



Project Summary

Source Resolution of Polycyclic Aromatic Hydrocarbons in the Los Angeles Atmosphere: Application of a Chemical Species Balance Method with First Order Chemical Decay

Marc Maurice Duval and S. K. Friedlander

The chemical mass balance method that was originally developed for source resolution of chemical elements was extended in this study to chemically reactive compounds in atmospheric aerosols. The basic theoretical equation was formulated to incorporate atmospheric decay factors for reactive species. The method was tested with selected polycyclic aromatic hydrocarbons using source emission data and atmospheric concentrations reported in the literature. Absolute atmospheric concentrations of coronene, benzo(a)pyrene, benzo(e)pyrene, benzo(g,h,i)pyrene, and anthanthrene measured at 13 sites in the Los Angeles basin were apportioned between automobile and refinery emission sources.

Refinery emission patterns of polycyclic aromatic hydrocarbons in the Los Angeles basin were computed from an analysis of auto emissions data and ambient data from a refinery area. Rates of atmospheric degradation of these hydrocarbons were calculated from an analysis of auto emission and ambient air data. Literature reports on major emissions of polycyclic aromatic hydrocarbons

from combustion sources were reviewed and evaluated.

This Project Summary was developed by EPA's Environmental 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

Polycyclic aromatic hydrocarbons (PAH) and a variety of other toxic organic and inorganic chemical species can be found in the aerosols commonly present in ambient air. These aerosols have been associated with adverse health effects on the human populace as well as visibility degradation and damage to vegetation and materials. When toxic materials are present in the atmosphere in amounts that represent an unacceptable health risk or other adverse effects, it is important to identify the sources of these pollutants so that appropriate control measures can be taken. By assessing the contribution of individual emission source categories to pollutant concentrations in the atmos-

phere, control strategies can be selectively directed toward those sources found to contribute significantly to the observed environmental effects.

Control agencies have been using dispersion modeling for many years to estimate the impact of a particular source on pollutant concentrations at a receptor site. However, quantitative accuracy of these models has been limited by the variability and uncertainties in the meteorological, emission, and other parameters. In recent years, receptor models of various types have been developed as an alternative to source resolution and apportionment of air pollutants. In this approach, analysis of the chemical composition of aerosol samples from both the receptor site and the source is used to retrospectively generate a source apportionment of chemical elements and species. Source apportionment requires a chemical mass balance (CMB) calculation that, as originally developed, assumes conservation of mass and the emission of characteristic patterns of chemical elements from each class of sources. The CMB method has been successfully applied to the apportionment of chemical elements in aerosols from several parts of the United States. In this study, the CMB method is extended to chemically reactive organic species, viz., PAH.

The basic equation for the CMB method can be expressed as:

$$\rho_i = \sum_{j=1}^p c_{ij} m_j$$

where ρ_i = mass concentration of species i measured at the receptor site

where c_{ij}

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c_{ij} = mass fraction of species i present in the mass from source j at the point of emission

m_j = mass concentration of the emissions from source j measured at the receptor site

For species that may react in the atmosphere the basic equation must be reformulated as follows:

$$\rho_i = \sum_{j=1}^p \alpha_{ij} x_{ij} y_{ij}$$

where α_{ij} = dimensionless decay factor (fraction of species i emitted from source j remaining in the aerosol at the receptor site)

x_{ij} = dimensionless ratio of mass of species i to the reference species l in the emission from source j

y_{ij} = mass concentration of reference species l (non-reactive) from source j at the point of measurement

Working with an overdetermined system of n equations with p unknowns ($n > p$), the solution to the least squares fitting is found from:

$$(Z)(Y) = (Q)$$

where (Z) = $p \times p$ matrix whose generic term on the j th row and m th column is:

$$z_{jm} = \sum_{i=1}^n \frac{\alpha_{ij} x_{ij} \alpha_{im} x_{im}}{\sigma_{\rho_i}}$$

(Y) = $p \times l$ matrix whose term on the j th row is y_{ij}

(Q) = $p \times l$ matrix whose generic term on the j th row is:

$$q_j = \sum_{i=1}^n \frac{\rho_i \alpha_{ij} x_{ij}}{\sigma_{\rho_i}}$$

The decay factor, computed from the ratio of atmospheric concentrations found at the receptor site to the corresponding concentrations measured at the point of emission, was shown to be related to the reaction rate coefficient, assuming first order kinetics and conditions for a continuous stirred tank reactor.

Polycyclic aromatic hydrocarbons are produced in combustion processes.

Because of their high boiling points, they are readily adsorbed onto the particulate phase as they cool down. Because of their carcinogenicity and because they are found concentrated on particles in the inhalable size range, they are of particular concern in health studies of ambient aerosols. Because lower molecular weight PAH have sufficiently high vapor pressures to warrant concern about vaporization losses during sampling, this study has been confined to PAH with molecular weights ≥ 252 amu.

Major combustion sources emitting PAH include coal combustion, coke production, incineration, wood combustion, open burning, and gasoline-powered engines. Since automobile emission characteristics depend on many variables, survey results from a large number of vehicles were used to compute a representative PAH emission profile. Although the source resolution study was conducted in Los Angeles, California, results from a survey of German auto emissions were employed because of the unavailability of such data for American cars.

Previously published data on atmospheric samples taken in Los Angeles near a freeway junction were used to obtain decay factors for four PAH involved in the study (Table 1). A fifth compound, benzo(e)pyrene, was assumed to be a stable species. Decay factors were obtained from a comparison of PAH-coronene ratios from the German auto fleet and the Los Angeles atmosphere. The deviation was assumed to be a first order decay in all species of interest. Additionally, reaction rate constants were calculated

Table 1. PAH Decay Factors^a

PAH	Decay Factor
Benzo(a)pyrene	0.48 ± 0.21
Benzo(e)pyrene	1.04 ± 0.29 ^b
Benzo(a)fluoranthene	0.98 ± 0.26
Benzo(g,h,i)perylene	0.83 ± 0.19
Anthanthrene	0.21 ± 0.11

^aArithmetic mean, within 68% confidence.

^bBenzo(e)pyrene was assumed to be a stable species in the source resolution analysis.

assuming atmospheric residence times equal to those for a continuous stirred tank reactor or plug flow reactor and compared with data reported in the literature.

Refinery emissions of PAH were determined from ambient air data reported in the literature for an area in Los Angeles downwind from a concentration of petroleum refineries and chemical plants. The area was assumed to receive contributions from both refineries and automobiles. Emissions attributable to the refineries were obtained by computing the difference between the observed concentration for each PAH and the corresponding calculated PAH concentration attributable to auto emissions. The automotive contribution was determined using lead concentrations as a tracer for auto emissions in this area together with lead-PAH ratios determined at a Los Angeles site assumed to be totally dominated by auto emissions. The calculated refinery emissions of PAH and the measured German auto emissions, corrected for their decay, constituted the concentration matrix that was used in computations of source apportionment by the chemical species balance method (Table 2).

Data from two different studies involving 13 sites in the Los Angeles basin were analyzed for source contributions assuming that autos and refineries were the only significant sources for the PAH. Significant refinery contributions were found at four of the sites. The measured concentration for each PAH was compared to the total calculated PAH concentration (auto plus refinery contribution) to provide a measure of the accuracy of the results. Average deviations are within -11 to +7%. The CMB method did not

yield reasonable results with literature data from a third study. Errors in the ambient concentration vectors are considered to be the most likely cause of the slightly negative refinery contributions obtained in the source apportionment computations.

Recommendations

The results of this study have shown that the incorporation of decay factors into the CMB method is a promising approach for apportioning the concentrations of reactive organic species in the atmosphere to their various emission sources. Additional studies with more accurate data and fewer assumptions are needed to assess the accuracy of this approach.

- Subsequent studies should utilize United States' auto fleets to insure the representatives of the emission patterns of PAH and other species of interest.
- Improvements are needed in the determination and validation of decay factors.
- Studies should be extended to other areas of the United States with a more complex mix of emission sources.
- The combination of factor analysis with CMB should be investigated as an approach for obtaining improved source resolution.

Table 2. Source Concentration Matrix.

PAH	PAH-Benzo(e)pyrene Ratio	
	Automobiles	Refineries ^a
Benzofluoranthenes	1.08 ± 0.36	1.43
Benzo(a)pyrene	0.98 ± 0.36	3.85
Benzo(g,h,i)pyrene	3.10 ± 0.87	2.46
Anthanthrene	0.57 ± 0.27	2.12
Coronene	1.96 ± 0.46	0.23 ^b

^aAll PAHs were corrected for decay.

^bBased on small coronene concentrations.

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The complete report, entitled "Source Resolution of Polycyclic Aromatic Hydrocarbons in the Los Angeles Atmosphere: Application of a Chemical Species Balance Method with First Order Chemical Decay," (Order No. PB 82-121 336; Cost: \$9.00, subject to change) will be available only from:

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