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"ATMOSPHERIC NITROUS AND NITRIC ACIDS AND THEIR ABSORPTION
BY RAIN AND SURFACE WATER."

A THESIS

SUBMITTED TO THE FACULTY

of the

COLLEGE OF ARTS AND SCIENCES

of the

UNIVERSITY OF LOUISVILLE

through

PROFESSOR C. J. ROBINSON

IN CANDIDACY FOR THE DEGREE

of

"MASTER OF SCIENCE"

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by

ALEXANDER Y. LEE

1912

Atmospheric Nitrous and Nitric Acids and Their Absorption by
Rain and Surface Water.

Having been born and brought up in China, an empire, where the people are utterly ignorant of the vital importance of a good system of public water supply, and having decided to take chemistry as my profession, I feel intensely interested in the examination of water for the purpose of convincing our people in the far east to pay proper attention to sanitation on a chemical basis. The average life period there has been roughly estimated to be thirty years, and we have now in the Middle Kingdom a population of 450 000 000. It means in each century we have approximately 1 000 000 000 of people there to drink water, not a drop of which has ever been examined to ascertaining whether is free from germs that cause dangerous diseases. In every Summer there break out disastrous epidemics of cholera which frequently result from the use of polluted water, and the people attribute such periodic calamities to the mischief of evil spirits. Persons with typhoid fever, which is also scattered by contaminated waters, are shut up in small rooms with windows and doors closed, thinking cold air to be the ultimate cause of such a malady. By experience they found out that the habit of using cold drinks would injure their health, and thus their favorite beverage has for a few thousands of years been a cup of hot tea. Being ignorant of the baneful consequences, they wash their rice and clothes in the same pond five feet apart. Turbidity, or suspended matters is the only thing that looks offensive to them, and consequently centuries ago they discovered the peculiar property

of alum for coagulation, and the latter substance has been extensively manufactured in China for the purpose of purifying their drinking water. Alum, as a good agent for coagulation, has been the chief domestic drug in the Chinese homes, for to any person who is seized abruptly with a serious disease is invariably given a lump of this substance dissolved in a cup of hot water, thinking that the constituents of the sickness in the patient's stomach could be coagulated. Consequently no Chinese home is without a box of alum kept in readiness for emergencies, and large lumps of it are thrown into the water tank when the turbidity of river water is great. Those whose residences are not situated in the vicinity of any stream use water drawn from wells.

Shortly after I entered the University of Louisville, I considered myself exceedingly fortunate in obtaining an opportunity of working in the water plant of the city. Having worked for a few months with those who carry out their daily routine of analysis in the laboratory, I began to take such interest in the work that I wished I could write my thesis on some phase of the work at the suggestion of Prof. Robinson. My attention was directed to the occurrence of nitrites and nitrates in nature waters and rain water, and the fact that the absorption of these substances from the air has not received a great deal of attention from chemists. These seemed also to be a possibility that the presence of these substances in some surface waters might be entirely accounted for by such absorption from the air. Chemists generally assert that these substances occur in water because of oxidation of organic matter with which

the water has become contaminated.

Historical- Very little has been done in the determination quantitatively of both nitrites and nitrates in natural waters aside from two or three cases in which some general statement of the existence of these two substances in rain water is made with reference to specific localities without giving any clear origin from which these substances could be procured. In Sir H. E. Roscoe's Treatise on Chemistry, concerning the subject, the following statements are given.

"The average amount of nitrogen contained in country rain water as ammonia, organic nitrogen, nitrous and nitric acids is about .7 parts per million, whilst the rain of London (Hyde Park) contains 2.2 parts per million"

Roussinga-ult, on the other hand, found in the rain of Paris 4 parts of ammonia in one million, and nitric acid .2 in a million. Dr. Edward Bartow, Director of State Water Survey of Illinois, gives the following suggestion.

"In our interpretation of results, we take into consideration the fact that nitrites may occur in well waters containing iron because of the reduction of nitrates by means of ferrous salts. It would be very interesting if you (Prof. Robinson) can show that nitrites in water, otherwise pure, may be present because of absorption from the air. It would seem to me that the amount would be small because of the almost immediate oxidation of the nitrites to nitrates by means of the dissolved oxygen present. If something could be added to the water which could prevent this oxidation, the nitrite content might

possibly be increased. The nitrite content in pure river and lake water is usually very low. If nitrites are present in quantity, they are usually accompanied by other indications of contamination such as albuminoid ammonia, high oxygen consuming power, high bacterial content and the presence of gas former". In the Annual Report of the State Agricultural College of Kansas for the year 1889, Prof. J. T. Willard gave the results of the analysis of nitrites and nitrates in the rain water of the four previous years. It is stated that the nitrogenous compounds in the rain waters were then analyzed under two divisions. In any sample nitrogen as ammonia was first tested, and then all the nitrites and nitrates were reduced to the form of ammonia, which was again tested, and the difference of these two determinations was attributed to nitrates. This explained why no nitrites were mentioned in the rain waters in former times. However in the year 1887 Prof. Willard did make quantitative qualitative nitrite determinations in the rain waters, and his results are quoted as follows.

"In the time mentioned"-from May 1887, to September 1889-"one hundred and seventy-one rains were tested for nitrites. Of these one hundred and twenty-eight gave the reaction for nitrites without concentration; twenty-nine gave no reaction and fourteen were doubtful. There were one hundred and thirty-two rains in the six months from April to September, inclusive. Nitrites were present in 86 per cent, of these, and absent or doubtful 14 per cent. There were thirty-nine rains in the remaining six months, October to March, inclusive. In 36 per cent. of these nitrites were present and in 64

per cent., absent or doubtful." The result of these four years determinations is stated as follows.

Mean rainfall for four years.....29.14 inches

Nitrogen in NO_2 & NO_3 1.06 pounds per acre

Nitrogen in ammonia..... 2.63 pounds per acre

From the preceeding quotations it is seen that chemists seem to agree that there are traces of nitrates in natural waters that have their origin in the atmosphere, but as to nitrites, they seem to have been investigated very slightly. In Roussingault's conclusion he stated the presence of nitrate and ammonia in rain water, but said nothing about nitrites, and I have no way of getting his paper to find out details of his experiments. So far as concerns the experiments I have made, conclusions to be drawn are some what different from his, and will be treated a little later.

Fresh natural waters are generally classified as rain water, surface water, subsoil or ground water, and deep or artesian water. Water in any form of dew, frost, snow, or hail that finds its contaminations only through the atmosphere is grouped in the first class. portions of water collected in various low places-rivers, or small streams, lakes, or ponds-in free contact with the atmosphere belong to the second class. Portions of water percolating through soil or rock at moderate distances below the surface and not in free contact with the atmosphere are called subsoil water under the third class. Portions of water accumulated at great depths below the surface are named deep water under the

fourth class. With reference to the amount of nitrites and nitrates contained in each class, I find a table in "Examination of Water", by Leffman, as follows. In the following table the numbers designate parts per million.

	Rain	Surface	Subsoil	Deep
Nitrogen in Nitrites	traces or none	.03 to none	.03 to none	traces or none
Nitrogen in Nitrates	traces	.75 to 1.25	1.5 to 5.0	none to 3.0

The preceding data will be discussed again. In regard to the origin of these two nitrogenous compounds existing in the natural waters, I find, in Leffmann's "Water Examination" the following remarks.

Nitrites are present in water as the result either of incomplete nitrification of ammonia, or the reduction of already formed nitrates under the influence of reducing agents or microbes. Nitrates are the final point in the oxidation of nitrogenous organic matter, especially animal matter." Quoting Roscoe and Shorlemmer's "Treatise on Chemistry": "If water be impregnated with animal matter, this will be indicated by the presence of nitrogen in solution, either in the form of albumin or albuminous matter, if the animal matter be contained in the water unchanged, or, if the animal matter has undergone oxidation, in the form of ammonia, or nitrous or nitric acid."

We can safely agree with the above-mentioned authors that at least part of the nitrites and nitrates present in water is derived from the animal matters. But the question here arises:

What per centage of these two substances in water can be attributed to animal matter? In other words, does the atmosphere contribute some nitrates and nitrites to the water? A satisfactory answer to this question does not seem to be found in any chemistry or in any water analysis, and apparently this problem has never been solved. In order to find a solution for this problem, it is necessary to seek for experimental proofs, for with speculation alone, a person could never accomplish this task even though he had a Greek mind. It is, therefore, my task to devise methods by means of which I may be able to interpret the answer which the silent nature gives only to experiments.

Before entering into discussions of the apparatus and my experimental results, I wish to describe the methods with which I test my nitrates and nitrites. All my determinations of these two radicals are made in accordance with the directions given by Leffmann in the book entitled "Examination of Water for Sanitary and Technic Purposes." The method with which to determine nitrates is devised by A. H. Gill. It is volumetric and the estimation of minute quantities of the substance is very effective and accurate.

"Solution Required:

Phenoldisulphonic Acid

Sulfuric Acid 111 grams

Phenol..... 9 grams

The mixture is heated for six hours in the water bath. The resulting compound often solidifies to a white mass on standing, but can be easily liquefied on the water bath during the evapora-

tion of the samples to be tested.

Standard potassium nitrate (0.722 gram of potassium nitrate), previously heated to a temperature just sufficient to fuse it, dissolved in water, and the solution made up to 1000 c.c. One c.c. of this solution will contain 0.0001 gram of nitrogen.

Analytic Process:

A measured volume of the water is evaporated just to dryness in a porcelain basin about six centimeters in diameter. One c.c. of the phenoldisulphonic acid is added and thoroughly mixed with the residue by means of a glass rod. The liquid is then diluted with about 25 c.c. of water, ammonium hydroxide added in excess, and the solution made up to 50 c.c.

One c.c. of the standard solution of potassium nitrate is now similarly evaporated in another basin, treated as above, and made up to 50 c.c. The color produced is compared to that given by the water, and one or the other of the solutions is diluted until the tints of the two agree. The comparative volumes of the liquids furnish the necessary data for determining the amount of nitrates."

Picric acid is formed by reaction of phenoldisulphonic acid- $C_6H_5OH(HSO_3)_2$ with nitrates in whatsoever form. By adding to a sample of water containing nitrates phenoldisulphonic acid, we, therefore, have picric acid produced; and on adding ammonium hydroxide these results potassium picrate, which imparts to the solvent a yellow color, the intensity of which is directly proportional to the amount present. The amount of nitrates in the sample is estimated by comparing the color of the sample with that of the

standard solution. The reactions taking place during this process can be represented by the following equations.

The method for the determination of nitrites in water is Ilosvay's modification of Griess's test. The direction of the analysis is as follows.

"Solutions Required:

1-4-Amidobenzenesulfonic Acid Solution (Sulfanilic Acid)-0.5 gram dissolved in 150 c.c. of diluted acetic acid, sp. gr. 1.04

Alpha-Amidonaphthalene Acetate Solution.

Standard Sodium Nitrite-One c.c. of which contains 0.00001 gram. of nitrogen.

Analytic Process:

Twenty-five c.c. of the water are placed in one of the color comparison cylinders, and two c.c. of each of the test solutions are dropped in. It is convenient to have pipet for each solution, and to use it for no other purpose.

One c.c. of the standard nitrite solution is placed in another clean cylinder, made up with nitrite-free water to 25 c.c., and treated with the reagents as above. In the presence of nitrites the liquid becomes pink. At the end of five minutes the two solutions are compared, the color equalized by diluting the darker, and the calculation made as explained under the estimation of nitrates."

In the preceding test the estimation is based upon the pink

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color produced in the water by azo-alpha-aminonaphthalene-1-4-benzenesulphonic acid ($C_6H_4HSO_3N_2C_{10}H_7NH_2$). The density of the color is also proportional to the amount of nitrites present. The reaction consists in the conversion of the sulfanilic acid- $C_6H_4NH_2HSO_3$ -into diazobenzenesulphonic anhydride- $C_6H_4N_2SO_3$ -by the nitrite present. This substance is then in turn converted, by aminonaphthalene- $C_{10}H_7NH_2$ -into azo-alpha-aminonaphthalene-1-4-benzenesulphonic acid. The following equations represent the changes.

In addition to the chemical changes, I wish to explain my modification of the test in regard to time. The customary procedure is the use of standardized solution of sodium nitrite with 0.00001 gram of nitrogen as the smallest unit, and at the end of five minutes the colors should be equalized. By experience I found that in water an amount of nitrites less than 0.03 part per million would be overlooked by applying a limit of five minutes for its development. Theoretically the pink color depends upon the existence of azo-alpha-aminonaphthalene-1-4-benzenesulphonic acid, and to a sample of water, containing no nitrites on adding the reagents, no diazobenzenesulphonic anhydride could be formed. The absence of the latter means the impossibility of forming azo-alpha-aminonaphthalene-1-4-benzenesulfonic acid, and the same sample could be kept in an enclosed bottle for ever with these two reagents and yet without pink color. And this theory was checked by experiments, for I placed 100 c.c. of distilled

(11)

nitrite-free water in one of the color-comparison cylinders with the usual reagents and kept it closed for two days and found no pink color. Consequently the limit of five minutes is only an arbitrary time to hasten the test. For technical purposes a moderate accuracy of estimation is only required, hence the limit of five minutes. However for research work time is not ^{so} much emphasized as accuracy, and it would be advisable to remove the limit of five minutes. Often times I had to use sodium nitrite solution with the strength of 0.000001 gram nitrogen in one c.c. and allow 30, or 40, or sometimes an hour for its development. The cylinders were always kept closed during this time by corks.

Hehner's cylinders (fig 1) are used for the tests, and the results are recorded in terms of parts per million.

In our attempts to throw some light on the question of the extent of absorption of nitrous and nitric acids from the atmosphere, experiments along three lines have been carried out as follows.

(1) Determination of the amount of nitrites and nitrates in the atmosphere.

(2) Determination of the amount of nitrites and nitrates in rain water.

(3) Determination of the rate of absorption of the nitrites and nitrates of the atmosphere by water

(1) Nitrites and nitrates in the atmosphere:

The apparatus which I devised for the purpose of measuring directly the amount of nitrites and nitrates in the atmosphere is represented in fig A. FI? MN, and PQ are three bottles, each of

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which has a capacity of 500 c.c. In PQ I placed 200 c.c. of distilled water containing 0.1122 gram of calcium bicarbonat, and in FI 200 c.c. of distilled water with twice as much calcium carbicarbonate as in the bottle MN, but in PQ I placed 200 c.c. of distilled water without any calcium salt. They are well closed by rubber corks and connected in series by glass tubes as indicated in the figure. RUV is a long piece of glass tubing one end of which is connected with the bottle PQ, and the other end passes through the window and extends out in the open air above the roof. HED is another piece of glass tubing connecting the small bottle FI with the large bottle AB which has a capacity of about 20 liters. WX is another piece of glass tubing connected with a piece of rubber tubing XY, a piece of large glass tubing YZ, another piece piece of rubber tubing Zd, and finnally another piece of small glass tubing ds..chab is a stand upon the holder ch of which is attached by means of wire an empty glass sphere with a wide opening at k, and a small outlet at g. When the large bottle AB is filled with water up to a mark k which indicates a fixed volume found by measurement to be 18500 c.c. The filling of water is done by attaching the glass tubing ds to a water faucet, and open the rubber cork r, and when the bottle is filled up to the mark l, the water is turned off and the cork r is replaced. Then the glass ~~tubing~~gx tubing ds is disconnected from the faucet, and the water in the bottle AB begins to siphon out. Immediately the jet of water is introduced into the glass sphere through the mouth k, and the portion of rubber tubing is placed across the holder ch of the

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No. of Experiments		Volumes of Air (Liters)	Temperature $^{\circ}$
1	N as NO ₂	18.5	?
1	N as NO ₃	18.5	?
2	N as NO ₂	37.0	?
2	N as NO ₃	37.0	?
3	N as NO ₂	55.0	?
3	N as NO ₃	55.0	?
4	N as NO ₂	74.0	20-30
4	N as NO ₃	74.0	20-30
5	N as NO ₂	92.5	10-30
5	N as NO ₃	92.5	10-30
6	N as NO ₂	195.0	10-40
6	N as NO ₃	195.0	10-40
7	N as NO ₂	390.0	10-60
7	N as NO ₃	390.0	10-60
8	N as NO ₂	585.0	16-60
8	N as NO ₃	585.0	16-60
9	N as NO ₂	1000.0	20-60
9	N as NO ₃	1000.0	20-60
10	N as NO ₂	693.0	50-77
10	N as NO ₃	693.0	50-77
11	N as NO ₂	740.0	70
11	N as NO ₃	740.0	70
12	N as NO ₂	925.0	60-70
12	N as NO ₃	925.0	60-70
13	N as NO ₂	2000.0	50-80
13	N as NO ₃	2000.0	50-80

(14)

Parts per million in Bottle PQ.	p.p.m. in MN	Milligrams of N as NO ₂ & NO ₃ abs.	Milligrams of N as NO ₂ & NO ₃ in per 1000 liters of air.
none	none		
none	none		
none	none		
none	none		
none	none		
trace	none		
none	none		
trace	none		
none	none		
trace	none		
none	none		
0.03	none	0.006	0.0165
none	none		
0.03	none	0.006	0.0110
none	none		
0.12	trace	0.024	0.0240
trace	none		
0.09	none	0.018	0.0252
trace	none		
trace	none		
none	none		
0.10	b none	0.020	0.0238
trace	none		
0.28	trace	0.066	0.055
0.05	none		

stand, and twine which suspends the glass sphere is placed across the rubber tubing at m. At first the water because of its high pressure siphons out very rapidly, and there is more water running out from s into the glass sphere than its outlet g could let out, and as a consequence of this condition, the water in the sphere is accumulating all the time. The more water accumulates in the sphere, the heavier the sphere becomes, and the weight of the sphere which bears on the rubber tubing m tends to choke the water from running ~~out~~ out of the bottle AB at m. Consequently an equilibrium is established which serves as a regulator to give a constant flow, so that the stream of air passing through the small bottles shall be constant, in order to insure perfect absorption of nitrites and nitrates. As soon as the first bottle of water is siphoned out, I remove the glass tube from the glass sphere, and attach it again to the faucet, and let the water run in the bottle AbB very slowly till the water in the bottle FI begins to rise in the tube HJ, for there is a partial vacuum in the bottle AB. As soon as the partial vacuum is filled with water, I turn off the faucet and open the cork r, and fill the bottle AB with water from a graduated cylinder up to the mark I. Thus the volume of ~~the~~ air which is forced in from V through these three bottles into the large bottle is known (18500 c.c.). By repeating the same process one is able to draw over a volume of air as large as one pleases, and when the volume passes through PQ, MN, and FI, the nitrites and nitrates are all absorbed in the water contained in the bottle PQ. Occasionally I found a trace of nitrites in MN, but none

in FI, and no nitrates in either MN or FI. The results of my experiments are given in the page (13) and (14).

In order to test or determine the rate at which the nitrites would be oxidized into nitrates by the oxygen dissolved in water, I placed in the bottle MN 100 c.c. of sodium nitrite solution with the strength of 0.1 part nitrogen per million, 200 c.c. of hard water in PQ, and 200 c.c. of hard water in FI. Then I drew a certain volume of air through these bottles by siphoning the water out in AB as I did before. The small amount of nitrites and nitrates in the atmosphere is absorbed in the bottle PQ, and if there should be any nitrite that is sucked over, it is held in the bottle FI. Having thus drawn over a volume of air, 92.5, liters, through these three bottles, I found that there was not a trace of nitrite in the bottle MN oxidized into nitrate. Then I repeated the experiment by drawing over a volume of air, 195 liters, I found there was but a trace of nitrate present in MN.

(2) Nitrites and nitrates in rain water.

Rain water in different showers is collected in different clean beakers that are set out on a certain roof. Water caught in the first six hours is designated "During the first 6 hour", and water caught in the next six hours "During the second 6 hours". etc. As a matter of fact there was no rain continued over two, or three days, but a period of five, or six days without sunshine, and rain now and then, is designated as "During the 1st day, During the 2nd day etc"

(17)

The results of my experiments are as follows;

Experiment	p.p.m. of N as NO ₂ in rain	p.p.m. of N as NO ₃ in rain	
1	0.18	trace	During the 1st 6 hours
	0.02	none	During the 2nd 6 hours
	0.01	none	During the 3rd 6 hours
2	0.10	trace	During the 1st 6 hours
3	0.12	trace	During the 1st 6 hours
	0.01	none ?	During the 2nd 6 hours
	trace	trace ?	During the 3rd 6 hours
	trace	none	During the 2nd day in rain
	trace	none	During the 3rd day
	trace	none	During the 6th day
4	0.16	0.04	During the 1st 2 hours
	0.08	0.01	During the 2nd two hours
	0.05	trace	During the 3rd 2 hours
	trace	none	During the 6th 2 hours
5	0.18	0.05	During the 1st 2 hours
6	0.20	0.14	Thunder storm

Snow is gathered from the surface of the ground, and the time is recorded like that given in the rain.

Experiment	p.p.m. of N as NO ₂ in snow	p.p.m. of N as NO ₃ in snow	
1	0.05	none	During the 1st 6 hours
	trace	none	During the 2nd 6 hours

Experiment	p.p.m. of N as NO ₂ in snow	p.p.m. of N as NO ₃ in snow	
1	trace	none	During the 3rd 6 hours
2	0.06. 0.02 0.01 trace	trace? none none none	During the 1st 4 hours During the 2nd 4 hours During the 4th 4 hours During the 7th 4 hours
3	0.05 trace	trace none	During the 1st 6 hours During the 2nd 6 hours
4	0.05	trace	During the 1st 4 hours
5	0.04	none	During the 1st 6 hours
6	0.04 0.04? trace	Trace trace none	During the 1st two h During the 2nd 2 hours During the 7th 2 hours
7	0.05	trace	During the 1st 6 hours

(3) Absorption of nitrous and nitric acids from the atmosphere by water

To what extent does water in free contact with the atmosphere absorb nitrous and nitric from the air? This question was investigated by setting a few pans, containing distilled water, in a place freely accessible to the open air. The apparatus I devised for such purpose is represented in the fig b. MN is a long wooden box at the four corners of which I put four legs, so that it stands about three feet above the floor. The bottom of the box is represented by the plane CEND two strips of which, namely CEPO, and RQND are sawed off for the purpose of allowing air to circulate in the box very freely. On the front side, FNDL, I sawed off a piece of board represented by SKHT, and the same is attached on the box at KH by means of two hinges. SKHT is, therefore, used as a door, and

when it is open, it takes the position IJKH. Four pans represented by A, A', B and B' are placed in the box as in the figure b. They are thus protected from rain, and in part from dust; but in the course of 15 days, they invariably accumulated enough dust and soot from the city air to make replacement of the water in them advisable. Whenever the water becomes very dirty before 15 days, it is filtered. Box and pans were placed on a roof about thirty feet from the ground level. The open surface of each of the pans is 29.84 square inches. A and A' contain 400 c.c. of distilled water; B and B' contain 400 c.c. of distilled water with three per cent of calcium bicarbonate. Every three days 50 c.c. of the water in each pan was drawn out to test for nitrites and nitrates, and 50 c.c. of these two kinds of solvent were replaced in each pan accordingly. The results are given as follows. c

(20)

Nitrogen as Nitrites

days	p.p.m.	p.p.m. taken out each time.	(A) acture p.p.m.	acture amount in 400 c.c.	weather conditions
3	none	none	none	none	raining and cold
6	.017	.002	.017	.0058	Cloudy and cold
9	.033	.004	.035	.0140	bright and cold
12	.048	.006	.054	.0216	bright and warm
15	.0063		.075	.0300	bright and warm

Nitrogen as Nitrites in (A')

3	none	none	none	none	raining and cold
6	.017	.002	.017	.0058	cloudy and cold
9	.033	.004	.035	.0140	bright and cold
12	.048	.006	.054	.0216	bright and warm
15	.064	.	.076	.0304	bright and warm

Nitr

Nitrogen as Nitrites in B

3	none	none	none	none	raining and cold
6	.025	.003	.025	.0100	cloudy and cold
9	.0045	.006	.048	.0192	bright and cold
12	.062	.008	.071	.0284	bright and warm
15	.076		.093	.0372	bright and warm

Nitrogen as Nitrites in B'

3	none	none	none	none	raining and cold
6	.025	.003	.025	.0100	cloudy and cold
9	.045	.006	.048	.0192	bright and cold
12	.062	.008	.071	.0284	bright and warm
15	.076		.093	.0372	bright and warm

Nitrogen as Nitrates in A

3	none	none	none	none	raining and cold
6	none	none	none	none	cloudy and cold
9	trace?	trace?	trace?	trace?	bright and cold
12	trace	trace	trace	trace	bright and warm
15	.01		.01	.0040	bright and warm

Nitrogen as Nitrates in A'

3	none	none	none	none	raining and cold
6	none	none	none	none	cloudy and cold
9	trace?	trace?	trace?	trace?	bright and cold
12	trace	trace	trace	trace	bright and warm
15	.01		.01	.0040	bright and warm

(21)

Nitrogen as Nitrates in B

days	p.p.m.	p.p.m. taken out each time	acture p.p.m.	acture amount in 400 c.c.	weather conditions
3	none	none	none	none	raining and cold
6	none	none	none	none	cloudy and cold
9	trace	trace	trace	trace	bright and cold
12	trace	trace	trace	trace	bright and warm
15	.014		.014	.0056	bright and warm

Nitrogen as Nitrates in B'

3	none	none	none	none	raining and cold
6	none	none	none	none	cloudy and cold
9	trace	trace	trace	trace	bright and cold
12	trace	trace	trace	trace	bright and warm
15	.014		.014	.0056	bright and warm

Experiment (2)

Nitrogen as Nitrites in A

3	.023	.003	.023	.0092	bright and warm
6	.043	.005	.046	.0184	bright and warm
9	.062	.008	.070	.0280	bright and warm
12	.078	.010	.094	.0376	bright and warm
15	.093		.119	.0476	bright and warm

Nitrogen as Nitrites in A'

3	.023	.003	.023	.0092	bright and warm
6	.042	.005	.045	.0180	bright and warm
9	.063	.008	.063	.0284	bright and warm
12	.079	.010	.095	.0370	bright and warm
15	.110		.120	.0480	bright and warm

Nitrogen as nitrites in B

3	.032	.004	.032	.0128	bright and warm
6	.058	.007	.062	.0248	bright and warm
9	.078	.010	.090	.0360	bright and warm
12	.095	.012	.116	.0456	bright and warm
15	.108		.141	.0564	bright and warm

Nitrogen as Nitrites in B'

3	.032	.004	.032	.0128	bright and warm
6	.058	.007	.062	.0248	bright and warm
9	.078	.010	.089	.0356	bright and warm
12	.095	.012	.116	.0456	bright and warm
15	.107		.140	.0568	bright and warm

Nitrogen as Nitrates in A

days	p.p.m.	p.p.m. taken out each time.	acture p.p.m.	acture amount in 400 c.c.	weather conditions
3	none	none	none	none	bright and warm
6	.010	.001	.010	.0040	bright and warm
9	.021	.003	.022	.0088	bright and warm
12	.031	.004	.035	.0140	bright and warm
15	.042	.	.050	.0200	bright and warm

Nitrogen as Nitrites in A'

3	none	none	none	none	bright and warm
6	.010	.001	.010	.0040	bright and warm
9	.021	.003	.022	.0088	bright and warm
12	.031	.004	.035	.0140	bright and warm
15	.042	.	.049	.0200	bright and warm

Nitrogen as Nitrates in B

3	none	none	none	none	bright and warm
6	.014	.002	.014	.0056	bright and warm
9	.027	.003	.029	.0116	bright and warm
12	.035	.004	.040	.0160	bright and warm
15	.045	.	.054	.0216	bright and warm

Nitrogen as Nitrates in B'

3	none	none	none	none	bright and warm
6	.014	.002	.014	.0056	bright and warm
9	.027	.003	.029	.0116	bright and warm
12	.035	.004	.040	.0160	bright and warm
15	.045	.	.054	.0216	bright and warm

Experiment (3)

Nitrogen as Nitrites in A

3	.025	.003	.025	.0100	bright and warm
6	.035	.004	.038	.0152	rain once, warm
9	.038	.005	.045	.0180	rain twice, cold
12	.035	.004	.047	.0188	rain and cold
15	.050	.	.066	.0264	bright and warm

Nitrogen as Nitrites in A'

3	.025	.003	.025	.0100	bright and warm
6	.035	.004	.038	.0152	rain once, warm
9	.037	.005	.044	.0176	rain twice, cold
12	.034	.004	.046	.0184	rain and cold
15	.049	.	.065	.0260	bright and warm

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Nitrogen as Nitrites in B

days	p.p.m.	p.p.m. taken out each time	acture p.p.m.	acture amount in 400 c.c.	weather conditions
3	.034	.004	.034	.0136	bright and warm
6	.049	.006	.053	.0212	rain once, warm
9	.052	.006	.062	.0248	rain twice, cold
12	.048	.006	.064	.0256	rain and cold
15	.063		.085	.0340	bright and warm

Nitrogen as Nitrites in B'

3	.034	.004	.034	.0136	bright and warm
6	.049	.006	.053	.0212	rain once and warm
9	.052	.006	.062	.0248	rain twice, cold
12	.048	.006	.064	.0256	rain cold
15	.063		.085	.0340	bright and warm

Nitrogen as Nitrates in A

3	.010	.001	.010	.0040	bright and warm
6	.012	.001	.013	.0052	rain once and warm
9	.012	.001	.014	.0056	rain twice, cold
12	?	?	?	?	rain cold
15	.021	.	.024	.0096	bright and warm

Nitrogen as Nitrates in A'

3	.010	.001	.010	.0040	bright and warm
6	.012	.001	.013	.0052	rain once and warm
9	.011	.001	.013	.0052	rain twice, cold
12	?	?	?	?	rain and cold
15	.021	.	.024	.0096	bright and warm

Nitrogen as Nitrates in B

3	.010	.001	.010	.0040	bright and warm
6	.014	.002	.015	.0060	rain once and warm
9	.013	.002	.016	.0064	rain twice, cold
12	?	?	?	?	rain and cold
15	.023	.	.028	.0096	bright and warm

Nitrogen as Nitrates in B'

3	.010	.001	.010	.0040	bright and warm
6	.014	.002	.015	.0060	rain once and warm
9	.013	.002	.016	.0064	rain twice, cold
12	?	?	?	?	rain and cold
15	.023		.028	.0096	bright and warm

n The numbers in the table show distinctly that both nitrites and nitrates of air are absorbed by pure water. The alkalinity present in the water seems to help it to absorb these substances more quickly than when pure. After 15 days the waters seem to be dirty enough to demand the use of a new set. Of the three sets of experiments two of them were performed in ^{the} bad weather. The average nitrogen absorbed by water in the forms of nitrites and nitrates is .15⁵ part ~~part~~ per million.

(4) Discussion of Results:

A careful study of the preceding results, obtained from the three kinds of experiments convinces me that the atmosphere must be of the sources contributing to the fresh waters both nitrites and nitrates. By comparing the figures I find out that the amounts of nitrites and nitrates vary according to the temperature, or in other words these two substances are carried here by winds from the region where thunder storms frequently occur. It appears that whenever a current of warm air comes to visit us from the South (Thunder storm region the atmosphere contains more nitrates and nitrites. Consequently I can draw the conclusion that the atmosphere toward the equator contains much more of these two substances than that from the North. My experiments were performed in the months of November, February, March and April, and the average of the results is .15 part per million. I had in the small bottle two hundred c.c. of water, and it, therefore, in every one hundred cubic meters of air there are three grams of nitrogen in the forms of nitrites and nitrates. If this average is used to measure ~~texxxx~~ the atmosphere

there are 8.6 tons of nitrogen in these two forms of compounds in every cubic mile of air.

The figures I obtained from the analysis of rain waters do not permit me to calculate the amount of nitrites and nitrates per acre in a year, for I did not observe the amount rain we had during the season. However it is sufficient to indicate the presence of these two substances in the rains, and consequently I can use these figure to prove that the atmosphere is one of the sources from which both nitrites and nitrates are produced.

The numbers I obtained from my experiment (3) tell us that water in free contact with the atmosphere does absorb nitrites and nitrates from air. The average amount of these two substances absorbed by water in the little pans whose diameters are 9.5 inches each within the limit of two weeks is .128 part per million. There are .128 p.p.m. or .0504g 52 weeks in a year. If we use the average value to measure the water surface absorption, we would have about two grams of nitrogen in the forms of these two compounds absorbed ~~gr~~ from the air by water in every acre of aqueous surface. I think it is not altogether improbable that the ground or meadows wet with dew are capable of absorbing nitrites and ~~n~~ nitrates from the atmosphere.

In regard to the manner in which the atmosphere acquires its own nitrites and nitrates, I think we have the well accepted theory which assumes that in every thunder storm sporks of electricity combine the oxygen and nitrogen in the air into these nitrogen oxides. If the formation of nitrogen oxides depends ultimately on sporks, we would have to assume that gas diffusion and winds carry

to our atmosphere, in the Winter, nitrites and nitrates that are produced by the thunder storms in the South. However we are sure that we do have difference in potential in our atmosphere as we are told in Ganot's physics, page 1157. Both Lord Kelvin and Dr. G. C. Simpson investigated the same subject and they both came to the conclusion that there are various difference of potential in the air from morning to evening. We may not be able to detect any spark in the atmosphere, but it is not inconceivable that some nitrites could be generated by such quiescent current. The numbers I obtained in the experiment (2) indicate some sort of local force which causes the union of nitrogen and oxygen to form these two compounds, for after six day's consecutive raining I still found a trace of nitrites in the rain water. Dr. Willard states that nitrites in the atmosphere are produced as the result of oxidation of ammonia.

We know that the nitrogen compounds are very essential to the tissues of both animal and vegetable organisms. With the exception of some kinds of microbes both plants and animals are incapable of absorbing nitrogen from the air to form nitrogenous compounds that are so essential to their existence, and in combustion both of plant and animal remains liberates free nitrogen. Therefore in every year there is a tremendous amount of nitrogen liberated from its compounds by combustion, and in the same year vegetation and animals grow as usual. In addition to the amount of nitrogenous compounds produced by thunder storms, I think the local generation of such compounds by the difference in potential in the atmosphere should be counted as a possible source for making up the annual loss of ni-

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trogen available for plant food. From the preceding results and d
discussion, I predict that fresh waters in hot places contain more
nitrogenous compounds than those in the cold regions.

It will also be noted that all my experiments were performed in
the city the atmosphere contains a great deal of smoke.

Alex. G. Lee