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THE INFLUENCE OF ATMOSPHERIC TRANSPORT ON PRECIPITATION CHEMISTRY AT TWO SITES IN THE MIDWESTERN UNITED STATES

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Abstract—Cluster analyses of two-dimensional mixed layer back trajectory data were used to determine what fraction of chemical variability in precipitation composition could be related to differences in atmospheric transport. Trajectories arriving at two different sites, Rockport, Indiana, and Gaylord, Michigan, were clustered to identify events occurring with similar transport patterns. It was found that certain transport situations resulted in significantly higher concentrations and depositions of the major ions, H^+, SO_4^-, NO_3^- and NH_4^+. At Rockport, the greatest fraction of acid deposition was associated with low wind speeds. At Gaylord, transport direction played a greater role than transport speed in influencing precipitation composition. Results presented here suggest that 10%–40% of the variability in ion concentrations may be related to differences in atmospheric transport. The residual variation in concentrations was correlated with differences in the occurrence of upwind precipitation, precipitation type, and variation in precipitation amount.

Key word index: Acid rain, cluster analysis, back trajectory, precipitation chemistry.

INTRODUCTION

A common practice described in the current literature is to assess the influence of meteorology on precipitation composition by stratifying the chemical data into subgroups based on specific meteorological conditions. Wolff *et al.* (1979), Raynor and Hayes (1982) and Topol (1986) classified precipitation events by synoptic scale weather conditions. Munn and Rodhe (1971) stratified precipitation data by geostrophic wind direction. Back trajectories have been used in several studies, as evidenced by the recent review and bibliography prepared by Miller (1987). Miller *et al.* (1978), Wilson *et al.* (1982) and Henderson and Weingartner (1982) used trajectories corresponding to precipitation events collected at MAP3S sites to create categories of wind sector, defining the octant of origin for the precipitating air masses. The sector approach was also applied to assess the long-range transport and wet and dry deposition of aerosols and gases to a remote receptor on the island of Bermuda (Chen and Duce, 1983; Miller and Harris, 1985; Wolff *et al.*, 1986; Church *et al.*, 1982; Jickells *et al.*, 1982; Galloway *et al.*, 1988).

This research has suggested that some portion of the chemical variability of precipitation can be explained by meteorological variability. However, there has not been a consistent effort to quantify these relationships, or to test their statistical significance. The specific objective of this investigation was to determine how much of the chemical variability in precipitation could be related to transport differences. It was designed to combine elements of these earlier studies with a more quantitative method of classifying precipitation events into subgroups representing similar transport patterns. Cluster analysis was applied as a pattern recognition technique to define these subgroups and non-parametric statistics were used to test for significant differences in chemical composition. This paper illustrates the utility of these tools in diagnosing multivariate relationships between wind speed and direction and precipitation composition.

DATA

Precipitation chemistry data used in this study were collected by the Utility Acid Precipitation Study Program (UAPSP, 1984). The UAPSP network of 19 sites covers the Eastern U.S. and collects samples on a daily basis. For each precipitation sample the UAPSP data base included the following information: date and time the first precipitation began and last precipitation ended, precipitation amount, field and laboratory pH, concentrations of major ions in solution, and

precipitation type (i.e. rain, snow, or mixed). Supplementary information not provided as part of the UAPSP was derived from precipitation gauge charts. This included the actual hours of precipitation, the maximum precipitation intensity and hour of its occurrence and the average precipitation intensity. The task of retrieving these parameters from the original strip charts was limited to two sites (Rockport, Indiana and Gaylord, Michigan), and 2 years (1982 and 1983).

These sites and years were chosen based on the availability of cloud data obtained from the U.S. Air Force. The Air Force Global Weather Central Automated Cloud Analysis model, an automated system for processing and interpreting a large volume of cloud data, provides a synthesis of conventional National Weather Service (NWS) surface reports, standard aircraft reports and satellite i.r. and visual imagery. A discussion of the influence of low cloud type on precipitation composition was presented in a published UAPSP report (Samson and Moody, 1987) and will not be addressed in this paper. The availability of these cloud data constrained the choice of UAPSP sites to those in the midwest for years 1982 and 1983.

Mixed-layer back trajectories were calculated for the Rockport and Gaylord sites using the Air Resources Laboratory Atmospheric Transport and Diffusion Model developed by Heffter (1980). Theoretically, these two-dimensional trajectories represent the most probable path of an air parcel advected with the mean motion of a vertically well-mixed layer. The transport layer was assumed to be between 300 m above the surface and the bottom of the first non-surface based inversion. When no elevated inversion was detected in the sounding data, the top of the mixed layer was set at 3000 m above the surface. NWS rawinsonde data were used to calculate these trajectories and to determine ambient atmospheric characteristics (i.e. pressure at the surface, and temperature and moisture content at the 850 mb level). Additionally, NWS hourly precipitation amounts were gridded and used to determine the occurrence of precipitation along trajectories enroute to the receptor locations (Keeler *et al.*, 1984).

A recent study by Billman-Stunder *et al.* (1986) illustrated the sensitivity of trajectory analyses of precipitation chemistry to the determination of when precipitation actually occurred. For the present study, the period of maximum precipitation intensity was used to match trajectory arrival times with each precipitation event. This provided a standard time, consistent from sample to sample, for determining atmospheric characteristics. It should be reasonably representative of the high deposition period of each precipitation sample collected.

METHODS

In an effort to use all available information, the multivariate technique of cluster analysis was applied, resulting in a quantitative classification that simultaneously considered the variation of wind speed and direction along trajectories. The goal of cluster analysis as applied here was to identify precipitation events which occurred under similar transport conditions.

In the work of researchers described in the introduction, subjective measures were used to categorize similar events (i.e. cold front, warm front designations; compass sectors of trajectory origin). In this paper, cluster variables were trajectory endpoints, these parameterize the wind speed and direction at 3-h intervals. The first six trajectory endpoints were used, representing transport 18 h upwind. The smaller the spatial variance of endpoints within a cluster, the more similar the trajectories. The step-wise optimal cluster routine measured similarity using the Euclidean distance between endpoints. A hierarchical clustering algorithm designed to minimize within-group variance (Ward's method, Gordon, 1981; Romesburg, 1984) was applied. The process continued grouping trajectories into clusters, until the increase in variance from joining two clusters was too great to warrant their combination. In the applications presented in this paper there were well defined discontinuities in the within-group variance signalling an optinal number of clusters.

Once transport clusters were defined, statistical comparisons of precipitation composition were made. Non-parametric statistics were necessary for two reasons, the distributions of chemical species exhibited significant departures from normality, and the sample sizes of data subgroups were often too small ($n < 30$) to rely on asymptotic normality. Non-parametric tests (Conover, 1980) were used to distinguish differences in the concentration and deposition distributions of the major ions in solution (H^+, NH_4^+, SO_4^{2-}, NO_3^-). Significant differences among transport groups were reported when the null hypothesis of no difference in distributions could be rejected at the 95% confidence level using the Kruskal–Wallis test, a non-parametric one-way analysis of variance. When the null hypothesis that the cluster data represent random samples from the same population was rejected, then a Mann–Whitney two-sample test was employed to test for significant differences between any two of the clusters.

Along with making non-parametric comparisons of distributions among clusters, a parametric analysis of variance was used to estimate what fraction of the variability in each ion could be explained by differences in atmospheric transport (Seilkop, pers. comm., 1988). These tests were not used for significance testing, but only to partition variance into measures of within cluster variability and between cluster variability.

SEASONAL VARIATIONS

Given the objective of determining how much variation in chemical composition could be explained by accounting for differences in atmospheric transport, the degree of variability in the chemical data has been established. Figures 1a and b illustrate the per event concentrations of sulfate at Rockport and Gaylord, respectively. These figures show concentrations ranging from 5 μmole ℓ^{-1} to 150 μmole ℓ^{-1}. The other major ions showed similar variation from event to event. However, superimposed on this daily fluctuation in $SO_4^=$, a seasonal pattern can be discerned. In general, the lowest and less variable concentrations occurred during the colder months at both sites. Highest concentrations occurred in warmer months.

In order to study the influence of transport on precipitation composition apart from this seasonal variation, the cluster analysis was performed by sea-

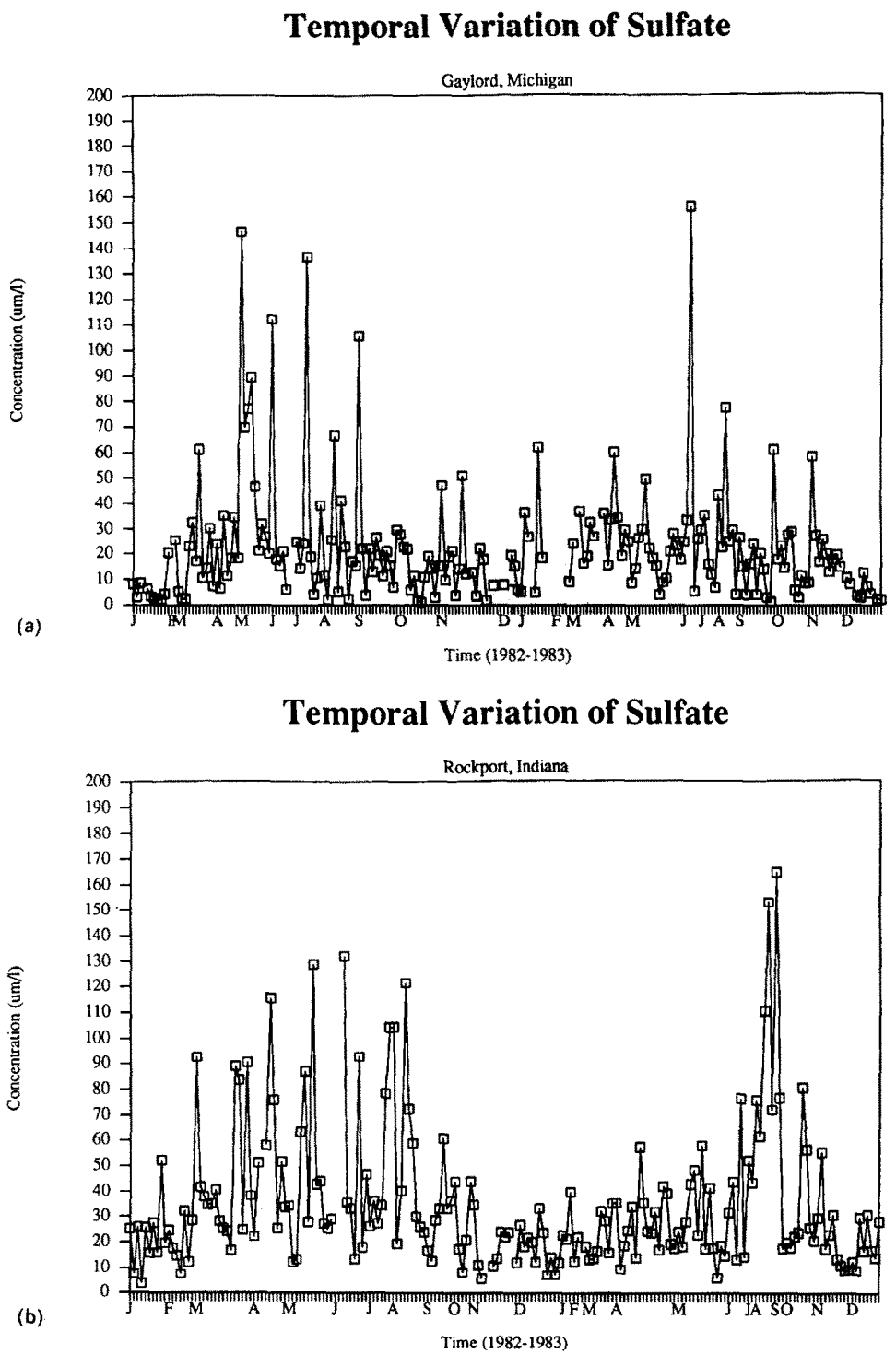


Fig. 1. Time sequence of per event sulfate concentrations from January 1982 to December 1983 recorded at (a) Gaylord, Michigan, and (b) Rockport, Indiana.

son. Two general periods were defined to account for seasonal differences in chemistry and still retain enough data to determine statistical relationships. The warm season events occurred between 1 April and 30 September. Cold season events occurred between 1 October and 31 March.

Table 1 contains the volume weighted average (VWA) concentrations for the two sites by season. This table suggests both interseason and intersite differences in chemistry. For both sites, SO_4^{2-}, H^+ and NH_4^+, were lower on the average in the cold season events. Nitrate showed very little seasonal variation.

Table 1. Average precipitation amount (cm) and volume weighted averages (μmole/ℓ^{-1}) of major ions by season

Rockport	Precipitation	SO_4^{2-}	NO_3^-	NH_4^+	H^+
Cold	81.4	23.5	18.1	16.7	49.1
Warm	88.8	34.1	22.5	21.8	74.4
Gaylord	Precipitation	SO_4^{2-}	NO_3^-	NH_4^+	H^+
Cold	52.7	15.1	21.6	13.4	36.5
Warm	87.6	23.9	22.4	21.0	41.7

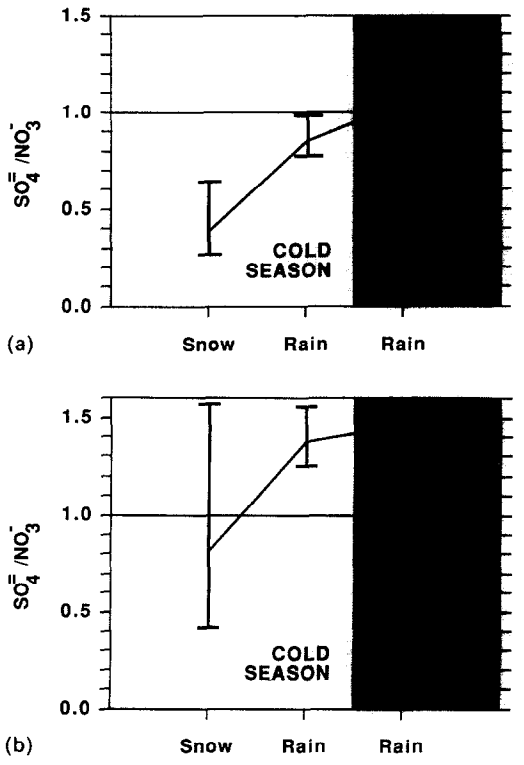


Fig. 2. Median and 95% confidence interval of the molar sulfate–nitrate ratio by season and precipitation type, for (a) Gaylord, and (b) Rockport.

The magnitude of VWA NO_3^- and NH_4^+ was similar between sites however the SO_4^{2-} and H^+ concentrations were lower at Gaylord in both seasons, similar to results reported by Richardson and Merva (1976).

At Gaylord, NO_3^- concentrations were similar to SO_4^{2-} in the warm months. However, during the colder months, molar concentrations of NO_3^- were higher than SO_4^{2-}. This difference was not observed in the Rockport data where SO_4^{2-} concentrations were typically > NO_3^-. These seasonal differences and differences in precipitation type have been summarized in Figs 2a and b, plots of the median molar ratio of SO_4^{2-}/NO_3^-, with 95% confidence intervals, by site. Figure 2a illustrates a large difference between cold season snow events and cold season rain events at Gaylord. During snow events, the molar concentration of NO_3^- was > SO_4^{2-}. Topol (1986), Raynor and Hayes (1983) and Dasch (1987) noted similar results for other locations, although Dasch identified that some of the difference in NO_3^- may be related to differences in event volume. At Gaylord, the NO_3^- concentrations were highly correlated with H^+, indicating the relative importance of HNO_3 in determining precipitation pH. This difference between precipitation types was not significant at Rockport (Fig. 2b). However, < 10% of the Rockport precipitation events fell as snow in the 2 year period, vs 50% of the Gaylord events.

ROCKPORT CLUSTER RESULTS

Trajectory data 18 h upwind were used to define clusters. For Rockport, 80 cold season events were clustered into six transport regimes. The flow patterns of each cluster are represented in Figs 3a–3f. Each trajectory segment plotted represents the distance travelled in 6-h intervals. The length of the arrowheads is proportional to the average wind speed for that duration. For clarity in identifying relative source regions, trajectories were plotted to depict transport 36 h upwind. Using the warm season data, 83 events were classified into five clusters, depicted in Figs 4a–4e. Significant differences in meteorological variables have been summarized in Table 2a for the cold season, and 2b for the warm season clusters. Transport describes the general wind direction and relative wind speed. Precipitation characteristics include the per cent of water deposition, the relative amount per event, and the relative precipitation intensity. Finally, ambient characteristics include the relative surface pressure and relative temperature and moisture content at 850 mb.

The results depicted in these figures and tables indicate that clustering trajectory endpoints was an effective technique for defining periods of similar transport. The meteorological characteristics of each cluster were relatively distinct. Along with the differences in wind velocity that defined the clusters, significant differences in precipitation amount, temperature and surface pressure were noted. These clusters also distinguished differences in precipitation chemistry.

In order to consider both the relative volume weighted ion concentrations in each cluster, and the contribution of each cluster to the seasons total deposition, a relative concentration factor (RCF) was calculated for each ion by cluster (see Appendix, Moody and Galloway, 1988). These factors represent the volume weighted average concentrations of each ion by cluster normalized relative to the VWA concentration of each ion by season (Table 1), and have been plotted for each season in Figs 5a and b. For example, when a RCF was >1, volume weighted concentrations of that ion were enhanced relative to the VWA of

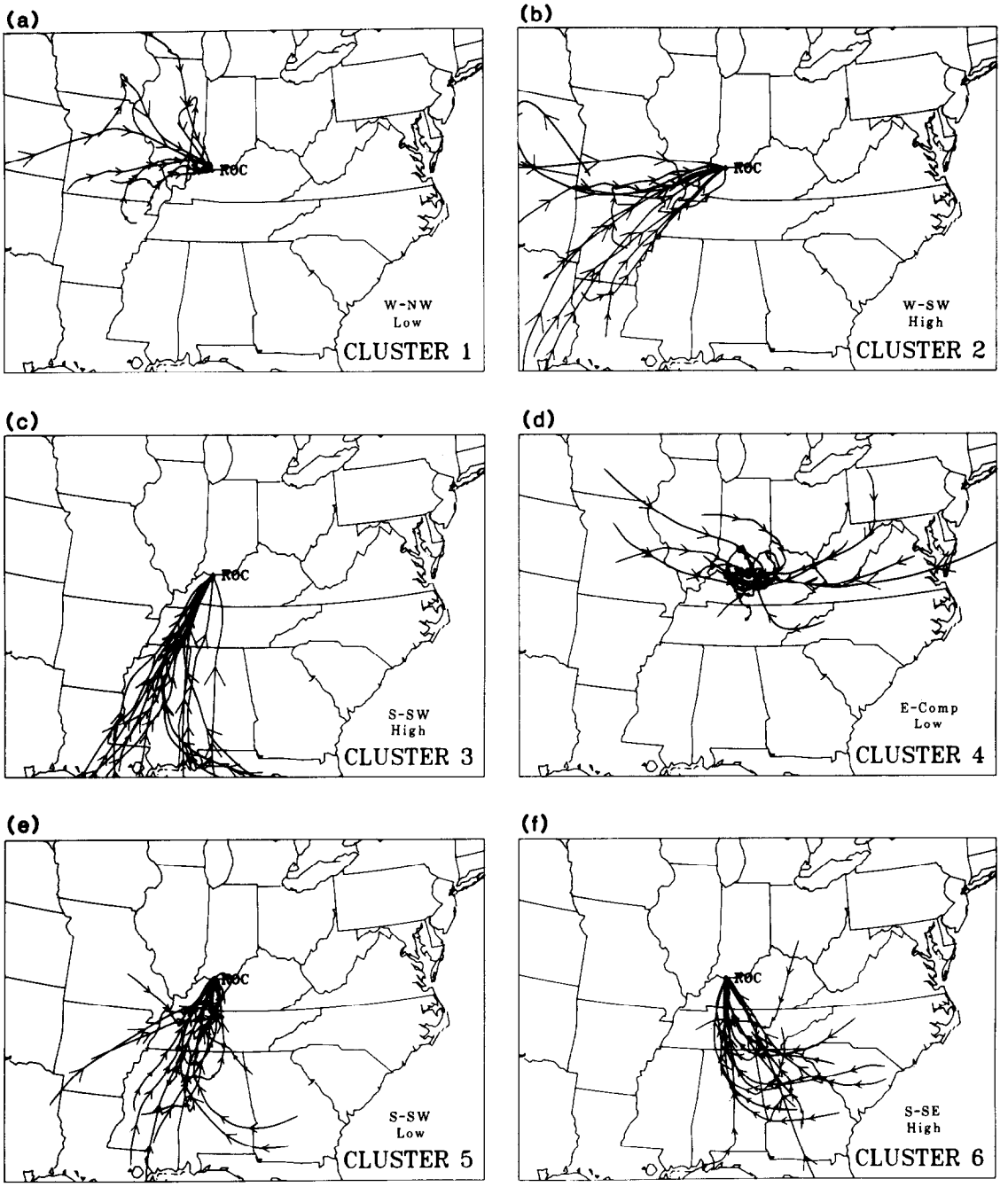


Fig. 3. Clusters depicting similar transport 36 h upwind formed using mixed layer back trajectories arriving in Rockport during cold season precipitation events; arrowheads denote 6-h intervals. The general wind direction and relative speed associated with each cluster is noted in panels a–f.

the ion for the season. Additionally, when these factors are multiplied by the per cent of water deposition in each cluster, the per cent of ion deposition occurring in that cluster results. This allows for the relatively concise representation of both concentration and deposition information. For easy comparison between clusters, total ion deposition by Rockport cluster has been summarized in Tables 3a and 3b.

Significant differences in VWA's could not be statistically tested, therefore distributional tests were performed. The Kruskal–Wallis test compared ion concentrations between all clusters within a season. For ions with distributions which differed among clusters, two-way cluster intercomparisons were made.

Results presented in these figures and tables are discussed by season in the following sections.

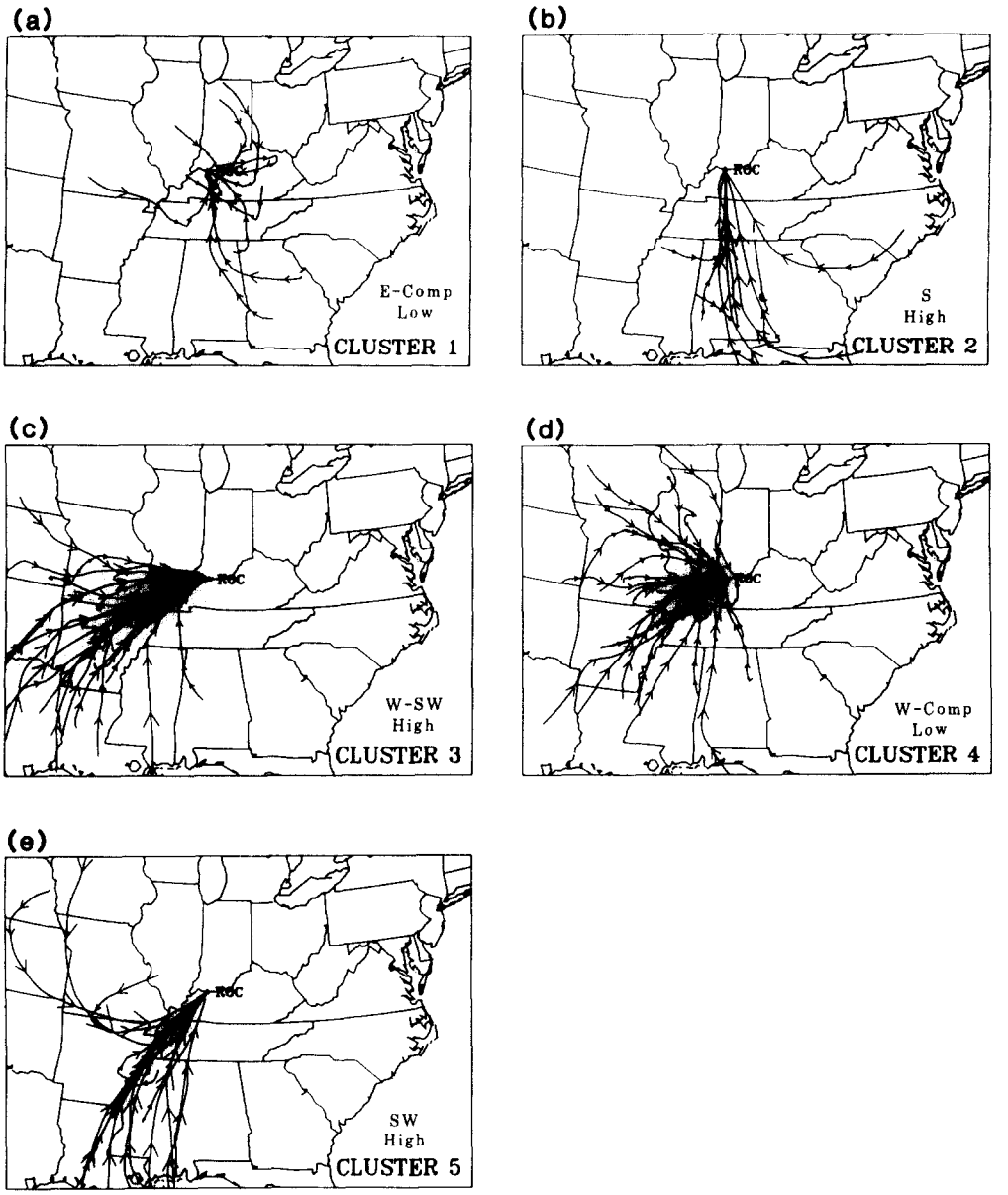


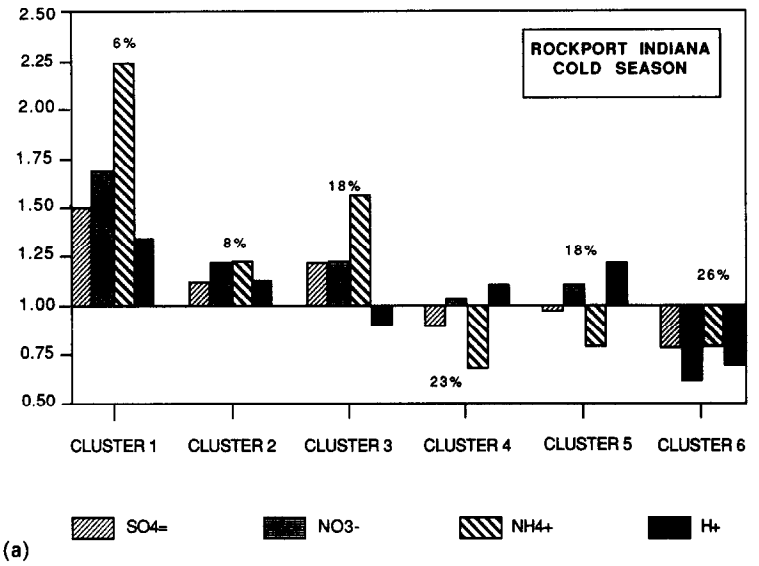
Fig. 4. Cluster depicting similar transport 36 h upwind form layer back trajectories arriving in Rockport during warm season precipitation events; arrowheads denote 6-h intervals. The general wind direction and relative speed associated with each cluster is noted in panels a–e.

Table 2a. Rockport cold season significant meteorological characteristics

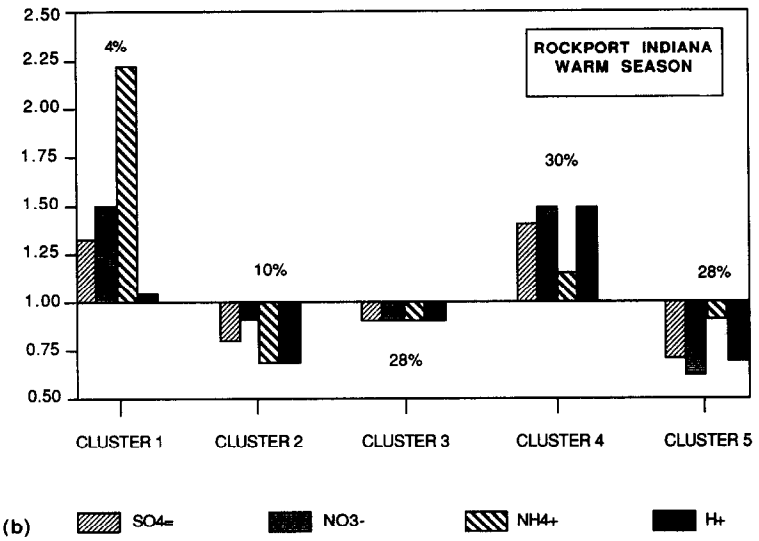
	Transport	Precipitation	Ambient
Cluster 1 $n=9$	From W–NW Low speed	6% Deposition	
Cluster 2 $n=10$	From W–SW High speed	8% Deposition Low amount/event	Low Sfc pressure
Cluster 3 $n=15$	From S–SW High speed	18% Deposition	Low Sfc pressure warm
Cluster 4 $n=16$	E-component Low speed	23% Deposition	High Sfc pressure cold
Cluster 5 $n=16$	From S–SW Low speed	18% Deposition	
Cluster 6 $n=12$	From S–SE High speed	26% Deposition	Low Sfc pressure warm

Table 2b. Rockport warm season significant meteorological characteristics

	Transport	Precipitation	Ambient
Cluster 1 $n=9$	E-component Low speed	4% Deposition Low amount/event Low intensity	Cold and dry
Cluster 2 $n=8$	From S High speed	10% Deposition Low amount/event	Cold and dry
Cluster 3 $n=21$	From W–SW High speed	28% Deposition Large amount/event	
Cluster 4 $n=28$	W-component Low speed	30% Deposition Large amount/event High intensity	Warm and moist
Cluster 5 $n=15$	From SW High speed	28% Deposition	



(a)



(b)

Fig. 5. Relative concentration factors of major ions by (a) Rockport cold season transport cluster, and (b) Rockport warm season transport cluster. These represent the volume weighted average (VWA) concentrations for each cluster normalized by the VWA concentration for the respective season.

Table 3a. Per cent of total ion deposition by Rockport cold season cluster. General wind direction and wind speed characteristics for each cluster are indicated

	C1 W–NW Low	C2 W–SW High	C3 S–SW High	C4 E-comp Low	C5 S–SW Low	C6 S–SE High
H^+	7.8	9.1	16.0	26.0	22.0	18.2
SO_4^{2-}	8.7	9.1	21.2	20.2	18.4	21.3
NO_3^-	10.2	9.4	20.9	22.3	21.6	16.4
NH_4^+	13.2	9.8	26.6	15.6	14.8	19.5
Precipitation	6.0	8.0	18.0	23.0	18.0	26.0

Table 3b. per cent of total ion deposition by Rockport warm season cluster. General wind direction and wind speed characteristics for each cluster are indicated

	C1 E-comp Low	C2 S High	C3 W-SW High	C4 W-comp Low	C5 SW High
H^+	4.0	7.0	23.8	45.9	19.9
SO_4^{2-}	5.0	8.0	25.2	42.9	19.9
NO_3^-	6.0	9.0	24.1	45.0	17.1
NH_4^+	9.0	7.0	24.1	33.9	26.0
Precipitation	4.2	10.0	28.0	30.0	28.0

Discussion of Rockport cold season

The high concentration factors in cold season precipitation (Fig. 4a) were associated with low volume events with transport from the west (clusters 1 and 2). In these events acidity was correlated with NO_3^- only ($r=0.87$ and 0.77, clusters 1 and 2, respectively), while SO_4^{2-} was correlated with NH_4^+. ($r=0.82$ and 0.97, respectively). In contrast, for low speed events with transport from the south southwest (cluster 5), and low speed events with an easterly component (clusters 4), SO_4^{2-} and NO_3^- were both correlated with H^+, and SO_4^{2-} explained more of the variation in H^+ ($r=0.98$ and 0.83, clusters 4 and 5, respectively).

When considering the entire cold season, SO_4^{2-} and NO_3^- were equally important in explaining the variability in precipitation acidity at Rockport (H^+ vs NO_3^-, $r=0.82$; H^+ vs SO_4^{2-}, $r=0.75$). However, the cluster results suggests ion relationships depend on transport. An important factor influencing these results may be the NH_4^+ concentration. Both Fig. 5a and statistical tests illustrated an apparent transport bias in NH_4^+, with concentrations highest in clusters 1, 2 and 3, and lowest in clusters 4, 5 and 6. Sulfate exhibited a similar pattern, suggesting that the SO_4^{2-} in clusters 1, 2 and 3 was present as an NH_4^+ salt.

Clusters 3 and 5 describe similar transport direction (southerly) but different transport speed (high and low, respectively). The low speed southerly events (cluster 5) were significantly more acidic. This cluster deposited 22% of the cold season acidity at Rockport over the 2 years. This illustrates that significant differences in concentration were correlated with differences in transport speed as well as direction.

Cluster 6 events were uniformly low in concentration and occurred with relatively high transport speeds. However, these events also delivered the largest fraction of cold season precipitation, suggesting other factors like dilution could play an important role. The greatest single contribution to cold season acid deposition at Rockport came from low speed events with an easterly transport component (cluster 4), which delivered 26% of the H^+.

Discussion of Rockport warm season

In the Rockport warm season, ion concentrations were relatively enhanced in clusters 1 and 4 (Fig. 5b). There were extremely high concentrations of NH_4^+ in low speed transport with an easterly component (cluster 1, Fig. 4a). The flow pattern associated with these events suggests an agricultural source of NH_4^+ over Kentucky and Tennessee. In spite of high concentrations, these events accounted for $<10\%$ of warm season ion deposition (Table 3b). A major fraction (46%) of the warm season acid deposition was delivered in low speed events with a westerly component (cluster 4). The acidity of these events was correlated with both SO_4^{2-} ($r=0.98$), and NO_3^- ($r=0.90$).

Clusters 1 and 4 were defined by different air mass characterisitics, precipitation characteristics and transport directions, however, they both exhibited relatively stagnant transport across regions of high emissions density. By comparison, in clusters 2, 3 and 5, which were all characterized by relatively high speed transport, concentrations were lower.

Stagnation has been recognized as an important factor leading to high concentrations of ambient SO_4^{2-}

aerosol (SURE, 1980). Recently, Haagenson *et al.* (1986) found that upwind stagnation also correlated with higher pH values in precipitation collected during the Acid Precipitation Experiment. Additionally, they found that the SO_2 content of the dry air upwind (calculated along trajectories) was significantly negatively correlated with pH. These results indicate the importance of upwind pollutant burden in determining precipitation acidity.

Another important factor which explained some of the variance in precipitation composition was the occurrence of upwind precipitation. The warm season data were stratified into events in which no precipitation fell within 12 h upwind of the time of maximum precipitation intensity, and events when it did. Based on this stratification alone, the concentrations of all ions in warm season events were significantly more concentrated when no upwind precipitation had occurred. These results are similar to Draxler's (1983), who found that the average rainfall amount along mixed layer trajectories describing transport to Washington, D.C. was significantly correlated with pH. The greater the amount of precipitation en route along the trajectory, the lower the acidity measured at the receptor. While there was no significant linear correlation with the upwind precipitation *amount* for the data used in the present study, its *occurrence* was important.

In high speed transport from the S (cluster 2) and W–SW (cluster 3), precipitation occurred upwind in 50% and 55% of the events, respectively. For both these transport patterns, when no upwind precipitation had occurred, the events were significantly more acidic. In high speed flow from the SE (cluster 5), concentrations of NH_4^+ and SO_4^{2-} were significantly higher when no upwind precipitation had occurred. This illustrates the importance of considering removal processes en route to a receptor.

The coincident dependence on upwind stagnation, and upwind precipitation exhibited in the Rockport warm season data tend to suggest that the warm season SO_4^{2-} was partially present as acid aerosol. If the rapid aqueous production of SO_2 were primarily important, one would not expect dependence on these parameters which are important in the formation and removal of particulate SO_4^{2-}.

Comparison between Rockport seasons

Visual comparison of Figs 3 vs 4 suggests that similar transport situations occurred in both seasons. The following discussion explores the seasonal differences in analyte concentration distributions for similar transport situations.

Maritime tropical flow. Figure 3c from the cold season, and Fig. 4e from the warm season exhibited qualitatively similar flow features. Both transport patterns were associated with relatively high wind speed, southerly transport generally following the Mississippi River from the Gulf of Mexico to Rockport. When the chemistry for these two transport situations was compared, there were no significant differences in the distributions of the four major ions. Thus the general pattern of higher SO_4^{2-} concentrations in the warm season noted for this site did not hold for this transport pattern.

Westerly flow. Figures 3b and 4c suggest similar high speed transport from the west in both seasons. Again, the concentration distributions for these two similar transport situations were not significantly different.

Stagnant easterly flow. Figures 3d and 4a indicate situations of relatively low wind speed flow from the east of Rockport occurred in both seasons. In this pattern, concentration distributions for the two seasons did show significant differences in composition. The concentrations of SO_4^{2-} and NH_4^+, in particular, were much higher under this transport situation in the warmer months. There were no significant differences in precipitation amount. The difference between warm and cold season concentrations of SO_4^{2-} were pronounced under these low wind speed conditions.

Stagnant westerly flow. Figures 3a and 4d indicate transport patterns in both seasons when the wind speeds were relatively low and arrived at Rockport from the west. The concentration distributions of NO_3^-, SO_4^{2-} and H^+ were significantly more concentrated in the warm season events, and there was no significant difference in the per event precipitation amount. Here again the warm season increase in SO_4^{2-} concentration was associated with lower wind speed conditions en route to the Rockport site.

This comparison of similar transport situations between seasons has shown that seasonal differences in the concentration distribution of SO_4^{2-} at Rockport were primarily associated with particular meteorological situations. Only those transport situations associated with lower wind speeds resulted in significantly higher warm season SO_4^{2-} concentrations, and higher weighted mean concentrations.

The seasonal difference in concentrations under stagnant conditions could be due to increased photochemical activity in the warm season over the relatively high emissions area surrounding the Rockport site. Alternatively, warm season clouds could have been more efficient at scavenging SO_4^{2-}. Another possibility is that enhanced vertical transport in the warm season could have made more of the local emissions available to the cloud environment.

The lack of a seasonal dichotomy in the higher wind speed transport situations may have resulted from transport from areas of lower emissions density. This type of analysis needs to be performed on more data to draw further conclusions.

GAYLORD RESULTS

The same type of analysis was performed for the Gaylord data. Six clusters were formed from the 94 cold season events. They have been plotted in Figs

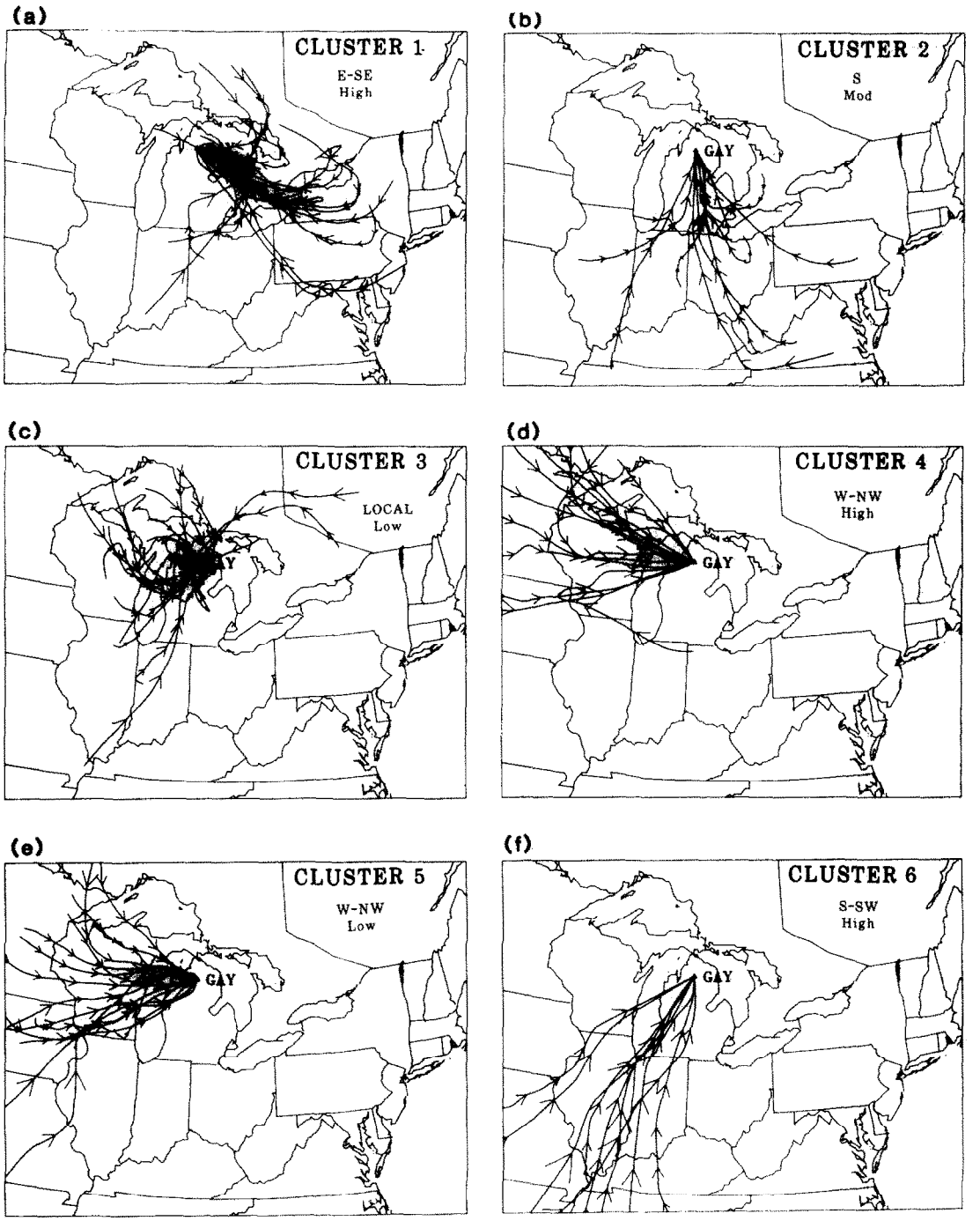


Fig. 6. Clusters depicting similar transport 36 h upwind formed using mixed layer back trajectories arriving in Gaylord during cold season precipitation events; arrowheads denote 6-h intervals. The general wind direction and relative speed associated with each cluster is noted in panels a–f.

6a–f. Using warm season data, 100 events were grouped into four transport clusters, depicted in Figs 7a–d. Meteorological characteristics by season are summarized in Table 4a and 4b. The RCFs are plotted in Figs 8a and b, and total ion depositions by cluster have been summarized in Tables 5a and b.

Discussion of Gaylord cold season

In cold season cluster 2, with relatively slow transport out of the south, deposition of ions was significantly enhanced (Fig. 8a). This cluster was significantly more acidic than every other cluster, and NO_3^-

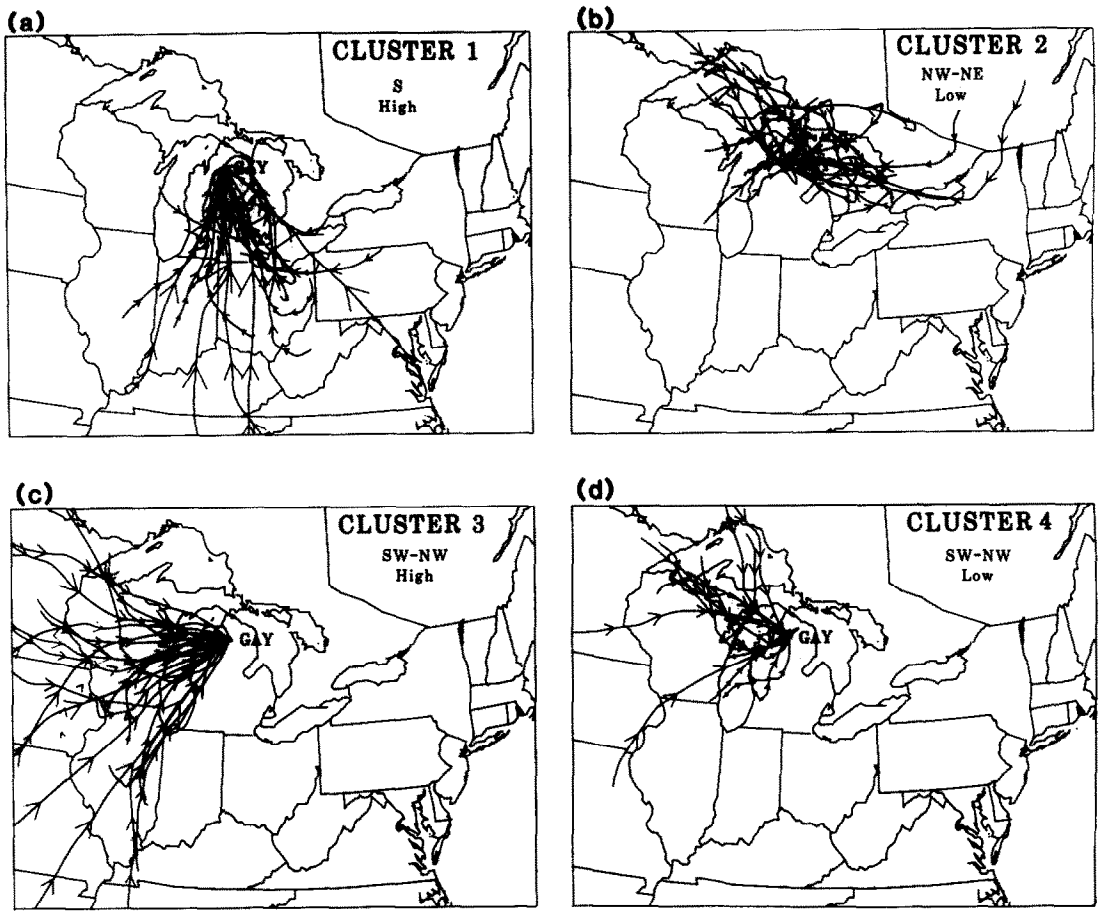


Fig. 7. Clusters depicting similar transport 36 h upwind formed using mixed layer back trajectories arriving in Gaylord during warm season precipitation events; arrowheads denote 6-h intervals. The general wind direction and relative speed associated with each cluster is noted in panels a–d.

was more concentrated in these events. Only NO_3^- was correlated with the H^+ ($r=0.80$), while SO_4^{2-} was correlated with NH_4^+ ($r=0.89$). Similarly, in the relatively low wind speed flow from the W–NW (clusters 3 and 5) only NO_3^- was correlated with acidity ($r=0.91$, $r=0.89$, respectively). By comparison, in relatively high speed flow from the E–SE (clusters 1), H^+ was more correlated with SO_4^{2-} ($r=0.81$) than NO_3^- ($r=0.57$). Events with very rapid transport from the south (cluster 6), were distinguished by high concentrations of SO_4^{2-} and NH_4^+ while NO_3^- and H^+ concentrations were low. This suggests the SO_4^{2-} was present as an aged aerosol.

Together, transport from the S, and E–SE (clusters 1 and 2) delivered almost 50% of the cold season acid deposition to Gaylord in 1982 and 1983 (Table 5a). Low speed flow from the W–NW (cluster 5) also made a significant contribution to ion deposition (20%) on the basis of precipitation volume. Concentrations for these events were relatively low. Cluster 4 events, with high speed transport from the W–NW were very clean, with the lowest relative concentrations and depositions for the season.

Statistically significant differences were noted in the chemical composition of the categories defined by this cluster analysis. It was shown previously that significant differences in the chemical composition of Gaylord cold season events were related to precipitation type. In most of the trajectory-defined clusters, there were relatively equal distributions of snow and rain events (with the exception of events with high speed flow from the SW, cluster 6, where 70% of the events were rain). When the events within these clusters were further stratified by precipitation type, there were no significant differences in the ion concentration distributions. This emphasizes the relative importance of transport over precipitation type in determining chemical concentrations. As with the Rockport cold season events, there were no significant relationships between concentrations and the occurrence of upwind precipitation during Gaylord cold season events.

Discussion of Gaylord warm season

During the warm season at Gaylord, high speed transport from the south, and SW–NW (clusters 1 and 3) deposited more precipitation per event, and the

Table 4a. Gaylord cold season significant meteorological characteristics

		Transport	Precipitation	Ambient
Cluster 1	$n=18$	From E–SE High speed	25% Deposition 52% Frozen	High Sfc pressure
Cluster 2	$n=9$	From S Moderate speed	10% Deposition 58% Frozen	Low Sfc pressure warm and pressure
Cluster 3	$n=17$	Local W–NW Low speed	20% Deposition 50% Frozen Low intensity	Low Sfc pressure
Cluster 4	$n=14$	From W–NW High speed	10% Deposition 56% Frozen	Cold and dry
Cluster 5	$n=15$	From W–NW Low speed	20% Deposition 54% Frozen	Warm
Cluster 6	$n=9$	From S–SW High speed	16% Deposition 33% Frozen	Warm and moist

Table 4b. Gaylord warm season significant meteorological characteristics

		Transport	Precipitation	Ambient
Cluster 1	$n=23$	From S High speed	33% Deposition Large amount/event High intensity	Low Sfc pressure
Cluster 2	$n=19$	From NW–NE Low speed	12% Deposition Low amount/event Low intensity	High Sfc pressure Cold
Cluster 3	$n=27$	From SW–NW High speed	32% Deposition Large amount/event High intensity	Low Sfc pressure
Cluster 4	$n=29$	From SW–NW Low speed	22% Deposition Low amount/event Low intensity	Cold and dry

precipitation occurred with significantly greater intensity relative to events in clusters 2 and 4 (Table 4b). Sulfate and H^+ concentrations were significantly higher in southerly flow, cluster 1, relative to every other transport pattern. The relative concentration factors were greatest in cluster 1 (Fig. 8b), although compared with the cold season, there was much less variation in the cluster volume weighted averages relative to the season average.

In all four transport clusters, the acidity was correlated with both NO_3^- and SO_4^{2-}, but SO_4^{2-} explained more of the variance. Similarly, both anions were correlated with NH_4^+, but NO_3^- explained more of the variance. Relatively high speed flow from the south (cluster 1) deposited almost 40% of the warm season acidity (Table 5b). In contrast low speed transport with a northerly component (cluster 2) contributed only 10% to warm season acid deposition in Gaylord.

Similar to the Rockport warm season results, when precipitation occurred within 12 h upwind along warm season trajectories, concentrations of NO_3^- and NH_4^+ were significantly less than when no upwind precipitation had occurred. However, more precipitation was deposited per event when upwind precipitation occurred, which would contribute to dilution and lower concentrations. No differences based on upwind precipitation were observed once the events were classified into transport clusters.

Comparison between Gaylord seasons

Southerly flow. Figures 6b and 7a events depict transport from southeastern Michigan and Ohio. Comparing these flow patterns between seasons, the cold season events were significantly more concentrated in H^+ relative to warm season events occurring with this transport. This cold season acidity was correlated with NO_3^-. However, warm season events contained significantly higher precipitation amounts per event, which would contribute to dilution. Greater per event ion deposition occurred with the warm season events.

East–northeasterly flow. Relatively similar transport patterns were defined by Figs 6a and 7b. There were no significant differences in the chemical concentrations between seasons. Relative to the seasonal mean values, the cold season event concentrations were above the cold season average while the warm season event concentrations were below the warm season average.

Westerly flow. Figures 6d and 7c were both characterized by relatively rapid transport from the west across Lake Michigan. There were no significant differences in the chemical concentration distributions between seasons. However, there was significantly more precipitation per event and higher depositions in warm season events relative to the cold season events.

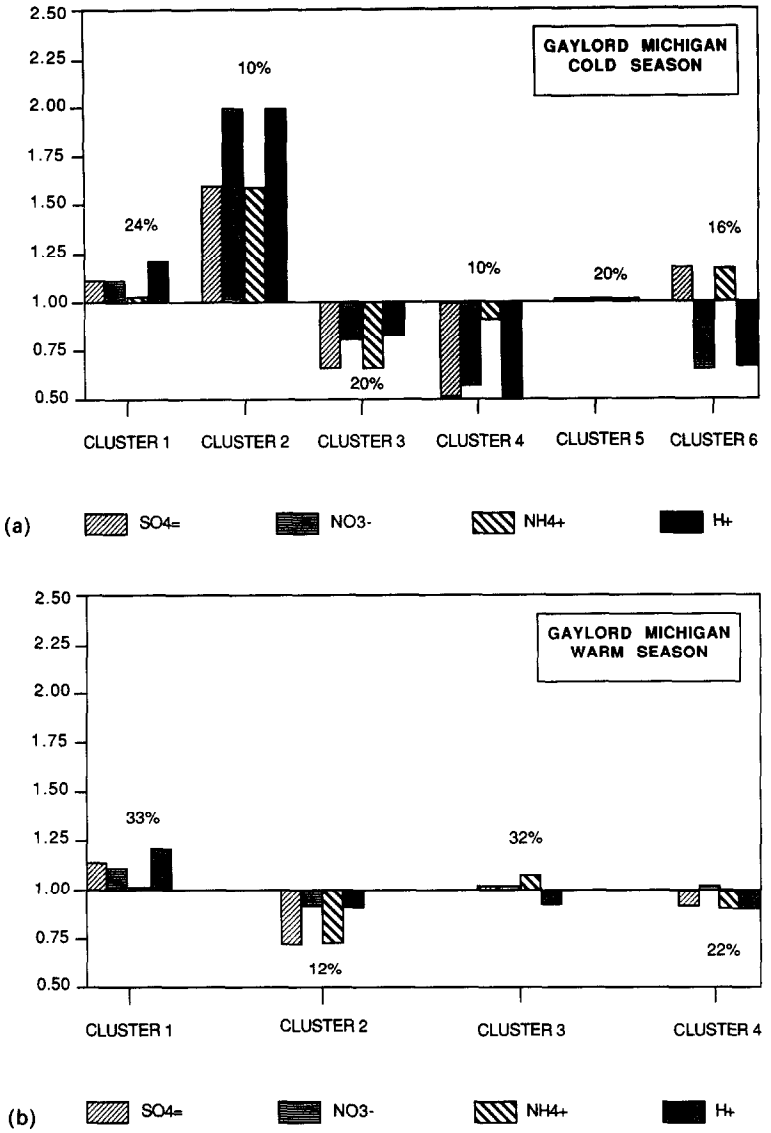


Fig. 8. Relative concentration factors of major ions by (a) Gaylord cold season transport cluster, and (b) Gaylord warm season transport cluster. These represent the volume weighted average (VWA) concentrations for each cluster normalized by the VWA concentration for the respective season.

Stagnant west–northwesterly flow. The clusters in Figs 6c and 7d illustrate relatively localized transport compared to the other clusters. The SO_4^{2-} and NH_4^+ concentrations were significantly higher in warm season events relative to cold season events.

As was observed for the Rockport data, even though on the average SO_4^{2-} and NH_4^+ ion concentrations were higher in the warm season, these differences appear to depend on transport characterisitics. For Gaylord differences in per event precipitation amount also played a role in determining the concentration, with higher precipitation amounts occurring in the warm season.

ANALYSIS OF VARIANCE

In order to identify what fraction of the total variability in ion concentrations for the season could be accounted for by differences in transport pattern, analyses of variance tests were performed. These result in an estimate of the amount of variability between clusters and within clusters. Table 6 contains a measure of the fraction of ion variability that could be accounted for by transport differences between clusters. These fractions represent the ratio of the between cluster variance to the total variance for each ion.

Table 6a illustrates that in both seasons at Rock-

Table 5a. Per cent of total ion deposition by Gaylord cold season cluster. General wind direction and wind speed characteristics for each cluster are indicated

	C1 ESE High	C2 S Mod	C3 W–NW Low	C4 W–NW High	C5 W–NW Low	C6 S–SW High
H^+	30.5	19.5	16.4	4.0	19.2	10.9
SO_4^{2-}	26.8	16.4	13.8	4.6	19.8	18.7
NO_3^-	28.0	19.5	16.6	5.0	20.2	11.4
NH_4^+	25.3	15.6	13.6	7.8	20.6	18.6
Precipitation	25.0	10.0	20.0	9.0	20.0	16.0

Table 5b. Per cent of total ion deposition by Gaylord warm season cluster. General wind direction and wind speed characteristics for each cluster are indicated

	C1 S High	C2 NW–NE Low	C3 SW–NW High	C4 SW–NW Low
H^+	39.6	10.8	28.8	19.8
SO_4^{2-}	37.3	8.4	32.3	19.8
NO_3^-	37.0	10.8	32.3	22.2
NH_4^+	33.3	8.4	35.2	19.8
Precipitation	33.0	12.0	32.0	22.0

Table 6a. Fraction of Rockport ion variability accounted for by differences between transport clusters

	Warm season	Cold season
H^+	27%	16%
SO_4^{2-}	21%	20%
NO_3^-	23%	23%
NH_4^+	13%	37%

Table 6b. Fraction of Gaylord ion variability accounted for by differences between transport clusters

	Warm season	Cold season
H^+	7%	32%
SO_4^{2-}	9%	22%
NO_3^-	7%	20%
NH_4^+	3%	*

* Not significant.

port, the differences in atmospheric transport could account for roughly 20% of the variability in concentrations of SO_4^{2-}, and NO_3^-. Acidity, however, appeared to be more dependent on transport differences in the warm season, with 27% of the variability related to differences between clusters. In the cold season, there was a strong transport bias observed from NH_4^+, with almost 40% of the variability potentially explained by the cluster groupings. However, in the warm season, the NH_4^+ concentrations were much less dependent on transport.

Table 6b contains results from similar tests performed on the Gaylord data. In general, transport differences explained a larger fraction of ion variation in the cold season, when roughly 20% of the SO_4^{2-} and NO_3^-, and 30% of the H^+ could be related to cluster differences. However, no significant fraction of the cold season variability in NH_4^+ could be accounted for by transport differences. This is very different from the Rockport results. In the warm season, a much smaller fraction (less than 10%) of the variability could be accounted for by transport differences.

SUMMARY AND CONCLUSION

These results illustrate that differences in transport potentially account for a significant fraction of variability in the composition of precipitation. However, there was residual variation which could not be related to differences in transport. It was already shown that some of this variability within groups could be accounted for by other processes such as upwind removal and differences in precipitation amount. Several other factors which were not addressed here could also have caused differences in composition even under conditions of similar transport. They include dry deposition rates, chemical transformation rates and the degree of vertical mixing of the atmosphere. However, these results do provide a reasonable estimate of the influence of different upwind regions based on the climatology of mixed layer transport associated with precipitation events for these two sites and years.

At Rockport, the greatest acid deposition was associated with low transport speed. At Gaylord, the greatest acid deposition was influenced more by transport direction than by transport speed. It was basically found that transport differences could identify clusters of events with uniformly low concentrations but not uniformly high concentrations. This is a reasonable result, considering that only wind speed and direction were used to define clusters.

A comparison of clusters between seasons indicated that similar transport situations occurred in both seasons. The significant differences between warm and cold season SO_4^{2-} concentrations were found to result primarily from differences in concentrations under stagnant wind flow conditions, particularly for Rockport. This suggests the seasonality in SO_4^{2-} concentration may be primarily associated with particular meteorological conditions.

In conclusion, these results have demonstrated that it is possible to quantitatively define periods of meteorological similarity, and to do so in a relatively objective manner. Statistically significant differences in the chemical composition of precipitation under different transport situations are indicative of the influence that meteorology can have on precipitation chemistry. These results suggest that transport differences (both wind speed and direction) may explain 10–40% of the variability in ion concentrations. They also indicate that the residual variation (within cluster variability) could be related to upwind stagnation which generally occurred with higher concentrations, upwind precipitation occurrence which potentially influenced lower concentrations, and precipitation amount which was generally inversely correlated with concentration.

This study has shown it is possible to interpret a significant portion of the variability in the chemical composition of precipitation using independent meteorological information. This method of analysis should be useful both for defining the long term chemical climatology for precipitation sites (Moody and Galloway, 1988) and identifying conditions which make the greatest contribution to acid deposition.

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