

THE CHEMICAL CONTENT
OF RAINFALL AT DEWEY, OKLAHOMA

OKLAHOMA
AGRICULTURE & MECHANICAL COLLEGE
LIBRARY
JUL 17 1937

THE CHEMICAL CONTENT
OF RAINFALL AT DEWEY, OKLAHOMA

by

Claude Earnest Boatman

Bachelor of Science

Central State Teachers College, 1929

A

Thesis

in

Chemistry

Submitted to the Department of Chemistry
in Partial Fulfillment of the Requirements for the
Degree of
MASTER OF SCIENCE

Oklahoma

Agricultural and Mechanical College

Stillwater, Oklahoma

LIBRARY
OF THE
AGRICULTURAL AND MECHANICAL COLLEGE
STILLWATER, OKLA

OKLAHOMA **1.**
AGRICULTURE & MECHANICAL COLLEGE
LIBRARY
JUL 17 1937

Approved by W. G. Sellers
Advisor

Approved by Otto M. Smith
Head of the Department of Chemistry

Approved by D. C. M. Fisher
Dean of the Graduate School

ACKNOWLEDGEMENT

The author wishes to express his heartfelt appreciation to Dr. V. G. Heller, whose kindness and generosity made it possible to carry on this investigation; to the entire faculty of the chemistry department for the kindness that has been extended to him; for the cooperation of his wife, who in his absence took especial interest in the collection of the samples; and to his superintendent, Mr. G. E. Spraberry, who through his sympathetic understanding made it possible to carry on the work in the Dewey High School laboratory.

PREFACE

It is common knowledge that much impurity is washed from the air during a rain storm. It is fairly well known that in this section considerable amounts of many common nutrient materials are leached from the soil annually through drainage of the rain waters. Very little is known as to how much is added through rainfall. The Department of Agricultural Chemistry Research of Oklahoma Agricultural and Mechanical College was asked to make a survey relative to this problem. The data in this thesis is the report of a similar study conducted at Dewey, Oklahoma.

What effect do dust storms and meteorological conditions have on the chemical content of rain water? What effect do the fuel used and the proximity to industrial plants have on the chemical content? It is hoped that the investigation connected with this work will help to answer these questions.

TABLE OF CONTENTS

	<u>Page</u>
History of the Problem - - - - -	1
Experimental Procedure - - - - -	14
Tables - - - - -	18
Conclusions - - - - -	26
Bibliography - - - - -	29

TABLES

		<u>Page</u>
Table I	Comparison of Chemical Content of Rainfall in Pounds per Acre as Pre- viously Reported - - - - -	13
Table II	Date and Climatic Conditions at Time of Collection - - - - -	18
Table III	Ammonia Nitrogen - - - - -	19
Table IV	Nitrate Nitrogen - - - - -	20
Table V	Nitrite Nitrogen - - - - -	21
Table VI	Total Nitrogen - - - - -	22
Table VII	Chloride - - - - -	23
Table VIII	Sulphate - - - - -	24
Table IX	The Total Quantity of Substances Washed from the Air by Rain - - - - -	25

HISTORY OF THE PROBLEM

In his report on the chemical composition of rain water at Rothamstead, England, Miller¹ reviews the early history of the problem. As early as 1749-50 Marggraf found that the water collected during the winter contained nitric acid, chlorine, and lime. This work was followed by that of Bergman who analyzed rain and snow, later Saussure noticed that rain water contained ammonia. Several analyses were made in Europe between 1820-1825. Hermbsteadt detected organic matter; Mulder and Zimmerman found chlorine and several other substances in rains at Utrecht and near Giessen. Liebig detected nitric acid and ammonia in Zimmerman's samples. Brandes determined the total solids and found chlorine, sulfates, ammonia, and other substances. Dalton had already determined the chlorine content of the waters collected at Manchester. Payen in 1845-1846 first determined ammonia in rain water. From this date most of the analyses were made in France with no reference to the magnitude of the precipitation. Boussingault and Borral reported the quantity of rainfall in their determinations. For fifty years most of the work was done in Europe. These investigations were carried on for a very short period of time which gave inadequate data for comparative conclusions. At Rothamstead the chemical content of rainfall was measured as early as 1853-1854. In 1877 another series of experiments was started and continued until 1885. The analyses were made on monthly samples. In 1886 another series was started for the determination of nitric acid which was continued until 1905. In 1877

¹ M. H. J. Miller, The Amount of Nitrogen as Ammonia and as Nitric Acid, and of Chlorine in Rain Collected at Rothamstead. J. Agri. Sci. p.280, 1905

analysis of the chlorine content on monthly samples was started and continued up to the time of the article (1905). The sulfuric acid content was measured monthly from 1881-1887. In addition to these analyses, Sir Edward Frankland analyzed about eighty samples.

Miller's own analysis showed that in two years, 1888-89 to 1900-01, the average amount of ammonia plus the nitrate nitrogen per acre per annum was 3.84 pounds, 70 percent of which was in the form of ammonia. There was a variation of from 3.31 pounds to 4.43 pounds. The conclusion was that the variations probably depended in part on the distribution of the rainfall and had no definite relation to the quantity; however, the lowest was coincident with the least precipitation. It was further found that the amount of nitrogen depended on the temperature, since the magnitude of precipitation was greater in the summer months. It was also found that the quantity of nitric acid washed from the air in the two seasons remained constant, while the ammonia varied widely. The conclusion was also drawn that the climate is not coincident with variation of rain composition since the tropical rains do not add more nitrogen than do those of the temperate climates.

The nitrogen in the form of nitrites was considered usually insignificant, in fact in many samples negative results were encountered. From December until March only 28 percent were positive, but from June until September 80 percent showed positive results. These results do not indicate production or conservation of the nitrites.

The chlorine analysis showed that the total precipitation per annum is independent of the magnitude of rainfall. The amount varied, however, from month to month. The total quantity was affected by the

proximity to the sea. The same relation was shown in the sulfuric acid content.

From 1890 to 1900, Harrison² analyzed the rain water collected at Georgetown, British Guiana. His analysis showed that 34.8 percent of the nitrogen was in the form of ammonia and 65.2 percent in the form of nitrates. The total rainfall was 99.27 inches which furnished 1.01 pounds of nitrogen as ammonia, 1.89 pounds of nitrogen as nitrates, and 129.2 pounds of chlorine per acre.

Aufrey³ collected 123 samples in the Botanic gardens in Hanoi from April, 1902, to March, 1905, and 313 samples from open spaces in the middle of town from June, 1906, to September, 1909. Upon the assumption that the composition was constant, the amount of nitrogen per acre for the six year period was 16.24 pounds.

In Canada, Shutt⁴ determined the quantity of nitrogen in rain and snow. He found that the nitrogen increased with the use of bituminous coal. A total of 4.323 pounds of nitrogen per acre was precipitated, 74 percent of which was in the form of ammonia and the remainder as nitrates. The rain contained more nitrogen than snow. In a subsequent report⁵ he states that in 1911 the rainfall was 19.67 inches and the

² J. B. Harrison, Composition of Rain Water in British Guiana, *Expt. Expt. Agri. Work, Dept. Sci. and Agri., British Guiana*, pp 15-18, 1909-1910

³ M. Aufrey, Amount of Ammonia and Nitric Acid in Rain Water in Tonquin *Bull. Econ. Hanoi-Haiphong*, 12, pp 595-616, 1909

⁴ F. T. Shutt, Nitrogen Compounds in Rain and Snow, *Trans. Roy. Soc. Can III*, pp 181-185, 1910

⁵ F. T. Shutt, Fertilizing Value of Rain and Snow, *Ottawa Nat.* 25, pp 99-100, *Expt. Sta. Record* 25, p. 719

snow 7.3 inches, or a total rainfall of 26.97 inches. This precipitation furnished 5.271 pounds of nitrogen per acre. His reports show that of the average amount for 1908-1911, 84 percent was furnished by rain. The greater amount was in the form of ammonia.

Hudwig⁶ collected samples at Uithuizermeeden, Gronigen from July, 1908, to December, 1910, which he analyzed for nitrogen. There was a variation in the total nitrogen content of from .354 to 1.586 parts per million. Most of the total amount was in the form of ammonia. The nitrates and nitrites varied from .154 to .322 parts per million. He concluded that since the amount of nitrogen precipitated was small that it had very little fertilizing effect. He found that the amount washed from the air was dependent upon the amount of rain and the meteorological conditions.

In the rain waters collected at Lincoln, New Zealand, from July, 1907, to June, 1909, Gray⁷ found an average of 1.548 pounds of nitrogen precipitated annually with 50.9 percent of the total for 1907-1908 as ammonia and only 44.6 percent as ammonia for 1908-1909. As compared with earlier determinations the chlorine content was lower, due to a decrease in wind, and the sulfates higher, due to an increase in manufacturing.

In Russia, Vityn⁸ estimated the amount of chlorine and sulfuric acid in water collected at eight different places from April, 1909, to

⁶ J. Hudwig, The Amount of Nitrogen as Ammonia and Nitric (and Nitrous) Acid in Rain Water Collected at Uithuizermeeden, Gronigen, *J. Agri. Sci.* 4, pp. 260-9, 1921

⁷ Geo. Gray, Dissolved Matter Contained in Rain Water Collected at Lincoln, New Zealand, *Agri. Coll. Mag.* 1910. *J. Chem. Soc.* 100 II, p. 327

⁸ I. Vityn, Amount of Chlorine and Sulfuric Acid in Rain Water, *J. Chem. Soc.* 100 II, p. 432, 1911

March, 1910. The analysis was made on monthly samples. The average amount of chlorine was 11.355 pounds per acre, and that for SO_3 was 29.49 pounds per acre. There was a range of 7.45 pounds per acre at Pawlowska to 20.53 pounds at St. Petersburg for chlorine, and the SO_3 content varied from 5.13 pounds at Borowoje, Samara, to 70.88 pounds at Ohta. At four places, St. Petersburg, Ohta, Pawlowska, and Sepolje, the chlorine content was highest in the spring and autumn. The results seemed to be coincident with predominance of sea winds. At St. Petersburg, Ohta, and Marapol the sulfuric acid content seemed to be due to the combustion of wood and coal.

Anderson's⁹ determination of nitrates and nitrites in the waters collected at Canterbury near Melbourne, Australia, shows that these compounds are more abundant in tropical storms than in the antarctic type. With the latter type the amounts of nitrogen were from 0.002 to 0.005 kg per hectare. The tropical rains of the spring and autumn type gave 0.018 kg per hectare while the summer type gave 0.027 kg. The heat wave type furnished 0.039 kg. The results varied under the influence of each type of storm.

Growther and Rustan¹⁰ concluded from their experiments at Leeds and Garforth that the ammonia content of rain water was largely determined by the locality and the amount of rain. Their analysis showed

⁹ V. G. Anderson, Influence of Weather Conditions on the Amount of Nitric Acid and Nitrous Acid in Rainfall Near Melbourne, Australia. Rept. Brit. Assoc., p. 3389, 1914. Quart. J. Roy. Met. Soc. 41, pp. 99-122, 1915

¹⁰ Chas. Growther and A. Rustan, The Nature of Distribution and Effects Upon Vegetation of Atmospheric Impurities In and Near an Industrial Town. J. Agri. Sci. 4, p. 25, 1911

less ammonia in the summer than in the winter. Light rains were proportionately richer in ammonia than the more copious ones. There were 95.7 pounds of SO_3 per acre added to the soil annually. One station at Leeds showed 336 pounds of SO_3 per acre. About 26 percent of the total sulfur was in form less highly oxidized than sulfates. The conclusions drawn by them were: (1) In industrial centers the atmosphere is charged with impurities, many of which are injurious to plants. (2) The impurities are most abundant in the industrial centers of the city and are disseminated over a large area, especially in the direction of the prevailing winds. (3) Rain is rich in suspended matter, chlorides, sulfates, and nitrogenous compounds. (4) Suspended matter impairs the growth of plants by preventing the passage of gases in and out of the leaves through deposition on the leaves as well as reducing the exposure to sunlight. (5) Free acids harm the plants through the direct action on the leaves and indirectly by reducing the activity of the necessary ammoniacal fermentation of soil humus. The effect on the beneficial nitrifying and nitrogen fixing bacteria in soil is even more deleterious. (6) The acids cause timothy to become poorer in proteins and richer in crude fiber.

Schroeder¹¹ found in the samples collected at Montevideo (1909-1912) 6.86 pounds per acre of nitrogen per annum and 87.9 kg NaCl per hectare. He substantiated the observation of others that most of the nitrogen was in the form of ammonia.

¹¹ J. Schroeder, The Composition of Rainfall at Montevideo (1909-1912), Rev. Assoc. Rural Uruguay, 1915

In 51 samples of rain and snow collected at Mt. Vernon, Iowa, in 1916, Artis¹² found that the ammoniacal nitrogen varied from 0.13 to 0.80 parts per million. Albuminoid nitrogen varied from 0.12 to 1.19 parts per million; the nitrate nitrogen from 0.005 to 0.80 parts per million. The chlorides ranged from 3.5 to 21.3 parts per million and sulfates ranged from 1.7 to 38 parts per million. The literature gave no data as to the quantity in pounds per acre and since there was no data relative to inches of rainfall it was impossible to calculate the annual precipitation of these substances.

The report from the Charcot¹³ expedition to the Antarctic shows for different parts of the southern hemispheres an average of .225 parts per million of nitrates for rain and .223 parts per million for snow.

In discussing what has been done in this field only the foreign countries have been covered. No small amount has been done in the United States.

The earliest record that was obtainable shows that in Mississippi¹⁴ in 1894 and 1895 there were 40.7 inches and 47.49 inches of rainfall respectively. The amount of nitrogen added to an acre per year was 2.847 pounds and 3.308 pounds respectively. The conclusion was drawn that this was one half the amount found in commercial fertilizer. This would indicate a decided effect upon soil fertility as opposed to the

¹² B. Artis, Nitrogen, Chlorine and Sulfate in Rain and Snow, Chem. News 113, pp. 3-5, 1916

¹³ H. H. Fennell and H. W. Houghton, Soil Nitrogen Income from Rain Water, Panhandle Agri. Expt. Sta. Bulletin 23, 1931

¹⁴ Ammonia in Rain Water, Mississippi St. An. Rep. 1895, p. 102

views of Hudwig.¹⁵

Stewart¹⁶ determined the sulfur in rain waters in Illinois. He found that 40 to 51 pounds per acre were washed down annually by the rain as shown by his analysis over a seven year period. The average was 45.1 pounds of sulfur per annum or 3.8 pounds monthly. The source of sulfur was from burning coal, sulfur dioxide and hydrogen sulfide that were liberated from industrial plants and growth of vegetation. He found that the amount of sulfur collected depended upon the quantity of rainfall. The amount added is sufficient to compensate for that lost through leeching and plant growth.

Wilson¹⁷ found that, while the sulfur content was usually higher in industrial centers, sometimes the content was higher for agricultural districts.

Johnson¹⁸ determined the quantity of sulfur in rain water in seven localities in Kentucky. The samples were collected at Lexington (U. S. Weather Bureau), the Van Meter farm near Lexington, Lincoln Institute, Paducah (Lone Oak), Mayfield, Russellville, and Greenville. The average rainfall was 44.77 inches, which furnished an average of 29.52 pounds of sulfur per acre per annum. The year was divided into quarters for the purpose of comparing seasonal variations in sulfur content. The fol-

¹⁵ J. Hudwig, loc. cit.

¹⁶ Robert Stewart, Sulfur in Relation to Soil Fertility, Ill. Agri. Expt. St. Bulletin, p. 227, 1920

¹⁷ E. D. Wilson, Sulfur Supplied to the Soil in Rain Water, J. Amer. Soc. Agron. 13, p. 226, 1921

¹⁸ E. M. Johnson, Sulfur in Rain Water in Kentucky, J. Amer. Soc. Agron. 17, p. 335, 1925

Following table shows the results:

Quarter	Pounds per acre per quarter	Rainfall in inches
1. January, February, March	13.330	14.88
2. April, May, June	7.087	9.45
3. July, August, September	6.355	9.52
4. October, November, December	9.337	11.63

These data show that the sulfur content is greater in the winter than in the summer.

Freeman¹⁹ analyzed samples collected at the same places in Kentucky as those of Johnson²⁰ for nitrogen. It was found that an average rainfall of 42.76 inches for the year April 1, 1922, to April 1, 1923, furnished an average of 18.78 pounds of nitrogen per acre. 11.61 pounds were in the form of ammonia and 7.17 pounds in the form of nitrates.

Eaton and Eaton²¹ cite the work of McIntyre and Young, who found 94.5 pounds of sulfur precipitated annually in the center of Nashville, while only 51.5 pounds were washed from the air 1.5 miles away, as a verification of their observation that the amount of sulfur is dependent on the proximity to industrial plants. They found more sulfur in the winter months and a direct relationship to the kind of coal burned.

¹⁹ J. F. Freeman, Nitrogen in Rain Water at Different Points in Kentucky, *J. Amer. Soc. Agron.* 15, p. 356, 1924

²⁰ E. M. Johnson, loc. cit.

²¹ S. V. Eaton and J. H. Eaton, Sulfur in Rainfall-Plant Physiol, pp. 1-77, January 1926

The work of Erdman, who found that more sulfur was brought down during the growing season (March to October), is also cited. Erdman explains this phenomenon by the fact that more hydrogen sulfide is evolved in the summer. These workers found that the percentage of sulfur was greater in small rains and varied inversely to the amount of rain. They believed that more sulfur was lost annually than was increased through rainfall and that the results may be disastrous.

In New York, Wilson²² analyzed samples from Ithaca, Brockport, and Alfred. An average of 7.13 pounds of ammonical nitrogen and .81 pounds of nitrate nitrogen from an average rainfall of 29.46 inches for an eleven year period was found at Ithaca. The amounts of ammonical nitrogen for Brockport and Alfred over a three and a two year period respectively were: for an average rainfall of 31.7 inches and 32.4 inches, 2.6 pounds and 12.75 pounds. Over this same period the nitrate nitrogen for Brockport and Alfred were .23 pounds and .25 pounds respectively. The waters at Ithaca furnished an average of 38.25 pounds of sulfur and those of Brockport and Alfred 77.53 pounds and 49.75 pounds respectively. These investigators verified the observation of others that the sulfur content was greater in the winter than in the summer. They observed that the amount of sulfur varies from station to station but remains constant at the same station.

N. Knight,²³ et al.,^{24 25 26} found the following amounts of nitro-

²² B. D. Wilson, Nitrogen and Sulfur in Rain Water in New York, J. Amer. Soc. Agron. 18, p. 1108, 1926

²³ N. Knight, Nitrogen in Rain and Snow, Proc. Iowa Acad. Sci. 18, pp. 75-77, 1911

^{24 25 26} (see following page)

gen per acre: January to April and September to December 1910, 13.71 pounds; February 22nd to January 5, 1912, 6.27 pounds; October 4, 1913 to January 12, 1914, 3.70 pounds; October 1, 1922 to June 1, 1923, 3.93 pounds.

Finnell and Houghton²⁷ furnishes the only report of work done in Oklahoma. Their work was carried on at Goodwell which is free from contamination. Their results show a greater quantity of ammonia when the rain is preceded by a dust storm. Thirty-two rains were grouped according to the intensity of electrical discharges to find the correlation between the amount of lightning and nitrate delivery. The results are:

	No lightning	Moderate lightning	Excessive lightning
Nitrate Content	.0048	.0111	.0281

The above data would indicate that the nitrate content is greater when the storm is accompanied by lightning. Twenty rains were analyzed for nitrite nitrogen. Those from February to April furnished .0042 pounds per acre and those from May to August .0004 pounds per acre. They believe that complete oxidation is dependent on the temperature. The

²⁴ W. K. Knox, Nitrogen and Chlorin in Rain and Snow, Chem. News, 111 1915, No. 2880, pp. 61-62

²⁵ J. H. Weehlk, Nitrogen and Other Substances in Rain and Snow, Chem. News, 127, 1923, No. 3330, p. 30

²⁶ G. H. Wiesner, Nitrogen and Chlorin in Rain and Snow, Chem. News, 109, 1914, No. 2830, pp. 85-87

²⁷ Finnell and Houghton, Nitrogen Content of Rain Water, Panhandle Agri. Expt. Sta. Bull. 34, 1935

data indicates that the oxidation is more complete in the cooler months.

The total amount of nitrogen furnished to the soil at Goodwell in 1931 with an average rainfall of 15.45 inches was 1.42 pounds per acre.

Comparative results of these investigations will be found in Table I.

LIBRARY
JUL 17 1937

COMPARISON OF CHEMICAL CONTENT OF RAINFALL IN POUNDS PER ACRE AS PREVIOUSLY REPORTED

Location	Period Collected	NH ₃ -N	NO ₂ -N	NO ₃ -N	NO ₂ -N	Total N	Sulfur	Chlorides
Rothamstead, Eng.	1889-1901	2.690	1.150	---	---	---	6.86	20.040
Georgetown, Brit. G.	1890-1900	1.010	1.890	---	---	---	---	129.200
Hanoi	1902-1905	---	---	---	16.240	---	---	---
Quebec	1909-1910	2.999	1.324	---	4.323	---	---	---
Quebec	1911	---	---	---	5.271	---	---	---
Uithuizermeeden	1906-1910	(Total nitrogen varied from .354 to 1.586 ppm. No data as to inches of rain.)						
Lincoln, New Zealand	1884-1888	---	---	---	---	---	5.98	---
Lincoln, New Zealand	1907-1909	0.788	0.860	---	1.548	---	---	---
8 places in Russia	1909-1910	---	---	---	---	11.80	---	11.355
Garforth	1906-1909	---	---	---	---	---	38.27	---
Leeds	1907-1908	---	---	---	---	---	64.41	---
Montevideo	1909-1912	---	---	---	---	6.86	---	46.8
Mississippi	1894	---	---	---	---	2.847	---	---
Mississippi	1895	---	---	---	---	3.308	---	---
Illinois, Urbana	1913-1919	---	---	---	---	---	45.100	---
Kentucky	1924	---	---	---	---	---	29.520	---
Kentucky	1922-1923	11.610	7.170	---	18.780	---	---	---
Ithaca, N.Y.	1915-1926	7.130	0.810	---	7.940	38.250*	---	---
Brockport	1923-1926	2.600	0.230	---	2.830	77.530	---	---
Alfred	1923-1925	12.750	0.250	---	13.000	49.753	---	---
Mt. Vernon, Ia.	1910	---	---	---	13.710	---	---	---
Mt. Vernon, Ia.	1912	---	---	---	6.270	---	---	---
Mt. Vernon, Ia.	1913-1914	---	---	---	3.700	---	---	---
Mt. Vernon, Ia.	1922-1923	---	---	---	3.930	---	---	---
Goodwell	1930	---	---	---	0.509	---	---	---
Goodwell	1931	0.991	0.321	.108	1.420	---	---	---

*8 year period

TABLE I

EXPERIMENTAL PROCEDURE

Dewey, a city of about 2000 population, is located in Washington county about midway between the north and south boundaries and about two miles from the western boundary. It is four and one-half miles northeast of Bartlesville. It lies in the valley of the Caney river. Most of the winter storms come from the north and northeast, while in the spring and summer the storms arrive from the northwest. The most commonly used fuel is natural gas, though considerable wood and coal are used for heating purposes during the winter months. In Dewey the only industrial plant of importance is the cement plant. At Bartlesville is located the smelters of the National Zinc Company. Tulsa, sixty-five miles to the south, has many industrial plants including refineries; Joplin, Pitcher, Coffeyville, and Miami to the north have many smelters; Blackwell and Ponca City to the west have smelters and refineries which liberates sulfur during their operations. In view of the fact that dust is known to have crossed the Atlantic ocean it is not too presumptuous to assume that sulfur is carried from these places by the wind.

The water for these experiments was collected in the garden plot at the rear of the residence of the author. Three large granite dish pans were used to catch the rainfall. These pans were placed on a rack about four and one-half feet above the soil so that the contamination from the soil due to the splattering of the rain would be reduced to the minimum. Care was taken to prevent contamination from roofs, trees, or other sources. Before each rain, dust and other debris were wiped carefully from the pans. The sample, it is believed, fairly well represented the true chemical content due to the washing of the atmosphere.

The inches of rainfall were measured in a large graduate which was calibrated in 1/10 inches, however, for the calculations involved the climatological report was used to determine the inches of rainfall for that vicinity.

No attempt was made to devise new methods of analysis since the methods in practical usage were considered adequate for these determinations.

To determine the ammonia¹ a 250 cc sample was distilled, the distillate being collected in 50 cc portions. These portions were Nesslerized and compared with standards prepared from a solution of ammonium chloride which contained .01 mg of N per cc.

For nitrates the phenol disulfonic acid² method was used on a 50 cc sample. The only variation from the method outlined was the addition of a few drops of a 10 percent solution of sodium carbonate. This was done on the assumption that, during the process of nitrogen fixation, some volatile nitrates (HNO_3) were formed which would be dissipated by evaporation. This would hold the nitrates as the sodium compound. It was actually observed that the nitrate content was greater in samples of the same rainfall that had been treated in this manner than those that had not been.

In the determination of the amount of nitrite nitrogen the sulfanilic acid, Naphthylamine³ method was used. The treated samples were

¹ American Public Health Association, Standard Methods of Water Analysis, pp. 15-16, 1917

² Ibid, pp. 23-24

³ Ibid, p. 22

compared to a standard color disc.

The Kjeldahl method was used to determine the organic and nitrate nitrogen. A 250 cc sample of the rain water was evaporated to about 5 cc, treated with 35 cc of a mixture of sulfuric acid and salicylic acid and allowed to stand for at least thirty minutes. At the end of this period 5 g of sodium thio sulfate was added in order to reduce the nitrate, and the mixture heated for five minutes after which it was allowed to cool. When the temperature had been sufficiently reduced, 10 g of $\text{CuSO}_4 - \text{Na}_2\text{SO}_4$ mixture was added and the digestion carried on at least two hours until the solution became a sparkling perfectly clear green color. The mixture was then allowed to cool and 250 cc of distilled water was added. To the final solution 60 cc of concentrated NaOH was added. A piece of zinc was placed in the flask to prevent bumping. The solution was distilled into 15 cc of $1/7 \text{ N H}_2\text{SO}_4$. After about two-thirds of the liquid had distilled over into the receiving flask the excess acid was neutralized with $1/14 \text{ N NaOH}$. Twice the volume of the acid minus the volume of the base was the volume of $1/14 \text{ N}$ acid neutralized by the ammonia from the digested sample. Since 1 cc of $1/14 \text{ N H}_2\text{SO}_4$ has a nitrogen titre of 1 mg, then the volume multiplied by 1 was the quantity of organic and nitrate nitrogen in 250 cc of the sample.

Chlorides were determined according to standard methods.⁴ Care must be taken in titration since the color change may not be so perceptible. It was found to be advisable first to run a blank on dis-

⁴ American Public Health Association, op. cit., pp. 42-43

tilled water to which 1 cc of potassium dichromate solution was added to find how much silver nitrate was necessary to produce a distinguishable color change. It was found that .15 cc of the AgNO_3 solution was necessary for this observer. In the calculations this volume was subtracted from the total volume AgNO_3 to obtain the true volume necessary to react with the chlorides in the sample.

The sulfates⁵ were precipitated as BaSO_4 and weighed as such, 41.1 percent of the total weight being the amount of sulfate (SO_4).

The following tables show the result of the observation running from November 1935 until January 1, 1937. The reports are all calculated as mg per liter and converted to pounds per acre.

⁵ American Public Health Association, op. cit., p. 58

DATE AND CLIMATIC CONDITIONS AT TIME OF COLLECTION

No.	Form of Prec.	Temperature	Amount of Rain-fall Observed	Prevailing Wind Direction	Dust	Lightning	Total per No.
1	Nov. 25, '35	45°F	1.00	South	none	none	1.00
2	Dec. 5-6, '35	40°F	1.21	South	none	none	
3	Dec. 26-29, '35	30°F	0.15	N.E.	none	none	1.36*
4	Jan. 1-2, '36	45°F	0.60	South	none	none	.60
5	Feb. 1 & 4, '36	43°F	0.20	N.W.	none	none	
6	Feb. 26, '36	61°F	1.00	N.E.	some	yes	1.20
March							
Precipitation too slight to catch sample							
7	April 9, '36	50°F	0.45	varied	some	yes	
8	April 21-28, '36	75°F	1.30	South	some	yes	1.75
9	May 1, '36	89°F	3.50	South	none	yes	
10	May 8, '36	84°F	2.60	South	none	yes	
11	May 11, '36	76°F	.80	South	none	none	
12	May 18, '36	86°F	.85	North	none	none	
13	May 22-24, '36	85°F	.50	South	none	yes	8.25
14	June 5-6-7, '36	93°F (hail)	5.10	North	none	yes	
15	June 17 & 30, '36	107°F (av)	1.00	South	none	yes	6.10
July							
Precipitation too slight to catch sample							
August							
Precipitation too slight to catch sample							
16	Sept. 1, '36	99°F	1.10	West	yes	excessive	
17	Sept. 7 & 12, '36	101.5°F	1.00	N.E.	some	yes	
18	Sept. 16-19, '36	83°F	4.50	S.E.	none	yes	
19	Sept. 20, '36	87°F	2.70	hard south	none	yes	
20	Sept. 23, '36	91°F	.90	South	none	yes	
21	Sept. 26-28, '36	80°-61°F	2.70	N.E.	none	none	12.90
22	Oct. 6-8, '36	65°F	5.80	North	none	yes	
23	Oct. 21-22, '36	75°F	1.00	N.E.	none	none	6.80
24	Nov. 2, '36	75°F	1.90	S.W.	none	none	1.90
25	Dec. 1-2, '36	35°F	.70	N.E.	none	none	
26	Dec. 5, '36	40°F	1.30	South	none	none	
27	Dec. 11, '36	40°F	1.00	South	none	none	3.00

*Gov. report

TABLE II

AMMONIA NITROGEN

Sample No.	Inches of Rain-fall per Rain	mg. N. per 1000 ml.	Pounds of N per Acre per Rain	Pounds of N per Acre per Mo.
November and December 1935				
1	1.00	.272	.0616	
2	1.21	.320	.0877	
3	.15	.220	.0075	.1568
January 1936				
4	.60	.140	.0190	.0190
February 1936				
5	.20	.740	.0335	
6	1.00	.400	.0906	.1241
April 1936				
7	.45	.520	.0530	
8	1.30	.380	.1119	.1649
May 1936				
9	3.50	.180	.1428	
10	2.60	.100	.0589	
11	.80	.040	.0073	
12	.85	.060	.0116	
13	.50	.140	.0159	.2365
June 1936				
14	5.10	.092	.1063	
15	1.00	.024	.0054	.1117
September 1936				
16	1.10	.276	.0688	
17	1.00	.260	.0589	
18	4.50	.040	.0408	
19	2.70	.320	.1958	
20	.90	.200	.0408	
21	2.70	.040	.0245	.4296
October 1936				
22	5.80	.220	.2891	
23	1.00	.160	.0363	.3254
November 1936				
24	1.90	.080	.0344	.0344
December 1936				
25	.70	.040	.0063	
26	1.30	.020	.0059	
27	1.00	.120	.0272	.0394

TABLE III

NITRATE NITROGEN

Sample No.	Inches of Rain-- fall per Rain	mg. N. per 1000 ml.	Pounds of N per Acre per Rain	Pounds of N per Acre per Mo.
November and December 1935				
1	1.00	.75	.1700	
2	1.21	.75	.2056	
3	.15	.10	.0034	.3790
January 1936				
4	.60	.04	.0054	.0054
February 1936				
5	..20	.08	.0036	
6	1.00	.16	.0363	.0399
April 1936				
7	.45	.30	.0306	
8	1.30	.30	.0884	.1190
May 1936				
9	3.50	.06	.0476	
10	2.60	.04	.0236	
11	.80	.02	.0036	
12	.85	.10	.0193	
13	.55	.06	.0068	.1009
June 1936				
14	5.10	.06	.0693	
15	1.00	.40	.0906	.1599
September 1936				
16	1.10	1.20	.2991	
17	1.00	.02	.0045	
18	4.50	.14	.1428	
19	2.70	.04	.0245	
20	.90	.36	.0734	
21	2.70	.14	.0857	.6300
October 1936				
22	5.80	.08	.1051	
23	1.00	.10	.0227	.1278
November 1936				
24	1.90	.00	.0000	.0000
December 1936				
25	.70	.30	.0476	
26	1.30	.10	.0295	
27	1.00	.34	.0770	.1541

TABLE IV

NITRITE NITROGEN

Sample No.	Inches of Rain-fall per Rain	mg. N. per 1000 ml.	Pounds of N per Acre per Rain	Pounds of N per Acre per Mo.
November and December 1935				
1	1.00	.007	.0016	
2	1.21	.007	.0019	
3	.15	.025	.0008	.0043
January 1936				
4	.60	.017	.0023	.0023
February 1936				
5	.20	.075	.0034	
6	1.00	.040	.0091	.0125
April 1936				
7	.45	.002	.0002	
8	1.30	.014	.0041	.0043
May 1936				
9	3.50	.010	.0079	
10	2.60	.010	.0059	
11	.80	.010	.0018	
12	.85	.010	.0019	
13	.50	.007	.0008	.0183
June 1936				
14	5.10	.004	.0046	
15	1.00	.002	.0005	.0051
September 1936				
16	1.10	.002	.0005	
17	1.00	.014	.0032	
18	4.50	.010	.0102	
19	2.70	.016	.0098	
20	.90	.002	.0004	
21	2.70	.018	.0110	.0351
October 1936				
22	5.80	.002	.0026	
23	1.00	.022	.0050	.0076
November 1936				
24	1.90	.014	.0060	.0060
December 1936				
25	.70	.007	.0011	
26	1.30	.034	.0100	
27	1.00	.002	.0005	.0116

TABLE V

TOTAL NITROGEN

Sample No.	Inches of Rain-fall per Rain	mg. N. per 1000 ml.	Pounds of N per Acre per Rain	Pounds of N per Acre per Mo.
November and December 1935				
1	1.00	1.03	.2334	
2	1.21	.80	.2193	
3	.15	1.00	.0340	.4867
January 1936				
4	.60	.20	.0272	.0272
February 1936				
5	.20	4.00	.1813	
6	1.00	1.60	.3626	.5439
April 1936				
7	.45	4.00	.4079	
8	1.30	2.80	.8248	1.2327
May 1936				
9	3.50	.15	.1190	
10	2.60	.15	.0884	
11	.80	.07	.0127	
12	.85	3.40	.6549	
13	.50	5.60	.6345	1.5095
June 1936				
14	5.10	.16	.1849	
15	1.00	.43	.0974	.2823
September 1936				
16	1.10	1.48	.3689	
17	1.00	1.00	.2266	
18	4.50	3.00	3.0591	
19	2.70	.38	.2325	
20	.90	.56	.1142	
21	2.70	.20	.1224	4.1237
October 1936				
22	5.80	.30	.3943	
23	1.00	.28	.0634	.4577
November 1936				
24	1.90	.09	.0387	.0387
December 1936				
25	.70	2.54	.4029	
26	1.30	.70	.2062	
27	1.00	.46	.1042	.7133

TABLE VI

CHLORILE

Sample No.	Inches of Rain-fall per Rain	mg. Cl. per 1000 ml.	Pounds of Cl. per Acre per Rain	Pounds of Cl. per Acre per Mo.
November and December 1935				
1	1.00	.500	.1133	
2	1.21	.000	.0000	
3	.15	2.028	.0689	.1822
January 1936				
4	.60	.608	.0827	.0827
February 1936				
5	.20	.508	.0230	
6	1.00	1.016	.2302	.2532
April 1936				
7	.45	5.560	.5670	
8	1.30	2.600	.7659	1.3329
May 1936				
9	3.50	2.600	2.0621	
10	2.60	3.000	1.7675	
11	.80	1.520	.2755	
12	.85	1.520	.2928	
13	.50	2.000	.2266	4.6245
June 1936				
14	5.10	1.520	1.7566	
15	1.00	3.500	.7931	2.5497
September 1936				
16	1.10	3.540	.8824	
17	1.00	4.060	.9200	
18	4.50	1.014	1.0340	
19	2.70	1.520	.9300	
20	.90	1.014	.2068	
21	2.70	.507	.3102	4.2834
October 1936				
22	5.80	1.520	1.9977	
23	1.00	.507	.1149	2.1126
November 1936				
24	1.90	.507	.2183	.2183
December 1936				
25	.70	2.540	.4029	
26	1.30	.507	.1494	
27	1.00	4.060	.9200	1.4723

TABLE VII

SULPHATE

Sample No.	Inches of Rain-fall per Rain	mg. SO ₄ per 1000 ml.	Pounds of SO ₄ per Acre per Rain	Pounds of SO ₄ per Acre per Mo.
November and December 1935				
1	1.00	6.8400	1.5499	
2	1.21	1.2340	.3383	
3	.15	5.8198	.1978	2.0860
January 1936				
4	.60	3.7717	.5128	.5128
February 1936				
5	.20	4.0073	.1816	
6	1.00	3.1670	.7164	.8980
April 1936				
7	.45	1.0302	.1050	
8	1.30	3.5871	1.0567	1.1617
May 1936				
9	3.50	5.1830	4.1106	
10	2.60	4.1550	2.4480	
11	.80	3.7840	.6860	
12	.85	7.2627	1.3997	
13	.50	15.9468	1.8068	8.6443
June 1936				
14	5.10	2.8359	3.2773	
15	1.00	7.6109	1.7246	5.0019
September 1936				
16	1.10	7.1306	1.7774	
17	1.00	11.7133	2.6542	
18	4.50	5.1830	5.2851	
19	2.70	2.0961	1.2824	
20	.90	1.9728	.4023	
21	2.70	3.0824	1.8859	13.2873
October 1936				
22	5.80	4.1355	5.4352	
23	1.00	16.1112	3.6508	8.0860
November 1936				
24	1.90	2.4249	1.0440	1.0440
December 1936				
25	.70	27.1671	4.3092	
26	1.30	19.7691	5.8236	
27	1.00	34.6642	7.8549	17.9877

TABLE VIII

THE TOTAL QUANTITY OF SUBSTANCES
WASHED FROM THE AIR BY RAIN

	November 1935 to January 1937	January 1936 to January 1937
Pounds of NH_3N per Acre	1.6418	1.4850
Pounds of NO_xN per Acre	1.7160	1.3370
Pounds of NO_2N per Acre	.1074	.1031
Pounds of Total N per Acre	9.4157	8.9290
Pounds of Cl per Acre	17.1118	16.9296
Pounds of SO_4 per Acre	58.7097	56.6237

TABLE IX

CONCLUSIONS

1. From the foregoing table one may safely conclude that the precipitation of ammonical nitrogen is greater during the spring months after which it dropped in value until the early fall when it again increased. In early winter the amount of ammonia decreased. As will be noticed sample number five shows a rather high ammonia content. The rainfall from which that sample was collected was very small, in fact it took several days to accumulate enough water on which to run the analysis. The particles of water were suspended in the atmosphere as fog for a greater part of the time. That this would show a considerable larger quantity of ammonia would be expected since intimate contact between the gas and water was assured. Again in April we find a large quantity of ammonia. This rain followed a dust storm. The results would seem to indicate a positive relationship between the dust storms and the quantity of ammonia precipitated. September furnished a rather high ammonia precipitation with the greater average per storm than in any month of the year. The two months preceding had been very hot and dry with only a bare trace of rainfall. The rain, in all probability, simply washed from the air an accumulated quantity of ammonia. It may be further observed that the greater quantity, expressed in parts per million, is coincident with the lesser rainfall.

2. That the nitrate nitrogen precipitation be increased when the storm is accompanied by electrical disturbances is to be expected because of the fixation of nitrogen. Table IV shows that as we proceed from winter to the spring months there is a decided increase in the amount of nitrate nitrogen. The largest quantity was precipitated in September. Most of these rains were accompanied by rather severe light-

ning. The increase in precipitation of nitrate nitrogen is coincident with the electrical disturbances.

3. The nitrite content is rather small. The results show that the amount of nitrite nitrogen is not perceptibly affected by the dust storms. Lightning would seem to increase the total precipitation as shown by the total quantity washed out during the months of May and September which exhibited an extensive electrical display. However, the quantity seems, in the case of February, to be somewhat dependent upon the temperature. September was the breaking of a long drouth accompanied by a high temperature range.

4. No attempt is made to account for the precipitation of organic nitrogen other than it must be from organic matter carried into the atmosphere by the wind.

5. The chloride content is greater during the spring and summer months than at any other time of the year. Many of our storms which show a high chloride content arrive from the northwest and west. The samples number seven and eight show a high chloride content following the dust storm in April. This fact would indicate that a rather large quantity of chloride was blown in by the dust.

6. The precipitation of sulfates is larger in the cooler months. The larger amounts are coincident with the increase in the quantity of fuel burned. The precipitation of sulfur is dependent to some extent upon the operation of the cement plant as shown by the figures for the months of December 1935, at which time the plant was not in operation, and December of 1936 when it was going at full production. The smelters of the National Zinc Company probably add some sulfates since the sulfate content increases when the wind is from the south or southwest,

however, the increase due to the wind from the northeast, which comes from the Dewey Portland Cement Company, is also apparent. There has also been an increase in the quantity of coal that is being used for home heating purposes.

BIBLIOGRAPHY

1. American Public Health Association. Standard Methods of Water Analysis. 1917.
2. Anderson, V. G. Influence of Weather Conditions on the Amount of Nitric Acid and Nitrous Acid in Rainfall Near Melbourne, Australia. Rept. Brit. Asso., 1914.
3. Artis, B. Nitrogen, Chlorine, and Sulfate in Rain and Snow. Chem. News 113, 1916.
4. Aufray, M. Amount of Ammonia and Nitric Acid in Rain Water in Tonquin. Bull. Econ. Hanoi-Haiphong, 12, 1909.
5. Crowther, Chas. and Rustan, A. The Nature of Distribution and Effects Upon Vegetation of Atmospheric Impurities in and near an Industrial Town. J. Agri. Sci. 4, 1911.
6. Eaton, S. V. and Eaton, J. H. Sulfur in Rainfall. Plant Physiol, January 1926.
7. Finnell, H. H. and Houghton, H. W. Soil Nitrogen Income from Rain Water. Panhandle Agri. Expt. Sta. Bull. 23, 1931.
8. Finnell, H. H. and Houghton, H. W. Nitrogen Content of Rain Water. Panhandle Agri. Expt. Sta. Bull. 34, 1935.
9. Freeman, J. F. Nitrogen in Rain Water at Different Points in Kentucky. J. Amer. Soc. Agron. 15, 1924.
10. Gray, Geo. Dissolved Matter Contained in Rain Water Collected at Lincoln, New Zealand. Agri. Coll. Mag., 1910.
11. Harrison, J. B. Composition of Rain Water in British Guiana. Rept. Expt. Agri. Work, Dept. Sci. and Agri., British Guiana, 1909-1910.
12. Hudwig, J. The Amount of Nitrogen as Ammonia and Nitric (and Nitrous) Acid in Rain Water Collected at Uithuizermeeden, Gronigen. J. Agri. Sci. 4, 1921.
13. Johnson, E. M. Sulfur in Rain Water in Kentucky. J. Amer. Soc. Agron. 17, 1925.
14. Knight, N. Nitrogen in Rain and Snow. Prec. Iowa, Acad. Sci. 18, 1911.
15. Knox, W. K. Nitrogen and Chlorin in Rain and Snow. Chem. News, 111, No. 2880, 1915.

16. Miller, H. H. J. The Amount of Nitrogen as Ammonia and as Nitric Acid, and of Chlorine in Rain Collected at Rothamstead. *J. Agri. Sci.*, 1905.
17. Miss. St. An. Rep. Ammonia in Rainfall. 1895.
18. Shutt, F. T. Fertilizing Value of Rain and Snow. *Expt. Sta. Record* 25.
19. Schroeder, J. The Composition of Rainfall at Montevideo (1909-1912). *Rev. Assoc. Rural Uruguay*, 1915.
20. Stewart, Robert. Sulfur in Relation to Soil Fertility. *Ill. Agri. Expt. St. Bulletin*, 1920.
21. Vityn, I. The Amount of Chlorine and Sulfuric Acid in Rain Water. *J. Chem. Soc.* 100, II, 1911.
22. Weisner, G. H. Nitrogen and Chlorin in Rain and Snow. *Chem. News*, 109, No. 2830, 1914.
23. Wilson, B. D. Sulfur Supplied to the Soil in Rain Water. *J. Amer. Soc. Agron.* 13, 1921.
24. Wilson, B. D. Nitrogen and Sulfur in Rain Water in New York. *J. Amer. Soc. Agron.* 18, 1926
25. Woehlk, J. H. Nitrogen and Other Substances in Rain and Snow. *Chem. News* 127, No. 3330, 1923.

Wyvonne Dyson