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CURRENT UNDERSTANDING OF ULTRA FINE PARTICULATE MATTER EMITTED FROM MOBILE SOURCES

FINAL REPORT

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COORDINATING RESEARCH COUNCIL, INC.
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EXECUTIVE SUMMARY

Ultra-fine particulate matter (UFPM) includes those particles that are less than 100 nm in diameter (or, for non-spherical particles, a characteristic dimension). There is currently some concern that UFPM may lead to adverse health effects in humans such as lung function decrease and cardio-vascular diseases. UFPM can be formed by nucleation of gases (e.g., sulfuric acid, some organic compounds) in the ambient atmosphere or by nucleation and condensation of gases during an emission process. (Nucleation is the formation of a new particle from gaseous molecules; condensation is the transfer of a molecule from the gas phase to an existing particle.) This review addresses UFPM associated with mobile source emissions. More emphasis is given to diesel engines than to spark-ignition engines because there are considerably more research results available for the former than the latter.

Measurements of UFPM emitted from mobile sources have been conducted in the laboratory (using chassis dynamometers), on roadways, and downwind of roadways. In addition, modeling of UFPM formation and evolution has been conducted and compared to available measurements. The great majority of the results of those measurement programs and modeling studies can be synthesized into a coherent description of the formation of UFPM in mobile source emissions and its subsequent evolution in the ambient atmosphere.

UFPM is produced in the exhaust of vehicles as the exhaust gas cools down. Lower temperature leads to a decrease in the saturation vapor pressure of gases and the least volatile gases (i.e., those with the lowest saturation vapor pressure) may then form new particles via nucleation. Sulfuric acid, which results from the oxidation of sulfur present in the fuel and lubricating oil, nucleates (probably through a ternary process that involves water and ammonia) to form very small aqueous particles of a few nanometers. Accordingly, UFPM emissions tend to increase as the sulfur content of the lubricating oil and fuel increase. Some organic gases and metals may also nucleate. It is possible that nucleation involves the ionized form (chemiions) of those species.

In the absence of a diesel particle filter (DPF), soot particles that are emitted directly from diesel engines are present in larger sizes but a significant fraction of that mode (the so-called accumulation mode, which ranges typically from about 20 to 200 nm in diameter) extends into the UFPM range (i.e., below 100 nm). DPFs control most of the soot emissions and, therefore, the accumulation mode is negligible in the emissions of diesel vehicles equipped with a DPF.

As the exhaust continues to cool down, gases may either continue to nucleate to form new nanoparticles or condense on existing particles (the accumulation mode particles, if no DPF is present, and/or the nanoparticles). Therefore, in the absence of a DPF, most sulfuric acid present in the exhaust will condense on the soot particles because those particles offer a larger surface area available for condensation than the new nucleated particles. Semi-volatile organic gases will preferentially condense onto organic particles formed from the nucleation of organic gases. Lubricating oil hydrocarbons are heavier than fuel hydrocarbons and, therefore, have lower volatility, which favors their gas-to-particle conversion.

The chemical composition of UFPM in diesel engine exhaust without a DPF consists mostly (>95%) of oil (e.g., C_{24} to C_{32} alkanes), a few percent of sulfate, about 1 % of unburned fuel (e.g., C_{15} to C_{23} alkanes) and <1% of combustion products (e.g., polycyclic hydrocarbons). The chemical composition of UFPM in diesel engine exhaust with a DPF consists mostly of sulfate with some ammonium, which suggests that semi-volatile organic compounds (SVOC) are oxidized in the DPF. The chemical composition of spark-ignition engine exhaust seems to consist mostly of carbonaceous compounds with little sulfate and other inorganic species.

Three size modes appear in the exhaust of motor vehicles: (1) a narrow nucleation mode around 10 nm that corresponds to nucleated particles that have grown by condensation of other gases, (2) a second larger nucleation mode around 20 to 30 nm, and (3) a wider accumulation mode of soot particles centered around 60 nm, that results from the combustion process. The two nucleation modes contain sulfate and SVOC whereas the accumulation mode contains soot (i.e., black carbon and some non-volatile organic compounds), sulfate, and SVOC. The organic compounds include alkanes (from lubricating oil and unburned fuel), and polycyclic compounds (e.g., PAH from combustion, hopanes and steranes from lubricating oil; diesel vehicle exhaust has more PAH than spark-ignition vehicle exhaust).

Cold-start conditions increase UFPM emissions in diesel engines without a DPF and spark-ignition engines. UFPM emissions tend to increase with high engine load (e.g., acceleration) for diesel engines without a DPF and for spark-ignition engines. Regeneration of the catalyst increases UFPM emissions in diesel engines with a DPF. Diesel engines without a DPF emit the most UFPM; diesel engines with a DPF emit about ten times less UFPM. Spark-ignition engines with low-emission rating or a three-way catalyst emit the least amounts of UFPM; their UFPM emissions are mostly associated with cold-start conditions.

Near a busy highway (>10,000 vehicles per hour), UFPM mass is typically a few $\mu g/m^3$ and the UFPM number concentration exceeds 10^5 particles/cm^3. After emission from the vehicle exhaust, UFPM evolves in the ambient atmosphere via a combination of the following processes as the exhaust plume becomes diluted: (1) volatilization of chemical species from the smallest particles (volatilization is favored from the smallest particles due to the so-called Kelvin effect), which then become even smaller, (2) coagulation of the smallest particles with larger particles (coagulation is faster when the difference in size between the two coagulating particles is larger), and (3) condensation of gases on particles as the plume cools. As a result of those processes, the number concentration decreases rapidly with distance. Typically, the smaller nucleation mode disappears within 100 m due to volatilization (that results from the dilution with ambient air) and subsequent coagulation with larger particles; accordingly, the UFPM number concentration typically decreases by at least half from 30 m to 100 m, possibly less under some stagnant winter conditions but significantly more during unstable summer conditions. Also, the UFPM concentration is generally not discernible from the background PM beyond 300 m from the highway. Noise barriers are very effective at minimizing exposure to UFPM because the highway plume does not impact the ground until several hundreds of meters beyond the barrier and UFPM is typically at background levels at such distances.

There are still some gaps in our scientific understanding of UFPM emissions from mobile sources and evolution in the atmosphere. Those gaps can be reduced by conducting additional experiments and theoretical calculations and some recommendations for possible avenues of further research are listed below.

Better understanding of the processes leading to the formation of UFPM: Theoretical models of UFPM formation show some promising results to explain the early evolution of UFPM; however, more work is needed to explain the various nuclei modes observed in the ambient atmosphere. Also, organic nucleation is possible and should be investigated, including the possibility of sulfate-organic heteronucleation and the role of chemiions.

Chemical composition of UFPM: Most work on the chemical composition of UFPM has focused on diesel engines without a DPF. A better understanding of the chemical composition of UFPM emitted from diesel engines with a DPF and from spark-ignition engines appears desirable.

Air quality modeling of UFPM: Model simulations of UFPM have been limited to case studies for specific conditions. Exposure assessment of UFPM will require the simulation of UFPM concentrations over a wide range of atmospheric conditions and emission scenarios. The development, incorporation and evaluation of UFPM modules in 3-D air quality models should be undertaken.

1. INTRODUCTION

There are several definitions of ultra fine particulate matter (UFPM): particles less than 1 μm in diameter and particles less than 0.1 μm in diameter are the two most common definitions. Here, we will use the definition of the U.S. Environmental Protection Agency (EPA), which is a particle less than 0.1 μm (i.e., 100 nm) in diameter (or characteristic dimension for non-spherical particles, such as the diameter of a spherical particle with the same volume to surface ratio). We will also refer to UFPM as nanoparticles since nanoparticles are defined as those particles with at least one dimension less than 100 nm (Biswas and Wu, 2005). There are several sources of UFPM including the manufacturing of nanomaterials, combustion sources, and nucleation events (Maynard, 2007; Kittelson et al., 1998; Weber et al., 1999). We will focus here on UFPM emitted from combustion sources, in particular those emitted from mobile sources. More emphasis is given to diesel engines than to spark-ignition engines because there are considerably more research results available for the former than the latter.

UFPM can penetrate into the lungs and there are some concerns that ultra fine particles may contribute to adverse health effects such as lung function decrease and cardio-vascular diseases. Both their large number concentrations and their chemical composition are considered to be potential causes for their adverse health effects (e.g., Oberdörster et al., 1995; Utell and Frampton, 2000; Ibald-Mulli et al., 2002; Oberdörster and Utell, 2002; Daigle et al., 2003; Colvin, 2003; Oberdörster et al., 2004; Delfino et al., 2005; Sioutas et al., 2005).

UFPM concentrations are mostly a source of concern in the immediate vicinity of emission sources (e.g., roadways) because those concentrations decrease rapidly as the ultra fine particles are removed. For example, Zhu et al. (2002a, 2002b) reported UFPM concentrations decreasing by about an order of magnitude within 100 to 300 m from freeways in Los Angeles.

Because UFPM comprises a large variety of chemical compounds and has a relatively short atmospheric lifetime, UFPM has not yet been thoroughly studied and there are still many gaps in our understanding of the sources, physico-chemical characteristics, atmospheric behavior, and health effects of UFPM.

This report addresses the emissions and the atmospheric fate and transport of UFPM emitted from mobile sources. Also, some recommendations to advance the state of the science with future measurements and modeling are provided.

2. EMISSIONS OF ULTRA FINE PARTICULATE MATTER

2.1 Characterization of the Emissions

The emissions of PM, including UFPM, from engines can be measured in the laboratory or in the ambient atmosphere. Measurements in the laboratory are generally conducted using a chassis dynamometer, which allows one to operate the vehicle at various speeds. Measurements can be done at a given speed (e.g., idling, low, medium or high load) or using a driving cycle that takes the engine through a predetermined series of different speeds. Measurements are made by sampling the air directly from the exhaust pipe through a sampling line and diluting the sampled air, typically through two successive dilution chambers, to approximate the dilution that takes place in the ambient atmosphere. Measurements in the ambient atmosphere are conducted on-road with suitably-equipped vehicles that sample the exhaust emissions after their release into the atmosphere. Since the sampling occurs in the atmosphere after initial dilution of the exhaust gases, there is no need for diluting the air samples. Laboratory and on-road measurements can lead to different results because sampling of the particle size distribution depends on the dilution and cooling process, which may differ between the laboratory and the atmosphere. Brown et al. (2000) found that, for a same dilution ratio (about 300:1), more nanoparticles were collected from an ambient exhaust plume sample than from a dilution tailpipe exhaust sample in the laboratory. Such differences must be kept in mind when reviewing results from laboratory experiments.

Sampling of the particle size distribution is often performed with scanning mobility particle sizers (SMPS). PM mass and chemical composition can be obtained from impactors that sample PM in selected size ranges, e.g., electrical low pressure impactors (ELPI) or micro-orifice uniform deposit impactors (MOUDI). McMurry (2000) presents a review of instruments used to measure the particle size distribution and collect PM by size ranges. Losses of UFPM occur on the sampling line and the instrument inlets. Such losses have been shown to be greater for the smaller particles than for larger particles. For example, Kittelson et al. (2006a) reported that for a SMPS the loss was less than 10% for particles greater than 100 nm in diameter, but about 20% for particles of 50 nm in diameter, 50% for particles of 20 nm in diameter and about 90% for particles of 10 nm in diameter. As a result, the measured UFPM size distribution significantly underestimates the actual UFPM size distribution. The use of so-called nano-SMPS and nano-MOUDI, which have been designed to minimize diffusion losses within the instrument, helps provide more accurate measurements of UFPM size distribution and size-segregated concentrations; however, losses in the sampling line are still an issue.

We first summarize the review conducted by Kittelson (1998) which presents the state of knowledge as of 1997. We then review the major studies in the peer-reviewed literature after 1997. Those studies cover experiments conducted in the United States, Europe, Japan and Australia. We focus here on the physical and chemical characterization of the emitted UFPM. We address the available information on the processes leading to UFPM formation in the following section. Finally, a summary of the current state of knowledge is presented.

Kittelson (1998) reviewed the formation of UFPM from internal combustion engines based on information available up to 1997. He concluded that nanoparticles may include hydrocarbons, carbon fragments, sulfate and metallic ash. The hydrocarbons result from the fuel, and atomized and evaporated lube oil that have not been oxidized during the combustion process and are released as hydrocarbons; they are sometimes referred to as the soluble organic fraction (SOF). Sulfate results from sulfur present in the fuel that is oxidized to SO_3, which subsequently is hydrolyzed to H_2SO_4. The metallic ash results from the presence of metal compounds in the fuel and lube oil. These metal compounds are mostly present as gaseous compounds in the hot exhaust gas but nucleate, condense or adsorb onto existing particles as the exhaust is diluted and cooled. Although the mass of UFPM is small compared to the total mass of PM emitted from an engine (particularly from a diesel engine without emission control), the number concentration of UFPM dominates the total PM number concentration. Figure 2-1 presents a hypothetical size distribution for the number and mass concentrations of PM. This figure highlights the fact that the $PM_{2.5}$ mass concentration is dominated by the mass of the accumulation mode (with little contribution from UFPM) whereas the UFPM number concentration is dominated by the nuclei mode.

Ristovski et al. (1998) investigated the UFPM emissions from spark ignition vehicles on a chassis dynamometer. UFPM size distributions were measured with a SMPS. UFPM number concentrations were in the range of 1 to 4 x 10^4 cm^{-3} for unleaded gasoline cars with catalyst exhaust control and 8 x 10^4 cm^{-3} for liquefied petroleum gas cars.

Burtscher et al. (1998) studied the formation of UFPM from a spark-ignition engine and two diesel engines. They found that the spark-ignition engine led to higher volatile UFPM fraction than the diesel engine and that the volatile fraction of diesel UFPM decreases with increasing load.

Tobias et al. (2001) used a combination of a differential mobility analyzer (DMA) with a thermal desorption particle beam mass spectrometer (TDPBMS) to analyze the emissions of UFPM (with diameter < 50 nm) emitted from diesel engines under laboratory conditions. Mass spectral analysis was used to identify and quantify the chemical components of UFPM. Sulfuric acid constituted a few percent of UFPM mass, with branched alkanes and alkyl-substituted cyclic alkanes contributing most of the UFPM mass. These organic compounds are representative of unburned fuel and lubricating oil. They proposed that UFPM is formed by nucleation of sulfuric acid (binary nucleation between sulfuric acid and water) or ammonia and sulfuric acid (ternary nucleation involving ammonia, sulfuric acid, and water), followed by condensation of organic compounds. They considered the nucleation of organic compounds to be unlikely; although the estimated vapor pressures of the least volatile organic compounds are on the order of 10^{-12} to 10^{-14} torr. They argued that an organic particle would be smaller than a sulfuric acid/water particle and the Kelvin effect (i.e., more volatilization from smaller particles) would inhibit the organic particle formation. They found that the volatility of the particles decreases with decreasing particle size, which is consistent with the Kelvin effect.

Sakurai et al. (2003a) investigated the chemical composition and volatility of emissions from a heavy-duty diesel engine under laboratory conditions using a TDPBMS and tandem
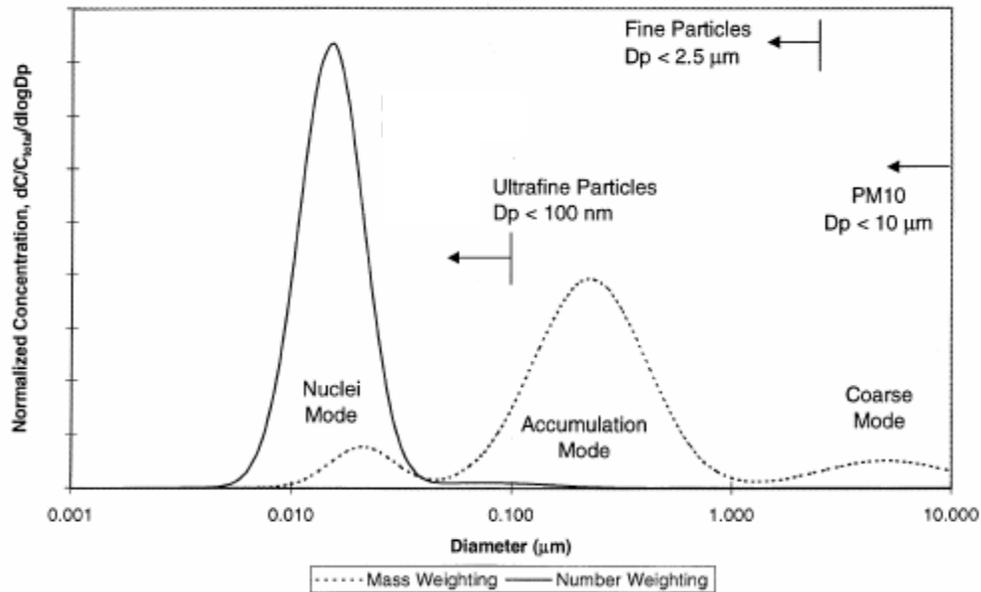
Figure 2-1. Definition of the modes and size ranges of hypothetical PM number and mass size distributions (Source: adapted from *J. Aerosol Sci*., **29**, Kittelson, D.B., "Engine and nanoparticles: a review", 575-588, Copyright (1998), with permission from Elsevier).

differential mobility analyzers (TDMA). Using mass spectral analysis of fuels (California low-sulfur fuel, Fischer-Tropsch very-low sulfur fuel and U.S. EPA fuel), oil, an oxidation product (palmitic acid) and sulfuric acid, it was estimated that the unburned fuel, combustion oxidation products and sulfuric acid contributed respectively about 1%, less than 1%, and only a few percent to the PM mass; unburned oil contributed at least 95% to the PM mass (see also Ziemann et al., 2002, for details on the experimental results). Fuel constituents are more volatile than lubricating oil constituents; since the more volatile components will be less abundant in smaller particles (due to the Kelvin effect), UFPM contains an even smaller fraction of unburned fuel than total PM. The TDMA volatility measurements suggest that the organic fraction of UFPM consists mostly of C_{24} to C_{32} organic compounds, which are typical of unburned oil.

Sakurai et al. (2003b) investigated the volatility of the components of diesel exhaust PM under laboratory conditions using TDMAs and an aerosol particle mass analyzer (APM). They identified that the particles could be separated into two overlapping modes with the smaller size mode containing particles that are almost completely volatile and the larger size mode containing particles with a non-volatile core. The characteristics of the two modes (peak diameter and magnitude) varied depending on the engine operating conditions. Most of the smaller size mode mass was below 100 nm and, therefore, consisted of UFPM, whereas most of the larger size mode mass was above 100 nm. Nevertheless, a significant fraction of the larger size mode mass was below 100 nm, implying that some UFPM contains a non-volatile core.

Kittelson et al. (2004) made SMPS measurements of UFPM concentrations on-road, i.e., near the source of their points of emissions. Those measurements were corrected for background PM concentrations by subtracting from the on-road measurements the PM concentrations measured at a nearby residential site upwind of the roadway. The corrected UFPM number concentrations ranged between 10^4 and 10^6 particles/cm^3. The UFPM number concentration increased with vehicle speed; also, the UFPM particle size decreased with increasing speed. Some of the increased UFPM was probably due to the release of material accumulated in the exhaust system at lower speeds. Measurements made under traffic congestion conditions (speeds less than 20 mph) showed lower UFPM number concentrations. These results are consistent with the fact that UFPM emissions increase with engine load, exhaust temperature and exhaust flow. UFPM number concentrations increased with the amount of diesel traffic.

Kwon et al. (2003) used a medium-size diesel truck on a chassis dynamometer to study the volatility of UFPM. Particle size distributions were measured with TDMA where an electric furnace was connected to the exhaust to vary the temperature of the sampled UFPM, thereby influencing the volatilization of the UFPM compounds. UFPM was found to contain both non-volatile and semi-volatile components. Under idling conditions, it appeared that there was a significant semi-volatile fraction (more than 90%) of UFPM present in the larger particles. Under half engine load conditions, the semi-volatile fraction of UFPM was negligible (less than 10%).

Zielinska et al. (2004) measured the phase and size distribution of polycyclic aromatic hydrocarbons (PAH) in the emissions of diesel and gasoline vehicle using a MOUDI. The diesel vehicles typically emitted more UFPM mass than the gasoline vehicle. The UFPM emissions included some non-volatile and semi-volatile PAH.

Vaaraslahti et al. (2004, 2005) investigated in the laboratory the effect of lubricant oils on emissions from a heavy-duty diesel engine with and without a continuously regenerating diesel particulate filter (CRDPF). Four types of oils were used with sulfur content varying from 1600 ppm to 9330 ppm. The PM size distributions were measured with a SMPS and an ELPI. Without a CRDPF, the highest UFPM number concentrations were observed at low load (number concentrations were about an order of magnitude less at high load). With a CRDPF, UFPM appeared in significant amount only at high load. The number concentrations were very sensitive to the sulfur content of the oil with a range of nearly two orders of magnitude among the four lubricating oils. The sulfur content of the fuel also had a strong effect on UFPM number concentrations. They concluded that without a CRDPF, UFPM formation results from nucleation/condensation of hydrocarbons from the fuel and oil, whereas with a CRDPF, UFPM formation was governed by sulfuric acid nucleation.

Mathis et al. (2004a) investigated the volatile component of UFPM for emissions from a diesel passenger car and a direct-injection spark-ignition passenger car on a chassis dynamometer. The diesel fuel contained 18 ppm sulfur and the gasoline fuel contained 33 ppm sulfur; the lubricating oil contained 6470 ppm sulfur. The particle size distribution was measured with a SMPS. Transmission electron microscopy (TEM) was used to identify the types of solid and volatile particles collected on the filters. Elemental analysis was also conducted to provide some information on the chemical composition of the particles. The particles appeared to fall into two categories, possibly hydrophilic and hydrophobic. Sulfur and potassium were associated with the hydrophilic component. The authors pointed out that direct-injection spark-ignition engines lead to 10% of the amount emitted by diesel engines equipped with a DPF.

Mathis et al. (2004b) investigated the effect of various volatile organic compounds (VOC) on the formation of UFPM in the exhaust of a light-duty diesel vehicle on a chassis dynamometer. Their objective was to understand how VOC in the exhaust may influence the formation of nanoparticles. Measurements were conducted using a SMPS. They injected ten different VOC, including two alkanes, two aromatics, one ketone, one ether, and four alcohols. They concluded that some organic compounds (alcohols and to a lower extent toluene) initiated and enhanced UFPM formation, that others (acetone, aniline and MTBE) inhibited UFPM formation, and that some (short-chain aliphatic compounds such as hexane and cyclohexane) had no significant effect. The significant effect of alcohols was attributed to their water solubility and their ability to decrease surface tension.

Mathis et al. (2005) studied four different light-duty passenger vehicle types: direct-injection and port-injection spark ignition vehicles with three-way catalysts and diesel (compressed-injection) vehicles with and without a DPF. The tests were conducted on chassis dynamometer with dilution sampling. The number size distribution was measured with an ELPI. Cold starts led to higher emissions of UFPM for the spark-ignition vehicles. The diesel vehicle without a DPF also showed high UFPM during cold starts (about 4 times greater than the spark-ignition vehicles) but the diesel vehicle with a DPF did not. However, high UFPM emissions were observed during the regeneration of the DPF. The DPF removed UFPM more efficiently than larger particles.

Kubo et al. (2006a, 2006b) used MOUDI instruments to sample size-distributed PM emitted from diesel exhausts and performed chemical analyses with gas chromatography/mass spectrometry (GC/MS) and time-of-flight secondary ion mass spectrometry (TOF-SIMS). The emitted UFPM ranged mostly between 3 and 30 nm. Kubo et al. (2006a, 2006b) concluded that hydrocarbons from lubricating oil and fuel were the main contributors to UFPM. They claimed that hydrocarbons from the oxygenated fuel ($>C_{19}$) dominated during idling conditions whereas lubricating oil hydrocarbons ($>C_{35}$) dominated during deceleration. Under high load conditions, sulfate dominated the chemical composition of UFPM.

The effect of an emission control device, the Johnson-Matthey continuously regenerating trap (CRT), on PM emissions was investigated experimentally by Grose et al. (2006). The particle size distributions were measured with SMPS and the PM mass and chemical composition was obtained from MOUDI samples. The volatility and hygroscopicity of the very small UFPM (4 to 15 nm in diameter) was measured with a TDMA. The fuels used contained 15 and 49 ppm of sulfur, respectively (the CRT requires low-sulfur fuel). The total UFPM number concentration and the mean particle diameter of the UFPM mode decreased with the fuel sulfur content. The measurements of the UFPM volatility suggested that those particles behaved more like ammonium sulfate particles than long-chain alkane (C_{28} to C_{32}) particles. Experiments on the hygroscopicity of the UFPM suggested that the larger particles (12 nm in diameter) behaved similarly to ammonium sulfate but that the very small particles (6 and 9 nm in diameter) behaved more like sulfate particles that are not totally neutralized (e.g., ammonium bisulfate), perhaps because of ammonia volatilization. However, experimental artifacts (partial neutralization of sulfuric acid particles in the TMDA) prevented a complete characterization of the degree of neutralization of the emitted UFPM. Nevertheless, it could be concluded that UFPM emissions from a diesel engine with CRT emission control consist mostly of sulfate, with some amount of ammonium; organic UFPM is not present in any significant amount, probably because organic compounds are oxidized in the CRT device.

Ristovski et al. (2006) investigated the influence of the sulfur content of diesel fuel on UFPM emissions from buses. Measurements were made on a chassis dynamometer using an SMPS. There was no DPF on the bus exhausts. Two different fuels (low sulfur and ultra low sulfur) were used with 500 and 50 ppm sulfur, respectively. The number concentration of particles in the 8 to 400 nm diameter range decreased by 30 to 60% when using the ultra low sulfur fuel compared to the low sulfur fuel. The effect was greater (but not quantified) for the UFPM fraction. The authors concluded that sulfur played a major role in the formation of UFPM, with the influence of sulfur content being greatest under high load conditions.

Kittelson et al. (2006a) investigated the size distribution and chemical composition of UFPM emitted from diesel engines on-road and in-the-laboratory (see Figure 2-2). Particle size measurements were made with a SMPS. A TDPBMS and a TDMA were used to characterize the physical and chemical properties of the particles. A major result of the work of Kittelson et al. (2006a) is the documentation of differences between laboratory and on-road measurements, with the latter showing greater UFPM concentrations (quantifying those differences is, however, complicated by the difficulty of accurately determining the dilution ratio of the on-road

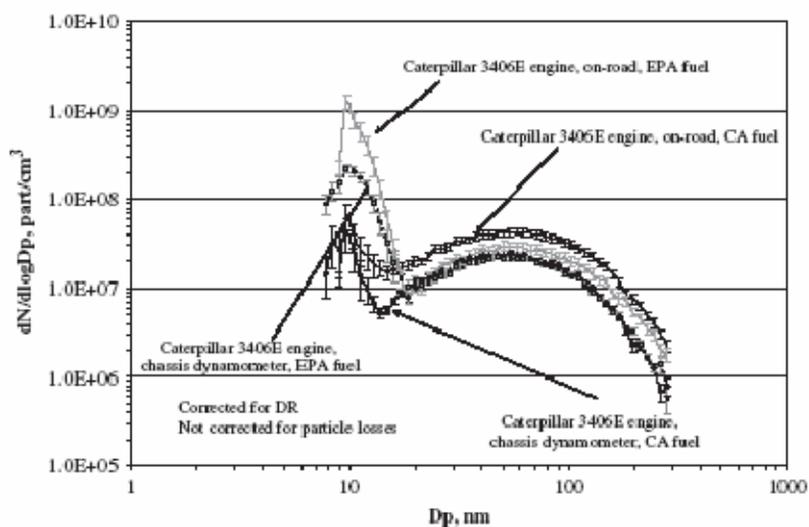Figure 2-2.   Particle number concentration distributions for diesel engines with EPA and California fuels sampled on-road and in the laboratory (Source: Reprinted from *J. Aerosol Sci.*, **37**, Kittelson, D.B., W.F. Watts and J.P. Johnson, "On-road and laboratory evaluation of combustion aerosols – Part 1: Summary of diesel engine results", 913-930, Copyright (2006), with permission from Elsevier).

measurements). They found that diesel engine emissions always show a nuclei mode under on-road conditions but not always under laboratory conditions. Measurements corresponding to a California fuel showed significantly less UFPM than those made with an EPA fuel; the authors assumed that the difference was due to the lower sulfur content of the California fuel. Most of the mass (>97%) of particles in the 12-30 nm range was volatile with properties consistent with C_{24}-C_{32} n-alkane compounds typical of lubricating oil. Hygroscopicity measurements were made to identify the sulfuric acid content of the UFPM. With high sulfur fuel (360 ppm sulfur), a significant fraction of sulfuric acid was found in UFPM, particularly in the smallest particles (20% for particles 6.5 nm in diameter and 5% for particles 30 nm in diameter). However, no hygroscopicity was detected with fuels that had less than 100 ppm sulfur content, suggesting that the sulfuric acid fraction in UFPM was then negligible.

Kittelson et al. (2006b) investigated the size distribution and chemical composition of UFPM emitted from spark-ignition engines on-road and in-the-laboratory (see Figure 2-3). A SMPS and an ELPI were used to measure the particle size distributions; a nano-MOUDI was used to collect size-segregated samples for chemical analysis. No significant particle signature was found under highway cruise conditions (about 88 km/h on-road); particle concentrations were greater under cold-start in cold weather, full-throttle acceleration (80 to 120 km/h on-road) and high-speed cruise (113 km/h, chassis dynamometer) conditions. The UFPM size distributions generated during acceleration were similar to those of modern diesel engines (i.e., with a CRDPF). At high speed, emissions of larger particles (> 100 nm in diameter) are lower, which favors the nucleation of fresh UFPM; in addition, continued high-speed operation will heat the exhaust and catalyst, which is also conducive to the release of volatile compounds from the exhaust system walls, thereby providing potential nucleation precursors. The difference in UFPM number concentrations between hot-start and cold-start in cold weather is approximately a factor of 3 to 10. Elemental carbon was a major component of PM in laboratory tests (but not of UFPM), except for one vehicle which was a high sulfate emitter. The latter emitted mostly sulfate UFPM. Trace metals emissions were associated with engine wear and not with lubricating oil emissions. Heavy-duty diesel vehicles produced greater UFPM number concentrations than spark-ignition light-duty vehicles.

Meyer and Ristovski (2007) studied the properties of diesel exhaust using a volatilization and humidification TDMA. Their results obtained under high load conditions suggest that UFPM consists of ammonium sulfate particles coated with a hydrophobic organic layer: water uptake occurs only after sufficient organic volatilization has taken place and the hygroscopic and volatilization properties of the hydrophilic component match those of ammonium sulfate. The hydrophilic component accounted for 5 to 10% of the UFPM particles (i.e., more than reported in some other studies, see above). At moderate loads, the authors suggested that UFPM consists of a mixture of inorganic and organic compounds, such as nucleated ammonium alkyl sulfates. At low loads, the authors suggested that UFPM consists mostly of lubricating oil hydrocarbons. The formation of UFPM of lower volatility at lower loads contradicts the results of Burtscher et al. (1998).

Robert et al. (2007a, 2007b) tested the PM chemical composition of light-duty gasoline vehicles and heavy-duty diesel vehicles on a chassis dynamometer using MOUDI instruments. For nine light-duty gasoline vehicles, sulfate UFPM emissions were small (0 to 340 ng/km);
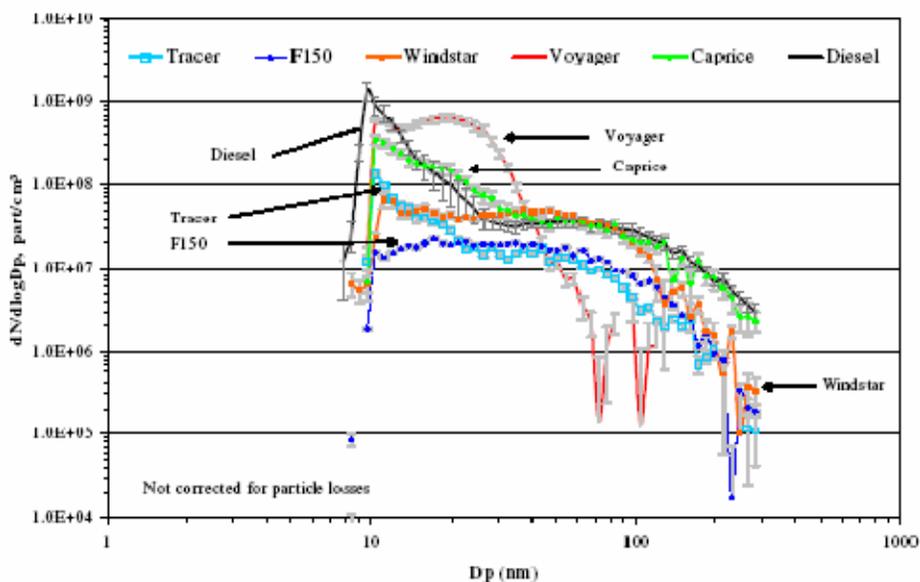
Figure 2-3. Average particle number concentration distributions from diesel and spark-ignition engines collected on-road during acceleration (vertical bars represent the standard deviation of the mean; values were corrected for dilution and background) (Source: Reprinted from *J. Aerosol Sci.*, **37**, Kittelson, D.B., W.F. Watts, J.P. Johnson, J.J. Schauer and D.R. Lawson, "On-road and laboratory evaluation of combustion aerosols – Part 2: Summary of spark-ignition engine results", 931-949, Copyright (2006), with permission from Elsevier).

ammonium and calcium UFPM emissions were 40 to 550 ng/km and 54 to 1620 ng/km, respectively. Using standard driving cycles, UFPM emissions ranged from 51 µg/km for the newest vehicles to about 10 mg/km for the oldest vehicles. The highest emission rates occurred for cold starts and accelerations. Emissions of black carbon ranged up to 800 µg/km, with most results in the range of 50 to 200 µg/km. Emissions of organic compounds were generally greater, ranging from less than 100 to 9,000 µg/km. Therefore, most UFPM mass consists of carbonaceous compounds. The low-emission vehicles and the vehicles equipped with oxidation catalyst and three-way catalysts emitted more UFPM during the cold start; the vehicles with no catalyst and the "smokers" (vehicles emitting blue smoke) emitted high UFPM levels during cold-start, accelerations and warm-start. The vehicles rated low-emissions and with three-way catalysts emitted the least amounts of UFPM.

For four diesel vehicles without a DPF, UFPM emissions per km were shown to vary significantly with the driving mode; highest emissions (about 200 mg/km) occurred during the creep mode, followed by the transient mode (about 100 mg/km) and the cruise modes (about 50 mg/km or less). For the California Air Resources Board five mode driving cycle, the UFPM emissions ranged from 24 to 72 mg/km. UFPM emissions from the diesel vehicles were about an order of magnitude greater than those from the gasoline vehicles. Inorganic UFPM emissions were in the ranges of 1 to 8, 3 to 9, 5 to 14, 4 to 54, and 4 to 81 ng/km for sulfate, sodium, ammonium, magnesium and calcium, respectively. Carbonaceous emissions dominated the UFPM mass with black carbon and organic compounds being commensurate in contribution for many conditions and vehicles.

2.2   Formation of Ultra Fine Particulate Matter

We address first several theories that have been proposed for the nucleation of nanoparticles. Then, we discuss briefly the oxidation of soot particles.

Nucleation

Kubo et al. (2006b) simulated the formation of organic nanoparticles using homogeneous nucleation and were able to reproduce their observations made with MOUDI instruments.

Shi and Harrison (1999) measured the size distribution of particles emitted from a heavy-duty diesel engine on a dynamometer with a SMPS. They simulated UFPM formation using homogenous nucleation theory for sulfuric acid and found that the nucleation rate was underpredicted by a couple orders of magnitude.

Tobias et al. (2001) considered the possibility of ammonium sulfate particle formation, which could occur via ternary nucleation (i.e., sulfuric acid, ammonia and water).

Yu (2001, 2002) proposed that chemiions are the main origin of the nanoparticles formed in the exhaust of mobile sources. Chemiions can be produced during combustion processes when positive ions and electrons are generated at high temperature; the electrons may subsequently attach to molecules to form large negative ions. Those ions may then react with certain molecules to form more stable electrically charged species. Recombination of positive

and negative chemiions leads to the termination of the reaction chain. This theory was used to simulate the nucleation of nanoparticles in diesel exhaust, predicting between 10^7 to 10^8 particles/cm^3 generated after 1 or 2 s, which is commensurate with measurements by Wei et al. (2001). Some experiments were conducted to confirm whether chemiions actually dominate the nucleation of nanoparticles in vehicle exhausts. Yu et al. (2004) measured ion concentrations of about 3 x 10^6 cm^{-3} in the exhaust of gasoline engines and 3 x 10^8 cm^{-3} in the exhaust of diesel engines. The ions measured in gasoline engine exhausts were less than 3 nm whereas those measured in diesel engine exhaust were larger than 3 nm and were thought to be charged soot particles; the smaller ions may consist of charged elemental carbon, sulfuric acid, nitric acid and hydrocarbons. Differences between the two types of engines were attributed to different residence times in the exhaust system and different soot particle concentrations.

Lee et al. (2006) investigated the processes that lead to the emission of metals (from fuel and lubricating oil) in UFPM. At normal metal concentrations in the fuel, the metals were found to be present in greater concentrations in smaller particles, in agreement with a condensation growth law, which suggests that metals condense on pre-existing soot particles. However, at high metal concentrations in the fuel (artificially enhanced for the purpose of the experiment), the metal concentration was found not to be correlated with particle size, thereby suggesting a coagulation process between soot particles and nucleated metal particles. Therefore, metals can contribute to UFPM both via condensation on existing soot particles or, when soot concentrations are low, via nucleation. The relative importance of these two processes will vary according to the engine operating conditions.

Meyer and Ristovski (2007) studied the properties of diesel exhaust using a volatilization and humidification TDMA, as discussed above. Their results suggested that nucleated particles consist of ammonium sulfate at high load (formed via ternary nucleation), ammonium alkyl sulfates at moderate load, and lubricating oil hydrocarbons at low load.

Kinetics of oxidation

Once soot particles have been emitted from the exhaust of a diesel engine, they undergo oxidation in the atmosphere by reaction with oxygen and other oxidants. This oxidation leads to some break-up of soot components and, as a result, a decrease in size of soot particles. Several studies have been conducted to understand the kinetics of soot oxidation.

Higgins et al. (2002) derived an expression for the kinetics of the oxidation of diesel soot particles as a function of size. Particle size was measured for selected monodispersed particle populations with a TDMA before and after oxidation at high temperature. The decrease in particle size was faster for the larger particles (130 nm) and slower for the smaller particles (40 nm). This difference in oxidation kinetics could be due to different effective particle densities, chemical composition, or a combination of both.

Higgins et al. (2003), Jung et al. (2003) and Kim et al. (2005) showed that the kinetics of diesel soot oxidation is influenced by the presence of metals from the lubricating oil. Metals such as calcium and iron were shown to enhance the number of active sites on the soot particles, thereby favoring the oxidation process.

2.3   Summary

For diesel vehicles without a DPF, UFPM is composed mainly (>95%) of unburned lubricant oil (C_{24} to C_{32} n-alkanes); unburned fuel (C_{15}-C_{23} alkanes) consists of more volatile compounds, which, therefore, are less conducive to gas-to-particle conversion (one study, however, reports that fuel hydrocarbons dominate during idling conditions). It is likely that nucleation of sulfuric acid particles occurs as the exhaust cools because of dilution. Organic compounds may then either condense on the sulfate particles or nucleate to form new particles. Condensation of organics should occur primarily on larger particles (e.g., diameter > 100 nm) that offer more surface area, as does sulfuric acid (since most sulfate is found in the larger particles). The relative amounts of organic nucleation and condensation on existing sulfate particles depend on the physical properties of the organic molecules and the surface area of existing particles available for condensation. Condensation of SVOC on aqueous sulfate particles seems inconsistent with (1) the fact that alkanes (identified as the major form of SVOC in vehicle exhaust) are not very water-soluble and (2) the fact that soot particles offer more available surface area for condensation than freshly nucleated particles do. Therefore, organic UFPM must result, to some extent, from nucleation of low-volatility organic molecules and possibly ternary nucleation with sulfuric acid. Metals could also serve as nuclei, although this has not been confirmed experimentally for engines under typical operating conditions.

There is little sulfate present in the UFPM (most of the sulfur mass is present as sulfate in the accumulation mode), but the presence of sulfur in fuel increases UFPM. This result is consistent with sulfate particles in the UFPM range acting as seeds for organic compound condensation and/or nucleation.

Most studies show that UFPM concentrations from diesel engines without a DPF and from spark-ignition engines increase with load (i.e., acceleration) and with cold start.

For diesel vehicles with a DPF, UFPM consists mostly of sulfate with some ammonium; there is little organic compounds in UFPM. Also, there is more UFPM generated during catalyst regeneration.

For spark-ignition vehicles, UFPM consists mostly of carbonaceous compounds with organic compound emissions generally greater than black carbon emissions.

Diesel engines without a DPF lead to the largest UFPM number concentrations. Diesel engines with a DPF have less UFPM emissions than those without a DPF. Spark-ignition engines with low-emission rating or three-way catalysts have the least amounts of UFPM emissions; their largest UFPM emissions are associated with cold starts.

3.   EVOLUTION OF ULTRA FINE PARTICULATE MATTER IN THE ATMOSPHERE

3.1   Ambient Measurements of UFPM

Measurements of UFPM with particle size distribution have been conducted in many areas, mostly urban areas. Sources of UFPM include primary emissions such as emissions from mobile sources, as discussed in the previous section, and secondary formation from the atmospheric oxidation of gaseous precursors such as sulfur dioxide (SO_2) and volatile organic compounds (VOC). (Note that primary emissions of UFPM correspond actually to emissions of gases that nucleate or condense during the emission process [i.e., within the exhaust system] or shortly after release to the atmosphere.) Secondary formation of UFPM in the atmosphere is generally referred to as nucleation events (Qian et al., 2007). Such events have been observed in several locations including the remote troposphere (e.g., over the ocean and a few km aloft; Weber et al., 1999), a beech forest in Denmark (Pryor et al., 2005) and urban areas such as Atlanta, GA (Smith et al., 2005; McMurry et al., 2005), Fresno, CA (Watson et al., 2006), Pittsburgh, PA (Stanier et al., 2004) and Mexico City, Mexico (Dunn et al., 2004); these nucleation events have been found to be associated with high SO_2 concentrations and, therefore, to correspond to the nucleation of sulfate particles (either binary nucleation of sulfuric acid and water or ternary nucleation of sulfuric acid, ammonium and water to form ammonium sulfate). Nucleation of organic particles is also possible, as observed, for example, in the Blue Ridge Mountains of Virginia (Went, 1960) or the Blue Mountains of New South Wales, Australia (Goldstein and Galbally, 2007). We focus here on the ambient measurements of UFPM related to mobile source emissions.

Shi et al. (2001) measured UFPM concentrations near a roadway and near a stationary source. They concluded that traffic, a stationary combustion source and secondary aerosol formation all contributed to UFPM concentrations.

Wehner et al. (2002) measured UFPM in a street canyon in Leipzig, Germany, with TDMA and condensation particle counter (CPC) instruments. They found ambient concentrations in excess of 10^5 cm^{-3} during morning hours (6 am to noon), which suggests that traffic is a source of UFPM. The peak of the particle size distribution occurred at about 15 nm in the street canyon. In the urban background, the UFPM number concentrations were about one order of magnitude lower with a peak at about 20 to 25 nm. Condensation of gases on UFPM was suggested as the reason for the growth of the UFPM peak. The evolution of the particle size distribution from the street canyon to the urban background was successfully reproduced with an aerosol dynamic model that treated dilution, condensation and coagulation.

Zhu et al. (2002a) measured particle size distributions and number concentrations with a SMPS and a CPC, respectively, near Interstate Highway 405 in Los Angeles. This freeway had an average traffic flow of about 14,000 vehicles/hr during the sampling periods with gasoline-powered vehicles constituting about 93% of the vehicle fleet and heavy-duty diesel trucks constituting less than 5%. Measurements were made at different distances from the highway (30,

60, 90, 150, 300 m downwind and 300 m upwind). The measurements showed a significant decrease in the UFPM number concentrations with distance from the highway. Measurements at 300 m downwind were similar to those made upwind, indicating that the highway emissions were nearly diluted to the urban background level at that distance. A trimodal size distribution was measured at 30 m downwind with mean number diameters at about 10, 30 and 60 nm. The smallest size mode (i.e., at ~ 10 nm) showed the highest particle number concentration (on the order of 10^5 cm^{-3}) at 30 m from the highway but its number concentration decreased rapidly with distance and was not significant beyond 60 m. Peak total number concentrations exceeded 10^5 cm^{-3} as far as 90 m from the highway, but dropped below 5 x 10^4 cm^{-3} at 150 m and below 10^4 cm^{-3} at 300 m.

Zhu et al. (2002b) measured particle size distributions and number concentrations with a SMPS and a CPC, respectively, near Interstate Highway 710 in Los Angeles. This freeway had an average traffic flow of about 12,000 vehicles/hr during the sampling periods with heavy-duty diesel trucks constituting about 25% of the vehicle fleet. Measurements were made at 17, 20, 30, 90, 150 and 300 m from the highway and 200 m upwind. The UFPM showed three distinct modes with mean number diameters at about 10, 20 and 60 nm at 17 m from the highway. The peak of the lowest mode (i.e., at 10 nm) was above 3 x 10^5 cm^{-3}. This peak decreased by about half with a growth to 15 nm at 30 m from the highway. The particle size distributions at 150 and 300 m downwind of the highway were not significantly different from the upwind measurements. A comparison of the measurements made downwind of Interstate 405 Highway (less than 5% heavy-duty diesel trucks; see above) and Interstate 710 Highway (25% heavy-duty diesel trucks) shows that the lower mode (around 10 nm) is greater near I-405 than near I-710, whereas the second mode (around 20 to 30 nm) is greater near I-710 than near I-405. The third mode (around 60 nm) is not significantly different from that of the upwind measurements. The mode at 10 nm is considered typical of UFPM from spark-ignition vehicles (Ristovski et al., 1998) and the mode at 20-30 nm is considered typical of diesel vehicles. Such a distinction may, however, be too simplistic as the UFPM size distribution measurements of Kittelson et al. (2006a, 2006b) suggest that both diesel and spark-ignition engines have a strong UFPM peak at 10 nm. The results from Zhu et al. (2002a, b) show that both aerosol dynamic processes (such as coagulation) and dilution play a role in shaping the evolution of the UFPM size distribution.

Zhu et al. (2004) extended the measurement programs reported above (which were conducted in summer 2001) by making measurements in winter 2001-2002 and by comparing the results of the two seasonal sets of measurements (see Figure 3-1). The particle number concentrations in the smallest size mode (around 10 nm) were significantly greater in winter than in summer; since traffic flow was similar in summer and winter, these results suggest that the lower wintertime temperature favors the nucleation and/or condensation of semi-volatile organic compounds. The decrease of the 10 nm mode with distance from the highway was slower in winter than in summer; this was due to less atmospheric dispersion (more stable conditions) in winter than in summer because a similar dilution pattern was observed in concentrations of carbon monoxide (CO) and black carbon (BC). The UFPM number concentration decreases by at least half from 30 m to 100 m during winter but by a factor of three or more during unstable summer conditions.

Fine et al. (2004) analyzed UFPM data obtained with a SMPS at three different sites in the Los Angeles Basin, CA (Riverside, Rubidoux and Claremont) and concluded that both vehicular traffic and secondary aerosol formation contributed to UFPM. The morning traffic led to increases in UFPM number concentrations and black carbon (BC). However, high UFPM number concentrations were observed also during summer afternoon periods.

Canagaratna et al. (2004) used a mobile laboratory to measure the chemical composition and size distribution of particulate matter emissions from municipal buses in New York City with an Aerodyne aerosol mass spectrometer (AMS). For UFPM, they found that sulfate and organic matter were the main contributors (black carbon was not measured in that study).

Kuhn et al. (2005) studied the volatility of outdoor (and indoor) UFPM using a TDMA system. The sampling site was located near the Interstate 405 Highway. The results showed the formation of two modes from the heating of particles of 45 and 90 nm in diameter, thereby indicating that those particles contain both volatile and non-volatile species. On the other hand, a single mode remained for particles of 18 and 27 nm, suggesting that those smaller particles contain only non-volatile species.

Sardar et al. (2005) analyzed the chemical composition of UFPM as a function of size at four Los Angeles urban sites (University of Southern California in downtown Los Angeles, Long Beach on the Pacific Coast, Upland and Riverside inland, CA). UFPM was collected with a nano-MOUDI. UFPM mass concentrations were in the range of 1 to 3.5 $\mu g/m^3$. The chemical composition of UFPM was as follows: 32 to 69% of organic carbon, 1 to 34% of black carbon, 0 to 24% of sulfate and 0 to 4% of nitrate. UFPM was clearly dominated by organic compounds, particularly since the OC results were not multiplied by a factor to convert from OC to organic compounds (typically a factor of 1.2 to 1.6 in an urban area; Turpin and Lim, 2001). The sulfate contribution was greater in summer at all sites, possibly suggesting a significant secondary component.

Geller et al. (2005) measured PM mass and number distribution in a tunnel near Oakland, CA, using SMPS-CPC and MOUDI instruments. The particle number distributions show a nuclei mode peaking at about 15 nm. Some individual size distributions show a second nuclei mode peaking around 25 nm and an accumulation mode peaking at 60 nm. The chemical composition of UFPM shows that carbonaceous compounds (some black carbon but mostly organic carbon) dominate. A significant fraction of ammonium sulfate is also present but ammonium nitrate is negligible.

Kerminen et al. (2007) investigated the spatial distribution of particle number concentrations at two distances (9 and 65 m) from a major roadway in Helsinki, Finland, using an ELPI. They found that under wintertime conditions with low wind speed and stable atmospheric conditions, the particle number concentration decreased slowly and, at 65 m, particle number could be as high as 70 to 90% of the concentration at 9 m from the roadway. These results indicate less spatial variation than reported for wintertime measurements conducted near freeways in Los Angeles, which show a decrease of about 25% between 30 and 60 m (i.e., potentially >25% between 9 and 65 m).

Ning et al. (2007) studied the diurnal variations of UFPM concentrations and chemical composition at an urban site (downtown Los Angeles, CA) using a MOUDI to collect two 3-hour samples daily (6-9 am and 1-4 pm). The UFPM mass concentrations ranged from about 3 to 7 $\mu g/m^3$. The morning samples were dominated by alkanes, PAH and hopanes (reflecting traffic emissions) whereas concentrations of sulfate and organic acids were significantly greater in the afternoon samples than in the morning samples. Organic acids are representative of secondary organic aerosol formation. Sulfate is representative of traffic emissions but its increase in the afternoon reflects atmospheric oxidation of SO_2.

Phuleria et al. (2007) analyzed the chemical composition of UFPM in Los Angeles near Highway 110 which represents purely gasoline-powered vehicle traffic and near Interstate 710 highway which includes a significant (~20%) heavy-duty diesel truck traffic. Contributions of hopanes, steranes and high-molecular weight PAH to UFPM were found to be similar for the two freeways. However, greater concentrations of black carbon (BC) and low-molecular weight PAH were found near the freeway with diesel traffic. These results were consistent for hopanes, steranes, BC and high-molecular weight PAH with those obtained in a highway tunnel near San Francisco (Phuleria et al., 2006).

Biswas et al. (2007) investigated the volatility of ambient UFPM collected near Interstate 710 highway in Los Angeles using a TDMA. Sampling was conducted at 10 m and 150 m downwind from the highway and the analysis was conducted for particles of 20, 40, 80 and 120 nm in diameter. The results showed a non-volatile fraction increasing with particle diameter and being negligible for particles of 20 nm. The nonvolatile fraction was greater for the site closer to the highway, probably because of condensation of semi-volatile compounds and coagulation of smaller particles as the distance from the highway increases.

Ntziachristos et al. (2007a) measured UFPM number concentrations and size distribution, along with carbonaceous PM, CO and CO_2 concentrations near Interstate 710 Highway in Los Angeles. They found a bimodal UFPM size distribution with a nucleation mode below 40 to 50 nm and an accumulation mode peaking at 70 to 80 nm. Such a bimodal distribution is typical of diesel engine emissions (see Zhu et al., 2002b, above). Using CO_2 as a tracer for the vehicle exhaust dilution, the authors compare their results with laboratory and on-road data. Some general agreement on the UFPM distribution was obtained in those comparisons although some factors such as secondary PM formation, diversity of vehicle types and variable meteorological conditions affect UFPM near roadways but not in the laboratory. Ntziachristos et al. (2007b) used a nanoMOUDI/MOUDI system to collect UFPM at the same location. Sulfur (35 ng/m^3) and iron (35 ng/m^3) were the most abundant trace elements. These elements represented small fractions of the UFPM mass.

Puustinen et al. (2007) measured UFPM number concentrations with a CPC in various locations of four European cities (Amsterdam, Athens, Birmingham and Helsinki). They found that UFPM number concentrations vary significantly spatially.

Bowker et al. (2007) have reported measurements of UFPM near Interstate 440 Highway in North Carolina. This highway is highly traveled (125,000 vehicles per day) and has a noise barrier located between the highway and the nearby residential area. The UFPM measurements

were performed in a mobile van with a DMA-CPC for 20 and 75 nm particles. The results showed that the noise barrier was very effective in deflecting the emissions from the highway as the UFPM (20 nm and 75 nm) concentrations near the highway (but beyond the sound barrier) were about half the concentrations measured 400 m farther downwind. At such large distances, one would expect UFPM concentrations to have reach background levels (see above).

Westerdahl et al. (2005) and Fruin et al. (2008) reported on-road measurements of UFPM and other pollutants emitted from mobile sources (BC, NO, and PAH) conducted on freeways and on major arterial roads using a mobile platform equipped with a CPC and a SMPS. They conclude that there are good correlations between UFPM and those other air pollutants and between UFPM and traffic counts. Diesel vehicles govern UFPM concentrations on freeways but hard acceleration of gasoline-powered vehicles governs UFPM on arterial roads. This latter result is consistent with the increase in UFPM emissions associated with high engine load for spark-ignition vehicles that was reported in Section 2.

Figure 3-1 shows typical UFPM concentration profiles as a function of distance from a freeway.

3.2   Modeling Atmospheric UFPM

The first two studies discussed below differ from the other modeling studies because they attempt to simulate the formation of UFPM during the emission process whereas the other modeling studies initiate the simulation at a few meters from the point of exhaust when some initial UFPM has already been formed.

Uhrner et al. (2007) simulated the evolution of UFPM in the exhaust plume of a diesel vehicle. The model simulation results were compared to measurements conducted with a SMPS. Aerosol dynamic processes being simulated included nucleation, condensation, evaporation, coagulation, turbulent diffusion and deposition. Emissions of solid soot particles and binary nucleation of H_2SO_4-H_2O were considered for the initial formation of UFPM. The simulated UFPM number concentrations within 1 m of the vehicle exhaust were commensurate with the measurements (in the range of 2 to 5 x 10^{13} cm^{-3}). However, the nucleated H_2SO_4 particles grew only to about 2.5 nm whereas the SMPS measurements showed a growth up to 7 nm. Adding two condensable hydrocarbons (C_8H_{18} and $C_{19}H_{29}$) with low saturation vapor pressure to the growth process of the nucleated particles led to particles growing up to 15 nm. These results highlight the importance of considering the interactions between H_2SO_4 and organic compounds to correctly describe the evolution of UFPM in vehicle exhausts.

Albriet and coworkers (Albriet, 2007; Albriet and Sartelet, 2007) have modeled the formation and evolution of UFPM from the point of exhaust to several tens of meters downwind. Albriet assumed that the nucleating species was sulfuric acid and used a binary nucleation algorithm. Nucleation of sulfuric acid particles produced UFPM, which did not grow beyond 5 nm in diameter. By taking into account the gas/particle partitioning of semi-volatile organic compounds (SVOC), UFPM could grow up to about 50 nm at 10 m from the exhaust and was in qualitative agreement with observed size distributions (Zhu et al., 2004). The SVOC chemical speciation was based on experimental data from Schauer et al. (1999, 2002) and was
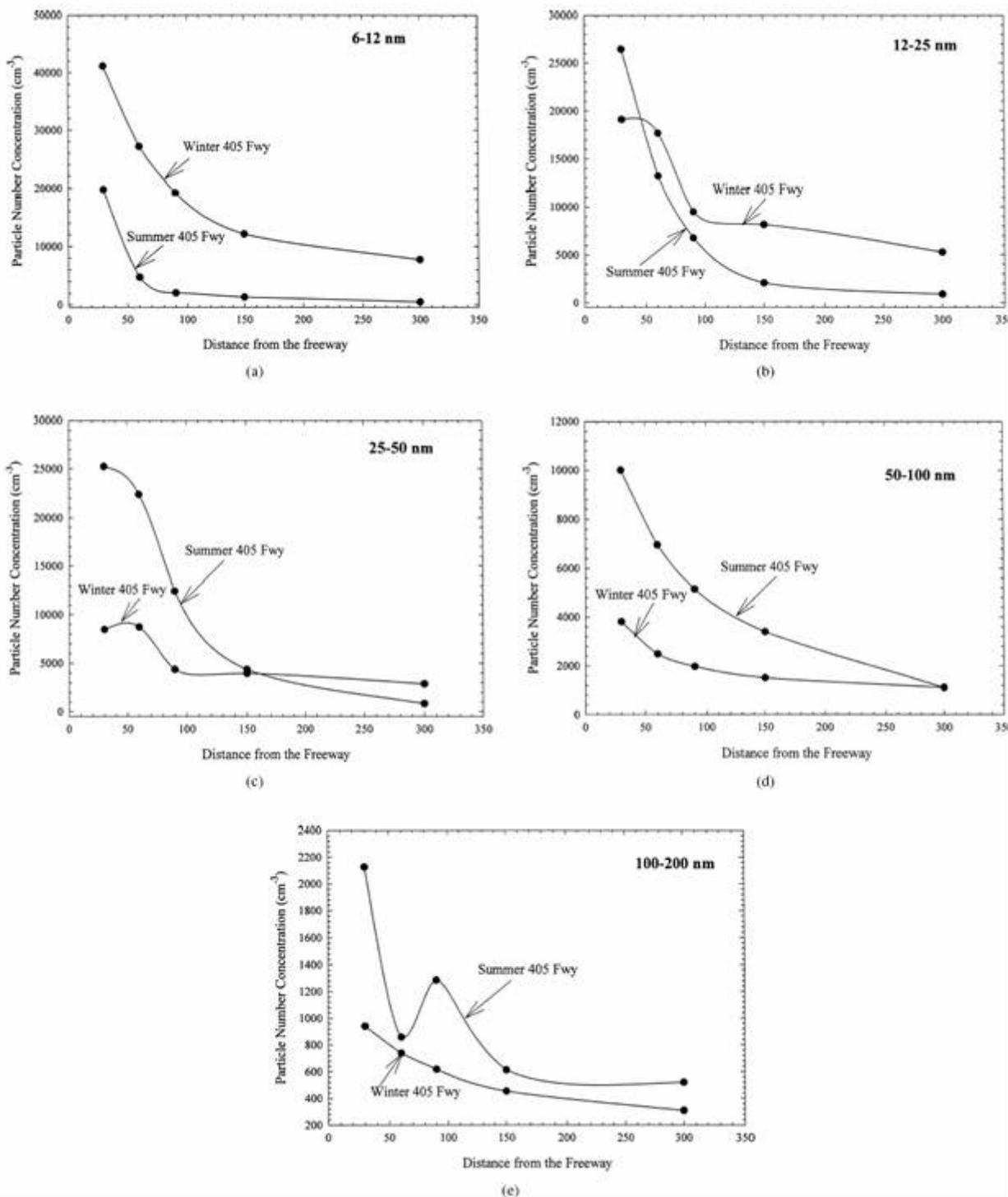
Figure 3-1. Concentrations of UFPM as a function of distance from a highway (Source: *Aerosol Science & Technology*: "Seasonal trends of concentrations and size distributions of ultrafine particles near major highways in Los Angeles", Zhu, Y., W.C. Hinds, S. Shen and C. Sioutas, 38 (S1):5-13. Copyright 2004. Mount Laurel, NJ. Reprinted with permission).

approximated using three surrogate species: n-nonadecane ($C_{19}H_{40}$) representing unburned fuel hydrocarbons, n-pentacosane ($C_{25}H_{52}$) representing lubricating oil, and pyrene ($C_{16}H_{10}$) representing products of combustion. Gas/particle partitioning of those SVOC was calculated assuming Raoult's law for absorption into an organic particulate phase.

Capaldo and Pandis (2001) simulated the evolution of diesel UFPM with a one-dimensional Lagrangian model. The model was initiated with a UFPM size distribution obtained from the measurements of Kittelson et al. (2004). The processes simulated included advection, vertical dispersion, coagulation and dry deposition. Condensation and evaporation were not treated. The UFPM concentration was calculated to decrease by one order of magnitude within 100 to 1,000 m from the point of emission.

Zhang et al. (2004, 2005) simulated the evolution of the UFPM size distribution by considering only condensation and evaporation processes with a box model. Although they were able to reproduce observed size distributions, some of their assumptions have been challenged (Jacobson et al., 2005). For example, they assumed a significant fraction of a low-volatility low-molar volume organic compound in the vehicle exhaust; available measurements suggest that such compounds constitute less than 1% of the organic mass (Tobias et al., 2001; Sakurai et al., 2003a).

Jacobson and Seinfeld (2004) used a 0-D model and a 3-D model with very fine spatial resolution to simulate the evolution of UFPM in vehicle exhaust. They considered only coagulation processes and ignored condensation and evaporation. Brownian coagulation could not explain the evolution of the size distribution. Adding the effect of Van der Waals forces and the fractal geometry of the particles increased the coagulation but still failed to give good agreement with the data of Zhu et al. (2002a).

Jacobson et al. (2005) used a model of aerosol dynamics and dispersion to simulate the evolution of the particle size distribution in vehicle exhaust plumes. The model was initiated with a particle size distribution at a few meters from the exhaust where the plume had cooled down to ambient temperature. Emissions of PM included the following chemical composition: sulfate, black carbon, C_{15}-C_{36} organic surrogates and oxalic acid (a surrogate for low volatility low molar volume organic compounds). The model used a 15 m x 15 m x 5 m spatial resolution and simulated the evolution of the particle size distribution due to condensation, evaporation and coagulation. The results showed that the small liquid particles (< 15 nm in diameter) lost SVOC by volatilization as the dispersion of the vehicle exhaust plume decreased the gas-phase concentrations of the SVOC. The decrease in size of those particles enhances their coagulation rate with larger particles by an order of magnitude (the coagulation rate increases as the size difference between the coagulating particles increases). This coagulation effect appears to be an influential factor for the evolution of the particle size distribution, particularly under daytime conditions when the greater ambient temperature favors the volatilization of SVOC from the small nanoparticles. Comparison of the model simulation results with measurements conducted near roadways showed good agreement when coagulation, condensation and evaporation were simulated (see Figure 3-2). Model performance deteriorated when one of those processes was not simulated (e.g., coagulation only or condensation/evaporation only). This simulation shows improvement over the previous modeling work of Zhang et al. (2004) and Jacobson and Seinfeld
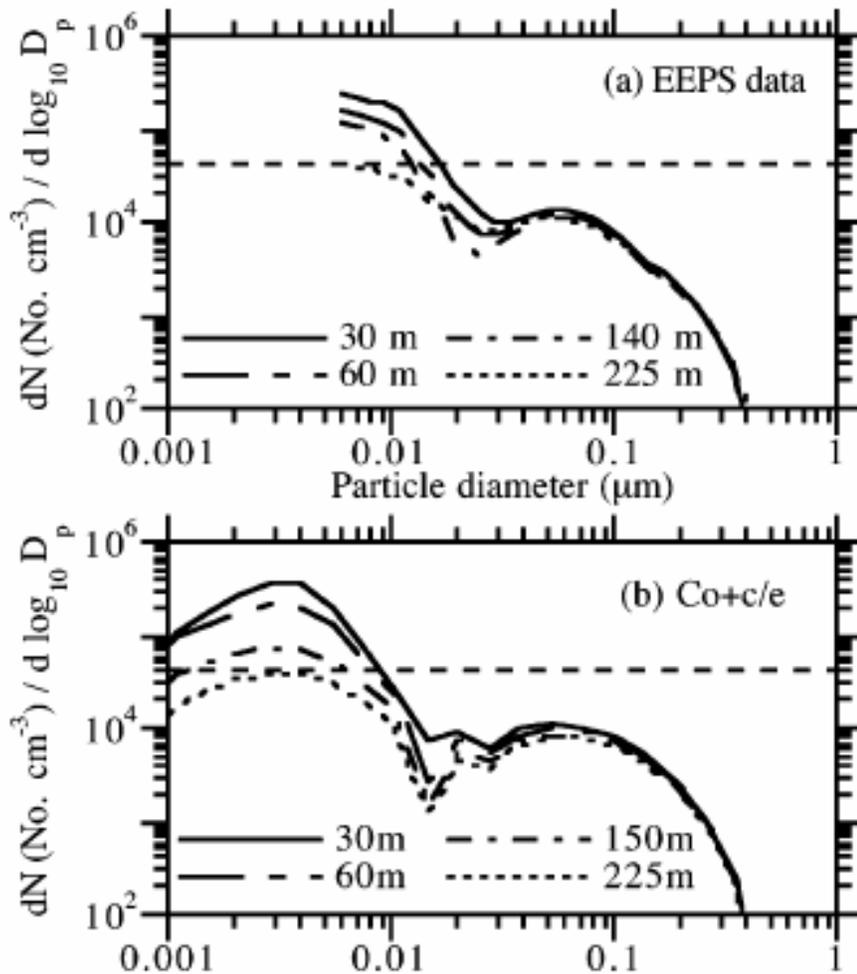
Figure 3-2. Comparison of (a) measured and (b) modeled particle number concentrations at different distances from a roadway (Source: Reprinted with permission from *Environ. Sci. Technol*., **39**, Jacobson, M.Z., D.B. Kittelson and W.F. Watts, "Enhanced coagulation due to evaporation and its effect on nanoparticle evolution", 9486-9492. Copyright (2005) American Chemical Society).

(2004) as it provides a good representation of the evolution of the UFPM size distribution using realistic inputs for the UFPM chemical composition.

3.3 Summary

Near a busy highway (>10,000 vehicles per hour), UFPM mass has been measured to be up to 3.5 $\mu g/m^3$ and the UFPM number concentration to exceed 10^5 particles cm^{-3}. Typically, the smaller nucleation mode disappears within 100 m due to volatilization (that results from the dilution with ambient air) and subsequent coagulation with larger particles; accordingly, the total UFPM number concentration decreases by at least half within 100 m, possibly less under some stagnant winter conditions but significantly more during unstable summer conditions. Also, the UFPM concentration is generally not discernible from the background PM beyond 300 m from the highway. Noise barriers are very effective at minimizing exposure to UFPM because the highway plume does not impact the ground until several hundreds of meters beyond the barrier and UFPM are typically at background levels at such distances.

There have been two theoretical studies of the formation and early evolution of UFPM in vehicle exhausts. These modeling studies reproduced the evolution of the nuclei modes of the UFPM size distribution by assuming (1) nucleation of sulfuric acid and (2) condensation of SVOC on the nucleated particles. However, nucleation of organic compounds was not considered.

Other modeling studies have addressed the evolution of the UFPM size distribution and chemical composition after the initial dilution from the vehicle exhaust (i.e., about 10 m from the exhaust point). After emission from the vehicle exhaust, UFPM evolves in the ambient atmosphere via a combination of the following processes as the UFPM plume becomes diluted: (1) volatilization of chemical species from the smallest particles (volatilization is favored from the smallest particles; the so-called Kelvin effect), which then become even smaller, (2) coagulation of the smallest particles with larger particles (coagulation is faster when the difference in size between the two coagulating particles is larger), and (3) condensation of background gases on particles. As a result of those processes, the number concentration decreases rapidly with distance. Modeling results are consistent with near-highway measurements.

4.   RECOMMENDATIONS

There are still some gaps in our scientific understanding of UFPM emissions from mobile sources and evolution in the atmosphere. Those gaps can be reduced by conducting additional experiments and theoretical calculations and some recommendations for possible avenues of further research are listed below.

Better understanding of the processes leading to the formation of UFPM: Little work has been done on developing a solid understanding of the physico-chemical processes that govern the formation and early evolution of UFPM. Theoretical models of UFPM formation show some promising results to explain the early evolution of UFPM; however, more work is needed to explain the various nuclei modes observed in the ambient atmosphere. Also, organic nucleation is possible and should be investigated, including the possibility of sulfate-organic heteronucleation and the role of chemiions.

Chemical composition of UFPM: Most work on the chemical composition of UFPM has focused on diesel engines without a DPF. Available results on UFPM emitted from diesel engines with a DPF suggest that UFPM consists mostly of sulfate. UFPM emissions from spark-ignition engines consist mostly of carbonaceous compounds. However, the experimental database for those engines is still relatively limited and a better understanding of the chemical composition of UFPM emitted from diesel engines with a DPF and from spark-ignition engines appears desirable.

Air quality modeling of UFPM: Model simulations of UFPM have been limited to case studies for specific conditions. Exposure assessment of UFPM will require the simulation of UFPM concentrations over a wide range of atmospheric conditions and emission scenarios. The development, incorporation and evaluation of UFPM modules in 3-D air quality models should be undertaken. This will require simulating the number size distribution of UFPM over fine spatial scales near major roadways. Although the numerical algorithms to address the various components of such a model (dynamics of the particle number size distribution; near-source atmospheric dispersion) are available, an air quality model that integrates those components in a single framework does not currently exist.

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6.   GLOSSARY

AMS: Aerosol mass spectrometer
APM: Aerosol particle mass analyzer
BC: Black carbon
CO: Carbon monoxide
CO_2:   Carbon dioxide
CPC: Condensation particle counter
CRDPF: Continuously regenerating diesel particulate filter
CRT: Continuously regenerating trap
DPF: Diesel particulate filter
ELPI: Electrical low-pressure impactor
EPA: Environmental Protection Agency
GC/MS: Gas chromatography/mass spectrometry
MOUDI: Micro-orifice uniform deposit impactor
NO: Nitric oxide
PAH: Polycyclic aromatic hydrocarbons
PM: Particulate matter
SMPS: Scanning mobility particle sizer
SOF: Soluble organic fraction
SVOC: Semi-volatile organic compound
TDMA: Tandem differential mobility analyzer
TDPBMS: Thermal desorption particle beam mass spectrometer
TEM: Transmission electron microscopy
TOF-SISM: Time-of-flight secondary ion mass spectrometry
UFPM: Ultra-fine particulate matter
VOC: Volatile organic compound