

THE RELATIONSHIP BETWEEN UPWIND SO₂ EMISSIONS AND SO₄²⁻ CONCENTRATIONS IN PRECIPITATION AT SIX SITES IN THE EASTERN U.S.A.

JEFFREY R. BROOK

Atmospheric Environment Service Downsview, Ontario M3H 5T4, Canada

and

PERRY J. SAMSON and SANFORD SILLMAN

Department of Atmospheric, Oceanic and Space Sciences, The University of Michigan, Ann Arbor, MI 48109-2143, U.S.A.

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Abstract—A method for estimating the upwind SO₂ emissions associated with individual wet SO₄²⁻ deposition events has been developed. The relationship between these estimates and wet SO₄²⁻ concentrations was examined at six Utility Acid Precipitation Study Program Sites (UAPSP) for the 1979–1986 period. Using Spearman correlation coefficients and the Bonferroni experimentwise criterion for statistical significance it was found that upwind emissions and concentrations were significantly related ($p < 0.05$). However, correlations were sensitive to site location, time upwind of the emissions and season, and ranged from -0.03 to 0.50. Correlations were weaker at sites located west of the high emission region in the midwestern U.S.A. and stronger at sites further away and to the east of this region. There was a decrease in the strength of the correlations from the warm season to the cold season. It was also found that differences in meteorology between events obscured the relationship between emissions and concentrations. The effects of variations in ambient temperature and precipitation amount on wet SO₄²⁻ concentrations were taken into account by calculating partial correlation coefficients. A higher percentage of the resulting correlations were found to be statistically significant and the differences between sites decreased. This suggested that meteorological variability had a confounding influence on the detection of a link between concentrations and emissions. This influence should be considered when studying source–receptor relationships.

Key word index: Acid deposition, wet sulfate deposition, precipitation chemistry, source–receptor relationships, trajectories, upwind emissions, long-range transport, air pollution meteorology.

INTRODUCTION

It is generally accepted that sulfate (SO₄²⁻) in precipitation in industrialized regions is associated with anthropogenic emissions of SO₂ rather than natural sources (e.g. Galloway and Rodhe, 1991). Consequently higher concentrations of SO₄²⁻ are expected in locations downwind from major anthropogenic sources. Recently, Hilst and Chapman (1990) showed that collectively, across sites in eastern North America, the monthly volume-weighted mean concentrations of SO₄²⁻ in precipitation and the SO₂ emissions within a 400–600 km radius were correlated. The magnitude of the correlation varied with season and geographic region with the strongest correlation existing in the summer months across sites situated in the midwest and mid-Atlantic states. At individual monitoring sites in North America a significant correlation between upwind SO₂ emissions and SO₄²⁻ concentrations (wet and dry) has been difficult to detect (Samson, 1980; Moody, 1986; Samson and Moody, 1986).

While intuitively such a relationship should exist, it has been obscured by a large amount of natural variability in precipitation chemistry from event to event. Trajectories and other meteorological data have therefore been necessary to study the link between ambient or precipitation concentrations and upwind emissions. Several such analyses have linked large levels of SO₄²⁻ in precipitation or air to areas with large SO₂ emissions (e.g. Samson, 1978; Raynor and Hayes, 1982; Henderson and Weingartner, 1982; Wilson *et al.*, 1982; Summers, 1987; Moody and Galloway, 1988; Zeng and Hopke, 1989; Moody and Samson, 1989). However, the results were generally of a circumstantial nature, i.e. when SO₄²⁻ levels were large, the precipitating air mass passed over areas with large emissions such as the midwestern U.S.A. Some approaches based on statistical receptor modeling have indicated that SO₄²⁻ in air is also influenced by areas with large SO₂ emissions (e.g. Thurston and Spengler, 1985; Hooper and Peters, 1989; Wolff, 1989; Keeler *et al.*, 1990).

This paper presents the results of an examination of the correlation between upwind SO₂ emissions and event measurements of wet concentrations of SO₄²⁻ for the 1979–1986 period from six Utility Acid Precipitation Study Program (UAPSP) sites. In order to calculate correlation coefficients a method for quantifying the upwind emissions associated with individual wet deposition events was developed. This method, which utilizes mixed-layer back-trajectories calculated with the NOAA-ARL model (Heffter, 1980), is described in this paper. The results discussed here were derived entirely from precipitation chemistry, emissions and meteorological data through direct statistical comparisons of upwind emission estimates and wet SO₄²⁻ concentrations. Correlations were calculated for each site using all valid wet deposition events during the 8-year period and separately, for events collected from the beginning of April to end of September (warm season) and for those collected during the other 6 months (cold season). Meteorological data were used to calculate trajectories and to treat the potential confounding influence of ambient temperature and precipitation amount, but no attempt was made to model the processes between sources and receptors. The object of this study was to test for a relationship between concentrations and emissions within the data itself.

DATA AND METHODS

Precipitation chemistry

To compare the relationship between upwind SO₂ emissions and concentrations of SO₄²⁻ in precipitation, samples of precipitation chemistry with fine temporal resolution were necessary. The data compiled during the Sulfate Regional Experiment/Utility Acid Precipitation Study Program (SURE/UAPSP) were selected because of their event or daily protocol (i.e. wet-only collection buckets were usually removed each day and actual precipitation start and stop times were recorded). This data set (referred to as UAPSP) is of very high quality due to rigorous quality assurance programs at the collection sites and laboratory and efforts to assure consistency among sites and years (Mueller *et al.*, 1988). Six sites, where collection commenced in 1979, were selected for this study. Their locations are displayed in Fig. 1 and specific information on each site is provided in Table 1. Precipitation chemistry measurements were taken from 1979 to 1987 with

the exception of the first three-quarters of 1981 when no data were collected at Tunkhannock, PA. The sulfate data from July to December 1987 were suspect at all UAPSP sites (Cleary and Topol, 1990), and were not used. Thus, the work presented here was based on the 8-year period from the beginning of 1979 to 1986.

The UAPSP measurements of sulfate concentration ($\mu\text{mol } \ell^{-1}$) were the main focus in this study. However, the concentrations of nitrate, chloride, ammonium, calcium, sodium, magnesium, potassium and hydronium ion (from the lab pH) were utilized for data validation purposes. A few meteorological parameters were reported with the UAPSP data. Of greatest importance was precipitation amount (cm) as recorded by a separate weighing bucket rain gauge (Topol and Schwall, 1987), because it had an influence on pollutant concentration and deposition. The UAPSP data also include precipitation type (rain, snow etc.) and occurrence of thunder. Precipitation event start and stop times were critical in matching the precipitation chemistry with the upwind SO₂ emissions and other sources of meteorological information. Along with concentrations, meteorological parameters and times, the UAPSP data contained various quality control flags signifying measurement error or malfunction and the presence or absence of contamination, particles and leakage. All the flagged data were examined for errors and outliers following the method of Endlich *et al.* (1986). These quality control procedures eliminated between 8 and 20% of the events depending upon location. Rockport, IN, had the highest percentage of valid data (92%) while at both Fort Wayne, IN, and Raleigh, NC, 20% of events were lost.

Meteorological data

Two additional sources of meteorological data were selected to complement the information provided by the UAPSP. Estimates of the mean ambient surface temperature in the vicinity of the receptors during precipitation events were calculated from the National Meteorological Center (NMC) gridded global analyses, obtained from the National Center for Atmospheric Research. These data were derived from a large variety of sources and were subject to extensive quality control procedures to insure accuracy and consistency (Trenberth and Olson, 1988). Measurements of wind speed, wind direction, temperature, dew point and geopotential height from the surface to 500 mb taken at the North American upper air observing sites were also utilized. These data, processed to facilitate back-trajectory calculation, were obtained from the National Climate Center. Trajectories were used to estimate upwind SO₂ emissions. Precipitation amounts (from UAPSP) and temperatures were examined because of the potential for the relationship between these variables and SO₄²⁻ concentrations in precipitation to influence the analysis of the source–receptor relationships.

Estimation of upwind SO₂ emissions

Trajectories were used in conjunction with Quantitative Transport Bias Analysis (QTBA; Keeler and Samson, 1989)

Table 1. Names, locations and length of record for the UAPSP precipitation chemistry sites used in this study

| UAPSP number | Site name and abbreviation | Dates | Latitude | Longitude |
|--------------|----------------------------|-------------|----------|-----------|
| 1 | Montague, MA (TFS) | 1/79–7/80 | 42°32' | 72°32' |
| | Turner Falls, MA | 8/80–7/87 | 42°36' | 72°33' |
| 2 | Scranton, PA (TUN) | 1/79–12/80 | 41°34' | 76°00' |
| | Tunkhannock, PA | 10/81–12/87 | 41°34' | 76°00' |
| 4 | Zanesville, OH (ZAN) | 1/79–12/87 | 39°59' | 82°01' |
| 5 | Rockport, IN (ROC) | 1/79–12/87 | 37°53' | 87°08' |
| 7 | Fort Wayne, IN (FWA) | 1/79–12/87 | 41°03' | 85°19' |
| 8 | Raleigh, NC (RAL) | 1/79–12/87 | 35°44' | 78°41' |

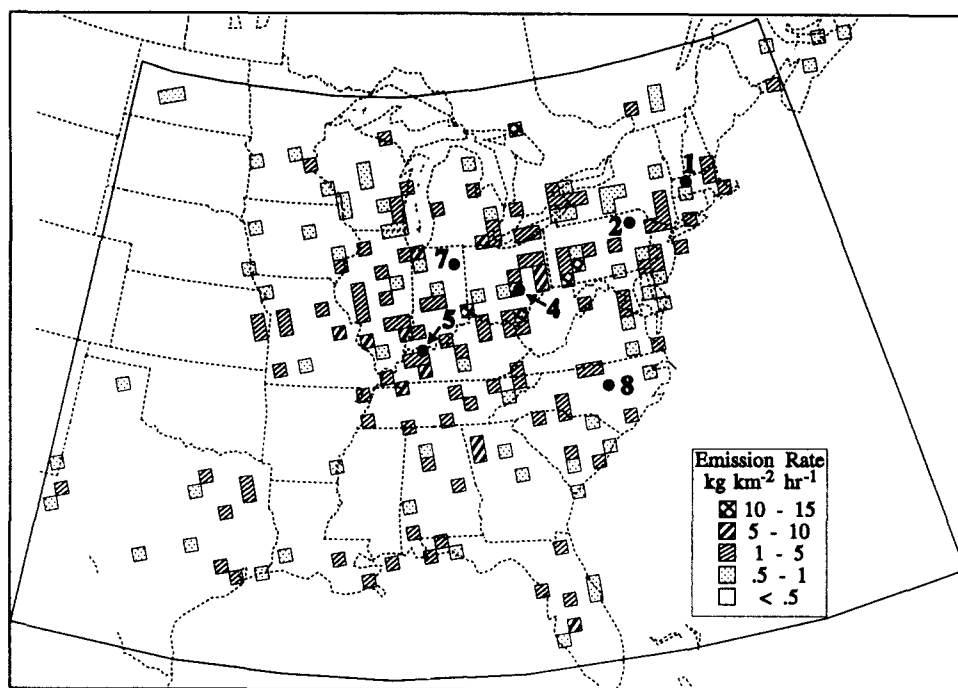


Fig. 1. The 1980 NAPAP SO₂ emissions used to estimate event-specific upwind SO₂ emissions. The domain of the model for calculating upwind emissions is shown as a solid line. Also shown are the locations of the six UAPSP sites used in this study (as indicated by the UAPSP site numbers in Table 1).

to determine the most probable history of the precipitating air masses. They were calculated using the Atmospheric Transport and Dispersion Model developed at the Air Resources Laboratory (ARL/ATAD) (Heffter, 1980). The model calculated the mean upwind track of the air within the "mixed-layer" of the atmosphere (a layer of variable height extending from the surface to approximately 1500 m above the surface in the summer and 800 m above the surface in the winter) using vertical profile data for wind, temperature and humidity obtained from the North American upper air network. These data had a spatial resolution of approximately 500 km and a temporal resolution of 12 h. The trajectory model interpolated the upper air data linearly in time and in space using a r^{-2} weighting where r was the distance between the trajectory and the upper air stations within 400 km of the receptor or previous trajectory end point. The interpolated information was used to determine the mean backward motion of the air within the mixed-layer. The model used this information to determine the position (latitude and longitude) of the air parcel at 3-h time intervals to a maximum of 72 h backwards in time (24 3-h segments or end points). Four trajectories corresponding to 00Z, 06Z, 12Z and 18Z arrival times were calculated for each day.

As with all methods for calculating trajectories, those employed in this study contain uncertainties due to the fact that the data were limited (Kuo *et al.*, 1985; Kahl and Samson, 1986; Draxler, 1987) and because it was not possible to model in detail all of the complex motions within the atmosphere. Previous studies have compared ARL-ATAD trajectories to data from the Cross-Appalachian Tracer Experiment (CAPTEX). The results showed lateral displacement uncertainties are on the order of 200 km at 24 h upwind and 400 km at 72 h upwind (Kahl and Samson, 1986). Uncertainties of this magnitude were shown not to be significantly different than those resulting from other methods of calculating trajectories (Draxler, 1987; Haagenson *et al.*, 1987).

The CAPTEX study focused on non-precipitating situ-

ations. With all methods for calculating trajectories, however, identification of the predominant SO₂ source region is more uncertain during precipitation events. The wind flow is generally more complex, especially when associated with cyclonic systems. Given that this study examines precipitation chemistry, it is important to consider the effect of using mixed-layer trajectories versus other types of trajectories (e.g. constant height or pressure surface trajectories or isentropic trajectories). For a limited number of cases, Haagenson *et al.* (1990) examined the influence of fronts on the accuracy of mixed-layer trajectories using the Across North America Tracer Experiment (ANATEX) data. They showed that when fronts were present along the transport path the trajectory uncertainty increased by a relatively small amount (16 km day⁻¹). With convective precipitation, mixed-layer trajectories are expected to be representative since these storms typically ingest air transported within the boundary layer. However, with developed cyclonic systems or severe storms vertical wind shear can be large (up to 180°). Mixed-layer trajectories and most other types of trajectories may not correctly identify the path of the air mass supplying the bulk of the pollutants to the precipitation. For example, precipitation falling in advance of a warm front is often generated in the warm air originating to the south, while at the surface, in the precipitation, the boundary-layer wind flow is often easterly. Clearly, a trajectory calculated from winds above the surface would be more appropriate. However, selecting the proper transport level is difficult and this level changes from one weather system to the next. Thus, the most appropriate type of trajectory is likely to vary from event to event and from site to site. The spatial and temporal resolution of the upper air stations do not provide enough detail (Kuo *et al.*, 1985) to justify attempting to resolve this issue in this paper. Therefore, it was assumed that mixed-layer trajectories would provide a reasonable approximation of the transport during all precipitation events and that they represented the most probable path of air parcels advected within mixed-layer. We also assumed that in most cases the

effects of wind shear, dispersion and trajectory uncertainty would be accounted for in the probability-based calculation of upwind emissions, described below.

The trajectories were used in conjunction with QTBA to calculate the transport potential or upwind probability field which identified which SO₂ emission regions were most and least likely to have contributed to the SO₄²⁻ observed in precipitation for a particular event. This method was developed by Small (1982) and was refined by Keeler and Samson (1989) to study the sources of ambient trace elements in eastern North America. It was also considered by Hidy (1984) as a possible method to test source-receptor relationships and applied in the NAPAP Aggregation Study (Samson *et al.*, 1990) for that purpose.

The transport potential for a given wet deposition event includes the mean transport computed using the trajectory model plus the horizontal spread imposed by atmospheric dispersion and uncertainty in transport estimates (Samson, 1980). The probability, $A_i(X, t)$, of a reactive, depositing tracer arriving at a point X at a time t , can be expressed as

$$A_i(X, t) = \int_{t-\tau}^t \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} T(X, t|X', t') dX' dt' \quad (1)$$

where $T(X, t|X', t')$, the potential mass transfer function in two dimensions, is defined by

$$T(X, t|X', t') = Q(X, t|X', t') R(t|t') D(X', t') \Lambda(X', t') \quad (2)$$

$Q(X, t|X', t')$ is the transition probability density function of an air parcel located at X' at time t' arriving at a receptor X at time t , $R(t|t')$ is the probability of the tracer not being reacted to another species from time t' to time t , $D(X', t')$ is the probability that the tracer was not dry deposited at (X', t') and $\Lambda(X', t')$ is the probability that the tracer was not wet deposited at (X', t') . The integration is conducted over time period τ .

The transition probability density function, $Q(X, t|X', t')$, is important in understanding source-receptor relationships since it describes the motion of the air transporting the pollutants. The probability functions treating the effects of deposition and chemistry between source and receptor (last three terms on the right side of equation 2) were set equal to one. These effects were neglected because our objective was to test for evidence of a relationship between upwind emissions and concentrations within the data itself, without imposing assumptions on the results. While developing detailed, event-specific functions for $R(t|t')$, $D(X', t')$ and $\Lambda(X', t')$ could improve the results, that was not the object of this study. As a consequence of neglecting these effects the upwind emission estimates were expected to represent an upper bound on the amount of SO₂ emissions influencing the SO₄²⁻ deposition for each event. However, since the upwind emissions were treated as relative statistical parameters and because the time upwind of emissions was fixed for each correlation calculation, the objectives of this study were not sacrificed.

The transition probability density function was approximated from the upwind trajectories. Sources along each trajectory were assumed to have the highest potential for contributing to the pollutant concentrations at the receptors. Away from the trajectory axis the spatial distribution of the transition probabilities was assumed to be normally distributed (Bolin and Persson, 1975) with a standard deviation that increased linearly with time upwind (Samson, 1980). This assumption was expected to account for dispersion, which generally depends upon the degree of vertical mixing, coupled with the magnitude of the wind velocity shear. For all events, transition probabilities were based on a sum of a number of individual trajectories that represented the beginning, middle and end of the event (a minimum of

two trajectories were used for each event). Calculation of transition probabilities is described in greater detail in the Appendix.

Transition probabilities were determined over a region extending from northwestern North Dakota to a point southeast of Bermuda. This region was divided into a 1° longitude by 2°/3 latitude grid (44 × 33) and transition probabilities were calculated for each grid point (P_i , $i=1,1452$). Probability fields corresponding to each wet deposition event and for different times upwind were determined and combined with the NAPAP 1980 SO₂ emission field for a typical summer weekday (EPA, 1986). The domain of the probability fields and the spatial variability of the SO₂ emissions within this region are displayed in Fig. 1. Upwind emissions for a given deposition event were calculated by summing the products of the total emissions, E_i (g h⁻¹ km⁻²), and probability, P_i , within grid box i , over the entire field:

$$\text{Upwind emissions}_t = \sum_{i=1}^{1452} P_i \times E_i \times A_i \times n \times \Delta t \quad (3)$$

where A_i was the area (km²) of each grid box, Δt was 3 h, corresponding to the time step of the trajectories and, n was the number of 3-h trajectory segments within the upwind region of interest.

Emissions were calculated for a variety of time periods so that the importance of source regions at varying times upwind could be assessed. Separate probability fields were determined for 0–12, 12–24, 24–36, 36–48, 48–60 and 60–72 upwind time periods ($n=4$), and for 0–48, 0–60, 0–72 and 12–48 (where $n=16, 20, 24$ and 12, respectively). Twenty-four hour puffs were also determined for selected events. The calculations were carried out by isolating the segments of each trajectory that fell within the different time ranges. Refer to the Appendix for more detail.

The individual time periods were visualized as puffs of probability upwind from the receptor. Figure 2 demonstrates what the 0–24, 24–48 and 48–72 h puffs would look like for an hypothetical event. Seventy-two hour back-trajectories are shown as heavy lines with open circles marking the end of 12-h segments. As indicated by the number of trajectories, this event would have had a duration of between 18 and 24 h. As a result, the potential area contributing to the upwind emissions is relatively large and uncertain, especially at greater times upwind. Within each of the 24 h puffs (areas A, B and C) the probabilities sum to one. The amount emitted into the air mass during the 72 h prior to precipitation would be estimated from the probability field defined by the entire shaded area in Fig. 2. The sum of the probabilities in this large area would also be constrained to a value of one.

The probability fields for the 0–24, 24–48 and 48–72 h upwind puffs for a 7-h event, that occurred on 13, March 1982, at Turners Falls, are shown in Fig. 3. The trajectories used to estimate the probability fields are also shown. The concentration of the SO₄²⁻ in the 0.51 cm of rain that fell was 5.4 mg l⁻¹. In this example, SO₂ emissions from many of the states in eastern North America could have had an influence on the composition of the precipitation at Turners Falls. However, the highest probabilities were along a corridor of about three to four states in width extending to the southwest. This region, which included portions of the Ohio River Valley, had the greatest potential for input into the upwind emissions burden for the event depicted. Three different estimates of upwind SO₂ emissions were determined from the probability fields shown. From 0 to 24 h upwind 64 × 10³ kg could have been input into the air mass influencing Turners Falls, between 24 and 48 h up to 748 × 10³ kg were input and 48–72 h prior to arrival at Turners Falls, 512 × 10³ kg of SO₂ could have been emitted into the air mass. These emissions had the potential to influence the composition of the precipitation collected at Turners Falls.

Changes in the emissions over time were not used because changes in wind flow had a much larger effect on the

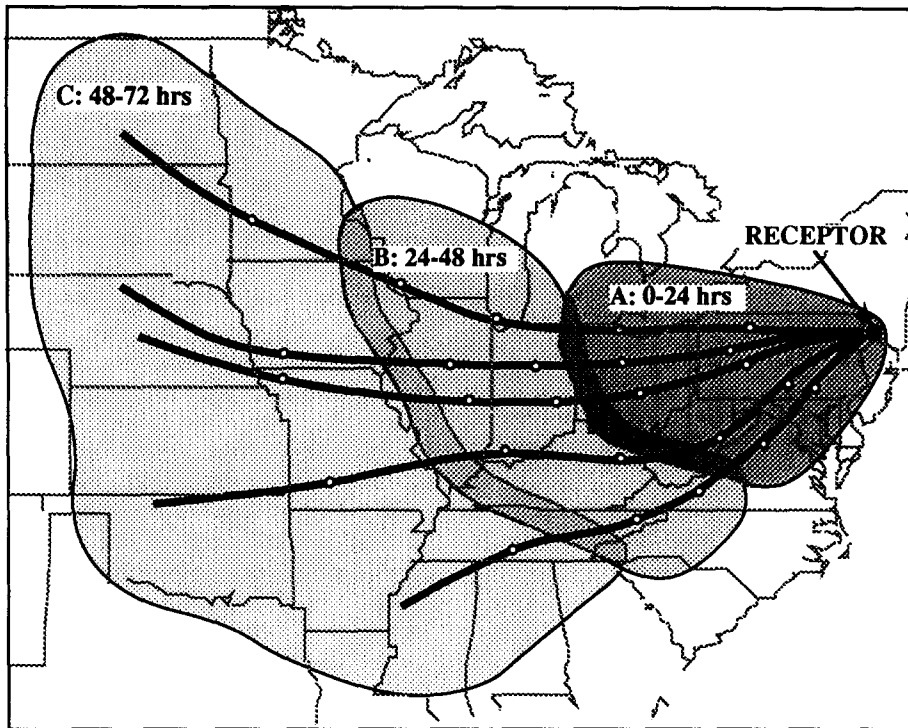


Fig. 2. Schematic of the puffs of probability that can be combined with an emissions inventory to estimate event-specific emissions for different upwind time periods. The air mass could have passed anywhere over region B 24–48 h prior of passing over the receptor during the wet deposition event.

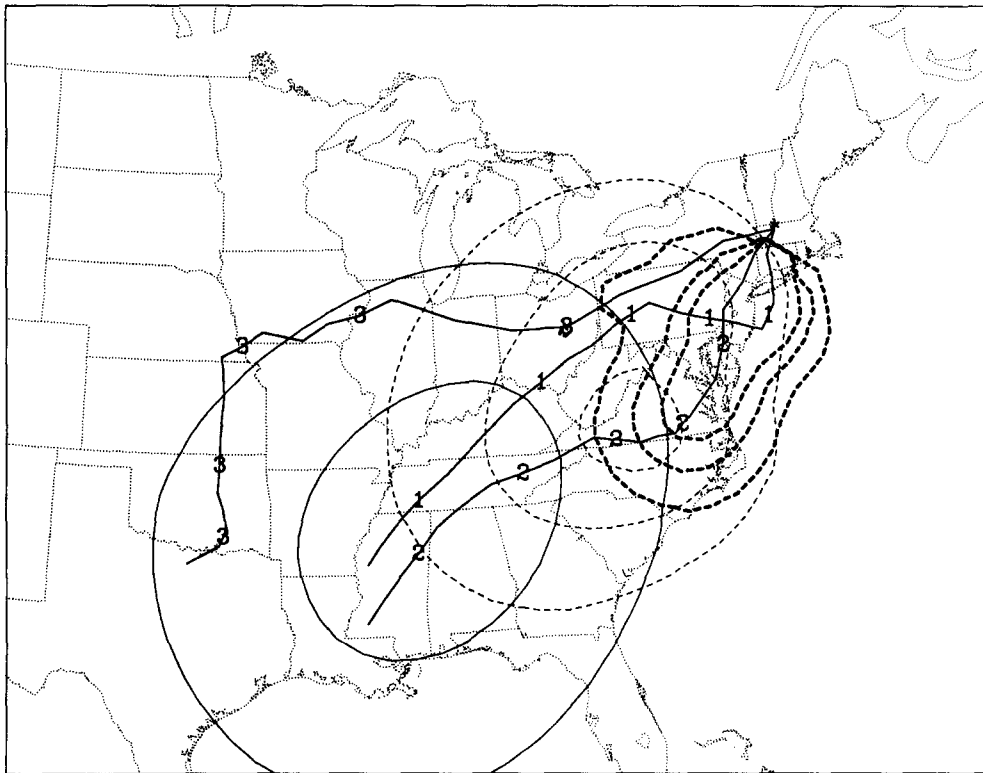


Fig. 3. The 0–24, 24–48 and 48–72 h upwind probability fields and trajectories associated with the wet deposition event reported on 13 March 1982 at Tuners Falls, MA. Twelve-hour segments of the trajectories are labeled with numbers indicating whether the trajectory arrived 1st, 2nd, 3rd, 4th, etc., with respect to the time period covered by the event. Heavy dashed contours correspond to the 0–24 h field. The light dashed contours are for the 24–48 h field and the solid contours are for the 48–72 h upwind probability field. Contour intervals, from outside to inside, are 0.5, 5.0 and 15.0 ($\times 10^{-7}$).

magnitude of the upwind emissions. From one event to the next estimates of upwind emissions varied by approximately 75% due to changes in wind velocity (see Table 4 later in this paper). From month to month, season to season and year to year emissions did not vary by much more than 20% (Lins, 1987; Kahout *et al.*, 1988). Therefore, differences in the upwind emissions between events were mainly a result of the spatial variation in the sources of SO₂. In this way, the use of trajectories and emissions provided a method for quantifying the effects of changes in wind velocity on precipitation chemistry.

Statistical tests

Correlation coefficients were calculated to evaluate the strength of the relationship between SO₄²⁻ concentrations measured in precipitation (hereafter referred to as concentrations) and the corresponding estimates of upwind SO₂ emissions (referred to as emissions). Spearman and Pearson coefficients were calculated, but because similar results were obtained, only the Spearman correlations are described in length. We focus on the Spearman's rank method of computing correlations (Harnett and Murphy, 1975) because of the log-normal behavior of concentrations and the lack of normality in the emissions distributions. Spearman's correlation coefficients, ρ , which downplay the influence of very large and small concentrations are more appropriate for comparing populations that are not normally distributed.

In addition to univariate values of ρ , partial correlation coefficients, ρ' , were used (Harnett and Murphy, 1975; SAS, 1990). They measure the strength of relationship between two variables, controlling for the effect of one or more other variables. In this study, partial correlations provided a means for adjusting for the effect of temperature and precipitation amount on the concentrations and on the emissions. Spearman's partial correlation coefficients were expected to provide a better indication of the relationship between

concentrations and upwind emissions and of the differences between sites.

RESULTS

Comparison of SO₄²⁻ concentrations and upwind SO₂ emissions.

A set of Spearman's rank correlation coefficients for each site were calculated using all of the events with valid concentration, emissions, temperature and precipitation data. The correlations between these variables for a variety of upwind regions are shown in Table 2. The observed significance levels (P values) and the sample size (*N*) are also included. In total, 150 concentration to upwind emission correlations are presented and compared to one another. They are therefore considered to represent a family of tests and statistical significances are judged according to the Bonferroni experimentwise error rate for simultaneous tests (Morrison, 1983). This criterion provides a much more conservative assessment of the significance of the correlations. Consequently, at the 95% significance level, the critical P value is 0.0003.

For two-thirds of the comparisons in Table 2 (36 of 54), the magnitude of the P values indicated that SO₄²⁻ concentration and upwind SO₂ emissions were significantly related ($P < 0.0003$). The strength of the correlations depended on the time upwind of the sources included in the emission calculation and varied from

Table 2. Spearman's rank correlation coefficients (ρ) for SO₄²⁻ concentrations versus upwind SO₂ emissions (Q), surface temperature (T) and precipitation amount (P). Top row—correlation coefficients. Bottom row—level of significance of correlation

| Time upwind | TFS (1) | TUN (2) | ZAN (4) | Sites ROC (5) | FWA (7) | RAL (8) |
|-------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| N | 488 | 522 | 772 | 582 | 573 | 437 |
| 0-12 h | 0.29 0.0001 | 0.21 0.0001 | 0.00 0.7930 | 0.18 0.0001 | -0.03 0.5513 | 0.29 0.0001 |
| 12-24 | 0.46 0.0001 | 0.44 0.0001 | 0.21 0.0001 | 0.11 0.0077 | 0.07 0.1153 | 0.38 0.0001 |
| 24-36 | 0.43 0.0001 | 0.40 0.0001 | 0.21 0.0001 | 0.08 0.0509 | 0.07 0.0766 | 0.36 0.0001 |
| 36-48 | 0.35 0.0001 | 0.31 0.0001 | 0.19 0.0001 | 0.08 0.0610 | 0.13 0.0026 | 0.31 0.0001 |
| 48-60 | 0.25 0.0001 | 0.23 0.0001 | 0.18 0.0001 | 0.09 0.0359 | 0.10 0.0200 | 0.22 0.0001 |
| 12-48 | 0.44 0.0001 | 0.43 0.0001 | 0.23 0.0001 | 0.09 0.0274 | 0.06 0.1562 | 0.39 0.0001 |
| 0-48 | 0.45 0.0001 | 0.43 0.0001 | 0.15 0.0001 | 0.15 0.0005 | 0.04 0.3840 | 0.40 0.0001 |
| 0-60 | 0.43 0.0001 | 0.42 0.0001 | 0.15 0.0001 | 0.13 0.0014 | 0.03 0.4457 | 0.39 0.0001 |
| 0-72 | 0.42 0.0001 | 0.41 0.0001 | 0.14 0.0001 | 0.12 0.0030 | 0.02 0.6214 | 0.39 0.0001 |
| Temp. | 0.48 0.0001 | 0.43 0.0001 | 0.38 0.0001 | 0.31 0.0001 | 0.24 0.0001 | 0.19 0.0001 |
| Precip. | -0.38 0.0001 | -0.39 0.0001 | -0.32 0.0001 | -0.35 0.0001 | -0.34 0.0001 | -0.46 0.0001 |
| Q vs T | 0.32 0.0001 | 0.33 0.0001 | 0.12 0.0004 | -0.22 0.0001 | 0.03 0.4074 | 0.05 0.2488 |
| Q vs P | -0.27 0.0001 | -0.08 0.0418 | 0.04 0.2960 | -0.01 0.7706 | 0.09 0.0232 | -0.17 0.0002 |

site to site. The strongest relationship was at Turners Falls (1), where the maximum ρ value was 0.46. Correlations were also relatively large at Tunkhannock (2) and Raleigh (8). In contrast, most of the correlations were not significant at Rockport (5) and Fort Wayne (7). Individually, the correlations were generally above the 95% level ($P < 0.05$) at Rockport, but at Fort Wayne (7) they were consistently low. Adhering to the Bonferroni critical level, one would conclude that any evidence of a correlation at these two sites, with the exception of the 0–12 upwind region at Rockport (5), was by chance. Significance levels exceeded the 95% level for all upwind times at Turners Falls (1), Tunkhannock (2) and Raleigh (8). All but one of the comparisons attained this level of significance at Zanesville (4). Since Spearman's correlation coefficients are based upon ranks it is not possible to determine the per cent of variance explained. However, Pearson correlation coefficients indicated that between 10 and 20% of the variation in concentrations could be explained by upwind emissions at Turners Falls (1), Tunkhannock (2) and Raleigh (8).

There appeared to be a geographical and temporal pattern in the concentration to emission correlations. Relationships were stronger at sites further away from the large SO₂ source areas in the Midwest and were essentially non-existent at the two sites west of this area. This behavior could have been an indication that transport and/or meteorology was more important at the more distant sites since upwind emissions were partially dependent on these factors. This is consistent with the pattern reported by Eder (1989). His analyses suggested that away from the high emission areas wet

SO₄²⁻ deposition was more dependent on transport. However, lack of correlation at Rockport and Fort Wayne could also have been a result of the failure of the trajectory calculation to represent accurately transport from sources located to the east during events with rapidly varying wind fields. There was a clear tendency for the correlations between emissions and concentrations to increase beyond 12 h upwind. This tendency could be due to inadequate resolution provided by the trajectories and QTBA or to limited conversion of SO₂ to SO₄²⁻ during the first 12 h of transport.

Scatter plots comparing upwind emissions and concentrations were examined for all six receptors. The comparison between emissions 12–24 h upwind and SO₄²⁻ for Turners Falls, MA, is shown in Fig. 4. Emissions do not explain a large fraction of the event to event variations in concentrations, even though ρ was 0.46. However, there was a clear tendency for concentrations to increase when upwind emissions increased. There also appeared to be fewer events with large concentrations when the emissions were small and vice versa. The plots were similar at most of the other sites.

Partial correlations between concentrations and upwind emissions

Given the number of factors influencing the transport, transformation and deposition of sulfur between source and receptor, it is not surprising that there is so much scatter in Fig. 4. The differences in the correlations between sites and between upwind regions were also likely due to these factors. Estimated surface temperature and precipitation amount were included

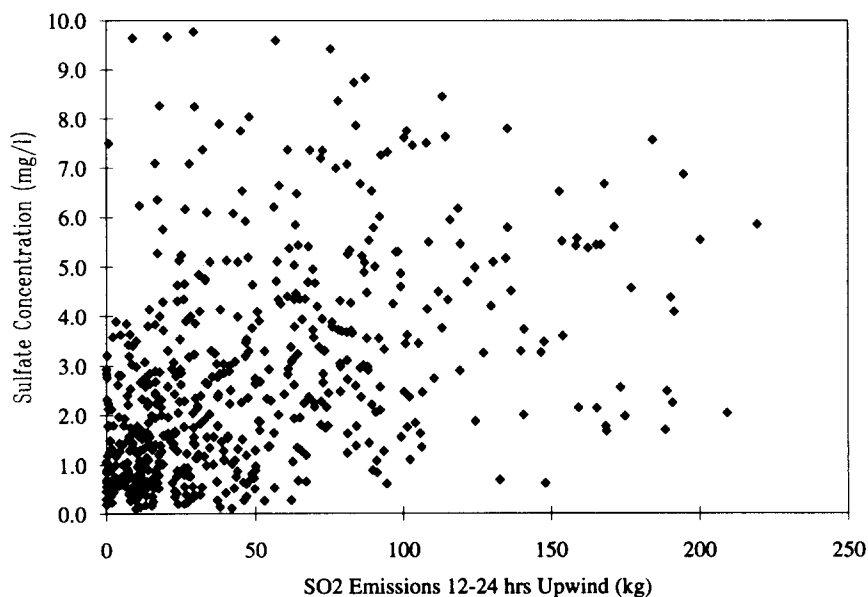


Fig. 4. SO₄²⁻ concentration in precipitation (mg l⁻¹) versus SO₂ emissions (10⁴ kg) from the 12–24 h upwind region for all events from 1979 to 1986 at Turners Falls, MA.

in the analyses in an attempt to account for some of their effects. There are well known, physically based reasons for both of these variables to have had an influence on the amount of SO_4^{2-} in precipitation (e.g. Scott, 1978; Lindberg, 1982; Skartveit, 1982; Seinfeld, 1986; Singh *et al.*, 1987). Accounting for temperature and precipitation was also expected to reduce the effect of links (causal or circumstantial) between emissions, temperature and precipitation, which could obscure the true relationship between concentrations and emissions. For example, relative to Turners Falls and Tunkhannock, the majority of the SO_2 sources were located in the southwest quadrant. As a result, there is a tendency for positive correlations between temperature and upwind SO_2 emissions since southerly winds often accompany increasing temperatures in the northeast.

At all six sites, estimates of surface temperature were significantly correlated with concentration. The estimated mean surface temperature during the deposition events was used as an indication of the temperature of the sulfur-containing air mass during transport between sources and receptors. The ρ values in Table 2 indicated that the strength of correlation varied from a high of 0.49 at Turners Falls to a low of 0.15 at Raleigh. A plot of temperature versus SO_4^{2-} using all events at Turners Falls is shown in Fig. 5. Although there was a large amount of scatter in the data, the expected increase in concentration with increasing temperatures was evident. Low concentrations were observed at almost all temperatures but there was a greater number of high concentration events when temperatures were warmer.

Precipitation amount and concentration were negatively correlated at all six sites. This agreed with

the dilution effect reported in the literature (e.g. Lindberg, 1982). In contrast to temperature, the ρ values shown in Table 2 for precipitation were not as variable between sites. The relationships were slightly weaker at the three midwestern sites, which suggests that proximity to the sources of SO_2 influenced the concentration-to-precipitation amount relationship. This could have been due to greater pollutant availability nearer the sources. As SO_4^{2-} was scavenged it would be replaced sooner over regions closer to the sources and thus, the dilution effect would not be as strong. The plot in Fig. 6 demonstrates the negative exponential relationship associated with dilution. The magnitude of the exponent (β_1) was determined for each site by least-squares fit of equation (4) to the data.

$$\ln([\text{SO}_4^{2-}]) = \beta_0 + \beta_1 \ln(P). \quad (4)$$

The value of the exponent varied, ranging from -0.17 in the midwest to -0.34 at the more distant sites. This range is generally in agreement with values reported elsewhere (e.g. Scott, 1978; MAP3S, 1982; Berge, 1988).

The correlations between temperature, precipitation and emissions (12–48 h upwind) were calculated to assess the potential for cross-correlation (see Table 2). As expected, there was a fairly strong positive relationship ($\rho \sim 0.32$) between temperature and emissions at Turners Falls and Tunkhannock. Consistent with its location, there was a significant negative correlation at Rockport. At the other three sites, the relationship between temperature and emissions was relatively weak. An inverse relationship between precipitation amount and emissions was detected at Turners Falls and Raleigh. This pattern could have been a result of their proximity to the Atlantic. Events

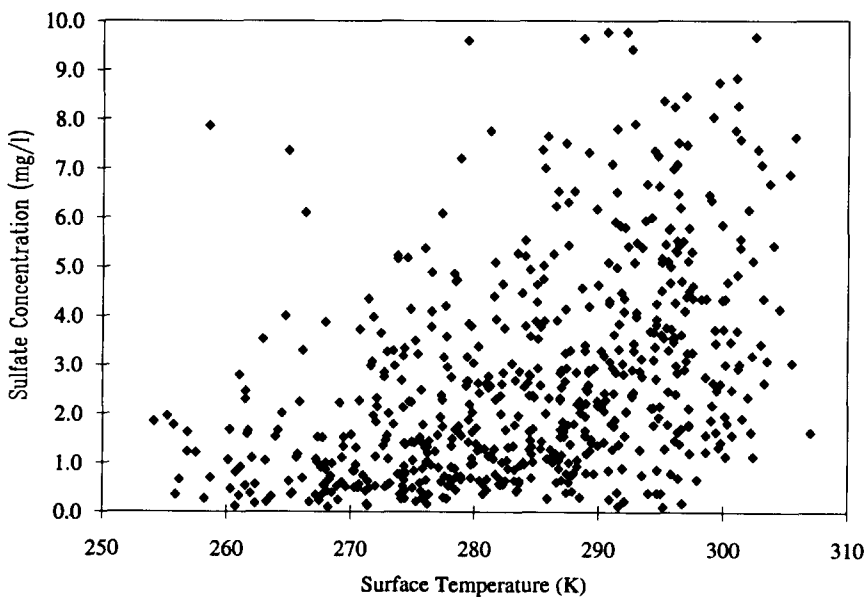


Fig. 5. SO_4^{2-} concentration in precipitation (mg l^{-1}) versus estimated mean surface temperature (K) for all events from 1979 to 1986 at Turners Falls, MA.

with large precipitation amounts are often associated with easterly winds and a maritime influence, which would have lead to reduced input of anthropogenic SO₂.

The Spearman's Rank coefficients were recalculated using partial correlation (ρ') to adjust for the effect of cross-correlation between variables previously regarded as independent (i.e. precipitation amount, temperature and upwind emissions). The results, summarized in Table 3, show a decrease in correlation between SO₄²⁻ concentrations and upwind emissions at some sites and increases at others. These changes

tended to reduce the variation between sites. Compared to the initial univariate analysis, a larger fraction of the correlations (81%) were found to be statistically significant. Overall, the weakest relationships were still found at Fort Wayne, but accounting for temperature and precipitation amount resulted in two statistically significant correlations where none were detected before. The strongest relationships were still found at the sites located further from the mid west.

The geographical pattern in the emissions-to-concentration relationship was not as evident. However,

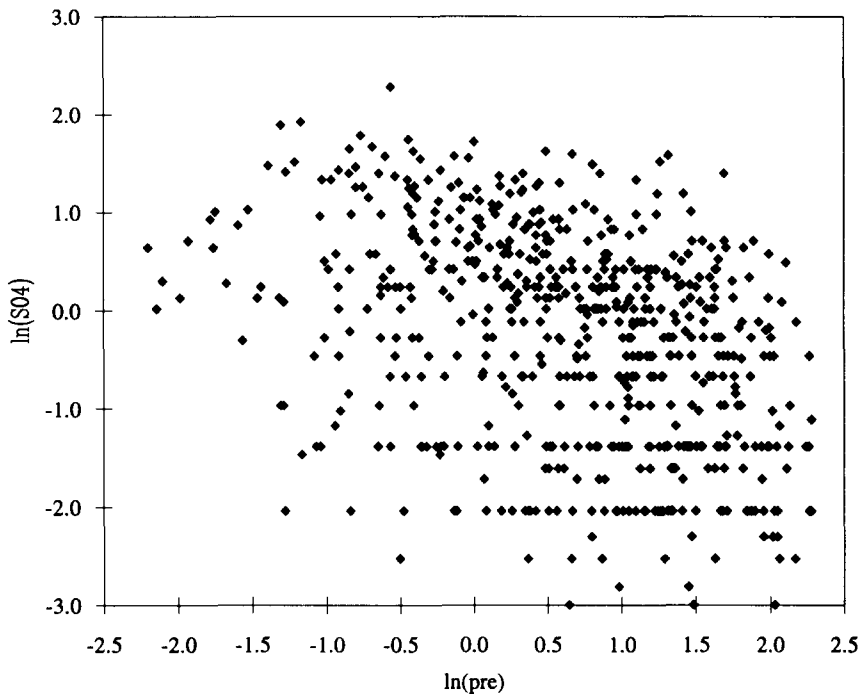


Fig. 6. Log of SO₄²⁻ concentration in precipitation (mg ℓ^{-1}) versus log of precipitation amount (cm) for all events from 1979 to 1986 at Turners Falls, MA.

Table 3. Partial Spearman's rank correlation coefficients (ρ') for SO₄²⁻ concentrations versus upwind SO₂ emissions. Partial correlations taken with respect to surface temperature and precipitation amount. Top row—partial correlation coefficients. Bottom row—P values

| Time upwind | TFS N=(481) | TUN (522) | ZAN (772) | ROC (582) | FWA (573) | RAL (437) |
|-------------|----------------|----------------|----------------|----------------|-----------------|----------------|
| 0-12 h | 0.22 0.0001 | 0.16 0.0004 | 0.10 0.0083 | 0.17 0.0001 | -0.01 0.8933 | 0.21 0.0001 |
| 12-24 | 0.31 0.0001 | 0.31 0.0001 | 0.12 0.0007 | 0.18 0.0001 | 0.05 0.2523 | 0.30 0.0001 |
| 24-36 | 0.31 0.0001 | 0.29 0.0001 | 0.22 0.0001 | 0.19 0.0001 | 0.10 0.0163 | 0.35 0.0001 |
| 36-48 | 0.27 0.0001 | 0.25 0.0001 | 0.26 0.0001 | 0.19 0.0001 | 0.18 0.0001 | 0.35 0.0001 |
| 48-60 | 0.20 0.0001 | 0.18 0.0001 | 0.26 0.0001 | 0.20 0.0001 | 0.17 0.0001 | 0.30 0.0001 |
| 12-48 | 0.32 0.0001 | 0.29 0.0001 | 0.20 0.0001 | 0.18 0.0001 | 0.11 0.01 | 0.36 0.0001 |

the site-to-site variation in the correlations continued to imply that the relationship between emissions and concentrations was dependent on distance and direction of the receptor from the source region. It would be necessary to include more sites to adequately test this hypothesis. This behavior is physically reasonable, however, because changes in wind flow, which are influenced by meteorology, would have a greater impact on the amount of upwind emissions at the more distant sites. Location, relative to the areas with the highest emission density, could have also led to the weaker correlations at Rockport and Fort Wayne. At these two sites, the transport patterns during events associated with large upwind emissions may have tended to be more complex because of the easterly winds necessary to produce this situation. Low pressure systems are most often responsible for easterly winds and as discussed earlier, the trajectory model may not have correctly resolved the transport due to large vertical wind shear. However, the actual cause of the poor correlation has not been determined.

Using partial correlations accentuated the tendency for correlations to increase beyond the first 12 h upwind. The values in Table 3 show that after adjusting for temperature and precipitation all six sites exhibited this pattern. Increases in correlation are consistent with the rate of atmospheric conversion of SO_2 to SO_4^{2-} , which for long-range transport situations ranges from 0.5 to 2% h^{-1} (Seinfeld, 1986). This rate can be greater in highly polluted atmospheres or in the presence of cloud and fog. However, during the first 12 h of transport only a relatively small fraction of the SO_2 was likely to have been converted.

There was also a relatively consistent difference in the time upwind of maximum correlation between the midwestern sites and the other three sites. Closer to the area of the highest SO_2 emissions the largest ρ' values were associated with longer travel times (> 36 h), while at the other sites, ρ' tended to be larger for shorter travel times (< 36 h). It is plausible that the behavior at the midwest sites was an indication that wind speed was more important than wind direction in governing SO_4^{2-} concentrations. Light winds would generally have been necessary to generate large SO_2 emissions within the 36–60 h region because Zanesville, Rockport and Fort Wayne are situated close to the large sources. Stronger winds would have moved the 36–60 h region away from the SO_2 sources. Therefore, changes in wind speed would have had a larger impact than changes in direction on the magnitude of the upwind emissions accumulated within the 36–60 h puff. This explanation suggests that stagnant situations were more conducive to large SO_4^{2-} concentrations than were particular wind directions at Zanesville, Rockport and Fort Wayne.

Partial correlation coefficients (ρ') were determined separately for the warm season events (1 April–30 September) and the cold season events (1 October–31 March). The relationship between concentrations and emissions was stronger in the warm season at a

majority of the sites. With the exception of Fort Wayne, maximum ρ' values were equal to or greater than 0.33. At Raleigh, the warm season partial correlation between concentrations and emissions encountered 36–48 h upwind attained a value of 0.5. Seasonal correlations are given in Figs 7a–7f, which show the variation in partial correlation coefficients as a function of time upwind and season. The critical ρ' values (ρ_{crit}) shown on the figures indicate the 95% significance level (Bonferroni rate) determined for the smaller of the two seasonal sample sizes (there were usually fewer events in the cold season). Substantial seasonal differences in correlations were found at Turners Fall, Zanesville, Rockport and Raleigh. No statistically significant correlations were detected during the cold season, but in the warm season they were significant for a number upwind times. The seasonal differences were small at Tunkhannock and Fort Wayne.

DISCUSSION

At best, upwind emissions were able to explain about 25% of the variability in concentrations (based upon Pearson Correlation Coefficients for the warm season at Raleigh, $r=0.5$). Reasons why upwind emissions did not have a stronger influence or why there

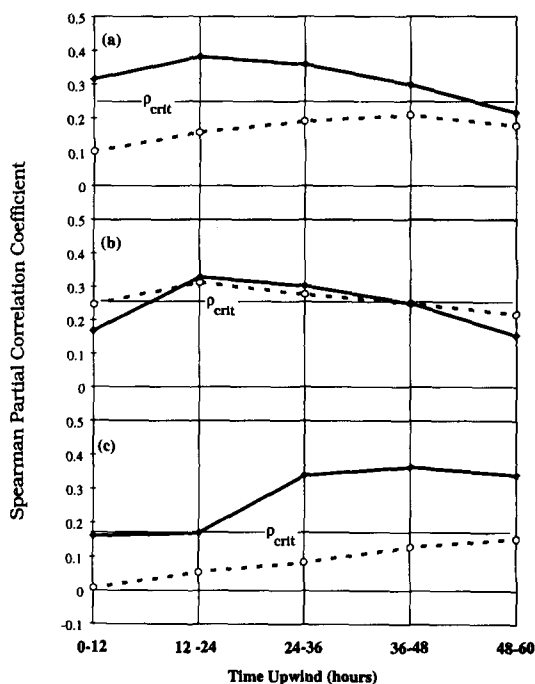


Fig. 7. (a)–(c) Spearman's partial correlation coefficients for upwind SO_2 emissions versus SO_4^{2-} concentrations in precipitation as a function of time upwind. Correlations calculated for both warm seasons (solid line) and cold seasons (dashed line) from 8 years of data. (a) Turners Falls, MA; (b) Tunkhannock, PA; (c) Zanesville, OH. The line through ρ_{crit} indicates the minimum value for the correlations to be significant with $\alpha=0.05$.

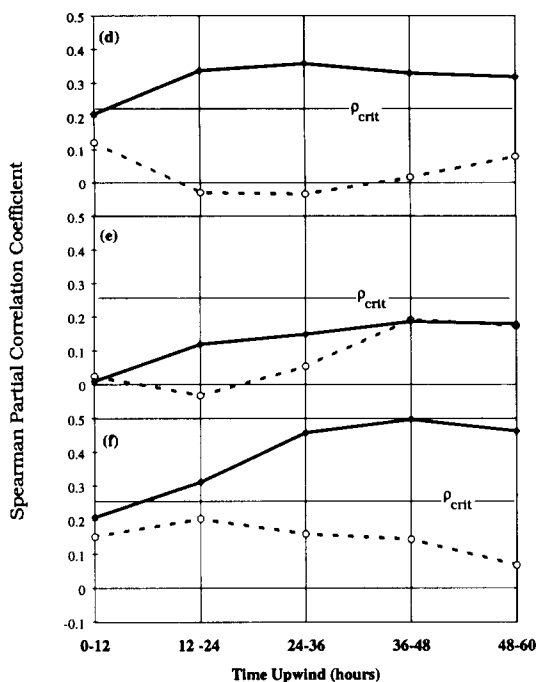


Fig. 7. (d)–(f) Spearman's partial correlation coefficients for upwind SO₂ emissions versus SO₄²⁻ concentrations in precipitation as a function of time upwind. Correlations calculated for both warm seasons (solid line) and cold seasons (dashed line) from 8 years of data. (d) Rockport, IN; (e) Fort Wayne, IN; (f) Raleigh, NC. The line through ρ_{crit} indicates the minimum value for the correlations to be significant with $\alpha = 0.05$.

were consistent site-to-site differences were difficult to determine. Obviously, a variety of atmospheric processes contributed to the large amount of event-to-event variation in the precipitation concentrations of SO₄²⁻. The relationships between upwind emissions and concentrations would likely have been more consistent if they (e.g. the loss of sulfur between the sources and receptor) had been taken into consideration. Uncertainties in the trajectories and in the approach used to estimate upwind emissions probably also masked the expected relationships.

A more involved analysis would have been necessary to explain more of the variability in concentrations and to strengthen the link with emissions. However, this would have ultimately lead to a Lagrangian-type model, which was not the object of this study. The main purpose here was to test the hypothesis that the emissions encountered upwind were related to the concentrations in precipitation downwind. Overall, the results of this study do indicate that a relationship existed. While the statistical tests indicated that the correlations were significant a majority of the time, it is of equal importance to note that these results were substantiated by our physical understanding of the processes. The geographic pattern, the weak correlation with emissions from the first 12 h and the decrease from warm to cold season agree with

physical and/or chemical conceptions of the factors influencing source–receptor relationships.

The seasonal behavior in the correlations shown in Figs 7a–7f agree with Hilst and Chapman (1990). They uncovered a spring–summer peak in the correlation between SO₂ emissions and the mean monthly precipitation concentrations of SO₄²⁻. The decrease in correlation between warm and cold seasons was probably partly due to differences in the meteorology between seasons. Seasonal changes in the spatial pattern of SO₂ emission rates may also have had an influence. Lins (1987) reported that the northern states experienced two peaks in emission rates (winter and summer), while in the southern states there was generally only one peak, which occurred in the warm season. However, relative to individual receptors these variations were much smaller than the event-to-event changes in upwind emissions and, therefore, they were not likely to have been important. There also could have been a bias towards more uncertain trajectories in the cold season since cyclonic systems are more frequent. This could have lead to unrepresentative estimates of upwind emissions. However, this should have lead to a decrease in correlation at Tunkhannock as well. Given the available information, it is not possible to specify which, if any, of these explanations is most probable.

Two potential ways that meteorological differences could have lead to a decrease in correlation between warm and cold seasons are changes in wind flow, leading to differences in upwind emissions regimes, and differences in temperature and ultra-violet insolation, which could alter the oxidant levels. The possibility that there were significant differences in upwind emissions between warm and cold seasons was explored using the Kruskal–Wallis test (Beyer, 1990). The emissions from the 0–12, 12–24, 24–36, 36–48, 48–60 h puffs were compared across seasons and the results of the test are indicated in Table 4 (Y-significant difference was detected at $P < 0.01$). While the results differed for each upwind puff, the emission regimes were generally not different between the warm and cold seasons at Rockport, Fort Wayne and Raleigh. There were differences at Turners Falls and Tunkhannock and at Zanesville no clear consensus could be determined. These results suggest that at Rockport and Raleigh, seasonal differences in the correlations between concentrations and emissions were not due to changes in the upwind emissions. Conversely, at Turners Falls and Zanesville the decrease in correlation from the warm to cold season could have been a result of changes the upwind emissions due to differences in the predominant source regions. However, at Zanesville, the changes in the correlations were largest for the 36–48 and 48–60 h puffs where the upwind emissions were not found to be significantly different between seasons. In contrast, the seasonal differences in the emissions beyond 12 h upwind were quite dramatic at Tunkhannock, but the changes in the correlations were very small. The

Table 4. Mean and coefficient of variation of the SO₂ emissions by site, season and time upwind. Results of the Kruskal–Wallis test (K.W.) comparing the behavior of the upwind emissions between seasons are indicated by a *N* if there was no significant difference ($P < 0.01$) and by a *Y* if a significant difference was detected

| Time upwind | Mean upwind emissions (kg × 10 ³) | | Coefficient of variation (%) | | K.W. test |
|----------------------|---|-------|------------------------------|------|-----------|
| | Cold | Warm | Cold | Warm | |
| Turners Falls | | | | | |
| 0–12 | 184.6 | 188.9 | 67 | 63 | N |
| 12–24 | 147.5 | 229.8 | 99 | 84 | Y |
| 24–36 | 155.3 | 226.6 | 94 | 78 | Y |
| 36–48 | 167.8 | 208.2 | 84 | 67 | Y |
| 48–60 | 167.2 | 188.5 | 67 | 59 | N |
| Tunkhannock | | | | | |
| 0–12 | 340.4 | 327.6 | 66 | 75 | N |
| 12–24 | 296.4 | 374.5 | 70 | 65 | Y |
| 24–36 | 232.6 | 300.4 | 70 | 61 | Y |
| 36–48 | 197.9 | 248.8 | 68 | 58 | Y |
| 48–60 | 174.9 | 210.1 | 66 | 56 | Y |
| Zanesville | | | | | |
| 0–12 | 694.8 | 559.4 | 76 | 69 | Y |
| 12–24 | 379.0 | 465.9 | 53 | 40 | Y |
| 24–36 | 259.6 | 300.8 | 63 | 54 | Y |
| 36–48 | 207.4 | 217.1 | 66 | 65 | N |
| 48–60 | 177.5 | 175.2 | 67 | 69 | N |
| Rockport | | | | | |
| 0–12 | 657.2 | 660.0 | 58 | 49 | N |
| 12–24 | 278.7 | 270.9 | 70 | 68 | N |
| 24–36 | 204.7 | 176.6 | 76 | 76 | N |
| 36–48 | 165.8 | 144.6 | 76 | 80 | N |
| 48–60 | 155.9 | 129.0 | 74 | 77 | Y |
| Fort Wayne | | | | | |
| 0–12 | 371.6 | 317.2 | 52 | 48 | Y |
| 12–24 | 339.2 | 353.6 | 55 | 52 | N |
| 24–36 | 238.2 | 248.4 | 68 | 61 | N |
| 36–48 | 193.8 | 191.9 | 69 | 70 | N |
| 48–60 | 171.0 | 157.8 | 68 | 72 | N |
| Raleigh | | | | | |
| 0–12 | 145.2 | 162.1 | 70 | 52 | N |
| 12–24 | 156.2 | 187.3 | 88 | 67 | Y |
| 24–36 | 182.4 | 200.5 | 83 | 70 | N |
| 36–48 | 188.6 | 186.3 | 77 | 72 | N |
| 48–60 | 184.8 | 171.7 | 67 | 69 | N |

number of cases where the change in the correlation between seasons was large but no significant seasonal difference in emissions was 9 out of a possible 13. This suggests that the decrease in correlations between warm and cold seasons were not due to systematic changes in the upwind emissions. This implies that other factors were responsible for the decrease in correlations from the warm to cold season.

The availability of oxidants could have lead to weaker correlations in the cold season. If there was a greater tendency for the SO₂ in the atmosphere to consume all the oxidants in the cold season, then increases in the SO₂ levels would not consistently be reflected in the amount of SO₄²⁻ in precipitation. This scenario is plausible given that lower temperatures and less sunlight in the cold season probably resulted

in a smaller amount of oxidants while the SO₂ emissions would not have changed substantially. Clark *et al.* (1987) hypothesized that the best potential for non-linear relationships between SO₂ emissions and SO₄²⁻ in precipitation would be in the cold season and would be greatest closer to major sources of SO₂. The seasonal changes in the correlation coefficients seem to substantiate this hypothesis.

Samson and Moody (1986) calculated Pearson correlation coefficients between precipitation concentrations of SO₄²⁻ and the SO₂ emissions potential (emissions within 500 km) at four UAPSP sites. For individual seasons during the 1979–1983 period (16 comparisons) only 3 of their 16 comparisons were found to be statistically significant ($P < 0.10$). This is in contrast to our results showing that 6 of 12 (2 seasons

and 6 sites) comparisons were statistically significant (12 of 12 have at least one significant correlation using significance criteria similar to Moody and Samson). It was not likely that the use of partial Spearman's correlation coefficients could explain the increased number of significant correlations. The main reason for the increased success in linking emissions and concentrations was probably the use of a more sophisticated method for estimating upwind emissions. The larger sample size was also likely to have had an influence. The methodological improvements were counteracted by more stringent significance criteria and the treatment of temperature and precipitation effects. These measures provided for a more demanding test of the upwind emissions to concentration linkage and, therefore, the significances of the partial correlations are even more noteworthy. It was evident that comparisons of upwind emissions and precipitation chemistry should be based upon partial correlation coefficients. The changes between ρ and ρ' and the degree of correlation between concentrations, emissions, temperature and precipitation amount indicated that univariate comparisons were subject to external meteorological effects. Neglecting these effects could produce an inaccurate picture of the relationship between upwind emissions and concentrations.

SUMMARY

An objective, trajectory-based approach to estimating upwind SO₂ emissions associated with wet SO₄²⁻ deposition events has been described and implemented for six UAPSP sites. Emissions for different upwind times were compared to SO₄²⁻ concentrations in precipitation for all valid events during the 1979–1986 period. Separate warm and cold season relationships were also examined and the effects of surface temperature and precipitation amount were factored into the comparisons.

On an annual basis, statistically significant partial Spearman correlations (Bonferroni, $p < 0.05$) were detected between upwind SO₂ emissions and SO₄²⁻ concentrations at all sites, but not for all upwind time periods. In general, the relationship between emissions and concentrations was stronger at sites further removed from the high emission areas in the midwest. The emissions from areas within 12 h of the receptors also tended to be less related to the concentrations. At four of the six sites, there was a noticeable decrease in the strength of the correlations between emissions and concentrations from the warm to the cold season. Tunkhannock was the only site where statistically significant correlations (Bonferroni, $p < 0.05$) were found in the cold season. An examination of the seasonal differences in the amount of upwind emissions suggested that systematic differences in transport were not entirely responsible for the decrease in correlation from the warm to the cold season. How-

ever, this comparison did not rule out the possibility of a greater frequency of uncertain trajectories in the cold season. More research is necessary to resolve this issue. Other meteorological factors, possibly contributing to a greater frequency of oxidant-limited situations, could have influenced the cold season relationship between upwind SO₂ emissions and the amount of SO₄²⁻ in precipitation.

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APPENDIX

Upwind emission calculation

In this Appendix the method used to calculate event-specific transition probability values (P_i , $i = 1, 1452$) by grid point for selected upwind time periods is described. The transition probability field for a given wet deposition event was determined from a series of back-trajectories that represented transport immediately before, during and immediately after the event. The grid point probability values, which summed to one over the domain, were based upon all identified trajectories. Probabilities were calculated according to equation (A.1). The number of trajectories used in the calculation are given by T , and s_1 and s_2 indicate which 3-h segments are to be considered. For example, if the upwind region of

interest was the 24–48 h region then s_1 and s_2 would equal to 8 and 16, respectively.

$$P_i = \sum_{t=1}^T W_t \sum_{s=s_1}^{s_2} \frac{1}{2\pi\sigma_x(t_s)\sigma_y(t_s)} \times \exp\left[-\frac{1}{2}\left(\frac{X_s''}{\sigma_x(t_s)} + \frac{Y_s''}{\sigma_y(t_s)}\right)^2\right] \quad (\text{A.1})$$

where $X_s'' = X - x'_s$ and $Y_s'' = Y - y'_s$ with (X, Y) being the coordinates of grid point, i . x'_s and y'_s are the coordinates of the endpoint of trajectory segment, s , for trajectory, t . When X_s'' or Y_s'' were greater than $3\sigma_x(t_s)$ or $3\sigma_y(t_s)$, which are defined below, then segment s was not counted at grid point i . It was assumed that $\sigma_x(t_s)$ and $\sigma_y(t_s)$ could be approximated by

$$\sigma_x(t_s) = \sigma_y(t_s) = a t_s \quad (\text{A.2})$$

with dispersion speed, a , equal to 5.4 km h^{-1} (Samson, 1980). t_s was the time upwind of trajectory segment, s .

In (A.1) trajectory weights, W_t , can also be assigned. In this study, weights were based upon the relationship between event start and stop times and trajectory arrival times (0, 6, 12 or 18Z). Greater weights were assigned to trajectories arriving closer to the middle of the events. Smaller weights were given to trajectories arriving just before and after the start and stop times. P_i values were normalized to 1 by dividing by

$$\sum_{i=1}^{1452} P_i \quad (\text{A.3})$$

which represented the sum of the probabilities across all grid points. The P_i values obtained through the above procedure were input into equation (3) to arrive at estimates of upwind emissions.