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OPERATION AND RESEARCH AT THE ITHACA MAP3S REGIONAL PRECIPITATION CHEMISTRY SITE

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ABSTRACT

The Ithaca MAP3S Regional Precipitation Chemistry Site has been in continuous operation since September, 1976. Event sampling was upgraded to daily sampling in March of 1989. From 1 May 1989 to 30 April 1990, 121 separate precipitation samples have been collected, a 50% increase in annual sample numbers when compared to event sampling. Annual sample volume, 120 cm, was approxamately 20% greater than the long-term average. Volume-weighted annual pH was 4.22 (mean annual average = 4.18), and annual deposition of H^+ was 712 eq/ha (mean annual deposition = 696 ± 58 eq/ha).

Recent research by MAP3S personnel includes an investigation of the relationship between declining emssions of SO2 and NOx, and their impact on precipitation chemistry. Results show: (1) no statistically significant ($p<0.10$) relationship between declining NOx emissions and annual NO_3^- concentrations in precipitation; (2) statistically significant relationships for declines in SO2 emissions and declines in annual precipitation $SO_4^=$ at Ohio ($p<0.05$), Illinois ($p<0.05$), Whiteface Mt., N.Y. ($p<0.10$), and Hubbard Brook, N.H. ($p<0.01$); and (3) statistically significant relationships between combined annual emissions of SO2 plus NOx and annual H^+ concentrations at Ohio ($p<0.05$), Illinois ($p<0.10$), Ithaca, N.Y. ($p<0.01$), and Hubbard Brook, N.H. ($p<0.01$). For the northeast and midwest as a whole a 19% decline in regional SO2 emissions has been accompanied by a 14% (±3% s.e.) decline in $SO_4^=$ concentration ($p<0.01$) in precipitation. For this same area an 18% decline in combined emissions of NOx plus SO2 has led to an 18% (±3% s.e.) in H^+ concentration ($p<0.01$).

Site Operation and Precipitation Characteristics

The Ithaca MAP3S Regional Precipitation Chemistry Site has been in continuous operation since September, 1976. Event sampling was upgraded to daily sampling in March of 1989. During the first full year of daily sampling, from 1 May, 1989 to 30 April, 1990, 121 separate samples were collected. This is approximately a 50% increase in the number of samples collected annually during the former period of event sampling. Precipitation amount for the previous year (1 May, 1989 to 30 April, 1990) was 120 cm, as compared to the long-term average of 103 ±5 (s.e.) cm/yr. Volume-weighted field pH for the previous year was 4.22, as compared to a long-term average of pH 4.18. Long-term deposition of H^+ is 696 ±58 eq/ha (s.e.)., while from 1 May, 1989 to 30 April, 1990 H^+ deposition was 712 eq/ha.

The data record for the site also includes various other meteorological parameters such as hourly precipitation amount, precipitation type, sample and predicted volume, and storm direction. Since 1987 detailed meteorological data have been archived for the site, including continuous hourly windspeed and direction, air temperature and delta temperature (a measure of atmospheric stability), relative humidity, and ozone concentrations. These meteorological data are part of the ongoing measurements associated with the National Dry Deposition Network (NDDN) and provide complimentary data to the MAP3S precipitation chemistry record.

The Ithaca site has been cited as one of the most consistently best-run stations in the MAP3S network by auditors of network operation (Barchet, 1987). In addition, the personnel associated with the site since its inception, have developed a productive research program that has addressed relevant questions in the field of preciptation and atmospheric chemistry, and ecological impacts (see Appendix A). Recent research, relating the effects of changing SO2 and NOx emissions on precipitation chemistry (discussed in detail below), addresses the DOE program objective of understanding the consequences of energy use and development (Wesely et al., 1990).

Recent Research- The Impact of Declining Emissions of NOx and SO2 on Precipitation Chemistry

The effect of reduced emissions of SO_2 and NO_x on precipitation chemistry, and on wet and dry deposition is of major concern especially in the eastern U.S. and Canada where acid-sensitive ecosystems are being impacted (e.g. Likens, 1987). A large effort has gone into modelling how changing emission scenarios would alter precipitation chemistry and wet deposition (Schwartz, 1989). Many current long-range transport-transformation models assume a proportional relationship between emission levels and consequent transformation to acid species (e.g. Fay et al., 1985; Irwin and Williams, 1988; Ellenton, et al. 1988). However, there are many physical and chemical factors that can alter this proportional relationship. These factors include: distance from source regions (Clark et al., 1987), short-term meteorology (Cape et al., 1984; Ellenton, et al. 1988; Dillon et al., 1988), longer-term climatic factors (Bradley, 1986; Irwin and Williams, 1988), the abundance of potential catalysts, hydrocarbons, and oxidizing agents such as O_3, H_2O_2, and OH, as well as other competing acid-forming species (Rodhe et al. 1981; Clark et al., 1987), precipitation pH (Cheng et al., 1971; Winkler, 1984; Fuhrer, 1985), and changing stack height levels (Popovics et al. 1987; Likens, 1984, 1987). All of these factors can affect rates of transport, transformation and deposition.

Both Rodhe and Granat (1984), and Leck and Rodhe (1989) observed that from 1955 to 1982 and from 1972 to 1986 respectively, changes in sulfate concentrations of precipitation in Scandanavia were consistent with changes in emissions of SO_2 in Europe. Dillon et al. (1988) have demonstrated a strong correlation between emissions of SO_2, and concentrations and rates of bulk deposition of $SO_4^=$ and H^+ in central Ontario from 1976 to 1985. Hedin et al. (1987) found significant decreasing trends in $SO_4^=$ concentrations at Hubbard Brook, N. H., and at 5 out of 8 National Atmospheric Deposition Program monitoring sites in the northeastern and midwestern U. S. since 1978. Likens et al. (1984) showed that from 1965 to 1978 a 39% decline in regional SO_2 emissions was accompanied by a 34% decline in $SO_4^=$ concentration at Hubbard Brook, N.H. Fay et al. (1985, and 1987), used an analytical emission-deposition model to calculate the long-term wet deposition of sulfate and nitrate, respectively, for eastern North America. Their model calculations compare favorably with the long-term data for $SO_4^=$ and NO_3^- concentrations in precipitation at Hubbard Brook.

Data Sources

To evaluate the effects of changing emission levels on precipitation chemistry we have used SO_2 and NO_x emission data compiled by Argonne National Laboratory (Fig. 1) for 1975 to 1987 (Kohout et al., 1989). The Argonne data set (Knudson, 1986 and Kohout et al., 1987, 1988 and 1989) represent the most comprehensive and up-to-date estimates of emissions by individual state and month for the contiguous U. S. (Lins, 1987). Other authors have attempted to estimate emissions of SO_2 and NO_x for the U.S. (Gschwandtner et al. (1985), Husar (1986)) for an extended time series, but their analyses extend only until 1980. It should be noted that during the overlapping time period of this analysis (1975-1980) the Husar SO_2 data set shows a somewhat different trend than the other two data sets, for the eastern U.S. Gschwandtner et al. (1985) show a downward trend in SO_2 consistent with the data used in this study (Kohout et al., 1989), while Husar (1986) shows no change or a slightly increasing trend from 1975 to 1980. Gschwandtner et al. (1985) and Kohout et al. (1989) used a similar consumption-oriented approach, while Husar (1986) used a source-oriented approach, tracking sulfur from coal production in mines through distribution over land to emission sources (Lins, 1987). For NO_x all three data sets show consistent patterns, with a rising, then falling trend for the period 1975 to 1980.

Combined emissions of SO_2 and NO_x were used to evaluate the relationship between total emissions and H^+ in precipitation. Emissions were combined by adding the moles of emission of NO_x

(assumed to be NO_2), to the moles of SO_2 emission multiplied by a factor of two. This latter step allows for the fact that the transformation of each mole of SO_2 has the potential to produce two moles of H^+ in precipitation.

Transport of SO_2 and NO_x and their transformation products from eastern Canada into the eastern U.S. is considered small. Estimates for this SO_2 import range from 3% to 7% of eastern U. S. emissions (Galloway and Whelpdale, (1980), Olson et al., (1982), Fay et al., (1985)) due to much lower emission rates in Canada (Pers. Comm., F. Vena, Environment Canada), and a net advective air flow toward Canada (Fay et al., 1987). For similar reasons Canadian NO_x emissions are assumed to have little impact on precipitation chemistry in the eastern U.S.. For example, Whiteface Mountain, located 75 km south of the Canadian border in northern N.Y. (Fig. 2), receives less than 6% of its wet nitrate deposition from eastern Canada according to a source apportionment study performed by Fay et al. (1987). Thus, Canadian emissions are not included in this analysis.

Source regions for the sites in this study are presented in Fig. 2. While it is difficult to assign source regions for each site with a great degree of precision we believe that these geographically large areas are an appropriate choice of source regions for the following reasons. Mean transport distances for oxides of sulfur and nitrogen, and their oxidation products, are on the order of 400 to 1200 km (Schwartz, 1989). Pack (1978) found a large amount of between site correlation for the four original MAP3S sites (Whiteface, Ithaca, Penn State, and Virginia), especially for monthly $SO_4^=$ and H^+ concentrations, suggesting long-range transport and regional-scale mixing for the eastern U.S. Dillon et al. (1988) found the strongest correlations between SO_2 emissions and $SO_4^=$ concentrations in Ontario, when all of eastern North America, rather than Ontario alone, was used as the source region. Altering the size of the source regions by ±20 % had little impact on the significance levels of regression slopes at any of the sites.

We have used high-quality empirical data from the MAP3S precipitation chemistry network (MAP3S/RAINE, 1982) which is the longest operating network in the U. S., and also from the Hubbard Brook Experimental Forest, N.H. which represents the longest continuous record of precipitation chemistry in North America (Likens et al., 1984). The MAP3S network began operation in the eastern U.S. in the fall of 1976 with 4 original sites (Whiteface Mountain, N.Y., Ithaca, N.Y., Penn State, Pa. and Charlottesville, Va.) (Fig. 2) and now contains 9 sites in the eastern and midwestern U.S. The sites were chosen to be representative regionally with no large sources of local pollution nearby. Precipitation (wet-only) is collected on an event basis and samples are analyzed for the major anions and cations at a central laboratory at Pacific Northwest Laboratory (PNL) in Richland, Washington. Quality of data are assessed and sample results are screened during initial chemical analysis at PNL and again when the data are entered into the Acid Deposition System (ADS) data base (Watson and Olson, 1984).

Monthly data summaries during the period of study for $SO_4^{=}$, NO_3^- and H^+ concentrations meet quality criteria except for H^+ concentrations from October 1985 through June 1986. For this nine-month period, all MAP3S sites show an estimated bias for H^+ concentration of -18% to -23%, due to laboratory error (Dana, 1988). Therefore the MAP3S 1986 H^+ concentration data are not used in this analysis. Annual H^+ concentration summaries for 1985 may be biased slightly lower in concentration by about 5% due to the inclusion of the H^+ data for last three months of 1985.

Precipitation samples at Hubbard Brook are bulk samples collected on a weekly basis (Likens et al. 1977). Comparison of bulk samples, with weekly wet-only data collected at Hubbard Brook from 1979-1982, show good agreement for most ions, including $SO_4^{=}$ and NO_3^- (Stensland et al., 1986). The bulk precipitation chemistry data set at Hubbard Brook extends from 1965 to 1987. Our analysis of the emission-concentration relationships for Hubbard Brook are limited by the length of the emission data set from Kohout et al. (1989) which begins in 1975. The average annual precipitation and precipitation chemistry record for the seven sites in this study are presented in Table 1. Unfortunately we have no continuous data on air concentrations of acid precursor gases or acidic aerosols at these sites.

Results and Discussion

The results of linear regressions of annual concentrations on the corresponding levels of emissions for two midwestern (Illinois and Oxford, Ohio) and four northeastern, continental MAP3S sites (Whiteface, Ithaca, Penn State and Virginia) plus Hubbard Brook, N.H. are summarized in Table 2, and data for three sites are presented in Fig. 3. Regressions significant at $P < 0.10$ are included because a high degree of variability in the precipitation chemistry, due to variability in meteorology (Munn and Rodhe, 1971; Rodhe and Granat, 1984) and/or climate (Bradley, 1986), is expected irrespective of emission changes. The use of annual data, rather than data on a shorter time scale, reduces some of this variability. However low R^2 values in Table 2 demonstate that a large amount of variability still remains and can not be explained by the regressions.

All significant regressions were tested for first-order autocorrelation (Durbin-Watson statistic). In no case was there positive autocorrelation.

Sulfur

The regression of $SO_4^=$ concentrations on emisssions of SO_2 for Illinois (1978-1987), Ohio (1979-1987), Whiteface Mt. (1977-1987) and Hubbard Brook (1975-1987) are statistically significant at $P <$ 0.05, 0.05, 0.10 and 0.01 respectively (Table 2 and Fig. 3). The Illinois and Oxford, Ohio sites are both located in the major source regions for SO_2 emissions and therefore are expected to be most influenced by emission changes in these areas (Wisniewski and Kinsman, 1988). This relation should be even stronger for dry deposition of sulfur which is deposited closer to emission sources than is $SO_4^=$ in precipitation (Irwin and Williams, 1988).

Hubbard Brook (Fig. 3) shows the strongest relationship between sulfur emissions and concentrations in precipitation ($P < 0.01$). A 23% decline in SO_2 emissions during 1975 to 1987 was accompanied by a 28% decline in precipitation $SO_4^=$. Whiteface Mt., the site closest to Hubbard Brook, also shows a statistically significant relationship ($p < 0.10$), although the relationship is not as strong as at Hubbard Brook. Wet $SO_4^=$ deposition at Hubbard Brook is also highly correlated with emissions ($p < 0.01$). Why is this so? Part of the answer may be that Hubbard Brook has the largest data set for this analysis (13 years at Hubbard Brook as opposed to 9 to 11 years for the other sites). Also, Hubbard Brook, the site located furthest downwind from the major pollution sources, may allow more opportunity for mixing, interaction with oxidants and consequent transformation to $SO_4^=$. In a similar situation, Rodhe and Granat (1984) found that $SO_4^=$ in precipitation at several sites in Sweden, located hundreds of kilometers from major emission sources, correlated well with changing SO_2 emission levels in Europe. Also, Clark et al. (1987), have concluded that emission-transformation relationships are more likely to be linear at greater distances from the source regions.

It should also be mentioned that the Hubbard Brook data for this analysis are derived from bulk samples, whereas the MAP3S data are derived from wet-only samples. Sulfate concentrations in high quality bulk precipitation samples may show a stronger relationship to changing SO_2 emissions because a small dry deposition component of $SO_4^=$ also may be included in the samples at Hubbard Brook (Eaton et al., 1980).

The remaining MAP3S stations show positive linear regression slopes, except Penn State which had a slope that was near zero. The lack of a strong relationship at these three sites ($P > 0.10$) may be the result of one or more possibilities. Meteorological variability, which in turn leads to a high level of variability in rainfall chemistry (MAP3S/RAINE, 1982), is certainly a factor. The use of annual volume-weighted mean concentrations reduces much, but not all of this variability, since high between-year variability also exists (Cape et al., 1984; Rodhe and Granat, 1984).

There is also the possibility that for some sites the emission-concentration relationship is not proportional because of the limitation of SO_2 oxidation by other factors. Limited availability of hydrocarbons, oxidants (OH, H_2O_2, O_3) and catalysts (Rodhe et al. 1981; Clark et al. 1987) may control $SO_4^=$ concentrations in precipitation. When oxidants or catalysts are not limiting then high rainfall acidity can limit aqueous phase SO_2 oxidation. Sites at Penn State and Ithaca have the highest rainfall acidity for the sites examined, with mean annual pH's of 4.15 and 4.18, respectively for 10 years of record. Liquid-phase oxidation of SO_2 to $SO_4^=$ appears to slow substantially below a pH of 4.2 because of decreased solubility of SO_2 in water droplets (Cheng et al. 1971; Winkler, 1984; Fuhrer, 1985). Thus declining emission levels may not influence these sites in a linear fashion until there has been a more substantial decrease in emissions. Hubbard Brook however has a volume-weighted mean pH of 4.24 for the period 1975 to 1986 and thus aqueous oxidation of SO_2 may be less limited by acidity of the precipitation.

Despite the differences in behavior among sites between SO_2 emissions and precipitation $SO_4^=$, an overall $SO_4^=$ to SO_2 relationship for all sites combined is apparent (Fig. 4(a) and Table 3(a)). For the northeastern, middle-Atlantic, and lower midwest as a whole, decreasing SO_2 emission levels are translated into lower $SO_4^=$ concentrations with an efficiency of 74% ±15% (s. e.). A strictly defined linear relationship should be 100%. The 74% slope, or efficiency ratio, is a conservative estimate since all seven sites, including Penn State, which shows no $SO_4^=$ to SO_2 relationship, and all years are included in the analysis.

The effects on the slope, standard error, and the R^2 values when certain years (1979) and/or sites (Penn State) are removed from the total data set are shown in Table 3(a). Surprisingly low sulfate concentrations were found at six of the seven sites during 1979 (see Fig. 4). The reasons for these low $SO_4^=$ concentrations during 1979 are not clear. Seasonal precipitation amounts and air temperatures were close to normal for the eastern U.S. during 1979 suggesting that factors other than meteorology were involved.

Excluding 1979 increases the efficiency ratio to 83%. Excluding Penn State increases the $SO_4^{=}$/ SO_2 conversion efficiency to 92%, and excluding data both from Penn State and from 1979 increases the efficiency ratio or regression slope to 102%.

Nitrogen

For the source regions of the midwestern and eastern U.S., emissions of NO_x from 1975 to 1987 have declined about 17% (Fig. 1 and Table 2). No site shows a statistically significant ($P < 0.10$) relationship between NO_x emission levels and NO_3^- concentration. The high degree of variability in the annual NO_3^- concentration data (Dana, 1988), make the analysis of relationships between emissions of NO_x and concentrations of NO_3^- difficult. Also, a faster atmospheric formation and removal rate of HNO_3, as compared with H_2SO_4, may make long-range transport of NO_3^- less pronounced than $SO_4^{=}$ (Rodhe et al., 1981).

Other workers also have not been able to establish significant trends in NO_3^- concentrations as related to changes in emissions.of NOx. Dillon et al., (1988) for a site in eastern Canada, concluded that NO_x emissions, and nitrate concentration and deposition had not changed significantly from 1976 to 1986. Rodhe and Rood (1986), also found no trend for NO_3^- in Sweden from 1972 to 1984, a period of minimal NO_x emission changes in Europe.

Hydrogen Ion

Hydrogen ions in continental precipitation are generally associated with $SO_4^{=}$, NO_3^-, non-sea salt Cl^-, and organic acid anions. However because samples for this study were not preserved with biocide, organic acids are a negligible component of the free acidity (Keene and Galloway, 1984). If we make the simplifying assumption that 100% of the H^+ were associated with $SO_4^{=}$, NO_3^-, and non-sea salt Cl^- in proportion to the concentrations of these anions, then we can estimate their relative contibutions to rainfall acidity. Sulfate accounts for an average of 62% (Hubbard Brook) to 68% (Oxford) of the acidity for the period of record. Nitrate accounts for 28% (Oxford) to 34% (Hubbard Brook) of the acidity, and non-sea salt chloride accounts for 4% of the acidity at all the sites.

An analysis of the regression of H^+ concentration in precipitation on the combined emissions of NO_x and SO_2 is included in Table 2. As mentioned earlier, the data for 1986 are not included for the MAP3S sites. Illinois ($P < 0.10$), Ohio ($P < 0.05$), Ithaca ($P < 0.01$), and Hubbard Brook ($P < 0.01$) all show a significant positive relationship. The remaining three sites all show a positive relationship, but the slopes are not significant at $P < 0.10$.

Not surprisingly, Hubbard Brook, which shows a strong relationship between sulfur emissions and concentrations in precipitation ($P < 0.01$), also has a very significant relationship between total emissions ($SO_2 + NO_x$) and H^+ concentration ($P < 0.01$). Hubbard Brook also shows significant relationships ($P < 0.01$) between respective emissions and $SO_4^=$ deposition, and H^+ deposition. None of the MAP3S sites show significant relationships ($P < 0.10$) between emission levels and deposition. Deposition increases variability by adding another factor, namely amount of annual precipitation, into a data set that, as mentioned earlier, is already highly variable.

The overall relationship between emissions of NO_x (in moles) plus SO_2 (2 x moles), and H^+ concentration is presented in Fig. 4(b) and Table 3(b). An efficiency of conversion ratio is indicated by the slope (100% ± 15% (s. e.)) using the same approach as was done for the overall SO_2 to $SO_4^=$ relationship. This analysis indicates that for the period of record, an 18% reduction in emissions has been accompanied by an 18% reduction in H^+ concentration throughout the study area. Thus, for the eastern U. S. as a whole, a strictly linear relationship appears to exist between emissions of SO_2 and NO_x and H^+ concentration in precipitation. Such a result suggests the importance of reducing both SO_2 and NO_x emissions in order to reduce total acid loading in the eastern U.S.

Ecological Implications

It appears that declines in emissions of SO_2 have led to significant declines in $SO_4^=$ concentration, and declines in NO_x plus SO_2 have led to declines in precipitation acidity, at least for some parts of the northeastern and midwestern U. S.. However, these declines, although ecologically important, are not large enough to prevent ecological damage in sensitive areas. For example, Hubbard Brook shows the greatest percentage decline in $SO_4^=$ concentration (28%, 53 ueq/l to 38 ueq/l) of the sites in this study. This decline has reduced average deposition (assuming average precipitation of 133 cm, (Likens et al., 1985)) from 33.8 kg $SO_4^=$/ha-yr to 24.3 kg $SO_4^=$/ha-yr. It has been proposed that to protect sensitive aquatic and terrestrial ecosystems, deposition of $SO_4^=$ should be no more than 9 to 14 kg $SO_4^=$/ha-yr (Schindler, 1988; Nilsson and Grennfelt, 1988). Thus, substantial additional reductions, on the order of 50% of present acid species concentrations and wet deposition, are necessary if the ultimate goal were to protect sensitive aquatic and terrestrial ecosystems.

Conclusions

Declining annual emission levels of SO_2 and NO_x (approximately 19% and 16% reductions, respectively) in the eastern and midwestern U.S. from 1975 to 1987 have produced significant declines in annual precipitation concentration of $SO_4^=$ ($P < 0.01$), and H^+ ($P < 0.01$) at Hubbard Brook, N.H. There are also strong relationships ($P < 0.01$) between respective emissions and deposition of $SO_4^=$, and H^+. Hubbard Brook is the site located furthest from the major source regions for emissions in this study and also has the longest period of record.

The two midwestern MAP3S precipitation chemistry sites, Illinois and Ohio, located nearest the major U.S. emission sources, show a significant direct relationship ($P < 0.05$) between lowered emissions of SO_2 and reduced $SO_4^=$ concentration, from the late seventies to 1987. Ohio and Illinois also show a significant direct relationship between emissions of SO_2 plus NO_x, and H^+ concentration ($P < 0.05$ and $P < 0.10$, respectively).

Two of the eastern continental MAP3S sites, from 1977 to 1987 show significant relationships. Whiteface Mt. has a significant relationship for $SO_4^=$ concentration regressed on SO_2 ($P < 0.10$), and Ithaca has a significant relationship for H^+ concentration regressed on combined emissions of SO_2 and NO_x ($P < 0.01$). Virginia and Penn State do not show statistically significant ($P < 0.10$) relationships, between emissions of SO_2 and/or NO_x and concentrations of $SO_4^=$, NO_3^- and H^+. Possible explanations for the lack of strong relationships at some of these sites intermediate in distance from the major source regions are:

1) record too short considering inherent variability in precipitation chemistry,
2) inappropriate choice of source regions,
3) incomplete mixing and interaction with appropriate oxidizing agents to produce transformation products,
4) substantial meteorological and/or climatological variability,
5) for Ithaca and Penn State, high levels of acidity may limit SO_2 uptake and thus produce non-linear emission-concentration relationships.

For the northeast, mid-Atlantic and lower midwest as a whole, changing SO_2 emission levels are translated into changing $SO_4^=$ concentratrions with an efficiency of 74% ± 15% (s. e.). A similar analysis for the relationship between SO_2 plus NO_x emissions and H^+ concentration indicates a 100% ± 15% (s. e.) conversion efficiency. An 18% decline in emissions has been accompanied by an 18% decline in H^+ concentration throughout the study region.

Even though Hubbard Brook, N.H. had a statistically significant decline in acid species from 1975 to 1987, large additional reductions in deposition, greater than 50% of present values, will be necessary to protect acid-sensitive ecosystems.

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TABLE 1 Average annual precipitation and volume-weighted chemistry for the sites used in this study. Numbers in parentheses are the standard deviations for the arithmetic means of the annual values.

TABLE 2 Percent decline in annual emission levels ((highest level minus lowest level)/highest level) for appropriate source regions for each site, and percent decline in annual volume-weighted concentrations of $SO_4^=$, NO_3^- and H^+ derived from linear regression equation. n indicates the number of years of record, all records are consecutive years ending in 1987 for (a) and (b). (c) has n-1 years of record (except for Hubbard Brook). NS indicates that the slope of the regression line was not significant at $p < 0.10$.

TABLE 3 Regression slopes for (a) $SO_4^=$ concentration (expressed as % of mean) regressed on SO_2 emissions (expressed as % of mean), standard errors, level of significance (P<), and R^2 for four different cases. These cases are: 1) all sites and all years (see also Fig. 4), 2) excluding Penn State, 3) excluding the year 1979, and 4) excluding both Penn State and the year 1979. n equals the number of data points used in each regression. (b) is a similar table of regression slopes for H^+ concentration (expressed as % of mean) regressed on the moles of emissions of NO_x plus twice the moles of SO_2 (expressed as % of mean). The slope values (X 100) are a measure of the efficiency with which changing emission levels have affected changes in concentration of $SO_4^=$ (a), and H^+ (b).

Table 1.

AVERAGE ANNUAL PRECIPITATION (cm) AND CHEMISTRY (ueq/l)

	Hubbard Brook, N.H. n=12	Whiteface Mt., N.Y. n=10	Ithaca N.Y. n=10	Penn State Pa. n=10	Virginia n=10	Illinois n=10	Oxford Oh. n=9
PRECIP	143.23 (19.1)	100.1 (15.7)	102.9 (14.5)	97.8 (16.6)	106.9 (22.2)	87.4 (12.8)	93.0 (12.6)
pH	4.24	4.34	4.18	4.15	4.27	4.27	4.24
$SO_4^=$	43.3 (5.8)	43.0 (5.8)	57.9 (6.7)	65.3 (6.0)	50.7 (8.6)	63.1 (5.4)	61.4 (8.5)
NO_3^-	23.5 (3.0)	21.1 (2.7)	30.3 (3.1)	31.2 (3.4)	24.1 (5.5)	26.8 (3.1)	24.9 (2.8)
Cl^-	6.2 (2.2)	4.7 (1.5)	6.0 (1.7)	6.9 (1.5)	8.9 (2.7)	6.7 (2.2)	6.2 (1.2)
H^+	57.4 (11.0)	45.9 (7.6)	66.1 (6.4)	71.5 (7.0)	53.8 (9.4)	54.2 (6.3)	57.5 (5.5)
NH_4^+	8.6 (1.2)	13.5 (2.2)	16.4 (1.9)	17.6 (4.1)	14.0 (3.2)	21.6 (2.7)	18.8 (3.0)
Na^+	3.5 (1.1)	1.8 (0.5)	2.0 (0.6)	3.2 (1.6)	5.4 (3.0)	3.0 (1.0)	3.0 (1.0)
K^+	1.0 (0.3)	1.4 (0.7)	1.1 (0.9)	1.4 (0.7)	1.4 (0.8)	1.4 (1.4)	1.5 (1.2)
Ca^{++}	3.6 (0.8)	4.7 (1.4)	5.6 (0.9)	6.8 (2.4)	3.7 (1.3)	12.8 (3.4)	8.3 (2.9)
Mg^{++}	1.8 (0.4)	1.4 (0.5)	1.5 (0.2)	1.8 (0.6)	1.8 (0.7)	2.7 (0.7)	2.1 (0.6)
$\frac{\text{anion sum}}{\text{cation sum}}$	0.96	1.00	1.02	1.01	1.04	1.01	1.01

Table 2.

	(a)				(b)				(c)			
	% SO2 decline	% [SO4] decline (from regression)	P<	R^2	%NOx decline	%[NO3] decline (from regression)	P<	R^2	%NOx + SO2 decline	% [H^+] decline (from regression)	P<	R^2
Illinois (n=10)	16	16	0.05	0.58	17	1	NS	0.001	16	17	0.10	0.40
Ohio (n=9)	15	26	0.05	0.51	15	14	NS	0.21	15	17	0.05	0.51
Whiteface (n=11)	23	18	0.10	0.28	18	11	NS	0.13	22	21	NS	0.27
Ithaca (n=11)	23	11	NS	0.16	18	-4	NS	0.02	22	19	0.01	0.62
Penn State (n=11)	28	2	NS	0.01	16	-10	NS	0.16	25	5	NS	0.03
Virginia (n=11)	28	13	NS	0.09	16	-4	NS	0.003	25	22	NS	0.26
Hubbard Brook (n=13)	23	28	0.01	0.69	18	14	NS	0.20	22	34	0.01	0.76

Table 2.

Table 3.

(a)

$SO_4^=$ Concentraion Regressed on SO_2 Emissions (expressed as %s of means)

	n	Slope	Standard Error	P<	R^2
All sites and all years	76	0.74	0.15	0.01	0.25
Excluding Penn State	65	0.92	0.17	0.01	0.32
All sites excluding 1979	69	0.83	0.15	0.01	0.30
Excluding Penn State and 1979	59	1.02	0.17	0.01	0.37

(b)

H^+ Concentration Regressed on $SO_2 + NO_x$ Emissions (expressed as %s of means)

	n	Slope	Standard Error	P<	R2
All sites and all years	70	1.00	0.15	0.01	0.39
Excluding Penn State	60	1.17	0.16	0.01	0.46
All sites excluding 1979	63	1.03	0.16	0.01	0.39
Excluding Penn State and 1979	54	1.20	0.18	0.01	0.46

FIG. 1 Annual emissions of sulfur dioxide and nitrogen oxides (assumed to be NO_2) for the eastern and midwestern United States from 1975 to 1987. The emissions area includes all states shown in Fig. 2(a). Maximum emission changes during the time period are 19% for SO_2 and 16% for NO_x.

FIG. 2 Locations of precipitation chemistry stations ( ), and source regions used in this study. The area with the dark outline in (a) represents the source region for the stations in Illinois and Oxford. The source region for Penn State and Virginia stations includes the area, 3, outlined in (b). Ithaca and Whiteface source regions include areas 2 and 3 in (b) and Hubbard Brook includes 1, 2 and 3. All precipitation chemistry sites, except Hubbard Brook, are part of the MAP3S Network. MAP3S sites not included in this study are the coastal sites at Brookhaven, N. Y. and Lewes, Del.; and the site at Oak Ridge, Tenn. which has only 7 years of record.

FIG. 3 Linear regression of annual volume-weighted ion concentrations (sulfate (A), nitrate (B), and hydrogen ion (C)) in precipitation on annual emissions for Hubbard Brook, N.H. (1975 to 1987), Ithaca, N.Y. (1977 to 1987), and Oxford, Ohio (1979 to 1987). The level of significance for graphs with slope lines (p at least < 0.10) is indicated.

FIG. 4 Linear regressions of annual volume-weighted $SO_4^=$ (a), and H^+ (b), concentration in precipitation for all sites (expressed as the % of each site mean *) on annual emissions for each appropriate source region (expressed as the % of the appropriate source region mean for each site**). The slope of the regression line (X 100) is a conservative estimate (see Table 3) of the efficiency of how changing emission levels affect changing levels of $SO_4^=$ and H^+ concentration over the entire study region. The slope is 0.74 ±0.15 (std. err.) for (a) and 1.00 ± 0.15 (std. err.) for (b). Circled data points represent the year 1979, when unusually low $SO_4^=$ values were found at most sites. The curved lines are simultaneous 95% confidence bands for the regression line .

* y = concentration expressed as a % of each site long-term mean for sulfate or hydrogen ion concentration

$$= \frac{y_i}{(\sum_{i=1}^{n} y_i)/n} \times 100$$

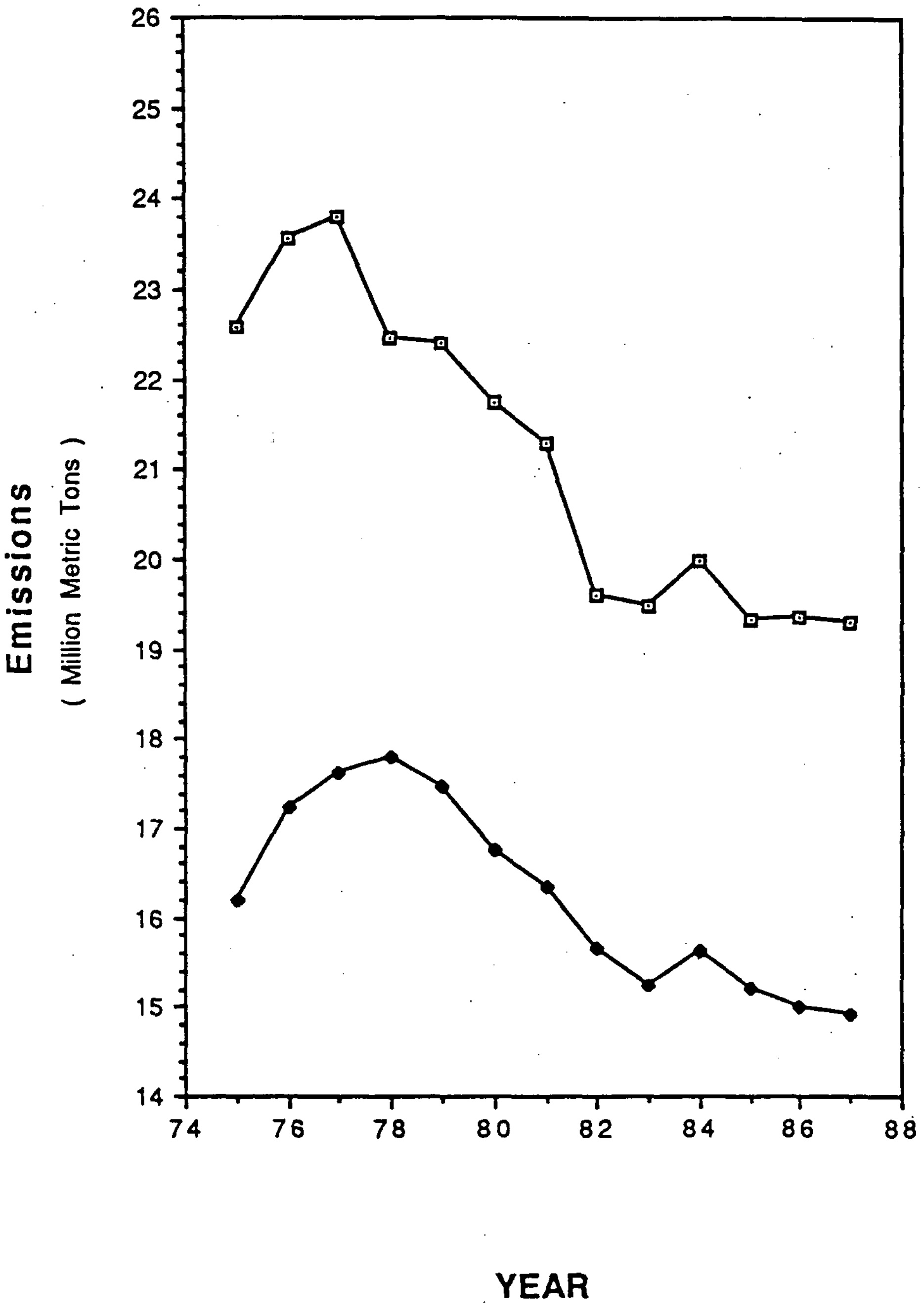
where y = annual mean volume-weighted sulfate or H^+ concentration for year i, and n = number of years of record.

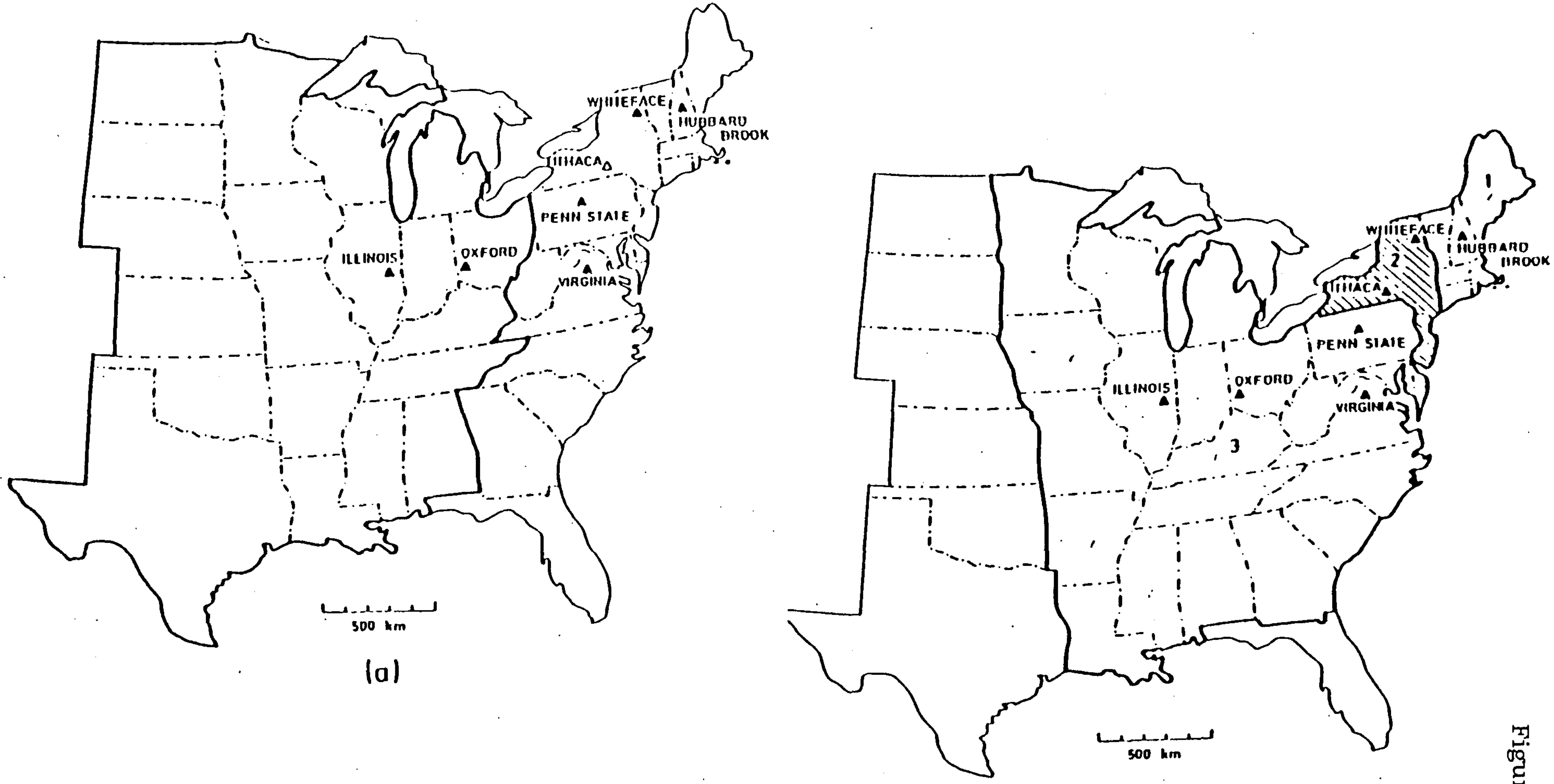
** x = emissions expressed as a % of each site long-term mean for SO_2 for (a) and NOx plus twice SO_2 in moles of emissions for (b)

$$= \frac{x_i}{(\sum_{i=1}^{n} x)/n} \times 100$$

where x = annual emission from appropriate source region for year i, and n = number of years of record.

Figure 1.


Emissions
(Million Metric Tons)
26
25
24
23
22
21
20
19
18
17
16
15
14
74
76
78
80
82
84
86
88
YEAR


WHITEFACE
HUBBARD BROOK
ITHACA
PENN STATE
ILLINOIS
OXFORD
VIRGINIA
500 km
WHITEFACE
HUBBARD BROOK
1
2
ITHACA
PENN STATE
ILLINOIS
OXFORD
3
VIRGINIA
500 km

(a)

(b)

Figure 2.

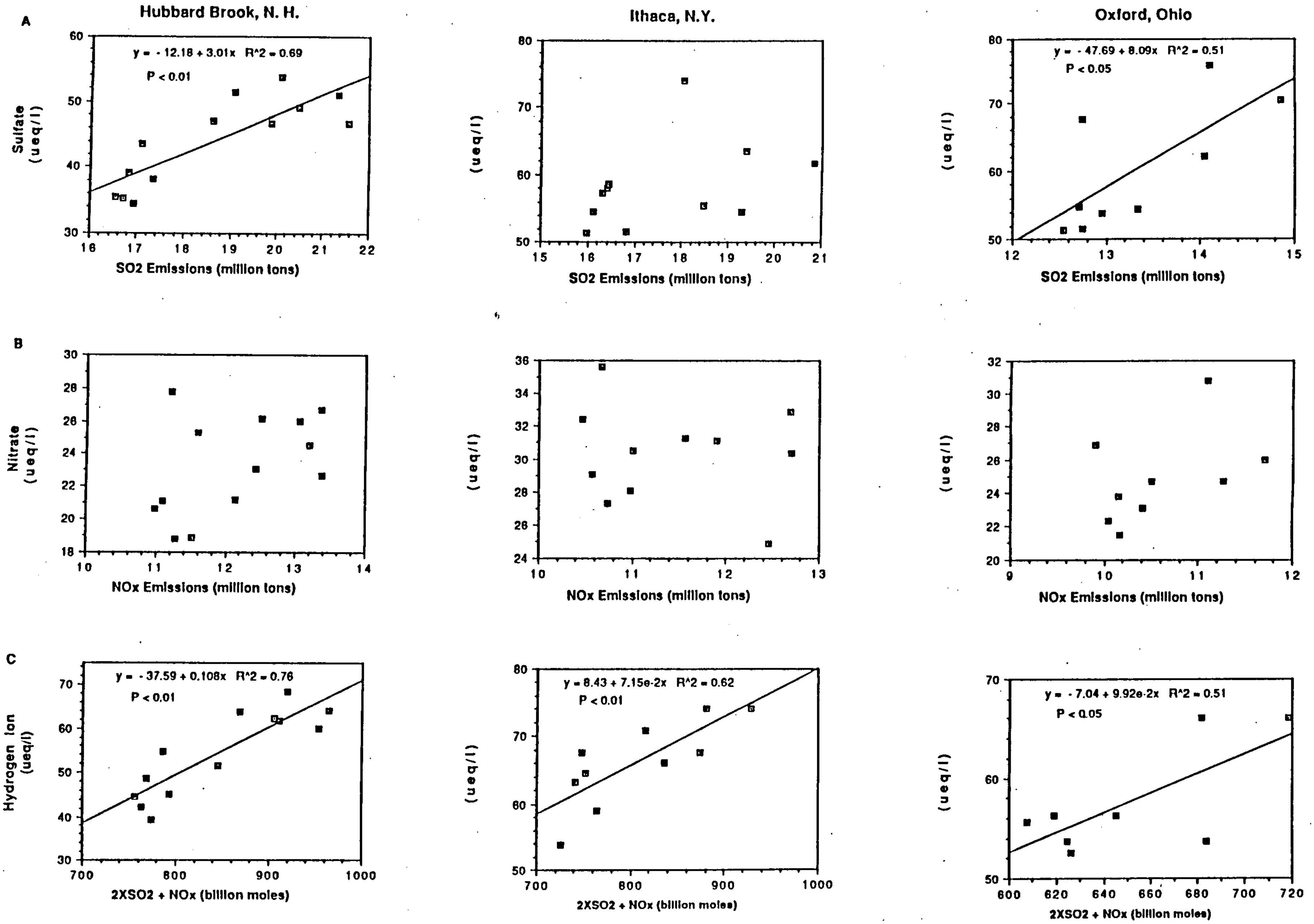
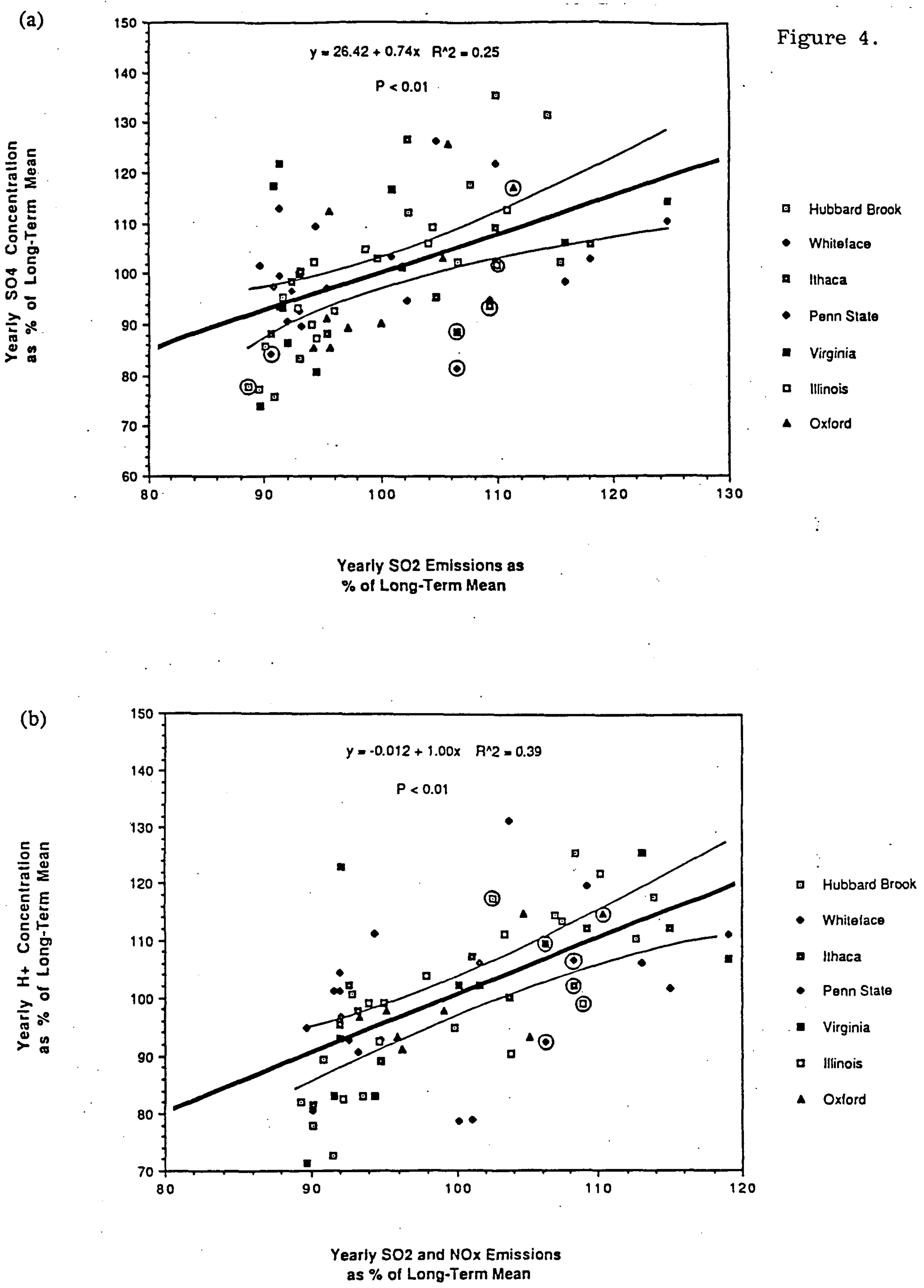

A
Hubbard Brook, N. H.
Ithaca, N.Y.
Oxford, Ohio
y = - 12.18 + 3.01x R^2 = 0.69
P < 0.01
Sulfate (ueq/l)
SO2 Emissions (million tons)
(ueq/l)
SO2 Emissions (million tons)
y = - 47.69 + 8.09x R^2 = 0.51
P < 0.05
(ueq/l)
SO2 Emissions (million tons)
B
Nitrate (ueq/l)
NOx Emissions (million tons)
(ueq/l)
NOx Emissions (million tons)
(ueq/l)
NOx Emissions (million tons)
C
y = - 37.59 + 0.108x R^2 = 0.76
P < 0.01
Hydrogen Ion (ueq/l)
2XSO2 + NOx (billion moles)
y = 8.43 + 7.15e-2x R^2 = 0.62
P < 0.01
(ueq/l)
2XSO2 + NOx (billion moles)
y = - 7.04 + 9.92e-2x R^2 = 0.51
P < 0.05
(ueq/l)
2XSO2 + NOx (billion moles)

Figure 3.

Figure 4.


(a)
y = 26.42 + 0.74x R^2 = 0.25
P < 0.01
Yearly SO4 Concentration as % of Long-Term Mean
Yearly SO2 Emissions as % of Long-Term Mean
150
140
130
120
110
100
90
80
70
60
80
90
100
110
120
130
Hubbard Brook
Whiteface
Ithaca
Penn State
Virginia
Illinois
Oxford
(b)
y = -0.012 + 1.00x R^2 = 0.39
P < 0.01
Yearly H+ Concentration as % of Long-Term Mean
Yearly SO2 and NOx Emissions as % of Long-Term Mean
150
140
130
120
110
100
90
80
70
80
90
100
110
120
Hubbard Brook
Whiteface
Ithaca
Penn State
Virginia
Illinois
Oxford

APPENDIX A

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