# REGIONAL TRACE ELEMENT AND SULFATE TRANSPORT

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**Abstract**—The goal of this paper was to investigate the transport of atmospheric sulfate and trace elements across the northeastern U.S.A. Data from a number of sites—Underhill (VT), Whiteface Mountain (NY), Mayville (NY), Laurel Hill and Allegheny Mountain (PA) and Deep Creek Lake (MD)—in August 1983 were considered. Sulfate was found to be regional in nature, displaying temporal variations which were similar at sites separated by large distances (several hundred kilometers) under certain meteorological conditions. Selenium was the only trace species investigated which displayed a regional character, though it too was influenced by local sources. Other elements, such as As and V displayed a somewhat regional nature but less than that observed for sulfate and selenium.

The 5-day period 16–20 August, a period of elevated sulfate at all sites, was investigated as to the generality of regional signatures, utilizing trace element ratios. The inter-site variabilities in elemental ratios among the Allegheny, Laurel, Deep Creek and Mayville sites were generally small (a factor of 2 or less) and well within the variabilities at a given site from one day to another. But there were exceptions, probably reflecting influences of local sources. Comparison with earlier trace-element data from the same region suggests that temporal variations may be less than spatial ones. Together the data indicate that it is important to obtain data from multiple sites and periods within a region in any effort to construct a regional signature.

An unusually clean period, 13–15 August, with steady air mass advection from the northeast to all sites, was investigated to evaluate the conservation of regional signatures into downwind regions. The inter-regional differences in trace element ratios proved to be far larger than the intra-regional ones—an order of magnitude in some cases, attributable mostly to addition of trace elements in the downwind region. The ability to identify in one region the signature from another region appears to be problematic. However, aerosol trace element ratios are found to be a powerful tool for investigating regional source influences when used in concert with meteorological information.

*Key word index*: Long-range transport, aerosols, size distributions, trajectories.

## INTRODUCTION

The results of major field measurement studies have documented the regional nature of elevated $SO_4^{2-}$ and haze episodes in the northeast U.S.A. (Lioy *et al.*, 1980; Mueller *et al.*, 1980). These studies primarily investigated the transport of $SO_4^{2-}$ and $SO_2$ at multiple sites across the northeast region. In this present work, the availability of trace element and $SO_4^{2-}$ measurements obtained simultaneously at multiple sites in the Northeast (Fig. 1) provides an opportunity to investigate the relationship between $SO_4^{2-}$ and trace elements transported in the atmosphere.

Previous studies have indicated sulfate concentrations that were similar at several northeastern sites separated by hundreds of kilometers (Lioy *et al.*, 1980; Pierson *et al.*, 1980, 1989; Stevens *et al.*, 1978; Tanner *et al.*, 1981). This pattern is apparent in the sulfate plots for six sites in the northeastern U.S.A. in August 1983 (Fig. 2). The sulfate concentration went through a general pattern of elevated sulfate concentrations at the beginning of the month followed by a relative minimum in concentration. This pattern was then repeated twice over the course of the month. The periods of elevated sulfate concentration were 3–5 days in duration. The widths of the relative maxima in concentration ($\sim 3$ days) were shorter for the three easternmost sites. The sites closer to the Midwest had elevated concentrations for longer durations ($\sim 3$–5 days). The peak concentrations were larger at the latter sites as well.

In an attempt to understand the variations in sulfate and trace element concentration, two contrasting periods are examined in more detail later in this paper. The first period (13–15 August 1983), indicated on Fig. 2 by the stippled band, was a relatively clean period at all of the sites, with air flow from the northeast. The second period of interest (16–20 August 1983), which followed directly after the first, was a relatively polluted period, with flow to the sites from the southwest.
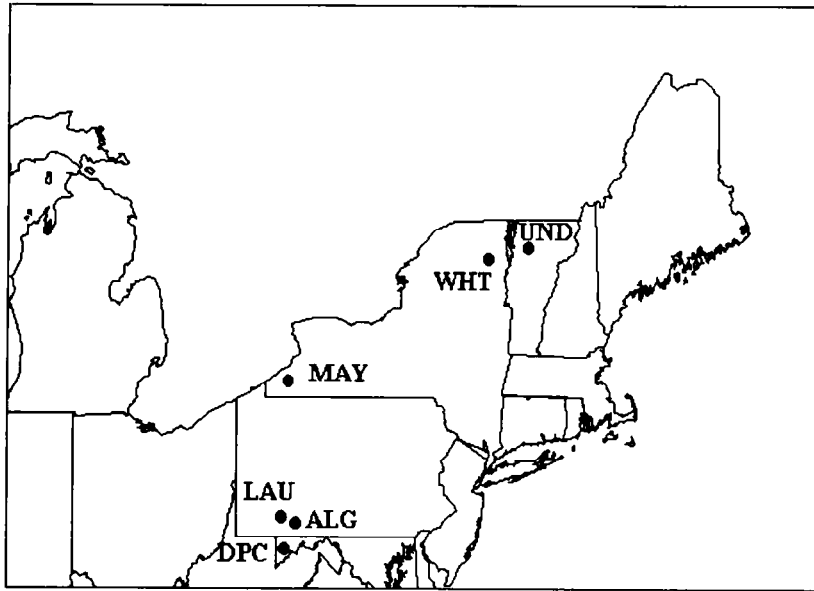
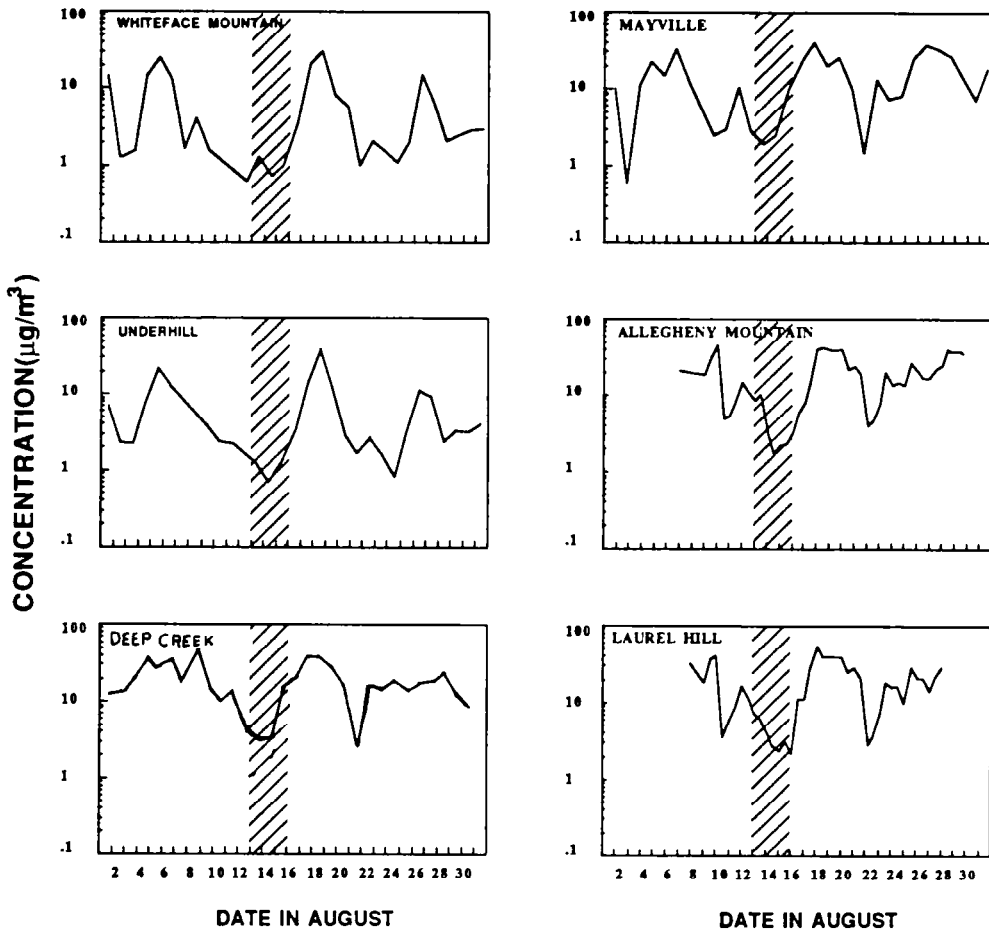Fig. 1. Location of northeastern U.S.A. sampling sites used in this study.



Fig. 2. Temporal variability in sulfate concentrations at six northeastern sites in August 1983. The hatched bar indicates the clean period with northeast winds at all sites.

*Inter-site correlations—five northeastern sites*

Trace element and sulfate data taken at each of six sites—Underhill (VT), Whiteface Mountain (NY), Mayville (NY), Laurel Hill (PA) and Allegheny Mountain (PA) and Deep Creek Lake (MD)—during August 1983 were investigated using simple correlation analysis and lag-correlation analysis. Inter-site sulfate correlations had been investigated (Mueller *et al.*, 1983) as part of the Sulfate Regional Experiment (SURE) using daily sulfate concentrations at a large number of sites across the northeastern U.S.A. The present analysis is, to our knowledge, the first to explore the inter-site correlations for trace element species as well as sulfate. The limitation in our analysis, as compared to the SURE analysis, was in the number of measurement sites available for comparison (nine SURE versus six here) and the length of sampling time (several months versus one month).

The spatial correlation patterns for the elements can be compared to one another and to sulfate to determine if any source inter-relationships exist. The inter-site correlations for sulfate and selenium will be discussed first, and then compared to the correlations found for the other elements of interest. The number of complete days for each of the sites was 20 (6–26 August). Therefore, all correlations discussed here are for the 20 observations in which data were complete for all of the sites.

Figure 3 shows the correlations between the sulfate concentrations measured at Underhill, VT, and the sulfate concentrations at the other sites. The strongest correlation for this site ($r = 0.95$) was found with the Whiteface Mountain site, located only 80 km from the Underhill site. This would be expected if the sources of the sulfate were located further upwind than the separation of the two measurement sites. The second highest correlation was found with the Allegheny Mountain and Laurel Hill, PA, sites ($r = 0.61$). Only one correlation coefficient is shown since the correlations were nearly identical between Underhill and each of these two sites. This relatively high correlation was rather surprising as Allegheny/Laurel are the furthest two of the sites from Underhill, VT. The sulfate measured at the Mayville site displayed a marginal correlation with the Underhill sulfate ($r = 0.48$).

Figure 3 also shows the correlation between the selenium concentration at Underhill and selenium at the other sites. The strongest correlation was again observed with the Whiteface Mountain site, though the degree of correlation was slightly less than for sulfate. Close inspection of the data reveals that this may simply reflect a difference in analytical sensitivity in the measurement of selenium by the two different laboratories. The correlations for the other sites shown actually increased slightly (though probably not significantly) for selenium relative to the sulfate correlations. Figure 3 indicates that the sulfate and selenium behave similarly at the sites being discussed, at least during this one month period.
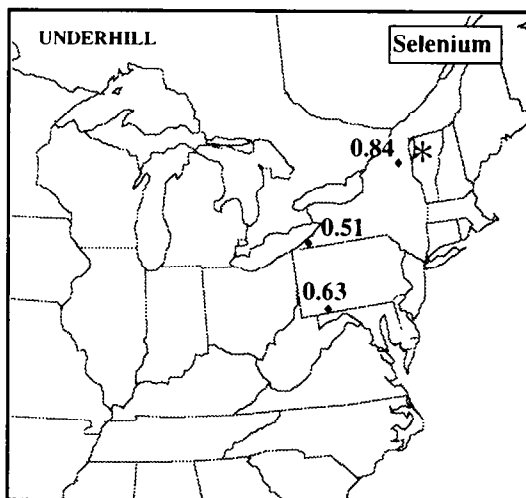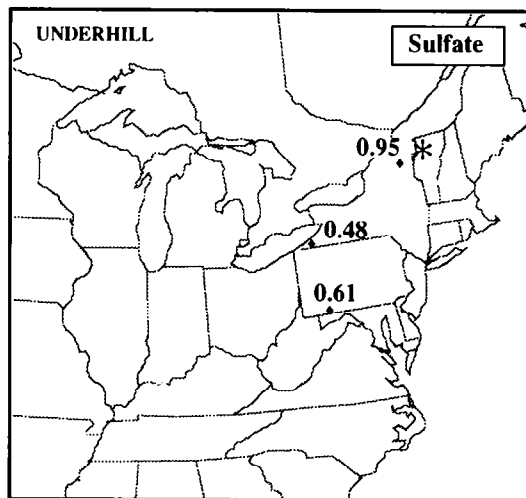


Fig. 3. Inter-site correlations of daily particulate sulfate and selenium centered on the Underhill, VT, site, August 1983. Laurel Hill is omitted since its results are substantially identical to those at Allegheny Mountain.

The inter-site correlations centered on the Mayville, NY, site are shown in Fig. 4. By far the best correlation for sulfate at this site was with the Allegheny/Laurel sites. Indeed, the correlations with the Whiteface and Underhill sites for sulfate were only marginal. A similar pattern was observed for selenium, except that the correlation with Allegheny/Laurel dropped considerably. One obvious possible explanation for the drop is as follows. The relatively high correlation for sulfate is consistent with the regionality of the sulfate, i.e. the sulfate measured at the Mayville and Allegheny/Laurel sites is a secondary material created gradually over a time long enough for widespread dispersion. The smaller correlation for selenium may indicate that either the Mayville site or the
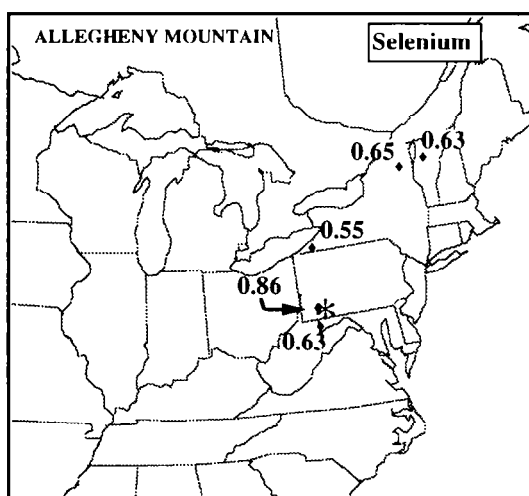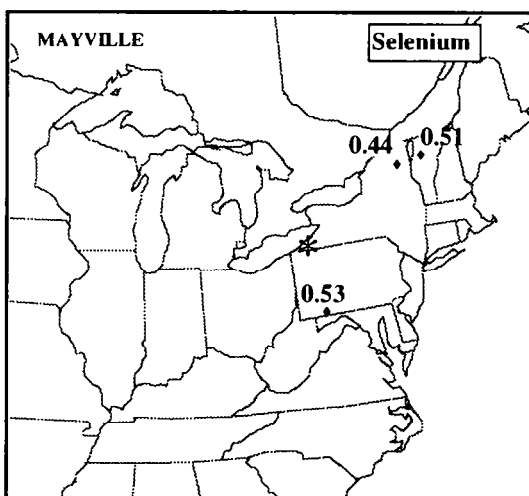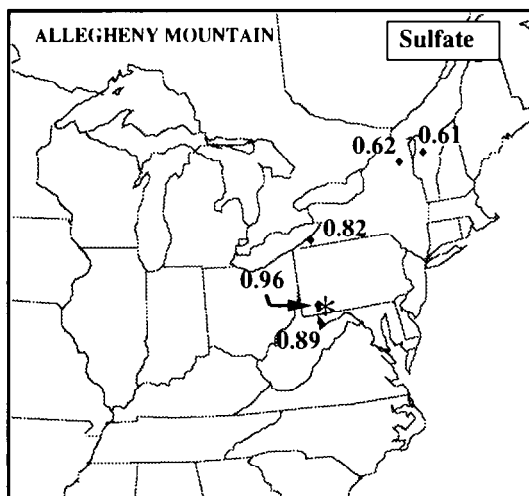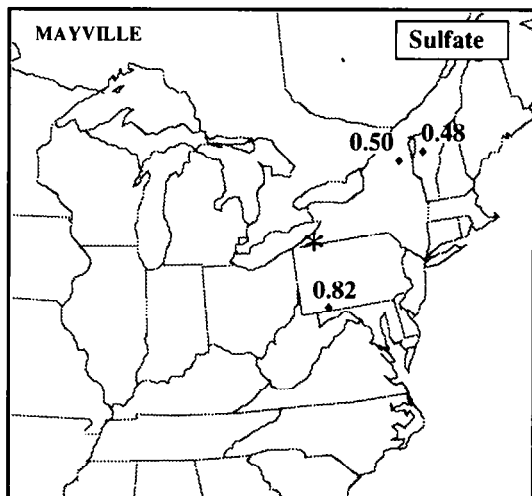
Fig. 4. Inter-site correlations of daily particulate sulfate and selenium centered on the Mayville, NY, site, August 1983. Laurel Hill is omitted since its results are substantially identical to those at Allegheny Mountain.

Fig. 5. Inter-site correlations of daily particulate sulfate and selenium centered on the Allegheny Mountain, PA, site, August 1983. Deep Creek Lake has also been included.

Allegheny/Laurel sites were periodically being influenced by a nearby selenium source, such as a coal-fired power plant. [There are seven large (> 1000 MW) coal-fired power plants within 100 km of Allegheny/Laurel/Deep Creek Lake.] The influence of these nearby power plants would degrade the selenium correlation but not the sulfate correlation. $SO_2$ emitted along with the Se would not have time to be converted into $SO_4^{2-}$ before reaching the sites.

Last, the inter-site correlations for sulfate and selenium centered about the Allegheny Mountain site are shown in Fig. 5. This time the Laurel Hill site was included separately and the site at Deep Creek Lake, MD (Vossler et al., 1989) was added to give an idea of the scale of correlation that can be expected in this area. The sulfate correlation between Allegheny and Laurel (35.5 km apart) was 0.96, and between Allegh-

eny and Deep Creek (59 km apart), 0.89. While the sulfate concentrations were slightly higher at Laurel than at Allegheny, the temporal behavior was almost identical for these two sites. A strong correlation is also seen with the Mayville site. Moderate correlations were seen for the Whiteface and Underhill sites.

Compared to sulfate, the selenium inter-site correlation centered on Allegheny was lower between Allegheny and Laurel (0.86), and much lower between Allegheny and Deep Creek Lake or Mayville (0.63, 0.55). Again, these sites were most likely influenced by the nearby power plants which would degrade the selenium correlation but not the sulfate correlation. One can be convinced on the basis of continuous $SO_2$ data that Laurel and Allegheny were indeed being influenced by power plant plumes. $SO_2$ concentrations reached over 100 ppb on several days with short

duration spikes of 20 min or less. No continuous $SO_2$ data exist for the Mayville site, however.

The inter-site correlations for other trace elements centered about each site for the 20 days were also calculated. Only As and V were significantly correlated between sites for the period studied. The As concentration measured at Underhill and Whiteface was moderately correlated ($r = 0.70$) but less than Se and sulfate. This was also true for As measured at the Allegheny and Laurel sites which had a correlation of $r = 0.77$. The second highest correlation found with the Allegheny Mountain and Laurel Hill, PA, sites was with the Whiteface Mountain site ($r = 0.61$). This moderate correlation was rather surprising as Allegheny/Laurel are two of the furthest of the sites from Whiteface. The As measured at the Mayville site displayed a weak and non-significant correlation with both the Underhill site $r = 0.34$ and the Whiteface Mountain Site ($r = 0.12$). The arsenic correlation between Mayville and the closer Allegheny and Laurel sites was also not significant ($r = 0.23$).

Vanadium measured at the six sites during the month of August also displayed some regional character during specific transport periods. Vanadium, however, displayed a somewhat different behavior than sulfate, selenium, or arsenic. However, the use of correlation analysis to investigate the regional nature of vanadium may be more limited in this study due to the limited transport during the month from the northeast where vanadium emissions are more extensive. The best vanadium correlation observed was between Mayville and Underhill ($r = 0.81$). Curiously, this correlation was better than that observed for sulfate and Se. Mayville and Allegheny Mountain vanadium were only moderately correlated ($r = 0.49$) as was Allegheny with Underhill ($r = 0.55$). Clearly, both arsenic and vanadium are transported on distance scales similar to sulfate and Se (Keeler and Samson, 1989), but it appears that local influences in the Northeast are sufficient to degrade the day-to-day correlation between sites.

### Time-lagged inter-site correlations

An analysis of time-lagged correlations was carried out with the daily sulfate concentrations. If air mass transport was significant during the month of August, time-lagged inter-site correlations should be greater than the correlation coefficients presented earlier. If long-range transport was as dominant a factor as has been reported for the SURE experiment, then a peak in the correlation coefficient at a lag time corresponding roughly to the transport time between sites should be evident. Since the sulfate concentrations are daily samples and transport times would rarely occur in multiples of days, the true transport time to concentration relationship may be hidden.

The time-lagged correlations for sulfate concentrations between the Underhill site and the Mayville, Whiteface Mountain and Allegheny/Laurel sites were

determined. As expected, the 1-day lag correlation with Allegheny/Laurel was the same as that calculated for a zero lag time. The inter-site correlation between Underhill and Mayville increased to 0.67 from 0.48 with a lag time of 1 day. The implied transport time of about 1 day between Mayville and Underhill is not unreasonable based upon the mixed layer wind speeds recorded during the period.

The selenium lag correlations again showed a somewhat similar pattern. Allegheny and Laurel were found to have the largest correlations to one another with zero lag times. The inter-site correlations for the Whiteface and Underhill sites increased with a lag time of 1 day, but the increase was greater. The lag correlations for Se between the Mayville and Whiteface and Underhill sites were 0.66 and 0.67, respectively. These inter-site correlation coefficients were equal to the lag correlation coefficients found for sulfate at the Whiteface and Underhill sites.

The analysis just presented is limited in several ways. Daily samples mask the variations due to rapidly changing atmospheric processes, and hence limit our understanding of the transport and chemistry taking place. While it is extremely difficult to compile one month of trace element and other pollutant data which are of high quality, a month of data is probably not enough to investigate adequately the inter-site trace element and sulfate fluctuations. The time-lag correlation analysis is limited in that there were too few cases if one attempts to stratify the data into periods of similar transport, e.g. transport from the Midwest to the Whiteface Mountain site. If the number of cases was larger, these cases could then be investigated to see if the correlation coefficient did peak at specific lag times. However, statistical analysis may yield meaningless results when working with such small sample sizes, i.e. $n = 5$. Time-lagged correlations were found to be difficult to interpret in the SURE analysis and other methods of investigating transport processes were utilized (Henry and Hidy, 1983).

### Elemental ratios used to identify source regions

The trace element content of aerosol particles may be useful in diagnosing the sources of these aerosols. The development of regional signatures several years ago (Rahn and Lowenthal, 1984, 1985) stirred up considerable controversy at the time as to the applicability of these signatures in apportioning distant and local ambient sulfate. The basis for the regional signatures was the idea that regional differences in fuels (coal vs oil for example), industrial types and land use were sufficiently different to give certain regions a characteristic mixture of trace elements. While air masses can have distinctive trace element compositions (Husain et al., 1984), problems arise in determining regional signatures in cases where the emissions of one area mix with the emissions of another area.

The task of determining the signature for a complex source region is not an easy one. A seven-element

tracer system proposed by Rahn and Lowenthal (1984) was based upon the assumption that the elemental ratios of V, non-crustal Mn, Zn, As, In and Sb to Se can uniquely characterize large regions of North America. Rahn and Lowenthal's method for determining the source signatures involved taking daily high-volume samples of aerosol at several sites thought to be regionally representative, i.e. non-urban sites with no strong local sources. Frequency distributions were then constructed over a selected set of samples, as shown in Fig. 6. Surface meteorological maps were used to explain the various modes found in the frequency distributions, i.e. to determine whether the mode represents local or transported aerosol. Rahn and Lowenthal also used surface maps to identify periods of local stagnation, and then they calculated ratios for only those samples to estimate the "signature" for the region of the sampling site.

For example, Rahn and Lowenthal's *Upper Midwest* (UMW) signature was determined from aerosol samples collected at two sites, Hartville and McArthur, OH. The As/Se ratio was found to have the clearest modes, and is shown in Fig. 6. The UMW signature was calculated by combining those samples which fell into the upper two As/Se modes seen in this figure. Samples which were determined to be unrepresentative, owing to "anomalously" high non-crustal V/Se ratios or Sb/Se ratios, were removed from the grouped samples.

Rahn and Lowenthal's *Lower Midwest* (LMW) signature was determined from aerosol samples taken on the tower at Allegheny Mountain from 10 to 25 August, during the middle of the 1983 Allegheny–Laurel Experiment, using a high-volume sampler with no size segregation. The LMW signature was then generated from those samples taken only from the 16–20 August period, a period of high sulfate concentration at all sites (Fig. 2). Simultaneously, Pierson *et al.* (1989) employed dichotomous samplers to measure

the trace element content of the ambient aerosol segregated into fine (aerodynamic diameter $< 2.5 \mu$m) and coarse (aerodynamic diameter 2.5–10 $\mu$m) size fractions.

It is instructive to look at the frequency distributions of the elements in the Rahn and Lowenthal tracer system as determined from the dichotomous sampler data at Allegheny and Laurel. In this way, it can be determined whether or not the sampling method biased the observed elemental ratios. Ratios calculated using only the fine fraction samples can be compared to the ratios calculated using the total aerosol samples to determine the sensitivity of the ratios to size fraction. Figure 7 shows the frequency distribution of the total (fine plus coarse) As/Se concentration ratio as measured on dichotomous sampler filters at Allegheny Mountain and Laurel Hill. While there does appear to be a mode corresponding to the *Lower Mode* shown in Fig. 6, there is no strong evidence for an *Upper Mode* in this figure. This was also true when looking at the aerosol data obtained at Deep Creek Lake during the same period (Vossler *et al.*, 1989). The aerosol was overwhelmingly Lower Midwest in nature. Rahn and Lowenthal determined that the upper mode in Fig. 6 is representative of the Upper Midwest Region. They suggested that the lower mode was probably indicative of a mixed aerosol from their Upper and Lower Midwest regions. This assessment is probable as the "typical" air mass arriving at Allegheny Mountain should pick up some of the "Lower Midwest's" emissions. From the limited amount of data discussed in the present analysis, it appears unlikely that the Upper Midwest signature and Lower Midwest signature could ever be independently observed in this part of southwestern Pennsylvania.

To investigate this further, the frequency distributions (not shown) of the ratios of all six tracer species to Se were plotted for these two sites. There is no
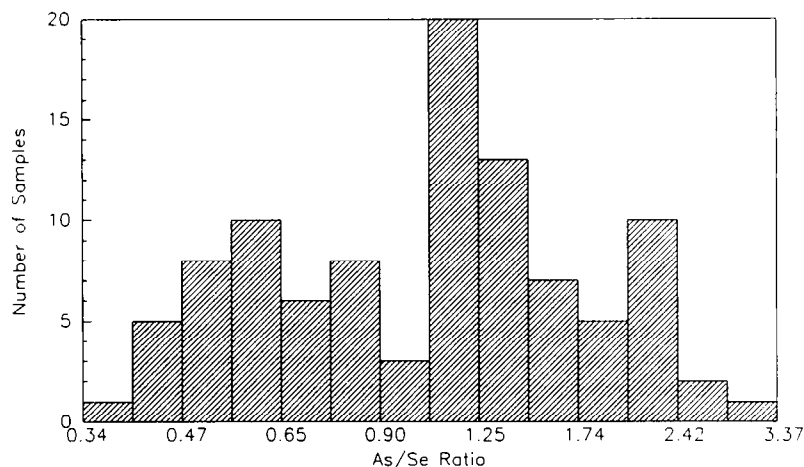


Fig. 6. Logarithmic frequency distribution of As/Se in aerosol samples from McArthur and Hartville, OH, January–March 1984. (After Rahn and Lowenthal, 1984).
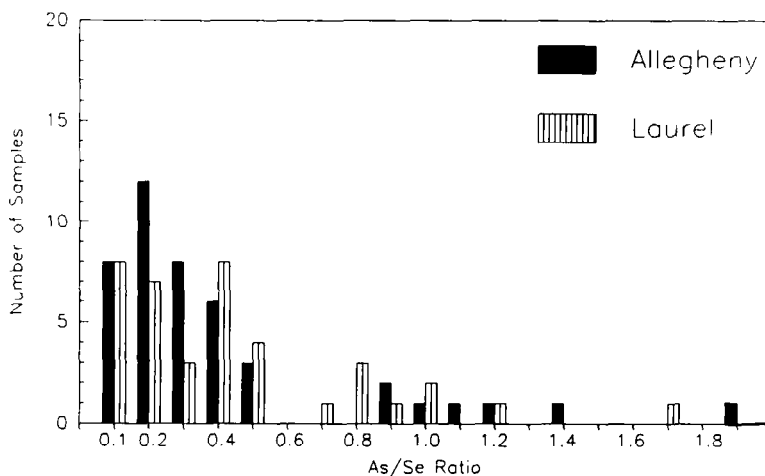
Fig. 7. Frequency distribution of As/Se in aerosol samples measured at Allegheny and
Laurel during August 1983.

evidence at Allegheny and Laurel for bimodal dis-
tributions for any of the ratios. While the distributions
observed were for fine-fraction elemental ratios, there
was no significant difference when the total aerosol
(fine + coarse fractions) was used in the calculations.
The exception to this was the In/Se ratio, which was a
factor of 2 higher when the total aerosol concentra-
tions were used. Tuncel (1986) and Dutkiewicz et al.
(1987) performed similar analyses on data obtained at
various sites and also failed to observe bimodal dis-
tributions in the six elemental ratios to Se.

Rahn and Lowenthal defined the Lower Midwest
(LMW) signature from 5 days of sampling at Allegh-
eny Mountain, PA, 16–20 August. This signature is
thought to be representative of the coal-combustion
aerosol from the Lower Midwest area. In determining
a region's signature, the specific location of the sam-
pling site within the region should be unimportant,
except that the site must be representative. Elemental
ratios were calculated from samples taken simultan-
eously at four sites over the 5-day period to determine
the inter-site variability in the regional signatures, i.e.
how representative the signature is when determined
at only one point in the region. The elemental ratios
calculated for the period 16–20 August using concen-
tration data from the various sites are given in Table 1.
It should be noted that the Allegheny, Laurel and
Deep Creek concentrations were measured with
dichotomous samplers while the Mayville and
URI-Allegheny concentrations were measured with
high-volume samplers.

Calculating the LMW signature from any of the five
sets of data resulted in similar elemental ratios, within
a factor of two for most elements. The factor of two is
well within the variability of each individual element's
ratio to Se. In general, while the inter-site signature
variability may not be that large, for individual pairs
of elements the variability in ratio can be quite large.
The Zn/Se ratio, for example, varied from 2.1 to 22.8

(Deep Creek and Mayville, respectively). The Mayville
value not only was an order of magnitude different
from the Deep Creek value, but was also four times the
value suggested to be representative of the LMW area.
The higher Zn/Se ratio consistently seen at Mayville
probably reflects a local Zn source, as the Se concen-
trations at this site were slightly higher on average
than at Allegheny (2.7 vs 2.1 ng m$^{-3}$). The ratios given
in Table 1 reflect the spatial variability in the LMW
signature, since the samples used in the determination
were from the same 5 days.

The temporal variation in the LMW regional signa-
tures was also investigated. Table 2 lists the elemental
ratios calculated by other researchers for the Lower
Midwest. Tuncel (1986) calculated elemental ratios
from a set of samples taken during the Ohio River
Valley Study carried out by EPA in 1980 (Shaw and
Paur, 1983). Samples were re-analysed by neutron
activation analysis (Tuncel et al., 1985), and the results
presented here are from that analysis. The second
column is the estimate from Dutkiewicz et al. (1987)
for the Ohio River Valley region (their Region III).
Differences were observed in the ratios calculated for
the different sites. The ratios found by Tuncel (1986)
and Dutkiewicz et al. (1987) were more similar to each
other than to the Rahn and Lowenthal ratios, except
for the Mn/Se ratio. The ratios of Tuncel and Dutkie-
wicz appear to be more similar to the average of the
Allegheny, Laurel, Deep Creek ratios, and to the
Mayville ratios, than to the ratios defining the LMW
signature. This indicates that it is important to obtain
data from multiple sites within a region in order to
characterize that region's signature adequately (if in-
deed regions do have characteristic "signatures"). The
number of samples also appears to be important in
characterizing a region's emissions. The ratios calcu-
lated by Tuncel and by Dutkiewicz et al. were the
average ratios from different years of data. The LMW
ratio, as already mentioned, was determined from 5

Table 1. Inter-site comparison of derived LMW signatures. Average elemental ratios 16–20 August 1983

|  | Allegheny | Laurel | Deep Creek† | Mayville | URI-ALG |
|---|---|---|---|---|---|
| As/Se | 0.31 ± 0.23 | 0.34 ± 0.26 | 0.34 ± 0.34 | 0.34 ± 0.24 | 0.23 ± 0.05 |
| Sb/Se | 0.27 ± 0.12 | 0.25 ± 0.11 | 0.32 ± 0.07 | 0.25 ± 0.10 | 0.15 ± 0.04 |
| V/Se | 0.38 ± 0.24 | 0.27 ± 0.08 | 0.21 ± 0.19 | 0.78 ± 0.33 | 0.16 ± 0.06 |
| Zn/Se | 5.46 ± 3.90 | 4.70 ± 2.60 | 2.1 ± 0.9 | 22.85 ± 9.0 | 5.30 ± 0.90 |
| Mn/Se | 1.55 ± 1.09 | 1.81 ± 1.09 | 1.27 ± 0.48 | 3.72 ± 1.37 | 1.10 ± 0.69 |
| In/Se* | 2.00 ± 3.00 | 1.00 ± 1.00 | 0.66 ± 0.60 | ND | 1.00 ± 1.00 |

* Value × $10^3$.
† Ratios of fine fraction concentrations.
ND, not determined in the analysis.

Table 2. Comparison of derived LMW signatures with other studies

|  | Tuncel (1986) | Dutkiewicz et al. (1987) | Average† | URI-ALG |
|---|---|---|---|---|
| As/Se | 0.57 | 0.74 | 0.33 | 0.23 |
| Sb/Se | 0.32 | 0.23 | 0.24 | 0.15 |
| V/Se | 0.34 | 0.37 | 0.29 | 0.16 |
| Zn/Se | 12.0 | 17.0 | 5.20 | 5.30 |
| Mn/Se | 1.60 | 5.90 | 1.54 | 1.10 |
| In/Se* | 4.20 | ND | 1.22 | 1.00 |

* Value × $10^3$.
† Average of Allegheny, Laurel and Deep Creek Lake.
ND, not determined in the analysis.

days of sampling. The fact that the data from the various studies were taken during different years and were still in fairly good agreement suggests that the temporal variation in the signatures may not be as large as the site-to-site variations.

*Trajectory analysis of elemental ratios and sulfate*

The determination of regional signatures using daily aerosol samples must be approached carefully. The variation in elemental ratios used to define regional signatures can be quite large. Defining periods of similar meteorology is one of the crucial steps in choosing a set of samples which can be used to characterize a region's emissions. Air mass trajectories were utilized in this analysis as a means of identifying periods of similar meteorology. Regional transport patterns were generally a result of migrating synoptic systems with time scales on the order of 2–5 days. Periods of similar meteorology, therefore, will have durations on the order of 2–5 days. Daily samples taken at the beginning and end of periods of similar meteorology may not be representative of a single region. They may represent the period of transition from one area's influence to another. While this transitional period cannot be avoided, the use of shorter duration samples can reduce the problem.

The period 13–15 August 1983 was a particularly "clean" period in the northeast U.S.A. (Fig. 2). This period was chosen as the wind flow for all 3 days was quite persistent, with winds at each of the sites from the northeast. Low concentrations were measured at Allegheny and Laurel beginning on the night of the

12th, when flow from the northeast began. The similarity in elemental ratios observed at the various sites on a given day was studied to identify the degree of spatial homogeneity in the ratios.

A day was selected where each site appears to have been influenced by air flow from the same region. Figure 8 shows the back mixed-layer trajectories from four sites in the Northeast on 13 August. The trajectories were calculated by means of the NOAA ARL-ATAD trajectory model (Heffter, 1980), which calculates the upwind track of the wind for the "mixed layer" of the atmosphere from the surface to the height of the first non-surface-based inversion (or an arbitrary 3000 m if no elevated inversion is detected below that) as deduced from vertical temperature profiles. These trajectories can be thought of as center-of-mass probabilities for air transport to the receptor site (Samson and Moody, 1981). The stars (***) for the Sb/Se ratio in Fig. 8 indicate that the Sb concentration at Whiteface Mountain was reported as zero for this day's measurements.

For each site, four 3-day (72-h) backward trajectories are shown (air masses arriving at 0Z, 6Z, 12Z and 18Z), as well as the daily measured concentrations of sulfate and elemental ratios. The figure indicates flow arriving at the sites from the northeast. Sulfate concentrations were extremely low, relative to the norm for these sites. The concentration data shown for the Allegheny site were from the University of Rhode Island URI analysis of high-volume samples taken at the Allegheny site. The URI high-volume samples were used so that inter-site comparisons with the other
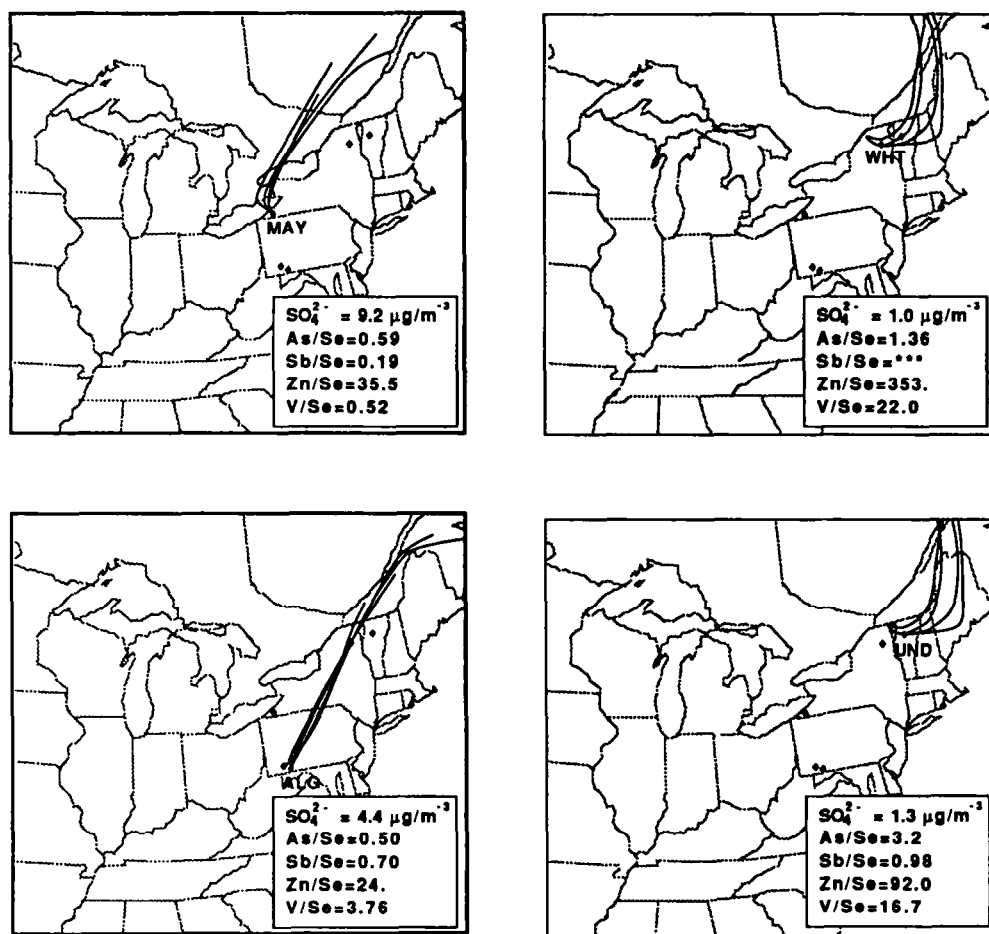
Fig. 8. Mixed-layer 72-h back trajectories and associated sulfate and elemental ratios at four sites on 13 August 1983.

daily high-volume samples would be consistent. Several fundamental questions concerning the use of elemental ratios can be investigated. If regions do have characteristic ratios, how do these elemental ratios behave after transport to another region?

Before the $SO_4^{2-}$ concentrations and elemental ratios measured at sites in different regions can be compared, the intra-regional variation should be addressed. Here, we are generally following the definitions of region given by Rahn and Lowenthal (1984, 1985). The Underhill (VT) and Whiteface (NY) sites show nearly identical sulfate concentrations and elemental ratios. The Sb/Se and V/Se ratios differed by less than a factor of two between these sites. For the most part, the two sites appear to be "seeing" the same trace element ratios. Similarly, the Mayville and Allegheny sites show similar sulfate concentrations and Zn/Se and V/Se ratios; the As/Se ratio, however, was the one exception, being a factor of four higher at Mayville.

The inter-site variation for sites in the same general region under this meteorological pattern does not appear to be great. However, the inter-regional differences were much larger. The sulfate concentrations

measured at the four sites were not very different, being at most a factor of two higher in the downwind region. The V/Se ratio was the most different between regions, being almost an order of magnitude larger for the two northeasternmost sites. The V concentrations at the four sites ranged from about 0.50 to 2.0 ng m$^{-3}$ — a factor of four different from highest to lowest. The lower V/Se ratios observed at Allegheny and Mayville were partially the result of somewhat higher Se concentrations there.

The higher Se concentrations observed at Allegheny and Mayville lowered other ratios as well. The As/Se ratio at Whiteface and Underhill was ~4 to 6 times larger than that observed at the Allegheny and Laurel sites for this day and the Zn/Se ratio dropped from ≥ 50 to ~30.

The next day, 14 August (Fig. 9), had meteorology similar to the 13th. Flow was again observed from the northeast for the entire day. Sulfate concentrations were again quite low at the four sites. The As/Se ratio at Mayville was twice that found at Allegheny, again indicating a local As influence near Mayville. The Sb/Se ratio at the two downwind sites showed the closest agreement of any of the ratios. The non-crustal
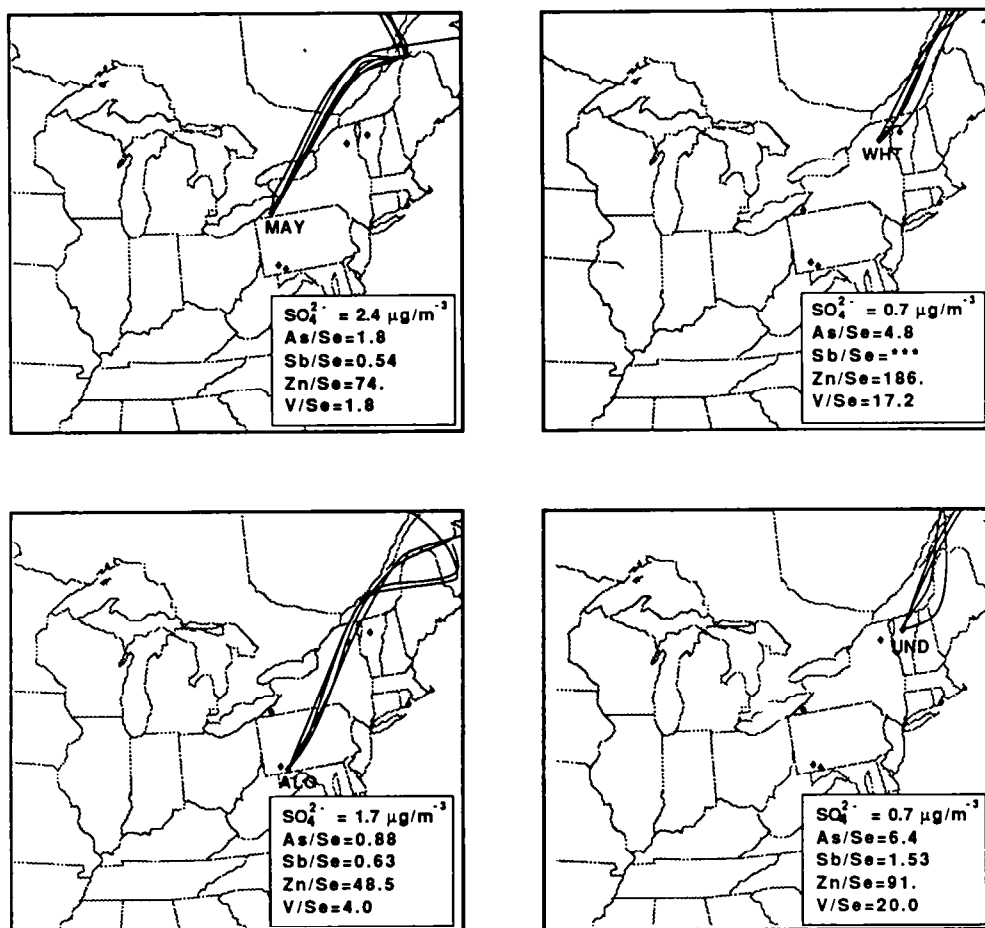
Fig. 9. Mixed-layer 72-h back trajectories and associated sulfate and elemental ratios at four sites on 14 August 1983.

Mn/Se ratio, not shown in the figures, was significantly different between Mayville and Allegheny, 8.0 vs 1.53 and 38.1 vs 1.0, on the 13th and 14th, respectively. Even though the air masses reaching the two sites originated in the same approximate area, the two sites ultimately measured slightly different elemental compositions.

The inter-regional differences were slightly larger on the 14th, with the Zn/Se and V/Se ratios showing the greatest difference. The V concentrations at the four sites were not very different, except that the V concentration measured at Allegheny was almost twice that measured at the other sites. The air reaching Mayville and Allegheny had higher concentrations of Se than the air reaching Underhill or Whiteface. The Zn concentrations measured at Mayville and Allegheny were, respectively, ~5 and 2 times the concentration measured at the Underhill site, again indicating that Zn was added to the air during transport.

Figure 10 shows the transport patterns and concentrations for 15 August at the four sites. The general air flow was still from the northeast, but was much slower. Sulfate concentrations remained low at the eastern

sites, but increased at the other two sites. The Whiteface Mountain and Underhill sites showed similar ratios for V/Se, but differed in the other ratios. The two downwind sites, while displaying similar As/Se ratios, appear to be "seeing" different air mass influences. The sites were probably being influenced more by local sources due to the more stagnant conditions on the 15th. The 15th would be a marginal day for determining a regional signature based upon this analysis.

Inter-regional differences were again apparent on the 15th. The As/Se ratios at Whiteface and Underhill were higher than those observed at Mayville or Allegheny. The Zn/Se and V/Se ratios were also higher at the upwind sites. The Sb/Se ratio was found to be very similar at Allegheny and Underhill, but lower at Mayville. The ratios and trajectories both indicate that the sites located in the East were being influenced by different air masses from the two sites closer to the Midwest.

In comparing the observed ratios from the 13th, 14th and 15th, some general patterns were observed with flow from the northeast. The V/Se ratio was
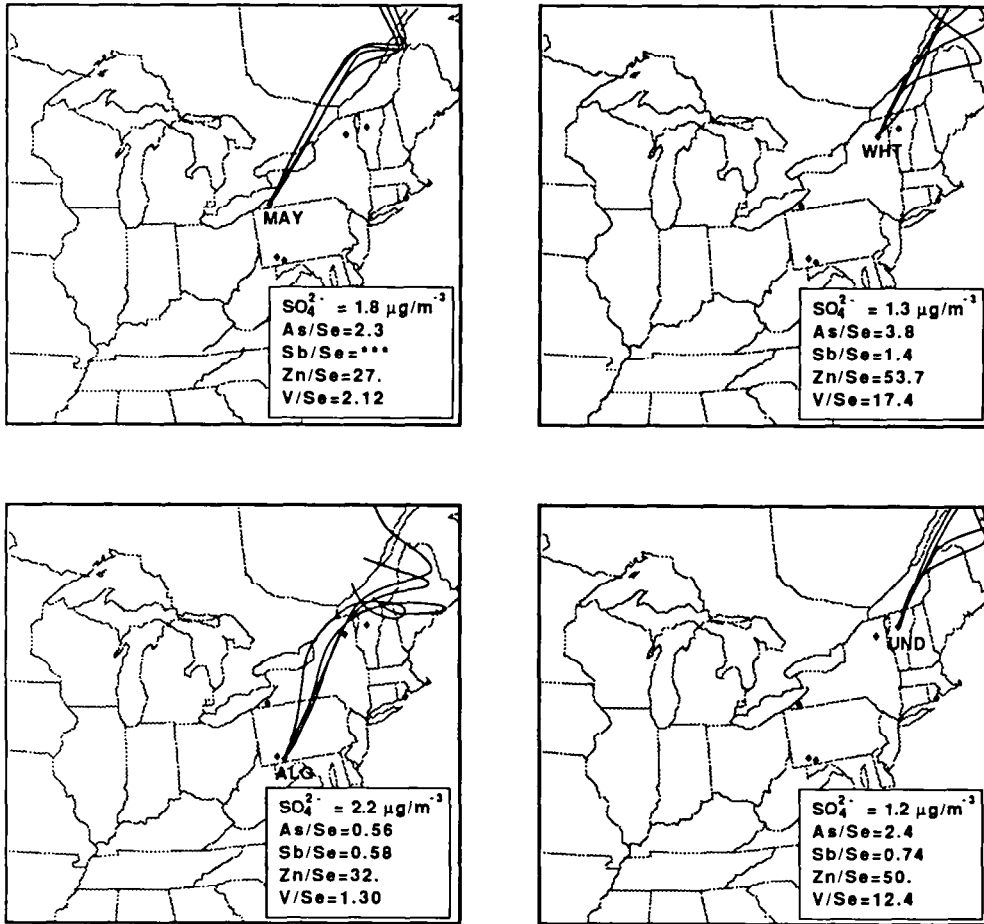
Fig. 10. Mixed-layer 72-h back trajectories and associated sulfate and elemental ratios at four sites on 15 August 1983.

consistently higher at the two upwind sites (Whiteface and Underhill), mainly due to the much lower Se concentrations measured at these sites. The Zn/Se ratio was consistently higher at the upwind sites, although the magnitude varied considerably over the 3-day period. Mayville appeared to be influenced by local sources of As and Zn. While sulfate concentrations were uniformly low at all sites on the 13th and 14th the concentrations increased at the downwind sites on the 15th. Elemental ratios showed less inter-site variability on the first 2 days while showing more variability on the 15th. Table 3 shows the average of the elemental ratios, calculated over the 3-day period just discussed.

The last day investigated using trajectory and elemental ratio analysis was 16 August. This was the first day of the period used to define the LMW signature, as discussed earlier. The sulfate concentrations, elemental ratios and associated trajectories are shown in Fig. 11. The 16th was a transitional day meteorologically. A low pressure system moved further off the coast decreasing its influence gradually. A high-pressure system began to be the dominant meteorological influence starting on the evening of the 15th.

Mixed-layer wind speeds decreased and large areas of stagnation were observed, as was evident in the trajectories for this day.

The sulfate concentrations were much higher on 16 August than they had been on the previous 3 days, approximately 3–7 times greater at all of the sites. The Whiteface and Underhill elemental ratios were found to be similar to each other, perhaps slightly more similar than the Mayville and Allegheny ratios were to each other. This may be due to the lack of local sources, most important under periods of high pressure or local stagnation, in the vicinity of Whiteface and Underhill.

The meteorology on the first half of the 16th was different from the meteorology for the second half. Elemental ratios calculated using daily samples can hide the short duration variations in the elemental ratios as seen in Table 4. The total concentration (fine plus coarse) ratios calculated from dichotomous samples taken twice per day were compared to the ratios determined using daily high-volume samples taken concurrently. The uncertainty in elemental signatures taken using daily samples can thus be investigated by comparing the two sets of ratios. The ratios calculated

Table 3. Comparison of trace element ratios 13–15 August 1983

|        | Allegheny | Mayville | Whiteface | Underhill |
|--------|-----------|----------|-----------|-----------|
| As/Se  | 0.65      | 1.56     | 3.32      | 4.00      |
| Sb/Se  | 0.64      | 0.37†    | ‡         | 1.10      |
| V/Se   | 3.02      | 1.47     | 18.9      | 16.4      |
| Zn/Se  | 34.8      | 45.5     | 198.0     | 77.7      |
| Mn/Se  | 1.31      | 17.2     | 20.5      | 17.9      |
| In/Se* | 8.07      | ND       | ND        | 25.4      |

* Value $\times$ $10^3$.
† Average of only two samples.
‡ Concentration of Sb = zero.
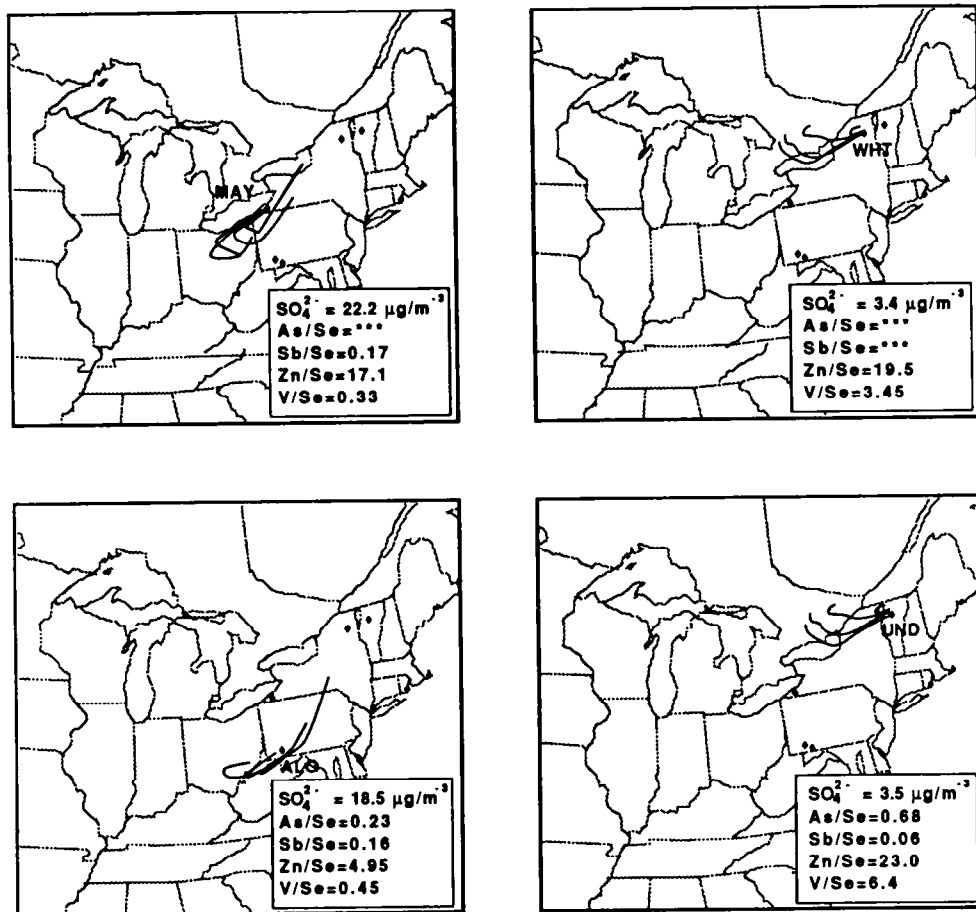ND, in concentration not determined.



Fig. 11. Mixed-layer 72-h back trajectories and associated sulfate and elemental ratios at four sites on 16 August 1983.

for the two shorter duration samples, at both Allegheny and Laurel, differed from each other by as much as a factor of 2–3 for some of the elements (Sb, V). The average of the two shorter samples at Allegheny compared favorably, within the analytical uncertainty, with the values calculated from the daily sample analysed by URI. This would indicate that some of the variability in the regional signatures could be reduced by utilizing shorter duration samples and eliminating those which fall into transitional periods between meteorologically similar periods. The elemental ratios calculated for Laurel Hill are also shown in Table 4 to give an idea of the inter-site variability that was observed on a transitional day like 16 August. It is apparent that the inter-site variability could also be reduced by using shorter duration samples, as the

Table 4. Elemental ratios calculated using short duration and daily samples. $SO_4^{2-}$ concentration and elemental ratios calculated at Allegheny/Laurel, August 16

| Ratio | Laurel | | | Allegheny | | | URI-ALG |
|---|---|---|---|---|---|---|---|
| | Day | Night | Average | Day | Night | Average | Daily |
| As/Se | 0.43 | 0.41 | 0.42 | 0.38 | 0.20 | 0.29 | 0.23 |
| Sb/Se | 0.35 | 0.18 | 0.27 | 0.46 | 0.33 | 0.40 | 0.16 |
| V/Se | 0.38 | 0.18 | 0.28 | 1.03 | 0.35 | 0.69 | 0.45 |
| Zn/Se | 2.44 | 3.10 | 2.77 | 3.51 | 3.60 | 3.56 | 4.95 |
| Mn/Se | 0.74 | 2.41 | 1.58 | 0.25 | 0.26 | 0.26 | 0.22 |
| In/Se* | 1.5 | ‡ | ‡ | ‡ | 0.8 | ‡ | 1.4 |
| $SO_4^{2-}$† | 28.24 | 55.52 | 41.88 | 14.98 | 40.39 | 27.69 | 18.5 |

\* Value $\times 10^3$.

† Units are $\mu g\,m^{-3}$.

‡ In concentration $= 0$.

Laurel Hill ratios (i.e. V/Se, Mn/Se) and sulfate concentrations were about a factor of two different from those determined for Allegheny Mountain. The ratios and sulfate concentrations were in closer agreement from the 17th to the 19th (not shown) presumably because the sites were truly being influenced by the same regional sources.

## SUMMARY

The goal of this paper was to investigate the transport of atmospheric sulfate and trace elements across the northeast U.S.A. Sulfate was found to be regional in nature, displaying temporal variations which were similar at sites separated by large distances under certain meteorological conditions. Selenium displayed the strongest regional character of the trace elements, though it was likely influenced by local sources. Vanadium and As were the only other trace elements found to have a somewhat regional character, though to a lesser extent than sulfate and selenium. For vanadium, this was probably due to limited transport during the month of August from the Northeast where vanadium emissions are more extensive.

The 5-day period 16–20 August, a period of elevated sulfate at all sites, was investigated as to the generality of regional signatures, utilizing trace element ratios. The inter-site variabilities in elemental ratios among the Allegheny, Laurel, Deep Creek and Mayville sites were generally small (a factor of two or less) and well within the variabilities at a given site from one day to another. But there were exceptions, probably reflecting influences of local sources. Comparison with earlier trace-element data from the same region suggests that temporal variations may be less than spatial ones. Together the data indicate that it is important to obtain data from multiple sites and periods within a region in any effort to construct a regional signature.

An unusually clean period, 13–15 August, with steady air mass advection from the northeast to all sites, was investigated to evaluate the conservation of regional signatures into downwind regions. The inter-regional differences in trace element ratios proved to be far larger than the intra-regional ones — an order of magnitude in some cases, attributable mostly to addition of trace elements in the downwind region. The ability to identify in one region the signature from another region appears to be problematic. However, aerosol trace element ratios are found to be a powerful tool for investigating regional source influences when used in concert with meteorological information.

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