300	1,662
1273	Norrsundet	233	446	416	252	1,348
122	Vassbo	308	577	475	342	1,701
1897	Stjärnfors	408	722	621	503	2,254
209	Ultuna A_1	292	600	394	318	1,603
1345	Varpnäs	342	682	566	426	2,016
2014	Kvarntorp	271	618	442	292	1,623
1489	Stockholm	276	628	333	312	1,549
233	Högsjö	343	611	466	410	1,831
1433	Berga	324	565	427	380	1,697
1809	Lanna	307	550	434	306	1,598
1185	Kristineberg	415	592	672	563	2,242
270	Bjärka-Säby	348	522	360	348	1,578
570	Tovehult	360	443	440	439	1,682
246	Flahult	411	611	642	561	2,225
1976	Rossared	455	709	750	636	2,549
1806	Ambjörnarp	468	649	857	665	2,638
1817	Skärshult	396	671	643	533	2,243
1983	Halmstad fl.	449	533	678	556	2,217
305	Svartingstorp	266	416	409	331	1,422
1336	Bräkne-Hoby	270	478	405	366	1,518
358	Kolleberga	456	566	573	674	2,268
925	Ugerup	318	465	415	417	1,615
347	Alnarp	362	443	394	409	1,608

Table 2

Station number	Number of precipitation days during the whole period $^{1}/_{10}$ 1947—$^{30}/_{9}$ 1950					
	≧ 0.1 mm	≧ 1 mm	≧ 5 mm	≧ 10 mm	≧ 20 mm	≧ 40 mm
1	612	515	214	72	17	1
1539	386	262	102	38	5	
2083	346	280	104	47	10	3
1469	480	315	103	31	5	
1846	449	289	105	39	10	1
1273	373	234	90	40	5	1
122	355	289	112	50	12	
1897	488	359	151	61	16	
209	417	289	108	35	8	
1345	476	298	124	60	12	2
2014	351	278	105	49	8	2
1489	484	291	101	33	9	
233	477	306	119	56	9	1
1433	416	283	109	45	12	1
1809	438	299	99	40	5	
1185	410	338	157	74	14	
270	387	286	112	44	3	
570	400	278	118	54	6	
246	521	381	155	60	11	
1976	414	349	185	87	22	
1806	527	412	192	81	12	1
1817	492	368	159	57	8	1
1983	544	384	157	57	9	
305	401	283	88	33	7	
1336	384	311	100	29	5	1
358	463	360	164	64	10	
925	446	321	106	31	6	
347	490	317	115	31	7	

which absorption in the gasous state is certainly not to be totally neglected.

A great problem seems now to be concerned with the way in which the fixed nitrogen in precipitation is created. HUTCHINSON (1944) in his survey gives the following summary of the sources for combined nitrogen which can be imagined, namely:

a) From soil and the oceans
b) From fixation of atmospheric nitrogen
   (1) Electrically
   (2) Photochemically
   (3) In the trail of meteorites
c) From industrial contamination

It seems evident from what is well known concerning these phenomena, that they all to some extent are able to produce fixed nitrogen. The question, however, is: what must be regarded as a chief agent? Hutchinson excludes in this respect, as it seems on well founded reasons, c. This source gives fixed nitrogen to some degree but it is far from sufficient to explain the actual transfer.

If we consider only our own material of observations, here treated, we must state, that there is no indication that an electrical production plays an important part. If that would be the case we would expect the concentration to be rather large in summer, when thunder and atmospheric electrical discharges occur, and very small in autumn, winter and spring, at which times, in our climate, practically no such phenomena occur. Now, as we have shown, there is a pronounced maximum of the concentration in spring in

Table 3

Station Number	$\alpha_{NH_4\text{-}N}$				
	Spring	Summer	Autumn	Winter	Year
I	0.006	0.020	0.004	0.007	0.009
1539	0.022	0.022	0.021	0.018	0.021
2083	0.029	0.024	0.008	0.008	0.016
1469	0.032	0.025	0.018	0.012	0.022
1846	0.049	0.032	0.015	0.022	0.029
1273	0.021	0.014	0.012	0.015	0.015
122	0.047	0.020	0.018	0.022	0.025
1897	0.038	0.019	0.019	0.019	0.023
209	0.046	0.025	0.027	0.022	0.029
1345	0.092	0.043	0.050	0.025	0.050
2014	0.089	0.078	0.089	0.082	0.084
1489	0.036	0.022	0.026	0.022	0.026
233	0.038	0.016	0.015	0.011	0.019
1433	0.035	0.024	0.022	0.014	0.025
1809	0.038	0.032	0.023	0.027	0.030
1185	0.033	0.019	0.021	0.020	0.023
270	0.039	0.026	0.022	0.018	0.026
570	0.042	0.026	0.019	0.014	0.024
246	0.047	0.045	0.025	0.027	0.035
1976	0.039	0.027	0.025	0.030	0.030
1806	0.043	0.029	0.034	0.017	0.031
1817	0.025	0.027	0.017	0.013	0.020
1983	0.032	0.025	0.030	0.027	0.029
305	0.045	0.047	0.024	0.018	0.033
1336	0.057	0.024	0.020	0.016	0.027
358	0.037	0.060	0.038	0.015	0.036
925	0.047	0.059	0.041	0.031	0.044
347	0.036	0.033	0.038	0.019	0.032

Table 4

Station Number	Total amount of NH_4-N kg/ha				
	Spring	Summer	Autumn	Winter	Year
I	0.20	0.74	0.15	0.18	1.27
1539	0.40	0.37	0.38	0.35	1.50
2083	0.53	0.38	0.19	0.18	1.28
1469	0.61	0.63	0.41	0.24	1.89
1846	1.00	0.72	0.36	0.43	2.51
1273	0.31	0.28	0.23	0.21	1.03
122	0.68	0.51	0.42	0.42	2.03
1897	0.78	0.56	0.52	0.48	2.34
209	0.80	0.61	0.56	0.40	2.37
1345	1.56	1.11	1.24	0.50	4.41
2014	1.30	1.79	1.84	1.47	6.40
1489	0.64	0.57	0.55	0.43	2.19
233	0.68	0.42	0.41	0.26	1.77
1433	0.62	0.50	0.52	0.30	1.94
1809	0.65	0.76	0.56	0.51	2.48
1185	0.67	0.43	0.61	0.56	2.27
270	0.68	0.65	0.43	0.34	2.10
570	0.67	0.41	0.43	0.27	1.78
246	0.99	1.20	0.74	0.78	3.71
1976	0.80	0.73	0.73	0.84	3.10
1806	1.08	0.86	1.24	0.50	3.68
1817	0.55	0.71	0.52	0.30	2.08
1983	0.76	0.58	0.92	0.85	3.11
305	0.72	0.95	0.46	0.32	2.45
1336	0.84	0.53	0.44	0.36	2.17
358	0.81	1.36	1.02	0.46	3.65
925	0.84	1.27	0.91	0.71	3.73
347	0.73	0.71	0.91	0.45	2.80

our country. This speaks against an electrical source, even if we also have to consider that tropical air masses are coming from regions where other electrical conditions prevail.

In seeking for an explanation of the nitrogen content of precipitation within the temperate zones, it seems to us that there are chiefly two rather important facts, which ought to be kept in mind. The first one concerns the almost constant ratio of one against two, in which NO_3-N appears compared with NH_4-N. Hutchinson has given a graphical demonstration of this fact, largely based on a table by Miller. It is strongly supported by the observations here treated. The high correlation shows that it is in Sweden characterized by a rather high regularity.

The second fact which seems important concerns the similarity between the laws governing the decrease in concentration of nitrogen compounds in precipitation on the one side, and the chlorides on the other one. It suggests a similarity in the way in which the two kinds of compounds occur, viz. as some form of particles or drops.

The constant ratio seems to us to show that in our regions the productions of NH_4-N and NO_3-N are intimately bound to one another, and that when the one compound is produced the other automatically is produced also. The simplest way in which this would occur would be through a photochemical process, occurring for instance in small droplets, where the free nitrogen of the atmosphere, according to the laws of gaseous absorbtion of nitrogen in water, must be present to a concentration

Table 5

Station Number	Mean concentration of NH_4-N mg/L				
	Spring	Summer	Autumn	Winter	Year
1	0.11	0.23	0.04	0.12	0.13
1539	0.29	0.32	0.29	0.31	0.30
2083	0.43	0.30	0.10	0.12	0.22
1469	0.49	0.34	0.36	0.22	0.36
1846	0.84	0.37	0.22	0.43	0.44
1273	0.39	0.19	0.16	0.31	0.24
122	0.66	0.27	0.23	0.36	0.34
1897	0.57	0.23	0.25	0.30	0.32
209	0.83	0.30	0.41	0.38	0.44
1345	1.37	0.49	0.66	0.43	0.68
2014	1.44	0.87	1.30	1.52	1.20
1489	0.69	0.27	0.49	0.43	0.43
233	0.58	0.20	0.24	0.17	0.27
1433	0.57	0.27	0.35	0.24	0.34
1809	0.64	0.42	0.36	0.50	0.46
1185	0.49	0.22	0.26	0.28	0.30
270	0.59	0.37	0.33	0.31	0.40
570	0.66	0.35	0.31	0.23	0.38
246	0.76	0.59	0.34	0.43	0.51
1976	0.52	0.31	0.30	0.37	0.36
1806	0.66	0.40	0.40	0.24	0.41
1817	0.41	0.31	0.24	0.19	0.28
1983	0.51	0.36	0.41	0.44	0.43
305	0.80	0.68	0.36	0.33	0.54
1336	0.94	0.33	0.33	0.29	0.43
358	0.54	0.72	0.52	0.20	0.48
925	0.79	0.82	0.66	0.56	0.71
347	0.60	0.48	0.64	0.36	0.52

Table 6. Frequency numbers of simultaneous values of nitrogen amount s expressed in gr/ha. Totally 117 different cases.

NH_4-N \ NO_3-N	1—5	6—10	11—15	16—20	21—25	26—30	31—35	36—40	Σ
1—5	13								13
6—10	22	5	1						28
11—15	13	7	1						21
16—20	4	7	3	1					15
21—25	1	1	2	1					5
26—30		6	4	2	1				13
31—35		1	3	3	1				8
36—40			2	1					3
41—45			1			1			2
46—50					1	1	1		3
51—55				1	1		1		3
56—60									
61—65									
66—70					1				1
71—75									
76—80									
81—85				1					1
86—90								1	1
Σ	53	27	17	10	5	2	2	1	117

of about 15 mg/lit. A simple reaction according to the formula:

$$12\,N + 18\,H_2O = 4\,NH_4NO_3 + 4\,NH_4OH + O_2 \quad (6)$$

evidently gives us just the result found to exist, namely two times as much NH_4-N as NO_3-N in the drop. If such a process actually takes place it can occur in many ways, possibly with one or more intermediate steps. What here seems worth to point out is that in a water particle, either solid or liquid, all the material is already at hand if the agency able to produce such a reaction comes into play. The possibility of certain sea water salts acting as catalysers or even part-takers must be taken into consideration. The process suggested above only needs to transform about 3 per cent of the nitrogen present in the drop in free state, in order to give the concentration of fixed nitrogen found to exist in precipitation. Experiments are evidently needed in order to decide this question. If such a chemical action is found actually to be produced by some wave lengths of sun light entering the troposphere, such a result will evidently be of utmost importance. Not only will it explain the constant ratio relationship found at high latitudes, but it will also explain the similarity of the washing out process in the cases of chlorides on the one side and nitrogen compounds on the other. Further it will suggest the possibility of a new kind of cosmical influences on processes of biological nature through variations in the composition of sun radiation.

REFERENCES

HUTCHINSON, G. E., 1944: Nitrogen in Biochemistry of the Atmosphere. *American Scientist*, pp 178—195.

MIYAKE, Y. and SIGIURA, Y. 1950: The Mechanism of Dissolution of the Atmospheric Chloride into Rain Water. *Papers in Meteorology and Geophysics*, **1**, No. 2—4.

SUGAWARA, KEN, OANA, SHINYA and KOYAMA, TADASHIRO 1949: Separation of the Components of Atmospheric Salt and their Distribution. *Bulletin of the Chemical Society of Japan*, **22**, No. 2.

WOODCOCK, ALFRED H. 1952: Atmospheric salt particles and raindrops. *Journal of Meteorology*, **9**. No. 3.

ÅNGSTRÖM, A. and HÖGBERG, L. 1952: On the Content of Nitrogen (NH_4—N, and NO_3—N) in Atmospheric Precipitation. *Tellus*, **4**, No. 1.