



## Project Summary

# Receptor Models for Airborne Organic Species

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The purposes of this study were (1) to critically review existing source emissions data to determine if variations in the organic composition of such emissions can be used to distinguish sources of airborne particulate matter and particulate organic matter, (2) to attempt to develop receptor source apportionment models for three fractions of particulate organic matter and selected polycyclic aromatic hydrocarbons, using an existing set of ambient aerosol measurements made at the site in New York, and (3) to define critical needs for the development of receptor models for airborne particulate organic matter.

The literature search focused on polycyclic aromatic hydrocarbons (PAH), aliphatic hydrocarbons, carboxylic acids, aza-arenes, sulfur heterocyclic PAH, and nitro-PAH. As most of the reported data were PAH measurements, ratios of PAH to a reference compound were calculated and compiled for comparisons of source emissions profiles.

Receptor source apportionment models were successfully developed for three fractions of respirable ( $D_{50} = 3.5 \mu\text{m}$ ) particulate organic matter and two PAH using the factor analysis-multiple regression modeling technique. The models included adjustments for shifts in the vapor-particle distribution due to temperature changes.

The lack of adequate organic composition data for source emissions was found to be a critical limitation for receptor model validation and also for development of chemical mass balance models. Recommendations

were made for further development of receptor models for particulate organic species.

*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

There has been increasing interest in and development of receptor source apportionment models to assist in defining control strategies for particulate pollutants. Such models attempt to identify the principal sources of airborne particles and to determine their contributions to ambient aerosol mass concentrations using measurements made at sampling, i.e., "receptor" sites. Most of the work in this field has focused on particle mass and elemental composition; little work has been done on receptor models for particulate organic matter.

The organic fraction of the aerosol constitutes 10 to 40% of the airborne particles that can penetrate the human respiratory system. Extractable organic matter (EOM) and many of the subfractions and compounds within this fraction have been shown to be biologically active in both mammalian and bacterial bioassays. Thus, there is reason to suspect that the organic fraction may be of significance to human health and that control of the sources of these materials may be required.

The ultimate source of much of the primary and secondary particulate organic

matter in urban and suburban aerosols is combustion of fuels for transportation, heating, power production, and industrial processes. Recent trends toward increased utilization of diesel engines in light-duty trucks and autos and of coal and wood as fuels for home heating are of particular concern, since the emissions from these sources are rich in organic compounds and can impact large population centers with severe impacts in specific neighborhoods. At present, we lack the tools that would enable us to determine the amounts and classes of organic compounds (as they exist in the atmosphere) contributed to urban atmospheres by various types of sources.

The purpose of this study was to investigate the potential of receptor modeling techniques as tools for determining sources of airborne organic compounds or particulate organic mass. Specific objectives were (1) to review existing data and to determine if these data indicate that variations in the organic composition of source emissions could be used to distinguish sources of airborne particulate matter and particulate organic matter, (2) to empirically determine if receptor modeling techniques could be used to identify the sources of airborne particulate organic pollutants and estimate their contributions, and (3) to define critical needs in the development of receptor source apportionment models for particulate organic species. In addition, samples of inhalable ( $D_{50} \leq 15 \mu\text{m}$ ) particulate matter were collected during the Philadelphia Model Evaluations Study of 1982 and were analyzed for EOM and PAH.

### **Critical Review of Existing Particulate Organic Source Emissions Data**

Available literature on the organic composition of emissions from major sources of organic particulate pollutants were critically reviewed to determine if the existing data show significant differences among sources that would be useful in developing "fingerprints" for receptor source apportionment models and if so, for which classes of compounds and what source types. Data were also sought on unique organic or carbon species that could be used as source tracers. The adequacy of the existing data for receptor modeling was then evaluated.

Based on existing emissions inventories, emphasis was placed on obtaining particulate organic source emission data for motor vehicles, home heating (gas, oil, wood, and coal), industrial boilers, power

plants (oil, coal, gas), large incinerators, coke production, petroleum refining, and soil.

The classes of organic compounds selected for the literature search were those known to be present in the ambient aerosol or in source emissions that might be useful in distinguishing sources of particulate matter: PAH, aliphatic hydrocarbons, carboxylic acids, aza-arenes (nitrogen heterocyclics), sulfur heterocyclic PAH, and nitro-PAH.

Copies of approximately 180 publications were obtained and reviewed, but few of these reported data that were suitable for the purpose of this review. The majority of those that were suitable reported PAH measurements. For each source sample, the ratios of individual PAH to a reference compound, benzo(e)pyrene, were calculated and these data were compiled for comparisons among sources. Major factors to be considered when comparing the existing organic source composition data were reviewed and discussed. These include the effects of combustion conditions, sampling protocols, sample preservation, extraction, and analytical methods on the reported PAH or other organic compound profiles.

Despite their many limitations, the existing data were judged to provide certain useful information for receptor modeling. First, the PAH profiles of sources that have been repeatedly sampled and analyzed by the same investigators appear to be quite reproducible. Second, the existing data indicate that there are organic compositional differences that can be exploited in differentiating certain sources. Furthermore, the data provide indications of compounds that should be more fully investigated. The PAH, in particular, appear most promising. Their proportions in emissions (gas plus particle) from a given source type frequently vary over several orders of magnitude, which enhances their potential usefulness for source discrimination. There also appear to be several unique or almost unique PAH tracers that may be useful. The existing data provide a basis for selecting those compounds within this class that are likely to be most stable in the atmosphere. In addition, good sampling and analytical methods already exist for this class of compounds.

There are, however, many deficiencies in the existing data on the organic composition of source emissions. The data have generally been collected for the purpose of determining emission rates and are consequently inadequate for use in

receptor source apportionment modeling. Specific deficiencies are the following:

1. Data generally exist only for the PAH, and even these have not been adequately measured in many sources of interest. Other composition variables, e.g., other classes of organics, trace elements, carbon, and particle mass have rarely been simultaneously measured for the same source.
2. Existing organic composition data are rarely representative of the average emissions for a source type. Usually, they represent a single source and a single set of operating conditions for that source.
3. Sampling methods used for source emissions are frequently incompatible with those used for ambient samples collected at a receptor site. In the case of source sampling, organic vapors and emitted particles are both collected. For ambient samples, organic vapors are rarely collected with the particles. In addition, sampling duration and filter loading differ for the two types of samples; this may also affect composition.
4. Differences in the particle size cuts of collected samples affect composition.
5. The analytical methods and quality assurance practices used to collect existing source composition data vary widely. For receptor modeling, both accuracy and precision of the measurement are critical.

Finally, it should be recognized that changes in the composition of source emissions can occur as a consequence of regulation and technology; consequently, receptor and source sampling and analysis methods and measurements must be continuously updated for receptor modeling.

### **Development of Receptor Source Apportionment Models for Particulate Organic Matter**

To evaluate the feasibility of developing receptor source apportionment models for particulate organic matter, an existing set of ambient aerosol measurements was analyzed using a factor analysis-multiple regression modeling method that had been previously developed in this laboratory. This method was selected because the lack of adequate organic source emissions composition data precluded the development of chemical mass balance models.

Weekly samples of respirable ( $D_{50} = 3.5 \mu\text{m}$ ) particulate matter that had been collected on the roof of a 15-story

building in the Manhattan section of New York City during 1979 and 1980 had been analyzed for three fractions of EOM, PAH, several trace elements (V, Pb, Cu, Mn), and water-soluble sulfate. This data base was extended by X-ray fluorescence (XRF) analysis for additional trace elements (Fe, Mo, P, Br, Ti and Ni) and a second analysis (XRF) for Pb, V, and S. The concentrations of three organic fractions of increasing polarity were determined by sequentially extracting the particulate samples with cyclohexane (CX), dichloromethane (DCM), and acetone (ACE).

Factor analysis was used to identify major sources of airborne particulate organic matter and select source emissions tracers. Six to nine factors were obtained, depending on the number of variables included in the factor analysis. A consistent pattern of factors was observed; the following major sources were identified through the high factor loadings for certain source tracer elements: (1) oil burning (V); (2) motor vehicles (Pb, Br); (3) resuspended soil (Fe, Ti, Mn); (4) sulfate-related aerosol (SO<sub>4</sub><sup>2-</sup>, S); and (5) incineration (Cu). These factors were consistent with the known sources of airborne particulate matter in New York City, where residual oil is the major fuel used for power generation and space heating. Neither wood nor coal are currently used as fuels.

Multiple regression models of the form

$$[\text{Organic fraction}] = k_1T_1 + k_2T_2 + \dots + k_iT_i + R$$

were developed, where the T<sub>i</sub> are concentrations of source tracer elements selected from the factor analysis, the k<sub>i</sub> are multiple regression coefficients, and R is the portion of the concentration of organic matter that cannot be attributed to any of the sources in the model. The coefficients, which are determined from the ambient measurements, are proportional to the ratios of particulate organic matter to tracer elements in the source emissions. For model verification these coefficients were compared to available source emission data. The multiple regression models were then used to estimate the average contributions of various source types to each organic fraction.

The coefficients of the selected source emissions tracers and the values of R for the models are summarized in Table 1. The contributions of each source type estimated from the models are presented in Table 2. The models indicated that residual oil burning and resuspended soil were the major sources of respirable par-

**Table 1. Multiple Regression Coefficients of Extractable Organic Matter Models**

Organic fraction (dependent variable)	Coefficients of tracer elements of models ± S.E. <sup>a</sup>					
	V	Ti	Pb	S	Cu	R
CX	25 ± 3	20 ± 12	1.1 ± 0.4	<sup>b</sup>	<sup>b</sup>	1.2 ± 0.3
DCM	<sup>b</sup>	55 ± 13	<sup>b</sup>	0.11 ± 0.06	<sup>b</sup>	0.28 ± 0.29
ACE	29 ± 6	42 ± 24	<sup>b</sup>	0.28 ± 0.10	22 ± 10	1.4 ± 0.6

<sup>a</sup>Coefficients ± the standard errors of the coefficients are for independent variables expressed in units of micrograms per cubic meter.

<sup>b</sup>No statistically significant coefficient obtained.

**Table 2. Summary of Estimated Contributions of Various Sources to the Average Ambient Concentrations of Extractable Organic Matter in New York City for 1979 and 1980<sup>a</sup>**

Source Type	CX <sup>b</sup>	DCM <sup>b</sup>	ACE <sup>b</sup>	Total EOM <sup>c</sup>
Residual Oil	1.06 ± 0.13	<sup>d</sup>	1.26 ± 0.27	2.3 ± 0.4 (24%)
Motor Vehicles	0.55 ± 0.21	<sup>d</sup>	<sup>d</sup>	0.55 ± 0.21 (6%)
Resuspended Soil	0.33 ± 0.20	0.92 ± 0.22	0.71 ± 0.41	2.0 ± 0.8 (21%)
Incineration	<sup>d</sup>	<sup>d</sup>	0.54 ± 0.25	0.54 ± 0.25 (6%)
Sulfate-Related	<sup>d</sup>	0.44 ± 0.22	1.08 ± 0.39	1.5 ± 0.6 (15%)
Unattributed	1.17 ± 0.33	0.28 ± 0.29	1.36 ± 0.63	2.8 ± 1.2 (29%)

<sup>a</sup>Contributions reported in units of µg/m<sup>3</sup>; the last column of the Table presents the contributions of each source type as a percentage of total EOM.

<sup>b</sup>CX = cyclohexane-soluble organic matter; DCM = dichloromethane-soluble organic matter; ACE = acetone-soluble organic matter.

<sup>c</sup>Total EOM = CX + DCM + ACE.

<sup>d</sup>No statistically significant coefficient obtained.

ticulate organics at this site during 1979 and 1980. These two sources accounted for 24 ± 4% and 21 ± 8% of the total EOM (CX + DCM + ACE), respectively. Sulfate-related organic aerosol accounted for an additional 15 ± 6% of EOM, while motor vehicles and incineration each contributed 6% at this rooftop site in Manhattan.

The models indicated that the sources of organic aerosol can be different for fractions of different chemical composition. For example, sulfate-related organic aerosol was found only for the more polar DCM and ACE fractions, which would contain any secondary organic aerosol.

Twenty-nine percent of the total EOM could not be attributed to known sources but is suspected to originate in part from upwind urban and regional background sources. Unidentified sources and filter sampling artifacts may also contribute to the residual. The samples used for model development were collected over periods of one week in order to maintain continuity with total suspended particulate matter (TSP) sampling that was begun in 1967. For organic sampling, 12- or 14-h samples would be more appropriate as volatilization losses and filter reactions would be minimized.

Seasonal variations in temperature and aerosol surface area can affect the distribution of organics between the vapor and particulate phases and, thus, might

account for some of the residual, R, of the model for CX. A first-order approximation was used to correct for such effects and account for some of the residual. The results indicated that only 3-4% of the residual could be explained in this way.

The coefficients of the model for the CX-soluble organic fraction were in good agreement with the ratios of this fraction to the tracer elements in source emission samples in those instances in which source emissions data were available. No source emission data were available for such comparisons for the two other organic fractions.

Some exploratory work has been done on developing similar source apportionment models for individual PAH. Using a limited set of data, statistically significant models were developed for benzo(a)pyrene and chrysene. The coefficients of the models were in good agreement with the few data available for source emissions. Since the distribution of chrysene between particulate and vapor phases is strongly temperature dependent, a Langmuir model was used to determine total chrysene concentrations based on particulate concentrations, ambient temperature, and the heat of sublimation of this compound. A second chrysene model was then developed for total chrysene (vapor plus particulate). Work on PAH models is continuing with a much

larger set of PAH measurements. In addition, the use of target transformation factor analysis to develop source emissions profiles for particulate organics based on ambient measurements is under investigation.

### The Philadelphia Study

As part of the Philadelphia Model Evaluations Study of 1982, samples of inhalable ( $D_{50} \leq 15 \mu\text{m}$ ) particulate matter were collected for organic analyses. The purpose of this work was to provide information on the concentrations of EOM and PAH and, if possible, use these data for further model development.

Samples were collected every 24 h between July 25 and August 14, 1982 at the Fireboat Station located at the intersection of Delaware and Allegheny Streets; the Delaware River is to the east and Interstate Highway 95 is two blocks to the west of the site. Heavy diesel truck traffic was observed on Delaware and Allegheny Streets.

The geometric mean concentrations of the CX, DCM, and ACE fractions during this period were 2.4, 1.9, and  $7.6 \mu\text{g}/\text{m}^3$ , respectively; daily variations in concentrations are shown in Figure 1. The average concentrations for the CX and DCM fractions at this site were both  $0.4 \mu\text{g}/\text{m}^3$

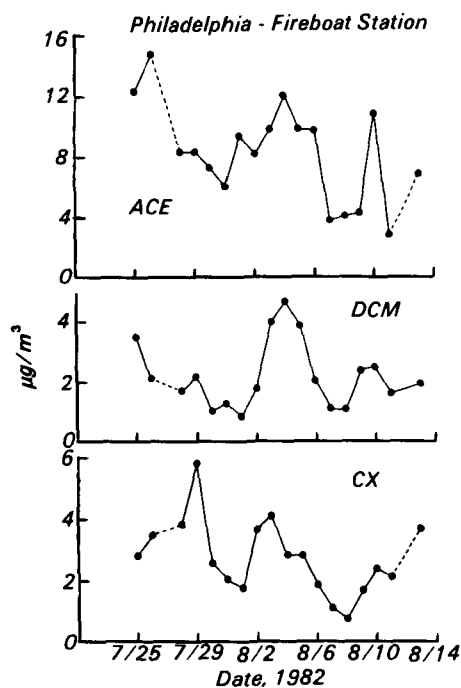


Figure 1. Variations in concentrations of cyclohexane (CX)-, dichloromethane (DCM)-, and acetone (ACE)-soluble organic matter at the Philadelphia Fireboat Station.

higher than those observed at our site located in Camden, NJ, to the south of this site; the ACE concentration at the Philadelphia site was  $1.6 \mu\text{g}/\text{m}^3$  higher. There was evidence of weekday-weekend variations in the concentrations of CX-soluble organic fraction; minima were observed on the weekends. Some inter-site (Philadelphia and Camden) correlation was apparent for all three fractions, but the strongest correlation ( $r = 0.70$ ,  $p = 0.01$ ) was observed for the polar ACE fraction, which contains oxidized hydrocarbons and secondary organic aerosol formed during summertime smog episodes.

The concentrations of 12 PAH (fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, and benzo(j)fluoranthene, benzo(e)pyrene, and benzo(a)pyrene, perylene, benzo(ghi)perylene and indeno(1,2,3-cd)pyrene were measured daily. The average concentrations of each compound during weekdays and weekends of the sampling period are presented in Table 3. Concentrations of individual compounds were generally less than  $1 \text{ ng}/\text{m}^3$ . The geometric mean concentration of benzo(a)pyrene during this period was  $0.13 \text{ ng}/\text{m}^3$ , and values ranged from 0.03 to  $1.07 \text{ ng}/\text{m}^3$ . The average concentration of all PAH was lower on the weekends than on weekdays.

Less motor vehicle traffic (diesels in particular) in this area on the weekends was hypothesized as the reason for lower concentrations of both CX-soluble organics and PAH compounds. Both PAH compounds and the CX fraction materials are directly emitted from combustion sources, i.e., they are primary aerosol species. Source apportionment modeling was not possible due to the lack of appropriate organic source emission data.

Table 3. Average Weekday and Weekend Concentrations of Polycyclic Aromatic Hydrocarbons\*

Compound	Weekdays	Weekends
Fluoranthene	$0.74 \pm 0.57$	$0.25 \pm 0.14$
Pyrene	$0.57 \pm 0.45$	$0.16 \pm 0.11$
Benz(a)anthracene	$0.35 \pm 0.41$	$0.05 \pm 0.04$
Chrysene	$1.09 \pm 1.29$	$0.35 \pm 0.31$
Benzo(b)fluoranthene	$0.40 \pm 0.35$	$0.10 \pm 0.08$
Benzo(k)fluoranthene	$0.28 \pm 0.36$	$0.05 \pm 0.05$
Benzo(j)fluoranthene	$0.50 \pm 0.36$	$0.19 \pm 0.12$
Benzo(e)pyrene	$0.16 \pm 0.79$	$0.20 \pm 0.18$
Benzo(a)pyrene	$0.36 \pm 0.37$	$0.06 \pm 0.04$
Perylene	$0.06 \pm 0.08$	$0.003 \pm 0.003$
Benzo(ghi)perylene	$0.63 \pm 0.55$	$0.16 \pm 0.16$
Indeno(1,2,3-cd)pyrene	$0.32 \pm 0.36$	$0.06 \pm 0.07$
Mean of Total PAH	$6.28 \pm 5.21$	$1.69 \pm 1.14$

\* $n = 13$  for weekdays;  $n = 5$  for weekends. In calculating the average concentrations  $\pm$  one standard deviation, one half of the detection limit was used for values less than the detection limit. Values in the Table are expressed in nanograms per cubic meter.

### Recommendations

The existing literature on the organic composition of source emissions, although somewhat limited, suggest that it may be possible to distinguish certain types of sources by differences in the organic composition of their emissions, e.g., emissions from diesel and spark-ignition engines, resuspended soil and coal combustion, residential oil, coal, and wood combustion, and motor vehicles and coke ovens. The results of the receptor source apportionment modeling work for three fractions of EOM and selected PAH indicate that it is feasible to develop such models to estimate the contributions of various types of sources to airborne particulate organics. However, it is clear from this study that further progress in these areas will require suitable organic composition data on important combustion sources. The following recommendations are made:

1. A source emissions sampler suitable for collecting particulate organics that are in temperature and pressure equilibrium with vapor phase organics and the vapor phase organics should be developed and field tested. Field testing should involve comparisons of such samples with those collected by the modified EPA method 5 and those collected downwind in plumes from sources.
2. It is recommended that a carefully designed winter (to avoid photochemical changes) field study be conducted using the PAH as model compounds in order to confirm that differences in organic source emissions exist that can be used for distinguishing sources of receptor modeling. Ambient and source samples should be collected at a site influenced

by just a few major source types such as automobiles, diesels, and oil heating. Source and ambient samples would have to be collected in such a way that the composition data would be comparable. Vapor phase and particulate PAH should be collected for all samples. The source samples must be sufficiently representative of the average conditions of each source type.

3. Portions of the samples or matched samples should be analyzed for trace elements and other composition variables. The best possible quality assurance practices should be used for all organic and inorganic analyses. In view of the impending loss of Pb and Br as tracers of motor vehicle emissions, more extensive chemical characterization of emissions from catalyst-equipped vehicles and diesel vehicles should be undertaken to try to identify individual compounds or patterns of organic compounds that might be useful as future tracers of motor vehicle emissions.
4. If the experiment outlined in recommendation 2 is successful, more extensive source emissions testing should be undertaken to define the organic and inorganic composition of important sources emitting toxic substances. Sampling equipment and protocols suitable for organics such as dilution samples should be used.

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*James L. Cheney is the EPA Project Officer (see below).*

*The complete report, entitled "Receptor Models for Airborne Organic Species," (Order No. PB 85-172 583/AS; Cost: \$19.00, subject to change) will be available only from:*

*National Technical Information Service  
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