

CRITICAL REVIEW OF SOURCE SAMPLING AND ANALYSIS METHODOLOGIES FOR CHARACTERIZING ORGANIC AEROSOL AND FINE PARTICULATE SOURCE EMISSION PROFILES

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Critical Review of Source Sampling and Analysis Methodologies for Characterizing Organic Aerosol and Fine Particulate Source Emission Profiles

Health and Environmental Affairs Department

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ACRONYMS

μm	micrometer (micron)
2-NF	2-Nitrofluoranthene
AAS	atomic adsorption spectrometry
AC	automated chromatography
API	American Petroleum Institute
ASME	American Society of Mechanical Engineers
b.p.	boiling point
BaP	benzo[a]pyrene
C	centigrade
$\text{C}_{15}\text{H}_{32}$	n-pentadecane
C_3H_8	propane
CA	California
CaCO_3	calcium carbonate
Caltech	California Institute of Technology
CARB	California Air Resources Board
CCU	catalytic cracking unit
Cl_2	chlorine (molecular)
cm	centimeter
CO	carbon monoxide
CO_2	carbon dioxide
D_{50}	50 percent cutoff diameter
DHS	Department of Health Services
DNPH	2,4 dinitrophenylhydrazine
DRI	Desert Research Institute
dscm	dry standard cubic meter
EASA	electrical aerosol size analyzer
EC	elemental carbon
ECD	electron capture detector
EER	Energy and Environmental Research Corporation
EPA	Environmental Protection Agency
ESP	electrostatic precipitator
F	Fahrenheit
FCCU	fluidized catalytic cracking unit
FID	flame ionization detector
ft	feet
FTIR	fourier transform infrared spectroscopy
$\text{g}\cdot\text{cm}^{-3}$	grams per cubic centimeter
GC/MS	mass spectrometric detector
GC	gas chromatography
H_2SO_4	sulfuric acid
HEPA	high efficiency particulate air
HEST	high efficiency sampling train
Hg	mercury
hivol	high volume
HNO_2	nitrous acid
HNO_3	nitric acid
HO_2	hydroperoxyl radical
HPLC	high performance liquid chromatography
HRSG	heat recovery steam generator
IC	ion chromatography
IC engine	internal combustion engine
ICP	inductively coupled plasma



INAA	instrumental neutron activation analysis
K_2CO_3	potassium carbonate
LC	liquid chromatography
lpm	liters per minute
mg	milligram
$MgCO_3$	magnesium carbonate
MOUDI	microorifice uniform deposit impactor
MS	mass spectrometry
Na_2CO_3	sodium carbonate
NAAQS	national ambient air quality standards
NaCl	sodium chloride
$NaNO_3$	sodium nitrate
NaOH	sodium hydroxide
Ncm	normal cubic meter (O°C)
NDIR	non-dispersive infrared
NEA	Nuclear Environmental Analysis, Inc.
NF	nitrofluoranthene
ng	nanogram
NH_3	ammonia
$(NH_4)_2SO_4$	ammonium sulfate
NH_4HSO_4	ammonium bisulfate
NH_4NO_3	ammonium nitrate
NMHC	non-methane hydrocarbons
NO	nitric oxide
NO_2	nitrogen dioxide
NO_3	nitrate (ion)
NO_x	oxides of nitrogen
NP	nitropyrene
O_3	ozone
OC	organic carbon
OH	hydroxyl (radical)
PAH	polycyclic aromatic hydrocarbons
PAK	polycyclic aromatic ketones
PAN	peroxyacetyl nitrate
PAQ	polycyclic aromatic quinones
PCB	polychlorinated biphenyls
PIXE	proton induced X-ray emission
PM	particulate matter
PM10	particulate matter equal to or smaller than 10 microns in diameter
PM2.5	particulate matter equal to or smaller than 2.5 microns in diameter
POM	polycyclic organic matter
ppbv	parts per billion (volume)
PSDS	plume simulation dilution sampler
PSVOC	particulate/semi-volatile organic compound sampler
PUF	polyurethane foam
PVC	poly vinyl chloride
RADS	reduced artifact dilution sampler
Re	Reynolds number
ROG	reactive organic gases
SCAQMD	South Coast Air Quality Management District
SCAQS	Southern California Air Quality Study
SCR	selective catalytic NOx reduction
sec	second

SFS	sequential filter samplers
SO ₂	sulfur dioxide
SO ₃	sulfur trioxide
SoCAB	South Coast Air Basin
SO _x	oxides of sulfur
SRI	Southern Research Institute
T	thermal
TA	thermal absorption
TCE	trichloroethylene
TEA	triethanolamine
TMO	thermal manganese oxidation
TOR	thermal/optical reflectance
TOT	thermal/optical transmission
TSP	total suspended particulate
URG	University Research Glassware
UV	ultraviolet
VOC	volatile organic compounds
v/v	volume per volume
WSPA	Western States Petroleum Association
XRF	X-ray fluorescence



EXECUTIVE SUMMARY

This report presents a critical review of sampling and analysis techniques for characterizing stationary source emissions of organic aerosols, fine particulate matter, and their precursors. This information is intended for use in designing future measurement programs for characterizing emissions from stationary sources which contribute to fine particle concentrations in the atmosphere. The review is based on relevant literature and discussions with technical/scientific experts in academia, industry and the regulatory community. The benefits and drawbacks of various measurement approaches are discussed, and a recommended approach for combustion sources is presented.

BACKGROUND

The recent change in the National Ambient Air Quality Standards (NAAQS) for particulate matter (PM) includes new annual and 24-hour standards for particles 2.5 μm or less in diameter, referred to collectively as PM_{2.5}. The geologic component of PM_{2.5} is typically 10 percent or less; the balance is typically sulfates, nitrates and carbon (e.g., sulfuric acid, ammonium bisulfate, ammonium sulfate, ammonium nitrate, and organic and elemental carbon). Organic compounds are important components of particulate matter and most of the particulate organic carbon is believed to reside in the fine particle fraction. For example, in an early study of the Los Angeles area, organic compounds constituted approximately 30 percent of the fine particle mass.

Particulate matter may be either directly emitted into the atmosphere (primary particulate) or formed there by chemical reactions and physical transformations (secondary particulate). The majority of primary particulate emissions from combustion are found in the PM_{2.5} or smaller size range, especially with clean burning fuels such as gas. Sulfates and nitrates are the most common secondary particles, although organic carbon also can result from reaction of volatile organic compounds. The gaseous precursors of most particulate sulfates and nitrates are sulfur dioxide, sulfur trioxide, and oxides of nitrogen. Secondary organic aerosol formation mechanisms are not well understood due to the multitude of precursors involved and the rates of formation which are heavily dependent on meteorological variables and the concentrations of other pollutants. It is believed, however, that atmospheric transformations leading to the formation of secondary aerosol from gas-phase primary organic emissions may be significant in some areas, particularly during the summertime. The chemical composition of PM_{2.5} strongly suggests combustion devices as the principal source in urban areas.

PETROLEUM INDUSTRY COMBUSTION SOURCES

Petroleum industry combustion devices likely are minor sources of carbonaceous aerosols in ambient fine particulate matter. An estimate of fine carbonaceous aerosol emissions from major sources in the Los Angeles area based on 1982 data showed that emissions from natural and refinery gas combustion (0.5 percent), petroleum industrial processes (0.7 percent), and coke calciners (0.6 percent) comprised a minor but significant fraction (1.8 percent) of total emissions.

Results of direct measurements of organic aerosol emissions from petroleum industry combustion devices are very limited. Petroleum industry combustion devices are found in both upstream (steam generators, heater treaters, reciprocating engines, etc.) and downstream (boilers, process heaters, gas turbines, thermal oxidizers, etc.) operations. Particulate emissions and particle size data from combustion processes indicate that a large fraction - often more than half - of the primary particles are PM_{2.5}. In addition, emissions data from several fluidized catalytic cracking units (FCCUs) indicate primary PM₁₀ emissions from FCCUs dominate total filterable particulate mass, accounting for 67 to 88 percent; primary PM_{2.5} comprises 40 to 70 percent of primary FCCU particulate emissions.

Volatile and semivolatile organic compounds are believed to be key contributors to secondary and condensable primary aerosols. The source profile of organic compound emissions also provides a powerful method of apportioning the contribution of various emission sources to ambient particle concentrations. Emissions of all organic compounds from petroleum industry combustion sources are not well-characterized. Previous emissions measurements for hazardous air pollutants (air toxics) provide an indication of the potential importance of different sources. For example, tests of petroleum industry combustion sources show that polycyclic aromatic hydrocarbon (PAH) emissions from reciprocating internal combustion engines and asphalt blowing units are approximately an order of magnitude higher than PAH emissions from boilers, process heaters, gas turbines, and coke calciners. Also, although organic hazardous air pollutant emissions data from gas-fired sources show extremely low emissions per unit of gas fired, the sheer quantity of gas fired in refineries could make a measurable if minor contribution to organic fine particulate. However, since hazardous air pollutant/air toxics measurements focus on a small subset of the total spectrum of organic compound emissions, they provide an incomplete picture of organic emissions.

TEST METHODS FOR AEROSOL/FINE PARTICULATE CHARACTERIZATION

Development of emission factors for primary particulate and secondary particle precursors requires emissions rates to be measured accurately. Also, the chemical composition of the emissions must be accurately measured to develop speciation profiles. Traditional stationary source sampling methods are capable of providing accurate data for criteria and many hazardous air pollutants, but may not completely characterize the fine particulate matter, especially organic aerosols, which forms as the stack gas mixes and reacts with the atmosphere. This critical review indicates that methods which dilute and age the stack gas sample in a manner roughly simulating stack plume conditions before collection of samples for analysis are better suited for characterizing such emissions. Dilution methods have long been employed as the standard for characterizing mobile source particulate emissions. A combination of traditional source stack sampling methods and dilution sampling methods for stationary combustion sources provides the opportunity to develop accurate emission factors/speciation profiles for evaluating the applicability of different fine particulate test methods to various source types. The data also could be used to identify less costly methods of measuring fine particulate emissions for future compliance, if required.

Due to the potential importance of organic aerosol emissions from gas-fired sources, a dilution sampler design developed and used specifically for characterizing organic aerosol emissions is recommended for future testing programs. The dilution sampling system should be designed using the following criteria.

- **Dilution ratio:** Dilution sampler emissions tests on an oil-fired furnace showed a dependence of aerosol size on dilution ratio, with larger particles resulting from higher dilution ratios and smaller ratios giving a larger number of smaller particles. Obtaining representative aerosol data requires not only uniform concentrations at the sampling point, but mixing in a manner that simulates local condensation conditions as closely as possible. It is recommended that dilution ratios of 40:1 or greater be used.
- **Residence time:** The characteristic time necessary for formation of secondary aerosol varies from a few seconds to several days, depending on the concentration and volatility of gaseous precursors, availability of primary particles and moisture droplets, sunlight intensity and radical species. It is recommended that the dilution chamber be configured to approximate time scales of actual plume mixing, when possible, and should be adjustable, to allow enough residence time for condensation processes to occur. An after-dilution residence time of at least 60 seconds should be used.

- Particle losses: Significant losses of charged particles to the electrically non-conducting surfaces (e.g., polyvinyl chloride [PVC] and Teflon®) of dilution samplers can be significant, and use of conducting surfaces wherever possible and installing charge neutralizers to avoid fine particle loss are recommended. To minimize line losses, sampler designs also should incorporate heated, temperature controlled probes and hoses to prevent condensation prior to mixing with dilution air.
- Sample contamination: Dilution samplers should be constructed of materials which will not dissolve or degrade during solvent rinsing or when exposed to caustic or corrosive stack gases. Use of rubber, plastics, greases or oils upstream of where the samples are collected should be avoided, since these materials may provide a source of organics within the sampler. Dilution air must either be thoroughly conditioned prior to introduction to the sample or pure gas mixtures must be used.
- Flow control and measurement: A reliable, field-verifiable method of flow measurement is important. Venturis and flow orifices are suitable for flow measurement, and are recommended. Since sample collection typically takes several hours, a computer data logger/ flow controller is also recommended.
- Field use: To minimize contamination and facilitate efficient use in the field, samplers should be lightweight, easy to take apart by a two person crew in a short amount of time for recovery and cleaning between sample runs, leak free without relying on greases or silicone and should have a small footprint which fits onto cramped stack platforms.

The dilution sampling technique should be combined with ambient air sampling and analysis methods to characterize fine particulate mass and chemical speciation. This will enhance comparability of source and ambient test measurement results. Traditional source stack sampling methods should be employed for measuring particulate mass, particle size distribution, chemical speciation and secondary particle precursor emissions. This will enhance comparability to previous source test data.

GOALS AND OBJECTIVES FOR FUTURE PROGRAMS

The overall goals of future measurement programs for characterizing stationary combustion source emissions which contribute to ambient fine particle levels should be to:

- Develop emission factors and speciation profiles for emissions of organic aerosols.
- Identify and characterize PM_{2.5} precursor compound emissions.

- Investigate surrogate monitoring parameters for aerosol formation based on in-stack concentrations of commonly measured species.
- Identify a method or methods for routine testing which is potentially inexpensive and relatively easy compared to present methods of dilution sampling.

Organic aerosol emissions and speciation are of special interest to the petroleum industry because of the predominance of natural and process gases as a fuel for process heaters and boilers in U.S. refineries. Organic aerosols are likely to comprise the majority of primary fine particulate emissions from gas-fired sources, and organic carbon is typically a significant fraction of fine particulate matter in the ambient air. Based on a review of the issues governing organic aerosol and fine particulate emissions, the following test objectives were identified to meet these goals:

- (1) Characterize primary aerosol emissions, including mass, size, organic carbon, elemental carbon, and organic species, after dilution and aging of stack emissions to simulate near-field atmospheric aerosol formation mechanisms.
- (2) Characterize in-stack total particulate mass and particle size distribution, including PM_{2.5}.
- (3) Characterize major gaseous PM_{2.5} precursors, specifically organic compounds (especially those with carbon number of 7 and above), oxides of nitrogen (NO_x), sulfur dioxide (SO₂), and ammonia (NH₃).
- (4) Develop organic speciation profiles from particulate matter collected on the filter media after dilution.
- (5) Provide data that can be related to existing ambient particulate data (i.e., of similar quality and completeness).
- (6) Compare total PM_{2.5} mass (filterable and condensable) using EPA reference methods and dilution sampling.
- (7) Analyze the in-stack total particulate matter for composition (including elemental carbon, nitrates, sulfate, and ammonium).
- (8) Characterize minor gaseous PM_{2.5} precursors, specifically sulfur trioxide (SO₃), sulfuric acid (H₂SO₄) and nitric acid (HNO₃).

The above objectives may be prioritized for a specific testing program. The Test Protocol should be designed to ensure that the planned measurements are appropriate for achieving the project objectives, that the quality assurance plan is sufficient for obtaining data of known and adequate quality, and that data generated will withstand scrutiny by the scientific and regulatory communities.

Section 1

INTRODUCTION

The Environmental Protection Agency's (EPA's) decision to revise the NAAQS for particulate matter may have significant impacts on the petroleum industry. The U.S. petroleum industry operates many stationary combustion devices such as process heaters, boilers, flares, fluid catalytic cracking unit regenerators, catalytic reforming unit regenerators, sulfur recovery units, steam generators, heater treaters, coke calciners, thermal oxidizers, stationary internal combustion engines such as gas turbines, and other devices. Most are gas fired, using process gases (refinery gas, casing gas, etc.) or natural gas. A small number of units are fired with distillate or residual oils, petroleum coke (e.g., catalyst regenerators for catalytic cracking units and catalytic reforming units), coal, or other petroleum refining byproducts. Those in urban non-attainment areas such as Los Angeles are almost exclusively gas-fired. Although gas is a relatively clean fuel, due to the target number and variety of gas-fired combustion devices and the range of process gas compositions even gas combustion may have significant potential to emit aerosol-forming organics. Organic aerosols are believed to contribute significantly to ambient particulate concentrations, especially in the very fine (below 2.5 micron) particle size range. Air emissions from combustion devices are important sources of organic aerosols, particulate matter and fine particle precursors.

Existing information regarding emission of organic compounds and aerosols from petroleum industry sources is sparse; therefore, API is conducting a two-phase program to characterize organic aerosol emission profiles for stationary petroleum industry combustion devices. The program also will seek to characterize emissions of other particles and particle precursors that contribute to fine particulate matter in the atmosphere. In Phase 1, the work includes: a critical review of sampling and analysis methodology (the subject of this report); development of an experimental design for characterizing organic aerosol emissions from petroleum industry combustion devices; and development of a test plan for implementation. In Phase 2, the test plan may be implemented.

The design of API's program requires a thorough understanding of the wide variety of available measurement approaches, regulatory agency and industry objectives, experimental design approaches, and combustion device characteristics. It should be noted that measurement of aerosols and aerosol precursors from stationary sources is not common practice; in fact, such

measurements are presently at the forefront of science and are thus subject to considerable uncertainty. Therefore, caution must be exercised in selecting a particular approach, to ensure that it is capable of achieving the project goals. Differing approaches to such measurements have been taken by various researchers, subject to differing research objectives. Ambient aerosols, especially fine aerosols, are dominated by particles which form after the exhaust gases leave the source stack. Since the mechanisms of aerosol formation are not yet completely known, interpretation of measurement results is subject to considerable uncertainty. This report provides a critical review of sampling and analysis methods to serve as important background for an effective test program design.

REPORT ORGANIZATION

This report is divided into seven sections as follows:

- Section 1 - Introduction. General overview of API program.
- Section 2 - Background. Provides overview of proposed fine particulate regulations, aerosol formation mechanisms, and past emissions data from petroleum industry combustion sources.
- Section 3 - Ambient Air Sampling and Analysis Methods. Overview of methods likely to be modified for dilution sampling.
- Section 4 - Traditional Stationary Source Emissions Measurement Methods. Overview of conventional stationary source testing methods relevant to this program.
- Section 5 - Aerosol Source Emissions Measurements. Review of dilution sampler designs and previous experience.
- Section 6 - Recommendations. Summary of Recommendations for Phase 2.
- Section 7 - References. Listing of literature reviewed to develop this report.

Section 2

BACKGROUND

Accurate measurements of organic aerosols and interpretation of test results will require an understanding of aerosol formation processes. Also, EPA's recent action to implement NAAQS for PM_{2.5} adds to the debate over the contribution of stationary combustion sources to ambient fine particulate concentrations. This section provides a brief overview of EPA's revised particulate standards and a review of ambient aerosol formation processes.

NATIONAL AMBIENT PM_{2.5} STANDARDS

On July 18, 1997, EPA published revisions to the NAAQS for particulate matter (62 Federal Register 38652). The revisions to the particulate standard were based solely on epidemiological studies without supporting toxicological and human clinical evidence. EPA's revisions include new annual and 24-hour standards for particles 2.5 micrometers (microns or μm) and smaller in diameter, referred to as PM_{2.5}. Combustion processes are the most likely source of PM_{2.5}.

EPA revised the previous primary (health-based) particulate standards by adding a new annual PM_{2.5} standard of $15 \mu\text{g}/\text{m}^3$ and a new 24-hour PM_{2.5} standard of $65 \mu\text{g}/\text{m}^3$. EPA is retaining the current annual PM₁₀ standard of $50 \mu\text{g}/\text{m}^3$, but has revised the form of the current 24-hour PM₁₀ standard of $150 \mu\text{g}/\text{m}^3$. The previous form of one exceedence has been replaced with a form based on the 99th percentile of 24-hour PM₁₀ concentrations in a year, averaged over 3 years. EPA has also revised its PM monitoring requirements to account for the new standards, including a reference test method for monitoring ambient PM_{2.5} (discussed later in Section 3). In addition, the sampling frequency for PM₁₀ monitoring has been extended to once in 3 days.

PARTICULATE MATTER IN THE ATMOSPHERE

Particles or particulate matter may be either directly emitted into the atmosphere or formed there by chemical reactions; they are called primary and secondary particles, respectively. The relative importance of primary and secondary particles depends mainly on the geographical location, with its particular mix of emissions, and on the atmospheric chemistry. For example, in areas where wood is burned as heating fuel during the wintertime, most of the particles are primary in nature, whereas during summertime photochemical episodes, a substantial fraction of the particulate matter is attributed to secondary reactions in the atmosphere (Grosjean and Friedlander, 1975). As

shown in Figure 2-1, these particles are formed via several pathways, which are discussed in the sections below.

Particle Size

Atmospheric particles may be solid or liquid, with diameters between approximately 0.002 and 100 μm (Finlayson-Pitts and Pitts, 1986). Particles with diameters of approximately 0.002 μm are the smallest size detectable by condensation nuclei counters. The upper end of this range corresponds to the size of fine drizzle or very fine sand. These particles are so large that they do not remain suspended for a significant amount of time and quickly fall out of the atmosphere. The most important particles with respect to atmospheric chemistry, physics, and health effects related issues are in the 0.002-10 μm range.

Aerosols are defined as relatively stable suspensions of solid or liquid particles in a gas. Thus aerosols differ from particles in that an aerosol includes both the particles and the gas in which they are suspended.

A particle's size affects many of its properties such as volume, mass and settling velocity. Size is expressed in terms of effective diameter, which depends on a physical rather than a geometric property. The most commonly used physical property is the aerodynamic diameter, D_a , which is defined as the diameter of a sphere of unit density ($1 \text{ g}\cdot\text{cm}^{-3}$) which has the same terminal falling speed in air as the particle under consideration (Finlayson-Pitts and Pitts, 1986).

Factors Affecting Ambient Particle Size and Composition

Suspended particles congregate in different sub-ranges according to their method of formation (Whitby *et al.*, 1972). Figure 2-2 (from Chow, 1995) shows the major features of the mass distribution of particle sizes found in the atmosphere. The "nucleation" range (also termed "ultrafine particles") consists of particles with diameters less than approximately 0.08 μm that are emitted directly from combustion sources or that condense from cooled gases soon after emission. The lifetimes of particles in the nucleation range are usually less than 1 hour because they rapidly coagulate with larger particles or serve as nuclei for cloud or fog droplets. This size range is detected only when fresh emission sources are close to a measurement site or when new particles have been recently formed in the atmosphere (Chow, 1995, and references therein).

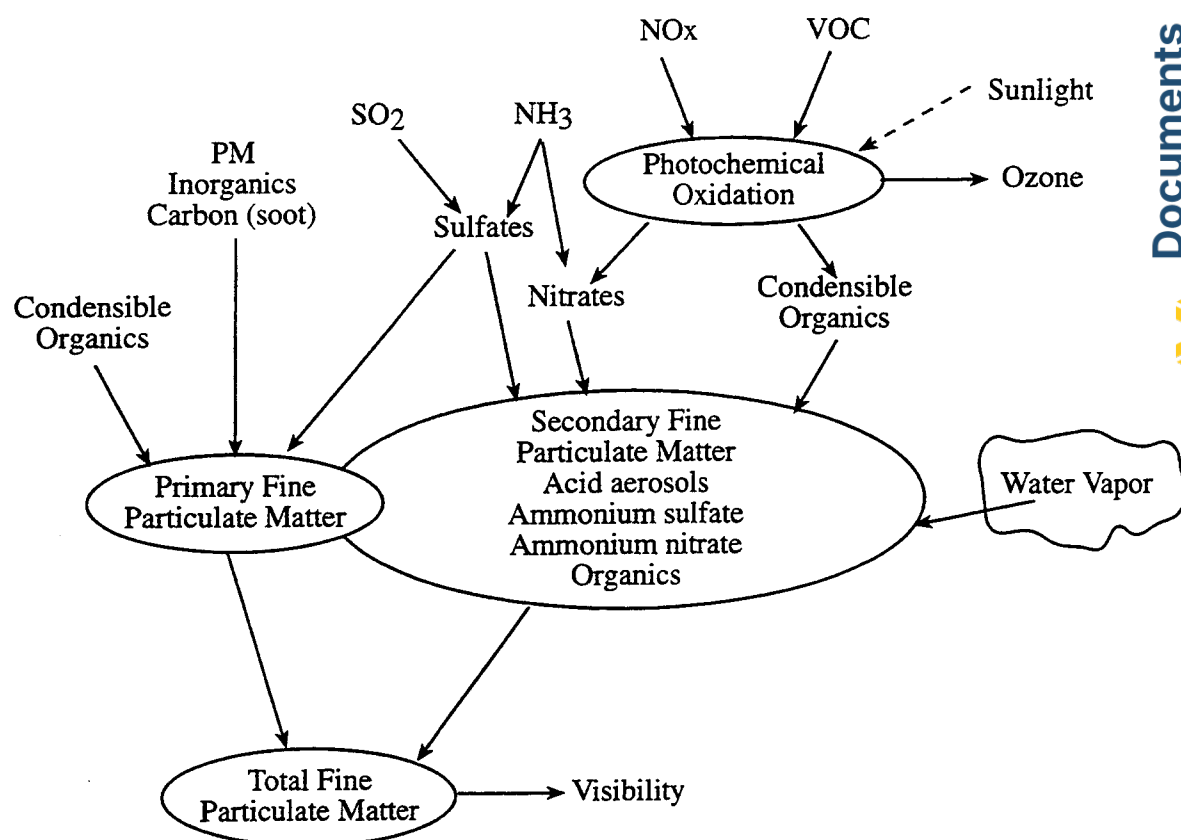


Figure 2-1. Fine Particulate Formation Pathways.

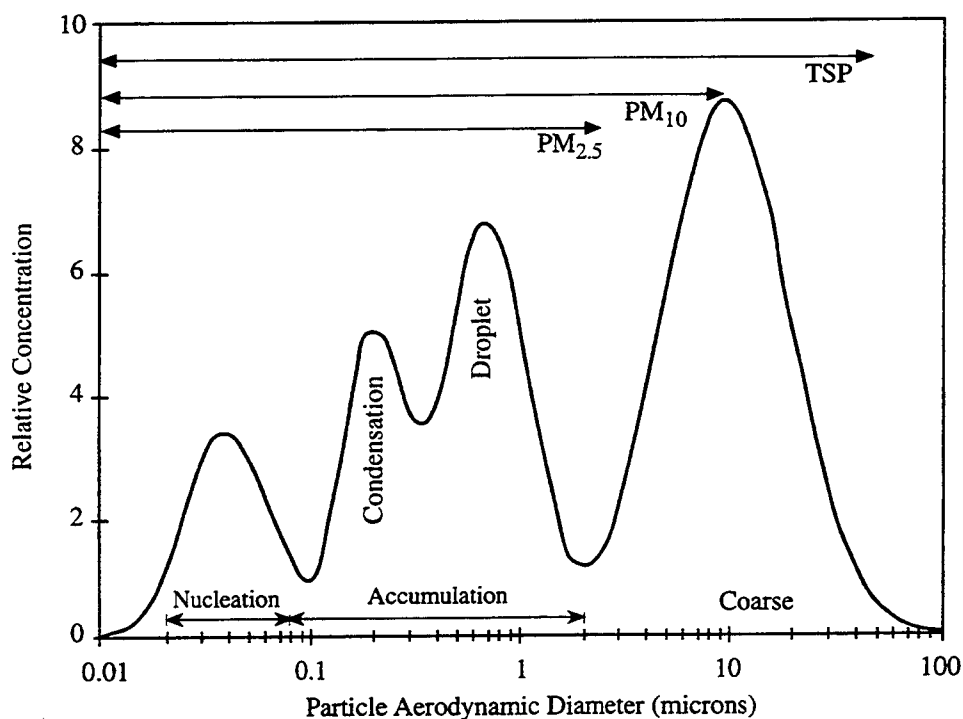


Figure 2-2. Idealized Size Distribution of Particles in Ambient Air (From Chow, 1995).

The "accumulation" range consists of particles with diameters between approximately 0.08 and 2 μm . These particles result from the coagulation of smaller particles emitted from: 1) combustion sources; 2) the condensation of volatile species; 3) gas-to-particle conversion; and 4) finely ground dust particles. The nucleation and accumulation ranges constitute the "fine particle size fraction," and the majority of sulfuric acid, ammonium bisulfate, ammonium sulfate, ammonium nitrate, and organic and elemental carbon is found in this size range. Particles larger than approximately 2 or 3 μm are called "coarse particles"; they result from grinding activities and are dominated by material of geological origin. Pollen and spores also inhabit the coarse particle size range, as do ground up trash, leaves, and tires. Coarse particles at the low end of the size range also occur when cloud and fog droplets form in a polluted environment, then dry out after having scavenged other particles and gases (Chow, 1995, and references therein).

Particle size fractions commonly measured by air quality monitors are identified in Figure 2-1 by the portion of the size spectrum that they occupy. The mass collected is proportional to the area under the distribution within each size range. The *total suspended particulate* (TSP) size fraction ranges from 0 to approximately 40 μm , the PM₁₀ fraction ranges from 0 to 10 μm , and the PM_{2.5} size fraction ranges from 0 to 2.5 μm in aerodynamic diameter. No sampling device operates as a step function, passing 100 percent of all particles below a certain size and excluding 100 percent of the particles larger than that size. Instead, the cut-point of a sampling device is the diameter where 50 percent of the particles are collected, so a fraction of those particles larger than the size cut also will be collected.

Figure 2-3 shows calculated residence times in the atmosphere for particle sizes within each size range, based on gravitational settling in still and stirred chambers (Hinds, 1982). Particles in the fine particle (PM_{2.5}) size fraction have substantially longer residence times, and therefore greater potential to affect PM concentrations further from emissions sources, than particles with aerodynamic diameters exceeding 2 or 3 μm . In this regard, fine particles behave more like gases than coarse particles.

Figure 2-2 shows the accumulation range to consist of at least two submodes, which is contrary to many other presentations that show only a single peak in this region. Recent measurements of chemically specific size distributions show these submodes in several different urban areas. John *et al.* (1991) interpreted the peak centered at approximately 0.2 μm as a "condensation" mode, containing gas-phase reaction products, and the approximately 0.7 μm peak as a "droplet" mode,

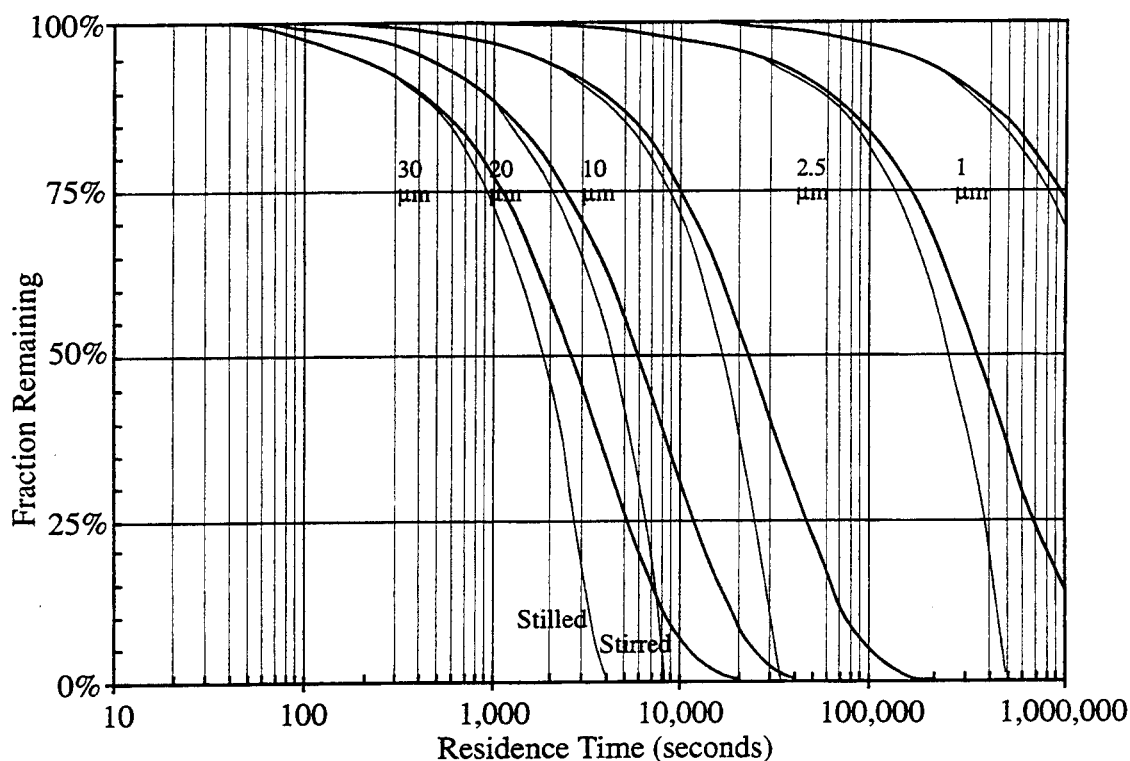


Figure 2-3. Aging Time for Homogeneously Distributed Particles of Different Aerodynamic Diameters in a 100 m Deep Mixed Layer. Gravitational Settling is Assumed for Both Still and Stirred Chamber Models (Hinds, 1982).

resulting from growth by nucleation of particles in the smaller size ranges and by reactions that take place in water droplets. The liquid water content of ammonium nitrate, ammonium sulfate, sodium chloride, and other soluble species increases with relative humidity. This behavior is especially important when relative humidity exceeds 70 percent. When these modes contain soluble particles, their peaks shift toward larger diameters as humidity increases (Chow, 1995, and references therein). The peak of the coarse mode may shift between approximately 6 and 25 μm . A small shift in the 50 percent cut-point of a PM₁₀ sampler has a large influence on the mass collected because the coarse mode usually peaks near 10 μm . On the other hand, a similar shift in cut-point near 2.5 μm has a small effect on the mass collected owing to the low quantities of particles in the 1 to 3 μm size range (Chow, 1995).

Chemical Composition

Six major components account for nearly all of the PM₁₀ mass in most urban areas: 1) geological material (oxides of aluminum, silicon, calcium, titanium, and iron); 2) organic carbon (consisting of hundreds of compounds); 3) elemental carbon; 4) sulfate; 5) nitrate; and 6) ammonium. Liquid water absorbed by soluble species is also a major component when the relative humidity exceeds approximately 70 percent, but much of this evaporates when filters are equilibrated prior to weighing. Water-soluble sodium and chloride are often found in coastal areas, and certain trace elements are found in areas greatly influenced by industrial sources.

Although total mass measurements depend somewhat on sampling and analysis methods (Chow, 1995), mass concentrations of PM₁₀ and PM_{2.5} can be reproduced within experimental precision (typically 20-30 percent) by summing the measured concentrations of these six chemical components. Approximately half of PM₁₀ is composed of geological material. However, geological material often constitutes less than approximately 10 percent of the PM_{2.5} mass concentrations, as most of it is found in the coarse particle size fraction. The majority of sulfuric acid, ammonium bisulfate, ammonium sulfate, ammonium nitrate, and organic and elemental carbon is found in the "fine particle size fraction," PM_{2.5} size range.

Table 2-1 summarizes the chemical composition of particles directly emitted from several representative emission sources measured in California in 1993 (Watson *et al.*, 1997; Chow, 1995). Although the detailed chemical composition of particles emitted from these sources may differ somewhat in different parts of the country, the table gives a reasonable overview of primary emissions from different sources. It can be seen from this table that organic carbon (OC) and elemental carbon (EC) are important constituents of most of these emissions.

Table 2-1. Chemicals in Primary Particles Emitted Directly from Different Emission Sources.

Source Type	Dominant Particle Size	< 0.1%	0.1 to 1%	1 to 10%	> 10%
Paved Road Dust	Coarse	Cr, Sr, Pb, Zr	SO ₄ ⁼ , Na ⁺ , K ⁺ , P, S, Cl, Mn, Ba, Ti	EC, Al, K, Ca, Fe	OC, Si
Unpaved Road Dust	Coarse	NO ₃ ⁻ , NH ₄ ⁺ , P, Zn, Sr, Ba	SO ₄ ⁼ , Na ⁺ , K ⁺ , P, S, Cl, Mn, Ba, Ti	OC, Al, K, Ca, Fe	Si
Construction	Coarse	Cr, Mn, Zn, Sr, Ba	SO ₄ ⁼ , K ⁺ , S, Ti	OC, Al, K, Ca, Fe	Si
Agricultural Soil	Coarse	NO ₃ , NH ₄ ⁺ , Cr, Zn, Sr	SO ₄ ⁼ , Na ⁺ , K ⁺ , S, Cl, Mn, Ba, Ti	OC, Al, K, Ca, Fe	Si
Natural Soil	Coarse	Cr, Mn, Sr, Zn, Ba	Cl, Na ⁺ , EC, P, S, Cl, Ti	OC, Al, Mg, K, Ca, Fe	Si
Lake Bed	Coarse	Mn, Sr, Ba	K ⁺ , Ti	SO ₄ ⁺ , Na ⁺ , OC, Al, S, Cl, K, Ca, Fe	Si
Motor Vehicle	Fine	Cr, Ni, Y	NH ₄ ⁺ , Si, Cl, Al, Si, P, Ca, Mn, Fe, Zn, Br, Pb	Cl ⁻ , NO ₃ ⁻ , SO ₄ ⁼ , NH ₄ ⁺ , S	OC, EC
Vegetative Burning	Fine	Ca, Mn, Fe, Zn, Br, Rb, Pb	NO ₃ ⁻ , SO ₄ ⁼ , NH ₄ ⁺ , Na ⁺ , S	Cl ⁻ , K ⁺ , Cl, K	OC, EC
Residual /Crude Oil Combustion (including fires)	Fine	K ⁺ , OC, Cl, Ti, Cr, Co, Ga, Se	NH ₄ ⁺ , Na ⁺ , Zn, Fe, Si	V, OC, EC, Ni	S, SO ₄ ⁼
Incinerator	Fine	V, Mn, Cu, Ag, Sn	K ⁺ , Al, Ti, Zn, Hg	NO ₃ ⁻ , Na ⁺ , EC, Si, S, Ca, Fe, Br, La, Pb	SO ₄ ⁼ , NH ₄ ⁺ , OC, Cl
Coal-Fired Power Plant	Fine	Cl, Cr, Mn, Ga, As, Se, Br, Rb, Zr	NH ₄ ⁺ , P, K, Ti, V, Ni, Zn, Sr, Ba, Pb	SO ₄ ⁼ , OC, EC, Al, S, Ca, Fe	Si
Oil-Fired Power Plant	Fine	V, Ni, Se, As, Br, Ba	Al, Si, P, K, Zn	NH ₄ ⁺ , OC, EC, Na, Ca, Pb	S, SO ₄ ⁼
Smelter Fine	Fine	V, Mn, Sb, Cr, Ti	Cd, Zn, Mg, Na, Ca, K, Se	Fe, Cu, As, Pb	S
Antimony Roaster	Fine	V, Cl, Ni, Mn	SO ₄ ⁼ , Sb, Pb	S	None Reported
Marine (Natural)	Fine and Coarse	Ti, V, Ni, Sr, Zr, Pd, Ag, Sn, Sb, Pb	Al, Si, K, Ca, Fe, Cu, Zn, Ba, La	NO ₃ ⁻ , SO ₄ ⁼ , OC, EC	Cl ⁻ , Na ⁺ , Na, Cl

EC = Elemental Carbon

OC = Organic Carbon

Organic compounds are important components of particulate matter, whether in urban, rural, or remote areas. Most of the particulate organic carbon is believed to reside in the fine particle fraction. It has been reported (Gray *et al.*, 1986) that in the Los Angeles area organic compounds constitute approximately 30 percent of the fine particle mass. Rogge *et al.* (1993a) analyzed

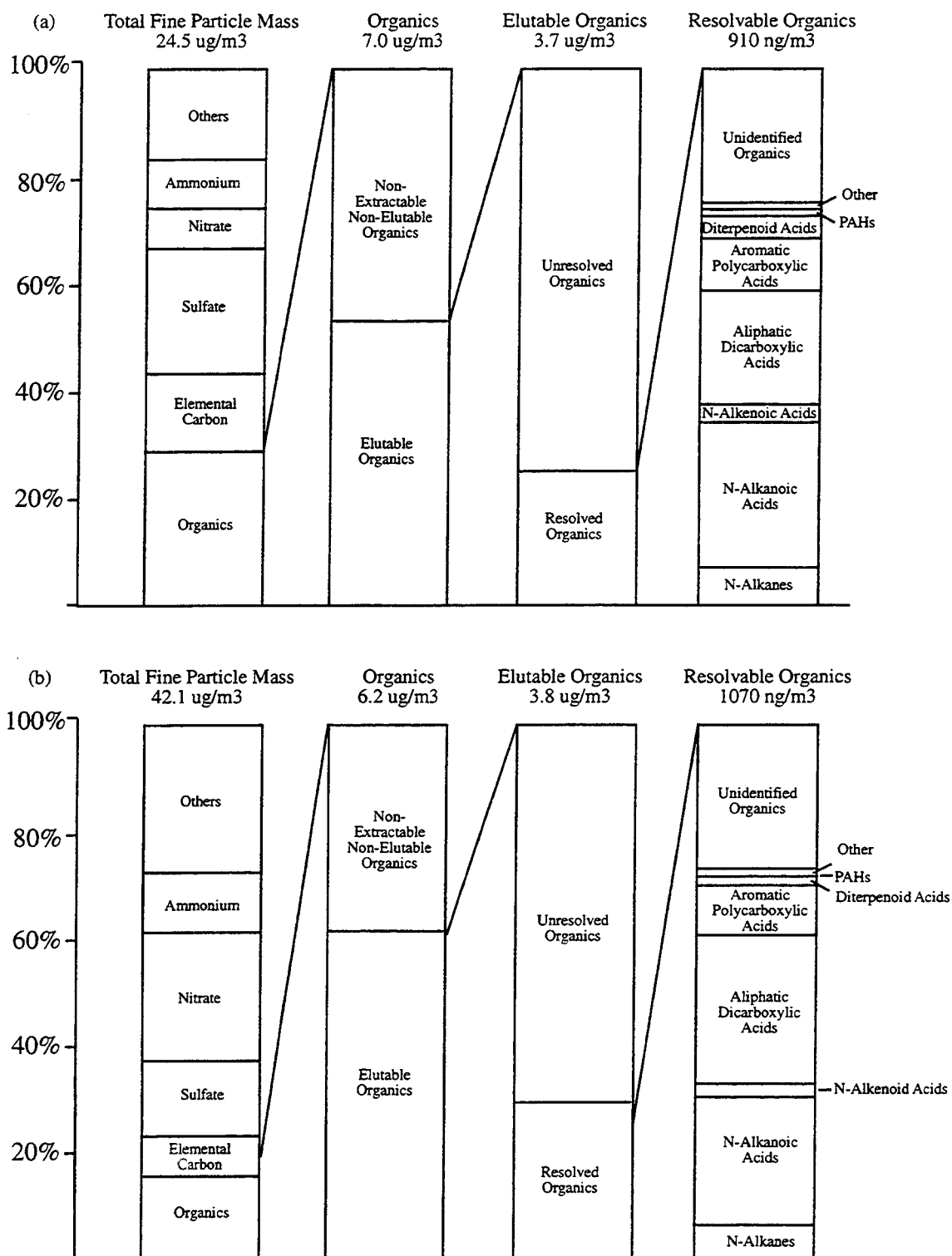


Figure 2-4. Mass Balance on the Chemical Composition of Annual Mean Fine Particle Concentrations, 1982, for (a) West Los Angeles and (b) Rubidoux (Riverside), California (Rogge *et al.*, 1993a).

atmospheric fine particulate samples collected at four urban locations in southern California in 1982 to quantify individual organic compounds. Figure 2-4 shows the material balances that describe the chemical composition of ambient fine particulate matter for the most western (West Los Angeles) and most eastern (Rubidoux) sampling sites. During the summer photochemical smog season, the prevailing winds are from west to east. Under this meteorological condition, West Los Angeles is often upwind of the city, whereas Rubidoux is far downwind of the metropolitan area. Consequently, the concentrations of total fine particles and the secondary formation products such as nitrates and dicarboxylic acids are higher in Rubidoux than in West Los Angeles.

Rogge *et al.* (1993a) identified and quantified more than 80 individual organic compounds found in the fine particles fraction, including n-alkanes, n-alkanoic acid, one n-alkenoic acid, one n-alkanal, aliphatic dicarboxylic acids, aromatic polycarboxylic acids, polycyclic aromatic hydrocarbons (PAH), polycyclic aromatic ketones (PAK), polycyclic aromatic quinones (PAQ), diterpenoid acids and some nitrogen-containing compounds. In general, many of the same organic compounds are found, in different proportions, in direct emissions from various sources, such as diesel and auto exhaust, charbroilers and meat cooking operations, cigarette smoke, biogenic sources, etc. (Rogge, 1993; Rogge *et al.* 1991, 1993b-e).

AEROSOL FORMATION

Primary Particles

Atmospheric concentrations of primary particles are, on average, proportional to the quantities that are emitted. Primary particles are emitted in several size ranges, the most common being less than 1 μm in aerodynamic diameter from combustion sources and larger than 1 μm in aerodynamic diameter from dust sources. Particles larger than 10 μm in aerodynamic diameter usually deposit to the surface within a few hours after being emitted and do not have a large effect on light scattering, unless high winds and turbulence resuspend the particles.

Emission source categories include: 1) major stationary (point) sources (e.g., boilers, process heaters, incinerators, and steam generators); 2) area sources (e.g., fires, wind-blown dust, petroleum extraction operations, meat cooking operations, and residential fuel combustion); 3) mobile sources (e.g., automobiles, buses, trucks, trains, and aircraft); 4) agricultural and ranching activities (e.g., fertilizers, herbicides, tilling operations, and ammonia emissions from livestock); and 5) biogenic sources (e.g., pollen fragments and particulate abrasion products from leaf surfaces).

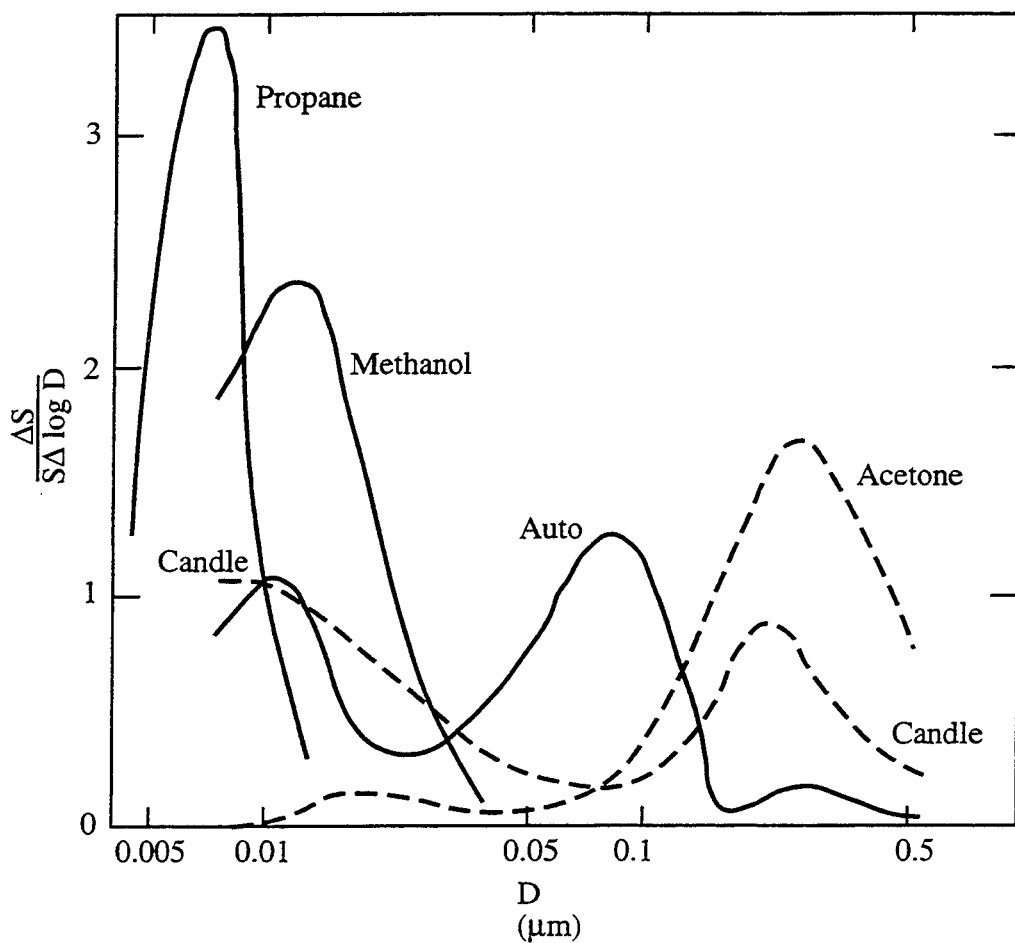


Figure 2-5. Surface Area Distribution of Particles from the Combustion of Several Organics and from Automobiles and a Candle (from National Research Council, 1979).

Combustion processes (e.g., power plants, incinerators, diesel engines) may produce particles not only in the nucleation range (less than approximately 0.08 μm) but also in the accumulation range. The relative numbers of particles produced in the nucleation range compared to the accumulation range depend on the nature of the combustion process (e.g., fuel, operating conditions) and air emission controls, as well as the conditions of cooling and dilution (Finlayson-Pitts and Pitts, 1986). Partitioning of particulate mass to the condensation and nucleation fractions is affected by the rate of cooling, the relative humidity of the diluting air, and the presence of other particles. Figure 2-5 shows the surface area distribution of particles produced by the combustion of several organic compounds, as well as by automobiles and a burning candle. The area under the curve represents the total particle surface area of the distribution. The "dirtier" flames (e.g., the candle and the acetone flame) produce significant numbers of particles in the accumulation mode, while the cleaner flames produce particles in the nucleation mode.

Secondary Particles: Chemical and Physical Transformation in the Atmosphere

Once released into the atmosphere, primary particle emissions are subjected to dispersion and transport and, at the same time, to various physical and chemical processes that determine their ultimate environmental fate. The role of the atmosphere may be compared in some ways to that of a giant chemical reactor in which materials of varying reactivities are mixed together, subjected to chemical and/or physical processes and finally removed. Primary emissions from various sources such as motor vehicles, residential wood combustion, meat cooking, etc., are very complex mixtures containing thousands of organic and inorganic constituents in the gas and particulate phases. These compounds have different chemical reactivities and are removed by dry and wet deposition processes at varying rates. Some of the gaseous species, by a series of chemical transformations, are converted into particles, forming secondary aerosols. Sulfates and nitrates are the most common secondary particles, though a fraction of organic carbon can also result from volatile organic compounds (VOC) via atmospheric reactions.

Atmospheric gases can also become suspended particles by absorption, solution, or condensation. Several of these mechanisms may operate in series in the process of secondary particle formation. In absorption, gas molecules are attracted to and adhere to existing particles. Sulfur dioxide and many organic gases have an affinity for graphitic carbon (e.g., activated charcoal is often used as a scrubbing agent for these gases), and most graphitic carbon particles in the atmosphere are usually found in association with an organic component. Most gases are somewhat soluble in water, and liquid particles will rapidly become saturated in the presence of sulfur dioxide, nitrogen dioxide,

and certain organic gases. Many hydrocarbons are emitted at elevated temperatures as a result of incomplete combustion and condense rapidly upon cooling to ambient temperatures. These are usually considered to be primary emissions if the condensation takes place rapidly, within approximately 1 minute of exiting the stack, but the particles formed can be sensitive to changes in temperature and the surrounding gas concentrations.

Chemical transformation and equilibrium processes for inorganic secondary aerosols are complicated, depending on many meteorological and chemical variables, and are not completely understood. Lurmann *et al.* (1988) and Lurmann (1989) summarize the different pathways from gas to particle conversion. Calvert and Stockwell (1983) have studied gas-phase chemistry. Stelson and Seinfeld (1982a; 1982b; 1982c), Russell *et al.* (1983), Russell and Cass (1984; 1986), Bassett and Seinfeld (1983a; 1983b), Saxena *et al.* (1986), Pilinus and Seinfeld (1987) and Wexler and Seinfeld (1992) provide good explanations of the equilibrium between gas and particle species in polluted environments.

The gaseous precursors of most particulate sulfates and nitrates are SO_2 , SO_3 , oxides of nitrogen (NO and NO_2 , the sum of which is designated NO_x) and ammonia. Ambient concentrations of sulfate and nitrate are not necessarily proportional to quantities of emissions since the rates at which they form may be limited by factors other than the concentration of the precursor gas (e.g., photo-chemical reactions). The majority of secondary sulfates are found as a combination of H_2SO_4 , ammonium bisulfate (NH_4HSO_4), and ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$). The majority of secondary nitrates in PM_{10} are found as ammonium nitrate (NH_4NO_3), though a portion of the nitrate is also found in the coarse particle fraction, usually in association with sodium. This is presumed to be sodium nitrate (NaNO_3) derived from the reaction of nitric acid with the sodium chloride (NaCl) in sea salt.

Secondary Sulfate Pathways

Sulfur dioxide changes to particulate sulfate through gas- and aqueous-phase transformation pathways. In the gas-phase pathway, sulfur dioxide reacts with hydroxyl radicals in the atmosphere to form hydrogen sulfite. This species rapidly reacts with oxygen and small amounts of water vapor to become sulfuric acid gas. Sulfuric acid gas has a low vapor pressure, and it either condenses on existing particles, nucleates at high relative humidities to form a sulfuric acid droplet or, in the presence of ammonia gas, becomes neutralized as ammonium bisulfate or ammonium sulfate. Though there are other gas-phase pathways, the hydroxyl radical pathway is

usually the most dominant. Calvert and Stockwell (1983) show a wide range of gas-phase transformation rates from less than 0.01 percent/hr to about 5 percent/hr. The transformation rate appears to be controlled more by the presence or absence of the hydroxyl radical and competing reactions of other gases than by the sulfur dioxide concentration. Hydroxyl radical concentrations are related closely to photochemistry. Gas-phase sulfur dioxide transformation rates are highest during the daytime and drop to less than 0.1 percent/hr at night (Calvert and Stockwell, 1983).

When fogs or clouds are present, SO_2 can be dissolved in a droplet where it experiences aqueous reactions which are much faster than gas-phase reactions. If ozone and hydrogen peroxide are dissolved in the droplet, the sulfur dioxide is quickly oxidized to sulfuric acid. If ammonia is also dissolved in the droplet, the sulfuric acid is neutralized to ammonium sulfate. As relative humidity decreases below 100 percent (i.e., the fog or cloud evaporates), the sulfate particle is present as a small droplet which includes a portion of liquid water. As the relative humidity further decreases below 70 percent, the droplet evaporates and a small, solid sulfate particle remains. The reactions within the fog droplet are very fast, and the rate is controlled by the solubility of the precursor gases. Aqueous transformation rates of sulfur dioxide to sulfate are 10 to 100 times as fast as gas-phase rates.

Secondary Nitrate Pathways

Directly emitted nitric oxide (NO) converts to nitrogen dioxide (NO_2), primarily via reaction with ozone. The principal gas-phase pathways for atmospheric nitrogen dioxide are that: 1) it can change back to nitric oxide in the presence of ultraviolet radiation; 2) it can change to short-lived radical species which take place in other chemical reactions; 3) it can form organic nitrates such as peroxyacetyl nitrate (PAN); or 4) it can oxidize to form nitric acid. The major pathway to nitric acid is reaction with the same hydroxyl radicals which transform sulfur dioxide to sulfuric acid. Nitric acid deposits from the atmosphere fairly rapidly but, in the presence of ammonia, it is neutralized to particulate ammonium nitrate. Calvert and Stockwell (1983) show a wide range of conversion rates for nitrogen dioxide to nitric acid, ranging from less than 1 percent/hr to 90 percent/hr. Though they vary throughout a 24-hour period, these rates are significant during both daytime and nighttime hours, in contrast to the gas-phase sulfate chemistry which is most active during daylight hours. Nitrate is also formed by aqueous-phase reactions in fogs and clouds in a manner analogous to aqueous-phase sulfate formation. Nitrogen dioxide dissolves in a droplet where, in the presence of oxidants, it converts to nitric acid and, in the presence of dissolved ammonia, to ammonium nitrate.

While ammonium sulfate is a fairly stable compound, ammonium nitrate is not. Its equilibrium with gaseous ammonia and nitric acid is strongly influenced by temperature and relative humidity. Russell *et al.* (1983) show that lower temperatures and higher relative humidities favor the particulate phase of ammonium nitrate. Their sensitivity tests demonstrate that the equilibrium is most sensitive to changes in ambient temperature and gaseous ammonia concentrations. The gas phase is highly favored when ambient temperatures approach or exceed 35 °C, while the particulate ammonium nitrate phase is highly favored when temperatures are less than 15 °C. When gaseous ammonia or nitric acid concentrations are reduced, some of the particulate ammonium nitrate evaporates to regain equilibrium with the gas phase. This phenomenon must be addressed in order to make accurate measurements of particulate nitrate and nitric acid, since ammonium nitrate particles on a filter may disappear during sampling or between sampling and analysis with changes in temperature and gas concentrations.

As noted above, gaseous nitric acid can also react with basic materials such as sodium chloride (from sea salt) and possibly alkaline dust particles. The products of these reactions (e.g., sodium nitrate) are usually stable and are often observed as coarse particles, since the original sea salt or dust was in that size range. Coarse particle nitrate accompanied by sodium and a deficit of chloride is a good indicator that this reaction has taken place.

Sulfur dioxide to particulate sulfate and nitrogen oxide to particulate nitrate reactions compete with each other for available hydroxyl radicals and ammonia. Ammonia is preferentially scavenged by sulfate to form ammonium sulfate and ammonium bisulfate, and the amount of ammonium nitrate formed is only significant when total ammonia exceeds sulfate by a factor of two or more on a mole basis. In an ammonia-limited environment, reducing ammonium sulfate concentrations by one molecule would increase ammonium nitrate concentrations by two molecules. This also implies that sulfur dioxide, oxides of nitrogen, and ammonia must be treated as a coupled system and cannot be dealt with separately. It also implies that reducing sulfur dioxide emissions might actually result in ammonium nitrate increases which exceed the reductions in ammonium sulfate where the availability of ammonia is limited.

Atmospheric water is another important component of suspended particulate matter. The liquid water content of ammonium nitrate, ammonium sulfate, sodium chloride, and other soluble species changes with relative humidity (Charlson *et al.*, 1969; Covert *et al.*, 1972), becoming especially important when relative humidity exceeds 70 percent.

Table 2-2. Calculated Atmospheric Lifetimes for Gas-Phase Reactions of Selected Gas-Phase Compounds with Atmospherically Important Reactive Species (From Atkinson, 1988, Unless Noted Otherwise).

Compound	Atmospheric Lifetime Due to Reaction with:				
	OH ^a	O ₃ ^b	NO ₃ ^c	HO ₂ ^d	hν ^e
NO ₂	2 days	12 hr	1 hr	2 hr	2 min
NO	4 days	1 min	3 min	20 min	-
HNO ₃	180 days	-	-	-	-
SO ₂	26 days	>200 yr	>4x10 ⁴ yr	>600 yr	-
NH ₃	140 days	-	-	-	-
Propane	19 days	>7,000 yr	-	-	-
n-Butane	9 days	>4,500 yr	9 yr	-	-
n-Octane	3 days	-	3 yr	-	-
Ethylene	3 days	9 days	3 yr	-	-
Propylene	11 hr	1.5 days	15 days	-	-
Acetylene	30 days	6 yr	>14 yr	-	-
Formaldehyde	3 days	>2x10 ⁴ yr	210 days	23 days	4 hr
Acetaldehyde	1 day	>7 yr	50 days	-	60 hr
Benzaldehyde	2 days	-	60 days	-	-
Acrolein	1 day	60 days	-	-	-
Formic acid	50 days	-	-	-	-
Benzene	18 days	600 yr	>16 yr	-	-
Toluene	4 days	300 yr	9 yr	-	-
m-Xylene	11 hr	75 yr	2 yr	-	-
Phenol	10 hr	-	20 min	-	-
Naphthalene	1 day	>80 days	80 days	-	-
2-Methylnaphthalene	5 hr	>40 days	35 days	-	-
2,3-Dimethylnaphthalene	4 hr	>40 days	20 days	-	-
Acenaphthene	2 hr	>30 days	~3 hr	-	-
Acenaphthylene	2 hr	~50 min	13 min	-	-
Phenanthrene	9 hr	-	-	-	-
Anthracene	2 hr	-	-	-	-
Fluoranthene ^f	6 hr	-	64 days	-	-
Pyrene ^f	6 hr	-	20 days	-	-

^a For 12-hr average concentration of OH radical of 1×10^6 molecule/cm³.

^b For 24-hr average O₃ concentration of 7×10^{11} molecule/cm³.

^c For 12-hr average NO₃ concentration of 2×10^8 molecule/cm³.

^d For 12-hr average HO₂ concentration of 10^8 molecule/cm³.

^e For solar zenith angle of 0°.

^f Lifetimes calculated from kinetic data given in Atkinson *et al.*, 1990.

Secondary Organic Aerosols

While the mechanisms and pathways for inorganic secondary particles are fairly well known, those for secondary organic aerosols are not well understood. Hundreds of precursors are involved in these reactions, and the rates at which these particles form are greatly dependent on the concentrations of other pollutants and meteorological variables. Organic compounds present in the gas phase undergo atmospheric transformation through reactions with reactive gaseous species such as OH radicals, NO₃ radicals, or O₃. Table 2-2 gives the calculated atmospheric lifetimes for some selected compounds present in direct gas-phase emissions due to known tropospheric

chemical removal reactions (from Atkinson, 1988). These lifetimes (i.e., the time for the compound to decay to 1/e or 37 percent of its original concentration) are calculated from the corresponding measured reaction rate constants and the average ambient concentration of the tropospheric species involved. Although the individual rate constants are known to a reasonable degree of accuracy (in general, to within a factor of two), the tropospheric concentrations of these key reactive species are much more uncertain. For example, the ambient concentrations of OH radicals at any given time and/or location are uncertain to a factor of at least 5, and more likely 10 (Atkinson, 1988). In addition, the concentration of OH radicals varies significantly not only diurnally but also with season and latitude due to varying penetration of solar ultraviolet light. The direct measurements by a ^{14}C -tracer method (Felton *et al.*, 1988) showed maximum midday OH radical concentrations in early to mid-October for pure and polluted air to be, respectively, 2.4×10^6 and 9.5×10^6 radicals cm^{-3} . Nighttime OH concentrations of less than 2×10^5 radicals cm^{-3} were measured.

Winter mid-latitude noontime maximum values on the order of approximately 2×10^6 radicals cm^{-3} are likely (Mount, 1992). The tropospheric diurnally and annually averaged OH radical concentrations are more certain, to possibly a factor of two. For this reason, the calculated lifetimes listed in Table 2-2 are approximate only and are valid for those reactive species concentrations which are listed in the footnotes. However, these data permit one to estimate the contribution of each of these atmospheric reactions to the overall rates of removal of most pollutants from the atmosphere.

As can be seen from Table 2-2, the major atmospheric loss process for most of the direct emission constituents listed is by daytime reaction with OH radicals. For some pollutants, photolysis, reactions with ozone, and reactions with NO_3 radicals during nighttime hours are also important removal routes. For alkanes, the atmospheric lifetimes calculated from the corresponding measured reaction rate constant and the average ambient concentration of OH radicals ranges from approximately 19 days for propane (C_3H_8) to approximately 1 day for n-pentadecane ($\text{C}_{15}\text{H}_{32}$). For aromatic hydrocarbons, lifetimes range from 18 days for benzene to a few hours for methylnaphthalenes (assuming average 12-hour daylight OH radical concentration of 1×10^6 molecule cm^{-3}).

Although the rate constants for OH radical reactions with most VOCs are known or can be deduced to a reasonable degree of accuracy (see, for example, Atkinson, 1986, 1989), relatively