19 April 1985, Volume 228, Number 4697 SCIENCE

Pollution Aerosol in the Northeast: Northeastern-Midwestern Contributions

Kenneth A. Rahn and Douglas H. Lowenthal

Summary. In recent years, atmospheric scientists have been endeavoring to determine the relative contributions of local and distant sources to pollution aerosol in eastern North America. Elemental analysis of aerosol from various sites in the northeastern United States has revealed a persistent northeastern "foreground" upon which pulses of midwestern aerosol are superimposed every few days, in response to large-scale meteorological features. Regional apportionment of tracer elements and sulfate in summer and winter samples from Narragansett, Rhode Island, and Underhill, Vermont, shows that most of the elements come predominantly from northeastern sources. Notable exceptions include arsenic and indium, for which Canadian nonferrous smelters are important sources, and sulfur and selenium, for which the Midwest is an important source. During 1982 and 1983, the Northeast and the Midwest contributed comparably to aerosol sulfate at Narragansett and Underhill, in spite of the fact that the emissions of sulfur dioxide in the Midwest were ten times those in the Northeast; Canadian smelters accounted for less than 10 percent of the total sulfate. During a major pollution episode in July 1982, northeastern and midwestern sources produced comparable sulfate concentrations in Rhode Island, whereas midwestern sources dominated northeastern sources in Vermont. Thus, although distant midwestern sources affect the quantity of pollution aerosol in the Northeast and may dominate episodically, nearer northeastern sources are comparably important on the long term.

One of the most important but most intractable problems of air quality in eastern North America continues to be determining the regional sources of its pollution aerosol and in particular the relative contributions of local versus distant sources. Until recently, it was necessary to deduce the major source areas from indirect approaches such as air-mass trajectory analysis (*1*), directional association (*2*), and long-range transport modeling (*3*), the sum total of which is suggestive but still inconclusive. In early 1984, however, we reported that certain areas have discrete regional signatures of pollution aerosol based on elemental ratios, from which it appeared possible to quantify the regional contributions to trace elements and sulfate in mixed aerosols of local or distant origin, or both (*4*). Regions of North America with distinct signatures included the East Coast, the Midwest, and the Sudbury Basin of Canada. Even though sulfate cannot be used as a true tracer element because so much of it is secondary in the aerosol (formed in the atmosphere from SO_2), its origins are important to understand because it contributes so much to fine-particle mass and acidic deposition.

Since that time, we have expanded and improved our signatures, solidified our statistical techniques for dealing with them, and added greatly to our data base. In this article, we demonstrate on the basis of extensive data from 1982 and 1983 that the Midwest and the Northeast contributed comparably to aerosol sulfate at two sites 300 km apart in the Northeast, in spite of the fact that the Midwest emitted ten times as much SO_2 as the Northeast. We show that these results are consistent with earlier studies wherever they overlap, but we extend them to create a more general picture of the large-scale movement of air pollution in the East. In effect, this study has already begun to meet some of the goals of the 5- to 10-year $100-million field and modeling experiment on artificial tracers that has been suggested recently as necessary to determine the source-receptor relations for acid deposition and its precursors in eastern North America (*5*).

Regional Elemental Signatures of Pollution Aerosol

Our elemental tracer system for pollution aerosol is based on the seven pollution-derived elements arsenic, selenium, antimony, zinc, indium, noncrustal vanadium, and noncrustal manganese (*6*). Regional signatures are developed and expressed as the ratios of the six elements to selenium (*7*), together with associated uncertainties (of the individual measurements, not of the mean). The uncertainties of ratios in a signature, which are roughly 40 percent, are controlled by sample-to-sample variability, because sampling and analytical errors are generally less than 10 to 15 percent. For subsequent statistical purposes, including regional apportionments, the signatures are generally used in the form of elemental concentrations scaled to unit selenium. This scaling is for convenience only because apportionments depend only on the compositions of signatures, not absolute concentrations. We construct the signatures by averaging the elemental ratios of high-volume samples chosen chemically and meteorologically to best represent the aerosol emitted by a given region while excluding the effects of adjoining regions (*4*). Although the samples representing a signature are of-

---

The authors are at the Center for Atmospheric Chemistry Studies, Graduate School of Oceanography, University of Rhode Island, Narragansett 02882.

Table 1. Regional elemental signatures for eastern North America. The values given are arithmetic means and standard deviations (in nanograms per cubic meter), scaled to unit selenium.

Element	Signatures				
			Current signatures		
	NENG (n = 4)*	CEC (n = 12)	LMW (n = 5)	UMW (n = 48)	SONT (n = 7)
As	0.136 ± 0.047	0.74 ± 0.26	0.23 ± 0.05	1.49 ± 0.46	2.8 ± 1.9
Sb	0.46 ± 0.13	1.14 ± 0.43	0.148 ± 0.038	0.43 ± 0.23	0.31 ± 0.16
Se†	1.00 ± 0.28	1.00 ± 0.37	1.00 ± 0.30	1.00 ± 0.30	1.00 ± 0.58
Noncr. V	11.6 ± 2.6	27 ± 11	0.160 ± 0.064	0.83 ± 0.32	4.4 ± 2.3
Zn	32 ± 5	29 ± 9	5.3 ± 0.9	24 ± 9	29 ± 8
Noncr. Mn	9.4 ± 2.4	3.7 ± 1.6	1.10 ± 0.69	6.7 ± 2.9	4.4 ± 2.4
In	0.0060 ± 0.0060	0.0046 ± 0.0029	0.0010 ± 0.0010	0.0045 ± 0.0039	0.095 ± 0.024
			Previously used signatures (4)		
	NYC (n = 3)	BOS (n = 3)	INT (n = 4)	SONT (n = 3)‡	
As	1.06 ± 0.11	0.49 ± 0.15	0.86 ± 0.22	8.1 ± 1.2	
Sb	1.65 ± 0.32	0.83 ± 0.41	0.31 ± 0.11	0.76 ± 0.11	
Se†	1.00 ± 0.22	1.00 ± 0.60	1.00 ± 0.44	1.00 ± 0.09	
Noncr. V.	10.6 ± 2.1	35 ± 6	1.91 ± 0.56	2.0 ± 1.3	
Zn	37 ± 9	37 ± 3	10.2 ± 4.5	57 ± 4	
Noncr. Mn	6.9 ± 0.6	4.2 ± 0.8	2.4 ± 1.3	14.1 ± 1.8	
In	0.0085 ± 0.0017	0.0050 ± 0.0040	0.0036 ± 0.0003	0.051 ± 0.025	

*Number of daily samples (semiweekly samples used for NYC and 2 of 12 for CEC). †Average Se for the samples used to derive the signatures: NENG, 0.37; CEC, 1.13; LMW, 3.6; UMW, 2.4; SONT, 0.38; NYC, 1.88; BOS, 0.59; INT, 1.78; SONT, 0.66. ‡Not used for any apportionments reported here.

ten few in number, they are chosen carefully from a much larger collection of samples. As illustrated in the rest of this section, the resulting signatures are reliable even though they are sometimes derived from relatively few samples. As far as we can tell, the signatures are free of bias or systematic error.

Our current and previous regional signatures from eastern North America are shown in Table 1. The New England (NENG) signature was derived from a period of unusual aerosol at Underhill, Vermont, during the summer of 1982 (*4*). Its most striking feature is its low arsenic value, the reason for which seems to be lack of significant coal combustion or nonferrous smelting in areas north of Vermont. The antimony and selenium values in the NENG signature are in normal proportions for eastern North America, but zinc, noncrustal vanadium, and noncrustal manganese are somewhat enriched. The high vanadium comes from oil combustion in the general area, but the origins of the high zinc and manganese are less certain. The area represented by NENG seems to be upper New England and parts of eastern Canada.

The Central East Coast (CEC) signature is new. It was derived from 12 samples taken during periods of meteorological stagnation at Narragansett, Rhode Island, two during the summer of 1979, four during the summer of 1982, and six during the winter of 1982–1983. The CEC signature thus reflects considerable temporal variation. It is similar to the average of the older Boston (BOS) and New York City (NYC) signatures [(*4*) and Table 1], which it replaces. It is more regionally representative, however, because it was derived from semirural Narragansett, which has no strong sources nearby. It is also based on more samples than the BOS and NYC signatures. Although one might fear that prevailing westerly winds would make it impossible to measure northeastern aerosol without perturbations from the Midwest, we have found that sampling in Canadian high-pressure areas stagnated over the Northeast effectively eliminates any influence of these upwind sources. Stagnation conditions occur frequently enough in all seasons that reliable northeastern signatures can be determined without difficulty.

The CEC signature is high in zinc, antimony, and noncrustal vanadium, and low to moderate in the other elements. The noncrustal vanadium originates from the abundant oil combustion along the East Coast. The zinc and antimony seem to be associated with regional urban and industrial emissions. The low selenium is linked at least partially with the lack of significant coal combustion in the region. Operationally, the CEC signature seems to represent the coastal strip from at least Boston through New York City, extending 200 to 300 km inland. On the basis of the distribution of oil-fired power plants and population, the CEC area may well include parts of Maine and Virginia.

The Lower Midwest (LMW) signature comes from a several day pollution episode at Allegheny Mountain, Pennsylvania, during August 1983 and represents midwestern aerosol from the southwest, that is, from the Ohio River Valley and southward. This aerosol was also seen in another southwestern episode at Allegheny Mountain and was later sensed repeatedly at the two Ohio sites discussed below. By comparison with the other signatures, it is very high in selenium, very low in noncrustal vanadium, and moderate in the other elements. The high selenium appears to be linked with the extensive coal combustion in the area; the low vanadium with the small degree of oil combustion.

The Upper Midwest (UMW) signature was derived from samples taken near McArthur and Hartville, Ohio, in rural southern and northeastern parts of the state, respectively, during the winter and spring of 1984. Although clearly high enough in selenium and low enough in noncrustal vanadium to be called midwestern, it is three to six times as enriched in arsenic, antimony, zinc, and noncrustal manganese as the LMW signature. Its character is thus coal-based but with a significant component from heavy industry. Synoptic analysis shows that this signature represents aerosol from the north and west, that is, from the more industrialized upper Midwest (northern Ohio-Indiana-Illinois, Michigan, Wisconsin, and perhaps parts of Minnesota and southwestern Ontario). The UMW signature carries much the same information as the earlier interior (INT) signature (*4*), which it replaces. The INT signature represented aerosol from the upper Midwest transported to Vermont and included aerosol from sources between the upper Midwest and Underhill. The newer UMW signature is for pure midwestern aerosol.

The SONT signature, as before, represents the Canadian nonferrous smelters of the Sudbury Basin of Ontario and Quebec but has been updated from measurements at Underhill, Vermont, during the summer of 1982. It is strongly enriched in arsenic and indium as compared to the other signatures. Because two of the smelters of this area, International Nickel Company and Falconbridge, were shut down during this period, we felt that a signature specifically for this period had to be determined and used. For the same reason, the contributions of the smelters to northeastern aerosol should be somewhat lower than normal during this period.

The five current signatures are distinct, are stable during transport, and include all the major types of aerosol that can be found in the Northeast. Their distinctness is shown by their lack of colinearity, as deduced from the diagnostic procedure of Belsley *et al.* (*8*). Their stability during transport seems to be a consequence of a similarity of particle sizes of the tracer elements coupled with effective transport of a broad range of particle sizes. In Narragansett, for example, 50 to 75 percent of the mass of the tracer elements is on submicron particles and hence is easily transportable. During transport, however, coarse (supermicron) particles will be removed somewhat faster than submicron particles. This will alter the proportions of elements that have different size distributions. An upper limit for this effect on element X is

$$(X/Se)_{\text{total aerosol}}/(X/Se)_{\text{submicron aerosol}}$$

which represents the factor by which its ratio to selenium would decrease if all coarse aerosol and no fine aerosol were removed. In Narragansett, the factors for five of the six tracer elements and sulfate are less than 1.5; only that for noncrustal Mn/Se is significantly higher, at 2.4.

These factors are worst-case estimates, because natural removal processes vary smoothly with particle size, not in a step function. Actual changes in ratios during transport seem to be very much less. For example, in 35 pulses of midwestern aerosol that we observed at Underhill during two summers and one winter, mean values of the Zn/Se, As/Se, and noncrustal Mn/Se ratios (all of whose elements come predominantly from the Midwest during episodes) fell within 20 to 25 percent of the mean of the LMW and UMW signatures, and the spread of the individual values was less than the spread of the two signatures. Thus, simple mixing rather than preferential removal controlled the proportions of arsenic, selenium, zinc, and noncrustal manganese during the 1000 km of transport. This lack of fractionation was particularly striking for the noncrustal Mn/Se ratio, which from particle-size considerations alone might have been expected to decrease frequently to values below both signatures. The popular division of aerosol into coarse and fine components at radius 1 μm, while meaningful from the chemical and inhalational standpoints, thus seems much less valid for transport purposes. Contrary to widespread opinion, studies of transported aerosol need not be limited to sampling only its fine-particle component.

Compositional Cycles and Intrusions of Midwestern Aerosol

Now we illustrate the inclusiveness of our signatures by showing that the major chemical features of northeastern and midwestern aerosols determined at the source are also the major features of aerosol measured downwind. One of the most striking features revealed by sequential daily aerosol samples throughout the Northeast is a ubiquitous and strong cycle of X/Se ratios. Because we have found this cycle wherever and whenever we have sampled, we presume it to be a characteristic feature of the northeastern atmosphere. Figure 1 shows typical summer cycles for Narragansett, Underhill, and Allegheny Mountain. Cycles of concentration, which have been recognized for many years and which stem from alternation of relatively clean air from the north or east with relatively dirty air from the west or south, are seen clearly. But the X/Se ratios also show regular cycles, several of whose amplitudes approach those of the concentration cycles. For example, the amplitude of the cycles of noncrustal V/Se and Sb/Se is nearly an order of magnitude, whereas that of Zn/Se is roughly a factor of 5. Of the cycles not shown in Fig. 1, that of noncrustal Mn/Se resembles the cycle of Zn/Se, while those of As/Se and In/Se are more irregular. Except for Allegheny Mountain,

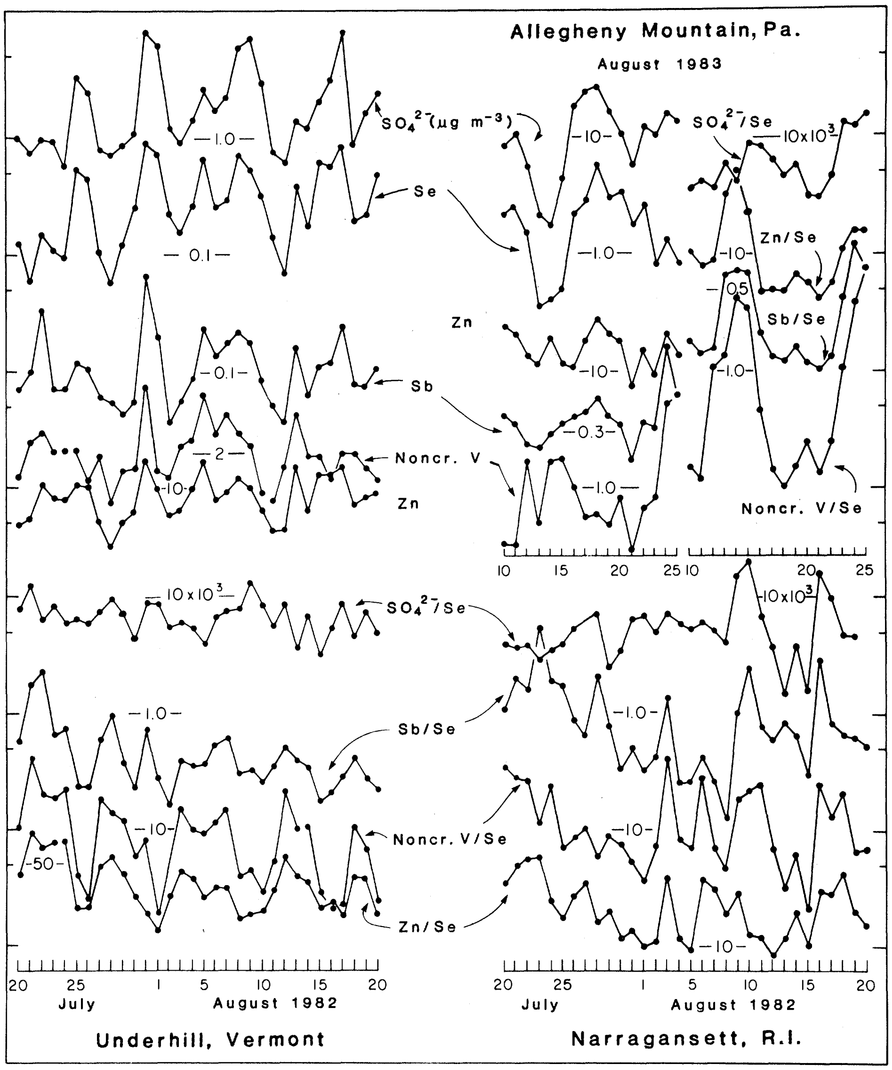

Fig. 1. Concentrations and ratios of trace elements in daily aerosol samples at three sites in the Northeast during summer.

the sulfate/Se ratio is nearly constant.

The cycles of noncrustal V/Se, Sb/Se, Zn/Se, and noncrustal Mn/Se are nearly in phase with each other. This means that an aerosol relatively rich in vanadium, antimony, zinc, and manganese is alternating with an aerosol rich in selenium and sulfur. In other words, organized compositional cycles rather than individual elemental cycles are being sensed. According to the ratios of Table 1, maxima and minima of the cycles correspond, respectively, to pure northeastern aerosol and midwestern plus northeastern aerosol (the latter because minima of noncrustal V/Se and Sb/Se, the two ratios most enriched in northeastern aerosol, do not reach pure midwestern values). Thus, pollution aerosol in the Northeast has two major regional components: a persistent northeastern "foreground" and a midwestern component which appears as superimposed pulses with durations of 1 to 4 days. The midwestern component is present in abundance about 40 to 50 percent of the time.

The fact that the two major extremes of pollution aerosol appearing at various northeastern receptor sites correspond closely to the two major types of aerosol (northeastern and midwestern) measured in eastern North American source regions constitutes the strongest evidence to date for the basic validity of our regional elemental tracer system. Other pieces of evidence discussed in this article include the link between chemistry and meteorology as well as the agreement between our results and those from independent studies.

The compositional cycles are strongest and most regular at Underhill and Allegheny Mountain, and weaker and more irregular at Narragansett. The contrast between Narragansett and Underhill is easy to understand, because Underhill is well removed from major pollution sources in both the Northeast and the Midwest and hence receives greater extremes of aerosol than Narragansett, which is closer to northeastern sources. The intensity and clarity of the cycles at Allegheny Mountain came as a surprise, however, because we did not expect to see such efficient transport of aerosol retrograde from Northeast to Midwest. The Allegheny Mountain results are consistent with more recent ones from outside Akron, Ohio, still farther to the west, where we have found regular transport of aerosol from the Northeast during winter.

It is reasonable to find regular exchange of aerosol between the Midwest and the Northeast, however, because the atmospheric residence times of submicron aerosol in mid-latitudes are commonly 4 to 7 days (*9*). Assuming wind speeds of 5 to 10 km hour^{-1} and linear trajectories, pollution sources would have a range of influence of approximately 500 to 2000 km, that is, the size of typical source regions within the eastern United States. Consequently, both the Midwest and the Northeast should affect each other's air quality.

The period of the compositional cycles is somewhat irregular and varies from 2 to 3 days to more than 1 week. It is generally shorter in winter than in summer. This finding suggests that the compositional cycles may be controlled by large-scale meteorological factors because in eastern North America the basic synoptic cycle (the time needed for a high-pressure area to be replaced by a low-pressure area and then by another high-pressure area) is roughly 1 week. Indeed, synoptic analysis confirms that the compositional cycles are linked very closely to the better known meteorological cycles, with the northeastern phase of the compositional cycle associated with stagnant air or winds from eastern Canada or the East Coast and the mixed midwestern-northeastern phase associated with flow from the interior, that is, with winds from the Midwest.

To illustrate this correlation between chemistry and meteorology, Fig. 2 shows simplified surface meteorological maps for a typical compositional cycle at Underhill, from 5 to 13 August 1982. General airflow near the surface is shown by broad arrows. The cycle consisted of 3 days of nearly pure northeastern aerosol, 3 days with a distinct midwestern component, and then 3 days of northeastern aerosol. Figure 2 shows that during the first 3 days, Underhill was influenced by a Canadian high-pressure area whose center was migrating from Hudson Bay to Pennsylvania. Air of the next 3 days, when midwestern aerosol was present, came from far to the southwest, in association with an intruding Bermuda high-pressure area and a cold front approaching from the west. During the last 3 days, the air again came from Canada and the American Northeast, as another large Canadian high moved into the area.

Thus, both theory and observation agree that neighboring regions affect each other's aerosol regularly and substantially. There can no longer be any doubt that midwestern sources contribute importantly to aerosol in the Northeast. On the other hand, coastal northeastern influences are felt not only along the coastal strip but also as far inland as Vermont, Pennsylvania, and Ohio.

Long-Term Regional Apportionments in Rhode Island and Vermont

By itself, alternation of two aerosols implies little about their relative contributions to the total, especially for individual elements or compounds. For this, long-term regional apportionments are needed. Using extensive data from the summer of 1982 and the winter of 1982–1983 at Narragansett and Underhill, we have apportioned our seven tracer elements and sulfate among the five current regional signatures of Table 1. The results are shown in Table 2. Together, they create a general picture of sources and transport for the Northeast that is both reasonable and defensible. Among their most interesting features is the first direct evidence that the Northeast contributes as much sulfate aerosol to itself as the Midwest does.

The number of daily samples per season and site ranged from 55 to 96. The seven tracer elements in each sample were apportioned by the standard least-squares chemical element balance model

$$C_i = \sum_{j=1}^{p} A_{ij}S_j \qquad (1)$$

for p sources, where C_i is the concentration of the ith species in the ambient sample, A_{ij} is the concentration of the ith species in the jth source, and S_j is the derived proportionality constant, or "regional coefficient," which represents the relative strength of the jth source. The regional coefficients were generated with the Environmental Protection Agency's Chemical Mass Balance Model program (*10*). If the initial apportionment gave any negative coefficients, they were set to zero and the sample was reapportioned; the process was repeated until all regional coefficients were positive or zero. Of the five starting signatures, only one or two were found to contribute to a typical sample. The program was modified to generate and use uncertainties for sources with coefficients of zero. We used the "effective variance" weighting option (*11*), which calculates regional coefficients for a sample and their uncertainties from the uncertainties in the signatures and the sample. Uncertainties were propagated through all subsequent calculations according to standard procedures (*12*). (Propagating uncertainties over a series of samples may give unrealistically low values, however.) The contribution of the jth source region to the ith element in a sample is the product of A_{ij} and S_j, that is, the concentration of the element in the signature multiplied by the coefficient of the signature.

Next, we apportioned sulfate by regressing its concentrations in a series of samples from a given season and site against the five regional coefficients S_j over the series

$$(\mathrm{SO_4}^{2-})_i = \sum_{j=1}^{p} S_{ij}E_j \qquad (2)$$

for p sources, where $(\mathrm{SO_4}^{2-})_i$ is the concentration of sulfate in the ith sample, S_{ij} is the regional coefficient of the jth source in the ith sample, and E_j is the derived "effective sulfate" for the jth source. The effective sulfate represents the mean sulfate associated with the jth signature over the series, that is, the initial sulfate near the source plus that formed from SO_2 during transport to the receptor. Because this regression also used effective variance weighting, both the set of effective sulfates and their uncertainties became functions of the uncertainties in both the measurements of sulfate at the receptor and the initial set of regression coefficients S_{ij}. The contribution of the jth source region to the sulfate of a sample is the product of E_j and S_{ij}, which is the effective sulfate of the signature multiplied by the coefficient of the signature.

Knowing that most sulfate of remote aerosols is secondary, one might wonder how it can be apportioned among primary elemental signatures without involving theoretical considerations such as rates of dry deposition of SO_2, rates of conversion of SO_2 to sulfate, relative oxidation of SO_2 in clouds versus the free atmosphere, and scavenging of SO_2 and aerosol during precipitation. Despite the many reasons why the link between primary signatures and secondary sulfate might be tenuous, the empirical relationships between sulfate and the five source areas are reproducible and reasonable at both Narragansett and Underhill. As expected, the uncertainties of apportionment shown in Table 2 are considerably larger for sulfate than for most of the primary tracer elements; however, the regional relationships with sulfate are real.

The reason for these regional associations seems to be that air masses reach quasi-stable proportions of secondary sulfate and primary tracer elements after only a few hundred kilometers of transport, in response to declining rates of transformation with time. In Eurasia, there are indications that this near-steady state is reached by about 1000 km (*13*). Underhill, which is roughly 1000 km from major midwestern sources of SO_2, seems to be nearer stable proportions than Narragansett, which is more influenced by northeastern SO_2.

The results shown in Table 2 have several main features: (i) Most of the zinc, antimony, noncrustal vanadium, and noncrustal manganese (50 to 98 percent) came from the Northeast. (ii) Arsenic and indium had significant components (25 to 80 percent) from the Midwest or the Canadian smelters, or both, particularly during winter. (iii) The influence of the smelters was greater at Underhill than at Narragansett. (iv) Annually, selenium and sulfate at both sites came roughly equally from the Northeast and the Midwest. (Even at Narragansett, sea-salt sulfate was unimportant, because it accounted for only 10 percent of

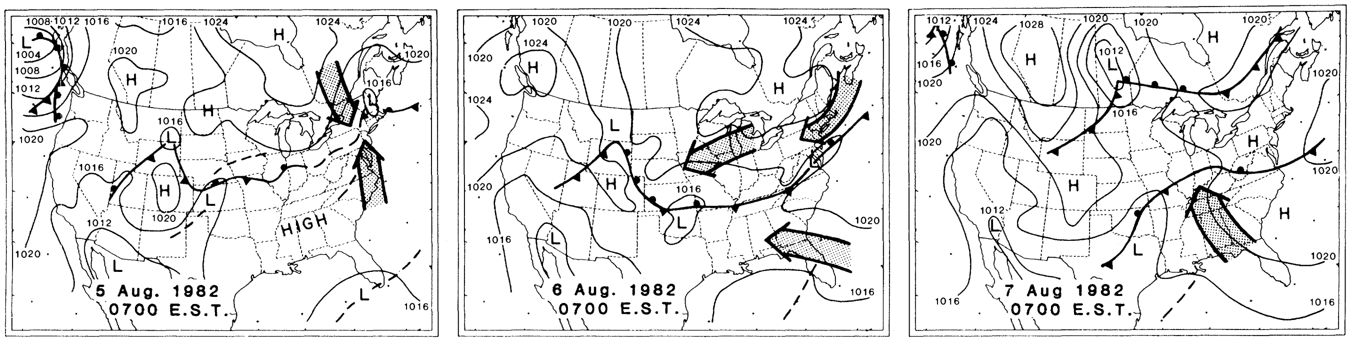

Fig. 2. Surface meteorological maps for 5 to 13 August 1982. Pressure is given in millibars.

the total sulfate in winter and 5 percent in summer.) (v) Only 3 to 5 percent of the annual average sulfate came from the smelters. (vi) The apportionments at Narragansett varied little with season, whereas those at Underhill were much more northeastern in winter than in summer. (This was particularly true for sulfate: in the winter of 1982–1983, 74 percent of the sulfate at Underhill came from the Northeast and only 21 percent from the Midwest; the previous summer, only 34 percent came from the Northeast and 62 percent from the Midwest. Thus, the relative contributions of the Northeast and the Midwest changed by a factor of 6 with season. At Narragansett, by contrast, the relative contributions changed by less than a factor of 2 but in the same direction.)

Seasonal average concentrations of the tracer elements were generally predicted to within 10 to 15 percent or so, whereas individual daily concentrations were predicted to within 20 to 50 percent. (The poorer daily predictions for indium are artifactual, because most of the points were upper limits.) Sulfate was predicted to within 10 percent for seasonal averages but only to within 50 to 60 percent for individual daily samples. Daily predictions were as good at Narragansett as at Underhill.

In summary, most trace elements in northeastern aerosol came from the Northeast itself. Only when an element

Table 2. Average regional apportionments of eight trace constituents in aerosol at two northeastern sites.

Component	Narragansett, Rhode Island			Underhill, Vermont		
	Summer 1982 (*n* = 75)	Winter 1982–1983 (*n* = 96)	Summer plus winter (*n* = 171)	Summer 1982 (*n* = 79)	Winter 1982–1983 (*n* = 56)	Summer plus winter (*n* = 135)
Sulfate						
Northeast (%)	54 ± 4	60 ± 4	55 ± 7	34 ± 3	74 ± 6	49 ± 4
Midwest (%)	45 ± 5	34 ± 4	42 ± 6	62 ± 7	21 ± 4	45 ± 5
Can. smelters (%)	0.8 ± 0.3	6 ± 1	2.5 ± 0.4	4 ± 1	6 ± 1	5 ± 1
Avg. pred. ($\mu g\ m^{-3}$)	5.8 ± 0.3	2.5 ± 1	4.2 ± 0.5	3.8 ± 0.3	2.5 ± 0.2	3.2 ± 0.2
Avg. obs. ($\mu g\ m^{-3}$)	6.1	2.3	4.2	4.0	2.3	3.2
Avg. obs./pred.	1.06 ± 0.57	1.01 ± 0.52		1.07 ± 0.57	1.11 ± 0.59	
Selenium						
Northeast (%)	50 ± 4	57 ± 5	53 ± 3	34 ± 4	47 ± 6	41 ± 4
Midwest (%)	48 ± 6	37 ± 6	43 ± 4	56 ± 8	40 ± 9	48 ± 6
Can. smelters (%)	2 ± 1	6 ± 1	4 ± 1	10 ± 2	13 ± 3	11 ± 2
Avg. pred. ($ng\ m^{-3}$)	1.00 ± 0.06	0.91 ± 0.06	0.96 ± 0.04	0.47 ± 0.04	0.53 ± 0.05	0.50 ± 0.03
Avg. obs. ($ng\ m^{-3}$)	1.06	0.91	0.98	0.45	0.50	0.48
Avg. obs./pred.	1.05 ± 0.24	0.99 ± 0.21		0.92 ± 0.27	0.85 ± 0.31	
Zinc						
Northeast (%)	79 ± 6	77 ± 7	78 ± 5	52 ± 6	67 ± 8	60 ± 5
Midwest (%)	18 ± 3	16 ± 3	17 ± 2	34 ± 4	16 ± 5	25 ± 3
Can. smelters (%)	3 ± 1	8 ± 1	5 ± 1	14 ± 2	17 ± 2	16 ± 2
Avg. pred. ($ng\ m^{-3}$)	18.9 ± 1.0	19.9 ± 1.2	19.4 ± 0.8	9.7 ± 0.6	11.3 ± 0.9	10.5 ± 0.5
Avg. obs. ($ng\ m^{-3}$)	19.4	20	19.7	9.9	12.4	11.2
Avg. obs./pred.	1.02 ± 0.22	1.04 ± 0.25		1.04 ± 0.28	1.10 ± 0.40	
Antimony						
Northeast (%)	83 ± 7	86 ± 8	84 ± 6	54 ± 7	75 ± 9	65 ± 6
Midwest (%)	16 ± 2	11 ± 2	13 ± 2	38 ± 5	17 ± 4	25 ± 3
Can. smelters (%)	1.1 ± 0.4	2.5 ± 0.4	1.8 ± 0.3	8 ± 2	8 ± 2	8 ± 1
Avg. pred. ($ng\ m^{-3}$)	0.55 ± 0.03	0.64 ± 0.04	0.60 ± 0.03	0.181 ± 0.014	0.25 ± 0.02	0.22 ± 0.01
Avg. obs. ($ng\ m^{-3}$)	0.82	0.66	0.74	0.185	0.24	0.21
Avg. obs./pred.	1.38 ± 0.59	0.94 ± 0.52		0.95 ± 0.30	0.92 ± 0.46	
Noncr. manganese						
Northeast (%)	76 ± 8	69 ± 9	74 ± 6	55 ± 6	70 ± 10	62 ± 6
Midwest (%)	22 ± 4	24 ± 5	23 ± 3	37 ± 5	18 ± 6	27 ± 4
Can. smelters (%)	2 ± 1	7 ± 1	4.6 ± 0.7	9 ± 2	12 ± 2	10 ± 2
Avg. pred. ($ng\ m^{-3}$)	3.6 ± 0.3	3.3 ± 0.3	3.4 ± 0.2	2.4 ± 0.2	2.4 ± 0.2	2.4 ± 0.2
Avg. obs. ($ng\ m^{-3}$)	2.9	2.3	2.6	2.9	2.4	2.6
Avg. obs./pred.	0.84 ± 0.22	0.73 ± 0.22		1.23 ± 0.52	0.96 ± 0.47	
Noncr. vanadium						
Northeast (%)	98 ± 10	98 ± 9	98 ± 7	88 ± 12	93 ± 11	92 ± 10
Midwest (%)	1.0 ± 0.2	0.8 ± 0.2	0.9 ± 0.1	4 ± 1	1.2 ± 0.4	2.2 ± 0.4
Can. smelters (%)	0.9 ± 0.3	1.7 ± 0.3	1.3 ± 0.2	8 ± 2	6 ± 1	6.6 ± 1.0
Avg. pred. ($ng\ m^{-3}$)	11.1 ± 0.8	13.4 ± 0.9	12.2 ± 0.6	2.7 ± 0.3	4.9 ± 0.4	3.8 ± 0.3
Avg. obs. ($ng\ m^{-3}$)	9.8	17.4	13.6	2.4	5.8	4.1
Avg. obs./pred.	0.99 ± 0.48	1.32 ± 0.39		0.94 ± 0.23	1.28 ± 0.44	
Arsenic						
Northeast (%)	54 ± 6	53 ± 5	53 ± 4	12 ± 2	26 ± 4	19 ± 2
Midwest (%)	34 ± 7	25 ± 6	29 ± 4	52 ± 8	25 ± 9	39 ± 6
Can. smelters (%)	11 ± 4	22 ± 4	17 ± 3	36 ± 9	49 ± 12	43 ± 8
Avg. pred. ($ng\ m^{-3}$)	0.50 ± 0.04	0.66 ± 0.05	0.58 ± 0.03	0.37 ± 0.04	0.38 ± 0.05	0.37 ± 0.03
Avg. obs. ($ng\ m^{-3}$)	0.44	0.76	0.60	0.41	0.66	0.54
Avg. obs./pred.	0.78 ± 0.40	1.06 ± 0.50		0.99 ± 0.43	1.30 ± 0.88	
Indium						
Northeast (%)	50 ± 8	31 ± 4	39 ± 4	15 ± 3	16 ± 3	16 ± 2
Midwest (%)	12 ± 3	7 ± 2	9 ± 2	9 ± 2	4 ± 1	6 ± 1
Can. smelters (%)	38 ± 12	62 ± 10	53 ± 8	75 ± 12	80 ± 12	77 ± 8
Avg. pred. ($pg\ m^{-3}$)	5.0 ± 0.6	7.9 ± 0.7	6.4 ± 0.5	5.9 ± 0.6	8.0 ± 0.8	7.0 ± 0.5
Avg. obs. ($pg\ m^{-3}$)	5.1	8.6	6.8	6.3	7.2	6.8
Avg. obs./pred.	1.17 ± 1.28	1.36 ± 1.80		1.64 ± 4.44	1.01 ± 0.38	

Table 3. Effect of regional signatures on the apportionment of sulfate (in percent) between northeastern and midwestern sources.

Signatures*	Narragansett, Rhode Island: Summer 1982	Narragansett, Rhode Island: Winter 1982–1983	Narragansett, Rhode Island: Summer plus winter	Underhill, Vermont: Summer 1982	Underhill, Vermont: Winter 1982–1983	Underhill, Vermont: Summer plus winter
			Sulfate from northeastern sources			
1	61 ± 4	68 ± 4	63 ± 3	35 ± 4	74 ± 7	57 ± 4
2	49 ± 3	60 ± 4	52 ± 3	33 ± 5	71 ± 9	48 ± 5
3	72 ± 5	69 ± 5	71 ± 3	34 ± 3	76 ± 6	50 ± 3
4†	54 ± 4	60 ± 4	55 ± 7	34 ± 3	74 ± 6	49 ± 4
Mean	59 ± 10	64 ± 5	60 ± 9	34 ± 1	74 ± 2	51 ± 4
			Sulfate from midwestern sources			
1	39 ± 4	29 ± 3	36 ± 3	62 ± 6	19 ± 3	44 ± 4
2	51 ± 5	36 ± 4	47 ± 3	63 ± 9	26 ± 7	48 ± 6
3	28 ± 3	25 ± 3	27 ± 2	62 ± 5	18 ± 3	45 ± 3
4†	45 ± 5	34 ± 4	42 ± 6	62 ± 7	21 ± 4	45 ± 5
Mean	41 ± 10	31 ± 5	38 ± 9	62 ± 1	21 ± 4	46 ± 2

*Signatures: 1, NENG, BOS, NYC, INT, SONT (oldest signatures); 2, NENG, BOS, NYC, LMW, UMW, SONT (old northeastern, new midwestern and smelter signatures); 3, NENG, CEC, INT, SONT (new northeastern and smelter, old midwestern signatures); 4, NENG, CEC, LMW, UMW, SONT (newest signatures. †Best values.

was strongly enriched in a distant source, such as arsenic and indium in the Canadian smelters and selenium and sulfur in the Midwest, did the distant source contribute significantly relative to the northeastern "foreground."

Are the apportionments of sulfate reasonable? It would appear so, based on the following evidence.

1) The apportionments are stable with respect to changes in the combinations of signatures used to generate them. Table 3 shows seasonal apportionments of sulfate at Narragansett and Underhill resulting from four different combinations of northeastern and midwestern signatures, ranging from our oldest to our most current. This is a severe (perhaps unrealistically so) test of our apportionment procedure, as it incorporates temporal and spatial variabilities in signatures as well as different numbers of signatures for the major source areas. The actual dispersion of the four estimates is not very different from the uncertainties calculated for each estimate, although the dispersion is greater at Narragansett than at Underhill. This suggests that our estimated uncertainties are reasonable. Seasonal apportionments of sulfate seem to be accurate to within 10 to 20 percent at both sites. The best apportionments, from the newest signatures, are within a few percent of the mean from all the combinations.

2) The apportionments of sulfate are not random but are related to those of other elements. The Northeast and the Midwest, which are the major sources of most of the tracer elements, are also the major sources of sulfate. The Canadian smelters, which are minor sources of all but arsenic and indium, are also minor sources of sulfate. This lack of sulfate from the smelters confirms earlier data (*14*), which showed that less than 1 μg of sulfate per cubic meter accompanies even strong smelter signals at Narragansett, and that the smelter signals appear less than 1 day per week.

3) The apportionments of sulfate most resemble those of selenium, to which sulfur is most similar chemically. At both Narragansett and Underhill, sulfate and selenium were apportioned within a few percent of each other (except for winter 1982–1983 at Underhill); these apportionments differed from those of the other elements. A number of other researchers have also found similar sources for sulfate and selenium in aerosol (*15*).

4) The reality of major northeastern contributions to sulfate in the Northeast is confirmed by "pure" northeastern samples (whose total midwestern contributions to sulfate are less than 10 percent of the observed value). At Narragansett, these "pure" northeastern samples contained about 10 percent of the sulfate in both summer and winter. At Underhill, they contained roughly 5 percent of the sulfate in summer and 10 percent in winter. These figures are estimates of the minimum effect of the Northeast on itself. Because only part of the northeastern sulfate will be associated with "pure" northeastern samples, the actual effect of the Northeast on itself should be larger.

5) The seasonal attributions of sulfate at Narragansett and Underhill are consistent with their locations and large-scale seasonal changes in meteorology. Narragansett, being east of the Midwest, is downwind of it during all seasons, whereas Underhill, being 300 km farther northwest, is much more easily cut off from the Midwest during winter, when the prevailing winds come from the northwest, rather than from the southwest as in summer. Moreover, the counterclockwise circulation around the intense coastal storms of winter carries aerosol from the coastal Northeast inland to Underhill in winter much more than in summer, when the storms are smaller, weaker, and less frequent.

6) Our apportionments for sulfate are consistent with results from independent studies. (i) Husain *et al.* have reported that 62 percent of the aerosol sulfate at Whiteface Mountain, New York (less than 100 km west of Underhill), was found by sector analysis to have come from the direction of the Midwest during an 18-month period (*16*). Our annual apportionment of 45 percent of Underhill's sulfate to the Midwest is in reasonable agreement with this figure, if we consider that the years and durations of the two studies differed and that results from sector analysis, because they include local effects, will always overestimate distant contributions. (ii) The United States–Canada Memorandum of Intent (MOI) Report (*3*) evaluated eight long-range transport models for the sulfur system. Data from seven of the eight models were reasonably consistent with one another (*17*) and can be used to predict that 56 ± 9 percent of the annual particulate sulfate in the Vermont–New Hampshire area during 1978 originated in the American Midwest, whereas 42 ± 10 percent came from the East Coast and eastern Canada. In view of the fact that these models are quite simplified, the similarity to our figures for 1982–1983 at Underhill, Vermont (45 percent of the annual aerosol sulfate from the Midwest and 49 percent from the East Coast plus eastern Canada), is encouraging.

Sources of Sulfate During Episodes

Sulfate episodes show many of the aspects of sources found from longer term apportionments. For example, consider an episode at both Narragansett and Underhill during the third week of July 1982. Figure 3 shows the course of elemental concentrations and X/Se ratios through this episode at the two locations, together with the northeastern and midwestern regional coefficients and the sulfate apportioned to each region. Figure 4 gives simplified surface meteorological maps for 12 to 20 July, which can be compared with the chemical record in Fig. 3.

During 12 to 14 July 1982, a midlatitude high-pressure area moved eastward into the Ohio–Pennsylvania–New York area behind a storm system. Simultaneously, a Canadian high moved eastward into Ontario and Quebec. To the southeast lay a warm and humid Bermuda high. Beginning on 14 July, these three highs fused. First, the Canadian and American highs merged and allowed air of mixed origin to enter New England from the northwest. Then, the Bermuda high pushed north and merged with a southerly lobe of this fused high. By 15 July, a stagnated high-pressure area covered all of eastern North America.

The air over the eastern seaboard stagnated from 14 to 16 July 1982. During that time, the aerosol at Narragansett showed rapidly increasing concentrations of certain northeastern elements, such as zinc, antimony, and noncrustal vanadium but lesser increases in selenium, arsenic, and noncrustal manganese, the first two of which come largely from inland sources. Consequently, the northeastern regional coefficients C_{NENG} and C_{CEC} also rose rapidly, while the midwestern coefficients C_{LMW} and C_{UMW}, which began with moderate residual values, decreased rapidly and disappeared on 16 July. This stagnation produced very high concentrations of sulfate aerosol (16 μg m^{-3}) almost immediately, as high as were seen at Narragansett until the following September. On 15 and 16 July, the sulfate at Narragansett was at least 90 percent northeastern.

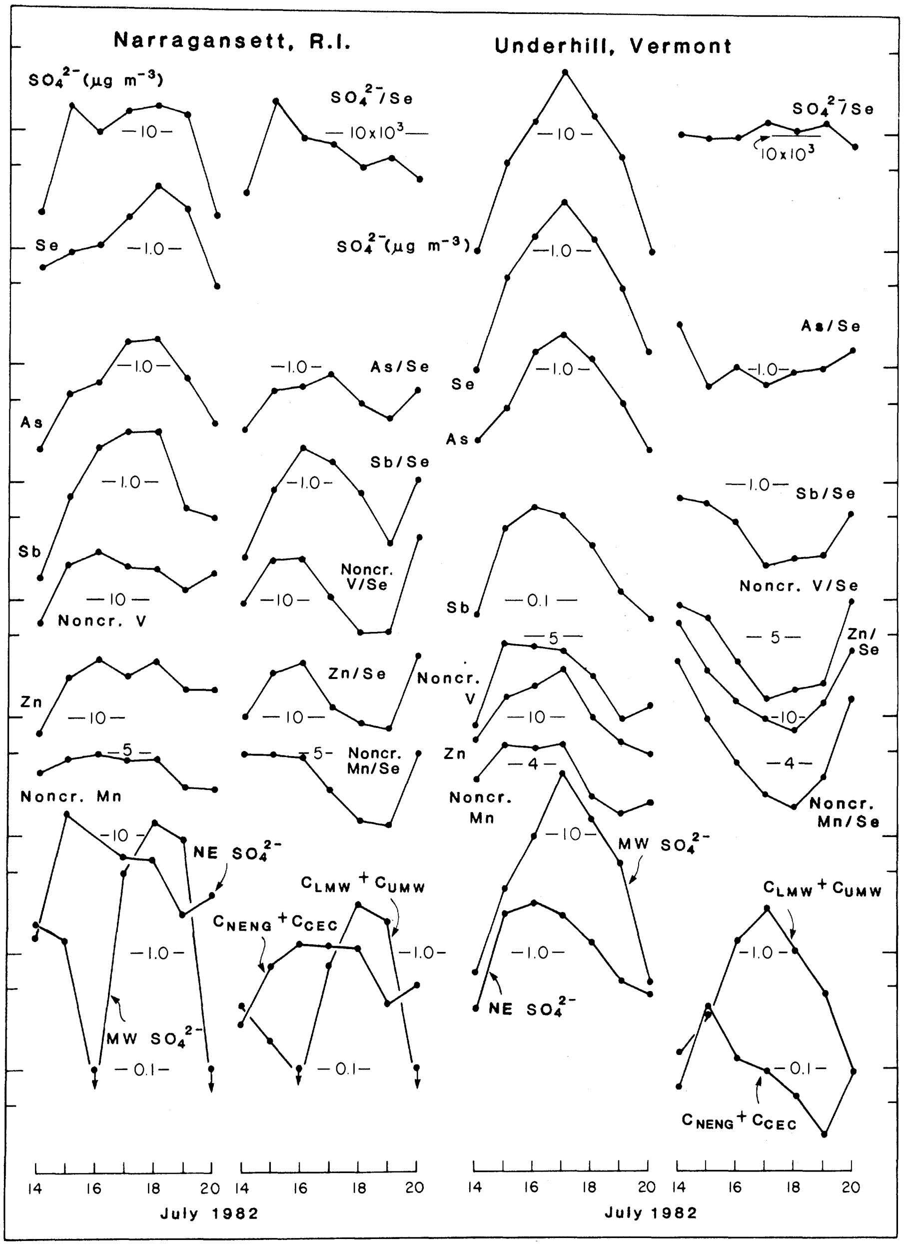

Fig. 3. Concentrations and ratios of trace elements, regional coefficients, and regional contributions to sulfate during the July 1982 sulfate episode at two sites in New England; MW, Midwest; NE, Northeast.

By contrast, this early period at Underhill was marked by steadily increasing concentrations of all elements and declining ratios to selenium. Accordingly, the midwestern regional coefficients rose steadily, whereas the northeastern regional coefficients rose on 15 July but decreased thereafter. Thus, the early part of the episode at Underhill was of mixed northeastern-midwestern character; only 20 to 40 percent of its sulfate was apportioned to northeastern sources. The lack of a strong northeastern phase at Underhill is understandable because there are relatively few local sources nearby whose aerosol could accumulate during stagnation.

At Narragansett, the second, or midwestern, phase of the episode took place on 17 to 19 July, as the large Bermuda high retreated southeastward, a low intensified and passed to the northwest, and a transport zone oriented southwest-northeast developed between the two. As this transport zone worked its way eastward, Narragansett came increasingly under its influence. Selenium, arsenic, and antimony reached their highest concentrations, whereas the other (northeastern) elements remained steady or decreased. Consequently, ratios to selenium took on their lowest values and the midwestern coefficients rose rapidly. Northeastern regional coefficients remained high during this period, however, because Narragansett, which is embedded in the Northeast, never really escapes local aerosol even when air flows in strongly from the outside. Sulfate concentrations were no higher during this second phase than during the first, or northeastern, phase. Although the sulfate was apportioned predominantly to midwestern sources during this second period, northeastern sulfate still accounted for 20 to 60 percent of the total for the episode. This figure compares well with the results of an earlier study in which it was found that the New York metropolitan area contributes roughly one-quarter of its own sulfate during summer at times when the air comes from the west-northwest (*18*).

Without regional tracers, this episode at Narragansett might well have been interpreted in terms of a single 5-day period. With the tracers, it is seen to have really been two episodes of different regional origins, which fortuitously produced equal sulfate. This episode is a microcosm of our longer-term finding that the weaker but closer northeastern

SO_2 sources create as much sulfate for the Northeast as the stronger but more-distant midwestern sources.

At Underhill, the greatest midwestern character was also found on 17 to 19 July. Sulfate, selenium, and arsenic were almost perfectly in phase with one another and peaked in concentration on 17 July. Although the highest sulfate concentration at Underhill, 35 $\mu g\ m^{-3}$, was double the high at Narragansett, average concentrations over the episode were very similar. During this second phase at Underhill, more than 90 percent of the sulfate was attributed to the Midwest. In view of the fact that the trajectories came from the west to southwest, this attribution is very reasonable. In contrast to midwestern sulfate, which varied from 0.5 to 33 $\mu g\ m^{-3}$ during the episode, northeastern sulfate formed a more nearly constant "foreground" of 0.5 to 2.5 $\mu g\ m^{-3}$.

By 20 July, a cold front had passed through the Northeast, sulfate concentrations had dropped to 1 to 2 $\mu g\ m^{-3}$, midwestern coefficients had fallen to very low values, northeastern coefficients had begun to rise, and the episode was over.

The results for this episode agree with the results of numerous other studies, which have shown that air masses bringing sulfate episodes to the Northeast during summer have passed over or stagnated over the Midwest (*19*). But our results extend this finding by showing that the Northeast can also be a strong source of episodic sulfate.

Summary

The regional elemental tracer system has shown that pollution aerosol in the Northeast is composed of a northeastern "foreground" plus superimposed pulses from the Midwest. When these pulses are strong enough, they form the classical episodes of midwestern aerosol. During periods of stagnation in the Northeast, however, aerosol produced locally can reach concentrations that rival or exceed those coming from the Midwest, even for sulfate. These two types of episodes can be distinguished clearly with elemental tracers.

Over the long term, the Northeast is its most important source for elements that are distributed broadly over eastern North America or enriched in northeastern emissions (vanadium, antimony, zinc, manganese, and probably many other elements not part of our tracer system). For elements enriched in distant sources, such as arsenic and indium from the Canadian nonferrous smelters and selenium and sulfur from the Midwest, the contributions of these distant sources may equal or exceed those from the Northeast. For sulfate, which is perhaps the most environmentally significant of these elements, transport models and other measurement programs confirm our basic conclusion that the Northeast and the Midwest contribute comparably to ambient levels in the Northeast. This amounts to a tenfold discrimination

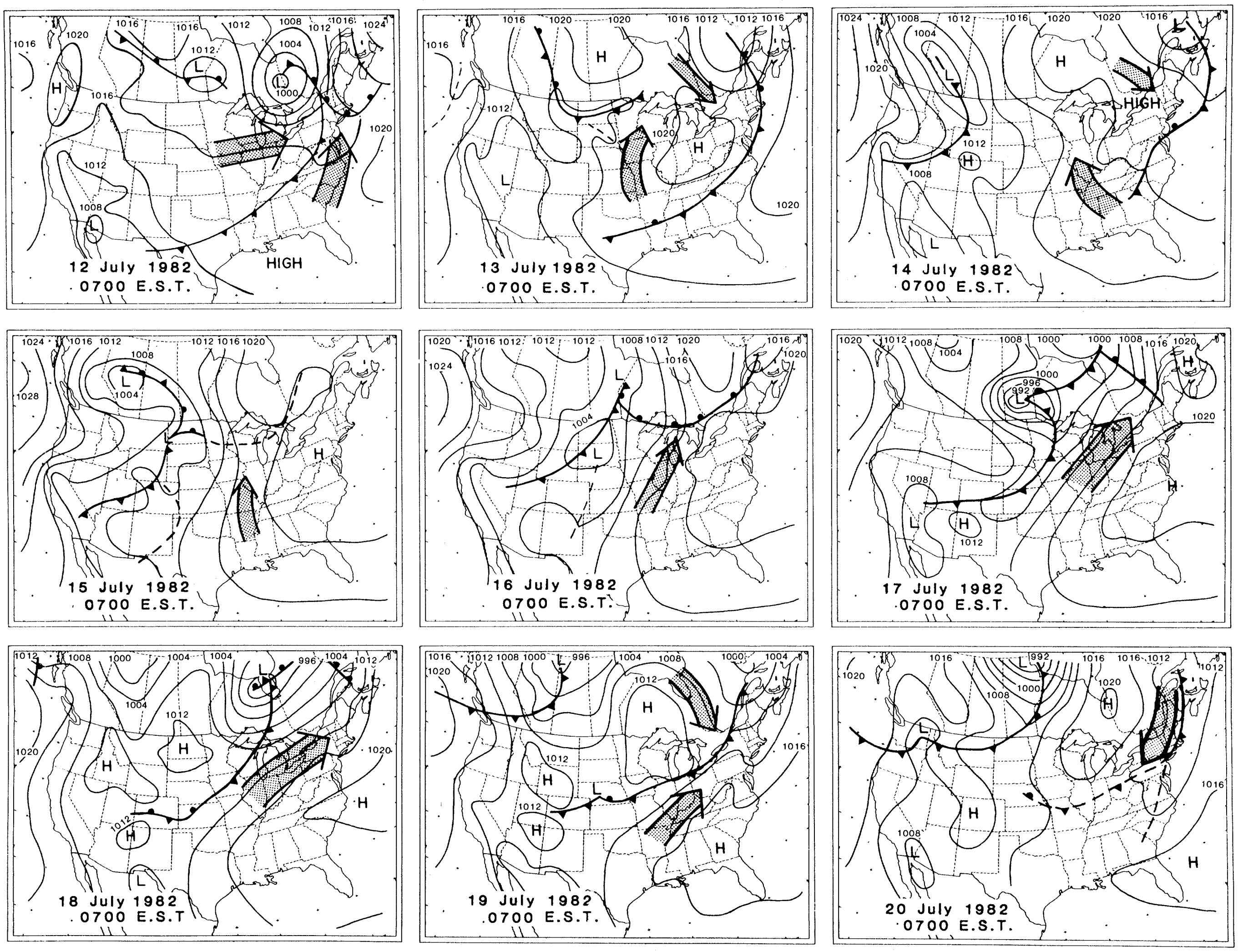

Fig. 4. Surface meteorological maps for 12 to 20 July 1982. Pressure is given in millibars.

against midwestern sources, which emit approximately 20 million tons of SO_2 annually versus 2 million tons for northeastern sources. A similar degree of discrimination with distance has been built into the MOI transport models (*20*).

More data are needed to refine our understanding of sources and transport of pollution aerosol in eastern North America. The elemental tracer system can and should be extended to other elements, to source regions farther from the Northeast, to additional seasons and years, and to precipitation. But the basic picture seems clear: even though strong pulses of transported aerosol reach the Northeast regularly from the Midwest, over the long term the Northeast is a major or dominant source of its pollution aerosol.

References and Notes

1. P. J. Samson, *J. Appl. Meteorol.* **19**, 1382 (1980); J. W. Wilson, V. Mohnen, J. A. Kadlacek, *Atmos. Environ.* **16**, 1667 (1982); R. G. Henderson and K. Weingartner, *ibid.*, p. 1657.
2. G. D. Thurston and J. D. Spengler, paper presented at the 74th meeting of the Air Pollution Control Association, Philadelphia, 21–26 June 1981.
3. A detailed discussion of eight long-range transport models is given in the Final Report (2F), Work Group 2 "Atmospheric Sciences and Analysis," United States–Canada Memorandum of Intent on Transboundary Air Pollution, 15 November 1982 [available from the Office of Environmental Processes and Effects Research (RD-682), Environmental Protection Agency, 401 M Street, SW, Washington, D.C. 20460].
4. K. A. Rahn and D. H. Lowenthal, *Science* **223**, 132 (1984).
5. G. M. Hidy, *J. Air Pollut. Control Assoc.* **34**, 518 (1984).
6. The noncrustal component of elements such as vanadium and manganese is used here to mean the mass present in excess of that expected from the earth's crust. It is calculated from a crustal reference element such as aluminum, silicon, iron, or titanium, assumed to be totally crustal in the aerosol (a) and a crustal reference material such as bulk rock or soil (r). The formula typically used to calculate the noncrustal component of element X is

$$\text{Noncrustal } X_a = \text{total } X_a - Al_a(X/Al)_r$$

In most cases, global mean crustal rock or soil is satisfactory as reference material; occasionally, local rock or soil must be used.
7. We originally chose to use selenium in the denominator because this element seemed to vary less from region to region than the other tracer elements. This selection was arbitrary, for both theory and actual experiment (*4*) show that different elements in the denominator are mathematically equivalent.
8. D. A. Belsley, E. Kuh, R. E. Welsch, *Regression Diagnostics* (Wiley, New York, 1980). For least-squares regressions weighted by effective variance [see (*11*) and associated discussion], the colinearity of signatures must be checked for each sample. According to the criteria of Belsley *et al.*, colinearity was not a problem in most of our samples. In some samples, however, weak to moderate near-dependencies were indicated between sources within a region, that is, NENG and CEC or LMW and UMW; dependencies between regions were rare. The program containing the technique of Belsley *et al.* for evaluating the colinearity of sources came from SAS-82, SAS Institute, Inc., Cary, N.C.
9. A review of residence times of atmospheric aerosol and the factors controlling them can be found in J. M. Prospero *et al.*, *Rev. Geophys. Space Phys.* **21**, 1607 (1983).
10. H. J. Williamson and D. A. DuBose, *Receptor Model Technical Series*, vol. 3, *User's Manual for Chemical Mass Balance Model* (Publication EPA-450/4-83-014, Environmental Protection Agency, Washington, D.C., 1983).
11. J. G. Watson, J. A. Cooper, J. J. Huntzicker, *Atmos. Environ.* **18**, 1347 (1984).
12. P. R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences* (McGraw-Hill, New York, 1969).
13. K. A. Rahn, C. Brosset, B. Ottar, E. M. Patterson, in *Particulate Carbon, Atmospheric Life Cycle*, G. T. Wolff and R. T. Klimisch, Eds. (Plenum, New York, 1982), pp. 327–342.
14. K. A. Rahn, N. F. Lewis, D. H. Lowenthal, in *Receptor Models Applied to Contemporary Pollution Problems* (Publication SP-48, Air Pollution Control Association, Pittsburgh, 1982), p. 163.
15. R. W. Shaw and R. J. Paur, *Atmos. Environ.* **17**, 2031 (1983); R. K. Stevens, T. G. Dzubay, C. W. Lewis, R. W. Shaw, Jr., *ibid.* **18**, 261 (1984).
16. L. Husain, J. A. Halstead, P. P. Parekh, V. A. Dutkiewicz, *Preprint Volume: Second Symposium on the Composition of the Nonurban Troposphere, May 25–28, 1982*; *Williamsburg, Va.* (American Meteorological Society, Boston, 1982), p. 218.
17. Regional Modeling Subgroup Report (2F–M), Work Group 2 "Atmospheric Sciences and Analysis," United States–Canada Memorandum of Intent on Transboundary Air Pollution, 15 October 1982 [available from the Office of Environmental Processes and Effects Research (RD-682), Environmental Protection Agency, 401 M Street, SW, Washington, D.C. 20460].
18. G. T. Wolff *et al.*, *Ann. N.Y. Acad. Sci.* **322**, 57 (1979).
19. L. Husain and P. J. Samson, *J. Geophys. Res.* **84**, 1237 (1979); P. J. Galvin, P. J. Samson, P. E. Coffey, D. Romano, *Environ. Sci. Technol.* **12**, 580 (1978); V. A. Dutkiewicz *et al.*, *Atmos. Environ.* **17**, 1475 (1983); P. P. Parekh and L. Husain, *ibid.* **15**, 1717 (1981).
20. R. B. Husar, "Possible Remedies to 'Acid Rain' " (Report 83P4, Center for Air Pollution Impact and Trend Analysis, Washington University, St. Louis, 1983).
21. We thank M. A. Voytek and K. R. Wunschel for technical assistance. Samples were provided by R. Poirot of the Vermont Agency of Environmental Conservation, F. Starheim and M. Fairchild of Ohio Edison, and J. McManus of American Electric Power. W. Pierson of Ford Scientific Laboratory graciously made his sampling site at Allegheny Mountain available. Samples were analyzed at the Rhode Island Nuclear Science Center, Narragansett. This work was supported by a grant from the Ohio Electric Utility Institute, contracts N00014-76-C-0435 and N00014-84-C-0035 of the Office of Naval Research, and cooperative agreement CR-810905 of the Environmental Protection Agency. Although the research described in this article has been funded in part by the Environmental Protection Agency, it has not been subject to Agency review and therefore does not necessarily reflect the views of the Agency; no official endorsement should be inferred.