Fine and coarse particles: chemical and physical properties important for the standard-setting process

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1. INTRODUCTION

Recent epidemiologic studies report statistical associations between a variety of health outcomes and indicators of particulate matter (PM). These findings lead to concerns about atmospheric aerosols (PM suspended in air) that are likely to continue well into the 21st century. The U.S. Environmental Protection Agency (EPA) has recommended augmenting the current PM_{10} (thoracic particle) standards with new fine particle standards (24-hour and annual). This recommendation largely resulted from the growing epidemiologic evidence for an association of health effects with indicators of the smaller size fraction of the atmospheric aerosol. Two possible indicators of the smaller size fraction for both research and standard setting are (1) fine-mode particles and (2) respirable particles. EPA scientists have preferred to use measurements of fine-mode particles in preference to measurements of respirable particles, primarily because of the significant distinctions between fine-mode and coarse-mode particles in regard to their sources, composition, and properties (physical, chemical, and biological).

As a result of the increasing concern with fine-mode particles, and with specific components of PM, new techniques for the measurement and analysis of aerosol mass and components are needed. Indicators that measure only one component of PM need to be augmented with measurements of the mass of all components. Sampling techniques are needed that capture and measure the semivolatile PM components, such as ammonium nitrate and organic components of particles in wood smoke, that partially are lost by most techniques in use today. Samplers are also needed that cleanly separate PM into fine-mode and coarse-mode fractions. Improved measurement techniques are needed to characterize the chemical and physical properties of aerosol, to determine compliance with standards, to determine sources of particles, to evaluate models, to assess exposure for acute and chronic epidemiology, to assess risk from PM exposure for setting standards, and to guide development of control strategies.

2. HISTORICAL TRENDS

Over the years, the PM components of interest and the PM measurement techniques used have changed; therefore, it is difficult to obtain long-term trends for PM indicators. EPA's National Air Quality and Emissions Trends Report[1] gives the annual average PM_{10} concentrations for the United States from 1988 to 1995, based on a consistent set of monitors from 955 sites. As shown in Figure 1, there is a small downward trend; however, it would be useful to know the relative changes in fine and coarse components of PM. Figure 2 shows annual average trends in Philadelphia for total suspended particles (TSP), PM_{10}, and $PM_{2.5}$.[2,3,4] TSP decreased significantly between 1973 and 1981 but increased slightly since 1981. There does not appear to have been a significant change in PM_{10} between 1987 and 1994. There appears to have been some improvement in $PM_{2.5}$ concentrations between 1980 and 1994; however, such a conclusion is uncertain because of the changes in $PM_{2.5}$ monitors and monitoring sites.

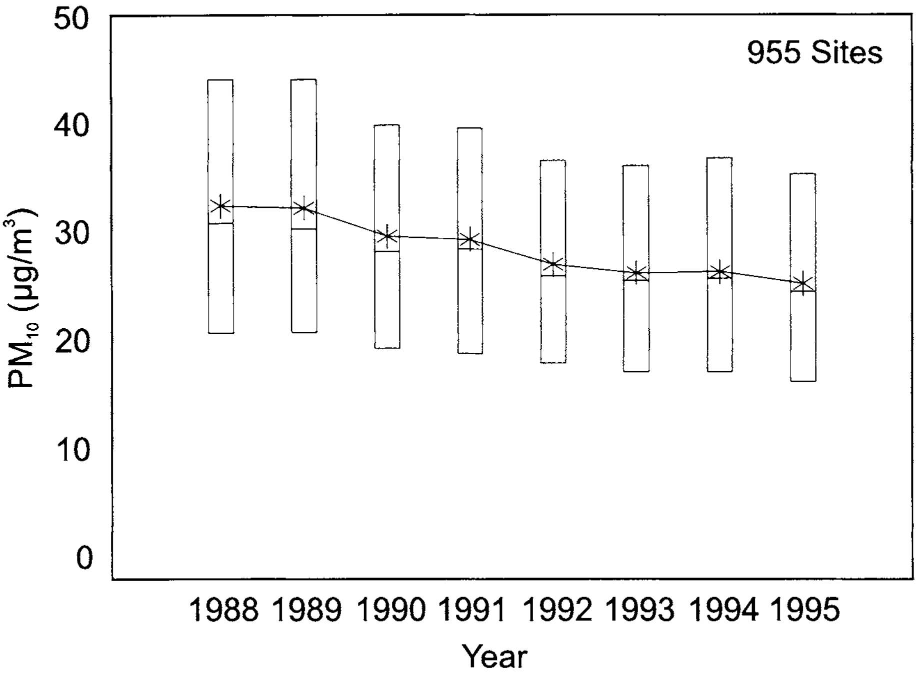

Figure 1. PM_{10} concentration trend from 1988 to 1995, based on yearly averages at 955 monitoring sites in the United States; bars show 90th percentile (top) and 10th percentile (bottom), the asterisk is the mean, and line is the median.[1]

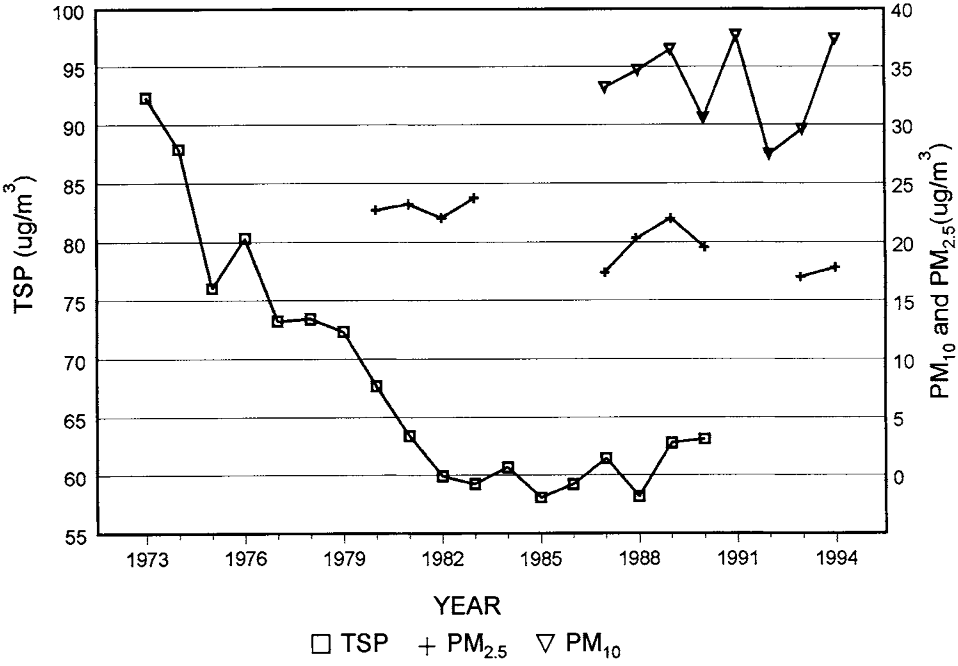

Figure 2. PM trends in Philadelphia, PA, 1973-1994; TSP, PM$_{10}$, and PM$_{2.5}$ (1987-1990) measurements from the Aerometric Information Retrieval System (AIRS);[2] PM$_{2.5}$ (1992-1994) from Harvard Philadelphia Study;[3] and PM$_{2.5}$ (1979-1983) from IPN.[4]

One source of information on long-term trends in fine particle pollution is the visibility distance data collected routinely at airport weather stations.[5] Visibility distance data, corrected for snow, rain, and relative humidity effects and transformed into the etinction coefficient, provide an indicator (known as 'haze') that increases as fine particle concentrations increase. This indicator, plotted as the 75th percentile, is shown in Figure 3 for several regions of the United States for the period 1948-1992.

Haze trends differ by season and region. In the winter, haze has declined in the Upper Midwest and Northeast but has increased in the Southeast and remained about the same in the Mid-Atlantic region. In the summer, however, there has been a dramatic increase in haze in all regions. A major increase in haze began in the 1950's; this increase accelerated in the 1960's but began to level off in the 1970's.

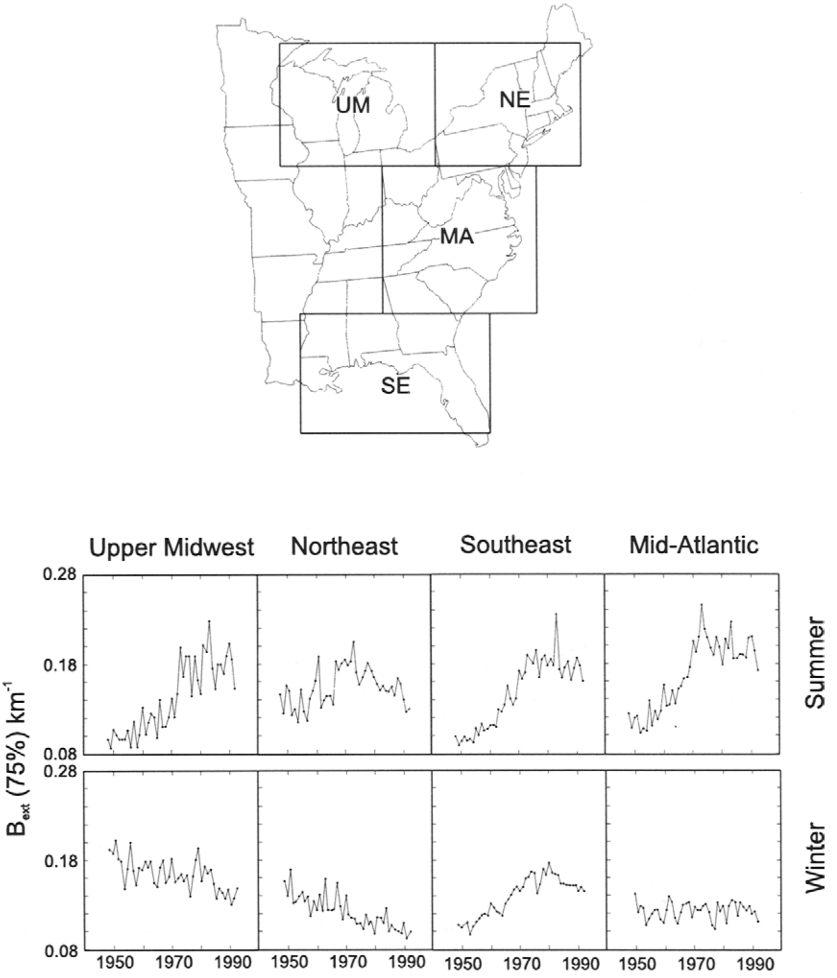

Figure 3. Haze trends in four regions of the United States from 1948 to 1992, shown as the 75th percentile of the extinction coefficient, corrected for relative humidity effects and with days with snow or rain removed.[5]

Because of the decrease in winter and the remarkable increase in the summer, the haze peak in the United States has shifted from winter in the upper Midwest to summer in the Mid-Atlantic region. This may be attributed to an overall decrease in industrial emissions and an increase in emissions of sulfur dioxide (SO_2) and nitrogen oxides (NO_x) in the summer resulting from increased demand for electricity for air conditioning.

The increase in haze since 1950 indicates that the potential exists for significant reductions in fine particles in the United States.

Developed countries, such as the United States, Canada, Japan, and those in Western Europe, will need to continue to be concerned with particle pollution. Megacities in developing countries will experience much greater concentrations of air pollution as industry and traffic expand in the 21st century. Regional pollution from developing countries will continue to impact developed countries.[6]

3. SIZE FRACTIONS

3.1. Fine-mode and coarse-mode particles

Before proceeding further, it will be useful to define the various size fractions that are used in discussions of PM. PM is not a single pollutant; rather it is composed of many different components. PM also may be divided into a variety of size fractions. Many different parameters have been used as indicators of the various size fractions and components of PM. One useful distinction has been to consider PM as two separate classes of pollutants, (1) fine-mode particles and (2) coarse-mode particles. In addition to size, fine-mode and coarse-mode particles differ in sources, formation mechanisms, composition, atmospheric lifetimes, spatial distribution, indoor/outdoor ratios, and temporal variability.[7] Current research is developing evidence that fine-mode and coarse-mode particles also differ in biological effects.[8-11]

The definition of fine-mode and coarse-mode particles is an operational one. It is based on measurements of size distribution, beginning in the early 1970's, that yielded bimodal distributions of particle mass with a minimum between 0.7 and 3.0 μm diameter.[12,13] An idealized distribution, showing the normally observed division of ambient aerosols into fine-mode and coarse-mode particles, is presented in Figure 4. *Aerosol* refers to a suspension of solid or liquid particles in air; however, aerosol is sometimes used to refer to the particles only. Fine-mode and coarse-mode particles may overlap in the intermodal region between 1 and 3 μm.[14]

3.2. Inhalable, thoracic, and respirable particles

It is also possible to define size fractions in terms of their entrance into the various compartments of the respiratory system. This convention classifies particles into inhalable, thoracic, and respirable particles. In a general sense, *inhalable particles* refer to particles with the potential of entering the respiratory tract, including the head airways region. *Thoracic particles* refer to particles with the potential of entering the tracheobronchial region (i.e., lower respiratory tract, including the trachea, bronchi, and the gas-exchange region of the lung). *Respirable particles* are particles with the potential of entering the gas-exchange region. Depending on the particle size, only a portion of the inhalable, thoracic, or respirable particles will enter the target compartment, and portion will be removed higher in the respiratory tract. Also only a portion of each size fraction will be deposited in the target compartment, and a portion will be exhaled. In the past, exact definitions of these terms have varied among organizations.[15] As of 1993 a unified set of definitions was adopted by the American Conference of Governmental Industrial Hygienists (ACGIH),[16] the International Standards Organization (ISO),[17] and the European Standardization Committee (CEN).[18] A historical account of the development of size-selective samplers for collecting size fractions that reach various portions of the respiratory system is given by Lippmann.[19] The particle separation curves for inhalable, thoracic, and respirable particles are shown in Figure 5. Also shown are the separation curves for PM_{10} and for the new Federal Reference Method (FRM) for $PM_{2.5}$ currently being developed.

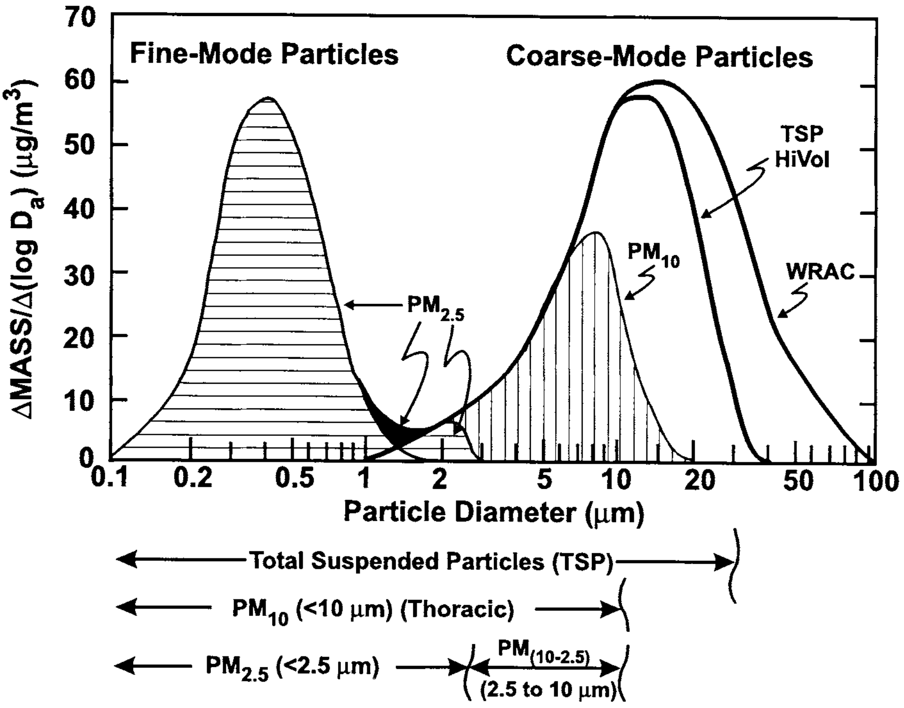

Figure 4. An idealized size distribution of ambient particulate matter showing fine- and coarse-modes and the portions collected by samplers with various size cut points.[7]

3.3. Particle samplers

Samplers have been designed to collect specific portions of the particle size-distribution. For example, TSP is defined by the design of the High Volume Sampler (HiVol), which collects all of the fine particles but only part of the coarse particles. The upper cut-off size of the HiVol is undefined, except by the design of the sampler, and varies with wind speed and direction. Extraordinary measures, such as were undertaken with the Wide Range Aerosol Classifier (WRAC), are required to collect the entire coarse mode.[20] Samplers also have been designed to collect the inhalable, thoracic, and respirable fractions.

The sample collected with a $PM_{2.5}$ cut is sometimes referred to as fine. In this paper, samples specified by relatively sharp cuts will be described numerically (i.e., PM_{10} or

$PM_{2.5}$). That portion of PM between $PM_{2.5}$ and PM_{10}, as shown in Figure 4, will be called $PM_{(10-2.5)}$). Because fine and coarse have lost the precise meaning intended by Whitby,[12] the addition of "mode" is used to emphasize reference to the fine- or coarse-mode particles shown in the distributions in Figure 4. Thus, $PM_{2.5}$ may be considered an indicator of fine-mode particle mass; PM_{10}, an indicator of the thoracic component (the fraction of PM that enters the thorax); and $PM_{(10-2.5)}$, an indicator of thoracic coarse-mode particles (i.e., that portion of the coarse-mode particle mass that reaches the thoracic compartment). In the proposal for new fine particle standards, EPA recommended maintaining the PM_{10} standards and sampling network, with PM_{10} becoming a marker for thoracic coarse-mode particles. However, research studies likely will determine $PM_{(10-2.5)}$ either directly or as the difference between PM_{10} and $PM_{2.5}$. Because of the overlap of fine- and coarse-mode particles in the intermodal region (1-3 μm), $PM_{2.5}$ is only an approximation of fine-mode particles, and $PM_{(10-2.5)}$ is only an approximation of thoracic coarse-mode particles.

In this paper, fine particles and coarse particles will refer to fine-mode particles and thoracic coarse-mode particles, respectively, not to the approximations given by $PM_{2.5}$ or $PM_{(10-2.5)}$. Also, diameter normally will refer to the aerodynamic diameter.

PM regulation began in the United States in 1971 with a TSP standard defined by the HiVol.[22] To focus regulatory concern on those particles small enough to penetrate and deposit in the lower respiratory tract (thoracic region), the indicator for the National Ambient Air Quality Standard for PM was changed in 1987 from TSP, as measured by the HiVol, to PM_{10}.[23] PM_{10} samplers collect all of the fine particles and part of the coarse particles. The upper cut point is defined as having a 50% collection efficiency at 10 ± 0.5 μm diameter. The slope of the collection efficiency curve also is defined.[24] Samplers with upper cut points of 3.5, 2.5, 2.1, and 1.0 μm are also in use. Dichotomous samplers split the particles into smaller and larger fractions that may be collected on separate filters. Detailed information on the design and use of particle samplers may be found in the review by Chow.[25]

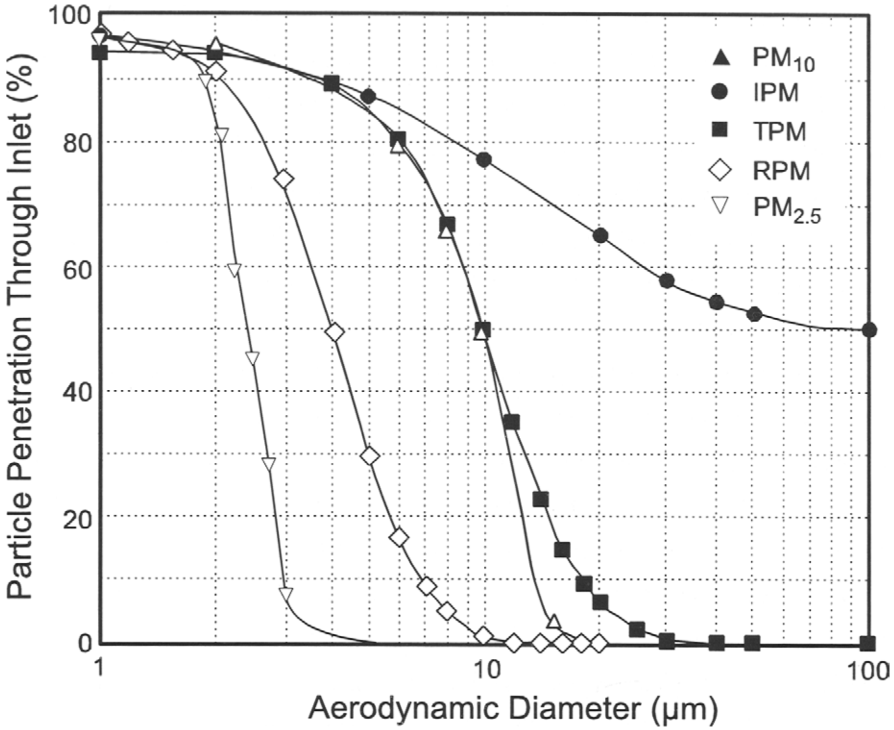

Figure 5. Particle separation curves for inhalable (IPM), thoracic (TPM), and respirable (RPM) particles and for PM_{10}[14] and $PM_{2.5}$.[21]

3.4. $PM_{2.5}$

Interest in fine and coarse particles, as distinct components of the atmospheric aerosol, began in the early 1970's, largely because of size distribution studies by Whitby and co-workers.[12,13] In 1979, EPA scientists endorsed the need to measure fine and coarse particles separately.[26] Based on limitations of existing technology, 2.5 µm, rather than 1.0 µm, was chosen for the cut point between fine and coarse particles. The $PM_{2.5}$ sample contains all of the fine particles but, especially in dry areas or during dry conditions, may collect a small but significant fraction of the coarse particles.[14] In 1979, EPA initiated the Inhalable Particle Network (IPN),[4] which included measurements of fine and coarse particles using dichotomous samplers with upper cut points of 15 and 2.5 µm. $PM_{2.5}$, as well as indicators of coarse particles measured in the Regional Air

Pollution Study in St. Louis, MO,[27] and the Harvard Six Cities Study.[28] Epidemiologic results from the Harvard Six Cities Study[28,29] that implicated $PM_{2.5}$ as being of special concern for health effects intensified interest in a fine particle standard. This interest was further intensified in 1994, when the American Lung Association brought a suit in U.S. Federal Court that forced EPA to begin a review of the PM standard.[30]

The first step in the review process is the preparation, by EPA's Office of Research and Development, of the Air Quality Criteria for Particulate Matter,[31] a critical review of scientific knowledge of PM. In this document, EPA recommended that '... fine and coarse particles should be considered as separate subclasses of pollutants. Consideration of formation, composition, behavior, exposure relationships, and sources argue for monitoring fine and coarse particles separately. Because fine and coarse particles are derived from different sources, it is also necessary to quantify ambient levels of fine and coarse particles separately in order to plan effective control strategies.'[32]

The second step in the review process is the preparation, by EPA's Office of Air Quality Planning and Standards (OAQPS), of the Review of the National Ambient Air Quality Standards for Particulate Matter: Policy Assessment of Scientific and Technical Information (the so-called OAQPS Staff Paper).[33] In this document, OAQPS recommended additional standards for fine particles and that 2.5 μm be used as the cut point between fine and coarse particles. The Clean Air Science Advisory Committee (CASAC), in their review of the staff paper, endorsed $PM_{2.5}$ as the indicator for fine particles.[34] EPA's National Exposure Research Laboratory is preparing the FRM that will include a design specification of the impactor, giving a sharp 50% cut at 2.5 μm aerodynamic diameter.[21]

3.5. EPA chooses $PM_{2.5}$ as the indicator for fine particles

During the review of the PM standard, there was some discussion of the possibility of choosing respirable particles for the new PM standards in order to harmonize U.S. and European particle measurements. However, EPA's decision to recommend a sharp, upper 50% cut point of 2.5 μm when it proposed new standards for fine particles[35] was based on different considerations than those of organizations (such as ACGIH, ISO, and CEN) that have recommended inhalable, thoracic, and respirable particle size fractions (Figure

5). Particle size fractions based on entrance into various compartments of the respiratory tract were developed originally for industrial hygiene purposes. In industrial applications, workers may be exposed predominantly to a single type of particle with a single size distribution. For these situations, inhalable, thoracic, and respirable size fractions may well be appropriate. However, in more complex situations, with more than one type of particle or size distribution, size fractions based on particle source or particle composition may be more appropriate. For example, coal miners are exposed to diesel soot, in the lower range of fine particles, and coal dust, in the coarse particle size range. Coal mining environments in the United States are monitored with a dichotomous sampler with a cut point between fine and coarse particles of 0.8 µm.[36] The ambient atmosphere is an even more complex situation with a wide range of particle sizes and sources. However, a separation into fine and coarse particles still gives useful information on particle sources that would be lost with a respirable sample.

The CASAC Technical Subcommittee for Fine Particle Monitoring[37] has encouraged EPA to 'give careful consideration to harmonizing the definition of PM_{10} with internationally accepted definitions of thoracic particulate matter'. The PM_{10} separation curve, although sharper than the inhalable particle curve, nevertheless gives a reasonable representation of inhalable particles. However, EPA, in its proposal for additional particle standards, choose fine particles instead of respirable particles. The preference for fine particles is based on the differences between fine and coarse particles, in terms of sources, composition, and properties. A respirable sample will combine both fine and coarse particles. However, a $PM_{2.5}$ sample, together with a PM_{10} or thoracic sample, allows a separate determination of fine and coarse particles. The difference between these two size-fractionation schemes is particularly important if fine and coarse particles have different sources and different biological properties. A thoracic and a respirable sample would not give information on which particle component was most prevalent. If one of these samples exceeded a standard, and a control program were required, this sampling scheme would provide little information as to which types of sources to control to most effectively reduce PM levels. A combination of PM_{10} and $PM_{2.5}$, however, would direct controls toward either fine or coarse particles. If fine and coarse particles have different biological properties, one city, whose high concentrations result from the more biologically active particle component, would have a different public health problem than would a city whose particle mix was dominates also easier to identify distinct source categories by factor analysis or chemical element balance if particles are first separated into fine and coarse. For example, potassium in fine particles is a tracer for wood burning, whereas potassium in coarse particles comes from soil.

3.6. Respiratory tract deposition

The selection of a fine particle fraction instead of a respirable particle fraction, either for research or standard setting, might be influenced by the pattern of deposition, as a function of particle size, into two important compartments of the lung, (1) the alveolar (the unciliated, gas exchange) compartment and (2) the tracheobronchial (the ciliated airways) compartment. The respiratory tract deposition fractions for the alveolar (A) and tracheobronchial (TB) compartments, as functions of particle size for a healthy adult, are shown in Figure 6.[38] Thoracic particles, given by a broad particle separation curve with a 50% upper cut point at 10 μm diameter (Figure 5), provide an indicator of those particles that enter the thorax and then can deposit in either the A or TB compartments. Respirable particles, given by 50% upper cut point at 4.0 μm and a broad separation curve (Figure 5), will be dominated by particles that deposit in the A compartment but also will contain a small fraction of particles that deposit in the TB compartment.

A particle sample with a cut at 2.5 μm will have a smaller, although possibly significant, fraction of particles that deposit in the TB compartment. A cut at 1.0 μm could give a better separation of PM into coarse-mode particles, above 1.0 μm, which deposit in both the A and TB compartments, and fine-mode particles, below 1.0 μm, which deposit primarily in the A compartment. Thus the patterns of deposition in the respiratory tract provide no basis for choosing a respirable fraction rather than a fine particle fraction or choosing 2.5 μm rather than 1.0 μm as the cut point for the fine particle indicator.

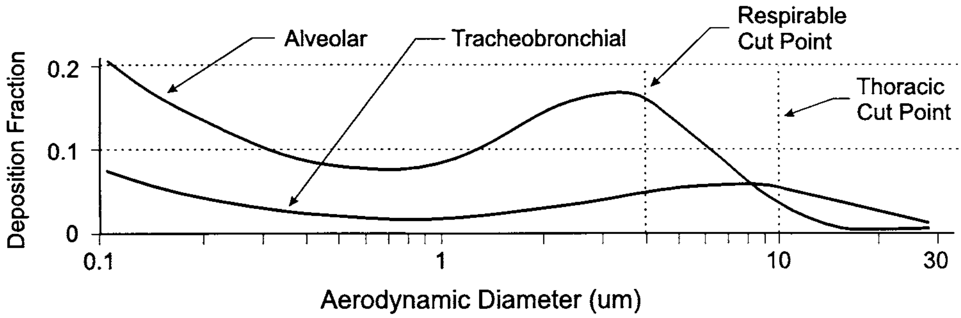

Figure 6. Calculated deposition fractions to the tracheobronchial and alveolar compartments of the respiratory tract for monodisperse aerosols as a function of aerodynamic diameter for quiet breathing (tidal volume = 750 ml, breathing frequency = 15 min^{-1}).[38]

Figure 6 shows the deposition fractions for a healthy adult breathing at a normal rate. The deposition fractions and patterns will change for different levels of exercise and for differences in lung size (e.g., deposition patterns for children will differ from those of adults).[39] Experimental studies also indicate differences in deposition fractions for various degrees of lung impairment.[39] Thus, the deposition fraction for 1-μm diameter particles was found to increase in going from normal subjects (0.14) to smokers (0.16) to smokers with small airway disease (0.21) to asthmatics (0.22) to subjects with chronic obstructive airway disease (0.28).[40] Major variations in deposition can occur even with healthy subjects, leading to local or regional enhancement of deposition.[41] Thus the variability in deposition fractions and patterns, especially for the entire population as opposed to workers, argues that fine particles, rather than respirable particles, are the most appropriate indicator for the protection of public health from the smaller size fraction of thoracic particles.

4. PM COMPOSITION

The major components of $PM_{2.5}$ mass are sulfate, nitrate, and ammonium ions; elemental and organic carbon; and mineral components. Also of potential importance are hydrogen ions or acidity and trace components, including toxic metals, transition metals, and polynuclear aromatic compounds. $PM_{(10-2.5)}$ mass is primarily mineral with a significant unknown fraction that may include biogenic materials. The composition of PM varies geographically. Mass apportionments for $PM_{2.5}$ and $PM_{(10-2.5)}$ in the eastern and the western United States are shown in Figure 7.[42] For $PM_{2.5}$, sulfate is greater in the eastern United States. Minerals, nitrates, and elemental and organic carbon are greater in the western United States. However, due to loss by volatilization, substances that exist in equilibrium with gas phase components, such as ammonium nitrate (NH_4NO_3), organic components of particles in wood smoke, and certain other organic compounds, may be underestimated. For $PM_{(10-2.5)}$, the mineral component is greater in the western United States. Because of the high concentrations of coarse particles in the western United States, it is of concern to measure fine particles with minimum intrusion of coarse particles.

5. DIFFERENCES BETWEEN FINE AND COARSE PARTICLES

The EPA proposal to retain the PM_{10} standard for protection from exposure to coarse particles, and to set new particle standards based on fine particles instead of on respirable particles for protection from smaller particles, is based largely on the desire to consider fine and coarse PM as different pollutants. Fine and coarse particles appear to differ in health effects, as indicated by epidemiology and toxicology; they also differ in sources, composition, and properties (physical, chemical, and biological). Exposure differences, in terms of temporal variability, regional uniformity, and infiltration factors (the ratio of the concentration of ambient particles that have penetrated indoors and remain suspended to the concentration of ambient particles outdoors), make it desirable to measure fine and coarse particles separately for exposure assessment for epidemiologic studies.[7] Some of the various differences between fine and coarse particles are summarized in Table 1.[7]

6. PM INDICATORS

6.1. Single-component measurements

Some PM indicators that have been used for research and epidemiologic studies measure only a single component of the atmospheric aerosol. British Smoke (BS) is a technique frequently used in European studies.[43] It has an upper 50% cut of approximately 4.5 μm diameter, but it can collect some particles up to 10 μm in diameter.

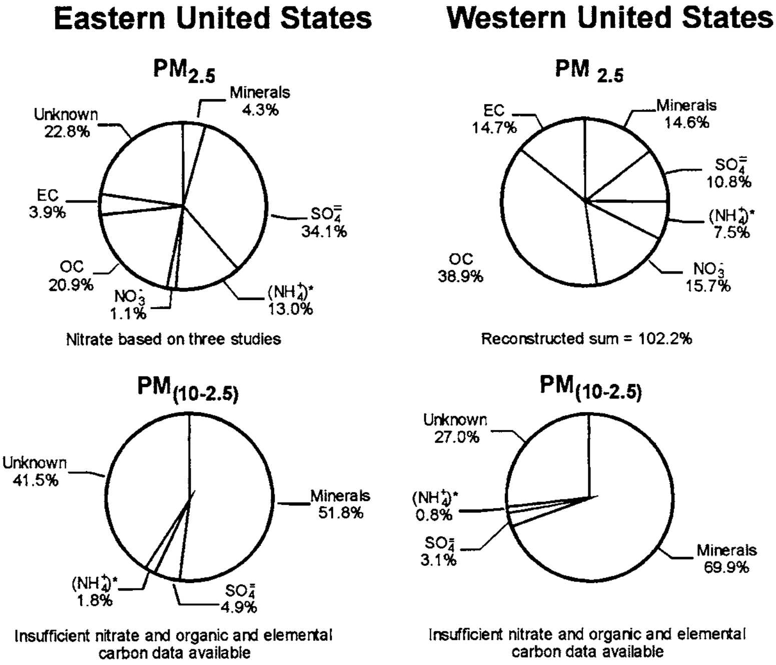

Figure 7. Major chemical components by mass for PM$_{2.5}$ and PM$_{(10\text{-}2.5)}$ particles in the western and the eastern United States.[42] (NH$_4^+$) represents the concentration of NH$_4^+$ that would be required if all SO$_4^=$ were present as (NH$_4$)$_2$SO$_4$ and all NO$_3^-$ as NH$_4$NO$_3$; therefore, (NH$_4^+$)* represents an upper limit to the true concentration of NH$_4^+$.

However, because BS is based on an optical measurement of blackness, it responds primarily to elemental carbon (EC). In Britain in the 1950's and 1960's, most EC came from the burning of coal for producing electric power and for home heating. This is still the major source of EC in some eastern European countries. In western Europe, however, EC now comes mostly from diesel exhaust. As a result, the relationship between BS and PM mass will vary regionally, locally, and seasonally. BS measurements can be credibly expressed in micrograms per cubic meter only if site specific calibrations between the BS reflectance readings and collocated gravimetric measurements are available for locations and time periods with relatively similar mixes of PM components. The relationship between BS and PM mass also will vary diurnally. Therefore, BS may not be used as an indicator of hourly PM mass.

Sulfate also may be used as an indicator for fine PM mass. It is a larger component of PM than is EC, but, because of the variation in the nitrate and organic components, the relationship of sulfate to fine PM mass is also variable. Indicators that depend on the measurement of one component of PM are generally not good indicators of PM mass unless the relationship is determined experimentally on a routine and frequent basis. Certain components, such as hydrogen ions, transition metals, polyaromatic hydrocarbons, number of ultrafine particles, etc., may be measured because of their potential health impact even though they are not significant in terms of mass. Measurements of the individual components of PM are useful; however, for most studies, it also will be important to measure a parameter that is closely related to total particle mass.

6.2. Loss of semivolatile components

Several major components of fine PM exist in the atmosphere in equilibrium with gaseous species. These are known as semivolatile materials (SVM). Examples are NH_4NO_3, organic components of particles in wood smoke, and certain other organic compounds. Changes in temperature or atmospheric composition during sampling can lead to losses of these semivolatile components of PM. Some components of fine PM are hygroscopic or deliquescent and will contain liquid water (particle-bound water [PBW]). The amount of PBW increases as relative humidity increases, but, for regulatory purposes, water is not considered a component of PM mass. The difficulty arises in removing the PBW without also removing the other semivolatile PM components.

Table 1

Comparison of ambient fine- and coarse-mode particles

	Fine-Mode Particles	Coarse-Mode Particles
Formed from:	Gases	Large solids/droplets
Formed by:	Chemical reaction or vaporization Nucleation, condensation on nuclei, and coagulation Evaporation of fog and cloud droplets in which gases have dissolved and reacted	Mechanical disruption (crushing, grinding, abrasion of surfaces, etc.) Evaporation of sprays Suspension of dusts
Composed of:	Sulfate, nitrate, ammonium, and hydrogen ions Elemental carbon Organic compounds (e.g., polyaromatic hydrocarbons) Metals (e.g., lead, cadmium, vanadium, nickel, copper, zinc, manganese, iron) Particle-bound water	Resuspended dust (soil dust and street dust) Coal and oil fly ash Oxides of crustal elements, (silicon, aluminum, titanium, and iron) $CaCO_3$, NaCl, and sea salt Pollen, mold, and fungal spores Plant/animal fragments Tire wear debris
Solubility:	Largely soluble, hygroscopic, and deliquescent	Largely insoluble and nonhygroscopic
Sources:	Combustion of coal, oil, gasoline, diesel fuel, and wood Atmospheric transformation products of NO_x, SO_2, and organic compounds, including biogenic organic species (e.g., terpenes) High-temperature processes, smelters, steel mills, etc.	Resuspension of industrial dust and soil tracked onto roads and streets Suspension from disturbed soil (e.g., farming, mining, unpaved roads) Biological sources Construction and demolition Coal and oil combustion Ocean spray
Atmospheric half-life:	Days to weeks	Minutes to hours
Travel distance:	100s to 1000s of km	<1 to 10s of km

The most frequently used indicator for fine particles in the United States is $PM_{2.5}$. Its definition includes, in addition to the 50% cut point diameter and the shape of the particle separation curve, specifications for sampling and equilibration. Those PM components with significant vapor pressure that survive the sampling and handling process also can be lost during the equilibration process. The FRM for PM_{10} calls for an equilibration period of 24 hour at a temperature between 10 and 25°C and a relative humidity between 15 and 45%.[44] There are no specifications on the temperature during the collection and handling of the PM_{10} sample. It is possible that the FRM for the proposed $PM_{2.5}$ standard will impose limitations on the allowable temperature increase above ambient during sampling and handling and will specify tighter limits on temperature and relative humidity during equilibration. This should increase the precision of the method but will still allow significant loss of SVM.

Nitrate loss has received considerable theoretical and experimental study.[45,46,47] Examples of the observed losses are shown in Figure 8.[48] Nitrate loss can be avoided by a sampling system in which gas-phase nitric acid is removed by a denuder and nitrate particles are collected on a nylon filter, which will absorb nitric acid as it vaporizes from NH_4NO_3 particles.[49] Similar results can be obtained with a Teflon® filter, followed either by a nylon or glass fiber filter impregnated with a basic substance such as potassium carbonate.[50,51]

Organic losses, both in terms of specific, toxic SVM and total organic mass, are also of concern.[45] A variety of after filters or absorbents have been used to collect organic species that are distributed between the particle and gas phases.[45,52] Quartz filters are used when an analysis of elemental and organic carbon by combustion is required. A positive artifact, resulting from the absorption of organic vapors by the quartz filter media, has received much attention.[53] Techniques have been proposed for correcting for this artifact by use of a back-up filter.[54] However, organic material may evaporate from particles, either as cleaner air passes through collected particles on the filter or as the filter and collected particles are equilibrated in an atmosphere that has less organic material in the gas phase than was present during sampling. This evaporation of semivolatile organic material causes a negative artifact.

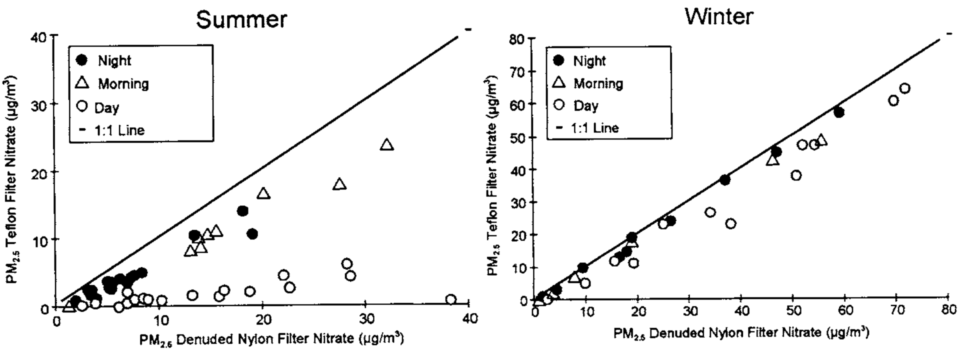

Figure 8. Comparison of nitrate measurements in Los Angeles; $PM_{2.5}$ samples collected on Teflon® filters versus samples collected on nylon filters after removal of nitric acid by denuders.[48]

This is especially a problem with a Teflon® filter, but also may be a problem with quartz filters.[55,56,57] Particles in wood smoke apparently contain a variety of semivolatile organic compounds.[55,58] Techniques for determining the mass and composition the organic semivolatile phase have been developed by Eatough and co-workers.[59,60,61]

Several continuous PM measurement techniques have been developed that deal with SVM in different ways. The Tapered Element Oscillating Microbalance (TEOM®)[62] measures the change in the mass of material collected continuously on a filter that is normally changed only after collecting material for a week or more. However, the collected material is kept at 50°C, a temperature high enough to prevent significant collection of water by hygroscopic or deliquescent materials. Otherwise, mass changes resulting from changes in PBW, as relative humidity (RH) changed, would dominate the mass changes caused by collection of new PM. The TEOM®, therefore, measures that component of the atmospheric aerosol that is nonvolatile at 50°C but excludes NH_4NO_3 and other SVM, including a significant fraction of organic particles in wood smoke.[56]

Two other techniques for continuous PM measurement remove PBW by dehumidification with a diffusion drier before collection. Koutrakis et al.[63] developed a technique based on the change in pressure drop across a filter as particles are collected. The filter surface is changed every 20 min, so that losses resulting from changes in temperature or atmospheric composition will be minimized. Obeidi et al.[64] developed a system that also uses a diffusion drier to remove PBW, but that depends on a carbon-impregnated filter to collect both nonvolatile and semivolatile PM. A denuder must be used before the filter to remove SVM in the gas phase. Then, any material evaporating from semivolatile particles will be collected on the carbon-impregnated filter and correctly measured as PM mass. To reduce the demands on the denuder, Obeidi et al.[64] concentrate the particles with a 0.1-μm virtual impactor before dehumidifying, denuding, and collecting them.

6.3. Cut point for separating fine particles from coarse particles

During the preparation of the PM criteria document, EPA considered whether 2.5 μm, or some smaller diameter such as 1.0 μm, would be the most appropriate size for separating fine and coarse particles.[14] Two considerations led to a preference for 2.5 μm. First, most of the epidemiologic studies of fine particles used $PM_{2.5}$ as the fine particle indicator; no epidemiologic data and little, if any, concentration data were available with a 1.0-μm cut. Secondly, during very high RH conditions, such as in fog or clouds, particle size distributions, measured by impactor-type classifiers, indicated that some fine-mode nitrate and sulfate particles were greater than 1 μm in diameter, presumably because of growth with increasing RH. PM concentrations were high during such periods, and a lower cut point size might result in missing some fine-mode mass. The existence of such large particles outside of fog and clouds has not been confirmed by techniques that measure single particles. The development of techniques to dehumidify aerosols makes it possible to remove some or all of the PBW and to use a lower cut point to more cleanly separate fine and coarse particles. However, it has not yet been demonstrated to what extent PBW can be removed without also removing some SVM.

7. FINE PARTICLE RESEARCH IN THE 21ST CENTURY

EPA has proposed, as a fine particle indicator for determining compliance with the new standards, a $PM_{2.5}$ cut and equilibration to remove PBW.[35] However, a new approach is need for research measurements of fine particles in the 21st century.[65] It is hoped that new techniques can be developed that will remove PBW but not lose SVM (such as ammonium nitrate and some organic component particles in wood smoke) and that will cleanly separate fine particles from coarse particles. Such techniques will be needed for a variety of research applications, including measurement of exposure for epidemiologic studies. Time-series epidemiologic studies of acute health outcomes will be needed for 24-hour and continuous (or hourly average) measurements. Chronic epidemiologic studies will need long-term measurements that integrate samples for a week, a month, or possibly longer periods.

Under the Clean Air Act, EPA is required to review the PM standards every 5 years.[66] Research with improved particle monitoring must begin soon so that new and useful information will be available for the next review. Hopefully, the 21st century will bring a new, improved indicator for the next U.S. fine particle standard. Countries that have not set a fine particle standard should consider carefully what fine particle indicator to use in research and for subsequent standard setting.

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