Journal of the Air & Waste Management Association

ISSN: 1096-2247 (Print) 2162-2906 (Online) Journal homepage: http://www.tandfonline.com/loi/uawm20

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To cite this article: Cheol-Heon Jeong , Greg J. Evans , Philip K. Hopke , David J. Chalupa & Mark Utell (2006) Influence of Atmospheric Dispersion and New Particle Formation Events on Ambient Particle Number Concentration in Rochester, United States, and Toronto, Canada, Journal of the Air & Waste Management Association, 56:4, 431-443, DOI: 10.1080/10473289.2006.10464519

To link to this article: http://dx.doi.org/10.1080/10473289.2006.10464519

Published online: 29 Feb 2012.

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TECHNICAL PAPER

ISSN 1047-3289 *J. Air & Waste Manage. Assoc.* **56**:431–443
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Influence of Atmospheric Dispersion and New Particle Formation Events on Ambient Particle Number Concentration in Rochester, United States, and Toronto, Canada

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ABSTRACT

Continuous measurements of particle number concentrations were performed in Rochester, NY, and Toronto, Ontario, Canada during the 2003 calendar year. Strong seasonal dependency in particle number concentration was observed at two sites. The average number concentration of ambient particles was 9670 ± 6960 cm^{-3} in Rochester, whereas in Toronto the average number of particles was 28,010 ± 13,350 cm^{-3}. The particle number concentrations were higher in winter months than in summer months by a factor of 1.5 in Rochester and 1.6 in Toronto. In general, there were also distinct diurnal variations of aerosol number concentration. The highest weekdays/weekends ratio of number concentration was typically observed during the rush-hour period in winter months with a ratio of 2.1 in Rochester and 2.0 in Toronto. The correlation in the total particle number concentrations between the two urban sites was stronger in winter because of the common urban traffic patterns, but weaker in summer because of local sulfur dioxide (SO_2)-related particle formation events in Rochester in the summer. Strong morning particle formation events were frequently observed during colder winter months. Good correlations between particle number and carbon monoxide (CO) as well as temperature suggested that motor-vehicle emissions lead to the formation of new particles as the exhaust mixes with the cold air. Regional nucleation and growth events frequently occurred in April. Local SO_2-related particle formation events most frequently occurred in August. SO_2 and UV-B were highly correlated with particle concentration, suggesting a high association of photochemical processes with these local events. A high directionality in a northerly direction was observed for particle number and SO_2, indicating the influence of point sources located north of Rochester.

IMPLICATIONS

Current regulation for PM2.5 mass provides little information about number concentration of UFP, but epidemiological studies suggest that the effect of UPF number concentration may be even more relevant concerning health effects than mass concentration. No significant correlation between UFP and PM2.5 indicates a need for collocation. Particle number concentration was typically 50% higher in winter than in summer. Strong relationships between UFP number and traffic activities as well as SO_2 were observed in two urban environments. The study describes the sources of UFP and the formation characteristics in these urban areas.

INTRODUCTION

Recently, attention has focused on sources of primary fine particles in the troposphere because of their impact on radiation transfer through the atmosphere of the Earth and global climate change.[1,2] Ambient particles have also been proposed as a contributor to climate change by acting as cloud condensation nuclei (CCN) for the formation of clouds.[3] Because of the complex chemistry of ambient aerosols, large uncertainties exist in understanding the temporal and seasonal influences on the number and size distributions of the urban ambient aerosol.

Over the past decade, epidemiological and laboratory studies have consistently shown relationships between adverse human health effects, including increases in mortality, morbidity, and symptoms of certain illnesses, and exposure to ambient particulate matter.[4–8] The correlations between particles less than 2.5 μm in diameter ($PM_{2.5}$) and all-cause mortality are stronger during the warm season than those during the cool season in the United Kingdom, suggesting significant seasonal dependency of adverse health effect.[7]

Several PM components have been hypothesized to play a role in toxic responses, including acid aerosols, metals, sulfates, nitrates, and ultrafine particles. A number of studies have investigated the effects of ultrafine particles (UFP, particle diameter [dp] <100 nm) on health effects.[9–13] Seaton et al.[9] reported that UFP can penetrate

Figure 1. Location of sampling sites in Rochester, NY, and Toronto, ON.

pulmonary interstitial spaces, provoking inflammation. The high specific surface area of UFP, which can catalyze reactions and adsorb many toxic substances, makes them a carrier of these substances into the deep lung during inhalation. In addition, toxicological studies have made considerable progress to provide explanations and evidence for the adverse health effects associated with exposure to UFP as determined in epidemiology.[13] To accurately assess the impact of atmospheric aerosols on climate and health, a better understanding of the formation, transformation, and removal processes of UFP in the atmosphere is essential. It is also important to compile long-term measurements to identify temporal and spatial variations of particle number concentrations to provide a basis for assessing the influence of UFP on human health and thereby start to develop appropriate guidelines or regulations.

Particle number concentration measurements of the size distributions and number concentrations of UFP were conducted for 25 months in Rochester, NY. In the previous study of UFP number size distributions in Rochester, NY, during 2002, significant diurnal and seasonal differences in the number concentration of UFPs were found.[14,15] The differences were ascribed to differences in nucleation events, sources, and atmospheric dispersion conditions. In the present study, number size distributions collected throughout 2003 are presented and compared with a year of number concentration data from a high-population city, Toronto, Ontario, Canada. The difference in particle number concentrations between these two urban sites could show differences in the contributions of local sources and removal mechanisms, thereby providing a better understanding of the dynamics of UFP.

The formation and growth of atmospheric aerosol particles as small as 3 nm in diameter have been observed frequently in a number of locations around the world.[16–19] To identify seasonal differences and examine specific factors that might influence the formation of UFP, nucleation events in the continental boundary layer need to be compared with the concentrations of other pollutants and relevant meteorological parameters. This project focused on identifying new particle formation and their subsequent particle growth and assessing the influence of gaseous pollutants, particle mass, and meteorological parameters on particle formation.

MATERIALS AND METHODS

Monitoring Locations

Particle number concentration measurements were conducted at two urban sites, Rochester, NY, and Toronto, Ontario, Canada, from January 1 to December 29, 2003. Locations of the sampling sites in Rochester and Toronto are shown in Figure 1. The Rochester site was located at the New York State Department of Environment Conservation (NYSDEC) downtown air monitoring site (latitude 43.16, longitude −77.60). This site was surrounded by an inner-loop road within 1 km of downtown Rochester and ~50 m from the nearest major road. Sampling was performed on the roof of the central fire station, ~10 m in height. In addition to the particle size distribution and number concentration, hourly averaged $PM_{2.5}$, sulfur dioxide (SO_2), carbon monoxide (CO), wind speed, and wind direction data operated by NYSDEC were obtained at this site. Ozone (O_3), ambient temperature, and relative humidity (RH) were obtained from the NYSDEC Rochester primary air monitoring site (latitude 43.17, longitude −77.55), ~4 km east of the downtown Rochester site. Solar radiation data, UV-B, was obtained from the U.S. Department of Agriculture (USDA) UV-B monitoring station at Geneva, NY (latitude 42.86, longitude −77.02), located 55 km southeast of the downtown Rochester site.

Table 1. Statistical characteristics of $PM_{2.5}$ and gaseous pollutants in Rochester, NY, and Toronto, Ontario, Canada, January 1–December 29, 2003.

	Rochester				Toronto					
	$PM_{2.5}$ ($\mu g\ m^{-3}$)	SO_2 (ppb)	O_3 (ppb)	CO (ppm)	$PM_{2.5}$ ($\mu g\ m^{-3}$)	SO_2 (ppb)	O_3 (ppb)	CO (ppm)	NO (ppb)	NO_2 (ppb)
Mean	11.2	5.4	25.0	0.55	8	3	24	0.49	9	23
SD	7.1	5.8	16.4	0.23	8	4	16	0.21	17	12
Min	0.3	0.1	0.1	0.02	0	0	0	0	0	0
5%	4.0	1.3	1.7	0.26	0	0	3	0.20	1	8
25%	6.6	2.4	12.3	0.40	3	1	11	0.35	1	14
Median	9.1	3.5	24.4	0.52	6	2	22	0.47	3	21
75%	13.7	6.1	34.5	0.65	11	4	33	0.60	9	30
95%	26.0	15.2	54.6	0.95	25	11	53	0.86	35	46
Max	65.2	76.7	99.1	2.82	65	54	115	2.40	266	87
N[a]	8693	8448	8423	8607	8610	8638	8623	8142	8541	8544

[a]Valid number of hourly averaged values.

Ambient aerosol number concentration measurements in Toronto were performed in the Wallberg building at the University of Toronto in downtown Toronto located ~150 km northwest of the Rochester site. The Toronto site (latitude 43.66, longitude −79.39) was situated 2 km north of Gardiner Expressway, 3 km west of Don Valley Parkway, and at the intersection of local streets having high traffic volumes during most of the day (9:00 a.m.–6:00 p.m.). Meteorological data, gas-phase pollutants (SO_2, nitric oxide [NO], nitrogen dioxide [NO_2], CO, O_3) and $PM_{2.5}$ mass were obtained from the Ontario Ministry of the Environment (MOE) Toronto Downtown site (latitude 43.66, longitude −79.38), 1 km northeast of the Toronto site.

Particle Size Distribution and Number Concentration

In Rochester, number and size distributions of particles with a range of 10–500 nm were measured using a scanning mobility particle sizer (SMPS) consisting of a differential mobility analyzer (DMA; model 3071, TSI Inc.) and a condensation particle counter (CPC; model 3010, TSI Inc.). The time resolution of the SMPS data with 32 size bins from 10 to 500 nm was 5 min, giving 288 distributions a day. Total particle number concentrations in Rochester were integrated from the measured size distributions. The data for each size distribution were inspected and anomalous distributions were omitted from the analysis. To minimize instrument uncertainties, the lowest range (<11 nm) and the highest range (>470 nm) of size distributions were excluded. Regular flow checks were made to ensure that the system was functioning properly. The quality of the SMPS measurement was ensured throughout the study using laboratory aerosols; several side-by-side measurements were made comparing results with another similar SMPS system.

Total particle number concentrations in Toronto were measured using a CPC (model 3020, TSI Inc.). Hereafter, concentrations measured by this CPC will be referred to as the total number concentration in Toronto. The scanning time was 10 min, and measured CPC data were converted into hourly means for comparison with other hourly averaged results. The CPC had a lower cutoff at 7-nm diameter at which 50% of particles were counted, indicating that the CPC could measure the particles beyond the size range covered by the SMPS in Rochester. Thus, the CPC concentration could be larger than the total concentration measured by the SMPS in the presence of particles below the 11-nm lower size limit of the SMPS. The maximum detectable concentration was 10^7 cm^{-3}. The 3020 CPC used single-particle counting for concentrations below 10^3 cm^{-3} and used a photometric method for higher concentrations.

Air Pollutants and Meteorological Parameters

Table 1 shows statistical characteristics of $PM_{2.5}$ and gaseous pollutants at the two sampling sites. NYSDEC monitored $PM_{2.5}$ using a tapered element oscillating microbalance (TEOM; model 1400a, R&P) at the downtown monitoring site in Rochester, NY. The TEOM system directly measures particle mass collected on a filter by drawing ambient air through a filter at a constant flow rate, continuously weighing the filter and calculating high time resolution mass concentrations at 50 °C. No corrections were made to the TEOM data to account for the well-known disadvantage: losses of semivolatile compounds (semivolatile organic compounds [SVOCs]). At the MOE Toronto downtown site, $PM_{2.5}$ was measured using a TEOM with a system equilibration system at 30 °C to minimize the loss of SVOCs. Although Rochester is a smaller city as compared with Toronto, annual average concentrations of SO_2 were significantly higher in Rochester by a factor of 2, suggesting the high impact of fossil fuel or other industrial combustion sources near the city of Rochester.

In addition to $PM_{2.5}$ and gaseous pollutants, the variations of meteorological parameters (wind speed, wind direction, temperature, RH) were compared at the sampling sites. Annual average wind speed in Rochester was ~2.7 m sec^{-1}. The average wind speed in winter months (December–February) was ~24% higher than the average in summer months (June–August). Over the study period, the most frequent wind direction was from the northwest (280–300°). The same pattern of wind direction was observed in the winter and summer months. Because a major coal-fired power plant is located northwest of the

downtown Rochester site, atmospheric pollutant concentrations measured at the monitoring site were likely influenced by the plume from the coal power plant. In Toronto during 2003, the average ambient temperature was ~7.6 °C, ranging from −30.2 °C to 33.1 °C. The wind speed in Toronto reached a high of 11.7 m sec^{-1}, with an average value of 2.9 m sec^{-1}. The prevalent wind direction was west (250–270°), although yearly wind directions tended to be more evenly distributed in Toronto. Only winds from northeast and south were not as common.

Correlation Analysis

Spearman rank–ordered correlations were performed between hourly particle number concentration and ambient pollutants as well as meteorological parameters measured in the study. A nonparametric procedure replaces the variables by their ranks in the calculation of the correlation coefficient. Spearman correlation coefficients, rho (r), are obtained as follows:

$$r = 1 - 6 \sum_{i=1}^{n} \frac{d_i^2}{n(n^2 - 1)}$$

where d is the difference in the ranks of two variables and n is the number of data points. All correlations analyses were performed for pairs of data. The Spearman rank correlation coefficients and P values were calculated using the nonparametrics procedure in the STATISTICA software.

PARTICLE NUMBER CONCENTRATION

Average Particle Number Concentration Comparison

For the Rochester particle size distribution data, the measured data over the sampling period were classified into the three size ranges, UFP_{11-50} (11 < dp <50 nm), UFP_{50-100} (50 < dp <100 nm), and fine particles ($FP_{100-470}$; 100 < dp <470 nm), and the number concentrations of ambient particles in the size ranges 11–50 nm (N_{11-50}), 50–100 nm (N_{50-100}), and 100–470 nm ($N_{100-470}$) were estimated. This separation into three size ranges facilitated comparison with results of other UFP size-distribution studies.[11,14]

Statistical values of the number concentration of ambient particles in the three size ranges from January to December 2003 in Rochester are shown in Table 2. N_{11-50}, showing the highest standard deviation (SD), accounted for ~70% of total number concentration of particles (N_{11-470}), whereas the $N_{100-470}$ contributed only 11% of the total number concentration. The average ratio of N_{11-100} ($N_{11-50} + N_{50-100}$) to N_{11-470} was ~0.89, which is comparable to the values reported in European cities, where the contributions of UFP (10 < dp <100 nm) to total particle number concentration (10–500 nm) ranged from 88 to 94%.[20] Note that the number concentrations of the smallest size range in the study (10 nm) were excluded to reduce uncertainty introduced by measurements near the detection limit of the SMPS system. The volume-based concentrations were dominated by the $FP_{100-470}$ that comprise 86% of the total volume concentration of particles (11–470 nm), whereas only 3% of the total volume was due to UFP_{11-50}.

Table 2. Statistical characteristics of particle number concentrations in Rochester, NY, and Toronto, Ontario, Canada, during the measurement period, January 1–December 29, 2003.

	Rochester, Diameter Range (nm)				Toronto, Diameter Range (nm)
	11–50	50–100	100–470	11–470	<1000
Mean	6720	1870	1080	9670	28,010
SD	5770	1380	760	6960	13,350
Min	220	70	80	730	2180
5%	1170	380	230	2310	10,500
25%	2920	910	500	5100	18,140
Median	5060	1540	880	7900	26,070
75%	8600	2420	1440	12,030	35,530
95%	17,710	4570	2580	22,870	52,460
Max	78,280	11,880	5270	85,800	99,890
N[a]	7876	7876	7876	7876	7281

[a]Valid number of hourly averaged values.

The annual mean, SD, and median of the total number concentrations measured in Toronto using a CPC are also given in Table 2. On average, the total number concentration was higher in Toronto than in Rochester by a factor of around 3. This difference is reasonable because the monitoring site in Toronto was located on a busy street affected by a high number of motor vehicles. The average number concentration was comparable to values reported in Helsinki, where the total number concentrations using a CPC ranged from 2000 to 80,000 cm^{-3} with an average of 20,000 cm^{-3}.[21] In comparable U.S. eastern cities, average particle number concentrations were ~23,100 cm^{-3} (3–2000 nm) in Atlanta and 22,000 cm^{-3} (3–500 nm) in Pittsburgh.[18,19] In contrast, the present variation in the total number concentration was higher in Rochester (mean/SD = 1.4) than in Toronto (mean/SD = 2.1), suggesting that there was less fluctuation in the production and/or removal rates in Toronto.

Seasonal Variation in Particle Number Concentration

Box and whisker plots for the total particle number concentrations based on hourly averages in Rochester and Toronto are presented in Figure 2. The upper and lower dots in the plot represent the 95th and 5th percentiles. The average data capture rate, the fraction of the time for which measurements were available in Rochester, was ~89% in Rochester, with the lowest value of 64% in December, whereas the rate in Toronto ranged from 41 to 100% with an average of 84%. The lowest data capture rate was in July, which produces a larger uncertainty for the July monthly average value at the Toronto site. In Rochester, the highest monthly average of total number concentration (N_{11-470}) was observed in February, with a value of 10,100 ± 8140 cm^{-3} (mean ± SD), whereas the lowest average was detected in July, with a value of 5100 ± 3570 cm^{-3}. This seasonal dependency in number concentration was also found in Toronto, with the highest average (40,360 ± 10,910 cm^{-3}) in February and the

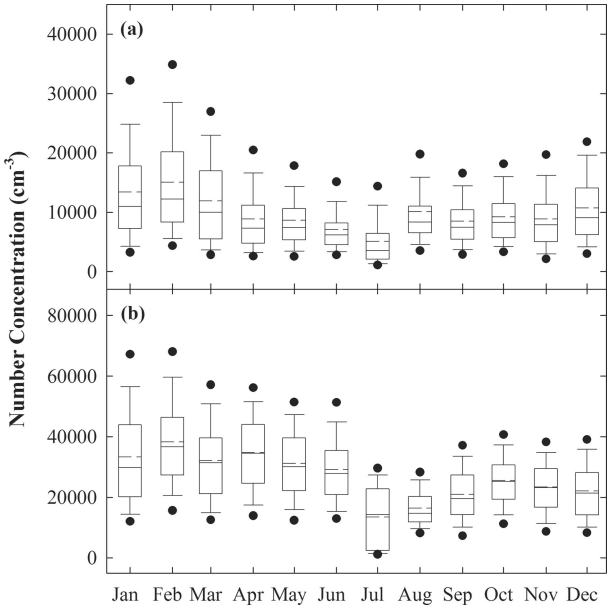

Figure 2. Monthly statistics of hourly averaged particle number concentrations in Rochester and Toronto from January to December 2003. Box and whisker plot indicate median and quartile (box), mean (dot lines), 90% quartile (whiskers), and 5/95% (dots).

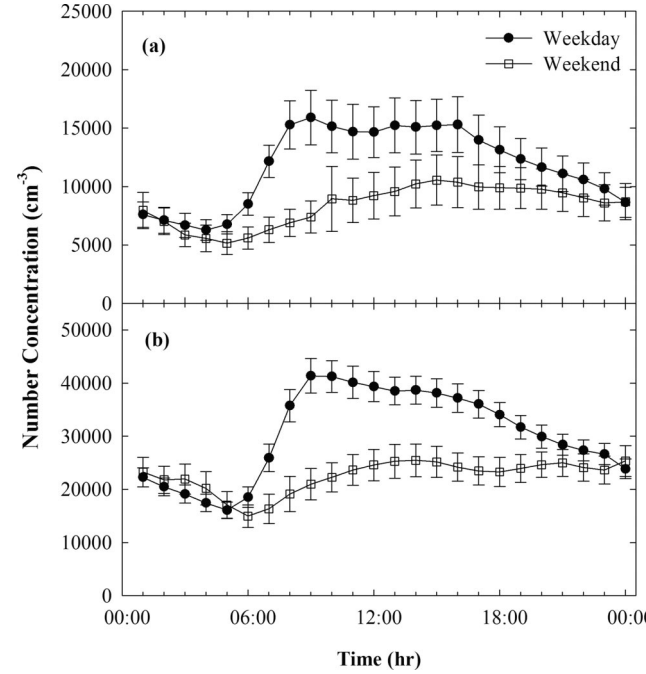

Figure 3. Diurnal variations of particle number concentrations on weekdays and weekends in Rochester (a) and Toronto (b).

lowest value (13,460 ± 10,720 cm^{-3}) in July, indicating a strong seasonal variation of the particle number concentrations in the urban areas. Although the monthly average concentrations in winter and early spring were higher than the averages in summer months, the highest episodic concentrations were often observed in summer months because of particle formation events in the presence of strong photochemical activity. Particle formation events are discussed in the section Particle Formation Events in Rochester. This seasonal variation is quite consistent with results of previous aerosol number concentration studies.[14,22] In the 2002 study, the monthly mean number concentrations were inversely proportional to ambient temperature and a similar trend was also found in this study, suggesting that ambient temperature is one of the critical factors that affect the dispersion and formation of UFP in the atmosphere. One hypothesis for a seasonally dependent particle formation mechanism is that the formation of new particles can be enhanced by the mixing of air parcels with large temperature and RH differences. Shi and Harrison[23] reported that the cooling of motor-vehicle emissions led to higher binary nucleation rate. In the processes of the dilution and cooling of freshly emitted gaseous combustion exhaust in the atmosphere, UFP formation appears to be enhanced by low temperatures in the winter months.

Seasonal variations of particle number concentrations are also affected by atmospheric physical properties such as mixing height. Seasonal and diurnal dilution ratios resulting from the differences in mixing heights between the warm and cold seasons were also examined to evaluate the seasonal dependency of aerosol number concentrations. To clarify the seasonal dependency of aerosol number concentrations, mixing heights were estimated by using the Global Final (FNL) archive of the National Oceanic and Atmospheric Administration (NOAA) Air Resource Laboratory (www.arl.noaa.gov/ready). However, the findings were inconclusive. It was recognized that the mixing heights derived from the regional NOAA data likely did not capture the complex meteorology within these two lakeshore urban environments. Use of mixing height values based on local measurements would have been preferable but these were not available. Hence, quantitative evaluation of the influence of mixing height on number concentration was not possible.

Diurnal Variation of Particle Number Concentration

The diurnal variations of particle number concentration on weekdays and weekends are presented in Figure 3. The diurnal patterns of number concentration showed a strong relationship between a recurring morning increase and traffic activities in the two cities. On weekdays, the increase usually occurred between 7:00 and 10:00 a.m., consistent with the traffic morning rush hour. The concentration of UFP remained elevated until the late afternoon despite an increase in mixing throughout the day. The afternoon concentrations of UFP might be more associated with both vehicle emissions and nucleation events. In addition, the morning rise in UFP concentrations was more prominent in Toronto than in Rochester, suggesting a more significant impact of traffic sources on the particle number concentration in this highly populated area. On weekends, the diurnal variation of particles was characterized by less temporal variation with lower concentrations, suggesting a weekly pattern in the formation of ambient UFP in urban areas.

Average ratios of the weekday to weekend aerosol concentrations are shown in Figure 4 for the different

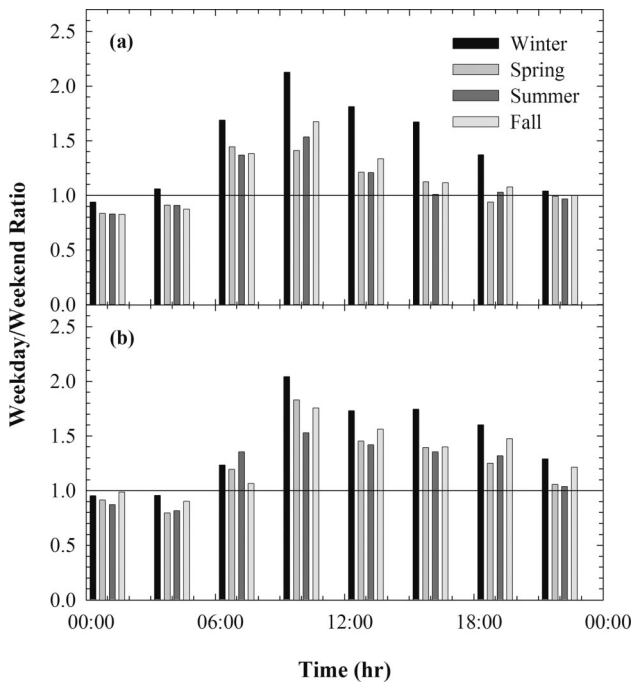

Figure 4. Diurnal variations of weekday/weekend ratios for particle number concentrations in Rochester (a) and Toronto (b).

seasons in Rochester and Toronto. The weekdays/weekends ratio during the winter months (December–February) was the largest, varying from 0.9 to 2.1 with an average of 1.2 in Rochester and from 1 to 2 with an average of 1.2 in Toronto. The ratios are comparable to the value of 1.26 reported for an urban site in Australia.[24] The highest ratio was observed between 7:00 and 10:00 a.m. during the winter months, indicating a significant impact of motor-vehicle emissions in the winter months. Based on the analysis of data from Rochester, the average CO concentration for weekdays was higher than the average for Saturdays and Sundays (14% and 23%, respectively), whereas there were no significant differences in $PM_{2.5}$ and SO_2 between weekdays and weekends. A similar trend was also found for the analysis of the Toronto data: NO and NO_2 concentrations were 41% and 26% higher on weekdays than on weekends, indicating that most of these pollutants were related to vehicular emissions.

Correlation between Particle Numbers at Two Monitoring Sites

The Spearman rank order correlations were performed to evaluate correlation between hourly averaged particle number concentrations at the two sampling sites during different seasons. The Spearman correlation coefficient (r) ranged from 0.15 to 0.52 with a mean of 0.40, showing the highest correlation in winter months (December–February) and the lowest correlation in summer months (June–August). This apparent relationship can be explained by the common traffic patterns (similar morning and evening rush hours) in the two urban areas, especially in the winter months. The lowest correlation between particle numbers during the summer months was likely because of newly formed particles from local SO_2-related sources in Rochester. In the previous Rochester study, there were severe local nucleation events along with high SO_2 peaks in summer.[14] As indicated in Table 1, the annual SO_2 concentrations, based on hourly averages, were 5.4 ± 5.8 and 3 ± 4 ppb in Rochester and Toronto, respectively. A large coal-fired power plant was located ~10 km north of the Rochester site and was likely the dominant local source of SO_2 in Rochester. In Toronto, SO_2 in winter was higher by a factor of 2 compared with the summer months, whereas SO_2 in Rochester was almost constant over the year, indicating a different seasonal dependency. The role of SO_2 in the particle formation process is discussed in more detail in the section, Local SO_2-Related Particle Formation Event.

Table 3. Correlation coefficients (r) between hourly averaged particle number concentrations and ambient pollutants during the different seasons.

	Winter	Spring	Summer	Fall
Rochester				
$PM_{2.5}$	0.22 (1798)	0.31 (2010)	0.14 (2020)	0.31 (1988)
SO_2	0.19 (1768)	0.50 (1928)	0.26 (1977)	0.31 (1988)
O_3	−0.15 (1776)	−0.16 (1985)	0.02 (1927)	−0.21 (1863)
CO	0.42 (1781)	0.33 (2001)	0.36 (1982)	0.48 (1975)
Toronto				
$PM_{2.5}$	0.31 (1819)	0.20 (2110)	0.16 (1410)	0.06 (1870)
SO_2	0.21 (1824)	0.15 (2114)	0.07 (1420)	0.08 (1873)
O_3	−0.11 (1817)	−0.08 (2111)	−0.01 (1419)	−0.18 (1870)
CO	0.61 (1817)	0.36 (2069)	0.25 (1178)	0.34 (1831)
NO	0.54 (1819)	0.57 (2114)	0.41 (1415)	0.44 (1817)
NO_2	0.48 (1819)	0.34 (2114)	0.29 (1416)	0.36 (1816)

Notes: Numbers in the parentheses indicate the number of samples for each combination: winter (December–February), spring (March–May), summer (June–August), and fall (September–November).

Correlation between Particle Number and Ambient Pollutants

A summary of the correlation coefficients between hourly averaged particle number concentration and the other ambient pollutants is presented in Table 3. The patterns of NO and CO in Toronto were highly correlated with total number concentrations in winter months, with coefficients of 0.54 and 0.61, respectively. In Rochester, the correlation coefficient between CO and particle number concentration was also higher in winter than in summer, as shown in Table 3. As postulated previously, particle formation may be enhanced when motor-vehicle emissions are released into cold ambient air. The lower correlation in summer was due in part to more dispersion, but it may also suggest a seasonal dependency in the formation of ambient particles, probably because of either different atmospheric conditions or different types of particle formation events.

The correlation between $PM_{2.5}$ and total number concentration was generally weak and variable with coefficients ranging from 0.14 to 0.31 in Rochester and from 0.06 to 0.31 in Toronto. In the previous study in Rochester, there was no correlation between UFP_{11-50} and $PM_{2.5}$, whereas $FP_{100-470}$ was highly correlated with $PM_{2.5}$ (r = 0.77), indicating that the mass-based measure, $PM_{2.5}$, is only representative of larger particles. Clearly, current

$PM_{2.5}$ monitoring provides little information about number concentrations. and collocated number measurements are needed if the influence of UFP on human health is to be assessed. In fact, one might hypothesize that an inverse relationship could exist between $PM_{2.5}$ and UFP. Particle nucleation is related to the existence of condensable vapors such as soluble/insoluble organic matter or inorganic acids.[25,26] Condensable vapors can be effectively scavenged by the condensation onto larger-sized particles (i.e., $PM_{2.5}$) and, thus, the formation of UFP could be reduced by pre-existing fine particles.

In general, associations between total number concentration and O_3 were either negative or insignificant. A good correlation between SO_2 and total number concentration was observed during the spring months (March–May) in Rochester, supporting the hypothesis that photochemical reactions of SO_2 contributed to new particle formation processes. Gas-to-particle conversion of sulfuric acid via oxidation of SO_2 is an important process in the atmosphere.[27,28] UV radiation can result in increased tropospheric hydroxide (OH) radical concentrations, which is one of the most effective oxidants in the lower troposphere leading the oxidation of SO_2 and the formation and growth of particles.[29,30] In Rochester, the effect of SO_2 tended to be strong compared with the trend in Toronto. The stronger correlation might have been because of the significant impact of freshly emitted plumes from local SO_2 sources on particle formation events in warmer months in Rochester.

PARTICLE FORMATION EVENTS IN ROCHESTER

Event Classification and Characteristics

On the basis of the size distributions of ambient particles (11–470 nm), three types of rapid increase in particle number concentration were observed during the daytime hours of 2003 in Rochester. The bursts of particle number were classified into morning and afternoon events in the previous nucleation study for the year 2002 in Rochester.[14] The afternoon particle formation events were also separated into regional nucleation events (regional events) and local SO_2-related particle formation events (local events) based on their behavior and likely sources. A similar classification was possible for the particle formation events observed in this study in 2003.

Figure 5 illustrates the size distribution and number concentration for a day that had morning, regional, and local events: the color scale shows the concentration of particles in each size class (in dN/dlogDp), whereas the logarithmic vertical axis shows the particle diameter in nanometers and the horizontal axis represents the time of day. The particle number concentrations are shown using the hottest color to represent the highest concentrations. As can be seen in Figure 5, the morning events had very high concentrations of UFP in the size range of 15–30 nm but were relatively brief in duration, indicating that the events were localized. In contrast, nucleation events with banana-shaped growth curves of longer duration were often observed near midday (Figure 6). The 6- to 12-hr duration of these events indicated that nucleation was occurring over a reasonably large area. Hence, these events were referred to as regional. It should be noted that, because of a limitation of the SMPS used in the

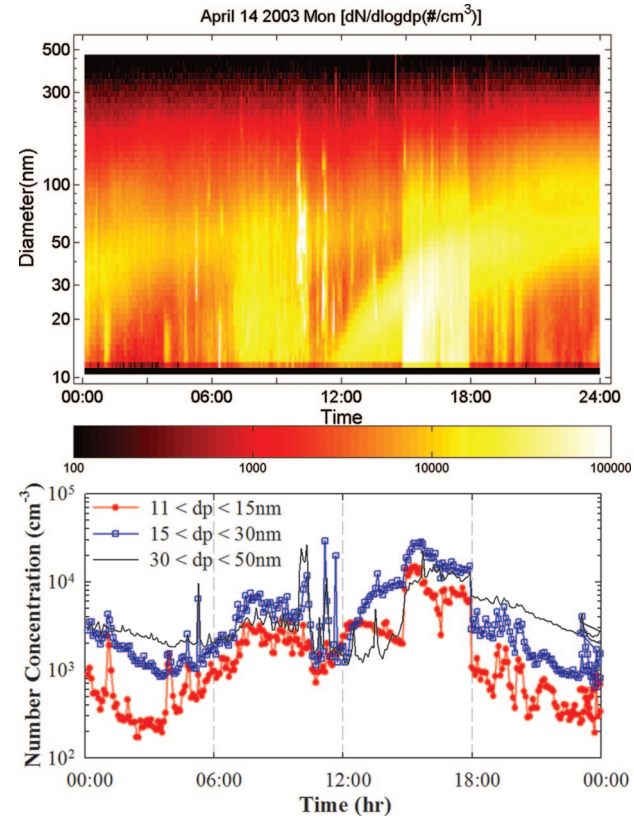

Figure 5. New particle formation events on April 14, 2003, in Rochester, NY. Diurnal evolution of particle size distribution and number concentrations.

detection of the smallest particles, the exact initial time for the nucleation and growth events could not be determined. The other important type of particle formation event in Rochester was an apparently strong formation of particles (11–15 nm) observed around 3:00 p.m. through 6:00 p.m. without further growth. SO_2 increased by a factor of 4 during these events, whereas the N_{11-50} also increased by a similar factor, and wind direction suddenly changed from south to north. Wind from the north was consistent with the location of the large-scale SO_2 point sources around Rochester, indicating the influence of local sources (Figure 5). Thus, this particle formation event was considered as a local event related to a high concentration of SO_2.

Morning Particle Formation Event

Morning particle formation events resulted in significant increases of UFP with modes ranging from 25 to 30 nm from 7:00 to 9:00 a.m. local time (the morning rush hour) over the entire measurement period. This rise in particle number concentration in the early morning was in good agreement with other field studies at urban sites.[18,19,31,32] These events produced particles in the size range of 11- 30 nm with a mode ranging from 22 to 32 nm.[32] It is clear that motor-vehicle emissions are responsible for the morning particle formation events.

To determine the frequency of morning particle formation events, the measured size distributions were classified based on their maximum concentration of UFP_{11-50} during the morning rush hour. Every morning from 7:00

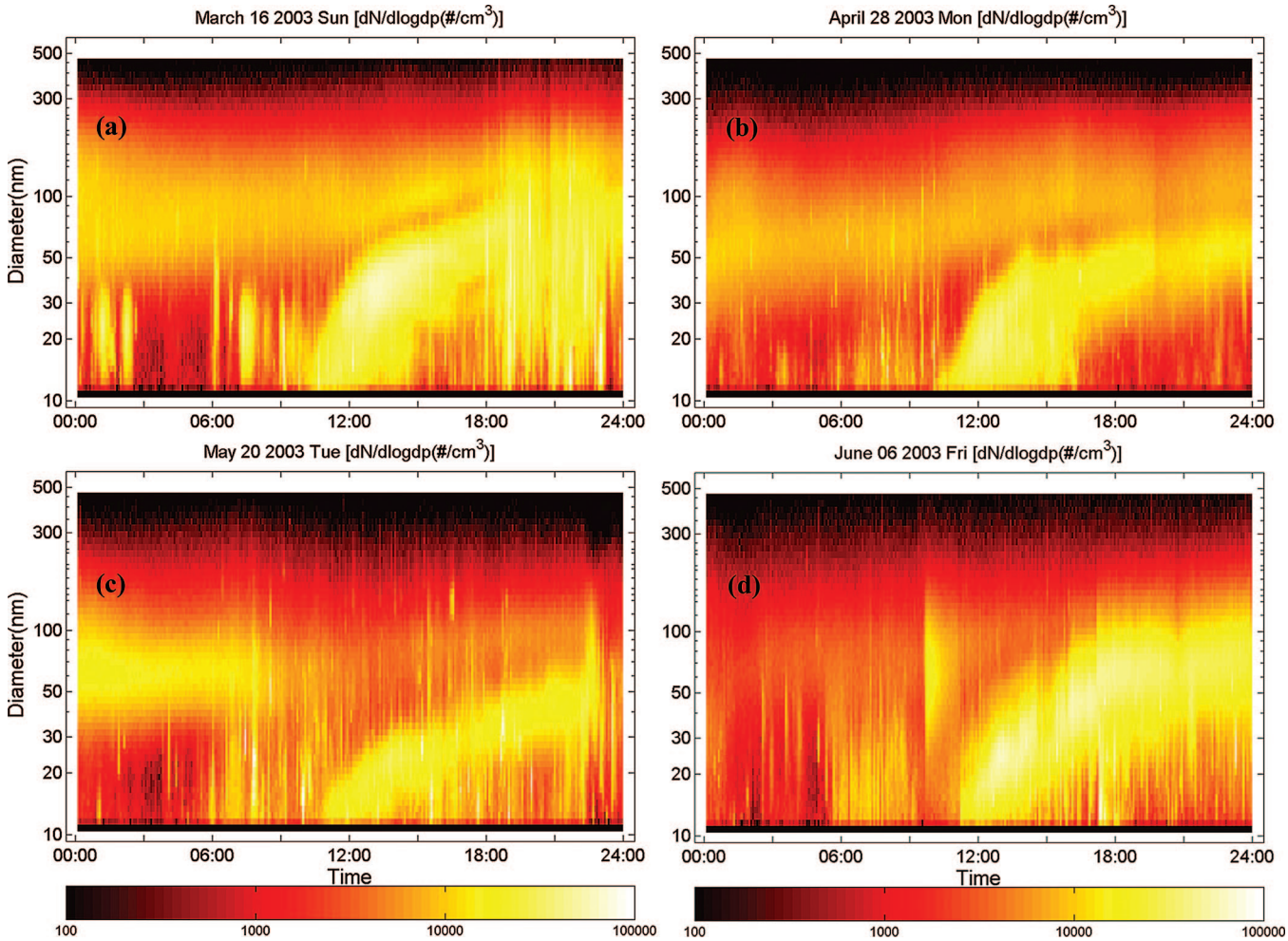

Figure 6. Regional nucleation and growth processes of ultrafine particles in Rochester, NY.

to 9:00 a.m. throughout the year was examined and categorized into four classes: maximum $N_{11-50} > 15{,}000$ cm^{-3} was classified as a strong morning nucleation event, N_{11-50} from 10,000 to 15,000 cm^{-3} was classified as a moderate event, $N_{11-50} > 8000$ cm^{-3} was classified as a weak morning event, and $N_{11-50} < 8000$ cm^{-3} was classified as no event. Figure 7 shows the frequency of morning event days from January to December 2003 applying the above-described scheme. Note that the data coverage in December 2003 was lower than 75% because of an instrument malfunction and regular maintenance of the SMPS system, so the nucleation event count might be underestimated for this month. Overall 165 morning event days out of 321 measurement days were observed (~51% of total the measurement days). Whereas strong morning events occurred for 56 days (17%), moderate and weak morning event days were 69 (21%) and 40 (12%), respectively. Generally, the maximum number concentrations during the morning events were higher in winter than in summer, as shown in Figure 7. The strong morning events were most frequently observed from December to March, and the highest hourly average concentration of UFP was ~37,500 cm^{-3} at approximately 9:00 a.m. on December 3, 2003.

The Spearman correlation coefficients between maximum N_{11-50} during the morning rush hour from 7:00 to 9:00 a.m. and other parameters including gaseous pollutants, UV-B, temperature, and RH are shown in Table 4. A good correlation was found between particle number concentration and CO for the morning event days, whereas

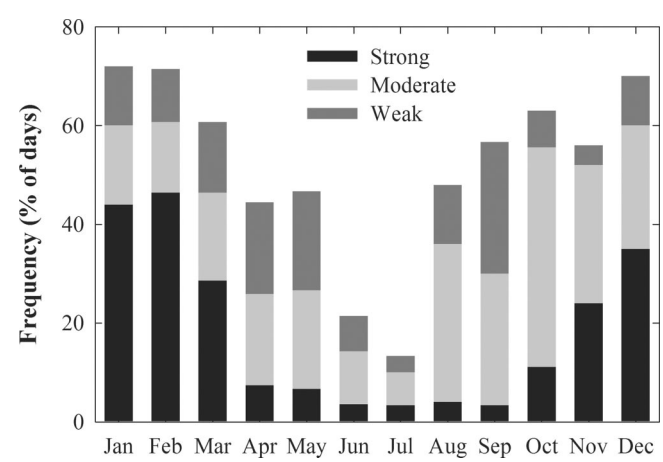

Figure 7. Frequency of morning nucleation events in Rochester, NY. The particle formation events were classified based on the maximum particle number concentration during the events (strong: $N_{11-50} > 15{,}000$ cm^{-3}; moderate: 15,000 $cm^{-3} > N_{11-50} > 10{,}000$ cm^{-3}; and weak: 10,000 $cm^{-3} > N_{11-50} > 8{,}000$ cm^{-3}).

Table 4. Correlation coefficients (*r*) between hourly averaged particle number concentrations and gaseous concentrations as well as meteorological parameters during rush hours on morning particle formation event days in Rochester.

	CO	SO_2	O_3	UV-B	Temp	RH
N_{11-50}	0.38	0.22	−0.50	−0.09	−0.42	0.09
N_{50-100}	0.36	0.34	−0.45	−0.03	−0.14	0.08
$N_{100-470}$	0.42	0.33	−0.36	0.01	0.11	0.15

no clear correlation was found between maximum N_{11-50} and either UV-B or RH. The negative correlation between the smallest particles (N_{11-50}) and temperature can be explained in terms of the lower ambient temperature being an important factor in the formation of new particles during the morning event days. Temperatures during the rush hour on morning event days varied between −18 °C and 26 °C with a mean of ~4 °C. As compared with the means of the pollutants during the entire year, average CO was 23% higher on the event days with a mean of 0.67 ppm, whereas there were no differences in the averages of SO_2 and $PM_{2.5}$. In general, motor vehicles emit gas-phase organic compounds along with small amounts of sulfur compounds and ammonia,[33,34] all of which may contribute to nucleation and particle growth. As previously mentioned, particle number concentration during the morning rush hours tended to increase as ambient temperature decreased. Nilsson and Kulmala[35] reported that the mixing of different air parcels such as the hot exhaust and cool ambient air in the morning significantly promotes nucleation rates. Thus, the emission of low and semivolatile compounds released during the rush hour would favor the formation of new particles when the exhaust mixes with cool ambient air. Tobias et al.[36] suggested in the study of volatile UFPs that organic compounds from unburned fuel or lubricating oil were involved in the nucleation of UFPs. Low volatile organics are typically originated from lubricating oil. Sakurai et al.[37] also reported that organic compounds in UFPs emitted from a diesel engine was comprised of medium-molecular-weight hydrocarbons derived from unburned lubricating oil.

Our data clearly showed a relationship between increased UFP number concentrations in the morning and vehicles, both in terms of weekday/weekend ratios and correlation with CO. In addition, for the days with morning particle formation events, the predominant wind directions was southwest (220–230°), the direction of the higher traffic density in downtown Rochester. However, the available data was not adequate to isolate the location of nucleation, specifically whether it was only occurring within the vehicle exhaust plumes. It is possible that nucleation was also occurring over a larger region covering locations at some distance from the roadways. Particles formed within a vehicle exhaust plume are often volatile, and their concentration decreases dramatically away from roadways because of both dilution and evaporation. However, we have observed high UFP concentrations on quiet residential streets, away from traffic, suggesting a larger spatial footprint for UFP than that consistent with formation within exhaust plumes alone. It is possible that secondary nucleation was also significant, as a result of oxidization of organic compounds in the exhaust at locations some distance from the point of emission. Hence, it is possible that nucleation and growth were also occurring well away from the roadway because of vehicle exhaust dispersed throughout the urban region. Further studies are needed to determine the spatial scale of particle formation from vehicular exhaust emissions in urban environments.

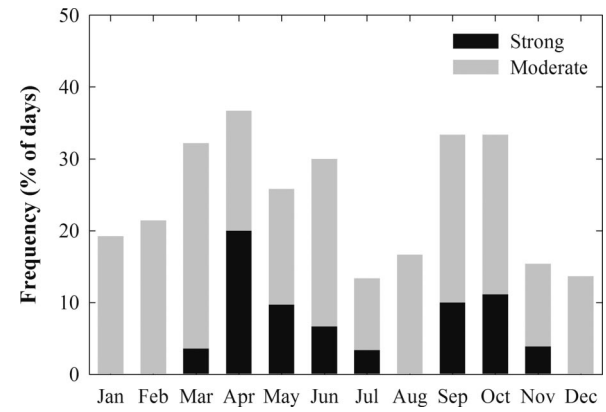

Figure 8. Frequency of regional nucleation and growth events in Rochester, NY.

Regional Nucleation Event

As described previously, regional nucleation can be characterized by the formation of particles N_{11-50} that subsequently grow for several hours, reaching sizes of up to 100 nm. Typical examples for regional nucleation events observed in Rochester are illustrated in Figure 6. Regional nucleation events have been reported in many different locations.[16,17,19] Stanier et al.[19] showed a good example for the regional scale of these nucleation events by comparing size distribution data at different sites during the Pittsburgh Air Quality Study (PAQS). They found that on February 25, 2002, at both an urban and a rural site 40 km away, similar nucleation occurred at the same time around 10:00 to 11:00 a.m., followed by the growth of the UFP to ~50 nm. Interestingly, a similar regional nucleation event was also observed in Rochester, NY, on the same day approximately 370 km northeast of the PAQS sampling site.

To characterize regional nucleation events, the observed event days were categorized into two groups, strong and moderate events, based on the clarity of the event. The strong regional nucleation events showed a clear nucleation mode and subsequent growth, whereas events with a high variation in the size distribution during the nucleation and growth events were classified as moderate events. The overall frequency of the classified days with respect to the regional events is presented in Figure 8. There were 82 regional event days out of a total of 321 valid days, of which 20 had strong events and 62 had moderate events. The overall frequency of regional events showed that the events frequently occurred in spring and fall months, especially in April, whereas the frequency

Table 5. Correlation coefficients (r) between hourly averaged particle number concentrations and gaseous concentrations and meteorological parameters during strong regional nucleation as well as growth event days in Rochester.

	CO	SO_2	O_3	UV-B	Temp	RH
N_{11-50}	0.02	−0.11	0.28	0.24	0.16	−0.49
N_{50-100}	0.10	−0.05	−0.01	−0.08	−0.01	−0.14
$N_{100-470}$	0.13	0.12	−0.01	−0.14	−0.02	0.04

of the particle formation events showed a summer minimum (July–August). This trend, a high event frequency in spring and a low frequency in summer, was also observed at a remote site as well as an urban site.[16,19] The lower frequency of the regional nucleation events in summer months could be the result of a number of factors. As postulated previously, condensable vapors such as organics photochemically produced as a source term of nucleation would be most intense in warmer months, but there are also enhanced sinks (condensational sink on pre-existing particles) of the condensable vapors. Pirjola et al.[29] found that the intensity of the sink term increased as temperature increased and RH decreased, suggesting a more favorable condition in summertime for loss of condensable vapors. Birmili et al.[38] also reported that intensity of the pre-existing condensational sink was relatively higher in summer than in winter months, which is a limitation term for the low nucleation frequency in summer.

To estimate an average growth rate of UFP in the 11- to 80-nm size range during the events, the entire dataset was re-examined. Observed growth rates of UFP ranged from 5 to 13 nm hr^{-1} with a mean of 8 nm hr^{-1}. For comparison, the growth rates of particles in the size range of 3–11 nm observed at an urban site in the U.K. and at a rural site in Germany were ~4 nm hr^{-1} and 2 nm hr^{-1}, respectively.[38,39]

The diurnal variations of number concentrations were compared with atmospheric pollutants and meteorological parameters during the daytime from 10:00 a.m. to 7:00 p.m. on the 20 strong regional nucleation days (Table 5). The highest correlation was observed between the smallest particles (N_{11-50}) and O_3 as well as UV-B intensity, whereas there were no significant correlations for the bigger particles (N_{50-100} or $N_{100-470}$), suggesting a high association between new particle formation and photochemical reactions leading to higher production of condensable vapors. During the nucleation events, ambient temperature tended to be at its daily peak, whereas a negative correlation between RH and N_{11-50} was observed, which is consistent with the reported results by Pirjola et al.[29] In general, there were no significant relationships between gaseous pollutants (CO, SO_2) and the nucleation events. Local wind direction distribution during the daytime from 10:00 a.m. to 7:00 p.m. on the strong nucleation event days (20 days) showed that predominant wind direction was the northwest (280–310°) with a probability of 30%.

Local SO_2-Related Particle Formation Event

Local SO_2-related events were characterized by a significant increase of N_{11-50} during a short time period (2–3 hr) in the presence of a high concentration of SO_2. In contrast with the characteristic of regional nucleation events described earlier, local events were usually found without the growth of newly formed particles. Local particle formation events exclusively occurred during the daytime, especially around noon, and persisted for approximately 2–3 hr. Because the concentrations of new particles formed during these local events were usually much higher than the value during the regional nucleation events, they could be easily separated from other nucleation events.

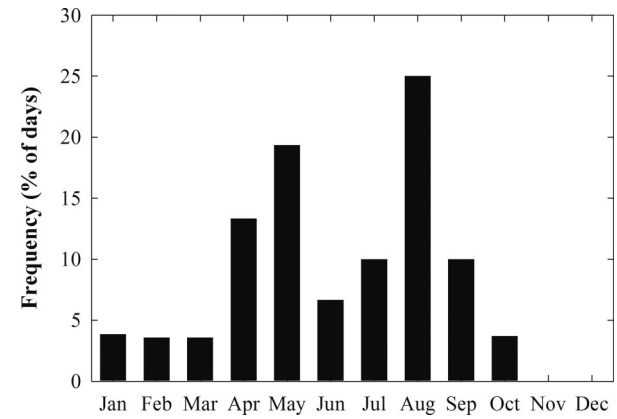

Figure 9. Frequency of local SO_2-related nucleation events in Rochester, NY.

To identify the favored conditions and sources of the local particle formation events, strong local SO_2-related events were defined by the criterion that the net formation rate of N_{11-50} exceed 9000 cm^{-3} hr^{-1} (2.5 cm^{-3} sec^{-1}) based on a day-by-day analysis of the entire year. Such local events were found on 26 days out of total 321 valid days (8% of all days). Figure 9 shows the frequency of the local particle formation events throughout 2003 in Rochester. The frequency of the events had a maximum in August with a probability of 25%, whereas the lowest frequency was in the winter months. The average total particle number concentration for the 26 local particle formation event days was 12,500 ± 10,400 cm^{-3}, which is around 30% higher than the average value during the measurement period. During local nucleation events, the observed maximum particle formation rates ranged from 9300 to 51,500 cm^{-3} hr^{-1} (2.6–14.3 cm^{-3} sec^{-1}) with a mean of 19,800 cm^{-3} hr^{-1} (5.5 cm^{-3} sec^{-1}). Also, NC_{11-50} increased over a few hours by factors ranging from ~2 to 13 from the average value. The concentration of SO_2 increased at a rate that varied between 10 and 60 ppb hr^{-1} with a mean of 20 ppb hr^{-1}, whereas there was no increase in CO.

Table 6 presents the Spearman correlation coefficients between particle number concentrations in the three size ranges and atmospheric parameters measured during strong local nucleation event days. Data from 12:00 a.m. to 9:00 a.m. were excluded to remove the impact of background concentrations and traffic-related morning particle formation events in this correlation analysis. In contrast to the correlation for RH during regional nucleation events, there was no significant correlation between RH and particle number concentration, indicating that RH was not an important factor for the

Table 6. Correlation coefficients (*r*) between hourly averaged particle number concentrations and gaseous concentrations as well as meteorological parameters during local particle formation event days in Rochester.

	CO	SO_2	O_3	UV-B	Temp	RH
N_{11-50}	0.05	0.64	−0.10	0.31	−0.13	−0.06
N_{50-100}	0.40	0.31	−0.20	−0.06	0.06	0.15
$N_{100-470}$	0.45	0.12	0.12	−0.01	0.38	0.20

local particle formation events. Unlike the morning rush hour events, there was also no significant relationship between particle number and ambient temperature during the local events.

Compared with the correlation for overall days, a correlation coefficient between N_{11-50} and SO_2 was significantly higher ($r = 0.64$), whereas in the case of larger-size particles, N_{50-100} and $N_{100-470}$, the correlation coefficient dramatically decreased, suggesting that particles were newly formed in the atmosphere rather than mixed in from long-range transport of a polluted air to the measurement site. A statistically high correlation was also found between N_{11-50} and UV-B, suggesting that the local particle formation events were favored by photochemically active conditions. UV-B values at which local nucleation events occurred were in the range 0.12–21.51 mW m^{-2} with a mean of 6.46 mW m^{-2}, whereas the mean value for the entire measurement period was 5.58 mW m^{-2}, indicating a 14% higher value of UV-B radiation on local nucleation days. The newly formed particles in the present study can be considered as secondary particles formed from the photochemical reaction of SO_2. Although there were some days with high UV-B and no nucleation events resulting in a low statistical correlation, UV-B was one of the important factors to trigger local nucleation events. This result is consistent with an observation of Pirjola et al.[29] who reported the strength of the nucleation event increased as a function of UV-B irradiation penetrating into the troposphere and stimulating the SO_2 oxidation process. In a laboratory experiment result very recently reported by Berndt et al.,[30] sulfuric acid was effectively produced in situ by photochemical reactions of SO_2 in the presences of O_3, hydrocarbons, and UV radiation, at levels comparable to those reported for the atmosphere. In the study, formation of new particles was observed only in the presence of SO_2, suggesting that the reaction of SO_2 with OH radicals photolyzed from O_3 would be one of critical factors in particle nucleation processes at SO_2-polluted sites.

Figure 10 shows the concentration distributions of UFP number and SO_2 on the local particle formation days observed for 2003 in Rochester. Northwesterly and northerly winds were prevailing on the local event days; high number concentrations of UFP_{11-50} were generally observed when the wind direction was from the north (0–30°). As can be seen in Figure 10, strong peaks of SO_2 were also observed when wind direction was from the north, indicating the influence of polluted air parcels including higher SO_2 from several point sources located north of the Rochester sampling site. These results suggest that SO_2-related formation events were distinct in that nucleation may have occurred within the plume from a coal-fired power plant, producing an increase in the particle concentration number that was only observed on summer days when this plume passed over the sampling site. Nucleation would have required that the sulfuric acid (H_2SO_4) concentration exceed some threshold value. The H_2SO_4 concentration within the plume would have depended on the relative rates of SO_2 oxidation and dilution

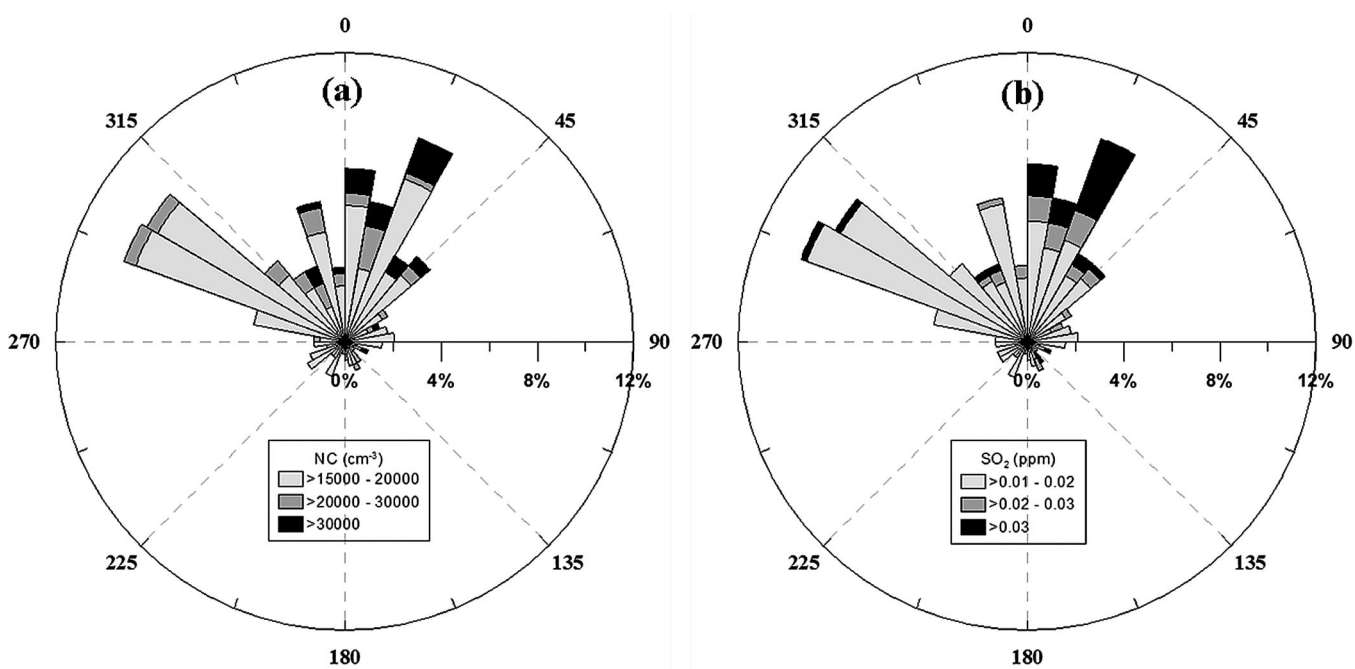

Figure 10. Concentration distributions of UFP number (a) and SO_2 (b) depending on wind directions on local particle formation event days in Rochester, NY.

during transport. Hence, nucleation was likely occurring within the plume at some distance downwind of the plant, giving these particles limited time for growth while subsequently being carried by the plume to the nearby sampling site.

CONCLUSIONS

To identify the characteristics of ambient UFPs, continuous measurements of particle number concentrations were performed at two urban sites, Toronto and Rochester, throughout 2003. The average number concentration of ambient particles ($11 < dp < 470$ nm) was 9670 ± 6960 cm^{-3} in Rochester, whereas in Toronto the average number of particles (dp <1000 nm) was 28,010 ± 13,350 cm^{-3}. Strong seasonal dependency in the particle number concentration was observed at the two sites with the highest values in February and the lowest in July. Particle number concentration was typically higher in winter months than in summer months by a factor of 1.5 in Rochester and 1.6 in Toronto. In general, there were also distinct diurnal variations of aerosol number concentrations with a rise during the morning rush hour. The ratio of particle number concentrations during the rush hour to the value during the early morning ranged from 1.6 (Rochester) to 1.9 (Toronto). The highest weekdays/weekends ratio of total number concentration was observed during the rush hour in winter months with a ratio of 2.1 in Rochester and 2.0 in Toronto.

A higher correlation between the total particle number concentrations of the two sites was observed in winter, whereas the lowest correlation was found in summer months. The correlation in winter was explained in terms of the common traffic patterns at both urban sites. The weaker correlation in summer may have been due in part to the impact of frequent local SO_2-related particle formation events observed during summer in Rochester.

A good correlation was found between total number concentrations and NO as well as CO during winter in Toronto. There was also a high correlation between CO and particle number concentration during winter and fall in Rochester, suggesting particle formation can be enhanced by motor vehicle emissions into cold ambient air. A good correlation between SO_2 and total number concentration was observed during spring in Rochester, whereas the correlation was weaker in Toronto. The high correlation in Rochester was explained in terms of the impact of local SO_2 sources on particle formation events at the site.

Particle formation events observed in Rochester were classified into three types according to formation event starting time, formation rates, correlation of gaseous species, and growth types. Strong morning particle formation events starting during the morning rush hour were frequently observed during colder months. Good correlations between particle number and CO as well as temperature suggested that motor-vehicle emission would favor the formation of new particles as the exhaust mixes with the cool ambient air.

Regional nucleation events, characterized by new formation of particles N_{11-50} and subsequent growth for several hours, frequently occurred in spring and fall, especially in April. The frequency of these particle formation events showed a summer minimum. The highest correlation was observed between N_{11-50} and O_3 as well as UV-B, whereas a high negative correlation for RH was observed, suggesting the association of photochemical reactions with the nucleation events. There were no significant relationships between CO, SO_2, and these nucleation events.

Local SO_2-related particle formation events having high N_{11-50} for 2 or 3 hr with high SO_2 levels frequently occurred in August, May, and April. The lowest event frequency was observed during winter. Compared with the result from the average value, particle number increased by a factor ranging from 2 to 13 during the local events. The average increase rate of SO_2 during the local event time period was 20 ppb hr^{-1}. Correlation was also observed between N_{11-50} and SO_2 (and UV-B), suggesting that local particle formation events are also favored by photochemically active conditions. In contrast to the correlation for RH during regional nucleation events, RH did not influence the local particle formation. A high directionality in a northerly direction for particle number and SO_2 concentrations was found at the site, indicating the influence of SO_2-polluted air parcels from point sources located in the north part of Rochester.

ACKNOWLEDGMENTS

This work was sponsored in part by the New York State Energy Research and Development Authority, the U. S. Environmental Protection Agency, the Canadian Foundation for Climate and Atmospheric Sciences, and the Ontario Ministry of the Environment. The authors would like to thank the NOAA Air Resources Laboratory and the U.S. Department of Agriculture for providing meteorological data and UV data. We also acknowledge Mike Fila at the University of Toronto for maintaining the instruments.

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