Molecular Identification of Organic Compounds in Atmospheric Complex Mixtures and Relationship to Atmospheric Chemistry and Sources

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This article describes a chemical characterization approach for complex organic compound mixtures associated with fine atmospheric particles of diameters less than 2.5 μm ($PM_{2.5}$). It relates molecular- and bulk-level chemical characteristics of the complex mixture to atmospheric chemistry and to emission sources. Overall, the analytical approach describes the organic complex mixtures in terms of a chemical mass balance (CMB). Here, the complex mixture is related to a bulk elemental measurement (total carbon) and is broken down systematically into functional groups and molecular compositions. The CMB and molecular-level information can be used to understand the sources of the atmospheric fine particles through conversion of chromatographic data and by incorporation into receptor-based CMB models. Once described and quantified within a mass balance framework, the chemical profiles for aerosol organic matter can be applied to existing air quality issues. Examples include understanding health effects of $PM_{2.5}$ and defining and controlling key sources of anthropogenic fine particles. Overall, the organic aerosol compositional data provide chemical information needed for effective $PM_{2.5}$ management. *Key words:* air pollution, analysis, atmospheric chemistry, chemical composition, emission sources, fine particles, organic compounds. *Environ Health Perspect* 110(suppl 6):995–1003 (2002). http://ehpnet1.niehs.nih.gov/docs/2002/suppl-6/995-1003mazurek/abstract.html

The atmosphere is a processing unit for organic compounds. Many important, complex chemical and physical processes occur in the atmosphere that modify, transport, and deposit organic compounds emitted from natural and man-made sources. One component of interest is atmospheric fine particles with nominal diameters of less than 2.5 μm ($PM_{2.5}$). These particles consist of complex mixtures of organic compounds exhibiting a wide spectrum of physical properties such as molecular weight, polarity, and pH. Fine particles vary in abundance and composition both spatially and temporally, with concentrations highest typically in urban atmospheres (*1–4*). Organic aerosols comprise approximately 10–30% by mass of the total fine particulate matter present in urban and rural U.S. atmospheres (*4–18*). However, higher ambient concentrations of combined organic carbon (OC) and elemental carbon (EC) are possible in urban atmospheres. For example, OC and EC were measured in Mexico City during a 1997 intensive measurement study and contributed approximately 50% of the ambient fine-particle mass (*19*).

The organic chemical composition of airborne fine particles is an important, multidisciplinary research area for several reasons. First, controlling fine-particle atmospheric concentrations requires an understanding of the emission sources. Organic complex mixtures contain molecular tracers that can be linked to specific emission sources or are byproducts from dominant atmospheric photochemical reactions. Identifying the mass contribution of key source markers in $PM_{2.5}$ complex mixtures and coupling this information with chemical mass balance (CMB) models provides a quantitative approach for estimating individual emission source inputs to urban atmospheres (*5–7,20–28*). Second, full chemical descriptions of organic mixtures collected as $PM_{2.5}$ have not been achieved. Approximately 20% of the masses of organic complex mixtures are resolved quantitatively as individual compounds (*5,6,9,10,29*). The remaining 80% of this organic complex mixture mass may contain individual compounds with great significance as ambient indicators representing particulate matter exposure. Incomplete chemical descriptions of fine-particle complex organic mixtures have slowed progress in establishing critical links between specific toxic constituents of airborne particles with health indicators (*8,17,30*). According to a recent National Research Council (NRC) panel, significant uncertainty exists in terms of what chemical components require reduced atmospheric emissions to achieve cost-effective reductions in health risks to populations (*17,30*). The same NRC panel recommended an aggressive research agenda to examine the chemical composition of ambient fine particles, fine-particle emission source chemistry, and toxicological and epidemiological research to identify the most biologically relevant $PM_{2.5}$ constituents that produce several acute health end points.

From an analytical chemistry perspective, atmospheric fine particles continue to present significant challenges, given the large molecular assemblages and variable concentrations of the associated organic complex mixtures. The analytical protocol must be robust and account for various forms of organic compounds (chemical functional groups and compound classes). The analytical method must have low-level detection capability at the low- to sub-ppb level. Bulk chemical and molecular properties of the fine-particle $PM_{2.5}$ carbonaceous material must link quantitatively to each other to distinguish among individual sources of fine carbonaceous particles to urban atmospheres. Finally, the measurement protocol must have good statistical control so meaningful data are produced (*31*).

A comprehensive chemical assessment of $PM_{2.5}$ complex organic mixtures is fundamental to understanding associated health effects and to developing engineering technologies for effective air quality management. This article presents a general discussion of the complex chemical composition of organic aerosol particles that are the result of many types of emission sources to the atmosphere. The discussion of fine-particle chemical composition is followed by an overview of a chemical species mass balance analytical approach for measuring the organic chemical composition of fine particulate matter from bulk chemical constituents to ultimately the molecular level. This analytical approach is the underlying method for SuperSite $PM_{2.5}$ characterization studies funded by the U.S. Environmental Protection Agency. Finally, the article describes techniques for relating chemical properties of the complex mixtures to ambient trends and emission sources using data reduction and modeling procedures.

Influence of Emission Sources on Chemical Composition of Organic Aerosol Particles

A general understanding of major source categories is useful in developing a descriptive basis for fine-particle organic chemistry. Primary emissions to the atmosphere are from man-made and natural sources. These primary organic compounds are modified by chemical oxidation reactions involving either single-phase reactants (homogeneous reactions) or multiphase reactants (heterogeneous reactions). Gas-phase organic compounds reacting with ozone is an example of homogeneous reactions, whereas reactions involving $PM_{2.5}$ organic surface layers and a gas-phase inorganic oxidant compound (hydroxyl radical) is an example of a multiphase reactant system (heterogeneous reactions). The reaction by-products of either homogeneous or heterogeneous processes are regarded as secondary atmospheric organic compounds formed within the lower troposphere. Figure 1 shows a simple representation of the major interconnections between primary biogenic and anthropogenic atmospheric compounds, photochemical conversion processes, and resulting secondary gas-phase and particle-phase organic matter. Typically, compounds emitted from primary biogenic sources are reduced (higher elemental C:H compositions) than either anthropogenic or secondary emissions. Atmospheric organic matter undergoing photochemical reactions becomes oxidized via reactions with several major oxidizing species in the atmosphere: the hydroxyl radical, the nitrate (NO_3) radical, and ozone (32–34). The oxidation process decreases the elemental C:H and adds oxygen-containing functional groups such as carbonyl, carboxylic acid, and nitro groups to reactive hydrocarbons. Examples of biogenic compounds found as $PM_{2.5}$ include epicuticular plant waxes ranging from n-$C_{23}H_{48}$ to n-$C_{33}H_{68}$ (C:H = 1.0:2.1). Polycyclic aromatic hydrocarbons (PAHs) are combustion-derived organic marker compounds often identified with urban $PM_{2.5}$. PAHs are emitted from primary emission sources such as motor vehicle and diesel truck exhaust (see Table 1 references). Typical PAH compounds emitted from vehicular sources include phenanthrene ($C_{14}H_{10}$; C:H = 1.0:0.71), benz[a]anthracene ($C_{18}H_{12}$; C:H 1.0:0.67), and coronene ($C_{24}H_{12}$; C:H = 1.0:0.5). Examples of secondary, photochemical organic tracers found as $PM_{2.5}$ are dicarboxylic acids such as malic acid (hydroxy butanedioic acid; $C_4H_{16}O_5$, C:H = 1.0:1.5), glutaric acid (pentanedioic acid; $C_5H_8O_4$, C:H = 1.0:1.6), adipic acid (hexanedioic acid; $C_6H_{10}O_4$, C:H = 1.0:1.67), and azelaic acid (nonanedioic acid; $C_9H_{14}O_4$, C:H 1.0:1.8) (5,35).

The presence of oxygen-bearing functional groups has important consequences for aerosol hygroscopicity. Groups such as carbonyls (aldehydes, ketones), alcohols, and carboxylic acids are polar carbon–oxygen bonds, which serve to increase compound solubility in polar solvents, including atmospheric water vapor and droplets. Hence the term "polar organics" is used to designate the oxygen-containing compounds. Increased polarity is thought to increase the uptake and retention of fine particles within the respiratory system, leading to undesirable health effects for persons with asthma, children, and individuals with respiratory illnesses (8,17,30).

Much effort has been devoted to identifying the composition and sources of organic aerosols (5–7,9,15,21,35–54). Other research on the chemical composition of fine particles from major urban sources of atmospheric organic aerosols has provided mass inventories describing bulk-level to molecular-level compositions. Details of the quantitative mass emission characteristics corresponding to each of the source types were published in earlier work (25,52–77). Table 1 provides a summary of emission studies corresponding to major urban sources of fine carbonaceous particles (specific references included in Table 1). Typically, several hundred individual molecules have been identified with each emission source type. However, only a small suite of individual compounds from each source is used in subsequent mathematical models for source apportionment. The modeling applications using specific organic compounds for urban sources of fine particles have been published (6,20).

Chemical Mass Balance

CMB inventories have been developed for urban fine particles and major emissions sources (Table 1). This approach documents the relative mass contribution of compound classes within a sample and describes at different compositional levels the various components within a complex mixture. It relates quantitatively the total carbon (TC) mass to constituent subgroups, functional group types, and individual molecules (marker compounds). Any one component or combinations of components can be used in comparing aerosol chemistry, emission source chemistry, and biogenic aerosol chemistry, or to track changes involving a chemical process. To illustrate the mass balance approach for ambient $PM_{2.5}$ organic components, Figure 2 shows the chemical species composition for the 1982 annual mean fine-particle concentrations for fine particles collected from West Los Angeles, California. Total organics contained within the total fine-particle mass (column I) is described
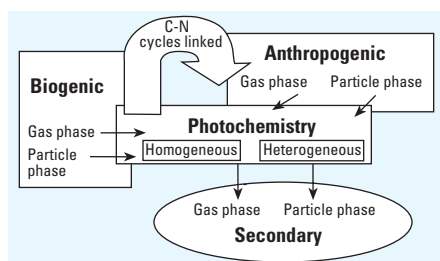

Figure 1. Relationship of atmospheric organic matter emitted from biogenic and anthropogenic primary sources to photochemical processing and subsequent production of secondary atmospheric organic matter.

Table 1. Urban sources of fine carbonaceous aerosol particles.

Source study	Reference
Anthropogenic sources	
Oil-fired boiler (No. 2 fuel oil)	(57,69)
Fireplace	
Natural wood (soft and hard woods)	(57,58,60,62,71,74–76)
Synthetic log	(57,58,71)
Vehicles	
Catalyst-equipped	(55–57,59,64,77)
Noncatalyst–equipped	(55–57,59,64,77)
Diesel trucks	(55–57,59,64,73,77)
Home appliances	
Natural gas	(57,65)
Meat cooking	
Charbroiling (extra-lean and regular ground beef)	(57,58,61,63,72)
Frying (extra-lean and regular ground beef)	(57,58,61)
Road dust	(57,67)
Brake dust	(57,67)
Tire dust	(57,67)
Cigarettes	(57,58,68)
Hot asphalt roofing tar pot fumes	(57,70)
Biogenic sources	
Vegetative detritus	
Cultivated and native plant composites (dead leaves)	(57,66)
Cultivated and native plant composites (green leaves)	(57,66)

quantitatively in various forms including in terms of intermediate complex mixture properties determined by high-resolution gas chromatography (HRGC) shown in column II (elutable organics and nonextractable, nonelutable organics) and column III (HRGC-resolved organics and unresolved organics). Column IV shows the molecular-level composition of the total fine-particle organics mass (7.0 $\mu g/m^3$) from column I that can be resolved analytically by HRGC/mass spectrometry (HRGC/MS). The total mass of column IV molecular organic compounds is 910 ng/m^3. By depicting the organic complex mixture in terms of bulk-level (column I), intermediate-level (columns II and III), and molecular-level chemical properties (column IV), it is possible to have quantitative descriptions for the complex organic mixtures collected as fine particulate matter and identify significant compositional chemical attributes. The CMB is a convenient chemical book-keeping method that can assist in mapping complex mixture chemistries measured for real atmospheric phenomena. By establishing a quantitative organizational framework for the chemical attributes (columns I–IV) of $PM_{2.5}$ organic complex mixtures, the data can be incorporated into CMB receptor models described in a later section.

Collection requirements for complex mixture chemical mass balance. Specialized sample collection procedures are required for the chemical constituent mass determinations corresponding to the four columns in Figure 2. An example of a typical fine-aerosol sampling system is shown in Figure 3. The sampling system is based on the Caltech fine-particle collector developed by Cass and coworkers (*22,78–80*). A number of dedicated filters are configured as part of the apparatus. The dedicated filters are composed of Teflon (Teflo membrane filters; Pall Corp., East Hills, NY, USA), other organic polymer membranes (polycarbonate membrane filters; Whatman Inc., Clifton, NJ, USA), and prefired quartz fiber filters (Tissuquartz fiber filters; Pall Corp.). Bulk organic carbon content and organic molecular-level measurements use only quartz fiber filters because this filter material can be processed thermally to achieve very low levels of TC background material.

The Caltech sampling system has been modified for $PM_{2.5}$ collection and is available commercially (Thermo Anderson RAAS2.5 Sequential Sample; Thermo Andersen, Smyrna, GA, USA). This and two other $PM_{2.5}$ speciation collectors (Met One SASS; Met One Instruments, Inc., Grants Pass, OR, USA), (URG Sequential Fine Particle Sampler, URG, Chapel Hill, NC, USA) were evaluated recently by the U.S. Environmental Protection Agency for suitability as $PM_{2.5}$ chemical species samplers (*81*). The performances of the three candidate samplers were found to be reasonable for preliminary use in the field. However, real differences were observed for the three $PM_{2.5}$ chemical speciation samplers for NO_3 and organic carbon components when compared with the reference IMPROVE collector (*81*). The differences in chemical species measurements were most notable for NO_3 and organic carbon and could have significant consequences when measuring ambient mass concentrations. Airflow through a filter (face velocity) is an active area of research by many groups because of an incomplete understanding of positive and negative artifacts associated with semivolatile compounds, especially the organic carbon fine-particle constituents (*82,83*). The current federal reference method for fine-particle organic carbon measurement sets a standardized face velocity to reduce measurement variability due to airflow. The standardized flow for organic carbon collection will result in similar negative sampling biases when collecting semivolatile organic carbon compounds (*81*). However, it is recommended that fine-particle chemical species samplers be configured with denuder systems upstream of the quart-fiber filters to remove potential volatile organic artifacts adsorbing onto the sample filters (positive sampling artifact).

Carbon species chemical mass balance and quantitative links. The analytical objective of the carbon mass balance approach is to establish quantitative links among measurable components of the complex mixture. Four
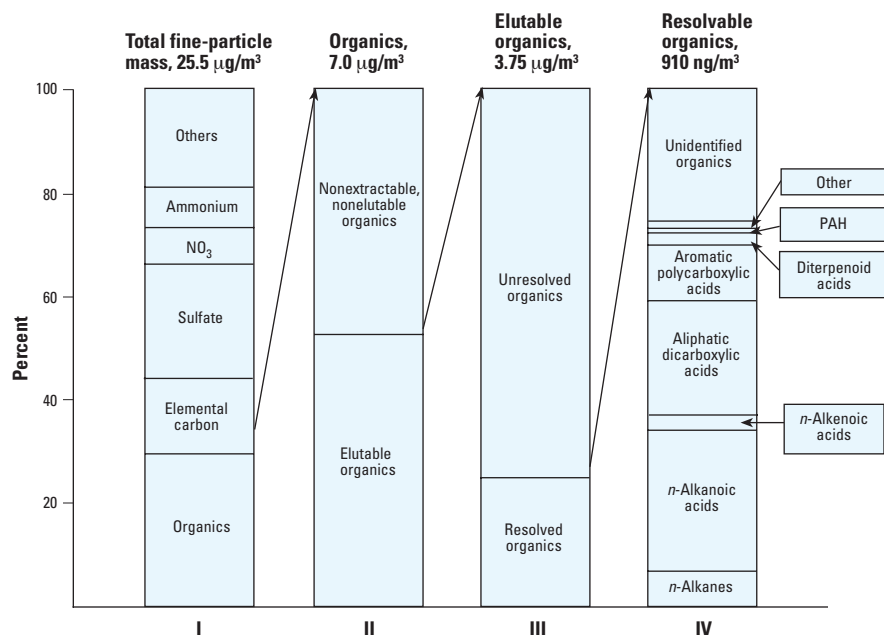

Figure 2. Mass balance for the CMB of 1982 annual mean fine-particle concentrations for West Los Angeles, California. Figure adapted from Rogge et al. (*5*).
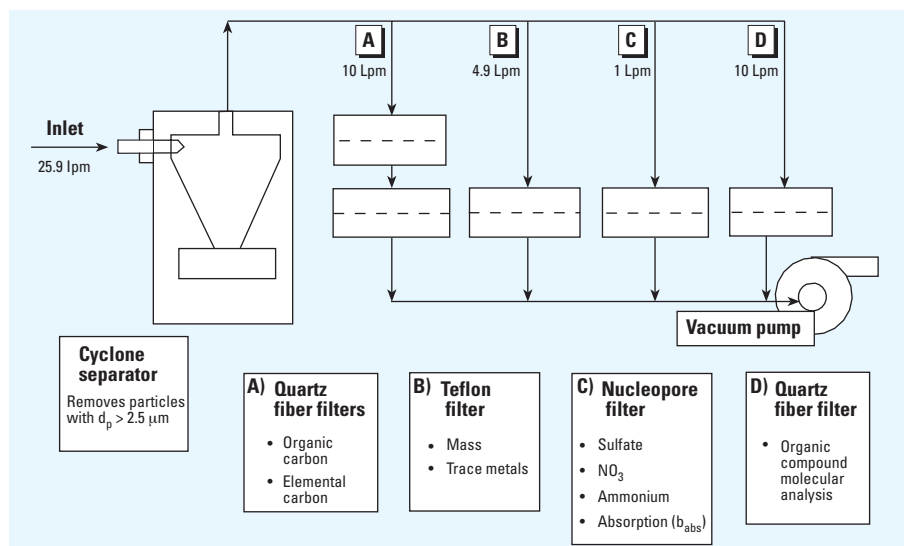

Figure 3. Fine-particle collection system for airborne chemical substances. Figure adapted from Gray et al. (*78*).

components of the PM$_{2.5}$ sample filters are measured typically: *a*) total mass, *b*) TC (organic + elemental), *c*) gas chromatography (GC)-elutable organic complex mixture, *d*) molecular tracers. By comparing these chemical properties from fine ambient particles with those measured similarly for emission sources of fine particles (Table 1), it is possible to quantitatively estimate emissions from individual sources. For example, work by Schauer et. al. (*6,7*) has shown that the mass of a key organic molecular tracer can be linked quantitatively to different sources types. Using the ratio of the molecular marker mass to the total organic fine-aerosol mass emitted from a single source type, it is possible to compute the contribution of the emission source type to an urban atmosphere. This source estimation is based on the mass balance relationship of a molecular tracer to the other major carbon-containing subfractions within the aerosol particulate sample (*25,57–59,61–77*).

Analytical Measurements for Fine-Particle Organic Complex Mixtures

The CMB fine-particle organic mixture requires several independent and interrelated chemical analytical measurements. Referring to the carbon mass balance in Figure 2, the total fine-aerosol mass is collected on preweighed Teflon filters. Using a microbalance, the total mass of fine aerosol is determined gravimetrically under conditions of constant temperature and humidity. TC analysis (Figure 2, column I) is performed by a combined pyrolysis/combustion measurement technique (*84,85*). The method provides a quantitative measurement of the mass concentrations of EC and organic carbon present on a sampled quartz microfiber filter and uses laser transmittance to correct for the conversion of OC to EC during the initial pyrolysis step. The organics mass (column II) is calculated using the mass of organic carbon determined by thermal evolution and combustion analysis (column I). The OC total mass is multiplied by a conversion factor to account for the mass of elements other than carbon present in the organic compounds. The OC conversion factors are calculated from the atomic mass compositions of organic compounds identified by HRGC/MS analysis (*86*). Typically, the conversion factors vary from 1.38 to 1.46 and reflect, in addition to carbon atoms, the mass concentrations of hydrogen and oxygen and trace amounts of nitrogen, chlorine, and phosphorus present in the organic compounds (*78*). Recent work by Turpin and Lim (*87*) has identified EC conversion factors for urban PM$_{2.5}$ (1.6 + 0.2) and for nonurban PM$_{2.5}$ (2.1 + 0.2). The

distinction between conversion factors for urban and nonurban PM$_{2.5}$ reflects a relatively greater contribution of biogenic organic compounds (e.g., higher plant waxes) to the fine-particle mass.

Quantitation of total solvent-soluble, elutable organics (i.e., lipids having 6–40 carbon atoms) (Figure 2, column III) is achieved by HRGC-flame ionization detection (HRGC/FID) analysis employing a surrogate standard (i.e., internal recovery standard, perdeuterated *n*-tetracosane) and a suite of *n*-alkane external standards (*9,57,86*). Individual molecular tracers (Figure 2, column IV) present in the total extracts from the source aerosol filters are identified and measured quantitatively by HRGC/MS analysis (*5,9,86*). Isolation of the GC-elutable organic complex mixture and the molecular marker components is described in the following sections.

Solvent extraction of fine-particle filters. Micromethods have been developed for the quantitative recovery of solvent-extractable organic matter (EOM) in fine particulate matter (*5,10,86,88*). The analytical protocol monitors losses associated with volatilization, incomplete extraction, or instrumental bias. To provide sufficient organic mass for the HRGC/FID and HRGC/MS analyses (i.e., minimum of 200 µg OC per filter composite for a single ambient composite), generally six 24-hr organic species filters are combined to form a filter composite with sufficient mass loadings for molecular marker measurement (Figure 2, column IV). The total volume of air sampled per composite is roughly 1000 m^3 (6.7 Lpm × 24 hr × 6 days). Before extracting the filter composite, an internal standard, *n*-C$_{24}$D$_{50}$, is added. The amount of *n*-C$_{24}$D$_{50}$ added is determined from the total mass of organic carbon contained on the filters as analyzed by pyrolysis/combustion (Figure 2, column II). The ratio of OC mass to the mass of *n*-C$_{24}$D$_{50}$ (surrogate standard) is 150 µg OC to 1 µg *n*-C$_{24}$D$_{50}$ (*86*).

The organic complex mixture is extracted from the filters by ultrasonic agitation using successive additions of hexane (two volume additions) and benzene/isopropanol (three volume additions). The serial extracts are filtered and then combined. The total extracts are reduced to volumes of 50–300 µL. The neutral fraction of the organics (neutral elutable organics) is defined operationally as the fraction that elutes from the bonded phase (J&W Durabond 1701 GC Column, 14%-cyanopropyl-phenyl-methylpolysiloxane; Agilent Technologies, Wilmington, DE, USA) of the analytical column and is detected by the FID of the GC without further derivatization. An aliquot of the total extract is derivatized by addition of diazomethane. This step converts reactive organic acids and

phenolic hydroxyl groups to the respective methyl ester or methyl ether analogs. Injection of the derivatized fraction onto the HRGC column produces chromatographic data for the acid plus neutral (acid + neutral) fraction (total acid + neutral elutable organics). The mass of the acid fraction (acidic elutable organics) of the solvent-soluble organics is determined by difference.

Quantitation of the total extracts is accomplished by computerized HRGC/FID analyses that incorporate the combined application of: *a*) area counts relative to a coinjection standard (1-phenyldodecane); *b*) relative response factor for the perdeuterated surrogate standard (*n*-C$_{24}$D$_{50}$); *c*) recovery of the perdeuterated surrogate standard for each source sample extract; and *d*) relative response factors for a suite of *n*-alkane external standards (17 *n*-alkane homologs from *n*-C$_{10}$H$_{22}$ to *n*-C$_{36}$H$_{74}$) (*10,57,86*).

Properties of organic complex mixtures by high-resolution gas chromatography. Major chemical features of the solvent-soluble organic aerosol fraction (carbon range of C$_8$ to C$_{36}$) are quantified and identified by HRGC/FID. In particular, bulk characteristics can be measured, revealing chemical information relating to carbon mass distributions and to the content of acidic compounds (polar organic compounds) present in the fine-particle complex organic mixtures. Figure 4 shows examples of HRGC-FID plots for total acid + neutral organics from fine particles collected at West Los Angeles, California (*88,89*). As seen in Figure 4, aerosol organics are complex mixtures of individual organic compounds, some of which can be measured quantitatively by HRGC/FID. Dominant peaks in the two West Los Angeles HRGC plots include normal alkanes (C$_{25}$–C$_{31}$) and normal alkanoic acids (C$_{12}$–C$_{28}$). These molecular determinations are based on comparison with HRGC analyses of external standards containing *n*-alkane and *n*-alkanoic acid methyl ester standards. Confirmation of the molecular markers is confirmed by HRGC/MS analysis using characteristic fragmentation patterns produced by electron impact ionization.

Although is it possible to identify a few dominant peaks in an HRGC plot of fine-particle acid + neutral organics using retention times compared with those of external standards, several important attributes identify additional chemical properties of the organic complex mixture. These properties are the mass distributions of elutable organics and the acidic and neutral components.

Elutable organics mass distributions. The fractions of solvent-soluble aerosol organics identified by HRGC/FID are referred to as "elutable organics" (Figure 2, columns II, III) and constitute a subfraction of the PM$_{2.5}$ EOM. Figure 2 shows the mass relationship

of EOM for West Los Angeles, California, which has a total ambient mass of 7.0 μg/m³ (column II). In this example, the organics mass comprises roughly equivalent masses corresponding to elutable organics and nonextractable and/or nonelutable organics. The nonelutable organics are carbonaceous substances that cannot be analyzed by the HRGC/FID procedure because of extremely high compound polarity and/or too high molecular weight (e.g., polymeric organic compounds; cellulose).

Elutable organics constitute 5–15% of fine-particle ambient mass concentrations but comprise 25–60% of the total mass of aerosol organics (5,6,10). Organics that are either solvent insoluble or do not elute from the GC analytical column used in this analytical protocol comprise the largest share of aerosol organics in most cases. With the carbon mass balance inventory, the elutable organics have a known and quantitative mass relationship to the total particle mass and various other forms of aerosol carbon present in fine-particle samples, including molecular marker compounds indicative of emission source types. Table 1 gives a summary of various emission source studies and the related references that incorporate CMBs shown in Figure 2. The reader is referred to these articles for CMBs corresponding to each of the urban sources of fine particles.

HRGC/FID analysis of fine-particle complex mixtures provides a quantitative measure of the elutable compounds as a function of retention time if chromatographic and instrumental conditions remain constant from one injection to the next. Examples of HRGC retention time analyses such as these are described in earlier studies of Los Angeles ambient fine particles (5,57,88–91) and in measurements of urban sources of fine organic aerosols (21,86,88). HRGC elutable organic "fingerprints" were constructed for individual emission sources and for ambient fine-particle samples in these cited studies. Figure 5 shows an example of a mass distribution histogram derived for HRGC-elutable organics isolated from fine particles sampled from heavy-duty diesel truck emissions (57,86).

In this approach, the histogram is constructed by summing the mass concentrations of all the organic compounds that elute between the successive elution points of the C_n–C_{n+1} normal alkanes over the range from n-C_{10} to n-C_{36} (88). The technique employs HRGC/FID response factors that correspond to 17 individual n-alkanes ranging from $C_{10}H_{22}$ to $C_{36}H_{74}$. The mass response factors generated by the n-alkane standard series are applied to 17 mass intervals, each containing a single n-alkane standard homolog. By dividing the mass of complex elutable organics into successive mass intervals (i.e., retention volumes) having separate mass response factors, more accurate measurement of the mass of total elutable organics is achieved (57,86,88–90).

Acidic and neutral complex mixture components. One other important bulk chemical characteristic of the elutable organics is the acidity or relative polarity of the organic components that can be studied by HRGC/FID. Conversion of HRGC/FID area counts to organic mass concentrations is calculated using the same procedure as the histogram
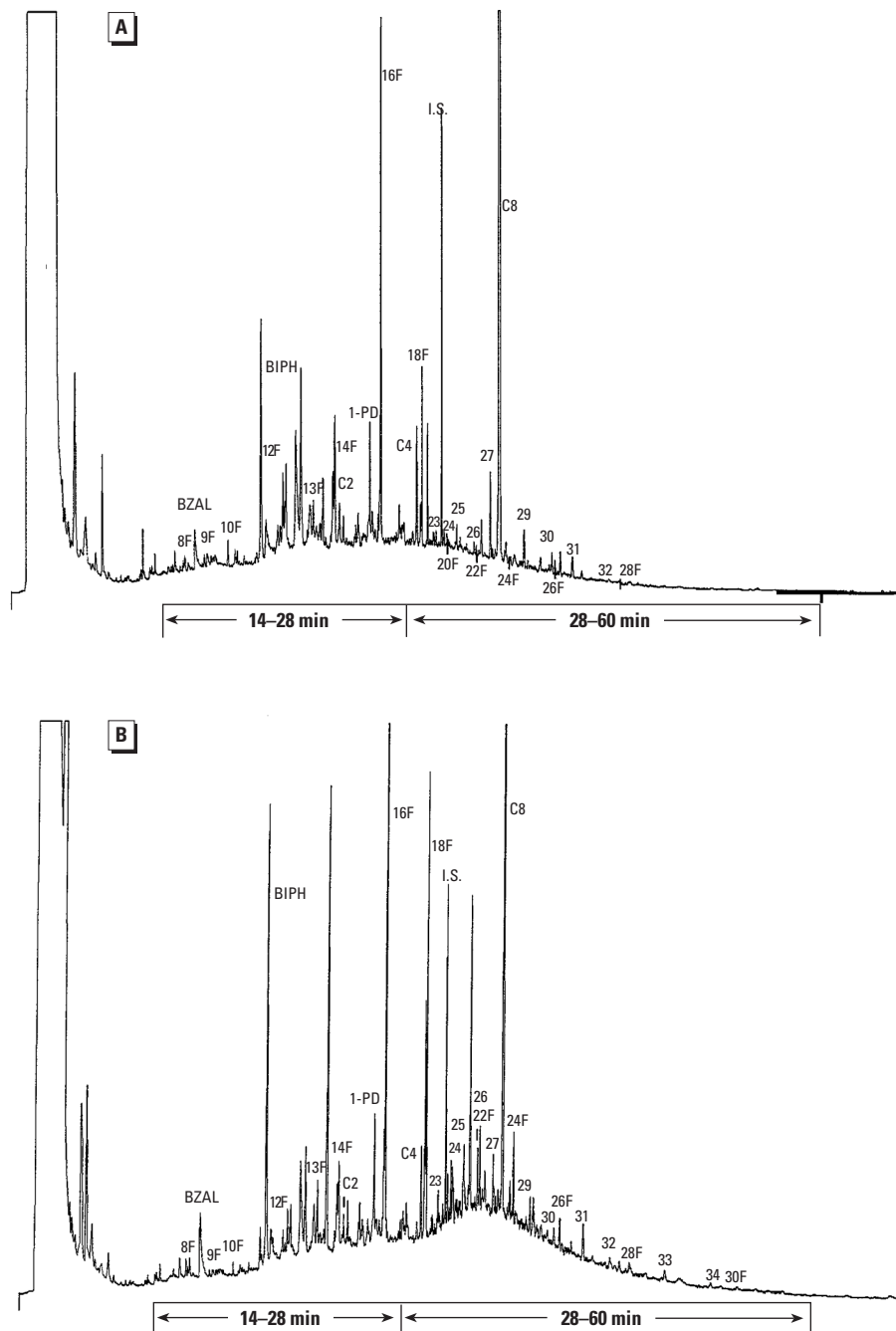

Figure 4. HRGC/FID plots of acid + neutral organics from monthly composites of fine-aerosol particles collected from West Los Angeles, California, for (*A*) August 1982 and (*B*) December 1982. Peak assignments are the following: *a*) n-alkanes (C_{23}–C_{32}) are designated by integer values corresponding to carbon chain length; *b*) n-alkanoic acids (C_8–C_{28}) are indicated by integer values followed by the letter "F" and represent the carbon chain length of the acid analog; *c*) phthalate esters (C_2–C_8) (sampling artifacts) are shown by C2, C4, or C8 and correspond to the carbon chain length of the ester group; *d*) benzaldehyde (BZAL) (solvent artifact); *e*) 1,1'-biphenyl (BIPH) (solvent artifact); *f*) 1-phenyldodecane (1-PD), coinjection standard; *g*) n-tetracosane-d₅₀ (IS), internal standard. Figure adapted from Mazurek et al. (*89*).

mass distribution plots between adjacent *n*-alkanes (*10,89*). Results of the computed mass distributions are combined into one plot for a sample's HRGC/FID analyses of neutral and acid + neutral aliquots. The mass of acid elutable organics for each mass interval is obtained by subtracting the mass of neutral elutable organics from the mass of acid + neutral elutable organics. In this HRGC/FID application, the acidic elutable organics fraction contains those organic compounds detected by FID only after undergoing a chemical derivatization step that selectively targets acidic hydrogen atoms attached to either aliphatic or aromatic carboxyl groups or to aromatic hydroxyl groups. The HRGC/FID analysis of acidic organics provides a mechanism for selectively evaluating the ambient mass concentrations and chemical distribution of the polar organic fraction.

As seen in Figure 6A, B, the two Los Angeles sites (West Los Angeles and downtown Los Angeles) exhibit compositional differences in terms of the ambient mass concentrations of complex mixture compounds and the relative proportion of acidic elutable organic compounds. Motor vehicle exhaust is the dominant emission source of fine particles for the downtown Los Angeles site. The mass of complex organics occurring between n-C_{22} and n-C_{36} (Figure 6B) exhibits a carbon number distribution characteristic of motor vehicle exhaust and engine lubricating greases and oils (*48,91–93*). The low ratio of acidic to neutral compounds for each carbon mass interval in Figure 6B shows relatively lower proportions of oxidized organic compounds compared with the West Los Angeles acid and neutral components. A vast majority of the downtown Los Angeles fine-particle organic mixture is from fresh vehicular emissions, whereas the acidic and neutral fractions from the West Los Angeles aerosol have other additional sources relative to motor vehicle emissions and are relatively more "aged" in terms of residence time within the urban atmosphere. Increased residence time allows for photochemical processing of primary organic material, forming aged and oxidized organic matter (polar organics).

Identification of fine-particle complex organic mixtures at a molecular level . Many individual organic compounds within the complex mixtures can be identified by HRGC/MS. For example, over 80 individual organic compounds were determined in the complex organic mixtures (elutable organics) from urban Los Angeles fine particles (West Los Angeles, 1982) (Figure 4A, B) (*5*). The compounds were identified by HRGC/MS analysis with electron impact ionization and a quadrupole mass analyzer (Finnigan MAT 4000 series GC/MS with Incos data system; Thermo Finnigan, San Jose, CA, USA).

Compounds were identified and confirmed by a sequential process. First, compound identification was conducted by comparing the unknown compound mass fragmentation pattern with the National Institute of Standards and Technology mass spectral library contained in the Finnigan 4,000 data-handling application. Second, confirming the identity of a compound was achieved by comparing the mass fragmentation patterns and elution times with those of external standards. Relative ion counts were converted to compound mass concentrations using relative response factors obtained by injection of external standards containing the compound of interest. Identifiable compound peaks were quantified

using the HRGC data system for compounds with mass abundances above 60–80 ng.

Major compound groups in the West Los Angeles fine-particle samples included *n*-alkanes, *n*-alkanoic acids, aliphatic dicarboxylic acids, aromatic polycarboxylic acids, PAHs, polycyclic aromatic quinones, diterpenoid acids, and nitrogen-containing compounds. Identifiable single compounds such as one *n*-alkenoic acid and one *n*-alkanal (aldehyde) were found also. These are common compound groups found in urban fine particles. In the West Los Angeles, California, 1982 example, the identified compounds account for 74–81% of the resolved organic mass comprising the fine-particle organic complex
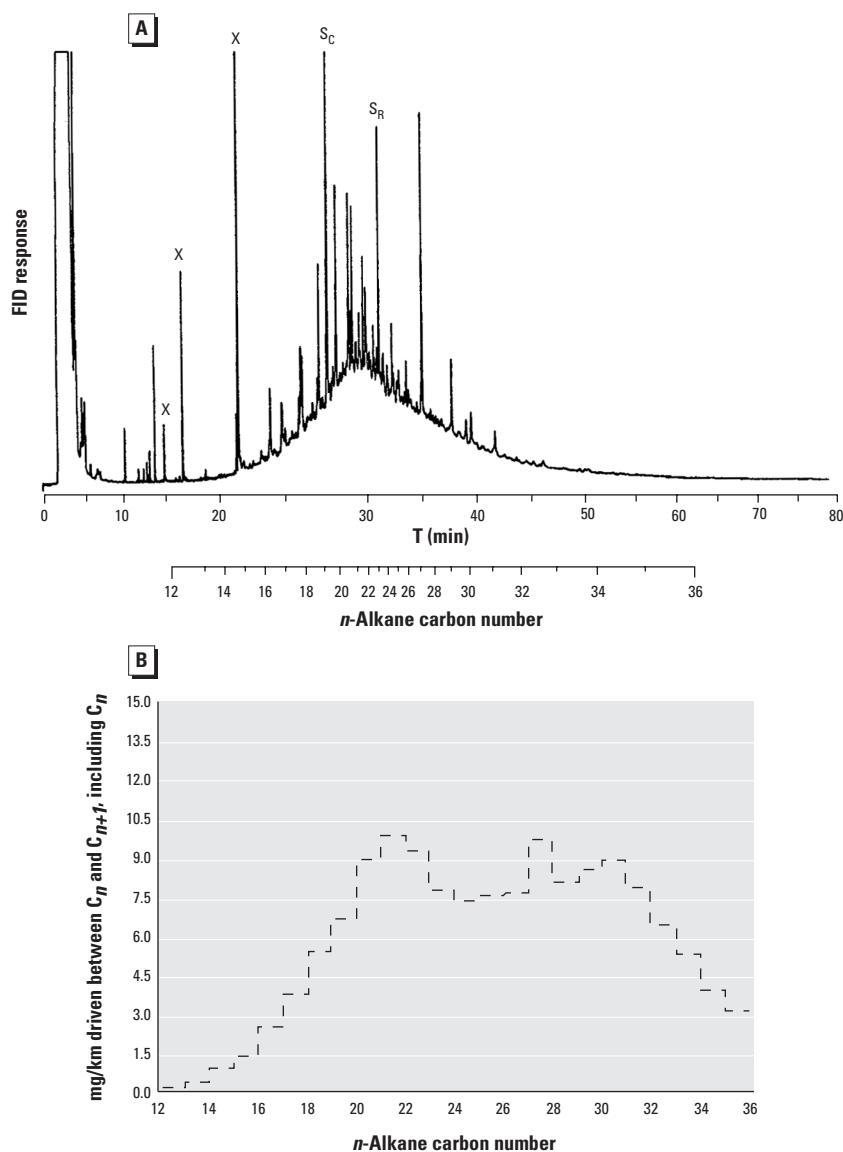

Figure 5. Illustration of organic mass distributions and conversion of (*A*) HRGC/FID plot of neutral elutable organics and (*B*) the computed mass distribution of the neutral elutable organics plotted versus normal alkane obtained from heavy-duty diesel truck fine-particle emissions. Labeled peaks are coded as solvent impurity (X); 1-phenyldodecane (S_C), the GC coinjection standard; and *n*-tetracosane-d_{50} (S_R), the surrogate recovery standard. Figure adapted from Mazurek et al. (*88*).

mixture (Figure 2, column III). Normal alkanoic acids, aliphatic dicarboxylic acids, and aromatic polycarboxylic acids are the major constituents of the resolved organic mass, with annual averages of 250–300, 200–300, and approximately 100 ng/m³.

Sources of organic compounds within fine-particle complex mixtures. The molecular marker content from fine particles collected from ambient samples and emission sources (Table 1) can be used in developing CMB receptor models. Receptor-oriented models infer source contributions by determining the best-fit linear combination of emission source chemical composition profiles that reconstruct the measured chemical composition of

ambient fine-particle samples (*6,21,51,94*). Once developed, the models provide assessments of the amount of fine-particle mass contributed by discrete sources to that receptor site (*6,7,12,15,20,21,51*).

Table 2 lists the source apportionment of fine-particle ambient mass concentrations for West Los Angeles and downtown Los Angeles (*6*). The data represent the computed 1982 annual average mass emissions from major sources of fine particles at the two metropolitan Los Angeles sites. The mass emissions are reported in terms of a computed CMB and refer to the fine-particle complex organic mixtures for the West Los Angeles, California (1982) example, whose analytical results are

shown in Figures 2, 4, 5, and 6. The sum of the computed ambient fine-particle annual average concentrations is 25.3 ± 1.4 μg/m³ and is within 3% of the measured annual average ambient fine-particle mass concentration.

Numerous manmade emission sources contribute to the atmospheric concentrations of fine particles at the West Los Angeles site. The largest contributor is diesel exhaust, followed by paved road dust, wood smoke, meat-cooking processes, and catalyst- and non–catalyst-equipped vehicles. Biogenic emissions from vegetation (waxy coatings from leaves) contribute seasonal emissions to fine-particle loadings. Photochemical processing of primary emissions from man-made and biogenic sources was about 6% of the total organic fraction and 4% of the total fine-particle ambient mass concentration.

Referring to downtown Los Angeles (Figure 6B), the 1982 annual average for secondary organics was estimated by the CMB model as 5% of the total organic fraction and 3% of the total fine-particle organic aerosol mass (Table 2). The CMB for downtown Los Angeles shows diesel exhaust contributing 50% of the total organic fine-particle fraction. Paved road dust and catalyst and noncatalyst vehicle exhaust contributed 16 and 9%, respectively. From the CMB sum of total vehicular and traffic-related emissions (diesel + catalyst and noncatalyst exhaust + paved road dust), the downtown Los Angeles site had an annual mass loading of 76% of the total organic fine particles and 49% of the total fine-particle annual average mass concentration.

The distribution of the complex mixture organics for downtown Los Angeles (Figure 6B) shows a chemical composition ranging from C_{12} to C_{36} with the most mass contributed by compounds in the C_{24} to C_{36} range. This complex mass distribution can be compared with the organics complex mixture mass distribution determined for diesel fine-particle emissions (Figure 5) (*56,64*). Although some of the more volatile complex mixture constituents (C_{16}–C_{22}) from the heavy-duty trucks are not apparent to the same degree as the higher molecular weight components, the downtown Los Angeles complex organic mixture (Figure 6B) contains substantial compounds in the C_{24}–C_{36}, mass interval. Even though the fine-particle complex mixture may not be fully characterized in terms of resolvable organics (Figure 2, column IV), major features of the mass interval distribution are comparable to those determined for the major emission sources measured similarly and reported in Table 1.

Figure 6. Distributions and ambient mass concentrations of acid and neutral elutable organics obtained from HRGC/FID analyses of (*A*) West Los Angeles, California, and (*B*) downtown Los Angeles, California, August 1982 monthly composites. Each bar shows the ambient mass of complex organic mixture constituents eluting between the elution points of the C_n and C_{n+1} *n*-alkanes, including the C_n alkane itself, where the alkane number (*n*) is stated below each bar. Figure adapted from Mazurek et al. (*10*).

Concluding Remarks

The organic chemical composition of airborne fine particles is complex, and currently less than two-thirds of its mass can be measured
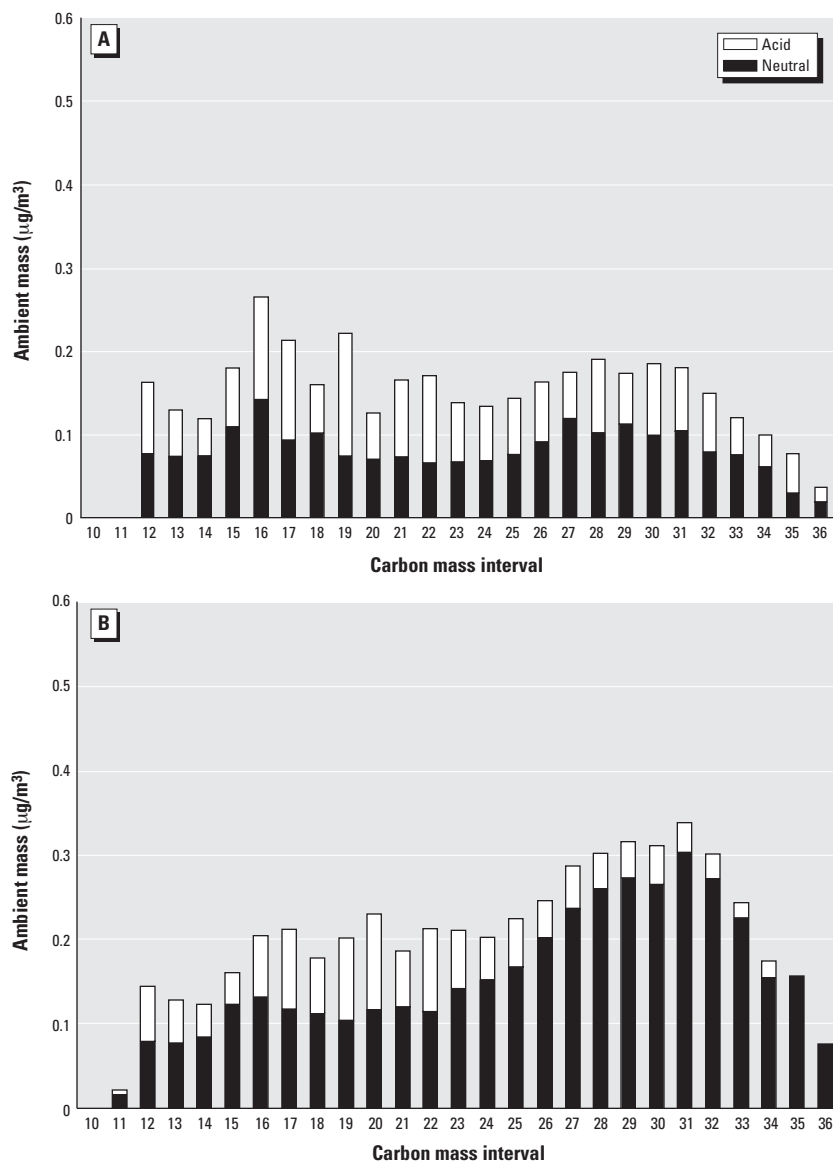
Table 2. Source apportionment of fine ambient particles for West Los Angeles, California, computed as the 1982 annual average. Data indicate computed ambient concentrations. Data from Schauer et al. (6).

Source	Computed ambient concentration (average ± SD, $\mu g/m^3$)	
	West Los Angeles	Downtown Los Angeles
Organic components		
Diesel exhaust	4.36 ± 0.64	11.6 ± 1.19
Paved road dust	3.00 ± 0.39	3.62 ± 0.46
Wood smoke	2.65 ± 0.41	1.85 ± 0.31
Meat charbroiling and frying	2.03 ± 0.39	1.74 ± 0.34
Catalyst and noncatalyst gasoline-powered vehicle exhaust	1.44 ± 0.16	2.12 ± 0.23
Organics (other + secondary)	1.03 ± 0.71[a]	1.16 ± 0.66[a]
Vegetative detritus	0.38 ± 0.11	0.24 ± 0.12
Tire wear debris	0.22 ± 0.09	0.22 ± 0.09
Cigarette smoke	0.20 ± 0.028	0.26 ± 0.045
Natural gas combustion aerosol	0.034 ± 0.016	0.040 ± 0.019
Total organic components	16.37	22.85
Inorganic components		
Sulfate ion (secondary + background)	5.9 ± 0.60	6.6 ± 0.65
Secondary NO_3 ion	1.9 ± 0.29	3.0 ± 0.54
Secondary ammonium ion	2.3 ± 0.23	3.0 ± 0.37
Sum (above computed values)	25.3 ± 1.4	35.5 ± 1.9
Measured (ambient concentrations)	24.5 ± 2.0	32.5 ± 2.8

[a]Not statistically different from zero with > 95% confidence.

and described at a molecular level. Despite the analytical limitations of current measurement technologies, much can be determined chemically for organic complex mixtures by using a CMB approach. Bulk chemical and molecular properties of the fine-particle $PM_{2.5}$ carbonaceous material can be linked quantitatively to each other using a CMB framework. This quantitative framework makes it possible to distinguish among individual sources of fine carbonaceous particles to urban atmospheres using receptor-oriented models based on best-fit linear combinations of source profiles. Very good agreement between computed and measured ambient concentrations of the source apportionment profiles have been achieved for fine-particle complex mixtures in metropolitan Los Angeles, California. The agreement for two sites is 3% (West Los Angeles) and 9% (downtown Los Angeles), for example.

An effective measurement and modeling procedure exists for understanding the sources and chemical composition of organic complex mixtures associated with ambient fine particles. However, much additional research is required that would link the various chemical attributes of complex mixtures to toxicological and epidemiological research on $PM_{2.5}$. For example, by using a CMB framework for fine-particle organic matter, it is possible to target specific chemical properties of the complex mixture by targeting properties described in columns I–IV (Figure 2) or by acidic or neutral properties that can be identified with additional chemical derivatization and chromatographic analysis (Figure 6A, B). Pursuing the interface between aerosol complex mixture chemistry and toxicological and epidemiological research on $PM_{2.5}$ is the great research challenge for understanding the most biologically relevant fine-particle constituents responsible for acute health end points.

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