United States
Environmental Protection
Agency

Atmospheric Sciences
Research Laboratory
Research Triangle Park NC 27711

Research and Development

EPA/600/S3-86/015 May 1986

EPA

Project Summary

Elemental Tracers Applied to Transport of Aerosol from Midwest to Northeast

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The main objectives of this Cooperative Agreement were to use a new regional elemental tracer technique to search for the signature(s) of midwestern aerosol, to use the resulting signature(s) to determine whether midwestern aerosol reaches the Northeast during summer, and to compare the transport of perfluorocarbon tracer gases with that of regional aerosol during the CAPTEX experiment. Secondary goals included testing various statistical aspects of the tracer system and evaluating stability of signatures during transport.

From samples in Ohio and Pennsylvania, two midwestern signatures were found and later used to show that aerosol is routinely transported from Midwest to Northeast in distinct pulses of 2-8 days. The tracer system was validated qualitatively during CAPTEX '83, where pulses of tracer gas from Ohio appearing in New England were always linked with pulses of midwestern aerosol.

Factor and cluster analysis were found to be only moderately useful for determining regional signatures. In eastern north America, As/Se, noncrustal V/Se, and In/Se have greater tracer power than Sb/Se, Zn/Se, and noncrustal Mn/Se.

Long-term apportionments showed that most elements in the Northeast come mostly from the Northeast, that As and In have large components from Canadian smelters, and that sulfate and Se have large components from the Midwest. Results for sulfate generally agreed within 20% with models and directional studies.

Regional signatures were found to be stable: during episodic transport from Midwest to Northeast, all four quantifiable elemental ratios changed by less than 25% on the average.

Regional least-squares apportionments were found to be insensitive to a variety of factors such as weighting scheme, scales of signatures, random elemental perturbations, duration of samples, and local sources of V.

This Project Summary was developed by EPA's Atmospheric Sciences Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Since 1980, the Arctic/Tracer Research Group at the University of Rhode Island has been developing an elemental tracer system to determine the source areas of pollution aerosol at sites far downwind. This capability is important for understanding long-range transport of aerosols and gases because at distances of 1000 km and more, traditional meteorological approaches such as trajectory analysis and synoptic analysis become very uncertain.

Elemental signatures have been used for many years to determine sources of urban aerosol because emissions from individual sources or types of sources have very different compositions. By contrast, aerosols from different regions are much more similar to one another because most regions contain similar mixes of sources. Nevertheless, significant elemental differences between regions can be found and exploited.

By late spring 1983, when this project was being proposed to EPA, the current seven-element tracer system (As, Se, Sb, Zn, In, noncrustal Mn, noncrustal V) had

been created and shown to be generally promising. Regional signatures, however, were still preliminary and needed to be developed further. The principal goals of this project were to seek to establish the elemental signature(s) of midwestern aerosol from samples taken in Pennsylvania and Ohio, use them to search for midwestern aerosol reaching the northeast during summer, and attempt to validate the tracer system by comparing the transport of perfluorocarbon tracer gases with that of regional aerosol during the Cross-Appalachian Tracer Experiment (CAPTEX) of September-October 1983. Secondary goals included testing various statistical aspects of the tracer system and evaluating the stability of elemental signatures during transport.

All these goals were met. Two distinct midwestern signatures were found, and were used to show that aerosol is transported routinely from the Midwest to the Northeast in pulses of a few days in duration. These pulses are related to particular configurations of large-scale meteorology, are most frequent in summer, and often come simultaneously to widely separated parts of the Northeast. During CAPTEX, pulses of tracer gas in Rhode Island and Vermont stemming from releases in Dayton, OH were always associated with pulses of midwestern aerosol; i.e., the elemental tracer system was validated qualitatively. High-volume aerosol samples were found satisfactory for our system of regional tracing in eastern North America: six of seven elemental ratios differed by less than 50% between fine and total aerosol; during episodic transport from Midwest to Northeast, none of the four quantifiable ratios changed by more than 25% on the average.

The geographical boundaries of the source regions are still only partially delimited. The sharpness of their boundaries is not yet known but is suspected to be fairly broad.

When necessary, signatures were determined from as few as 4-5 samples chosen carefully from much larger sets. When available, as many as 48 samples were used for signatures, however. Although the smaller numbers of samples appear to yield reliable signatures, the greater numbers are clearly preferable. Typical uncertainties of elemental ratios in regional signatures are 40%.

The least-squares regional apportionment procedure was shown to have little or no sensitivity to weighting scheme, scales of signatures, random perturbations in samples or signatures, typical duration of samples, strong local sources of V, and number of samples used to apportion sulfate. The apportionments did depend moderately on the combination of elements in the signatures and strongly on having representative signatures from each major region.

Long-term regional apportionments of aerosol at Narragansett and Underhill showed that most elements come mostly from the Northeast, that As and In have large components from the Canadian smelters, and that sulfate and Se have large components from the Midwest.

Absolute accuracy of regional coefficients cannot be fully verified at present, because no independent standard exists. Samples during CAPTEX confirmed the midwestern coefficients semi-quantitatively: strong maxima of midwestern aerosol in the Northeast were detected each time a pulse of perfluorocarbon gas from Dayton was measured. Where they overlap, long-term regional apportionments of sulfate in the Northeast agree within 20% to results from transport models and other field studies.

The Two Midwestern Regional Signatures

The Lower Midwest (LMW) signature was determined from a several-day pollution episode at Allegheny Mountain, PA during August 1983. LMW represents aerosol from the Ohio River Valley and southward. The same signature was also seen in the next southwestern episode at Allegheny Mountain, and was later sensed repeatedly at two sampling sites in Ohio. Because LMW is strongly enriched in Se relative to the other elements, it seems to be derived primarily from coal combustion.

The Upper Midwest (UMW) signature was determined from samples taken near McArthur and Hartville, OH during winter and spring 1984. It represents aerosol from the Ohio River Valley and northward. Compared to LMW, most elemental ratios to Se are markedly higher in UMW. Thus, UMW seems to be coal-based but with a significant component from heavy industry. This agrees with the relatively greater industrialization of the Upper Midwest.

Transport of Aerosol from Midwest to Northeast

The two midwestern signatures were used to detect aerosol transported to one or more sites in the Northeast according to the following procedure:

(1) At each site, a series of daily aerosol samples was taken and analyzed for the seven tracer elements. From the seven elemental concentrations, each sample was apportioned into its five regional contributions, two from the Northeast, two from the Midwest, and one from the Canadian smelters. The result was five "regional coefficients."

(2) Generalized northeastern and midwestern regional coefficients were then formed for each sample by summing the two northeastern coefficients and the two midwestern coefficients. The summed coefficients are proportional to the amount of primary pollution aerosol from the two major source regions.

(3) The generalized regional coefficients and the Canadian smelter coefficient were plotted for the series of samples. The resulting figure showed directly how the relative influences of the source areas varied over the time series.

Such plots for New England invariably have the same basic features:

(1) Northeastern aerosol is nearly always present and has relatively steady concentrations (the northeastern "foreground").

(2) Midwestern aerosol is much more variable. It usually appears as strong pulses of 2-4 days in duration. Between pulses, midwestern coefficients are very low. Pulses come roughly weekly.

(3) Canadian smelter aerosol appears much less often than midwestern or northeastern aerosol. It comes in spikes of 1-3 days in duration which are usually near-simultaneous in at least Rhode Island and Vermont.

Most variations in regional coefficient can be directly related to changes in large-scale meteorology. When air comes to New England from the north or east, or stagnates, northeastern aerosol dominates. When air flows in an organized manner from the interior, a midwestern component is superimposed on the northeastern aerosol. When air comes strongly from the northwest, usually behind a cold front, a Canadian smelter component is often seen.

Deriving Regional Signatures by Pattern-Recognition Techniques

Regional signatures are normally determined by a combination of chemical

and meteorological techniques. These procedures are still evolving and have not yet become standardized or fully objective. Scientific judgment is still required to select the most appropriate samples. To remedy this, alternative multivariate approaches such as factor and cluster analysis are being explored.

Cluster analysis of 100 samples from two sites in Ohio gave a "UMW" signature that did not differ from the original UMW in any systematic way, but an "LMW" with higher ratios than the original. Factor analysis of the same samples gave another "UMW" and "LMW," again with the "UMW" matching the original more closely than the "LMW" did. In addition, factor analysis of samples from Underhill, VT provided estimates of a northeastern and a transported midwestern signature.

The UMW and LMW signatures derived from factor analysis of Ohio samples fit the Vermont samples as well as the original UMW and LMW did, but the UMW and LMW derived from cluster analysis did not work as well. The Vermont samples were fit much more poorly by the "northeastern" and "midwestern" signatures derived from factor analysis of the Vermont samples themselves.

Concerning the feasibility of using pattern-recognition techniques to derive regional signatures of pollution aerosol, it thus seems that

(1) factor analysis within the source area works better than cluster analysis;

(2) factor analysis shows promise, at least for determining the major signature within a strong source region. The indeterminancy and arbitrary nature of the factor solution must be kept in mind, however.

Considering that there are at least some circumstances under which factor analysis gives reasonable signatures, its limits should be explored in more detail.

Long-Term Regional Apportionments in the Northeast

Extensive data from four seasonal experiments during 1982-83 at Narragansett, RI and Underhill, VT have been used to apportion sulfate and the seven tracer elements among northeastern, midwestern, and Canadian smelter sources. The results showed that

(1) most of the noncrustal V, noncrustal Mn, Zn, and Sb (50-98%) came from the Northeast;

(2) As and In had significant components (25-80%) from the Midwest and/or the Canadian smelters, particularly during winter;

(3) the influence of the smelters was greater at Underhill than at Narragansett;

(4) annually, Se and sulfate at both sites came roughly equally from the Northeast and the Midwest;

(5) only 3-5% of the annual-average sulfate came from the smelters;

(6) the apportionments at Narragansett varied little with season, whereas those at Underhill were much more northeastern in winter than in summer.

Seasonal average concentrations of the tracer elements were generally accounted for to within 10-15%, whereas individual daily concentrations were accounted for to 20-50%. Sulfate was accounted for to the 10% level for seasonal averages but to only 50-60% for individual daily samples.

In summary, most trace elements in northeastern aerosol actually came from the Northeast. Only when an element was strongly enriched in a distant source, such as As and In in the Canadian smelters and Se and S in the Midwest, did the distant source contribute significantly relative to the northeastern foreground.

Qualitative Validation of the Elemental Tracer System During CAPTEX '83

During CAPTEX '83, perfluorocarbon tracer gas was released from Dayton, OH and Sudbury, Ontario under meteorological conditions expected to bring it to the Northeast. Because signatures of aerosol from both Ohio and the Sudbury Basin were being developed, it seemed natural to see whether aerosol from these sources would be found to reach the Northeast simultaneously with the tracer gas. Tracer gas from Dayton should be accompanied by one or both of the midwestern signatures; tracer gas from Sudbury should be accompanied by the Canadian smelter signature.

Daily samples from Rhode Island and Vermont during CAPTEX (mid-September through October 1983) were analyzed for sulfate and trace elements and resolved into regional components as discussed above. The abundance of aerosol from the region of release, as measured at each site 1-2 days after the release, were used to predict whether the tracer gas should have been sensed at the sites. Of the 12 cases for which gas could be compared with aerosol, 10 agreed clearly. In one of the two other cases, midwestern aerosol was found without tracer gas, but this type of result was anticipated and did not constitute a problem. In the other case, smelter aerosol was absent, but moderate tracer gas from Sudbury was found. On this day, the strongest part of the tracer plume passed rapidly and briefly north of our sampling site. This probably explained why smelter aerosol was not observed.

Thus, qualitative predictions for tracer gas during CAPTEX were accurate in 11 of 12 cases, and the other case can be explained reasonably.

Stability of Regional Signatures

The stability of regional signatures during transport was examined in two ways. First, the relative particle sizes of the tracer elements were determined repeatedly at Narragansett, to address the question of how much elemental ratios would change if all coarse aerosol and no fine aerosol were removed during transport. Second, actual changes in ratios were examined by comparing signatures of aerosol in 34 midwestern episodes at Underhill, VT to the two original midwestern signatures.

To evaluate the relative particle sizes of the tracer elements and sulfate, 12 pairs of simultaneous samples of total aerosol and submicron aerosol were taken at Narragansett during May-June 1984. The X/Se ratios in total aerosol relative to the fine component ((X/Se) total/(X/Se) submicron), the factor by which the elemental ratio would decrease during transport if all the coarse aerosol and none of the fine aerosol were removed, were less than 1.5 for all ratios except noncrustal Mn/Se, for which it was 2.4. By contrast, elemental ratios vary by factors of 6-170 over the five North American signatures. Thus, the maximum changes expected during transport due to particle-size effects alone are far below the ranges already found for North American signatures.

During actual transport, elemental ratios seem to be even more stable than this, however. For 34 episodes of midwestern aerosol observed 1000 km downwind in Underhill, VT, average values of the As/Se, Zn/Se, and noncrustal Mn/Se ratios were within 25% of the mean of the midwestern ratios, and the average value of Sb/Se, after correcting for a 24% contribution from northeastern sources, fell within 10% of the midwestern mean. Thus, the

best empirical evidence showed that all four quantifiable elemental ratios changed by less than 25% on the mean during transport of 1000 km. Consequently, it appears that regional signatures may be applied with confidence to receptor samples taken far from the source under episodic conditions, even when the aerosol samples are not size-segregated.

Statistical Tests of the Regional Tracer System

A systematic series of tests of various statistical aspects of the elemental tracer system has confirmed its general stability and the general validity of the results derived from it:

(1) The number of samples used to derive a signature from a specific distribution has little effect on the final value. From sets of 48 and 12 samples used to construct two of the signatures, four random subsets of five samples each gave X/Se ratios that were statistically identical to the original signatures.

(2) According to a procedure for evaluating colinearity, or "near-dependency" of signatures, the five signatures for North America are not colinear.

(3) According to several tests, using different weighting schemes for the least-squares apportionments does not affect the resulting regional coefficients systematically. In cases where coefficients within the Midwest and the Northeast change, the total contribution from each region remains stable.

(4) Scaling regional signatures upward or downward by one to two orders of magnitude does not affect unconstrained apportionments (where negative coefficients are allowed), but may affect constrained apportionments slightly.

(5) The number of samples in a series used to apportion sulfate is not critical, as long as it is above 20 or so.

(6) By perturbing a Vermont aerosol sample and associated signatures randomly and repeatedly and apportioning with the perturbed data, it was shown that the perturbed coefficients overlapped the unperturbed coefficients; i.e., the tracer system is stable with respect to long-term effects of random variations.

(7) Within limits, length of sample does not influence apportionments: results from semi-weekly samples are nearly identical to apportionments of daily samples over the same period.

(8) Strong local sources of individual tracer elements affect apportionments minimally: doubling or halving the concentrations of individual elements changes the regional coefficients by factors several times smaller.

(9) Regional coefficients are robust relative to the mix of elements in the signatures: although removing elements changes regional coefficients somewhat, it does not alter the basic qualitative impressions about the regional makeup of the sample.

(10) Midwestern and northeastern signatures are not interchangeable in practice: mixtures need one signature from each area in order to fit them well, and aerosols from a single region must have a signature from the region to be fit properly.

(11) Bias introduced by constraining regional coefficients to non-negative values is insignificant, i.e., comparable to or less than the overall uncertainties of apportionment.

(12) Typical uncertainties (precisions) of the 1-2 largest regional coefficients in a given sample are 25-40%; uncertainties in minor coefficients can reach or exceed 100%.

Recommendations for Future Work

Although this study has helped to demonstrate that regional elemental tracers can now be used reliably to determine source areas of signature elements and sulfate in aerosol of eastern North America, the tracer system has not reached its potential, nor have its limits been probed. Much can still be done to expand and improve it. The following areas of research seem most important and promising:

(1) Add elements to the system, so that more signatures can be apportioned simultaneously and existing signatures discriminated more reliably.

(2) Investigate the extent to which existing regional signatures would be refined by more samples from more sites. Several sampling sites per major region, each with at least 100 samples, would be ideal.

(3) Determine additional signatures in North America, especially in the southern and western portions of the Midwest. This will help resolve the true effect of the more distant regions of the Midwest on air quality in the Northeast.

(4) Apply the tracer technique to additional sites in New Hampshire, Maine, and New York State. Only then will the conclusions about sources of pollution aerosol be generally valid for "the Northeast."

(5) This program should be continued until climatologically valid conclusions about source areas can be drawn for one or more sites in the northeast. This kind of conclusion requires data from at least five years.

(6) The utility of regional elemental signatures for sampling periods well under one day should be investigated. Situations under which the sources of northeastern aerosol may vary in significantly less than 24 hours include coastal storms which pass rapidly over New England and bring a cold sector, a warm sector, and a cold sector in less than a day, as well as frontal conditions in general.

(7) Multivariate statistical techniques for determining signatures should be pursued until their prospects are clarified.

(8) Synthetic data should be used to help determine the limits of detection of regional signatures in individual samples.

(9) The relative amounts of signature elements in submicron and total aerosol should be determined in the Midwest in the same fashion as already done in the Northeast. This will help evaluate potential changes in signatures during transport from Midwest to Northeast.

(10) Actual changes in regional signatures during transport should be further studied, under both episodic and nonepisodic conditions if possible.

(11) The extent of the association between regional signatures and large-scale meteorology should be investigated in detail, for chemistry and meteorology are inherently complementary and will be used together in future studies.

(12) The statistics of the regional tracer system need to be examined in greater detail than has been possible to date. Two examples of important topics are the extent of bias introduced by constraining the regional coefficients to non-negative values and the mathematical basis, strengths, limitations, and possible bias of the regression procedure for sulfate.

(13) In order to draw reliable conclusions about the origin of trace contaminants in deposition, the tracer technique must be extended to precipitation. This will be one of the most important applications of the tracer technique.

☆U. S. GOVERNMENT PRINTING OFFICE:1986/646 116/20825

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The complete report, entitled "Elemental Tracers Applied to Transport of Aerosol from Midwest to Northeast," (Order No. PB 86-168 812/AS; Cost: $16.95, subject to change) will be available only from:
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