Wet Atmospheric Deposition in Indiana

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Introduction

Atmospheric deposition of materials by precipitation has become an increasing area of concern. Although the role of this deposition in the environment and its sources are still largely uncertain (Miller, 1984), it is thought that precipitation chemistry, especially acidity, can be highly influenced by anthropogenic emissions of sulfur and nitrous oxides (Cogbill and Likens, 1974, Likens, 1976, Martin and Barber, 1977).

To monitor atmospheric deposition, several networks have been developed over N. America and Europe. Beginning in July, 1982, weekly precipitation samples were collected in West Lafayette, IN as a part of the National Atmospheric Deposition Program Network (NADP), organized under the USDA Cooperative State Research Service Interregional project IR-7. The network was created in 1978 and currently has a total of 177 stations across the U.S. The network has excellent common procedures for field work, standardized equipment at each site, and has all samples analyzed at a central laboratory location, minimizing procedural biases and enhancing the capability for regional and temporal comparisons.

Samples at the West Lafayette sites are taken weekly at the Purdue Agronomy Farm (11 km NW). On-site measurements of precipitation pH and specific conductivity are performed on a small aliquot. The remaining sample is shipped in its collection bucket to the NADP Central Laboratory for a detailed laboratory analysis including pH and conductivity, as well as soluble concentrations of Ca, Mg, K, Na, NH_4, NO_3, Cl, SO_4, and PO_4 ions. In addition, detailed on-site precipitation records are maintained, giving a thorough history of rainfall duration as well as collector performance. On-site pH and conductivity measurements were made only when the total precipitation sample weight exceeded 70g (1.03mm liquid precipitation equivalent), otherwise the entire sample is shipped to the Central laboratory.

Results and Discussion

The field pH measurements taken at the Agronomy Farm field site are shown in Figure 1 for the entire two-year period ending 10 July, 1984. Eighty-eight weekly, on site, observations were taken (out of 104 possible). In the remaining weeks there was either no precipitation or the volume was less than 70 ml. The data points and a moving three-week average line are shown for comparison. The scatter of the points is relatively high with a range from 3.21 to 4.93 pH hunits. Also, a definite periodicity can be seen these first two years, with pH maxima occurring in the winter months and pH minima occurring in the summer. The annual mean pH based on weekly, on-site measurements is 4.15.

The Central Laboratory data yielded similar results. At the time of writing this presentation, laboratory analyses were available up through the end of May, 1984 (98 weeks), on 86 samples from weeks with sufficient precipitation for analysis. The mean, volume-weighted pH for the laboratory measured samples was 4.36. Figures 2a and
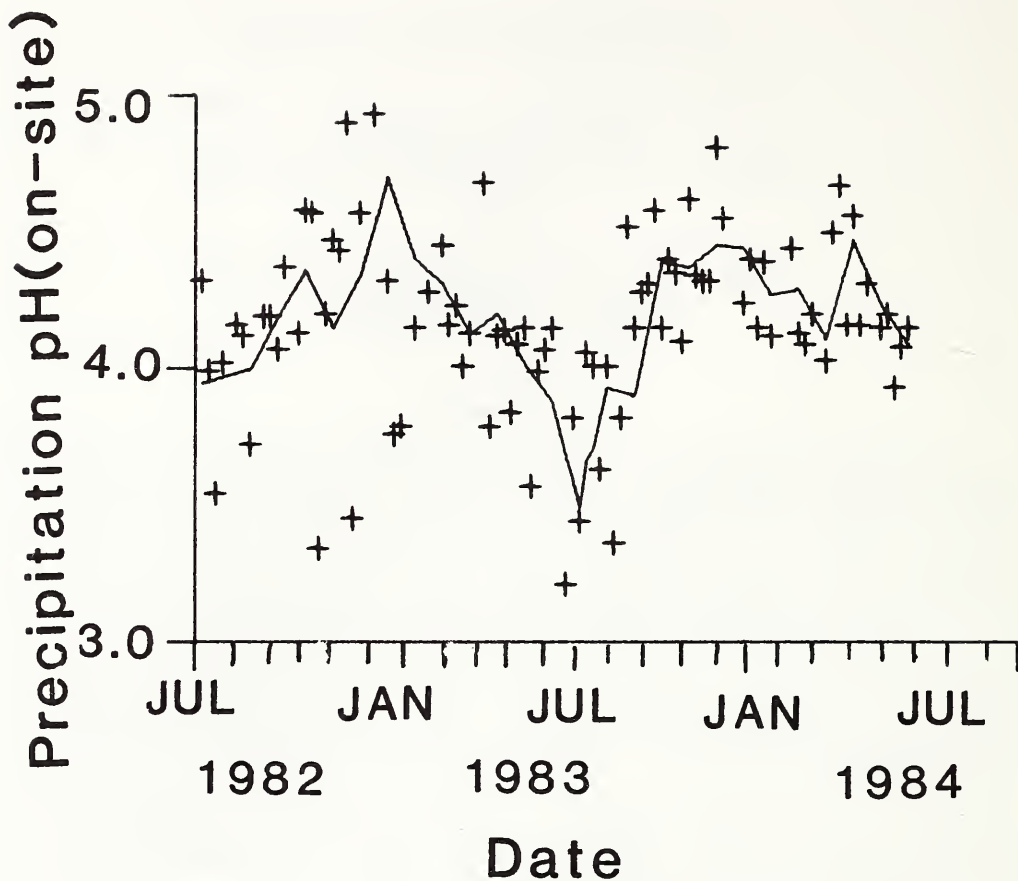
FIGURE 1.   On-site precipitation pH measurements at West Lafayette, In for the two-year period 13 July, 1982 - 10 July, 1984.

2b show the SO_4 and NO_3 deposition vs. time for the 98-week period. The SO_4 ion also shows some periodicity, but approximately 6 months out of phase with the pH plot, with summer maxima and winter minima. This would be "in phase" with an H^+ ion concentration plot. This seasonality (especially pH has been observed in other parts of the NADP network (Semonin and Stensland, 1984) and may be related to
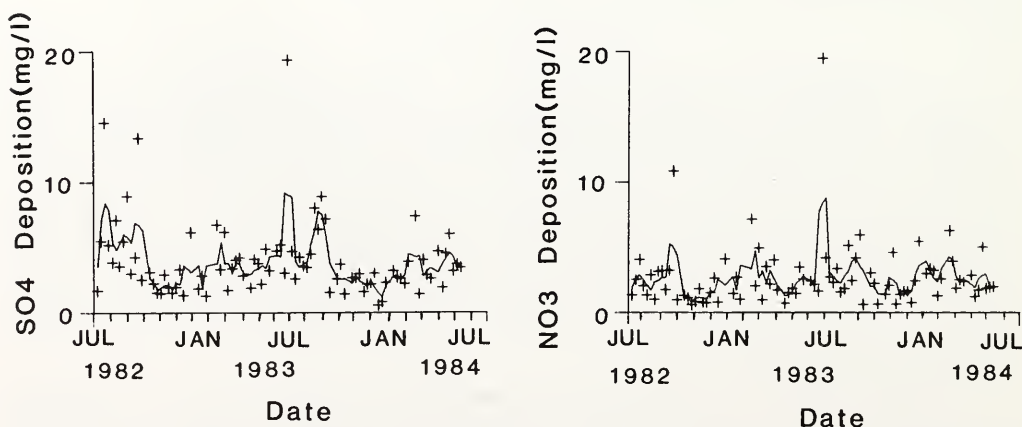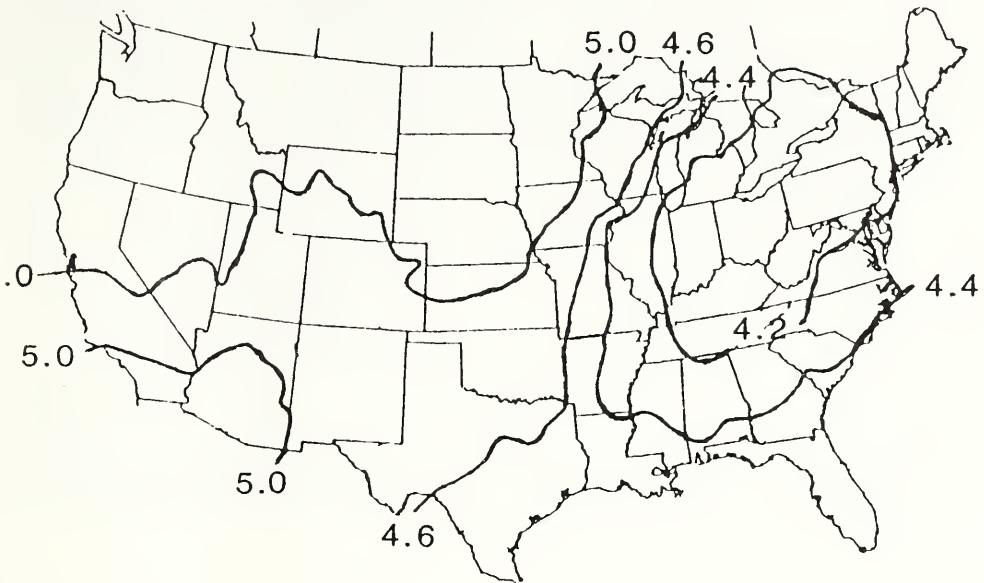

FIGURE 2.   a) Sulfate and b) Nitrate deposition at West Lafayette, In for the 98-week period 13 July, 1982 - 1 June, 1984.

temperature. The NO_3 ion, on the other hand, shows less seasonality and appears less random. NADP Network results for mean pH and SO_4 ion concentration in the summer and winter of the 1982 are shown in Figures 3 and 4. Again, the seasonal periodicity
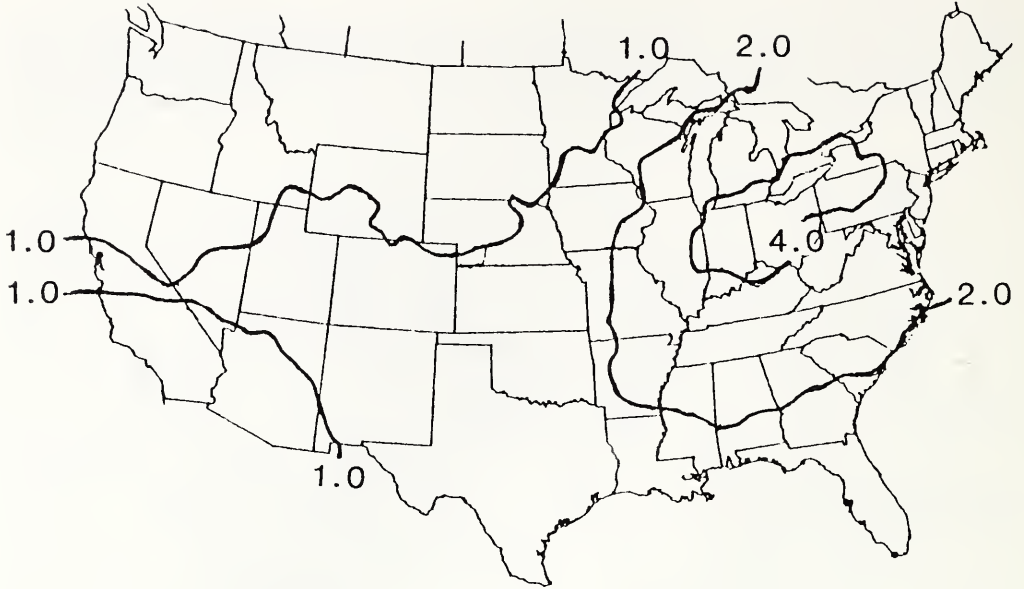

Summer 1982 Volume Weighted Mean pH
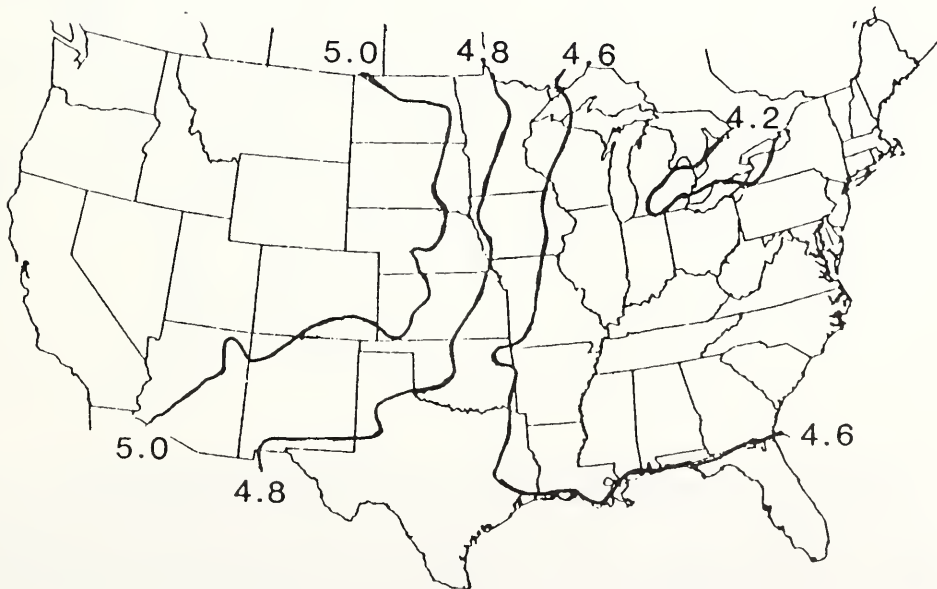
Winter 1982 Volume Weighted Mean pH

Figure 3. NADP Network results for mean precipitation pH in a) summer and b) winter, 1982 (NADP, 1984).

Summer 1982 Sulfate Ion Concentration(mg/l)
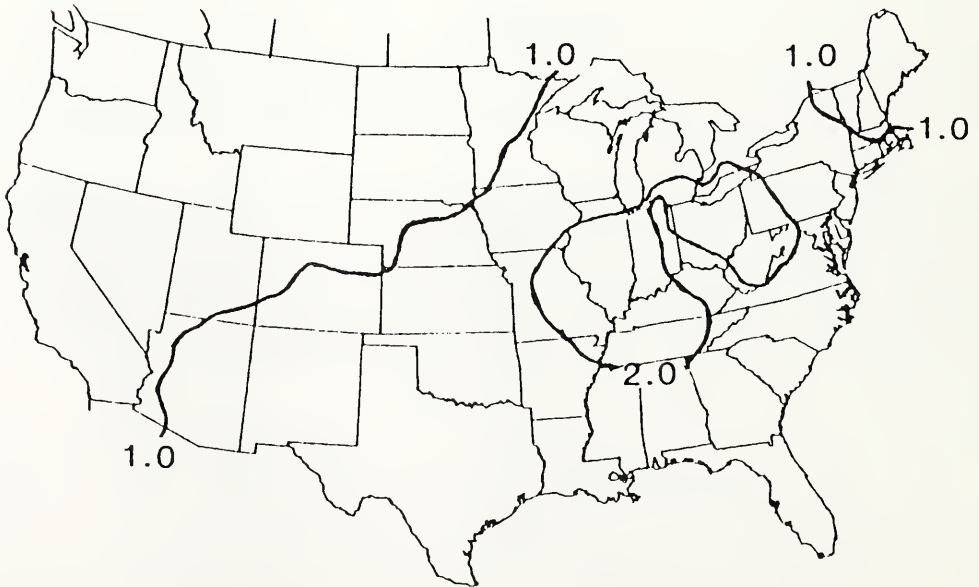
Winter 1982 Sulfate Ion Concentration(mg/l)

FIGURE 4.   NADP Network results for mean sulfate ion deposition in a) summer and b) winter, 1982 (NADP, 1984).

of both data sets is quite distinct. Indiana lies on the western fringes of the area of most acidic rainfall and highest SO₄ deposition with extends north and eastward into the northeastern U.S. and southeastern Canada.

Statistical Data Analysis

The laboratory results were analyzed with stepwise multivariate linear regression with computer programs from the Statistical Package for the Social Sciences (SPSS8.5.3) at the Purdue Univ. Computing Center. The initial results (with 86 observations) showed great variation in all variables. Careful scrutiny of the data revealed that most of the large concentrations of ions were obtained in small precipitation volumes. Martin and Stensland (1984) have suggested sample contamination may be a problem in very small samples in large containers due to chemical reactions with the material of the collecting bucket itself during the storage time before lab analysis. The enhanced scavenging effect of light showers would also contribute to high concentration in the small samples. When data from sample volumes of less than 70 ml were removed, reducing the number of observations to 76, the analysis gave more plausible results and drastically reduced the standard deviation of the ion concentrations, in some cases by as much as 480%.

The correlation coefficients for various ions and processes with H ion concentration are shown in Table 1. The listed ions were chosen on the basis of concentrations because the other measured ions were at least an order of magnitude less and were frequently below the detection limits of the instruments. The hydrogen ion concentration was estimated using the relationship:

$$H = 10 \exp(-pH_{lab}).$$

Weekly mean temperature (TEMP) at the site was included as a variable in hopes of seeing the effects of temperature-dependent oxidation on sulfur and nitrogen oxides. Precipitation volume (VOL) and the difference of summed anions and summed cations (IONDIF, in meq/l) were also used in the correlations. The IONDIF should be closely correlated with H if no organic ions are in the system and all important inorganic ions are being measured.

TABLE 1.   Correlation coefficients for ions and several processes vs. H ion concentrations.

	H	SO₄	NO₃	HN₄	Ca	VOL	pH_lab	TEMP
IONDIF	.596	.864	.582	.214	.205	-.216	-.718	.350
TEMP	.529	.541	.160	.243	.416	.024	.585	
pH_lab	-.857	-.686	-.550	-.187	-.412	.235		
VOL	-.250	-.242	-.450	-.187	-.389			
Ca	.510	.519	.547	.359				
NH₄	.084	.513	.588					
NO₃	.467	.575						
SO₄	.604							

The correlation coefficients show SO_4 to be significantly ($\alpha = .05$) correlated NO_3, Ca, NH_4, as well as being the best predictor of H, while nitrate shows significant correlation with SO_4, Ca, NH_4. This is not surprising as much research has found these two anions to be dominant in precipitation chemistry (Likens et al., 1979, Grannat, 1972) and a major source of its acidity (Baker et al., 1981). The higher correlations of SO_4 and NO_3 with the difference in summed anions and cations also support this. The positive correlation between SO_4 and temperature and the increased summer sulfate levels found at the site have been observed elsewhere (Musold and Lindqvist, 1983).

If the source of all SO_4 and NO_3 ions were SO_2 and nitrous oxides, then every

equivalent of NO_3 and SO_4 should have an equivalent of H originally associated with it, and as suggested by Skeffington (1984), the slope of a linear regression between H and the oxidized form should be very close to 1. Our data yielded regressions of $H = 1.09 \, SO_4 - .004$ for SO_4 ion in meq/l and $H = .180 \, NO_3 + .006$ for NO_3 ions in meq/l. The intercepts of both equations are near the origin, and in the case of SO_4, the slope is not significantly different from 1.0, which should be the case if SO_2 is the predominant source of SO_4. For NO_3, however, the slope is much less than unity, and we must infer that the source of much of the NO_3 is not from nitrous oxides, but from other sources. This makes sense as the site is relatively distant from any large point sources.

A surprising result was the intercorrelation of Ca with the other ions. We expected a negative or insignificant relation with H^+, as most terrestrial dust contains Ca in the form of $CaCO_3$, causing neutralization (Harrison and Pio, 1983). We found instead a significant positive correlation. This suggests a more neutral salt of sulfate or nitrate as the predominant Ca form. The acidic contribution (if any), however, is not apparent.

As expected, Volume shows a negative correlation with all ion concentrations, implying that the majority of the aerosols are scavenged during the initial phases of precipitation events.

Overall, if we use a multiple linear model to regress the data stepwise with H ion concentration, we obtain:

$$H = .013 \, SO_4 - .110 \, NH_4 + .025 \, NO_3 + .0014 \, TEMP + .027 \, Ca - .057$$

where all concentrations are in mg/l and temperature is in °F. Rejection in the stepwise method was at the $\alpha = .05$ level. The model yields an R^2 value of .78, with SO_4 explaining 36% of the H variance.

Impact on Indiana Soils

If we integrate the major ions (by mass), including SO_4, NO_3, and NH_4, we get average annual depositions of 8.43 kg S/ha and 6.18 kg N/ha. This corresponds well with the 8.0 kg S/ha deposited at Champaign-Urbana, IL in 1982. The S value may be a bit low as the averaging period did not include the last six weeks of the two-year period, when concentrations are usually higher than the average. The acidifying effect of these ions in precipitation is believed to have little, if any, impact on most Indiana soils due to the large buffering capacity present (CAST, 1984). While the N deposition represents a small fraction of total N used in agriculture, the S deposition may supply a significant portion of most agricultural needs. Most crops in Indiana remove approximately 18 kg S/ha annually (Terman, 1978).

Conclusions

Atmospheric deposition through precipitation has been monitored since the summer of 1982 at the Purdue Agronomy Farm as a part of the NADP network. The mean, volume-weighted precipitation pH is 4.36, while annual S deposition in the form of soluble SO_4 averaged 8.43 kg/ha, enough to meet some of the needs of growing crops in Indiana thus reducing the need for S fertilizers. Nitrogen deposition in the form of NH_4 and NO_3 is on the same order of magnitude, 6.18 kg N/ha, but represents a much smaller portion of the total plant needs.

The H and SO_4 ion concentrations show a definite seasonal trend, higher in the summer and lower in the winter. Multiple correlations indicate that Ca, SO_4 and NO_3 ion concentrations in precipitation are significantly correlated with H concentrations.

The concentrations and total deposition at this station fit the regional pattern portrayed by other network stations throughout the Midwest.

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