



Project Summary

Development and Evaluation of Composite Receptor Methods

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A composite receptor method for PM-10 apportionment was evaluated to determine the stability of its solutions and to devise cost-effective measurement strategies. Aerosol samples used in the evaluation were collected during summer, 1982, by dichotomous samplers at three sites in the vicinity of Philadelphia, PA. The composite receptor method consisted of a wind-trajectory method, chemical mass balance (CMB), and multiple linear regression (MLR). Several industrial sources were determined by CMB, and vehicle exhaust and a sulfur-component were determined by MLR. Measured Pb minus a CMB-derived correction for other sources was used as an independent variable in MLR, and MLR results for the Pb abundance in vehicle exhaust agreed with predictions of a model for vehicle emission factors. In resolving PM 10 into 11 components, scanning electron microscopy was essential for coal-fly ash and botanical matter, x-ray fluorescence (XRF) was needed for the sulfur-component and vehicle exhaust, and instrumental neutron activation analysis (INAA) was essential for fluidized catalytic crackers at refineries. The remaining components were determined well by either INAA or XRF. Ten to twenty samples were sufficient to determine average source contributions by CMB. At least 50 samples were needed to determine vehicle exhaust and the sulfur-component by MLR.

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

Receptor models are techniques for using data on the composition of atmospheric aerosol to resolve particulate mass concentration into components related to emission sources. The U. S. Environmental Protection Agency has specified that receptor models may be used with dispersion models to develop plans to meet its new PM-10 standard and has developed guidelines on how the chemical mass balance (CMB) receptor model is to be used. The present report explores how the resolution and accuracy of the CMB model can be improved by using it in conjunction with other receptor methods and by including measurement data by a variety of methods including x-ray fluorescence (XRF), instrumental neutron activation analysis (INAA), scanning electron microscopy (SEM), ion chromatography (IC) and x-ray powder diffraction (XPD).

This report is based on data obtained in a study intended to develop and improve the capabilities of receptor models. Ambient aerosol was collected in the PM-10 size range (particle diam $\leq 10 \mu\text{m}$) at three sites in the Philadelphia area during summer, 1982. Source emissions were collected using a dilution-cooling technique at seven major stationary sources. Surface soil and dust were collected at multiple sites and suspended by an aerosol generator. Ambient, source, and soil samples were deposited on filters by dichotomous samplers and analyzed by XRF, INAA, IC, pyrolysis, SEM and XPD.

The Philadelphia study led to the development of a composite receptor method that uses several different receptor methods in concert. It consists of a wind-trajectory method to identify significant sources of trace elements, CMB to determine their contributions to PM-10, and CMB

combined with multiple linear regression (MLR) to determine a sulfur-component and vehicle exhaust. The composite method was developed to overcome limitations that those receptor models have when used individually.

In developing the composite method, it was recognized that three criteria must be met for a chemical species to be included in a CMB:

- (1) All sources of the species must be included in the CMB.
- (2) The species' abundance in particulate emissions from all of those sources must be known.
- (3) Sources with collinear signatures (i. e. similar species abundances) cannot be determined individually and must be included in a broadly defined source category.

Although signature data have been compiled for more than 120 sources, collinearity becomes severe in a typical CMB if more than only 6 to 12 components are included. Thus, the wind trajectory method was valuable for selecting sources to include in CMB analyses. Components in CMBs for fine particles were crustal matter and emissions from municipal incinerators, oil-fired power plants, fluidized catalytic cracker, antimony roaster, and paint pigment manufacturing. Because signatures for coal-fly ash and soil were collinear, criterion 3 required that they be included in a broadly defined crustal source category. Elements included in CMB analyses were Si, Ti, Fe, Ni, Zn, Cd, Sn and Sb measured by XRF and Al, V, La, Ce and Sm measured by INAA.

Criterion 2 led to the exclusion of Pb and S from the CMB because their abundances were not known well for vehicle exhaust and a sulfur-component. The latter consisted of sulfate, cations and possibly water or organic matter. Multiple linear regression (MLR) can be used to estimate S- and Pb-abundances, but measured Pb could not be used as an independent variable in MLR because vehicle exhaust was not the only significant source of Pb. Thus, the above described CMB was applied to each ambient sample to determine non vehicular Pb, which was subtracted from measured Pb to yield a vehicle-exhaust tracer. This work describes application of MLR to various data subsets chosen to reveal any dependence on sampling site, sample size and measurement method.

Apportionments presented here include SEM results for botanical matter and coal-fly ash in coarse particles. SEM provided estimates for several other components including emissions from municipal incinerators. For samples heavily impacted

by municipal incinerators, SEM confirmed CMB results. However, cases were identified where CMB results indicated municipal incinerator emissions when none were detected by SEM. Evaluation of those cases suggested possible departure from criterion 1 because Zn, an important tracer for incinerators, had other possible sources not included in the CMB. Thus, this work includes an evaluation to determine the effect of cases with high Zn concentrations on the results of the composite receptor method.

Results

The composite method enabled PM-10 to be resolved into 11 components. The method provided an estimate of the average Pb abundance in vehicle exhaust when incinerators and oil combustion contributed a portion of the Pb. Final results indicate that the vehicle exhaust portion of PM-10 ranged from 5% to 10%. Stationary sources included in the CMB contributed less than 5% to PM-10. The sulfur-component contributed $54 \pm 10\%$ of PM 10. Wind-stratified data indicated that $80 \pm 20\%$ of particulate S was from regional sources beyond the Philadelphia area. Multiple linear regression of S vs. tracers Se and either V or Ni attributed 72 ± 8 and $16 \pm 5\%$ of particulate S to coal- and oil-fired power plants, respectively.

The combined use of XRF and INAA enabled more sources to be resolved than was possible when only one method was used. XRF data were essential for obtaining accurate determinations of the large sulfur-component and vehicle exhaust. INAA was essential for determining a $0.2 \mu\text{g}/\text{m}^3$ contribution by fluid catalytic crackers at refineries. SEM was essential for determining 0.2 and $2 \mu\text{g}/\text{m}^3$ contributions of coal-fly ash and botanical matter, respectively. Remaining components were determined well by either INAA or XRF data.

Conclusions

Evaluation of data for 156 samples from the Philadelphia study led to the design of a cost-effective plan for PM-10 apportionment by receptor models. Because INAA and SEM-EDX data were not directly used in MLR, it was only necessary to analyze enough samples to provide adequate estimates of the means. Standard errors computed from the standard deviations of CMB-derived component concentrations suggest that 10 to 20 randomly selected samples analyzed by INAA and SEM-EDX should be sufficient for major species. Both fine and coarse fractions should be analyzed by INAA rather than only the fine frac-

tion as was done in the Philadelphia study. It is appropriate that all samples were analyzed by XRF because XRF analysis is less expensive and many analyzed samples were needed for the composite of CMB and MLR. Analysis of data subsets by MLR indicates that the sulfur-component was determined well with as few as 31 samples, but the vehicle component required more than 50 samples.

Analysis of sulfate collected in dichotomous samplers was of little value in the present study other than to confirm that XRF could be used to measure S in sulfate. In future studies, it would be more useful to collect samples with annular denuder systems so that the nitrate volatilization problem can be avoided and both gaseous and particulate S and N compounds can be analyzed.

In the Philadelphia study, two dichotomous samplers were used to collect samples for XRF and SEM analyses. The use of two dichotomous samplers is not only expensive, but the resulting fine fraction samples are unsuitable for analysis by SEM. A modified dichotomous sampler was developed which enables one device to collect both fine and coarse particles that can be analyzed by XRF, INAA and SEM.

The abundance of S in the sulfur-component derived by CMB-MLR was at least 19% lower than that of S in pure sulfate salts. Measurement error can account for no more than half of the difference. Much of the difference may be due to water or carbon bound to sulfate particles.

If Pb is used to determine vehicle exhaust by CMB analysis, the Pb abundance needs to be determined. In the present study, it was shown that the abundance of Pb in vehicle exhaust could be derived by CMB-MLR, and the results agreed with predictions of a comprehensive emissions model. If the model and its parameters were fully validated, it could be used instead of an expensive set of field measurements to derive the Pb abundance. However, not all parameters in that model have been validated, and the model does not include particulate mass resulting from condensation of exhaust gasses in the atmosphere. Until the model is validated for use with CMB, a composite of CMB and MLR will be needed to determine the Pb abundance.

Decreasing use of Pb in fuel will make it difficult to use Pb as a tracer for vehicle exhaust in future years. The vehicle model predicts a factor of 20 decrease in Pb-emissions per unit of VMT between 1982 and 1990. Such a decrease implies that if

the measurements described in this report were repeated in 1990, vehicles would contribute only 20% of ambient Pb. Such a low vehicle contribution will be a difficult challenge even for the composite of MLR and CMB. One way to overcome this difficulty might be to use the composite of CMB and MLR to deduce the Pb abundance in vehicle exhaust sampled near a roadway. Because Pb emission rates differ widely among various classes of vehicles, it is important that the roadway sampling site represents the vehicle mix and driving speeds of areas where PM-10 is to be apportioned. An alternative would be to use another tracer for vehicles. A tendency for Br to volatilize in the presence of acid aerosol makes Br a tracer of questionable quality. Carbon monoxide may be a better one, but, in future years, as the proportion of vehicles with control devices for CO increases, non vehicular sources of CO are likely to interfere with CO from vehicles.

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The complete report, entitled "Development and Evaluation of Composite Receptor Methods," (Order No. PB 88-234 067/AS; Cost: \$14.95, subject to change) will be available only from:

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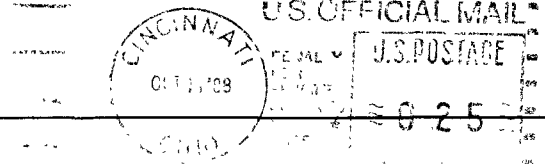
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