

## **Atmospheric Wet Deposition Relationships to Season and Precipitation in South Western Indiana**

R.H. GRANT

Department of Agronomy  
Purdue University, West Lafayette, Indiana 47907

### **Introduction**

The influences of acidic precipitation on the environment has been in the forefront of discussion across the United States for at least the past ten years. Precipitation at four sites within the state of Indiana has been collected for chemical analysis since 1984 as part of the National Atmospheric Deposition Program (NADP). Analysis of the concentrations and depositions of the various precipitation constituents helps describe the atmospheric environment and the impact the environment has on the ground surface chemistry. Of particular interest is the amount, variability and sources of acidity within the precipitation, as well as the climatology of the storm systems depositing the precipitation.

A description of the results for the NADP site at the Purdue Agronomy Farm near West Lafayette, Indiana (3) indicated that the sulfate deposition was largely accounted for by oxidation reactions on sulfur dioxide and that both sulfate and nitrate were highly correlated with the precipitation pH. The West Lafayette site is remote from large sources of sulfur dioxide, nitrous oxides or flyash, with only one power plant (to the south of the site) within 50km (13). This study described the wet deposition from October 1984 to December 1986 at the Southwest Purdue Agricultural Center near Vincennes, Indiana which is situated in the vicinity of six power plants (surrounding the site) within 50 km (13). Both sites are classified by (13) as rural.

### **Methods**

The Climatological Data for Vincennes, Indiana (18) were used to determine the normality of the precipitation during the period of study.

The wet deposition samples were collected according to NADP protocol (13) on Tuesday of each week. The water soluble hydrogen ( $H^+$ ), sulfate ( $SO_4^{2-}$ ), nitrate ( $NO_3^-$ ), ammonium ( $NH_4^+$ ), chloride ( $Cl^-$ ), magnesium ( $Mg^{2+}$ ), orthophosphate ( $PO_4^{2-}$ ), and calcium ( $Ca^{2+}$ ) concentrations of the wet deposition samples were analyzed by the Central Analytical Laboratory of the NADP in accordance with NADP procedures (11, 12). Precipitation amount were recorded using a Belfort weighing rain gauge.

Many sampling periods within the study period were not used due to high levels of contamination, negligible or no precipitation samples, or poor operation of the collector. If the sample had: a) no precipitation, b) precipitation less than 0.127 cm, c)  $PO_4^{2-}$  concentrations greater than 0.05 mg/L, or d) a sampler efficiency (defined as the percent of rain gauge-recorded precipitation collected in wet bucket sample) less than 75% it was not included in the data analysis. Of the initial 116 weeks included in the study period, 69 weeks passed the above criteria. These weeks were separated by season where December, January, and February defined the winter season and each season following was defined by three consecutive months (17). The 69 weeks of good wet deposition samples were distributed as 17, 15, 23, 14 in the spring, summer, fall, and winter respectively. Note that this is not a climatological series, but rather a set of precipitation periods over a 27-month period. Since the results

are based on a data set of 27 months, the overall averages are weighted unevenly with fall season precipitation contributing more data than the other seasons. Therefore the seasonal interrelationships of the precipitation chemistry are more reliable than the overall interrelationships.

Weekly precipitation was classified by amount into six categories: less than 0.5cm, 0.5 to less than 1 cm, 1 to less than 2.5 cm, 2.5 to less than 5cm, 5 to less than 10cm, and greater than or equal to 10 cm precipitation.

Concentrations reported here are weighted by the precipitation amount to adjust the relative importance of any given sample concentration to the total precipitation chemical content. For example, a precipitation weighted pH is defined as:

$$\text{pH} = \frac{\sum_{k=1}^n (P \cdot \text{pH})}{\sum_{k=1}^n P}$$

when  $n$  is the number of valid weekly samples and  $P$  is the amount of weekly precipitation.

Linear correlations between concentrations of the various chemical species and unpaired one-tailed  $t$ -tests on the differences in concentration of chemical species between seasons were made using the microcomputer version 6 of the Statistical Analysis System (microSAS).

The stepwise regression procedure of microSAS was used to determine which of the seven chemical constituents could best describe the variance in the  $\text{H}^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{Cl}^-$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$  concentrations. The criteria for entry and retention of a given dependent variable within the regression was set at an alpha of 0.05. The fraction of the independent variable variance associated with the dependent variable was defined as the partial  $r^2$  of the final regression. The association of the variance of any constituent by any other constituent may be due to precipitation chemistry or be coincidental.

## Results and Discussion

Departures from the normal (30 year average, 1951-1980) for precipitation at Vincennes, Indiana show 1984 and 1985 to be wetter than normal and 1986 to be near normal (Table 1). The fall seasons of 1984 and 1985 were very wet while the precipitation during the other seasons was within 20% of the normal. The unusually wet 1984 fall was a result of strong midlatitude westerlies with an active stormtrack through the Midwest (6). The unusually wet 1985 fall was a result of hurricane and tropical storm-related moisture (5) brought north from the Gulf of Mexico and the Atlantic (5). The distribution of precipitation by class amount shows that the fall season had a larger percentage of 1 to 10cm weekly precipitation periods than the other seasons (Table 1) for the 1984-1986 study period. As expected, winter had the greatest fraction of light precipitation periods.

### Hydrogen

The pH of the wet deposition for the period of study does not show a trend over time (Figure 1). The overall average precipitation-weighted pH was 4.32 with the average varying by season as 4.33, 4.14, 4.46, and 4.35 for spring, summer, fall, and winter respectively. The concentration of  $\text{H}^+$  was well correlated with  $[\text{SO}_4^{2-}]$  over the entire study period (Table 2). This correlation between  $[\text{H}^+]$  and  $[\text{SO}_4^{2-}]$ , as well as a fair correlation between  $[\text{H}^+]$  to  $[\text{NO}_3^-]$ , was greatest during the summer and winter. Correlations between  $[\text{H}^+]$  and  $[\text{SO}_4^{2-}]$  and  $[\text{NO}_3^-]$  were higher in this study than that found previously for West Lafayette, Indiana (3). Ammonium was also significantly correlated with  $[\text{H}^+]$  during the summer and winter (Table 2), unlike that found for West Lafayette (3).

TABLE 1 Seasonal precipitation for Vincennes, Indiana for indicated years

| Weeks<br>n   | Weekly precipitation amount (%) |              |                |              |               |          |         | Deviation    |        |       |       | 1951-80<br>Normal<br>(cm) |
|--------------|---------------------------------|--------------|----------------|--------------|---------------|----------|---------|--------------|--------|-------|-------|---------------------------|
|              | <.5cm                           | 0.5-<br><1cm | 1.0-<br><2.5cm | 2.5-<br><5cm | 5.0-<br><10cm | > = 10cm | 1984    | 1985<br>(cm) | 1986   | ----- |       |                           |
| Spring<br>17 | 15.4                            | 19.2         | 30.8           | 15.4         | 15.4          | 3.9      |         | + 6.04       | -0.71  |       | 31.80 |                           |
| Summer<br>15 | 26.9                            | 15.4         | 19.2           | 23.1         | 11.5          | 3.9      |         | + 1.22       | + 4.37 |       | 31.52 |                           |
| Fall<br>23   | 25.7                            | 8.6          | 25.7           | 20.0         | 17.1          | 2.9      | + 15.90 | + 32.16      | + 3.92 |       | 22.61 |                           |
| Winter<br>14 | 34.5                            | 17.2         | 13.8           | 20.7         | 13.8          | 0        | + 0.85  | + 2.16       | - 5.49 |       | 21.59 |                           |

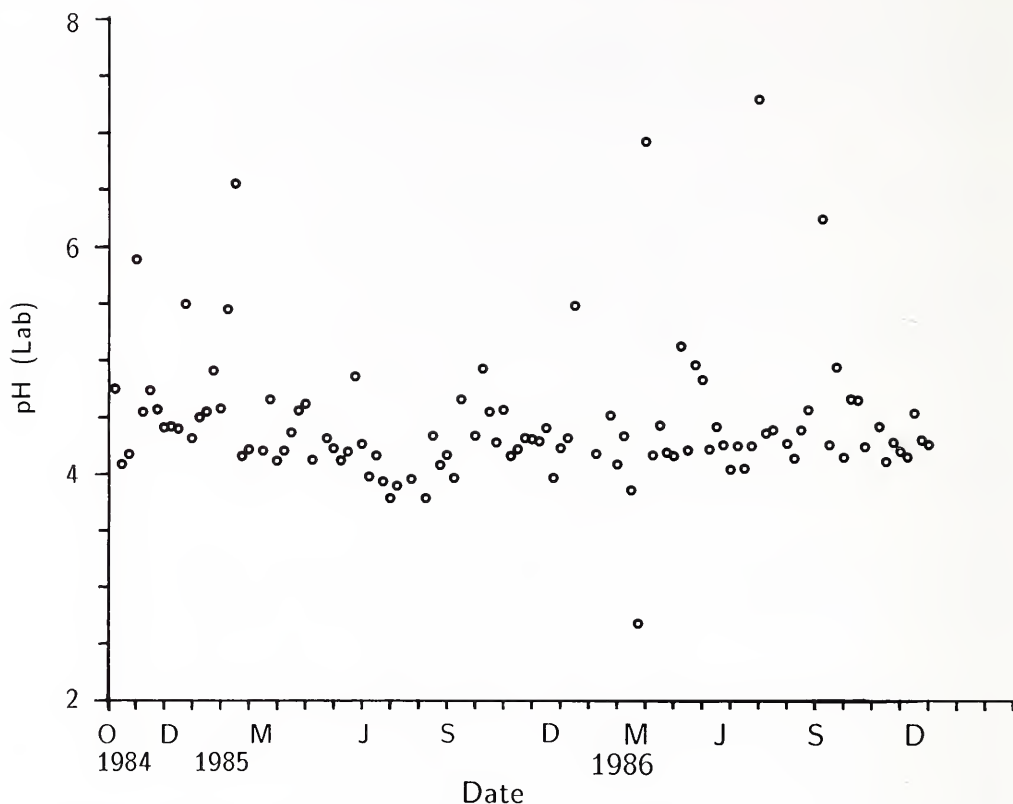


FIGURE 1. Variation in precipitation pH at Vincennes, IN.

The  $H^+$  concentration was regressed (using the stepwise procedure) against all constituents. Over the entire study period,  $[SO_4^{2-}]$  was associated with 62% of the  $[H^+]$  variation while  $[NO_3^-]$ ,  $[NH_4^+]$ , and  $[Ca^{2+}]$  were associated with 11, 5, and 1% of the  $[H^+]$  variation respectively. This is in contrast to the results of (3) that show  $[SO_4^{2-}]$  associated with only 36% of the  $[H^+]$  variation. Overall, the regression model accounted for 79% of the  $[H^+]$  variation. Although the variables used in the regression model here differ from those used in the West Lafayette study (3), the total variance accounted for is the same.

Regression of  $H^+$  concentration against all other precipitation constituents by season showed that the spring season  $NH_4^+$  concentration was associated with 10% of the  $[H^+]$  variation. The fall season regression was the only one in which  $[NO_3^-]$  or any cation other than  $[NH_4^+]$  was important in accounting for the precipitation  $H^+$  concentration (Table 3).

The pH of the weekly precipitation was influenced by the amount of precipitation (Figure 2) with low precipitation corresponding to large variances in pH over the study period. Classifying the weekly precipitation, we find that the  $[SO_4^{2-}]$  concentration was important in the estimation of  $H^+$  concentration for precipitation in all categories except for the 0.5 to 1.0cm per week category where  $[NO_3^-]$  was important in explaining the  $[H^+]$  variance (Table 4). It is believed that the importance of the nitrate concentrations in accounting for the  $[H^+]$  for this category of precipitation is probably an anomaly of the data set. While the scavenging of the particulates in the atmosphere is more efficient than that of gases (16), small weekly accumulations of precipitation do not show an expected greater importance in cations associated with soil dusts explaining the  $H^+$  concentration.

The positive correlations between  $[H^+]$  and  $[NH_4^+]$  as well as those between

TABLE 2 Simple correlation matrix of precipitation constituent concentrations  
(All listed correlations significant at  $\alpha=0.05$ )

|                 | NH <sub>4</sub> | SO <sub>4</sub> | NO <sub>3</sub> | Cl   | Ca    | Na   | K     | Mg   |
|-----------------|-----------------|-----------------|-----------------|------|-------|------|-------|------|
| H               |                 |                 |                 |      |       |      |       |      |
| Spring          |                 | 0.78            | 0.61            |      |       |      |       |      |
| Summer          | 0.89            | 0.94            | 0.90            |      |       |      |       | 0.81 |
| Fall            |                 | 0.52            | 0.39            |      | -0.45 |      | -0.52 |      |
| Winter          | 0.75            | 0.93            | 0.86            |      | 0.84  |      | 0.68  | 0.66 |
| NH <sub>4</sub> |                 |                 |                 |      |       |      |       |      |
| Spring          |                 | 0.72            | 0.89            |      | 0.57  |      |       | 0.58 |
| Summer          |                 | 0.91            | 0.86            |      | 0.58  |      |       | 0.91 |
| Fall            |                 | 0.70            | 0.69            | 0.79 | 0.44  |      | 0.75  | 0.72 |
| Winter          |                 | 0.84            | 0.89            |      | 0.89  |      | 0.75  | 0.78 |
| SO <sub>4</sub> |                 |                 |                 |      |       |      |       |      |
| Spring          |                 |                 | 0.83            | 0.53 | 0.75  | 0.49 |       | 0.76 |
| Summer          |                 |                 | 0.88            |      |       |      |       | 0.85 |
| Fall            |                 |                 | 0.58            |      |       |      |       | 0.54 |
| Winter          |                 |                 | 0.82            |      | 0.86  |      | 0.74  | 0.69 |
| NO <sub>3</sub> |                 |                 |                 |      |       |      |       |      |
| Spring          |                 |                 |                 |      | 0.63  |      |       | 0.65 |
| Summer          |                 |                 |                 |      | 0.62  | 0.61 |       | 0.87 |
| Fall            |                 |                 |                 |      |       |      |       |      |
| Winter          |                 |                 |                 |      | 0.97  |      | 0.81  | 0.87 |
| Cl              |                 |                 |                 |      |       |      |       |      |
| Spring          |                 |                 |                 |      | 0.50  | 0.77 | 0.76  | 0.56 |
| Summer          |                 |                 |                 |      |       |      | 0.96  |      |
| Fall            |                 |                 |                 |      | 0.56  | 0.60 | 0.67  | 0.76 |
| Winter          |                 |                 |                 |      |       | 0.83 |       |      |
| Ca              |                 |                 |                 |      |       |      |       |      |
| Spring          |                 |                 |                 |      |       |      |       | 0.99 |
| Summer          |                 |                 |                 |      |       |      |       |      |
| Fall            |                 |                 |                 |      |       |      | 0.60  | 0.86 |
| Winter          |                 |                 |                 |      |       |      | 0.85  | 0.89 |
| Na              |                 |                 |                 |      |       |      |       |      |
| Spring          |                 |                 |                 |      |       |      | 0.83  |      |
| Summer          |                 |                 |                 |      |       |      | 0.94  |      |
| Fall            |                 |                 |                 |      |       |      | 0.76  |      |
| Winter          |                 |                 |                 |      |       |      |       |      |
| K               |                 |                 |                 |      |       |      |       |      |
| Spring          |                 |                 |                 |      |       |      |       |      |
| Summer          |                 |                 |                 |      |       |      |       |      |
| Fall            |                 |                 |                 |      |       |      |       | 0.42 |
| Winter          |                 |                 |                 |      |       |      |       | 0.73 |

[H<sup>+</sup>] and [Ca<sup>2+</sup>], and [Mg<sup>2+</sup>] are probably coincidental. This is supported by the negative coefficients in the majority of [H<sup>+</sup>] regressions both by season and precipitation amount.

TABLE 3 Association of H concentration variation for indicated constituents by season (alpha = 0.05)

| Season  | Partial regression $r^2$ |                 |        |        |                     |      | Total $R^2$ |
|---------|--------------------------|-----------------|--------|--------|---------------------|------|-------------|
|         | SO <sub>4</sub>          | NO <sub>3</sub> | K      | Mg     | NH <sub>4</sub>     | Ca   |             |
| spring  | 0.60                     |                 |        |        | (0.10) <sup>1</sup> |      | 0.70        |
| summer  | 0.89                     |                 |        |        |                     |      | 0.89        |
| fall    | 0.31                     | 0.03            | (0.27) | (0.32) |                     |      | 0.93        |
| winter  | 0.86                     |                 |        |        |                     |      | 0.86        |
| OVERALL | 0.62                     | 0.11            |        | 0.05   |                     | 0.01 | 0.79        |

1/parenthesis indicate negative regression coefficients

### Sulfate

The weighted mean SO<sub>4</sub><sup>2-</sup> concentration was greatest during the summer season and least during the fall and winter seasons (Table 5). Stepwise regression of [SO<sub>4</sub><sup>2-</sup>] on all other constituents resulted in the accounted for 84% of the over all [SO<sub>4</sub><sup>2-</sup>] variance using three independent variables—[H<sup>+</sup>], [Mg<sup>2+</sup>], and [NH<sub>4</sub><sup>+</sup>]. The variation in H<sup>+</sup> concentration was associated with 62% of the variance in sulfate over the entire study period. Seasonal association of [H<sup>+</sup>] with [SO<sub>4</sub><sup>2-</sup>] variance was greatest during the summer and winter with 60, 89, 58, and 86% for the spring,

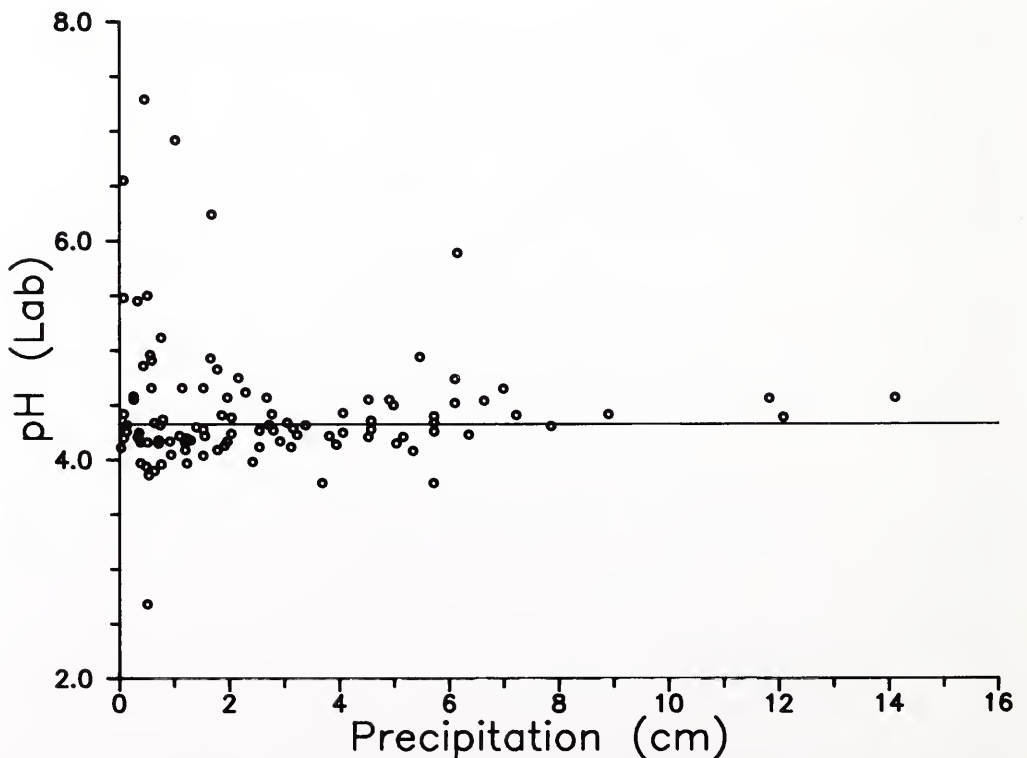


FIGURE 2. Effect of weekly precipitation amount on pH. Solid line designates the precipitation weighted mean pH.

TABLE 4 Association of H concentration variation with indicated constituent within precipitation amount ( $\alpha = 0.05$ )

| Weekly precip. (cm) | Partial regression $r^2$ |                 |                     |                  |        | Total $r^2$ |
|---------------------|--------------------------|-----------------|---------------------|------------------|--------|-------------|
|                     | SO <sub>4</sub>          | NO <sub>3</sub> | NH <sub>4</sub>     | Ca               | K      |             |
| 0.0-0.5             | 0.62                     |                 |                     |                  |        | 0.62        |
| 0.5-1.0             |                          | 0.79            | (0.14) <sup>1</sup> |                  |        | 0.93        |
| 1.0-2.5             | 0.63                     | 0.08            | 0.04                | (0.20)           |        | 0.89        |
| 2.5-5.0             | 0.92                     |                 |                     |                  |        | 0.92        |
| 5.0-10.0            | 0.69                     |                 |                     |                  | (0.27) | 0.96        |
| <10.0               |                          |                 | ---                 | (only 3 samples) |        | ---         |

1/parenthesis indicate negative coefficients

summer, fall, and winter seasons respectively. Homogeneous and heterogeneous oxidation of SO<sub>2</sub> by peroxides, oxygen, ozone, and hydroxyl compounds may explain the association of [H<sup>+</sup>] with the [SO<sub>4</sub><sup>2-</sup>] variance (8, 10). In general, SO<sub>2</sub> concentrations are greatest during winter period and lowest during summer period (1). Gas-phase oxidation of SO<sub>2</sub> has been estimated to be highest during the summer and lowest during the winter over St. Louis (7) while liquid-phase oxidation is approximately the same for all seasons (8, 14). The season of typically low SO<sub>2</sub> concentrations corresponds with a large fraction of the total annual precipitation, probably resulting in a proportionally higher liquid-phase versus gas-phase oxidation. The season of typically high SO<sub>2</sub> concentrations corresponds with a small fraction of the total annual precipitation (Table 1), probably resulting in proportionally higher gas-phase versus liquid-phase oxidation. This interplay of precipitation and gaseous concentrations may explain the apparent linkage of [H<sup>+</sup>] with [SO<sub>4</sub><sup>2-</sup>] during both summer and winter.

The magnesium concentration was associated with 6 and 30% of the SO<sub>4</sub><sup>2-</sup> concentration variance in the spring and fall regressions respectively. Sea salt spray particulates of MgSO<sub>4</sub> compounds (2) and soil dust entrainment are the primary sources of [Mg<sup>2+</sup>]. An indicator for determining the origin of the air mass depositing the sulfate is the sulfur to chloride (S/Cl) ratio. Maritime air consisting of sea salt spray typically has S/Cl ratios around 0.02 while continental air consisting of soil dust typically has S/Cl ratios of around 4. The average S/Cl ratio of the precipitation was 4.1,

TABLE 5 Selected seasonal anion and cation concentrations

|        | Ave. concentration <sup>1</sup> |                 |              |                 |      |
|--------|---------------------------------|-----------------|--------------|-----------------|------|
|        | SO <sub>4</sub>                 | NO <sub>3</sub> | Cl<br>(mg/L) | NH <sub>4</sub> | Ca   |
| Spring | 2.86                            | 1.29            | 0.20         | 0.33            | 0.28 |
| Summer | 3.64                            | 1.52            | 0.39         | 0.23            | 0.23 |
| Fall   | 2.34                            | 0.84            | 0.24         | 0.17            | 0.27 |
| Winter | 2.34                            | 1.21            | 0.25         | 0.20            | 0.10 |

Note: 1. precipitation weighted average

3.4, 2.9, and 2.9 for spring, summer, fall, and winter respectively. These high S/C1 ratios suggests a continental source for much of the  $[\text{SO}_4^{2-}]$ .

Ammonium explained 24 and 5% of the variance in  $[\text{SO}_4^{2-}]$  for the spring and winter seasons respectively. The primary sources of  $\text{NH}_4^+$  are naturally occurring products of decomposition. Ammonium sulfate is one of the components present in the water soluble part of fine particulate aerosols (4).

### *Nitrate*

The weighted mean  $\text{NO}_3^-$  concentration was greater during the summer and least during the fall season (Table 5). Stepwise regression of all constituents on  $[\text{NO}_3^-]$  resulted in the association of 73% of its variance with  $[\text{H}^+]$ ,  $[\text{NH}_4^+]$ , and  $[\text{Ca}^{2+}]$ .

Hydrogen concentration was associated with 12 and 14% of the  $[\text{NO}_3^-]$  variance in the spring and fall respectively and 80% in the summer season. One likely source of the association of  $[\text{H}^+]$  with  $[\text{NO}_3^-]$  in the summer is the gas-phase oxidation of  $\text{NO}_x$  by hydroxyl compounds and hydrocarbons (7). The primary product of these reactions is nitric acid vapor. In contrast to  $\text{SO}_2$  oxidation, liquid-phase oxidation does not appear to be significant within the atmosphere (7). Overall, the seasonal differences in  $\text{NO}_x$  oxidation, both gas and liquid-phase, is poorly understood.

Ammonium concentration was associated with 56 and 47% of the  $[\text{NO}_3^-]$  variation in the regressions for spring and fall respectively. Ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) is a common form of agricultural fertilizer applied in the spring and fall and as such is a potential cause for this apparent linkage in precipitation chemistry. As previously mentioned, natural decomposition is the primary source of naturally occurring  $\text{NH}_4^+$ . Some evidence exists to suggest that gaseous  $\text{NH}_3$ , gaseous  $\text{HNO}_3$ , and solid  $\text{NH}_4\text{NO}_3$  have a temperature sensitive equilibrium in the atmosphere which may provide the basis for this association (10, 15).

Calcium was associated with 3 and 10% the  $[\text{NO}_3^-]$  variance during the spring and summer. Calcium concentration in the precipitation was least during the winter (Table 5) yet was associated with 93% of the  $[\text{NO}_3^-]$  variance. Apparently the overall particle-acid chemistry in the winter is different from that of the other seasons.

### *Chloride*

The weighted mean  $\text{Cl}^-$  concentration was greatest during the summer season and least during the spring season (Table 5). Stepwise regression of all constituents on  $[\text{Cl}^-]$  resulted in the association of 82% of the variance with  $[\text{Na}^+]$ ,  $[\text{Mg}^{2+}]$  and  $[\text{Ca}^{2+}]$ .

Sodium was associated with 67% of the  $[\text{Cl}^-]$  variance for the overall study period. By season,  $[\text{Na}^+]$  was associated with 93, 8, 69, and 59% of the  $[\text{Cl}^-]$  variance in the spring, summer, fall, and winter respectively. The high association of  $[\text{Na}^+]$  with  $[\text{Cl}^-]$  variance in the spring and fall corresponds with the high association of  $[\text{Mg}^{2+}]$  and  $[\text{SO}_4^{2-}]$  reported above. The high associations may be a result of the prevalence of  $\text{Na}^+$  and  $\text{Mg}^{2+}$  in soil dust aerosols as well as salt sea spray. While road salt is another potential source of  $\text{Na}^+$  in conjunction with  $\text{Cl}^-$ , the high associations do not occur during periods of road salt use and road salt is not used in the vicinity of the collector. Furthermore the sodium to chloride ratio ( $\text{Na}/\text{Cl}$ ) can be used to differentiate road salt, sea salt spray, and soil dust. The expected sea salt ratio of  $\text{Na}/\text{Cl}$  is 0.56 (the solid line of figure 3). Studies of sea salt spray however show that the  $\text{Na}/\text{Cl}$  ratio is actually closer to 0.37 above the ocean (9). The  $\text{Na}/\text{Cl}$  ratio of road salt is 1.0 (the dotted line of figure 3) while that for soil dust is greater than 1.0. The average  $\text{Na}/\text{Cl}$  ratio for each season was



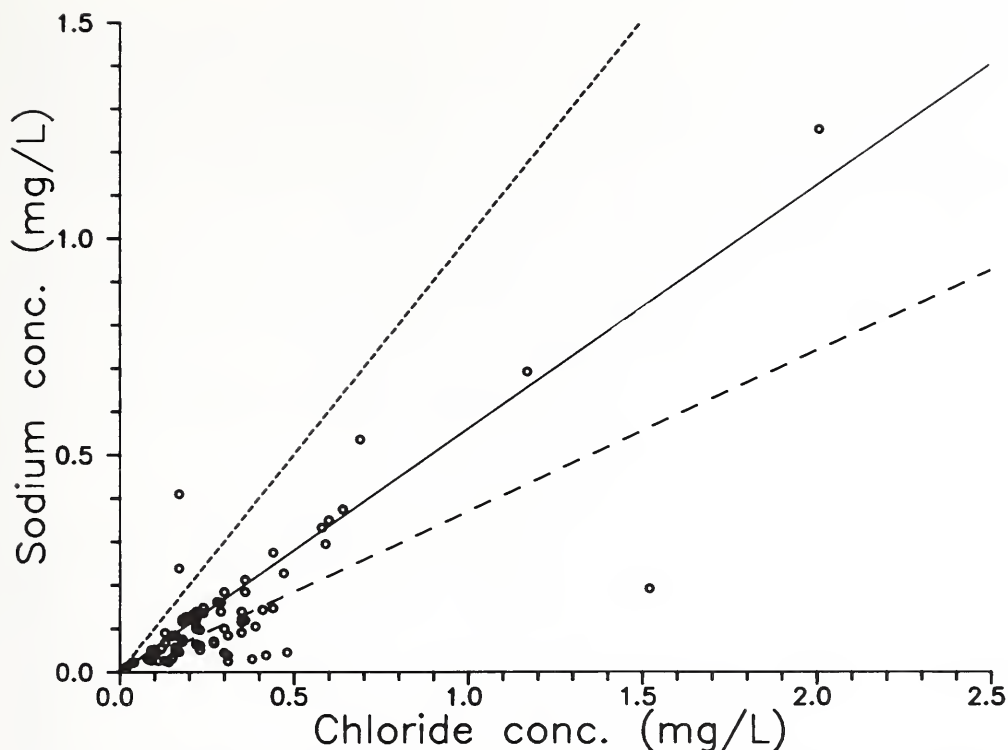


FIGURE 3. Sodium - chloride concentration relationships for weekly precipitation. The sea salt Na/Cl ratio of 0.56 is indicated by solid line. The sea salt spray Na/Cl ratio of 0.36 is indicated by the dashed line. The road salt Na/Cl ratio of 1 is indicated by the dotted line.

0.41, 0.40, 0.46, and 0.49 for spring, summer, fall and winter respectively—close to that expected from sea salt.

Magnesium was associated with 11% of winter  $[Cl^-]$  variation. A similar evaluation of the chemical components in association with the  $[Mg^{2+}]$  variance showed  $[Ca^{2+}]$  to be the dominant association during the winter. Calcium and  $[K^+]$  was associated with 3 and 2% of the overall  $Cl^-$  concentration variation respectively. These associations may be related to soil dust, fly ash, or sea salt spray (9). Seasonally,  $[K^+]$  was present in the stepwise regression in summer and winter while  $[Ca^{2+}]$  was not found in the final regression for any season. It is suspected that the variance in these metals is fortuitous as negligible  $[Cl^-]$  is present in flyash or soil dust (15).

Hydrogen concentration was associated with 13 and 18% of the fall and winter  $[Cl^-]$  variation. The explanation of  $[Cl^-]$  variation by  $[H^+]$  in the fall is probably not a result of gas-phase chlorine oxidation since the regression coefficient was negative. The winter partial  $r^2$  may be indicative of oxidation reactions producing hydrochloric acid. Hydrochloric acid is one of the components present in the water soluble part of fine particulate aerosols (4), originating largely from lead-based automobile exhausts.

#### Ammonium

The weighted mean  $[NH_4^+]$  was greatest during the spring season and least during the fall (Table 5). Ammonium tends to increase the pH of precipitation by reacting with  $SO_4^{2-}$  to form salts under conditions of high  $NH_3$  gas concentrations (4). Livestock waste and other organic matter decomposition are probably sources of most of the  $NH_4^+$ , but some  $NH_4^+$  is also found in sea salt spray. The variation in  $[H^+]$  associated with  $[NH_4^+]$  is particularly important during the fall.

### Calcium

The weighted mean  $\text{Ca}^{2+}$  concentration was greatest during the spring and fall seasons and least during the winter (Table 5). The relatively high correlations of  $[\text{Ca}^{2+}]$  with  $[\text{SO}_4^{2-}]$  and  $[\text{NO}_3^-]$  support the contention by (3) that the calcium is in the form of more neutral salts for all seasons but the fall (Table 2). It is generally assumed that the calcium found in precipitation is from soil dust entrained in the atmosphere or flyash (9). However an additional source is maritime sea salt (16). The dominance of a soil dust source is suggested by those results as flyash should be present heavily in summer and winter and less so in fall and spring as heating and cooling needs are slack. During the fall, the sea salt may be a significant contributor of  $\text{CaCO}_3$ . This however is unlikely since the mean cation to anion ratio for the fall season was 0.98 indicating some excess anions rather than excess cations in the precipitation.

#### 1985 Fall season anomaly

Fall is unique in the data set since the 1985 precipitation greatly exceeded the normal (Table 1), and the excess precipitation was largely associated with tropical storms and hurricanes (5). Precipitation from these storms resulted in rainout and washout of atmospheric gases and particulates largely originated from maritime regions. The fall of 1984 also has high precipitation but was derived from more typical midlatitude cyclones (6) with the precipitation causing rainout and washout of atmospheric gases and particulates advected from both maritime and continental regions.

The fall seasons of 1984 through 1986 had unusual positive correlations between hydrogen and the other cations (Table 3, 4). The importance of the cations is evident in the fall where the combined  $[\text{Mg}^{2+}]$  and  $[\text{K}^+]$  were associated with 33% of the  $[\text{SO}_4^{2-}]$  and 59% of the  $[\text{H}^+]$  variance in the precipitation samples. During this season, the pH is highest. For the 1984 and 1986 fall seasons ( $n=15$  weeks), the expected negative correlations between  $[\text{H}^+]$  and the variance cations appear (except  $[\text{NH}_4^+]$ ) and correlations between  $[\text{H}^+]$  and  $[\text{SO}_4^{2-}]$ ,  $[\text{NO}_3^-]$ , and  $[\text{NH}_4^+]$  improve. Only 25% of the  $\text{H}^+$  concentration variance in the 1984 and 1986 fall seasons was associated with  $[\text{Na}^+]$  and  $[\text{Ca}^{2+}]$ . For the 1984 and 1986 fall seasons, 32% of the  $\text{SO}_4^{2-}$  concentration variance was associated with cations ( $[\text{Mg}^{2+}]$  and  $[\text{Na}^+]$ ). For the 1985 fall season ( $n=7$  weeks), only  $[\text{NH}_4^+]$  was significantly associated with  $[\text{H}^+]$  variance, with only 69% of the  $[\text{H}^+]$  variance accounted for. The 1985 fall season  $[\text{SO}_4^{2-}]$  variance was primarily explained by  $[\text{Ca}^{2+}]$  (92%) with only 7% explained by the  $\text{H}^+$  concentration. The importance of  $[\text{Ca}^{2+}]$  in the 1985 fall regression may be due to  $[\text{Ca}^{2+}]$  present in maritime air sea salt particulates carried by the tropical storms of the season.

$\text{NH}_4^+$  concentrations accounted for most of the  $[\text{Cl}^-]$  and  $[\text{NO}_3^-]$  variance during the combined 3-year fall season while  $[\text{SO}_4^{2-}]$  and  $[\text{Mg}^{2+}]$  accounted for 90% of the  $[\text{NH}_4^+]$  variance. Removing the 1985 fall data results in a reduction of explained  $[\text{NH}_4^+]$  variance to 48%—all associated with  $[\text{NO}_3^-]$ . Looking exclusively at the 1985 fall samples, 99% of the  $[\text{NH}_4^+]$  variance and 88% of the  $[\text{NO}_3^-]$  variance is associated with the  $\text{Cl}^-$  concentration. This dominance of  $[\text{Cl}^-]$  in the variance of  $[\text{NH}_4^+]$  and  $[\text{NO}_3^-]$  for the 1985 fall season may be due to the reaction of sea salt spray particulates carried in the storms with  $\text{NH}_3$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$  and  $\text{SO}_2$  resulting in the replacement of  $\text{Cl}^-$  by  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  as seen in a remote maritime atmosphere (2).

Comparing the 1985 fall to the 1986 and 1984 fall season samples with one-tailed t-tests show significant differences between  $[\text{SO}_4^{2-}]$  and  $[\text{H}^+]$  (at 0.10 level) and in the  $\text{Na}/\text{Cl}$  ratio, the  $\text{S}/\text{Cl}$  ratio and the  $\text{Cl}$  concentration (at 0.15, 0.20,

and 0.20 level respectively). The 1985 season had higher concentrations of  $H^+$ ,  $Cl^-$ , and  $SO_4^{2-}$  and lower  $Na/Cl$  and  $S/Cl$  ratios than the 1984 and 1986 combined fall seasons. The average 1985  $Na/Cl$  ratio was 0.39 which is very close to the predicted ratio of sea salt spray, while the average 1984 and 1986  $Na/Cl$  ratio was 0.63 indicating more continental influence on the precipitation chemistry.

### Summary and Conclusions

The chemical composition of the precipitation at Vincennes, Indiana collector over the period of October 1984 through December 1986 appears to be of both natural and man-made origin. The variance in the precipitation pH was greater for weekly samples in which only 2cm of precipitation was collected than for samples of greater than 2cm of precipitation. Seasonally, the precipitation pH was lowest during the summer and highest during the fall with an overall precipitation weighted average pH of 4.32.

The oxidation reactions of  $SO_2$  (resulting in  $SO_4^{2-}$ ) appear to be the most important factor in explaining the acidity of the precipitation for all seasons except fall. The oxidation reactions of  $NO_x$  (resulting in  $NO_3^-$ ) however appear to contribute little to the precipitation acidity, but do appear to be more active during the summer than the rest of the year. The nitrate present in the precipitation is closely linked with the ammonium in the spring and fall suggesting that fertilizers and decomposition of natural materials are large contributors to the nitrate. The high correlations between  $[SO_4^{2-}]$  and  $[NO_3^-]$  existing throughout the seasons cannot be explained readily but is frequently observed. Based on the regressions, the precursors of  $SO_4^{2-}$  formation differ significantly from those of  $NO_3^-$  formation. This however must be tempered by the fact that associated variance of a given constituent to  $SO_4^{2-}$  or  $NO_3^-$  does not a priori mean chemical interaction.

The series of recurring major tropical storms in the fall of 1985 appeared to significantly alter the precipitation chemistry. Compared to the fall season of 1984 and 1986, the fall of 1985 had reduced pH and elevated  $SO_4^{2-}$  and  $Cl^-$  concentrations, an apparent reduced importance of oxidation reactions for  $SO_4^{2-}$  formation, and an increased importance of  $[Ca^{2+}]$ ,  $[Cl^-]$ , and  $[NH_4^+]$  in the precipitation chemistry.

Calcium,  $Mg^{2+}$ , and  $K^+$  are probably all primarily present as a result of soil dust entrainment. Evaluation of the 1985 fall season anomalous chemical relationships suggest an interaction of these cations with maritime air mass particulates. Excluding the 1985 fall season, the cations were still associated with 35% of the  $[H^+]$  variance including this fall season to be chemically unique within the period of study.

In comparison to a study of the wet deposition at West Lafayette, IN for an earlier period of time (3), the Vincennes site acidity ( $[H^+]$ ) appears to be much more associated with  $[SO_4^{2-}]$  than at the West Lafayette, IN site. However regression of  $[H^+]$  against all the chemical constituents for both Vincennes and West Lafayette showed the same fraction of the  $[H^+]$  variance accountable by the ions studied.

Future studies evaluating the trends in precipitation chemistry should take into account inter-annual variability in the storm tracks and the intensity and duration of the storms producing the weekly precipitation.

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