

## NUTRIENT CONTENT OF PRECIPITATION OVER IOWA<sup>1</sup>

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### ABSTRACT

Nutrient content and pH of precipitation samples collected at six sites during 1971-1973 were studied to determine the reaction of rainfall and snowmelt and the amounts of N, S, and P added by precipitation over Iowa. The amount of  $\text{NH}_4\text{-N}$  added by precipitation per hectare annually at each site was about equal to that added as  $\text{NO}_3\text{-N}$ . The amounts of inorganic N added per hectare per year ranged from 10 kg in north-central to 14 kg in west-central Iowa, and the annual amounts of  $\text{SO}_4\text{-S}$  added per hectare ranged from 13 kg in northeastern to 17 kg in north-central Iowa. It is estimated that, on average, precipitation adds about 0.6 kg of  $\text{NH}_4\text{-N}$ , 0.6 kg of  $\text{NO}_3\text{-N}$ , and 1.5 kg of  $\text{SO}_4\text{-S}$  per hectare monthly in Iowa. However, the data indicated that, on an annual basis, the contribution of precipitation to P in soil is very small; at the most, about 0.1 kg of water-soluble  $\text{PO}_4\text{-P}$  was added per hectare annually in Iowa. No  $\text{NO}_2\text{-N}$  could be detected in any of the precipitation samples analyzed.

Average pH value of the rainfall and snowmelt samples collected at each site during each year was about 6, individual samples seldom reached as low as pH 4. The data indicate that the concentration of  $\text{SO}_4\text{-S}$  in precipitation in this region is seasonal, high during fall and winter and low during spring and summer.

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## INTRODUCTION

The many facets of nutrients (e.g., C, N, and S) in the biosphere have become major environmental issues occupying the scientific and public sectors of our society for the past decade. Although this concern is justified by the increasing contamination of air and water resources by various substances on local levels, information on the amounts and concentrations of some of the substances present in air and natural water under normal conditions is needed. Such information is essential for our better understanding of the sources and fates of pollutants in the biosphere.

The atmospheric component of the cycles of nitrogen and sulfur often can be a significant part of the various pools of their respective cycles (Allison, 1965; Erickson, 1963; Feth, 1966; Gambell and Fisher, 1964; Meetham, 1950; Robinson and Robbins, 1970), but the atmospheric component of the phosphorus cycle seems to be of minor significance to the cycling of this element in the environment. Among the various chemical elements present in precipitation (e.g., N, S, K, Cl, and Ca), N and S deserve special attention because N added by precipitation may contribute to nitrate pollution of surface and ground water. Sulfur may cause acid rain that can lead to increased leaching from soils of Ca and other nutrient elements, deterioration of aquatic ecosystems, damage to vegetation and buildings, and other agricultural and urban problems. On the other hand, the limited amount of N and S brought down by precipitation might be useful to meet the requirements of crops for these elements in areas where soils have limited supplies of N and S (Allway et al., 1937; Erdman, 1923; Tabatabai and Bremner, 1972; Walker, 1969; Widdowson and Hanway, 1974).

Normal water in the atmosphere in equilibrium with prevailing CO<sub>2</sub> pressure will have a pH of about 5.7 (Barrett and Brodin, 1955), but much lower pH values (ca. 2) have been reported for precipitation in the northeastern United States. The low pH values of precipitation have been considered to indicate air pollution (Likens and Bormann, 1974).

Nitrogen is the most plentiful element in the atmosphere. It plays a key role in the life of all living organisms. There are several nitrogen compounds in the atmosphere. These include N<sub>2</sub>O, NO, NO<sub>2</sub>, NH<sub>3</sub>, and ammonium (NH<sub>4</sub><sup>+</sup>) and nitrate (NO<sub>3</sub><sup>-</sup>) aerosol. Large portions of the ammonia and nitrogen oxides (NO<sub>x</sub>) in the atmosphere may originate from biological processes, but the concentrations of these gases in the air are greatly affected by industrial activities, automobile traffic, and feedlot operations (Elliott et al., 1971; Hutchinson and Viets, 1969; Robinson and Robbins, 1970). Of the eight possible oxides of nitrogen (N<sub>2</sub>O, NO, N<sub>2</sub>O<sub>3</sub>, NO<sub>2</sub>, N<sub>2</sub>O<sub>4</sub>, N<sub>2</sub>O<sub>5</sub>, NO<sub>3</sub>, and N<sub>2</sub>O<sub>6</sub>) only three are important constituents of the atmosphere. Of these -- nitrous oxide (N<sub>2</sub>O), nitric oxide (NO), and nitrogen dioxide (NO<sub>2</sub>) -- the most plentiful in the atmosphere is the relatively inert nitrous oxide. Nitrogen dioxide

present in the atmosphere, however, can react with water vapor to form nitric acid, which, in turn, reacts with ammonia or particles in the air and forms nitrate salts, such as ammonium nitrate, which is brought down by precipitation. The major reactions involving the various gaseous nitrogen compounds are oxidation reactions of both  $\text{NH}_3$  and  $\text{NO}_2$  to form nitrates and neutralization of  $\text{NH}_3$  to form ammonium sulfate and ammonium nitrate aerosols. Atmospheric particles are frequently found to contain  $(\text{NH}_4)_2\text{SO}_4$ , and its formation from  $\text{NH}_3$  and  $\text{SO}_2$  in the atmosphere is probably a significant factor in the scavenging of  $\text{SO}_2$ . The major sources for the gaseous nitrogen compounds are biological action and organic decomposition in the soil and, to a lesser extent, in the ocean. Only  $\text{NO}$  and  $\text{NO}_2$  are emitted as pollutants, at an estimated annual world-wide rate of about 50 million tons (Robinson and Robbins, 1968). It has been estimated that, on a global basis, about 99% of the total atmospheric N is derived from biological processes and only 1% from combustion (Robinson and Robbins, 1970). The residence times for all the nitrogen compounds except  $\text{N}_2\text{O}$  are only a few days. For  $\text{N}_2\text{O}$  the residence time has been calculated to be 70 years if there was no loss in the biosphere. Biological reaction, however, may reduce the residence time to about one to three years (Robinson and Robbins, 1968).

Stewart (1970) found that a significant portion (90%) of the urea N excreted by animals in feedlots may find its way to the air as ammonia. An appreciable fraction of atmospheric ammonia, in turn, is absorbed by soil, plant, and water surfaces in the vicinity of feedlots (Elliott et al., 1971; Hutchinson and Viets, 1969). It has been shown that there is a tendency for more  $\text{NH}_3$  to be contained in precipitation near feedlots, but it seems that the amounts brought down by precipitation are insignificant compared with those directly absorbed by soil and water surfaces (Hoefl et al., 1972; Hutchinson and Viets, 1969).

Sulfur is one of the trace substances always found in the atmosphere. Sulfur enters the atmosphere as sulfur dioxide ( $\text{SO}_2$ ), hydrogen sulfide ( $\text{H}_2\text{S}$ ), sulfuric acid ( $\text{H}_2\text{SO}_4$ ), and various sulfates ( $\text{SO}_4^{2-}$ ). In unpolluted air, S occurs primarily in three compounds;  $\text{SO}_4^{2-}$  in aerosol and  $\text{SO}_2$  and  $\text{H}_2\text{S}$  gases. Hydrogen sulfide in the air is normally oxidized to  $\text{SO}_2$ , which, in turn, is oxidized to  $\text{SO}_3^{2-}$ . Sulfur trioxide dissolves in water droplets to form sulfuric acid, which may react further to form sulfate salts, such as ammonium sulfate. Both the sulfuric acid and sulfate salts thus formed exist in air as an aerosol and are removed by precipitation and, to a lesser extent, by gravitational settling. It is estimated that a given volume of  $\text{SO}_2$  that enters the air will be removed by these mechanisms, as acid or salt, in a time ranging from five days to two weeks (Erickson, 1963).

There are several sources for atmospheric S, these include sea spray,  $\text{H}_2\text{S}$  and volatile sulfides released from marshlands and sea, and S released by burning S-containing fuels (Coleman, 1966; Erickson, 1963). Junge's (1960) work on the S budget of the global atmosphere indicates that, excluding the  $\text{SO}_4^{2-}$  in sea salt particles, 30% of the

atmospheric S is of anthropogenic origin. Other estimates indicate that the S released from sea spray and S-containing fuels accounts for about 12 and 11%, respectively, and that the other 77% is released as H<sub>2</sub>S from marshlands and sea (Erickson, 1963). Hoeft et al. (1972) have shown that atmospheric SO<sub>2</sub> levels in both rural and urban locations in Wisconsin tend to be seasonal, low in summer and increased markedly in winter. They attributed this to the burning of S-containing fuels in winter months and slow release of S from soil and biological reactions during this time.

This paper reports results obtained from a monitoring program to assess the pH and concentrations of NH<sub>4</sub>-N, NO<sub>3</sub>-N, SO<sub>4</sub>-S, and PO<sub>4</sub>-P in precipitation over Iowa, to determine the quantities of these nutrients added annually by precipitation to land surfaces in this region, and to compare the values obtained in Iowa with those reported for other regions.<sup>2</sup>

#### MATERIALS AND METHODS

Six sampling stations were established in Iowa in September 1971. The sites selected were located on a line extending across the state from the northeast to the southwest. The sites were selected so that no major industrial activity directly influenced the nitrogen, sulfur, and phosphorus concentrations of the atmosphere of the sample-collection sites. Table I shows the sites, counties, and the general area where precipitation samples were collected for 27 months during 1971-1973.

The procedure used to collect precipitation samples and the methods used for the analyses reported are described by Tabatabai and Laflen (1976).

#### RESULTS AND DISCUSSION

The six sites selected for this study were located on a line extending from northeast to southwest of Iowa (Table I). The precipitation samples collected were analyzed for pH, NH<sub>4</sub>-N, NO<sub>3</sub>-N, NO<sub>2</sub>-N, PO<sub>4</sub>-P, and SO<sub>4</sub>-S. Because the concentrations of PO<sub>4</sub>-P were very small, ranging from 0 to 10 ppb, the results obtained were not summarized. Use of

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<sup>2</sup>A summary of part of the results presented in this paper was submitted for publication in Journal of Environmental Quality (Tabatabai and Laflen, 1976).

TABLE I  
Description of sampling sites.

Nearest city	Site		Proximity to nearest urban area km	Classification*
	County	Area of Iowa		
Ames	Story	Central	0	U
Boone	Boone	Central	10	R
Charles City	Floyd	NE	15**	R
Creston	Union	SW	4	R
Eldora	Hardin	N. Central	3	R
Guthrie Center	Guthrie	W. Central	12	R

\* U, urban; R, rural.

\*\* Late 1972 and all of 1973 samples were collected within 1 km of Charles City.

the maximum value to calculate the amount of inorganic P added by precipitation, however, indicated that, at the most, about 0.1 kg of P is added per hectare annually in Iowa. No NO<sub>2</sub>-N could be detected in any of the precipitation samples analyzed.

#### pH OF PRECIPITATION

Table II shows the average of pH values obtained for precipitation samples collected at the six sites for 27 months. The averages of pH values ranged from  $5.8 \pm 0.8$  to  $6.5 \pm 0.3$ , and the overall average pH value of the samples collected was  $6.2 \pm 0.5$ . Although a pH value of 4 was measured occasionally, no seasonal variation in pH values was observed. The pH values obtained in this study were markedly different from those reported for samples from northeastern United States and Sweden where pH values as low as 2 and 3 were measured (Likens and Bormann, 1974).

Normal water in the atmosphere in equilibrium with CO<sub>2</sub> will have a pH of 5.7 (Barrett and Brodin, 1955), and, if this pH value is considered as the neutral point for atmospheric water, most of the precipitation samples that we collected showed a slight net alkalinity; most pH values were above 5.7. The results obtained indicate that concentrations of SO<sub>4</sub>-S in precipitation over Iowa were much higher than those found in samples from the northeastern United States (Likens and Bormann, 1974). Because no consistent low pH values were found for

TABLE II

Annual means of some chemical properties of precipitation collected at six sites in Iowa.

Period	Site	Annual mean of chemical property specified*			
		pH	NH <sub>4</sub> -N	NO <sub>3</sub> -N	SO <sub>4</sub> -S
		----- ppm -----			
1971	Ames	6.11(0.38)	0.43(0.56)	0.36(0.24)	1.23(0.74)
	Boone	6.18(0.28)	0.38(0.48)	0.60(0.42)	1.08(0.58)
	Charles City	5.91(0.36)	0.61(0.41)	0.67(0.38)	1.70(0.70)
	Creston	6.15(0.48)	0.43(0.28)	0.59(0.32)	1.22(0.50)
	Eldora	6.33(0.20)	0.48(0.37)	0.43(0.28)	1.16(0.50)
	Guthrie Center	5.94(0.49)	0.64(0.59)	0.99(0.98)	1.37(0.97)
1972	Ames	6.21(0.66)	0.64(0.37)	0.74(0.36)	2.06(1.14)
	Boone	6.33(0.29)	0.55(0.29)	0.78(0.40)	1.81(1.05)
	Charles City	6.17(0.47)	0.79(0.78)	0.98(0.29)	1.44(0.82)
	Creston	6.15(0.48)	0.73(0.65)	0.59(0.30)	1.72(1.25)
	Eldora	6.46(0.30)	0.54(0.56)	0.50(0.33)	2.31(1.52)
	Guthrie Center	6.24(0.50)	0.76(0.94)	0.59(0.32)	1.44(0.82)
1973	Ames	6.00(0.39)	0.49(0.36)	0.57(0.29)	1.49(1.15)
	Boone	5.78(0.82)	0.53(0.24)	0.60(0.26)	1.48(0.96)
	Charles City	6.03(0.74)	0.86(0.53)	0.58(0.40)	1.19(0.90)
	Creston	6.53(0.29)	0.52(0.33)	0.44(0.28)	1.16(1.00)
	Eldora	6.25(0.36)	0.66(0.42)	0.55(0.29)	1.41(0.90)
	Guthrie Center	5.81(0.87)	0.70(0.51)	0.54(0.34)	1.50(1.12)
1971-1973 (all samples)	Ames	6.12(0.54)	0.55(0.42)	0.60(0.34)	1.68(1.11)
	Boone	5.97(1.20)	0.51(0.32)	0.69(0.38)	1.55(1.02)
	Charles City	5.98(0.95)	0.80(0.64)	0.60(0.35)	1.43(0.86)
	Creston	6.26(0.46)	0.62(0.54)	0.55(0.30)	1.48(1.09)
	Eldora	6.36(0.32)	0.57(0.48)	0.50(0.30)	1.81(1.25)
	Guthrie Center	6.05(0.67)	0.72(0.76)	0.62(0.47)	1.43(0.92)
	All sites	6.15(0.55)	0.63(0.55)	0.60(0.37)	1.55(1.04)

\* Figure in parentheses indicates standard deviation.

precipitation in this region, it seems that SO<sub>4</sub>-S in precipitation in Iowa exists as un-ionized particulate SO<sub>4</sub> or as ionized forms neutralized by equivalent amounts of bases. Also, the results obtained showed that the occasional low pH values were not associated with high concentrations of SO<sub>4</sub>-S in those samples. Data reported by Likens and Bormann (1974) for SO<sub>4</sub>-S content of rain and snow in New York indicate that present-day precipitation contains about 70% less S than precipitation preceding 1950, but it has lower pH values. From the results obtained for concentrations of SO<sub>4</sub>-S and pH values of precipitation in Iowa and those reported by Likens and Bormann (1974) for samples in the state of New York, it seems that a factor other than SO<sub>4</sub>-S is responsible for low pH values of some precipitation samples or that sufficient cations (e.g., NH<sub>4</sub>) are not present in precipitation where acid rain is found.

## INORGANIC N IN PRECIPITATION

The monthly average concentrations of  $\text{NH}_4\text{-N}$  and  $\text{NO}_3\text{-N}$  for the six sites studied ranged from 0.1 to 2.1 ppm and from 0.1 to 2.2 ppm, respectively. Figure 1 shows the monthly average concentrations of  $\text{NH}_4\text{-N}$

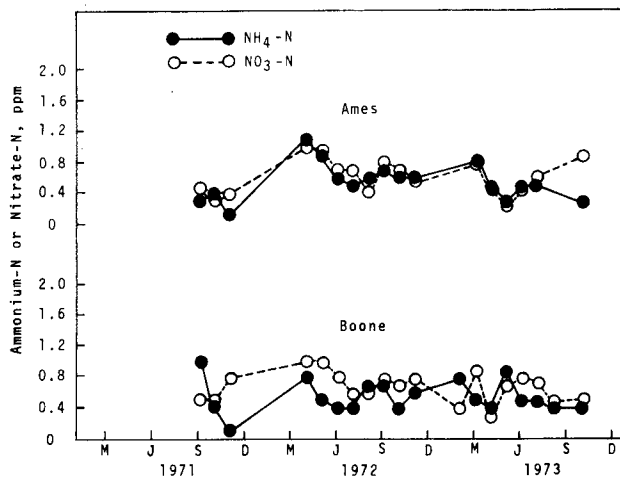


Figure 1. Monthly average concentrations of ammonium-N and nitrate-N in precipitation at two sites in Iowa.

and  $\text{NO}_3\text{-N}$  of precipitation samples from two of the six sites studied. The results indicate no seasonal variation in concentration of precipitation N over Iowa. The results were similar for the other sites studied.

The average annual  $\text{NH}_4\text{-N}$  concentrations in the precipitation samples studied ranged from  $0.38 \pm 0.48$  to  $0.86 \pm 0.53$  ppm, and the  $\text{NO}_3\text{-N}$  concentrations ranged from  $0.36 \pm 0.24$  to  $0.99 \pm 0.98$  ppm. The overall average of  $\text{NH}_4\text{-N}$  and  $\text{NO}_3\text{-N}$  concentrations of the six sites were  $0.63 \pm 0.55$  and  $0.60 \pm 0.37$  ppm, respectively (Table II). Generally, the concentration of  $\text{NH}_4\text{-N}$  was about equal to that of  $\text{NO}_3\text{-N}$ . The concentrations of inorganic N found in this study are similar to those reported by Taylor et al. (1971) for rainfall in Coshocton, Ohio. The highest  $\text{NO}_3\text{-N}$  concentration found for precipitation in Iowa (2.2 ppm) is similar to that reported for precipitation in Nebraska (Olson et al., 1973), but the highest value of  $\text{NH}_4\text{-N}$  (2.1 ppm) found in Iowa is much lower than that (3.3 ppm) reported for Nebraska (Olson et al., 1973) and for Wisconsin precipitation collected from sites removed from barnyards (Hoeft et al., 1972).

The ratio of  $\text{NH}_4\text{-N}$  to  $\text{NO}_3\text{-N}$  in precipitation samples studied was about 1:1. A similar ratio has been reported for precipitation samples

from urban areas and rural areas removed from barnyards in Wisconsin (Hoeft et al., 1972). Other studies, however, indicated a ratio of 2:1 for these forms of inorganic N in precipitation samples from Nebraska (Olson et al., 1973). The relative concentrations of  $\text{NH}_4\text{-N}$  and  $\text{NO}_3\text{-N}$  in precipitation samples in the Midwest are strikingly different from those found for coastal areas of the United States (Likens and Bormann, 1974; Tarrant et al., 1968). In studies of organic and inorganic N in precipitation samples in coastal Oregon, Tarrant et al., (1968) found very little (0-0.1 ppm) of  $\text{NO}_3\text{-N}$  and no trace of  $\text{NH}_4\text{-N}$ . The results obtained for inorganic N in precipitation samples from New Hampshire and New York, however, indicate significantly higher concentration of  $\text{NO}_3\text{-N}$  than  $\text{NH}_4\text{-N}$  (Likens and Bormann, 1974). This high concentration of  $\text{NO}_3\text{-N}$  in precipitation has been attributed to increased combustion of natural gas and motor fuels.

Table III shows the correlation coefficients (r) for paired relationships of some of the chemical properties of precipitation over Iowa. Statistical analyses indicated that, with a few exceptions, total inorganic N, ( $\text{NH}_4 + \text{NO}_3$ )-N, concentration in the precipitation collected during each year was significantly correlated with  $\text{SO}_4\text{-S}$  concentration, and  $\text{NH}_4\text{-N}$  was significantly correlated with  $\text{NO}_3\text{-N}$ . Statistical analyses of the pooled data collected at each site during the study period indicated that ( $\text{NH}_4 + \text{NO}_3$ )-N concentrations in the samples were also significantly correlated with  $\text{SO}_4\text{-S}$ . Statistical analyses of the relationship between pH and  $\text{SO}_4\text{-S}$ ,  $\text{NH}_4\text{-N}$ , or  $\text{NO}_3\text{-N}$ , however indicated that, with a few exceptions, pH was not correlated with  $\text{NH}_4\text{-N}$ ,  $\text{NO}_3\text{-N}$ , or  $\text{SO}_4\text{-S}$ . The strong relationship between inorganic N and  $\text{SO}_4\text{-S}$  and between  $\text{NH}_4\text{-N}$  and  $\text{NO}_3\text{-N}$  in precipitation over Iowa may indicate that nitrogen and sulfur in precipitation in this region are originating from similar source(s) or that chemical reactions of these elements in the atmosphere are producing compounds containing N and S. The strong relationship between  $\text{NH}_4\text{-N}$  and  $\text{NO}_3\text{-N}$  suggests presence of  $\text{NH}_4\text{NO}_3$ , and the strong relationship between inorganic N and  $\text{SO}_4\text{-S}$  suggests presence of  $(\text{NH}_4)_2\text{SO}_4$  along with ammonium nitrate in precipitation in this region. Use of the seasonal averages of  $\text{NH}_4\text{-N}$  and  $\text{NO}_3\text{-N}$  and of long-term annual precipitation (average annual precipitation in Iowa is 80 cm) to calculate the seasonal deposition of N by precipitation indicated that, on the average, between 9 and 12 kg of inorganic N/ha is deposited annually (Figure 2). Use of the measured annual precipitation for the study period indicated, however, that the annual amounts of inorganic N added by precipitation ranged from 10 kg/ha in north-central to 14 kg/ha in west-central Iowa (Table IV). Of these amounts, between 70 and 82% is deposited during spring and summer. The data also indicate that the amount of  $\text{NH}_4\text{-N}$  deposited annually at each site was equal to the amount of  $\text{NO}_3\text{-N}$ . The overall average annual addition of inorganic N (13 kg/ha) by precipitation in Iowa is similar to that in Nebraska and Wisconsin rural areas (Hoeft et al., 1972; Olson et al., 1973). In addition to these amounts of inorganic N added by precipitation in Iowas,  $\text{NH}_4\text{-N}$  could be directly absorbed by soil and water surfaces, especially in areas near feedlots.



TABLE III

Simple correlation coefficients (r) for paired relationships of some chemical properties of precipitation over Iowa.

Period	Variables	Site					
		Ames	Boone	Charles City	Creston	Eldora	Guthrie Center
1971	(NO <sub>3</sub> + NH <sub>4</sub> )-N vs. SO <sub>4</sub> -S	0.60*	0.85**	0.51	0.81**	0.54	0.96**
	NO <sub>3</sub> -N vs. NH <sub>4</sub> -N	0.52*	0	0.68*	0.39	0.79**	0.88**
	pH vs. SO <sub>4</sub> -S	0.50*	0.39	0	0.71**	0.54	0.84**
	pH vs. NH <sub>4</sub> -N	0.52*	0.17	0.17	0.66*	0.17	0
	pH vs. NO <sub>3</sub> -N	0.73**	0.22	0.28	0.83**	0.51	0.76*
1972	(NO <sub>3</sub> + NH <sub>4</sub> )-N vs. SO <sub>4</sub> -S	0.70**	0.72**	0.53**	0.36*	0.45*	0.66**
	NO <sub>3</sub> -N vs. NH <sub>4</sub> -N	0.79**	0.42*	0.41*	0.48**	0.84**	0.42*
	pH vs. SO <sub>4</sub> -S	0.14	0.10	0.17	0.10	0	0
	pH vs. NH <sub>4</sub> -N	0	0.30	0.25	0.14	0.30	0.30
	pH vs. NO <sub>3</sub> -N	0	0.30	0.25	0	0.22	0
1973	(NO <sub>3</sub> + NH <sub>4</sub> )-N vs. SO <sub>4</sub> -S	0.82**	0.39*	0.69**	0	0.10	0.76**
	NO <sub>3</sub> -N vs. NH <sub>4</sub> -N	0.57**	0.51**	0.28	0.35	0.28	0.77**
	pH vs. SO <sub>4</sub> -S	0.35	0.14	0.17	0.22	0.69**	0
	pH vs. NH <sub>4</sub> -N	0.51**	0.17	0.35	0.40	0.33	0.17
	pH vs. NO <sub>3</sub> -N	0.10	0	0.54**	0.25	0.41	0.10
1971-1973 (all samples)	(NO <sub>3</sub> + NH <sub>4</sub> )-N vs. SO <sub>4</sub> -S	0.75**	0.65**	0.57**	0.36**	0.33*	0.70**
	NO <sub>3</sub> -N vs. NH <sub>4</sub> -N	0.65**	0.33**	0.36**	0.42**	0.66**	0.46**
	pH vs. SO <sub>4</sub> -S	0.25*	0.10	0.64	0	0.37**	0.10
	pH vs. NH <sub>4</sub> -N	0.27*	0	0.25	0.14	0.25	0.20
	pH vs. NO <sub>3</sub> -N	0.17	0.14	0.28	0.17	0.30**	0

\* Significant at P < 0.05. \*\* Significant at P < 0.01.

Junge (1958) conducted a nationwide survey of NH<sub>4</sub>-N and NO<sub>3</sub>-N in rainwater samples of 60 sites in the United States during 1955 and 1956. He found an uneven distribution of both these forms of inorganic N in rainwater. Also, he found no correlation between these inorganic N forms in precipitation and thunderstorm activity, density of industry, population, or agricultural activity. He found, however, that areas

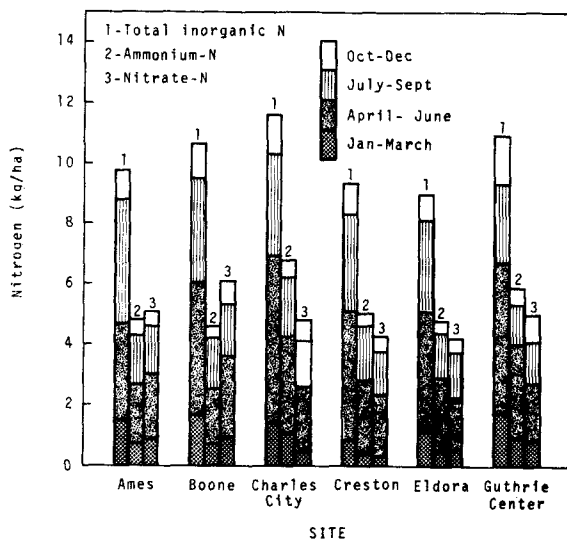


Figure 2. Seasonal addition by precipitation of total inorganic N, ammonium-N, and nitrate-N as six sites in Iowa.

having soils of low pH values correlated with areas having low concentrations of  $\text{NH}_4\text{-N}$  in precipitation and that alkaline-soils regions seemed associated with high concentration of  $\text{NH}_4\text{-N}$  in rainwater. The results obtained in our study were not aimed toward investigating such relationships, but the results obtained for concentrations of  $\text{NH}_4\text{-N}$  in precipitation samples at the six sites in Iowa do not seem to show any general trend to indicate such relationships.

#### SULFUR IN PRECIPITATION

The concentrations of  $\text{SO}_4\text{-S}$  found in the precipitation collected at the six sites during the study period ranged from 0.1 to 4.9 ppm, and the monthly average concentrations of  $\text{SO}_4\text{-S}$  in precipitation samples from the six sites ranged from 0.3 to 4.6 ppm. The annual average concentration of  $\text{SO}_4\text{-S}$  ranged from  $1.08 \pm 0.58$  to  $2.31 \pm 1.52$  ppm, and the overall average for the six sites was  $1.55 \pm 1.04$  ppm (Table II). The monthly average concentrations of  $\text{SO}_4\text{-S}$  in the samples collected at two of the sites studied are reported in Figure 3. These results show that the concentrations of  $\text{SO}_4\text{-S}$  in precipitation in Iowa is seasonal and inversely related to the amount of monthly precipitation. The inverse relationship between average monthly  $\text{SO}_4\text{-S}$  in precipitation and monthly addition of precipitation is shown in Figure 4 for three of the sites studied. The data obtained for the other sites showed similar relationships. The highest concentration of  $\text{SO}_4\text{-S}$  was found during the fall and winter when precipitation is low, and the

TABLE IV

Amounts of ammonium-N, nitrate-N, and sulfate-S added annually by precipitation at six sites in Iowa

Site	NH <sub>4</sub> -N	NO <sub>3</sub> -N	SO <sub>4</sub> -S
	----- kg/ha/year* -----		
Ames	6.0	6.0	16.8
Boone	6.0	7.2	15.6
Charles City	7.2	6.0	13.2
Creston	6.7	6.0	16.7
Eldora	5.0	4.8	17.3
Guthrie Center	7.1	7.2	16.1
Avg.	6.3	6.2	16.0

\* The values obtained for Creston, Eldora, and Guthrie Center were calculated from average annual nutrient concentration and percentage of the annual precipitation received during sampling period.

lowest concentration during the summer and spring when precipitation is high. Atmospheric S levels in Wisconsin at rural and urban sites also

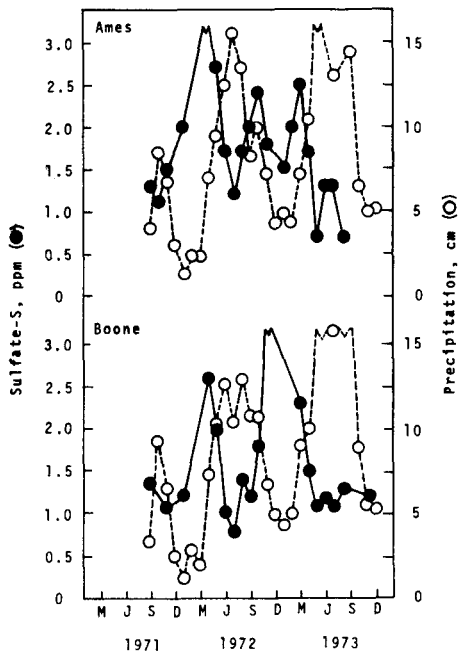


Figure 3. Relationship of monthly average concentration of sulfate-S in precipitation to amount of monthly precipitation at two sites in Iowa.

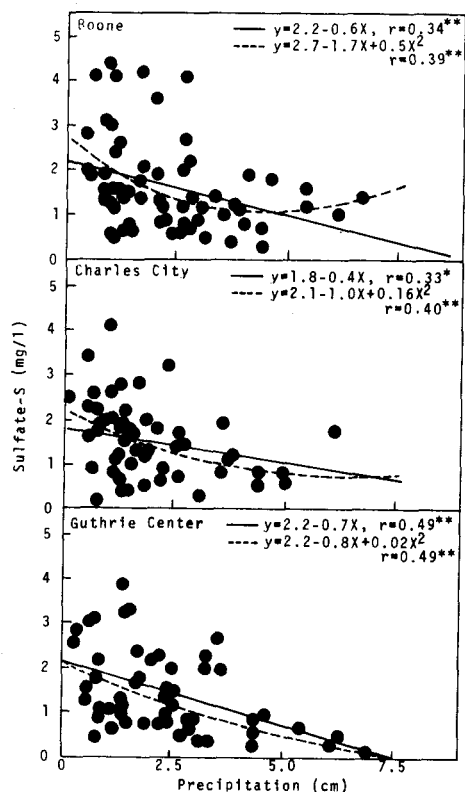


Figure 4. Relationship between monthly average concentration of sulfate-S in precipitation and amount of monthly precipitation at three sites in Iowa.

were found to be low in the summer and high in the winter (Hoeft et al., 1972). The high concentration of  $SO_4$ -S in precipitation during the fall and winter in Iowa could be due to home and business heating during these months. The low concentrations during spring and summer could be due to washing by precipitation and to lower concentration of S gases in the atmosphere resulted from direct absorption of  $SO_2$  and other S gases by the exposed soil and plant surfaces. These processes of addition and removal of S gases into and from the atmosphere seem to play major roles in the observed seasonal concentrations of  $SO_4$ -S in precipitation in Iowa. Use of the seasonal averages of  $SO_4$ -S and of long-term average of precipitation (80 cm) to calculate the seasonal deposition of S by precipitation indicated that, on the average, between 12 and 15 kg of S/ha is deposited annually. As was true of N, between 62 and 78% of these amounts of S are deposited during spring and summer (Figure 5).

Precipitation during 1971-1973 was abnormally higher than the normal annual average of each of the six sites studied. During the study period, the averages of annual precipitation of the six sites were between 10 and 45% higher than the long-term annual average. Use of the measured monthly precipitation and concentration of  $SO_4$ -S indicated that the monthly deposition of S ranged from 1.1 to 1.8 kg/ha (ave. 1.5 kg/ha). On this basis, the annual addition of S by precipitation at

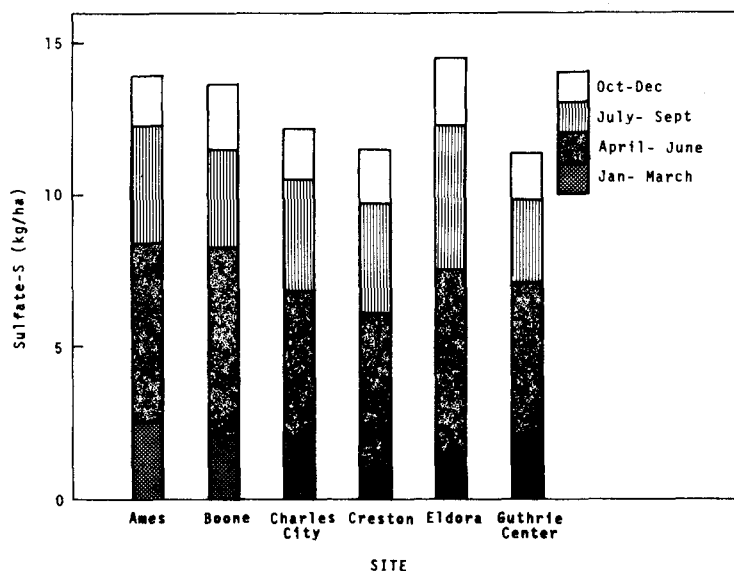


Figure 5. Seasonal addition by precipitation of sulfate-S at six sites in Iowa.

the six sites varied from 13 kg/ha in northeastern to 17 kg/ha in north-central Iowa. The average annual additions of S by precipitation (16 kg/ha) during the study period in Iowa (Table IV) is similar to that reported (17 kg/ha) for rural areas in Wisconsin (Hoeft et al., 1972). Present-day addition of S by precipitation in Iowa is similar to that reported a half-century ago. Erdman (1923) estimated the annual precipitation-originated S in Ames in 1923 to be 17 kg/ha, and the present estimate for this site is 17 kg/ha. Also, Harper (1942) summarized the data that were available before 1942, indicating that rural areas of the United States were receiving precipitation-originated S in amounts similar to those found in this study.

The 13 to 17 kg/ha of S added by precipitation in Iowa are of importance to crop production in this region because laboratory tests and greenhouse experiments have shown that Iowa soils do not contain sufficient plant-available S to meet crop requirements of this element (Tabatabai and Bremner, 1972; Widdowson and Hanway, 1974), yet no S-deficiency symptoms have been reported for crops grown under field conditions. In previous studies on S in soils, Tabatabai and Bremner (1972) found that Iowa soils have low reserve of plant-available S, and they suggested that studies to assess atmospheric contribution of S to crops and soils in Iowa be performed before recommending S fertilization of Iowa soils. From the results obtained in this work, it is evident that precipitation adds the small amounts of S required by many crops in this region. Also, some S gases are likely absorbed directly by soils and plants in Iowa because it is known that soils and plants absorb SO<sub>2</sub> directly from the atmosphere (Allway et al., 1937; Coleman,

1966; Faller, 1970; Olsen, 1957; Ulrich et al., 1967). A recent study in Wisconsin showed that, under optimum yield, 44% of the S in alfalfa was derived from atmospheric sources (Hoeft et al., 1972). The results of concentrations of S in precipitation and those reported for S in Iowa soils (Tabatabai and Bremner, 1972; Widdowson and Hanway, 1974) indicate that current concentrations of S in precipitation in Iowa are beneficial to crop production in this region.

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