Solid and liquid particles found in the atmospheric aerosol typically cover 4 to 5 orders of magnitude from nanometers (nm) up to 100 micrometers (µm). The size range of particles of most interest to human health effects are inhalable and typically fall below 10 µm.\textsuperscript{1,2} This article focuses on ultrafine particles (i.e., particles less than 0.1 µm or 100 nm).

Typical size distribution of ambient particles by particle number concentration (PNC) and mass (volume x particle density) is shown in Figure 1. As seen in this figure, most of the mass is found in the size range between 0.1 and 10 µm with a minimum between about 1 and 2.5 µm resulting from the different mechanism of formation.\textsuperscript{3,4} Conversely, most of the particles by count and a significant fraction of the surface area, although comprising little mass, are observed in the size range below 0.1 µm.\textsuperscript{5-7} This has led to the well-known three empirically-defined size fractions: coarse (i.e., particles with an aerodynamic diameter between 2.5 and 10 µm, PM\textsubscript{10}-PM\textsubscript{2.5}), fine (i.e., particles less than 2.5 µm, PM\textsubscript{2.5}), and ultrafine particles (i.e., particles less than 0.1 µm or 100 nm, UFP; note: units for particles less than 0.2 µm will be given in nm). [Editor’s Note: Characteristics of the three modes are summarized in Table S-1, which can be found in the online version of this article at www.awma.org.]

Depending on how the UFP size range is defined, particles less than 200 nm may be considered UFP.\textsuperscript{7} Definitions are usually based on PNC, where most of the particles, typically greater than 85–90% fall below 100 nm, as shown in Figure 1. This
Particles in Ambient Air

certainly is true near fresh emissions sources; however, downwind of a major urban area, such as Los Angeles, the median size range (mobility diameter) can be in the range of 90–150 nm during summer months, as summarized by Sioutas et al.\(^7\) Particles less than 10 nm are also referred to as nanoparticles. This article focuses on UFP, which are ubiquitous in air; although their PNC can vary widely depending on where and when the observation is made.\(^3,8\)

**Sources and Ambient Processing**

UFP have both natural and anthropogenic sources, including both primary emissions (directly emitted) and secondary aerosol formation from gas phase precursors.\(^3,4,9-11\) In urban areas, combustion sources, in particular, motor vehicle emissions, are a significant source of both primary and secondary UFP.\(^7,11-18\) Kittelson et al.\(^12\) indicate that diesel engines emit higher numbers of UFP than gasoline engines. Similar results were reported by Zielinska et al.,\(^18\) including diesel emissions having higher concentrations of UFP polycyclic aromatic hydrocarbons. UFP are formed through nucleation and gas-to-particle reactions and grow and shrink by a series of mechanisms, including condensation, coagulation, and volatilization.

Nucleation is ubiquitous in ambient air, including the free troposphere, marine air, and urban areas and is usually initiated through binary or tertiary mechanisms most often involving sulfuric acid and water, or also ammonia, respectively.\(^10,11,19,20\) Nucleation is favored when UFP concentrations are low, whereas high PM concentrations favor condensation of gases onto preexisting particles.\(^10,19,21\) Growth of smaller particles is often by condensation of low volatility organic components.\(^19,22\)

**Characteristics in Air**

UFP vary considerably in composition, PNC, and over space and time due to variations in emissions sources and formation processes and influenced by meteorology. Higher PNC typically occur in urban areas relative to rural areas, and within urban areas highest concentrations are observed near sources, such as on or near roadways; although concentrations fall off rapidly with distance.\(^7,8,11,23,24,25\)

UFP concentrations can vary significantly during the day and by season.\(^7,8,26,27\) Most urban areas observe a peak in UFP in the morning during rush hour associated with motor vehicle emissions and a second peak during the afternoon, enhanced during the summer, associated with photochemistry or one slightly later in the afternoon due to rush hour traffic that is enhanced during cooler conditions.\(^8,27\) A second morning peak up to several hours after sunrise, on clean sunny days is associated with regional nucleation events,\(^20,21\) and an evening event may occur due to evening home heating, including wood combustion.\(^28\)

In terms of population exposure, individuals living near freeways are impacted by high UFP levels, while secondary formation (nucleation and growth), being more regional in nature, impacts a larger population more uniformly. The latter likely

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*Figure 1. Typical number and volume distributions of atmospheric particles with the different modes.*

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results from the competing nucleation and growth processes (e.g., in urban areas). Kulmala et al.\textsuperscript{10} indicate formation rates for 3 nm particles is up to \(1 \times 10^2\) to as high as \(1 \times 10^5\) particles cm\(^{-3}\) s\(^{-1}\) followed by growth rates of 1–20 nm h\(^{-1}\).

Morawska et al.\textsuperscript{11} reported UFP concentrations from 71 studies across a range of environments, from clean background to tunnel with concentrations ranging from about \(3 \times 10^3\) to almost \(2 \times 10^5\) particles cm\(^{-3}\). UFP number concentrations obtained at different locations throughout the world were summarized by Wang et al.\textsuperscript{27} (see Table 1\textsuperscript{27}) with average UFP concentrations having a similar range (\(6 \times 10^3\) to \(6 \times 10^5\) particles cm\(^{-3}\)) to those reported by Morawska et al.\textsuperscript{11} In the latter study, the size range of particles measured varied from as low as 3 nm up to 3 µm depending on the study, with one study reporting an upper range of 10 µm. UFP number concentrations observed during nucleation events in Pittsburgh ranged from \(5 \times 10^4\) to \(1.5 \times 10^6\) particle cm\(^{-3}\)\textsuperscript{21}.

Several studies indicate that UFP mass and number typically correlate poorly with each other so PNC cannot be used as a surrogate for UFP mass. In addition, both UFP mass and PNC correlate poorly with PM\(_{2.5}\) or PM\(_{10}\) mass indicating that neither of these metrics can be used as a surrogate for UFP number or mass concentration.\textsuperscript{8,29} A poor correlation also was usually observed between gaseous pollutants (e.g., CO, NO, NO\(_x\), and O\(_3\)) at urban sites in Los Angeles, also indicating these pollutants should not be used as surrogates to assess human exposure to UFP.\textsuperscript{7}

The chemical composition of UFP varies over space and time due to changing source impacts, including primary particle emissions and gas-phase precursors, competition in formation and growth due to nucleation, coagulation, condensation, and volatilization, and meteorology.\textsuperscript{8,23} For example, these competing factors likely impact the chemical composition of UFP as particles generated on freeways by motor vehicles are transported to the near road environment and beyond.\textsuperscript{17,30-32} Zhang and Wexler\textsuperscript{32} show through modeling with good agreement to data, that motor vehicle exhaust experiences two distinct dilution stages after being emitted: “tailpipe-to-road” and “road-to-ambient.” In a follow up paper, Zhang et al.\textsuperscript{31} suggest that the competing factors and resulting number concentration changes must be impacting composition so individuals living near the freeway (< 90 m) are likely exposed to particle sizes and compositions that those living further away are not.

Results from the U.S. Environmental Protection Agency's (EPA) PM Supersites Program\textsuperscript{8,33} indicate that at most measurement locations, organic carbon was a major fraction of the UFP, except near industrial sources,\textsuperscript{15} where trace metals were abundant, and during regional nucleation events where UFP were initially dominated by sulfate followed by neutralization within about an hour or so by ammonia.\textsuperscript{20} Morawska et al.\textsuperscript{11} also summarize the composition of UFP at a number of locations. UFP composition varied by location with organic carbon, sulfate, elemental carbon, and sometimes ammonium and nitrate comprising the bulk of the composition.

Trace elements also have been reported as summarized in Morawska et al.\textsuperscript{11} and Solomon et al.\textsuperscript{8} and tend to include a number of potentially health relevant species, such as Ni, Fe, V, Cu, Pb, and Zn. Ning et al.\textsuperscript{34} describe organic components (e.g., PAH, hopanes and steranes, organic acids, and n-alkanes) and volatility of particles below 180 nm derived from secondary aerosol formation and associated with near roadway and photochemical production. PAH and n-alkanes were associated with morning rush hour whereas organic acids peaked in the afternoon associated with photochemical production. In the same study, UFP appeared to be highly acidic during both time periods as estimated by incomplete neutralization of sulfate and nitrate by ammonium.

Health Effects

It has become widely accepted that UFP are associated with adverse cardiovascular and respiratory health effects in humans.\textsuperscript{7,16,35,36} As summarized in Solomon et al.,\textsuperscript{2} UFP have significant access to the alveolar region of the lungs, unlike larger particles, where they more effectively deposit as a result of rapid diffusion and where clearance mechanisms may be relatively slow, allowing UFP to interact with cells of the lung lining and to translocate intact to other parts of the body. As well, UFP contain large amounts of toxic components and their adverse health effects potential would not be predicted from their mass alone. In fact, a number of studies indicate that number, surface area, and
chemical composition are more important than UFP mass as a health relevant metric.

UFP, as well as larger particles, also are deposited throughout the respiratory track, particularly at bifurcations and other bends (i.e., hot spots—high particle loadings in a small area (1 mm²) relative to adjacent lung tissue) due to secondary flows and impaction, respectively. UFP also have been shown to directly translocate to the brain along the olfactory nerves with yet to be determined health consequences. In addition, UFP can pass intact into cells and found free in cellular cytoplasm, where they can have direct access to cytoplasmic proteins and organelles, for example, the mitochondria impacting the respiratory chain and DNA in the nucleus, resulting in enhanced toxic potential of these particles. The composition of UFP includes a range of organic components (e.g., polycyclic aromatic hydrocarbons), elemental carbon, and trace metals (e.g., V, Ni, Fe, Cd) that have the potential to generate reactive oxygen species, which can result in oxidative stress, followed by inflammation resulting in cardiovascular and respiratory effects. This mechanism has gained considerable acknowledgement over the last decade.¹⁶

**Measurement Methods**

Considerable uncertainty remains as to what property or properties of UFP are of most concern with regard to adverse health effects although epidemiological and toxicological studies have made considerable advances over the last decade.⁷,¹⁶ Associations have been noted with mass, particle number, surface area (can also include surface composition), and chemical composition. This section will summarize measurement methods that are most often employed to measure these properties. More detailed information about these methods and others can be found in the literature.³⁷⁻⁴⁰

Particles that deviate from unit density (1.0 g cm⁻³) and are of irregular shape (not spherical) have pronounced effects on particle sizing methods. This has lead to reporting particle equivalent diameters (dₑ) for irregularly shaped particles.³⁷⁻⁴⁵ Different instruments report or measure particle properties based on different dₑ and this is especially important in the UFP size range where, for example, a significant fraction of the primarily emitted soot particles are irregularly shaped agglomerates. Aerosol mass spectrometers measure vacuum diameter (dᵥ), since the measurement is in the free molecular regime. The differential mobility analyzer (DMA), either by itself or as part of the scanning mobility particle sizer (SMPS) system, measures mobility diameter (dₘ) based on application of an electrical field to size the particles. Samplers that separate particles based on inertia, such as impactors or cyclones, measure aerodynamic diameter (dₐ). Mobility diameter can be related to dₑ if the effective density is known.⁴¹ Instruments that measure UFP typically report dᵥ and dₘ, since particles less than 200 nm are more influenced by diffusion than inertia. Larger particles most often report dₐ. Relating equivalent diameters requires knowledge of the particle mass, density, and a dynamic shape factor at a minimum and these parameters can be estimated by measuring two or more particle properties simultaneously.³⁷⁻⁴⁵ For example, it is possible to estimate effective particle density by combining measurements of dᵥ and dₘ.

Methods have now been developed to measure particle size distributions below 3 nm and ion mobility spectrometers measure clusters of particles below 1 nm.⁴¹,⁴⁶ Here the focus is on selected methods that measure properties of particles above 3 nm and these include UFP properties for mass, PNC, surface area, and chemical composition, since, as noted earlier, these appear to be the most relevant to health effects, and thus, implementation in monitoring networks would be beneficial to policy development designed to reduce potential adverse health effects from UFP.

Several reviews provide detailed discussion of the methods briefly described below.³⁷⁻⁴⁰,⁴⁴,⁴⁷ A number of other methods for determining the physical and chemical properties of UFP also are described in these reviews.

**Time-Integrated Measurements**

**Mass and Chemical Composition.** Widely used time-integrated substrate-based methods for UFP mass include the micro-orifice uniform deposit impactor (MOUDI)⁴⁸ and the nano-MOUDI (n-MOUDI).⁴⁹ These samplers are multi-stage (cascade) impactors operating at low pressure, allowing for collection of particles below 200 nm in several size ranges. Rotating disks allow for uniform deposit. Other low-pressure impactors collecting particles in several size ranges have been developed,⁵⁰,⁵¹ but only the MOUDI will be discussed here.
A variety of collection substrates can be employed, depending on the desired chemical analysis method. The MOUDI has advanced from an 8-stage impactor with the lowest cutpoint at 56 nm to a 13-stage impactor with the lowest cutpoint at 10 nm. The commercial instrument has an upper stage cutpoint of 18 µm, although various combinations of stages can be used. The n-MOUDI is used in combination with the MOUDI following the 56 nm size cut of the MOUDI to obtain three size fractions below 56 nm. Substrates can be weighed and analyzed for a range of chemical components. In Los Angeles, the MOUDI–n-MOUDI system was operated for two weeks to obtain time-integrated samples for the major components of UFP, whereas the system was combined with a UFP concentrator to obtain three, 3-hr samples (morning, midday, evening) for mass and chemical composition of UFP at a source and receptor site.

Particle Morphology and Chemical Composition. Electron microscopy and associated microanalysis provides a direct measure of particle size, shape, and chemical composition, some methods providing the latter for bulk particles, others for just the surface. Fletcher et al. provide a thorough review of these methods, which have historically provided important characteristics about ambient particles that until recently have not been able to be obtained by other readily available methods.

Continuous or Near Continuous Methods
These methods typically measure the property of interest at time intervals of one hour or less and for simplicity will be referred to only as continuous methods. Several reviews provide detailed discussions of the selected methods described below, as well as variety of other methods to measure a range of UFP properties, such as mass, PNC, size distribution, surface area, and chemistry.

Mass: Direct and Indirect Methods. A continuous UFP mass monitor was developed by preceding a Beta Attenuation Monitor with a low-pressure drop, 150-nm cutpoint impactor. The system operated on a 2-hr cycle. Comparison with the MOUDI showed excellent agreement (R² = 0.92), but the SMPS results were low and missed the daily rush hour peak, however, in general, the diurnal variation between the two methods agreed.

Indirect methods, such as the condensation particle counters and SMPS (described below) can be used to estimate UFP mass continuously if the density and shape of the particles are known.

Particle Number Concentration (PNC). Condensation particle counters (CPC) are widely used to measure the total number of particles above a minimum diameter, for example, 3 nm (~ 10⁻²⁰ g), up to greater than 10 µm. In the CPC, particles are grown by condensation using a range of working fluids, the most common of which are butanol and water. Particles are grown to a size that can be optically detected. Several water-based CPCs (WCPC) are described in a study comparing commercially available instruments to an UFP water-based CPC. The lowest detectable particle size in the default mode was 3 nm and the maximum PNC, within 10% accuracy, was 1 x 10⁵ particles cm⁻³, although the UFP WCPC was able to detect particles as low as 1.8 nm, depending on the configuration and particle chemistry used in testing. Evaluation of a pulse-height CPC indicated it was able to detect charged clusters with electrical mobility equivalent diameter down to ~1 nm.

Particle Size Distribution. Electrical mobility analyzers classify particles according to their electrical mobility. The DMA requires a detector, typically a CPC or other similar instrument. Modern DMA instruments typically measure size distributions in the range from approximately 3–10 to 500–800 nm. The lower and upper ranges depend on the instrument. A high-resolution DMA, able to measure particle sizes down to 1 nm, was used in an intercomparison of air ion spectrometers and the neutral cluster and air ion spectrometer that is able to measure neutral and ion clusters down to 1 nm. These measurements are important for understanding nucleation.

As noted above, the DMA requires a detector. The scanning mobility particle spectrometer (or sizer) (SMPS) is a commercial system that employs a DMA and CPC in one instrument designed to measure particles size distributions in the range of 10 to 800 nm dₘ. Size distributions can be obtained within about 2 min by ramping the classifying voltage continuously. A newer version SMPS, the nano-SMPS, uses a nano-DMA, which has a shorter mobility analyzer, to obtain size distributions in the particle size range of 3–150 nm.

Surface Area. UFP particle surface area may be an important variable with regard to understanding
the adverse health effects, since UFP contain a significant fraction of the total particle surface area, which is also available for chemical reactions in air. The epiphaniometer measures the diffusion-limited mass transfer rate of a gas to particles. These measurements provide information on the maximum possible rates of vapor condensation to or gas reaction with the particles. A comparison indicated good to excellent agreement between the epiphaniometer and an SMPS for Fuchs and geometric surface area when calibrated with sub-100-nm particles. Variations in nanoparticles (3–10 nm), including surface area are described in Fresno during a year beginning in August 2002, along with a summary of a number of other studies, where nanoparticle surface area was estimated through various methods. Summarized results indicated nano-particle surface areas ranged from 0.01 µm² cm⁻¹ in the free troposphere to 1000 µm² cm⁻¹, the latter as reported in Fresno.

Chemical Composition. Over the past 5–10 years the development and application of in-field particle mass spectrometry has undergone exponential growth. Single particle mass spectrometers and aerosol mass spectrometers provide size-dependent chemical composition of single particles or ensembles of particles below 1 µm, respectively, on short time frames. Recent advances with instruments that measure an ensemble of particles are able to determine the chemical components below tens of nanometers. Numerous approaches now exist that have provided a wealth of information on atmospheric chemistry. More details of a wide range of particle mass spectrometry methods and applications can be found in the above cited literature.

The Future of Air Monitoring
Over the last half decade or so research has moved forward in great strides to reduce the size and cost of monitors to obtain better information on the spatial and temporal aspects of gas and particulate pollutants in air. As a class, these mini-monitors are being referred to as sensors. White et al. (this issue, page 36) provide an overview of sensors and how they might be applied through mobile devices that allow the coupling of sensors to mobile platforms using digital applications (“apps”). These apps link air pollutant levels (some measured by miniature sensors located within the mobile device), location, Internet access, and other relevant variables to networks where advanced data analysis can occur and provide integrated and interpreted information back to the data user. Portable and wearable sensors that monitor UFP are being developed. Use of multiple sensors, containing multiple measurements, have the potential to greatly improve exposure estimates by providing both air quality and activity data simultaneously, as well as community monitoring by the general public empowering individuals to better protect their own health by avoiding adverse air pollution conditions.

Summary
The strong association between ultrafine particles (UFP) and adverse health effects—cardiovascular and pulmonary—are becoming widely recognized yet considerable uncertainty remains as to the metric(s) and the mechanisms that result in the adverse effects. UFP are ubiquitous in air varying in concentration by 3 orders of magnitude, in general, but are most pronounced in air near combustion sources with motor vehicles likely being the largest source in most urban areas. Nucleation events, some on regional scales, followed by particle growth to 100 nm and more are another important source of UFP.

Numerous measurement methods, some well established, provide a wealth of physical and chemical information about UFP, which, in turn, improve our understanding of their health and welfare effects. Recent research has focused on pushing the envelope to improve sensitivity, dynamic range, lower size limit of particles detected, and chemical composition, including the composition of particles below 50 nm at high time resolution, approaching seconds. Many of the well-established methods, such as number concentration and size distribution, are suitable for routine monitoring networks, as described in the reviews noted within. Wearable mini-monitors or sensors for UFP are on the horizon that will improve exposure estimates and empower communities to better protect their health. When more fully understood, policy-makers will be more informed as to how to reduce the adverse health effects from particulate matter, in particular those associated with UFP.
### Table S-1. Comparison of ambient ultrafine, fine, and coarse particles.

<table>
<thead>
<tr>
<th></th>
<th>Fine Ultrafine</th>
<th>Accumulation (0.1 to 2.5 µm size range)</th>
<th>Coarse</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formation Processes:</strong></td>
<td>Combustion, high-temperature processes, and atmospheric reactions</td>
<td>Condensation, coagulation, Reactions of gases in or on particles, Evaporation of fog and cloud droplets in which gases have dissolved and reacted</td>
<td>Mechanical disruption (crushing, grinding, abrasion of surfaces), Evaporation of sprays, Suspension of dusts, Reactions of gases in or on particles</td>
</tr>
<tr>
<td><strong>Formed by:</strong></td>
<td>Nucleation, Condensation, Coagulation</td>
<td>Condensation, Coagulation, Reactions of gases in or on particles</td>
<td>Mechanical disruption (crushing, grinding, abrasion of surfaces), Evaporation of sprays, Suspension of dusts, Reactions of gases in or on particles</td>
</tr>
<tr>
<td><strong>Composed of:</strong></td>
<td>Sulfate, Elemental carbon, Metal compounds, Organic compounds with very low saturation vapor pressure at ambient temperature</td>
<td>Sulfate, nitrate, ammonium, and hydrogen ions, Elemental carbon, Large variety of organic compounds, Metals: compounds of Pb, Cd, V, Ni, Cu, Zn, Mn, Fe, etc., Particle-bound water</td>
<td>Suspended soil or street dust, Fly ash from uncontrolled combustion of coal, oil, and wood, Nitrates/chlorides/sulfates from HNO3/HCl/SO2 reactions with coarse particles, Oxides of crustal elements (Si, Al, Ti, Fe), CaCO3, CaSO4, NaCl, sea salt, Pollen, mold, fungal spores, Plant and animal fragments, Tire, brake pad, and road wear debris</td>
</tr>
<tr>
<td><strong>Solubility:</strong></td>
<td>Probably less soluble than accumulation mode</td>
<td>Largely soluble, hygroscopic, and deliquescent</td>
<td>Largely insoluble and nonhygroscopic</td>
</tr>
<tr>
<td><strong>Sources:</strong></td>
<td>Combustion, Atmospheric transformation of SO2 and some organic compounds, High temperature processes</td>
<td>Combustion of coal, oil, gasoline, diesel fuel, wood, Atmospheric transformation products of NOx, SO2, and organic compounds, including biogenic organic species (e.g., terpenes), High-temperature processes, smelters, steel mills, etc.</td>
<td>Resuspension of industrial dust and soil tracked onto roads and streets, Suspension from disturbed soil (e.g., farming, mining, unpaved roads), Construction and demolition, Uncontrolled coal and oil combustion, Ocean spray, Biological sources</td>
</tr>
<tr>
<td><strong>Atmospheric half-life:</strong></td>
<td>Minutes to hours</td>
<td>Days to weeks</td>
<td>Minutes to hours</td>
</tr>
<tr>
<td><strong>Removal Processes:</strong></td>
<td>Grows into accumulation mode, Diffuses to raindrops and other surfaces</td>
<td>Forms cloud droplets and rains out, Dry deposition</td>
<td>Dry deposition by fallout, Scavenging by falling rain drops</td>
</tr>
<tr>
<td><strong>Travel distance:</strong></td>
<td>&lt; 1 to 10s of km</td>
<td>100s to 1000s of km</td>
<td>&lt; 1 to 10s of km (small size tail, 100s to 1000s in dust storms)</td>
</tr>
</tbody>
</table>

Source: Adapted from Table 2-2. Air Quality Criteria for Particulate Matter (October 2004); EPA 600/P-99/002aF-bF; National Center for Environmental Assessment, Office of Research and Development, U.S. Environmental Protection Agency Research Triangle Park, NC, 2004; available online at http://cfpub.epa.gov/ncea/cfm/recordisplay.cfm?deid=87903.

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