Ambient Air Quality Monitoring of Ultrafine Particles in Rochester, New York

Final Report 05-04
September 2005

New York State
Energy Research and
Development Authority

NYSERDA

NYSERDA

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AMBIENT AIR QUALITY MONITORING OF ULTRAFINE PARTICLES IN ROCHESTER, NEW YORK

FINAL REPORT

Prepared for the

NEW YORK STATE ENERGY RESEARCH AND DEVELOPMENT AUTHORITY

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PREFACE

The New York State Energy Research and Development Authority is pleased to publish "Ambient Air Quality Monitoring of Ultrafine Particles in Rochester, NY." The report was prepared by the principal investigator, Philip Hopke, the Bayard D. Clarkson Distinguished Professor at Clarkson University.

This report is one of the first characterizations of ambient ultrafine particles (UFPs) in the United States. It begins to build a database that can be used in epidemiological studies and complements ongoing work at the U.S. Environmental Protection Agency Particulate Matter Health Center at the University of Rochester Medical Center. The study was supported because little is known about UFP temporal variations. Future research is needed to understand spatial and temporal patterns of UFPs as well as particle nucleation and growth in other locations as well.

The work was funded by the New York Energy Smart^{SM} Environmental Monitoring, Evaluation, and Protection (EMEP) Program and is one of several studies characterizing particulate matter in New York State.

Abstract and Key Words

Recent epidemiological and laboratory studies have shown relationships between particulate matter (PM), the number of ultrafine particles (UFPs) per volume of air, and human mortality and morbidity. To create a database for future epidemiological research focusing on this connection, this study measured number and mass concentrations of PM and UFPs in Rochester, New York. Results from the first 13 months of data collection indicate that number concentrations of UFPs cannot be extrapolated from readily available data for mass concentrations of PM, and thus separate data on UFPs are needed. Ultrafine particles vary both seasonally and daily. Number concentrations were generally higher during winter than in summer, probably because of the cooling of combustion exhaust from motor vehicles combined with the atmospheric conditions typical of winter. Formation of large numbers of UFPs on summer mornings was related to motor vehicle emissions; that observed in afternoons appeared to be associated with sulfur dioxide from combustion sources, including a coal-fired power plant, northwest of the city. Average number concentrations of the smallest UFPs were significantly higher on weekdays than on weekends; the likely source of these particles was motor vehicles.

Key words:
air quality
ultrafine particles (UFPs)
particulate matter (PM)

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SUMMARY

Ambient particulate matter (PM) is a complex mixture of coarse particles (PM_{10}, with aerodynamic diameters greater than 10 microns, μm), fine particles ($PM_{2.5}$, with aerodynamic diameters <2.5 μm), and ultrafine particles (UFPs, with aerodynamic diameters <0.1 μm). PM has received growing attention in recent years as a possible factor in adverse health outcomes. Numerous epidemiological and laboratory studies have shown relationships between PM and such adverse human health effects as increased mortality, morbidity, and respiratory symptoms. The possibility that ultrafine particles may be more effective than larger particles in producing adverse health effects has prompted new research.

In this study, number concentrations (number of particles per unit volume) and size distributions of particles 0.010 to 0.500 μm (10 to 500 nanometers, nm) in diameter were measured at the New York State Department of Environmental Conservation (DEC) monitoring site in downtown Rochester, NY, from December 2001 through December 2002. This site is on the roof of the main fire station. At this site, carbon monoxide (CO), sulfur dioxide (SO_2), and $PM_{2.5}$ are also measured. Ozone is measured by DEC at another site, on the east side of Rochester.

A scanning mobility particle sizer (SMPS) was installed at the downtown Rochester site and particles were sampled from the glass manifold used to provide the samples to the gas monitors. This system provides the measurement of particle size distributions from 10 to 500 nm every five minutes so that it is possible to examine the dynamics of the atmospheric aerosol. The locations of the sampling site for this study, the DEC ozone site, and major sources are shown in Figure S1.

The smallest ultrafine particles, measuring 11 to 50 nm, accounted for more than 70% of the total number concentration, and 50 to 100 nm particles, approximately 20%. Figure

Figure S1. Locations of sampling sites and major local stationary sources as listed in the EPA point source emissions inventory.

S2 presents the annual variations of monthly average concentrations of 11 to 50 nm particles. The mean number concentrations in the winter months, December to February, tended to be higher than the values in July and August. The highest mean number concentration (11 to 50 nm) was found during December 2002, with a mean of 7,630 ± 3,710 (mean ± standard deviation) cm^{-3}; while the lowest mean concentration was observed during July, with a value of 4,280 ± 2,250 cm^{-3}.

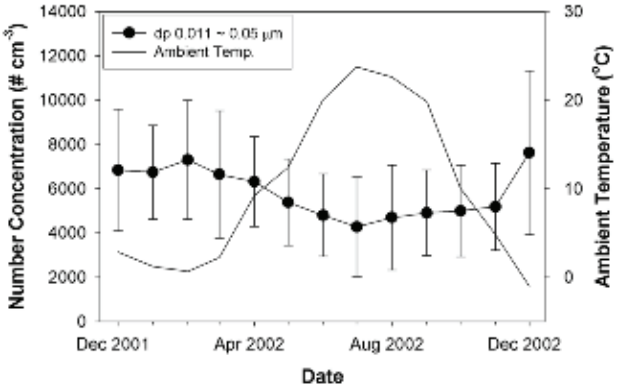

Figure S2. Monthly variations of total number concentration and ambient temperature in Rochester, NY.

Two peaks in the number concentrations were typically found in the size range of 11 to 50 nm as a function of time of day (Figure S3). The first event occurred around 8 A.M. During the winter months, this peak was associated with increased levels of CO. These particles appear to be from direct particulate emissions from motor vehicles during the morning rush hour. Increased number concentrations of particles of this size were also observed in the late afternoon during the evening rush hour, especially during the winter, when the mixing height remains lower than during the summer.

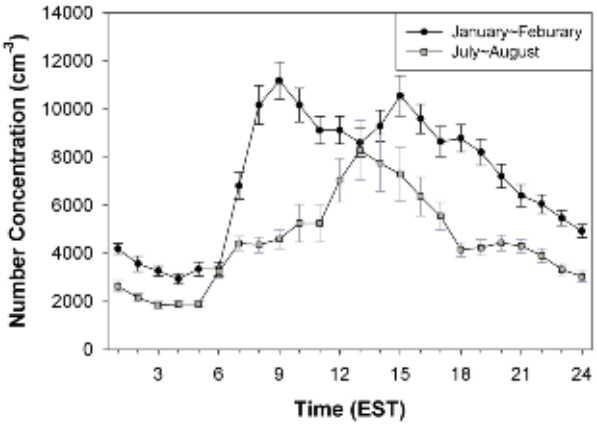

Figure S3. Comparison of diurnal variations in ultrafine particles in the size range of 11– 50 nm during winter months and summer months.

The second peak typically occurred between noon and 6 P.M. and was associated with nucleation events forming new ultrafine particles. These events were more likely in the spring and summer months. Sakurai et al. [2003] have found that particles emitted by diesel engines include both semivolatile and non-volatile components. Thus, in the winter, the semivolatile material will remain in the particulate phase while in the summer there could be vaporization and loss of particle numbers.

Nucleation events are observed in the form of sharp increases in the concentrations of 11 to 50 nm particles and were more likely in the spring and summer, particularly at midday, when photochemical activity is at its peak. Peaks of SO_2 concentrations were observed during the nucleation events when the wind direction

was from the northwest, where large SO_2 emissions sources are located (Figure S1); whereas there were no significant influences of $PM_{2.5}$ and CO on the nucleation events. It is hypothesized that the ultrafine particles are sulfuric acid and water from the oxidation of SO_2. The relationship between SO_2 and number concentrations of 11 to 50 nm particles is presented in Figure S4. Thus, these events are assumed to be primarily associated with local SO_2 emissions. There were also a more limited number of nucleation events, followed by particle growth up to approximately 100 nm.

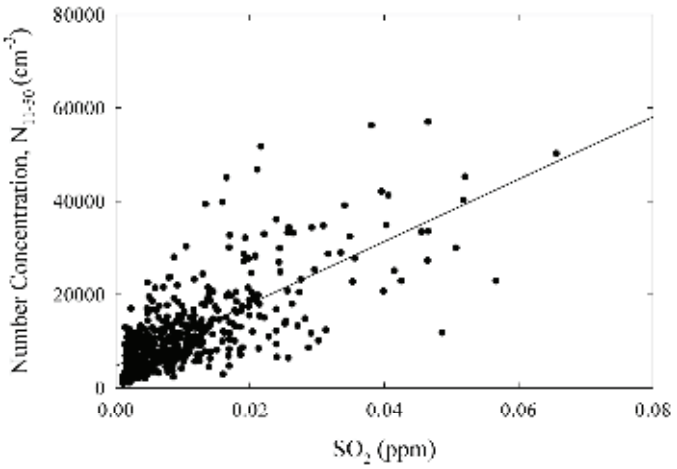

Figure S4. Correlation between number concentrations of ultrafine particles and SO_2 concentrations during the afternoon nucleation event from April to September 2002.

These nucleation and growth events have been associated with regional events as have been observed at several sites in Pennsylvania by Stanier *et al.* (2004). In order to have growth, there must be production of condensable vapor over a larger spatial domain. It is hypothesized that the larger domain provides adequate time to for photochemistry to convert volatile organic compounds into less volatile SVOCs that can then condense onto the particles and permit them to grow.

Clearly the inhabitants of Rochester are regularly exposed to high concentrations of ultrafine particles either coming from motor vehicle emissions or nucleation events. The most common nucleation events are clearly the result of emissions from local sources. Given the strong relationship with SO_2, the nucleation events are almost certainly related to the emissions from the local coal-fired power plant. The origins of the nucleation with growth events are not as clear.

The data from this project begins to build a base that can be used in future epidemiological studies. With several years of such data, it may be possible to explore the relationship between particle number concentrations and adverse health effects such as mortality, emergency room visits, and hospitalizations.

Other than Atlanta, Rochester is the only location in the United States where there could be sufficient data developed to permit an epidemiological study to be conducted, and we suggest that such a study be undertaken in the near future.

Section 1

INTRODUCTION

One of the major leading hypotheses that has been proposed for the cause of the observed effect of particulate matter on health is that high numbers of ultrafine particles—those with aerodynamic diameters less than 0.1 microns (μm), or 100 nanometers (nm)—rather than particulate mass is an important metric for exposure. Wichmann et al. (2000) found significant associations of elevated cardiovascular and respiratory disease mortality with various fine and ultrafine particle indices evaluated in Erfurt, Germany. Their study found significant associations between mortality and ultrafine particle number concentration (NC), ultrafine particle mass concentration (MC), fine particle mass concentration, and SO_2 concentration. The correlation between mass concentrations of fine particles ($MC_{0.01\text{-}2.5}$ μm) and number concentrations of ultrafine particles ($NC_{0.01\text{-}0.1}$ μm) was only moderate, suggesting it may be possible to partially separate their effects. Thus, measurements of ultrafine particle concentrations as well as particle mass are needed to examine these relationships. However, there are only very few locations for which such data are available. In the Wichmann et al. study, only particle counts were used. Thus, it is vital that we provide a clear record of the number concentration and size distributions of the ambient aerosol in the size range below a few hundreds of nanometers in particle diameter to provide critical data for evaluating the role of ultrafine particles in eliciting adverse health effects.

The objectives of this project are:

- to establish a monitoring site at which airborne particle size distributions from 10 nm to 500 nm are measured with near-real time resolution;
- to collect these particle data along with the continuous and filter-based PM_{10} and $PM_{2.5}$ mass values, $PM_{2.5}$ composition data, and O_3, SO_2, and CO data being collected by DEC; and
- to provide these data to the epidemiological collaborators in the U.S. Environmental Protection Agency's PM and Health Center at the University of Rochester, so that they can evaluate their potential health implications.

Across the United States, there are a number of efforts to measure the mass concentrations and compositions of integrated particle samples. However, there has been very little monitoring of particle size distributions. As part of the Aerosol Research and Inhalation Epidemiology Study (ARIES) program (Tolbert et al. 2000) examining the relationship between health effects and characteristics of airborne particulate matter in Atlanta, particle size distributions from 3 nm to 3 μm are being measured (Woo et al.

2001; McMurry and Woo 2002). These are the first such measurements to be made over an extended period (a total of 18 months when the project concludes). Particle size measurements have also been made at some of the seven Supersite monitoring stations around the United States but were scheduled for only a one-year period. Thus, most of the prior measurements cover a few days to a few weeks to one year. No body of measurements in the United States provides a clear record of particle number and size over a variety of various locations and over time periods of multiple years. There are no particle size distribution data for any of the smaller northeastern cities the size of Rochester, NY. It is this critical gap that this project was designed to address.

At the time that the revised National Ambient Air Quality Standard (NAAQS) for particulate matter less than 2.5 µm ($PM_{2.5}$) was promulgated, data on fine particle mass concentrations in urban areas across the United States were relatively limited, and no monitoring of particle size and number had been conducted except in limited-duration research studies. A network of mass concentration monitors was deployed in late 1998 to begin the monitoring necessary to determine the degree of attainment of the NAAQS. These monitors began regularly scheduled sampling in 1999 and are now providing limited 24-hour integrated mass concentration data, generally on an every third day basis. However, the New York State Department of Environmental Conservation (NYS DEC) chose a site in downtown Rochester (Figure 1) for continuous mass monitoring using tapered-element oscillating microbalance (TEOM) technology for both PM_{10} and $PM_{2.5}$. Both of these units operate at 50°C. At this site, DEC also monitors CO and SO_2 as well as $PM_{2.5}$ using a Federal Reference Method (FRM) sampler. Since particle mass and gases are already being measured at this location, it is an ideal site to measure particle size distributions to look for associations between such indicators of exposure and adverse health effects. Ozone is not measured at this site, but it is measured at another DEC site on the eastern side of Rochester as also shown in Figure 1.

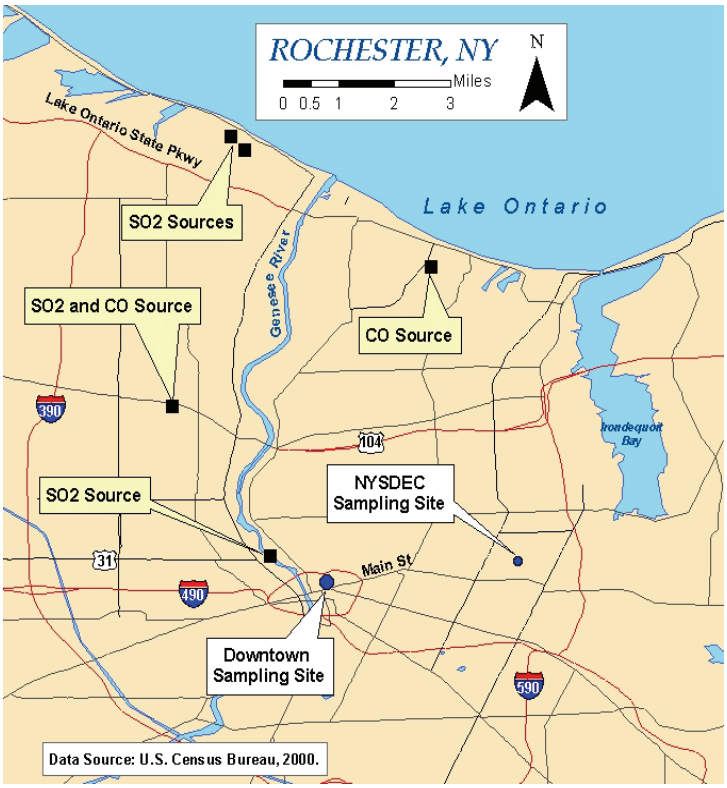

Figure 1. Locations of sampling sites and major local stationary sources as listed in the EPA point source emissions inventory .

With approximately 220,000 residents, Rochester is similar in population to Erfurt, Germany, site of the Wichmann et al. (2000) study. Although the power of both studies may be limited by the low number of deaths in cities of this size, this problem can be offset by having high-quality exposure data at a single, well-equipped site. This project was designed to examine the presence of ultrafine particles in a city in upstate New York and consider the processes that determine the concentrations and size distributions. It did not assess the health effects of the ultrafine particles, but rather developed a database of particle size data that could be employed in future epidemiological studies. This report focuses on the first 13 months of data collection, the period during which the work was supported by NYSERDA. Monitoring has continued with support from the University of Rochester PM and Health Center and the Electric Power Research Institute.

Section 2

BACKGROUND

HEALTH EFFECTS OF FINE PARTICLES

Epidemiological studies have linked fine particulate air pollution with increases in morbidity and mortality rates from cardiopulmonary complications (Wichmann et al. 2000). A strong and consistent association has been observed between adjusted mortality rates and ambient particle concentrations, with an increase in PM_{10} concentration of 50 $\mu g/m^3$ associated with a 3 to 8% increase in relative risk of death (EPA 1996). The strongest associations are seen for respiratory and cardiac deaths. Particulate air pollution is associated with asthma exacerbations, increased respiratory symptoms, decreased lung function, increased medication use, and increased hospital admissions (EPA 1996). Nevertheless, the mechanisms by which particulate pollution induces health effects at such low mass concentrations remain unclear. Determining the biological mechanisms involved has been identified as a high-priority research need by the EPA (1998).

Among the hypotheses proposed to explain which particles are responsible, considerable attention has focused on particle size, with particular interest on ultrafine particles (UFPs, with diameters less than ~100 nm) (Oberdörster et al. 1995; Seaton et al. 1995). Recent work at the University of Rochester Medical Center has focused on ultrafine particles for several reasons:

(1) UFPs are biologically more reactive than larger-sized particles and elicit effects at low concentrations (Ferin et al. 1992; Oberdörster et al. 1994).

(2) UFPs at the same mass concentration in the air have a much higher number concentration and surface area than larger particles. For example, in order to achieve the low airborne mass concentration of 10 $\mu g/m^3$, 2.4×10^6 particles/cm^3 with diameters of 20 nm are needed; in contrast, only one 2.5 μm particle/cm^3 is required (Oberdörster et al. 1995).

(3) Inhaled, 20 nm UFPs have a high deposition efficiency (about 50%) in the pulmonary region (ICRP 1994).

(4) UFPs have a high propensity to penetrate the epithelium and reach interstitial sites (Stearns et al. 1994).

Although few measurements of UFPs in ambient air have been made, a recent panel study of asthmatic subjects in Erfurt, Germany (Peters et al. 1997a), found that peak flow, a measure of lung function, varied

more closely with the five-day mean of UFP number than with fine particle mass concentration, suggesting that the UFP component of fine particle pollution contributes to airway effects in asthmatics.

Despite many epidemiological studies showing a relationship between particle exposure and cardiovascular mortality, no plausible mechanism has been established that would explain this association. Recent studies in healthy and compromised animals from EPA laboratories (Campen et al. 1997) and from Harvard (Godleski et al. 1997) have suggested that inhalation of particulate pollutants may induce changes in cardiac rhythm or repolarization, but the implications for humans are unclear. Seaton et al. (1995) have proposed that pollutant exposure induces a transient increase in blood coagulability as part of the acute-phase response associated with inflammation. This hypothesis is supported by the recent finding that plasma viscosity is increased on high-pollution days relative to low-pollution days in men and women aged 25 to 64 years (Peters et al. 1997b). Our monitoring study has generated new information providing near real-time resolution of airborne particle size distributions. The availability of this information is crucial if the mechanistic basis for particle effects is to be unraveled.

ATMOSPHERIC PROCESSES

Because of the importance of particle effects on climate, there has been increased interest in the formation of particles in the ambient atmosphere. Evidence of nucleation has been observed in a variety of places including the free troposphere (Raes et al. 1997), in the marine boundary layer (O'Dowd et al. 1998), in the vicinity of evaporating clouds (Hegg et al. 1991), in Arctic areas (Wiedensohler et al. 1996; Pirjola et al. 1998), in urban areas and stack plumes (Kerminen and Wexler 1996), and in boreal forests (Mäkelä et al. 1997). Similar events have been observed in Helsinki (personal communication, Markku Kulmala 2001). These events can be observed in terms of large numbers of very small particles (often less than 10 nm in diameter). Even at 10 nm, we will be able to infer the presence of nucleation events and particle growth in an urban area, for which such data are very rare.

Particle size has been measured in Atlanta (Woo et al. 2001; McMurry and Woo 2002) and Pittsburgh (Stanier et al. 2004). Woo et al. (2001) present the results of 13 months of measurements at an industrial-commercial area northwest of downtown Atlanta. They found that particle number concentrations tended to be higher on weekdays than on weekends. Concentrations of particles in the 10 to 100 nm and 100 to 2000 nm diameter ranges were higher at night than during the daytime and tended to reach their highest values during morning rush hour. Concentrations of 4 to 10 nm particles were elevated during rush hour when temperatures were <10°C. Annual average concentrations of particles in the 3 to 10 nm diameter range peaked between 11 A.M. and 2 P.M., because of very high concentrations at those times on a few days. They suggest that high concentrations result from nucleation events and identify three types of "ultrafine particle" events: (1) pronounced peaks of 3 to 10 nm particles typically occurred around noon in August

and April, when solar radiation was high; (2) significantly elevated concentrations of 10 to 35 nm particles were seen during the early morning and late afternoon hours in winter; and (3) relatively high number concentrations of 35 to 45 nm particles were detected several times. Elevated concentrations of SO_2 were observed during all three types of events. Nitrogen oxides (NO_x) were typically depleted during the formation of 3 to 10 nm particles and were more likely to be elevated during the formation of 10 to 35 and 35 to 45 nm particles. The sources of the particles are not yet known.

In Pittsburgh, particles measuring from 3 to 560 nm were measured using scanning mobility particle sizers from July 2001 to June 2002. The average Pittsburgh number concentration for 3 to 500 nm particles was 22,000 cm^{-3}, with an average mode size of 40 nm. Strong diurnal patterns observed in number concentrations were evident as a direct effect of the sources of these particles (atmospheric nucleation, traffic, and other combustion sources). New particle formation from homogeneous nucleation was found to be significant on 30-50% of study days and over a wide area (at least 100 kilometers). Rural number concentrations were a factor of 2 to 3 lower on average than the urban values.

Section 3

METHODOLOGY

PARTICLE MONITORING

Particle Size Distributions

In this study, the number and size of particles with diameters of 10 to 500 nm were measured every five minutes, using an electrostatic classifier along with a particle detector. Ambient aerosol particles are passed through a bipolar charging region produced by a 2 mCi ^{85}Kr source. This neutralizer yields an aerosol with an approximately Boltzmann charge distribution. To separate this charged aerosol into single particle size fractions, the aerosol is passed through a differential mobility analyzer (Knutson and Whitby 1975a, 1975b), as shown in Figure 2. This device attracts the positively charged particles toward a central electrode. As the voltage on the central electrode is increased, the particles of increasing mobility pass through an exit slit. Only a small range of mobilities can enter this slit, thus providing an essentially monodisperse aerosol. A continuous-flow condensation nuclei counter is used to condense butanol onto the particles, which grow to a size at which they effectively scatter light and can be detected. The central electrode voltage is continuously ramped to provide a sequence of measured particle counts from which a size distribution can be deduced (Wang and Flagan 1990). As part of the software that controls the voltage in the differential mobility analyzer, particle size distributions are calculated and stored on the hard drive. These data consist of the number of particles in each of a series of defined size intervals. The combination of a differential mobility analyzer, a condensation nuclei counter, and a computer with its related software is called a Scanning Mobility Particle Sizer (SMPS).

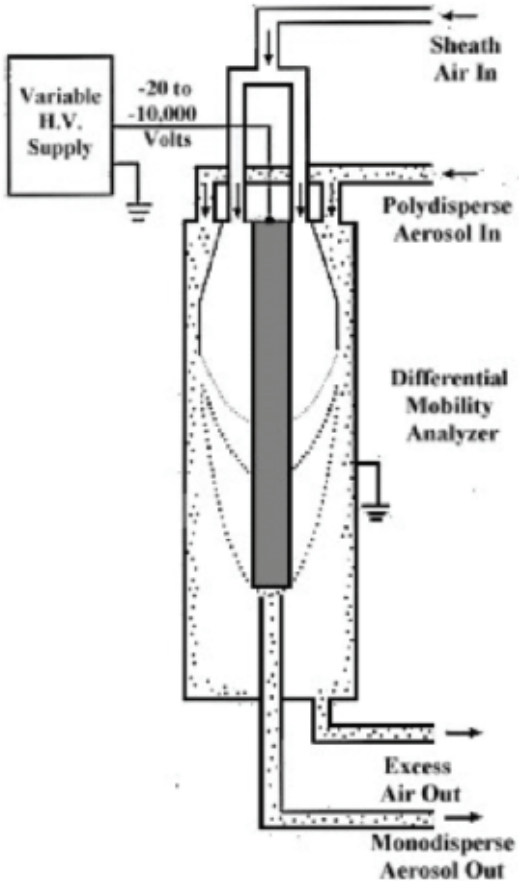

Figure 2. Schematic diagram of the TSI differential mobility analyzer that is part of the Scanning Mobility Particle Sizer used in this project.

To illustrate the type of data obtained from this system, Figure 3 shows a series of particle size distributions. The air sample was taken indoors, but the results illustrate the general shape of distributions that would be obtained from the ambient aerosol in an urban area. In general, there is a large accumulation mode around 100 nm. If there is a nuclei mode event, then a large number of particles in the size range of 10 to 20 nm would be observed. The size distributions depend on the particle sources and the extent of particle interaction in transit from the source to the sampling location.

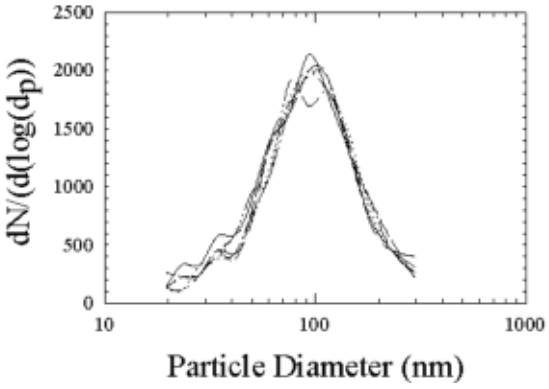

Figure 3. Illustration of particle size distributions measured using a SMPS.

Monitoring Site

The sampling location for this study is the Central Fire Headquarters in downtown Rochester (Figure 1). The firehouse is surrounded by an inner loop road within a half-mile and lies approximately 50 m from the nearest major road. Air is sampled on the roof of the building, 10.3 meters above the ground. The measurement system is set up inside, in a room that houses continuous gaseous monitors operated by DEC. Particles are sampled from the glass inlet manifold used to provide samples to the gaseous monitors. Power and a telephone line allow remote retrieval of the data from Clarkson University in Potsdam.

Particle Mass and Composition Data

DEC is currently monitoring PM_{10} and $PM_{2.5}$ using TEOM technology at the Central Fire Headquarters. Also at the site is a Rupprecht and Patashnick sequential FRM monitor for $PM_{2.5}$ that operates on an every-third-day basis.

Gaseous Pollutant Data

In addition to the PM measurements, gaseous pollutants are measured by the NYS DEC at several sites in the Rochester area. The downtown site (AIRS ID 360556001) is at the Central Fire Headquarters with continuous monitors for SO_2 and CO. Ozone concentration data are collected at another DEC site in the Rochester area. All of the gas concentration data used in this study were obtained from DEC.

QUALITY ASSURANCE

The site was visited at least every two weeks by a technician from the University of Rochester Medical Center, who filled the butanol reservoir and made the routine flow checks to ensure that the system was functioning properly. The data were regularly retrieved by personnel at Clarkson, and system problems were promptly detected and reported to the Rochester personnel. The result is a very high rate of data capture, following the initial shakedown period in December 2001, when minor problems arose and were largely solved by the installation of an uninterruptible power supply. The data for each size distribution were inspected, and anomalous distributions were omitted from the data set.

Section 4

RESULTS

SIZE DISTRIBUTIONS OF UFP

Particle size distributions were obtained every five minutes. To minimize instrument uncertainties, the lowest range, 10 to 11 nm, and the highest range, 470 to 500 nm, of size distribution were excluded. Particle concentrations were then classified into three size ranges, 11 to 50 nm, 50 to 100 nm, and 100 to 470 nm to characterize the variation of particle numbers in the various size ranges.

The data were then plotted in 24-hour contour plots, as shown in Figure 4. The figure shows the sequence of 12 measurements per hour over a 24-hour period. The vertical axis is the particle size plotted on a logarithmic scale. The concentration in a given logarithmic size interval, dN/d (log d_p), is shown by the brightness of color, ranging from low values in dark red through high values in white. In this particular case, a number of isolated events can be observed where there are short-term high concentrations of particles in the 10 to 30 nm size range. These very small particles are likely to be the result of local traffic in the vicinity of the sampling site. The site is in the central city surrounded by an inner loop road within a

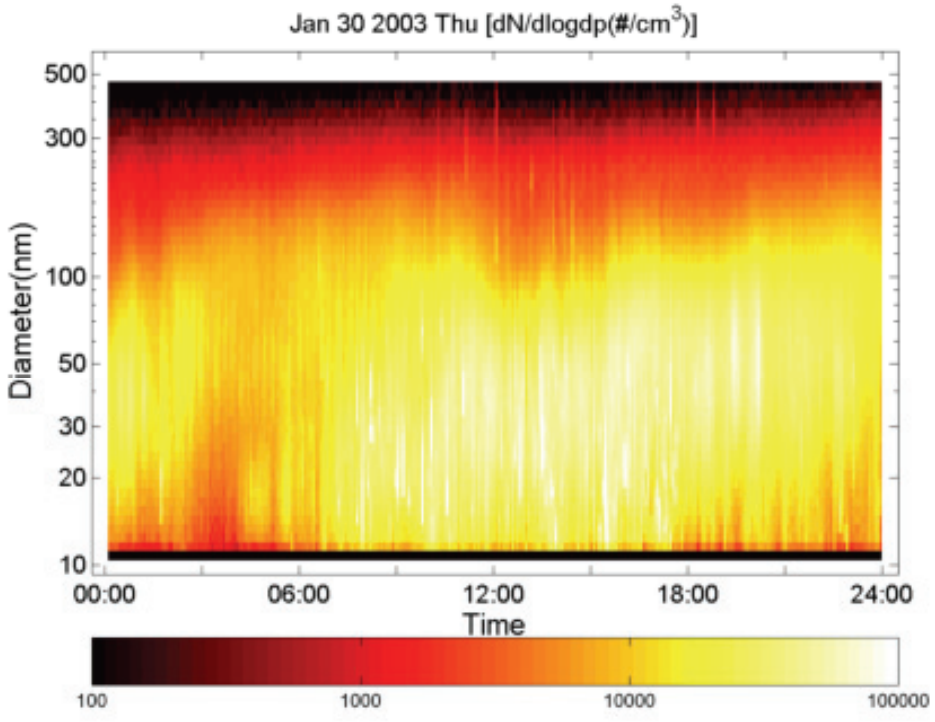

Figure 4. Illustrative example of the particle size distributions measured at the Rochester Central Fire Station for January 30, 2003.

half mile and approximately 50 m from the nearest major road. The size of the particles emitted from motor vehicles changes rapidly with distance from the source area (Kim et al. 2002; Zhu et al. 2002), so these smallest size particles are likely from local traffic. Recall that the samplers are located at the roof level of the three-story firehouse.

Table 1 shows the annual average number and volume concentrations and statistical parameters of the three size ranges measured in Rochester for the first 13 months of the study. The volume size distributions can be readily calculated from the number size distributions (Hinds 1999). This report will focus on only these first 13 months as that was the period during which the work was supported by NYSERDA. Monitoring has continued with support from the University of Rochester PM and Health Center and EPRI.

Table 1. Annual average number concentrations (# cm^{-3}) and volume concentrations (μm^3 cm^{-3}) of particles in the three size ranges, during the measurement period December 2001 to December 2002.

		Diameter			
		11 to 50 nm	50 to 100 nm	100 to 470 nm	Total
Number	Mean	5,800	1,510	880	8,160
	St. dev.	4,710	1,030	580	5,490
	Min	280	70	40	540
	Max	57,060	11,480	4,960	61,440
Volume	Mean	0.087	0.314	2.740	3.140
	St. dev.	0.065	0.218	2.036	2.155
	Min	0.004	0.014	0.142	0.180
	Max	0.688	2.280	19.420	19.545

The number concentrations of ultrafine particles in the size range 11 to 50 nm showed significant variability with a high standard deviation and accounted for approximately 71% of the total concentration of 11 to 470 nm particles. The average number concentration of 11 to 100 nm particles contributed around 90% of the total number concentration. The value is comparable to those reported in European cities, where the contributions of ultrafine particles in the size range 10 to 100 nm to the total number concentration of 10 to 500 nm particles ranged from 88% to 94% (Tuch et al. 1997; Pakkanen et al. 2001). Similar results have been seen in Atlanta (Woo et al. 2001) and in Pittsburgh (Stanier et al. 2004).

For comparison with daily $PM_{2.5}$ concentrations, the five-minute number concentration data were averaged to daily values. The correlations between the average daily ultrafine number concentrations in the two size ranges, 11 to 50 nm and 100 to 470 nm, particles and the measured daily mass concentrations of $PM_{2.5}$ are shown in Figure 5. The correlation between average particle number concentration and mass concentrations for the 50 to 100 nm particles had a value of $r = 0.20$ and was not plotted. Thus, there was no correlation between UFP number concentrations and $PM_{2.5}$ mass concentrations (Figure 5a). The number concentrations of 100 to 470 nm particles showed very little correlation with $PM_{2.5}$, with a squared correlation coefficient of 0.10 (Figure 5b). These results suggest that the collocated number measurements

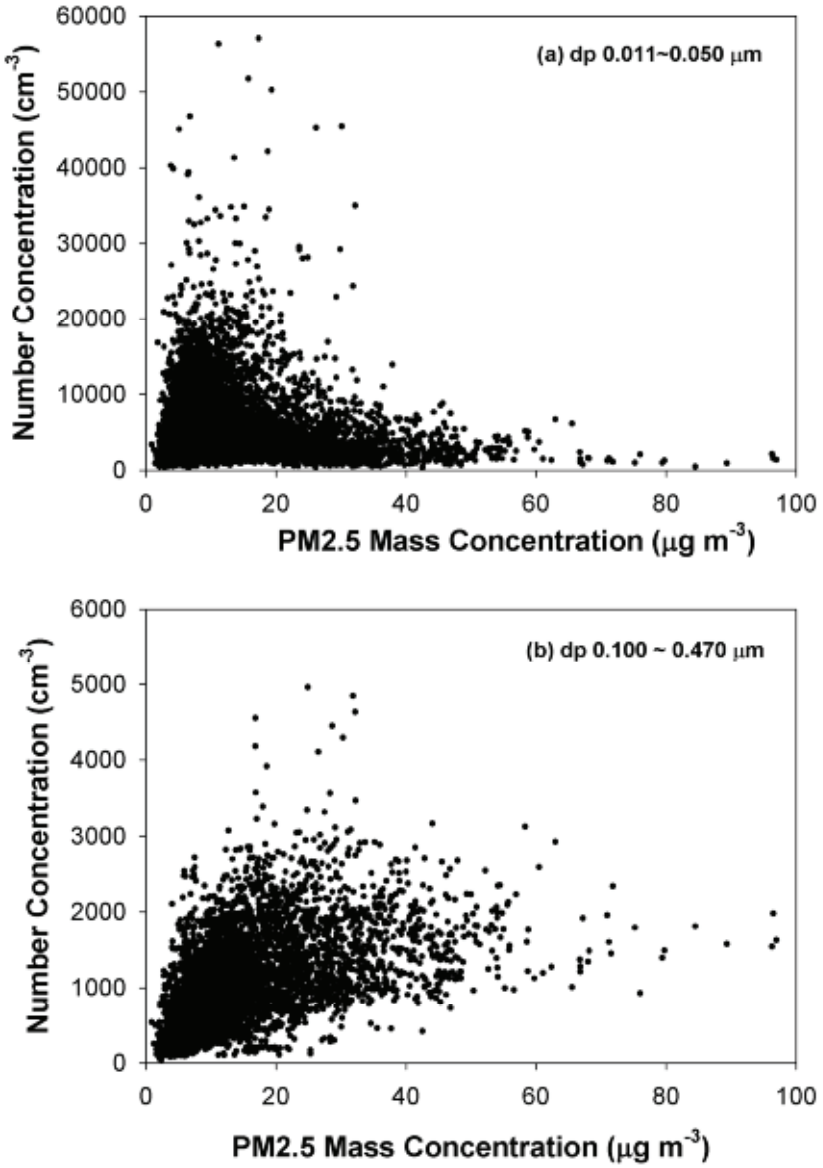

Figure 5. Correlation between number concentrations of particles in the size range of (a) 11 to 50 nm and (b) 100 to 470 nm and $PM_{2.5}$ mass concentrations during the measurement period December 2001 to December 2002.

of UFPs are needed to assess their effect on human health, since the number concentrations cannot be effectively estimated from the mass concentration measurements.

Mass concentration of ultrafine particles can be estimated by assuming that the average density of particles is 1,500 kg m^{-3} and all particles are spherical (Tuch et al. 1997). The estimated mass concentrations of particles in the size range 11 to 470 nm were closely correlated with mass concentrations of $PM_{2.5}$ (r^2 = 0.69), and their contribution to the $PM_{2.5}$ mass was approximately 27%, as shown in Figure 6.

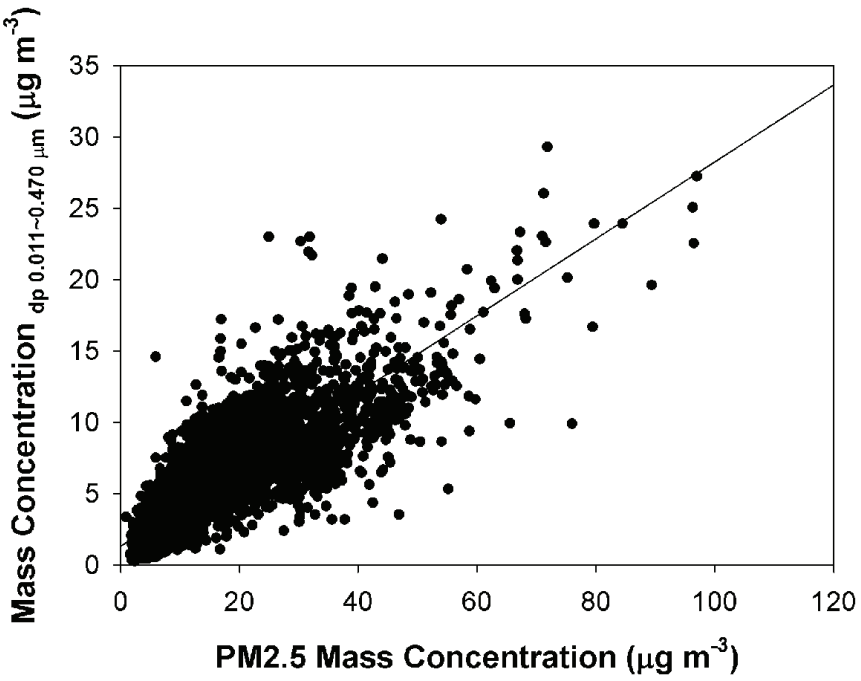

Figure 6. Comparison of mass concentrations of particles in the size range of 11 to 470 nm estimated by using a density of 1,500 kg m^{-3} and $PM_{2.5}$ mass concentrations determined with a 50°C TEOM system.

VARIATIONS IN NUMBER CONCENTRATIONS

The monthly average number concentration and standard deviations of all three particle size ranges (11 to 470 nm) are presented in Table 2. The highest and second-highest mean number concentrations were observed during December 2002 and February 2002, respectively. Although the mean number concentration for August was lower than the annual average concentration, 8,160 cm^{-3}, the highest number concentration was observed at 3 P.M. (EST) on August 26, 2002, with a maximum value of around 61,400 cm^{-3}.

Table 2. Statistical characteristics of monthly averages of particle number concentrations in the size range of 11 to 470 nm.

	Mean	Maximum	Minimum	Std. Dev.	Valid No.
December 2001	9,200	48,800	541	6,500	420
January 2002	9,240	29,000	1,080	4,700	593
February 2002	9,930	37,000	1,470	5,940	658
March 2002	8,910	35,400	865	5,880	700
April 2002	8,700	58,500	1,440	5,300	711
May 2002	7,430	44,600	724	4,700	563
June 2002	7,350	51,900	1,550	4,930	672
July 2002	7,040	57,800	615	5,310	732
August 2002	7,390	61,400	620	5,330	744
September 2002	7,490	48,900	600	5,380	638
October 2002	6,660	28,300	1,140	3,960	550
November 2002	6,950	25,200	950	3,890	721
December 2002	10,100	54,100	830	7,150	711

Figure 7 presents the variation in monthly average concentrations of ultrafine particles in the size range 11 to 50 nm. The mean number concentrations in the winter months, December through February, tended to be higher than the values in summer months, July and August. The highest mean number concentration was found during December 2002, with a mean of 7,630 ± 3,710 (mean ± standard deviation) cm^{-3} while the lowest mean concentration was observed during July, with a value of 4,280 ± 2,250 cm^{-3}. The variations of ultrafine particle number concentrations in the winter months were probably related to increased nucleation of combustion exhaust emitted from motor vehicles, as well as lower average mixing heights and frequent inversions that occur during the winter months. Also, the highest daily average

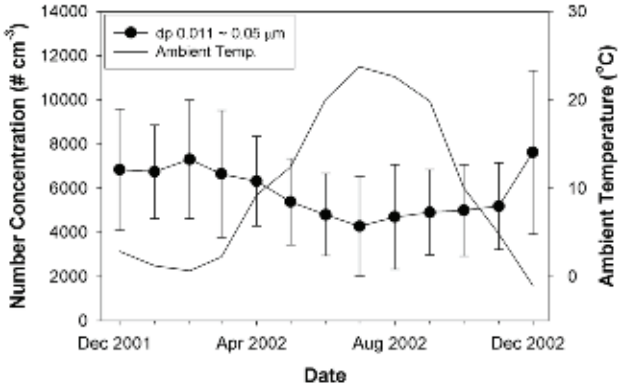

Figure 7. Monthly variations of total number concentration and ambient temperature in Rochester, NY.

ambient temperature, 24ºC, coincided with the lowest number concentration while the lowest ambient temperature, with a mean of 0.7ºC, occurred when the highest number concentration was observed. This suggests that the mean number concentrations were inversely proportional to ambient temperature and that ambient temperature is one of the critical factors that affects the dispersion and formation of ultrafine particles.

However, the highest coefficient of variation, 52%, was found during July, and the highest hourly concentration and abrupt peaks were typically observed during the summer, even though the mean concentration was lower than during the winter months. This indicates that nucleation events of ultrafine particles in the size range 11 to 50 nm are more likely to occur during midday in the warmer season, when photochemical activity is at its peak.

Comparisons of number concentrations of UFP in the three size ranges during weekdays and weekends are shown in Table 3. The average weekday number concentration of ultrafine particles in the size range of 11 to 50 nm was significantly higher than the average weekend values, by a factor of 1.2 to 1.7, and the value was significantly lower on Sundays. For the 50 to 100 nm particles, the average weekday number concentrations were somewhat higher than the average weekend values. But for the fine particles, measuring 100 to 470 nm, there was no difference between weekdays and weekends. The result suggests that one of the main sources of ultrafine particles is motor vehicles. The number concentrations of ultrafine particles are expected to be dominated by local emissions, whereas the variations in fine particles (100 to 470 nm) are expected to be related to regional sources.

Table 3. Number concentrations (#/cm^3) in the three size ranges during weekdays and weekends.

		Diameter		
		11 to 50 nm	50 to 100 nm	100 to 470 nm
Weekday	Mean	6,330	1,550	890
	St. dev.	4,960	1,050	574
Saturday	Mean	5,080	1,440	840
	St. dev.	4,330	1,020	548
Sunday	Mean	3,760	1,330	870
	St. dev.	2,620	947	664

Average number concentrations and standard errors in the three size ranges as a function of the time of day are presented in Figure 8. In the size range of 0.011 to 0.050 μm, the first peak usually occurred between 8:00 to 9:00 A.M. (EST) with a value of 7,700 ± 5,390 cm^{-3} (mean ± standard deviation); while the second peak appeared around 3:00 P.M. (EST) with a value of 8,400 ± 6,510 cm^{-3}. The first peak was present at times corresponding to morning rush hour; while the second peak might be related to nucleation events of ultrafine particles and to the afternoon rush hour when the mixing heights were higher and rush "hour" is more spread in time.

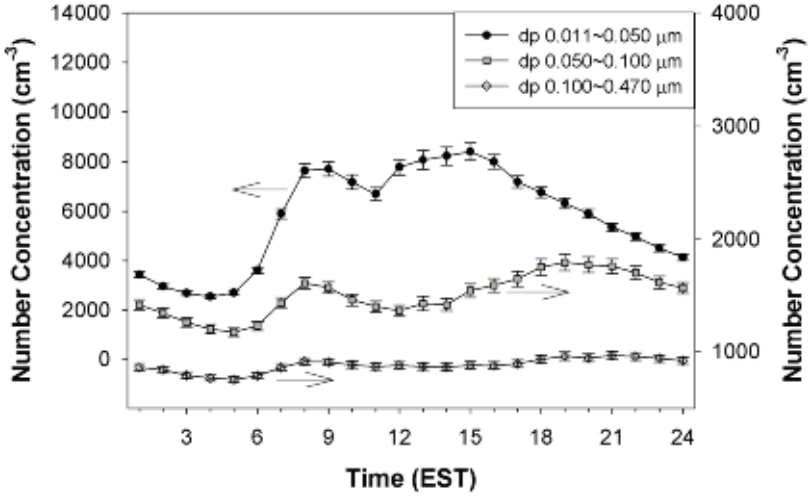

Figure 8. Diurnal variations of number concentrations of particles in the three size ranges during the measurement period December 2001 to December 2002.

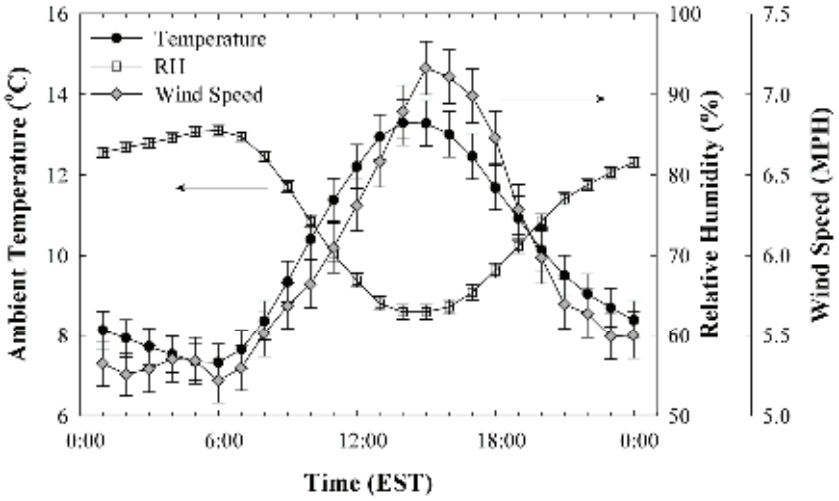

Figure 9. Diurnal variations of ambient temperature, relative humidity, and wind speed during the measurement period December 2001 to December 2002.

Figure 9 shows the variations of meteorological parameters during the same period. Wind speed can be a limited indicator of the mixing height because the diurnal patterns are similar. It appears that the lowest

mixing height when wind speed was at minimum corresponded to the expected traffic hours, so the morning peak of ultrafine particles was the result of the motor vehicle emissions combined with a lower mixing height and lower ambient temperature. However, the afternoon peak, observed during the maximum average wind speed and mixing height period, might be more associated with intensity of solar radiation, because high ambient temperature and low relative humidity strongly depend on the amount of solar radiation, making frequent nucleation events in the afternoon likely.

As seen in Figure 10, strong nucleation events tended to occur more frequently in the afternoon in summer than in winter. Typically, nucleation events of ultrafine particles were observed between noon and 4 P.M., and the result in Figure 10 shows much higher fluctuations of the ultrafine particle number concentrations in the afternoon during the summer.

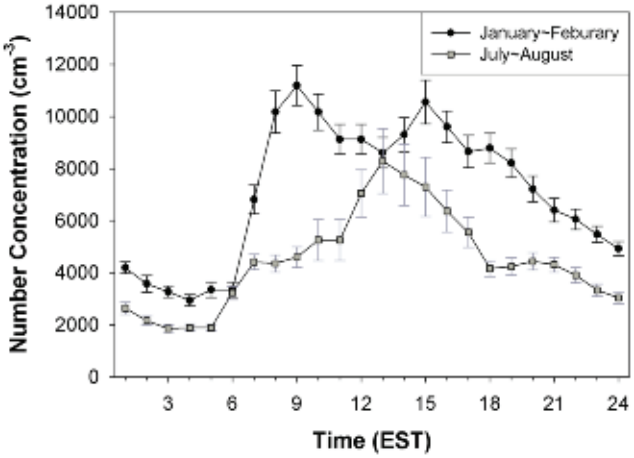

Figure 10. Comparison of diurnal variations in ultrafine particles in the size range of 11–50 nm during winter months and summer months.

In addition, the number concentrations of particles in the size range of 50 to 100 nm were also related to morning rush hour and evening rush hours, as shown in Figure 8. The second peak in the size range of 50 to 100 nm tended to occur after the second peak of ultrafine particles (11 to 50 nm). It might be that the formation of particles (50 to 100 nm) is associated with the coagulation and growth of ultrafine particles after evening rush hour. The hourly variations in fine particles (100 to 470 nm) were negligible, indicating more regional sources.

NUMBER CONCENTRATION AND SIZE DISTRIBUTION DURING NUCLEATION EVENTS

During the measurement period, we typically observed two peaks of rapid increase in the number concentrations of ultrafine particles. Figure 11 illustrates the typical pattern of the two types of nucleation peaks during a day. The color scale shown in Figure 11 shows the concentration of particles in each size class (in dN / dlogDp). The vertical axis is the particle diameter in nanometers, and the horizontal axis is time of day. The particle number concentrations are shown by the color, with highest concentrations being the hottest color. As shown in Figure 11, the first event usually occurred during the morning rush hour, 7 to 9 A.M., with high concentrations of ultrafine particles in the size range 20 to 100 nm (morning events). This size range suggests that these high concentrations are the result of direct emissions, which at that time of day are likely to come from motor vehicles. Another type of event occurred between noon and 6 P.M., with the dominant size of particles tending to be 11 to 30 nm (afternoon events).

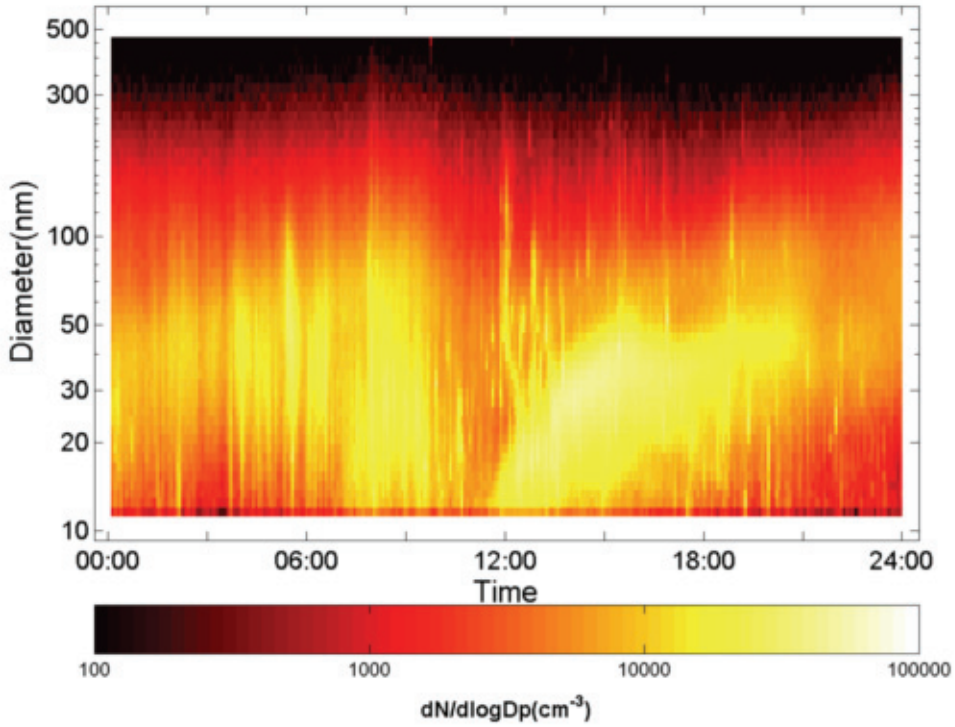

Figure 11. Size distributions and number concentrations of ultrafine particles for a typical type of the morning event and the afternoon nucleation event on April 11, 2002.

The morning events were observed throughout the 13-month period, especially in winter. As can be seen from Figure 12, the increased number concentrations during the events in winter were higher than the values in summer. Note, however, that data for 16 days in December 2001 and nine days in May and October 2002 are missing because of a system malfunction; the count of the nucleation events might be underestimated for these months. The number of morning events in which the number concentrations of

ultrafine particles (11 to 50 nm) exceeded 15,000 cm^{-3} is shown in Figure 12. The average number concentration of these ultrafine particles between 7 and 9 A.M. was approximately 8,600 cm^{-3} on weekdays, whereas morning events were rarely observed on weekends. Morning events were most frequently observed in December, and the highest concentration of ultrafine particles was approximately 30,000 cm^{-3} at 9 A.M. on December 11, 2002, a Wednesday.

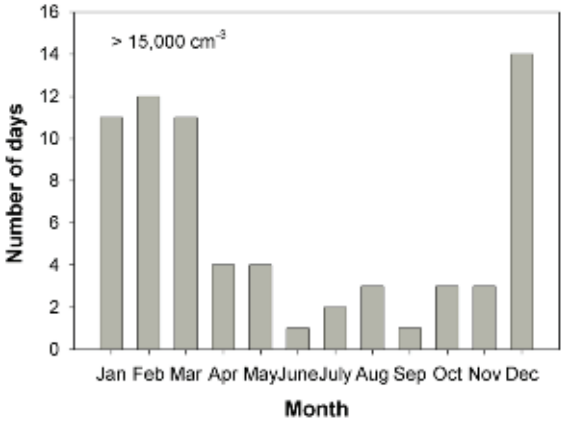

Figure 12. Frequency of morning event days with a number concentration of more than 15000 cm^{-3} during the events in the measurement period.

Seasonal variations tended to follow the typical pattern of mixing depths in winter, which is a season with low mixing depths, temperature inversions, and related low wind speeds. The lowest monthly average ambient temperature during the morning events was recorded in December, with a mean of –3ºC, and the highest temperature was observed in July, with a mean of 22ºC. The results also indicate that the intensity of the morning events was inversely proportional to the ambient temperature in the morning; the number concentrations of ultrafine particles during the events increased at low ambient temperature. The relationship suggests that there is a loss of semivolatile material during the summer months, leading to the evaporation of particles. Sakurai et al. (2003) have found that particles emitted by diesel engines include both semivolatile and nonvolatile components. In the winter, the semivolatile material remains in the particulate phase, whereas in the summer there could be vaporization and loss of particle numbers. In addition, it may be that in colder weather, gaseous emissions nucleate as the exhaust mixes with the cool ambient air (Shi and Harrison 1999). CO concentrations were generally higher during the morning events, as might be expected if both arise from the direct emissions of vehicles.

The afternoon events usually occurred between noon and 6 P.M. and were observed on 149 of the 344 measurement days during the 13-month measurement period. Figure 13 presents the maximum number concentrations of ultrafine particles and time of day. During the afternoon nucleation events, the number concentrations increased by factors ranging from 15 to 60 (usually >1,000 cm^{-3} in average base).

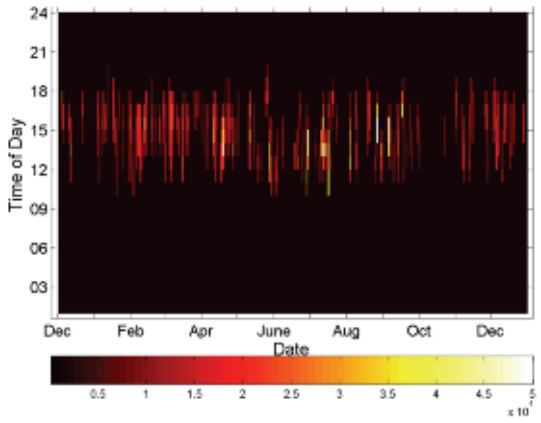

Figure 13. Number concentrations of ultrafine particles in the size range of 11–50 nm during afternoon nucleation events.

Afternoon nucleation events were most common in spring and summer, especially in April (18 days). Note that 16 afternoon events with number concentrations of more than 30,000 cm^{-3} were observed between April and September; while only one such afternoon nucleation event, in February 2002, occurred during the other months. Moreover, unlike the afternoon events in winter, which generally started around 2 P.M. (Figure 10), the nucleation events in summer tended to begin around noon. The results strongly suggest that there was significant seasonal dependence of the afternoon nucleation events.

Typical strong nucleation events were observed on June 29 and August 26, with peak concentration values of 42,000 cm^{-3} and 57,000 cm^{-3}, respectively. The variations of gaseous pollutants and meteorological data during these nucleation events are illustrated in Figures 14 and 15. June 29 was a Saturday, when the effect of motor vehicles was negligible with no morning traffic peak; August 26 was a Monday. In both cases, the nucleation events occurred when ambient temperature was at the maximum for the day and relative humidity ranged from 50% to 70%. Temperature can serve as a surrogate for solar radiation, which was not measured. Since nucleation is expected to occur as a result of oxidation of gaseous precursors like SO_2 to form aerosol sulfate, photochemical activity is expected to be strongly correlated with solar radiation and temperature.

Similar trends in the ambient temperature and relative humidity were observed during the summer nucleation events. The average peak of number concentrations in summer appeared earlier in the day than the afternoon peaks observed in winter, as shown in Figure 10. $PM_{2.5}$ mass and CO concentrations were poorly correlated with the number concentrations of ultrafine particles during the nucleation events ($PM_{2.5}$, $r^2 = 0.02$ and CO, $r^2 = 0.02$), whereas SO_2 increased dramatically as the number concentration of particles rose, as can be seen in Figures 14 and 15. Similar phenomena were observed for the strong nucleation events between April and September 2002.

To identify the effect of SO_2 on the nucleation events, data from April through September were extracted and then regressed against the SO_2 concentrations (Figure 16). As expected, the number concentrations of ultrafine particles during nucleation events were moderately correlated with the SO_2 concentrations ($r^2 = 0.48$). However, in cooler months, the correlation between SO_2 and ultrafine particle concentrations was much lower ($r^2 = 0.10$). These results suggest that local SO_2, mostly emitted and transported from stationary sources, such as the nearby coal-fired power plants, might affect the afternoon nucleation events in summer. Strong peaks of SO_2 were observed when wind direction was from the northwest, where two SO_2 sources are located. Thus, photochemical reactions oxidizing SO_2 to sulfuric acid and its subsequent nucleation with water and possibly ammonia appear to be primarily responsible for the nucleation events. The newly nucleated ultrafine particles can be considered secondary particles formed from the photochemical reaction of SO_2 on warm afternoons. During the rest of the year, there may not be sufficient photochemical activity to produce significant conversion of locally emitted SO_2, and thus more distant

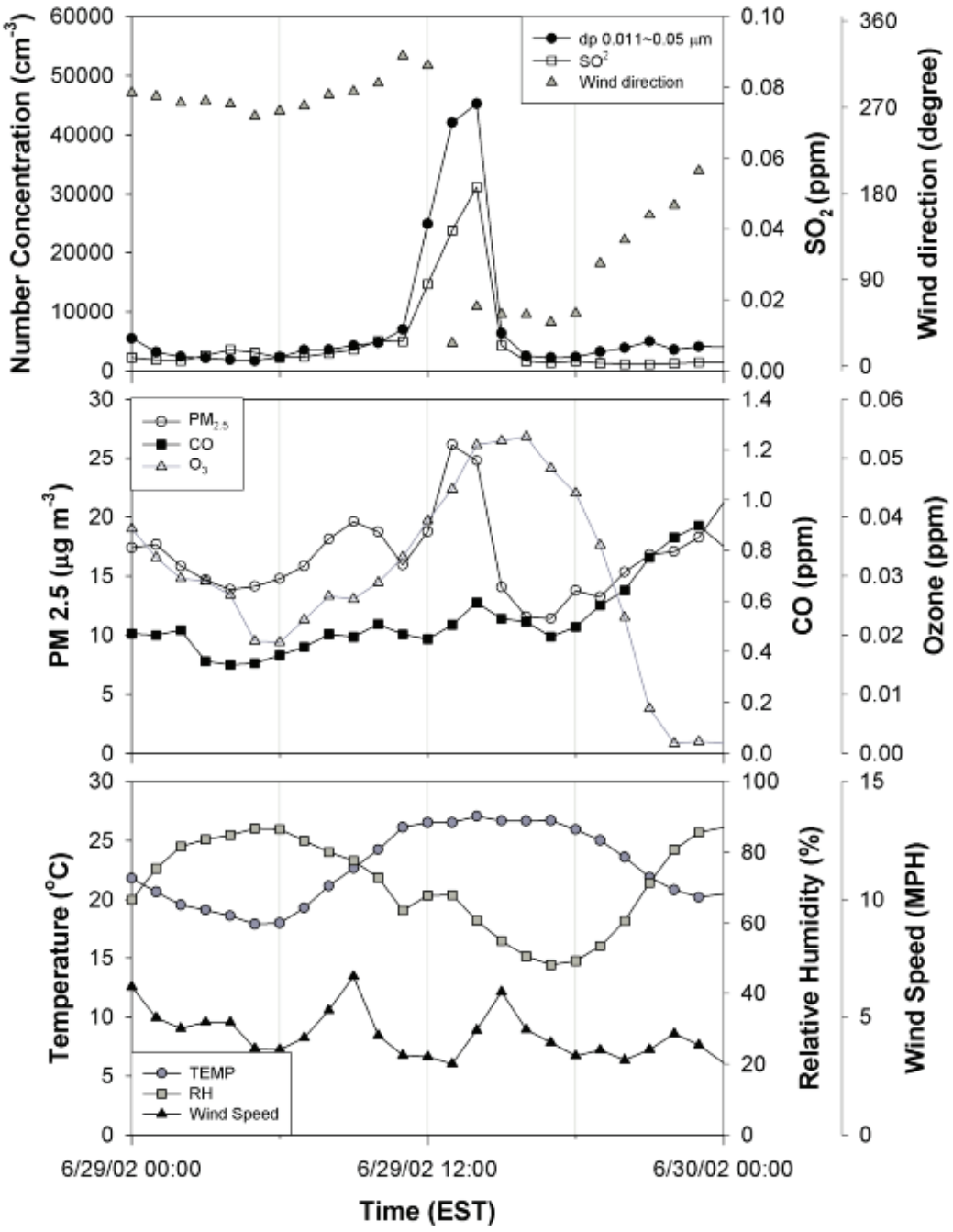

Figure 14. Comparison of number concentration, SO_2, CO, O_3, $PM_{2.5}$ mass, wind direction, and wind speed during an ultrafine nucleation event on June 29, 2002.

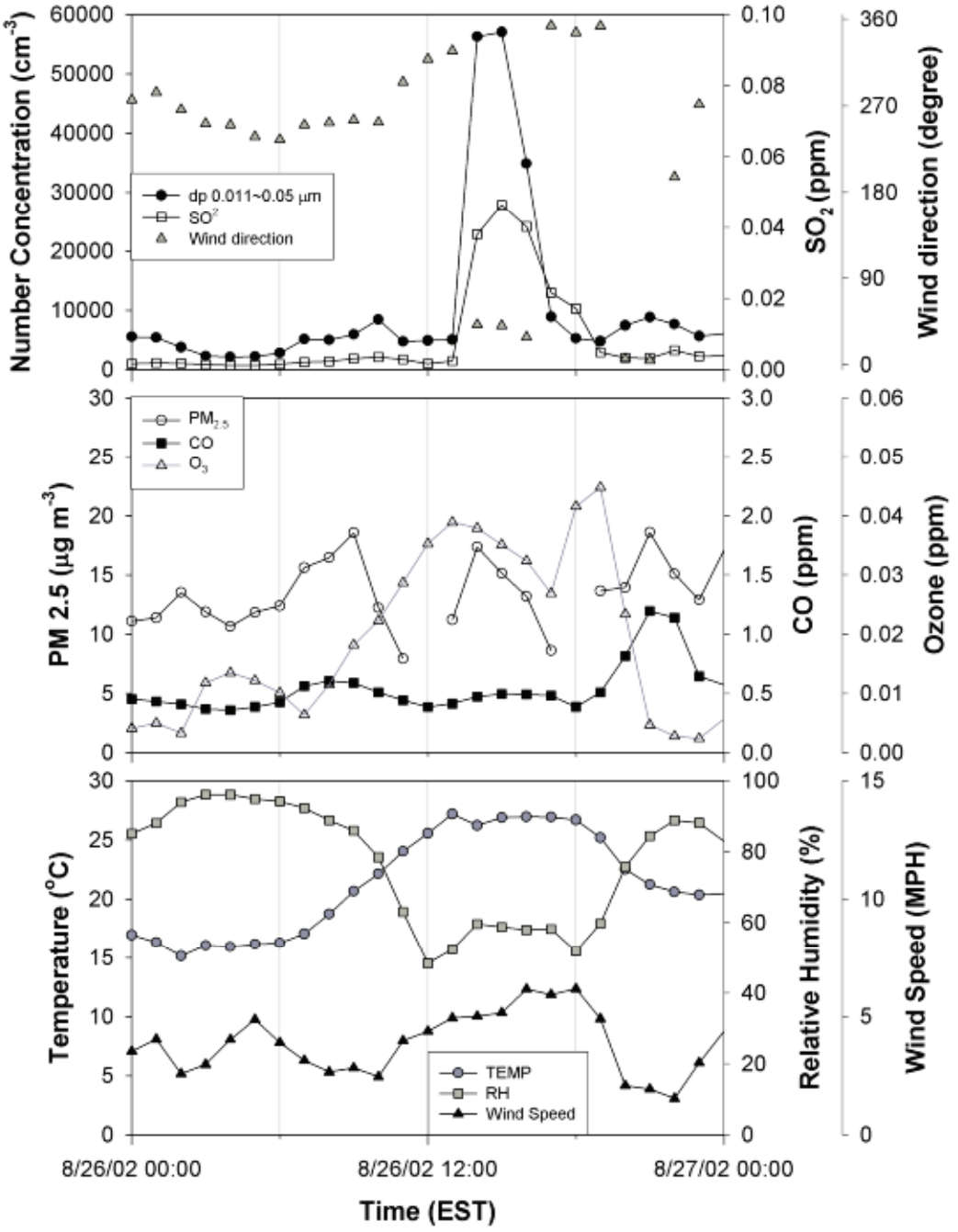

Figure 15. Comparison of number concentration, SO_2, CO, O_3, $PM_{2.5}$ mass, wind direction, and wind speed during an ultrafine nucleation event on August 26, 2002.

regional sources may contribute to background concentrations of sulfuric acid. In an urban area, there could be sufficient ammonia from human activities and traffic, along with some locally produced sulfuric acid, to promote the nucleation observed in the weak afternoon events.

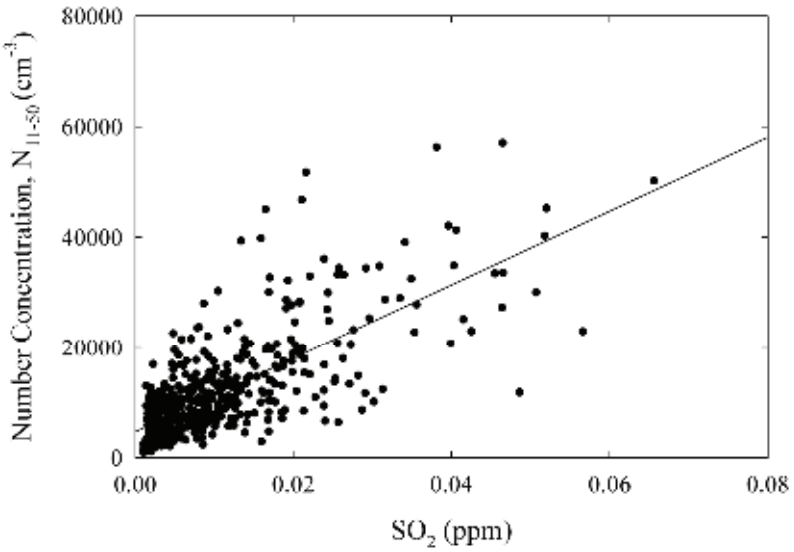

Figure 16. Correlation between number concentrations of ultrafine particles and SO_2 concentrations during the afternoon nucleation event from April to September 2002.

Although there was no direct correlation between ozone concentrations and UFP number concentrations during the nucleation events, the events coincided with higher ozone, and higher UV irradiation was also likely. The nucleation events seem associated with photochemical reactions with high solar radiation. This result is consistent with observations of Pirjola and Kulmala (1999), who reported that the strength of a nucleation event increased as a function of UV-B irradiation penetrating into the troposphere and stimulating the SO_2 oxidation process.

There were two types of afternoon nucleation events. One type involves only nucleation in the size range 11 to 30 nm; while the other type begins with nucleation followed by particle growth up to approximately 100 nm throughout the late afternoon and evening. The first type of event—described as a plume event by Woo et al. (2001)—is associated with local sources and little or no growth of the nucleated particles. Growth events are associated with more regional phenomena, as Stanier et al. (2004) observed at several sites in Pennsylvania. For growth to occur, condensable vapor must be produced over a large area, which may provide adequate time for photochemistry to convert volatile organic compounds into less volatile compounds that can then condense onto the particles and permit them to grow.

An example of a nucleation and growth event as shown by the banana shape of Figure 17: the growth events persisted for 18 hours up to approximately 100 nm in diameter after the nucleation began around noon, and then disappeared at the time of the morning event, around 7 A.M. The growth events were more

clearly observed in spring and summer, especially in April. This period of more common growth events may be the result of the combination of sufficient sunlight for photochemistry, emissions of biogenic precursors in the early spring, and lower temperatures at that time of year that result in lower saturation vapor pressures for the semivolatile organics that are responsible for the growth. The growth rates ranged from 5 to 13 nm/hr, with a mean of 8 nm/hr. During the growth events, average relative humidity and ambient temperature were approximately 53% and 17ºC, respectively, while main wind direction was southwesterly, with an average speed of 3 m/sec. In general, steady wind direction was responsible for the effective growth of ultrafine particles, whereas wind speed had little effect.

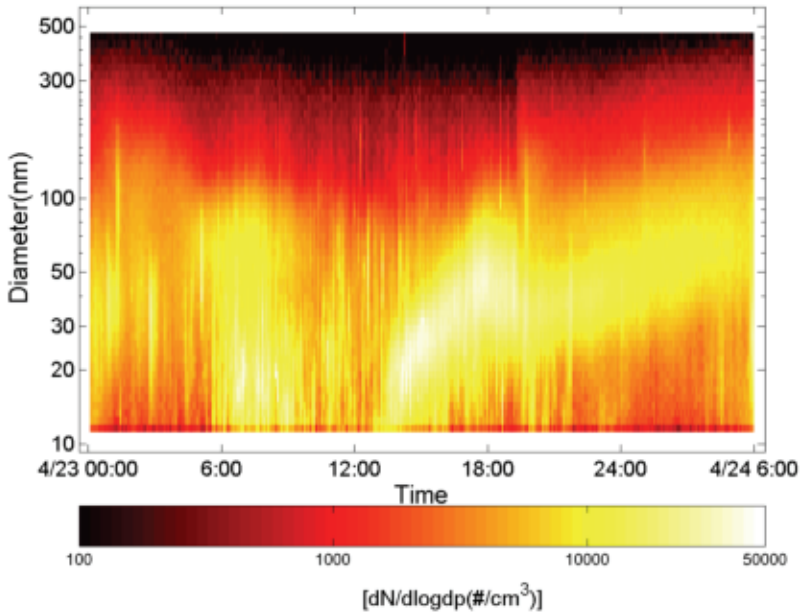

Figure 17. The typical growth event observed for 18 hours from 23 through 24 April 2002.

Section 5

CONCLUSIONS

The data collected in this 13-month study of fine and ultrafine particles, sampled in Rochester, NY, indicate that mass concentrations of $PM_{2.5}$ were poorly correlated with number concentrations of ultrafine particles, whereas fine particle number concentrations were likely correlated with $PM_{2.5}$ ($r^2 = 0.32$).

Ultrafine particles show both seasonal and daily variations. Mean number concentrations during winter were higher than the values in summer, probably because of the cooling of combustion exhaust of motor vehicles combined with the lower mixing heights and inversion episodes typical of winter. Strong nucleation events of ultrafine particles were generally observed in summer. It is anticipated that the particles associated with the morning events related to motor vehicles were likely carbonaceous. The afternoon nucleation events, however, were likely to be partially neutralized sulfate because of a strong association with SO_2 concentrations.

Two peaks in the number concentrations were typically found in the size range of 11 to 50 nm as a function of time of day (Figure S3). The first event occurred around 8 A.M. During the winter months, this peak was associated with increased levels of CO. These particles appear to be from direct particulate emissions from motor vehicles during the morning rush hour. The second peak typically occurred between noon and 6 P.M. and was associated with nucleation events forming new ultrafine particles.

The weekday average number concentration of ultrafine particles (11 to 50 nm) averaged during weekdays was significantly higher than the value averaged during weekends, whereas for 100 to 470 nm particles, there was no difference between weekdays and weekends. The likely source of the 11 to 50 nm particles is motor vehicles.

There were two types of nucleation events that usually occurred between noon and 6 P.M.; and were most evident between April and September. These nucleation events typically occurred when ambient temperature was high and relative humidity was around 60%. These events coincided with strong peaks of SO_2 and with northwesterly winds from the direction where three SO_2 sources are located, and were closely associated with peaks of number concentration of ultrafine particles ($r^2 = 0.48$). During weak nucleation events the correlation between SO_2 and number concentrations was poor, and there were no significant correlations between number concentrations and $PM_{2.5}$ or CO.

The afternoon nucleation events were often accompanied by the growth of ultrafine particles. Newly formed particles tended to grow into the accumulation mode of particles throughout the night, and diminished in the morning.

Clearly the inhabitants of Rochester are regularly exposed to high concentrations of ultrafine particles either coming from motor vehicle emissions or nucleation events. The most common nucleation events are clearly the result of emissions from local sources. Given the strong relationship with SO_2, the nucleation events are almost certainly related to the emissions from the local coal-fired power plant. The origins of the nucleation with growth events are not as clear.

The data from this project begins to build a base that can be used in future epidemiological studies. Rochester is somewhat larger in population than Erfurt and thus, with several years of such data, it may be possible to explore the relationship between particle number concentrations and adverse health effects such as mortality, emergency room visits, and hospitalizations. Other than Atlanta, Rochester is the only location in the United States where there could be sufficient data developed to permit an epidemiological study to be conducted, and we suggest that such a study be undertaken in the near future.

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