*Young and Keeler, Aerosol and Air Quality Research,* Vol. 7, No. 3, pp. 379-402, 2007

# Summertime Ultrafine Particles in Urban and Industrial Air: Aitken and Nucleation Mode Particle Events

**Li-Hao Young*, Gerald J. Keeler**

*Department of Environmental Health Sciences, University of Michigan, 109 South Observatory, Ann Arbor, Michigan 48109, USA*

## Abstract

The main objectives of this study are to develop a systematic approach for the identification and classification of ultrafine particle (UFP) events and to analyze the events for implications of sources and meteorological conditions conducive to elevated UFP number concentrations. UFP events are prolonged periods with elevated UFP number concentrations. Particle number size distributions, gas pollutants, and meteorological parameters were concurrently measured during the summers of 2003 to 2005 in Detroit, Michigan, USA. Among the 74 identified UFP events, 40 (54%) are Aitken mode particle events and 34 (46%) are nucleation mode particle events. Correlation results show that 65 out of the 74 UFP events were associated with plumes of combustion sources, including all the Aitken mode events and 25 out of the 34 nucleation mode events. These in-plume particle events were positively correlated with elevated NO, CO, particle surface area, and occasionally high levels of $SO_2$. The remaining 9 nucleation mode events, however, showed no such correlations, and hence referred to as secondary nucleation mode particle events. These secondary nucleation events occurred under relatively clean (i.e., low preexisting aerosols) and sunny conditions shortly after the breakup of nocturnal inversion and during midday. Overall, the results indicate that motor vehicles and industrial plumes are the major sources of elevated UFPs in urban/industrial air. Under favorable conditions, atmospheric secondary nucleation can occur in rather polluted urban/industrial air and become a major contributor of UFPs. The formation mechanisms, hence chemical composition, are likely different between the in-plume and secondary UFPs. Therefore, exposure assessments to ambient UFPs need to take into account the contributions from both types of particles.

***Keywords***: Urban air; Traffic; Industrial plume; Sources; Meteorology.

---

* Corresponding author.

Current address: Department of Occupational Safety and Health, China Medical University, 91, Hsueh-Shih Road, Taichung, Taiwan 40402. Tel: +886-4-2205-3366 ext. 6123, Fax: +886-4-2207-2187

E-*mail address*: lhy@umich.edu

# INTRODUCTION

As a subset of ambient particulate matter (PM), ultrafine particles (UFPs; < 0.1 μm) are attracting increasing attention in recent years due to their potential adverse effects on human and environmental health. Their large surface-to-volume ratio and ability to deposit deep in the respiratory tracts make UFPs potentially more toxic than their larger counterpart (Nel, 2005; Nel *et al.*, 2006). They can also affect Earth's radiation budget directly by light absorption and scattering and indirectly by becoming cloud condensation nuclei (Lohmann and Feichter, 2003; Bellouin *et al.*, 2005). UFPs nominally consist of two sub-modes: nucleation (0.003–0.02 μm) and Aitken mode (0.02–0.1 μm). These particles are either emitted directly from combustion processes (i.e., "in-plume" particles) or formed by nucleation from precursor vapors (i.e., secondary particles).

The major source of UFPs in urban/industrial areas is combustion processes. Many ambient studies have shown that elevated UFP number concentration ($N_{UFP}$) correlates with local traffic pattern, particularly the morning rush-hour traffic, and increases with increasing traffic volume (Alam *et al.*, 2003; Jeong *et al.*, 2004; Sardar *et al.*, 2004; Young and Keeler, 2004; Harrison and Jones, 2005; Virtanen *et al.*, 2006). Emissions of stationary combustion sources also contain high number concentrations of UFPs (Brock *et al.*, 2003; Maguhn *et al.*, 2003; Chang *et al.*, 2004). The characteristics of these in-plume UFPs is that the maximum number concentration typically occurs near the point of emission and decreases further downwind (Brock *et al.*, 2003; Zhu *et al.*, 2006). Nevertheless, highly concentrated particles in polluted plumes can have regional-scale impact. For example, particle numbers of up to $12 \times 10^4$ 1/cm$^3$ have been measured from a single industrial plume at a downwind distance of 18 km (Brock *et al.*, 2003).

Atmospheric nucleation (or new particle formation) is typically favored under conditions of low preexisting aerosols, of which the surface area serves as a condensation and coagulation sink of ambient vapors and small particles; high particle surface area suppresses nucleation. With that in mind, nucleation is not necessarily accompanied by high levels of co-pollutants typical of direct source emissions. A review by Kulmala *et al.* (2004) shows that nucleation events occur in various environments, including polluted urban areas (Woo *et al.*, 2001; Stanier *et al.*, 2004a; Young and Keeler, 2004) industrial plumes (Brock *et al.*, 2003) coastal regions (O'Dowd *et al.*, 1999) forests (Aalto *et al.*, 2001) and the free troposphere and lower stratosphere (Lee *et al.*, 2003; Young *et al.*, 2007). In polluted environments, the extremely high concentrations of precursor gases (e.g., $SO_2$, $NH_3$ and organics) potentially can overcome the nucleation barrier imposed by the high preexisting particle concentration. In particular, the involvement of vapor-phase $H_2SO_4$ in the nucleation processes has been widely implicated due to its low vapor pressure (< 0.001 torr at 300 K) (Curtius, 2006). The production of vapor-phase $H_2SO_4$ is initiated by the reaction between $SO_2$ and •OH. Because •OH is produced from the photolysis of $O_3$, nucleation events

are often correlated with solar radiation, i.e., photochemically-driven (Boy and Kulmala, 2002; Stanier *et al.*, 2004b).

In addition to the source strength, the sizes and concentrations of UFPs are strongly dependent on the source characteristics and meteorological conditions. On-road and laboratory source studies have shown the $N_{UFP}$ varies with engine operating conditions, fuel composition, and after-treatment (Maricq *et al.*, 2002; Kittelson *et al.*, 2006). In addition, higher particle number concentrations and emissions are often attributed to the lower temperature and mixing height in the winter (Jeong *et al.*, 2004; Harrison and Jones, 2005). Wind direction and speed also play an important role in the transport and dilution of ambient particles (Harrison and Jones, 2005; Hussein *et al.*, 2006). All of these potential modifying factors underscore the dynamic and transient nature of ambient UFPs.

UFP events are prolonged periods with elevated $N_{UFP}$. These events therefore potentially pose the greatest impact on human and environmental health. Studying these events would allow us to identify potential cause-effect relationships and develop effective control strategies. Here we first present a systematic and quantitative approach for the identification and classification of UFPs events, based on earlier studies of atmospheric nucleation events (Mäkelä *et al.*, 2000; O'Dowd *et al.*, 2002; Alam *et al.*, 2003; Birmili *et al.*, 2003; Vehkamäki *et al.*, 2004). Second, we present case studies of the resultant 74 UFP events for implication of sources and meteorological conditions conducive to elevated UFP number concentration in Detroit, Michigan, USA.

## EXPERIMENTAL METHODS

### *Sampling campaigns*

The sampling site is located in a southwest Detroit community (42.316 °N, 83.094 °W), on top of a mobile air research laboratory constructed inside a 16.2 m long trailer (Fig. 1). The site is in proximity to an interchange of two heavy-traffic interstate highways, I-96 and I-75, and the Ambassador Bridge, a major crossing between Canada and the US. Typical average daily traffic (ADT) volumes on nearby highways range from 73,000 to 121,000 vehicles/day (MDOT, 2005). Traffic backups are a common sight on the Ambassador Bridge (ADT ≈ 14,000 vehicles/day) and its connecting highways. The distances to the nearest highway (I-75) and the Ambassador Bridge are about 0.4 and 1.6 km, respectively. A number of major industrial sources are located to the southwest of the site. The second largest $SO_2$ point source is approximately 5 km to the southwest (Fig. 1). Therefore, the study area is impacted by not only traffic emissions but also industrial plumes in the summer when the prevailing winds are from the southwest. Three intensive sampling campaigns were carried out in the summer months of July 12–23, 2003, August 12–September 2, 2004, and July 28–August 4, 2005.

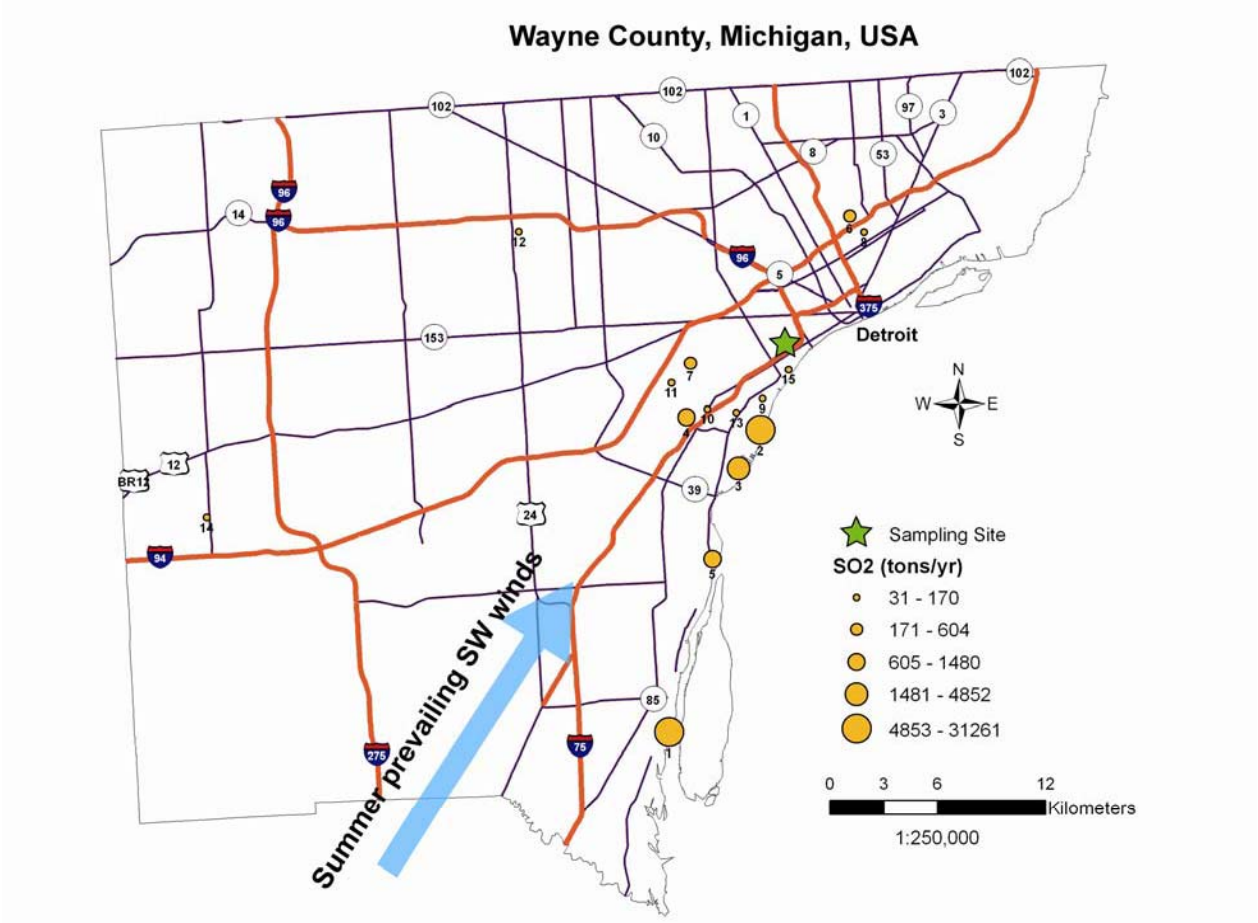


**Fig. 1.** A map of the sampling site (star) and major $SO_2$ point sources (circles) in Wayne County, MI. The size of the circles corresponds to the amount of $SO_2$ emissions. The number next to the circles is the rank of emissions.

***Instrumentation***

An ambient ultrafine particle sampling system was used to measure the particle number concentrations and size distributions in the size range of 0.01–0.41 μm at 5 min intervals (Fig. 2(a)). The system consists of a conductive tube that draws sample air into the mobile laboratory, an L-shaped inline sampling probe that isokinetically transports a small fraction of the sample air to a Scanning Mobility Particle Sizer (SMPS; TSI Model 3936), the SMPS for particle sizing and counting, and a pump. The SMPS system comprises a differential mobility analyzer (TSI Model 3081) and a butanol-based condensation particle counter (TSI Model 3010). The flow rates in the sampling system were maintained laminar and pre- and post-calibrated with an air flow calibration system (Gilian Gilibrator, Sensidyne). The flow residence time in the system was less than 2.5-s to minimize particle interactions. Furthermore, the effects of electrostatic attraction, thermophoretic and diffusiophoretic depositions on particle losses were minimized by using conductive tubes, insulator, and a temperature-controlled room. Particles in the size range of

0.001–10 μm were evaluated for entry, bend, and transport losses according to loss equations from published experimental studies (Baron and Willeke, 2001). The maximum sampling loss was estimated less than 10% for the smallest measurable particles of 0.01 μm (Fig. 2(b)).

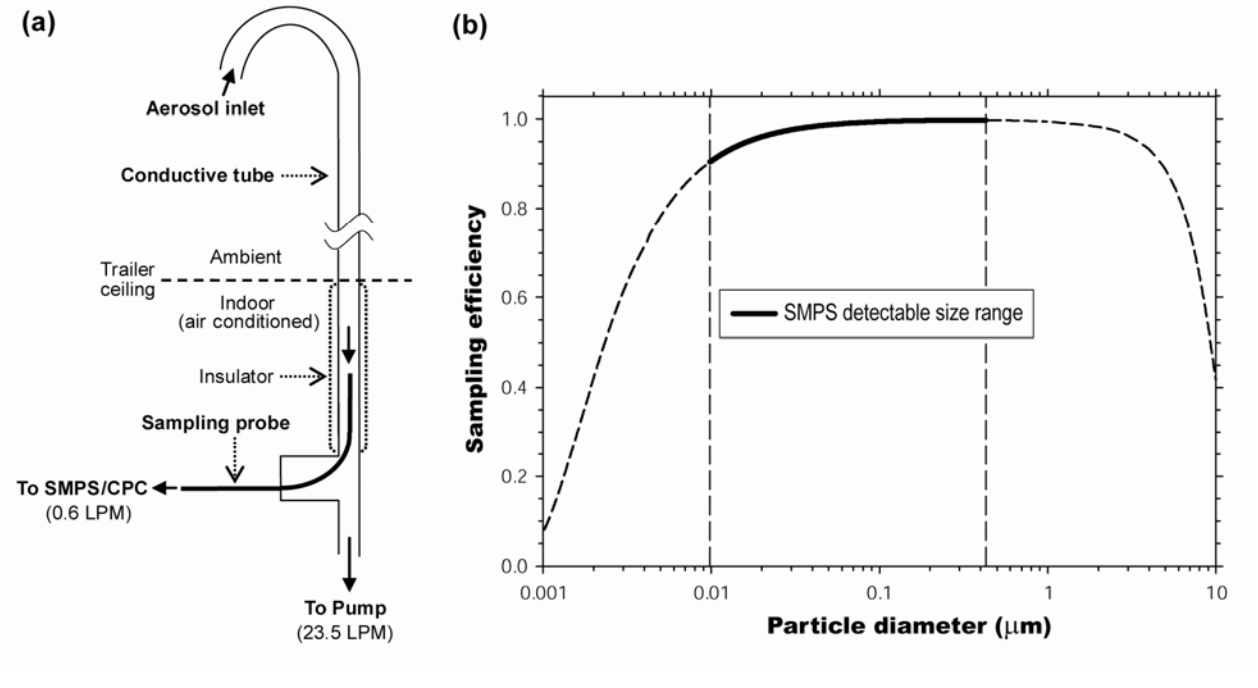


**Fig. 2.** Ultrafine particle sampling system: (a) a schematic diagram and (b) the modeled sampling efficiency; the product of inlet and transport efficiency.

A suite of gaseous species ($O_3$, $SO_2$, CO, and NO) were concurrently monitored at 5-min intervals by means of uv photometry (TEI 49C), pulsed fluorescence (TEI 43C), chemiluminescence (TEI 42C), and gas filter correlation infrared radiation (TEI 48C), respectively. The gas monitors were calibrated against zero air and multi-points of known concentration of standard gases with a dynamic multi-gas calibration system (TEI 146C). A Tapered Element Oscillation Microbalance (TEOM; Model 1400a, Rupprecht & Patashnick) with inlet line heated to 40°C was used to measure the $PM_{2.5}$. Meteorological parameters including ambient temperature, relative humidity, wind speed, wind direction, rainfall, and solar radiation flux were also monitored on-site atop a 10-m tower.

***Particle event parameters and criteria***

A common feature of particle events is a substantial increase of the number concentration ($N$) from background level. Such an increase can be quantitatively characterized by the following parameters: (1) the minimum number concentration and the time when it occurred, $N_{MIN}$ and $t_{MIN}$,

respectively and (2) the $N_{MAX}$ and $t_{MAX}$. According to these parameters the characteristics of a peak can be derived as follows. The net change of $N_{UFP}$ during an event is

$$\Delta N = N_{UFP[MAX]} - N_{UFP[MIN]} \tag{1}$$

The "intensity" of that net increase in relation to the background concentration can be expressed as a ratio

$$\frac{\Delta N}{N_{UFP[MIN]}} \tag{2}$$

The characteristic time for $N_{UFP[MIN]}$ to reach $N_{UFP[MAX]}$ is defined as

$$\Delta t = t_{MAX} - t_{MIN} \tag{3}$$

Using these parameters we developed a set of criteria for identifying and classifying major UFP events. It aims to identify prolonged periods with relatively high particle number concentrations. Fig. 3 shows a flow chart and criteria for the selection and classification of particle event. As shown, the data was first smoothed using centered moving arithmetic averages. Here, an UFP event satisfies all the following: (1) the $N_{UFP[MAX]}$ > the *daily* 75$^{th}$ percentile concentration ($N_{UFP[75th]}$); (2) the $N_{UFP[MAX]}$ > the *overall* median concentration ($N_{UFP[50th]}$); (3) the ratio of $\Delta N/N_{UFP[MIN]} > 0.5$; and (4) the $\Delta t > 1$ hr. The 1$^{st}$ and 2$^{nd}$ criteria are a measure of the strength of the event, and take into account the temporal (daily and annual) variation. In specific, the 2$^{nd}$ criterion sets the lower-limit concentration to exclude situations where the daily $N_{UFP[75th]}$ < the overall $N_{UFP[50th]}$ during low-background (clean) days. The 3$^{rd}$ criterion is a measure of intensity. The 4$^{th}$ criterion is a crude measure of the spatial extent of the event to exclude number concentration "spikes." The whole process was repeated for each summer intensive.

Identified UFP events were then classified as nucleation mode particle events if they satisfy the following criteria: (1) the $N_{Nucl[MAX]}$ > the *overall* $N_{Nucl[75th]}$; and (2) the ratio of $N_{Nucl[MAX]}/N_{UFP}$ > the *overall* 75$^{th}$ percentile value. Both criteria are to ensure only intense nucleation events are selected. UFP events that do not satisfy the above criteria are classified as Aitken mode particle events. Furthermore, if a nucleation mode particle event is correlated with elevated total particle surface area and CO, NO, or $SO_2$, it is categorized as "in-plume" nucleation mode event; otherwise, as a "secondary" nucleation mode event.

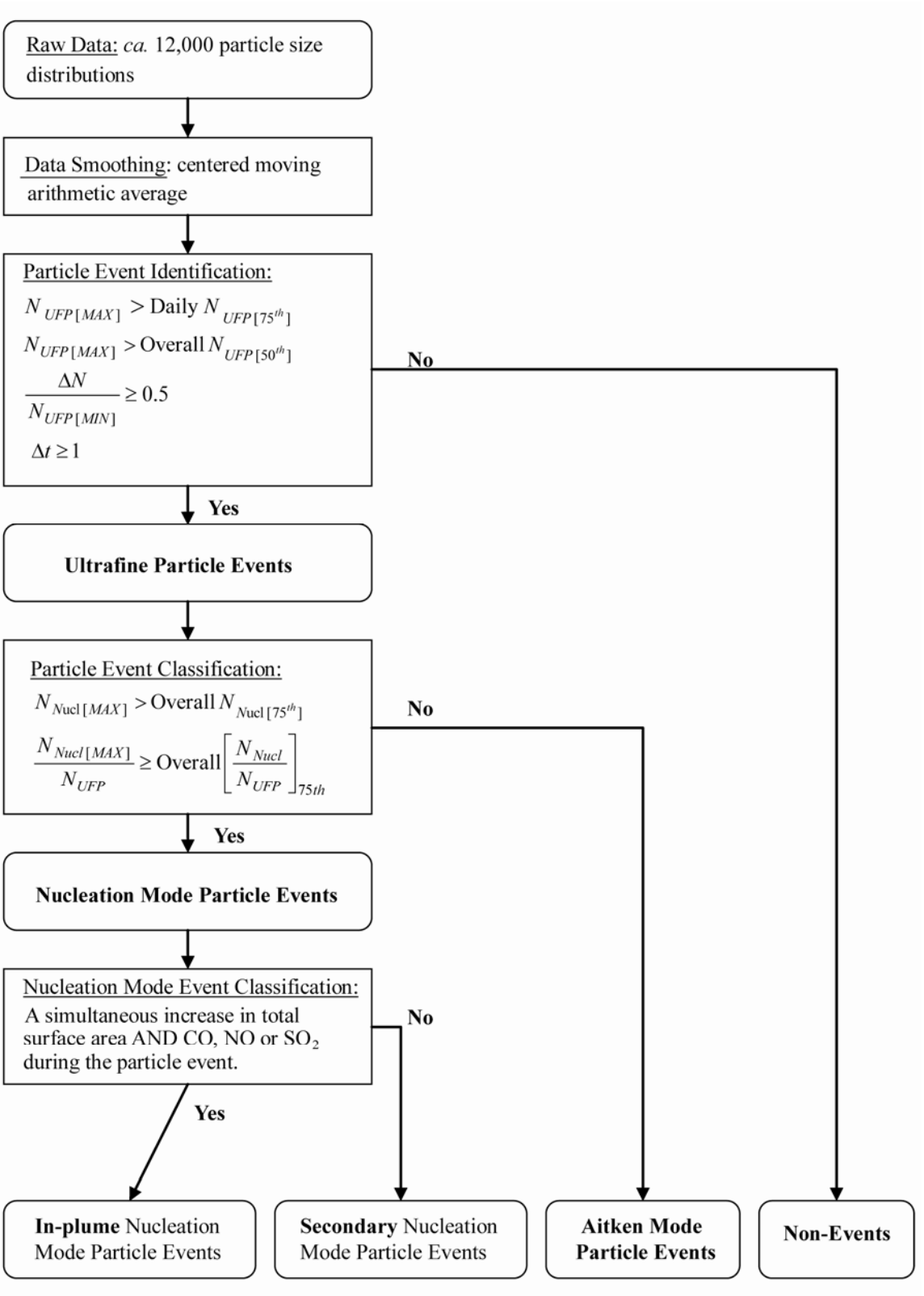


**Fig. 3.** A flow chart and the criteria for particle event identification and classification.

***Meteorological conditions***

The on-site meteorological conditions and their correlation coefficients ($r$) with the $N_{nucl}$ and $N_{UFP}$ are summarized in Table 1. During the summer months, the mean temperature, RH, absolute humidity, wind speed, and solar radiation were 21.8°C, 64.4%, 12.1 g/m$^3$, 1.3 m/s, and 205 W/m$^2$, respectively. The $N_{nucl}$ and $N_{UFP}$ showed little correlations with the meteorological parameters. The highest $r$ values are between the solar radiation and the particle numbers ($r_{Nucl}$ = 0.28, $r_{UFP}$ = 0.25).

**Table 1.** Summary statistics of the meteorological parameters in the summer months of 2003-2005 in southwest Detroit.

| Variable | Unit | Mean | SD[a] | Min | Medium | Max | $r_{Nucl}$[b] | $r_{UFP}$[b] |
|---|---|---|---|---|---|---|---|---|
| Temperature | °C | 21.8 | 4.6 | 12.4 | 21.5 | 35.7 | 0.18 | 0.18 |
| Relative humidity | % | 64.4 | 17.7 | 24.7 | 67.1 | 91.9 | -0.20 | -0.20 |
| Absolute humidity | g/m$^3$ | 12.1 | 2.8 | 4.9 | 11.9 | 19.8 | -0.04 | -0.04 |
| Wind speed | m/s | 1.3 | 0.7 | 0.4 | 1.3 | 4.1 | 0.15 | 0.05 |
| Wind direction | ° | Prevailing wind - Southwesterly | | | | | | |
| Global radiation | W/m$^2$ | 205 | 278 | 1 | 38 | 1073 | 0.28 | 0.25 |
| Precipitation | mm | 0.0 | 0.1 | 0.0 | 0.0 | 5.3 | -0.03 | -0.02 |

a. Standard deviation.
b. The correlation coefficients between the meteorological parameters and number concentrations of nucleation mode ($N_{Nucl}$) and ultrafine particles ($N_{UFP}$), respectively.

Although we experienced sporadic periods of rainfall, the dominant synoptic weather during the study was high-pressure system originating from the west and northwest. The prevailing wind direction was from the southwest. About 40% of the time the winds were below 1 m/s. Fig. 4 shows the diurnal pattern of the average wind speed and mixing height during the study. As shown, the atmospheric condition is typically very stable in the early morning. The wind picks up shortly after sunrise at ~ 0530 EDT, followed by the breakup of the nocturnal inversion at ~ 0800 EDT.

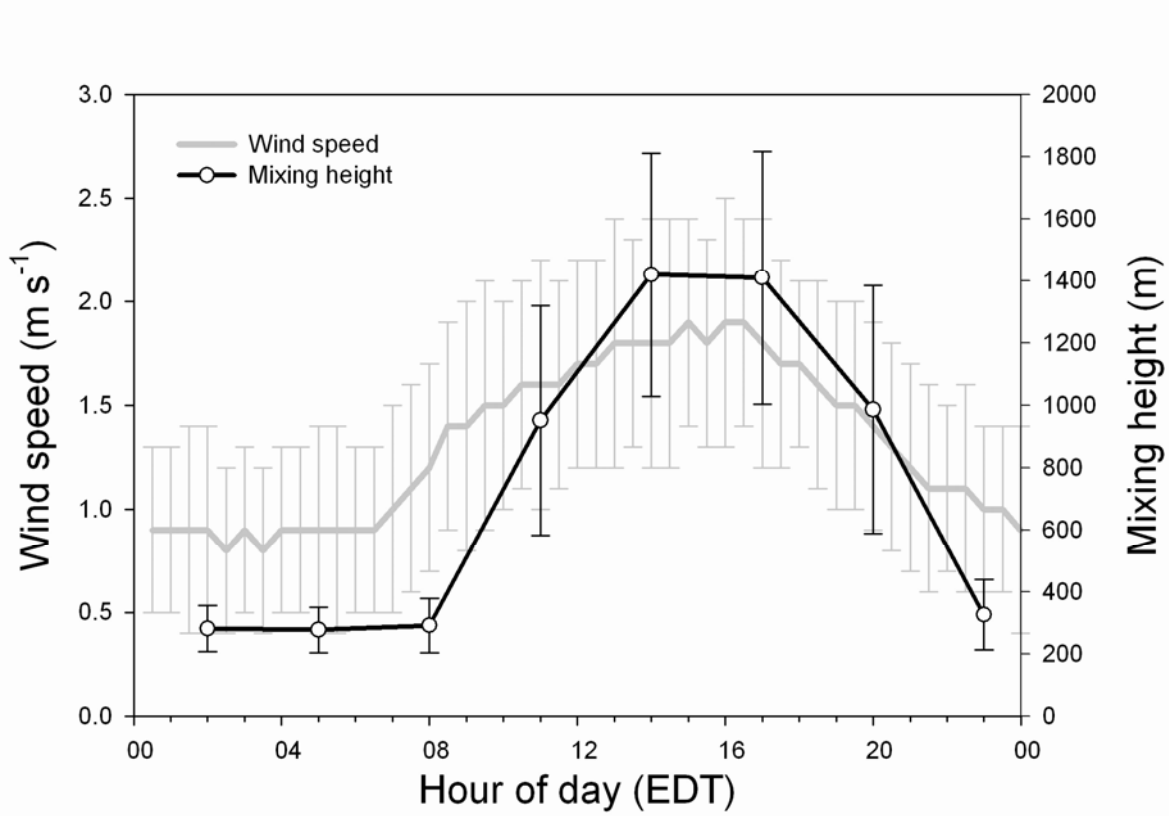


**Fig. 4.** The mean wind speed and mixing height during the entire study. The error bar is one standard deviation around the mean.

## RESULTS AND DISCUSSION

In the following, "total" particles refer to those within the SMPS measurable size range of 0.01 to 0.41 μm. In this range there are three sub-modes: nucleation (0.01–0.02 μm), Aitken (0.02–0.1 μm), and accumulation mode (0.1–0.41 μm). The first two modes combined represent the ultrafine particles; 0.01–0.1 μm.

### *Pollutant concentrations*

The summary statistics on the UFP number $N_{UFP}$, surface area $S_{UFP}$, and volume concentration $V_{UFP}$ during the 2003–2005 campaigns are given in Table 2. The particle summary statistics for each campaign are remarkably consistent with each other, including those obtained at the same sampling site in 2002 (Young and Keeler, 2004). The overall averages of $N_{UFP}$, $S_{UFP}$, and $V_{UFP}$ were $2.0 \times 10^4$ 1/cm$^3$, 119 μm$^2$/cm$^3$, and 1.3 μm$^3$/cm$^3$, respectively. On average, the UFPs contribute 88% of the total particle number, 40% of the total particle surface area, and 20% of the total particle volume. The large standard deviation (SD) values indicate strong influences from

local sources. The particle statistics in Table 2 are comparable to that in other urban areas (Jeong *et al.*, 2004; Stanier *et al.*, 2004a; Harrison and Jones, 2005).

**Table 2.** Summary statistics of the UFP number, surface and volume concentrations in the summer months of 2003 – 2005 in southwest Detroit.

| Year | $n$[a] | Mean | SD[b] | Min | Median | Max | Ratio[c] |
|---|---|---|---|---|---|---|---|
| UFP number, $N_{UFP}$ $\times 10^4$ (1/cm$^3$) | | | | | | | |
| 2003 | 3290 | 2.1 | 1.3 | 0.2 | 1.9 | 11.5 | 0.89 |
| 2004 | 6305 | 1.8 | 1.0 | 0.2 | 1.6 | 12.2 | 0.88 |
| 2005 | 2287 | 2.4 | 1.8 | 0.5 | 2.0 | 16.6 | 0.90 |
| Overall | 11882 | 2.0 | 1.3 | 0.2 | 1.7 | 16.6 | 0.88 |
| UFP surface[d], $S_{UFP}$ (μm$^2$/cm$^3$): | | | | | | | |
| 2003 | 3290 | 114 | 74 | 11 | 98 | 595 | 0.38 |
| 2004 | 6305 | 117 | 72 | 10 | 101 | 540 | 0.41 |
| 2005 | 2287 | 135 | 84 | 26 | 117 | 604 | 0.43 |
| Overall | 11882 | 119 | 75 | 10 | 104 | 604 | 0.40 |
| UFP volume[d], $V_{UFP}$ (μm$^3$/cm$^3$): | | | | | | | |
| 2003 | 3290 | 1.2 | 0.8 | 0.1 | 1.0 | 5.7 | 0.18 |
| 2004 | 6305 | 1.3 | 0.8 | 0.1 | 1.1 | 5.2 | 0.20 |
| 2005 | 2287 | 1.4 | 0.9 | 0.3 | 1.2 | 6.4 | 0.21 |
| Overall | 11882 | 1.3 | 0.8 | 0.1 | 1.0 | 6.4 | 0.20 |

a. Sample size.
b. Standard deviation.
c. Ratio of ultrafine particles (0.01-0.1 μm) to total particles (0.01-0.41 μm).
d. The mobility-equivalent *S* and *V* were derived from the *N*, assuming spherical particles.

The size-resolved particle number, $PM_{2.5}$, gas pollutants concentrations, and their correlation coefficients are given in Table 3. The highest particle number concentration ($0.9 \times 10^4$ 1/cm$^3$) resides in the Aitken mode size range of 0.02–0.05 μm. The increasing relative standard deviation (RSD) with decreasing particle size again underscores the transient and "localized" nature of the nucleation mode particles. In contrary, the accumulation mode particles are relatively stable, averaging $0.2 \times 10^4$ 1/cm$^3$. The low $r$ values (< 0.14) between the nucleation mode particles and particles larger than 0.05 μm are indicative of the differences in their origins. The UFPs, particularly the nucleation mode particles, showed virtually no correlations with the $PM_{2.5}$ and the gas pollutants ($r < 0.2$), except $SO_2$ ($r_{nucl} = 0.34$, $r_{UFP} = 0.52$). Clearly, in the present study, these pollutants are poor predictors of the particle number concentration and their relationships with UFPs cannot simply be described by a bi-variate linear relationship. Contrasting to our results, the hourly particle number concentration showed moderate correlations with CO and NO in several urban cities of Los Angeles ($r$ value up to 0.66) (Sardar *et al.,* 2004).

**Table 3.** Summary statistics of the concentrations of size-resolved particle number, total surface area, total volume, $PM_{2.5}$, and gas pollutants in the summer months of 2003–2005 in southwest Detroit.

| Variable | Unit | Mean | SD[a] | Min | Median | Max | RSD[b] | $r_{Nucl}$[c] | $r_{UFP}$[c] |
|---|---|---|---|---|---|---|---|---|---|
| $N_{0.01\text{-}0.02}$ ($N_{Nucl}$) | $\times 10^4$ 1/cm$^3$ | 0.59 | 0.54 | 0.03 | 0.45 | 7.08 | 0.92 | 1.00 | 0.79 |
| $N_{0.02\text{-}0.05}$ | $\times 10^4$ 1/cm$^3$ | 0.89 | 0.71 | 0.07 | 0.74 | 10.84 | 0.79 | 0.61 | 0.93 |
| $N_{0.05\text{-}0.1}$ | $\times 10^4$ 1/cm$^3$ | 0.51 | 0.36 | 0.04 | 0.41 | 3.02 | 0.71 | 0.14 | 0.60 |
| $N_{0.1\text{-}0.42}$ | $\times 10^4$ 1/cm$^3$ | 0.24 | 0.14 | 0.02 | 0.21 | 1.42 | 0.61 | 0.06 | 0.29 |
| $N_{0.01\text{-}0.1}$ ($N_{UFP}$) | $\times 10^4$ 1/cm$^3$ | 1.99 | 1.29 | 0.18 | 1.72 | 17.58 | 0.65 | 0.79 | 1.00 |
| $S_{Total}$[d] | μm$^2$/cm$^3$ | 301 | 163 | 32 | 272 | 1317 | 0.54 | 0.17 | 0.50 |
| $V_{Total}$[d] | μm$^3$/cm$^3$ | 7.0 | 4.1 | 0.6 | 7.1 | 37.7 | 0.59 | 0.06 | 0.26 |
| $PM_{2.5}$ | μg/cm$^3$ | 17.9 | 10.4 | b.d.l[e] | 14.7 | 84.7 | 0.61 | 0.01 | 0.11 |
| $O_3$ | ppb | 24.7 | 21.7 | b.d.l | 19.5 | 98.9 | 0.88 | 0.05 | 0.04 |
| CO | ppm | 0.96 | 0.51 | b.d.l | 0.83 | 7.30 | 0.53 | 0.01 | 0.20 |
| $SO_2$ | ppb | 7.2 | 10.3 | b.d.l | 3.9 | 155.9 | 1.44 | 0.34 | 0.52 |
| NO | ppb | 11.5 | 24.1 | b.d.l | 3.1 | 303.1 | 2.10 | 0.00 | 0.16 |

a. Standard deviation.
b. Relative standard deviation.
c. The correlation coefficients between the variables in the 1st column and the number concentrations of nucleation mode ($N_{Nucl}$) and ultrafine particles ($N_{UFP}$), respectively.
d. The subscript "total" refers to particles within the SMPS measurable size range: 0.01-0.41 μm.
e. Below detection limit.

***Ultrafine particle (UFP) events***

A total of 74 UFP events were identified in all but two sampling days in southwest Detroit during the summer months of 2003, 2004, and 2005. Among them 40 (54%) are classified as Aitken mode particle events and 34 (46%) as nucleation mode particle events. The average occurrence rate of UFP events was ~ 2 1/day. The particle number concentration characteristics during these events are summarized in Table 4. The maxima $N_{UFP}$ values during these events were, on average, two times higher than the overall mean $N_{UFP}$ value. The mean duration ($\Delta t$) for the $N_{UFP}$ to reach a maximum was 2.4 hr. This translates to a spatial scale of ~ 11 km assuming constant wind direction and wind speed of 1.3 m/s (Table 1). The mean UFP appearance rate ($\Delta N/\Delta t$) was 4.3 1/cm$^3$-s.

**Table 4.** Particle number concentration characteristics during ultrafine particle events ($n$ = 74).

| Unit | $N_{UFP[MAX]}$[a] $\times 10^4$ 1/cm$^3$ | $N_{UFP[MIN]}$[b] $\times 10^4$ 1/cm$^3$ | $\Delta N$[c] $\times 10^4$ 1/cm$^3$ | $\Delta N/N_{UFP[MIN]}$ ratio | $\Delta t$[d] hr | $\Delta N/\Delta t$ 1/cm$^3$-s |
|---|---|---|---|---|---|---|
| Mean | 4.0 | 1.2 | 2.8 | 2.6 | 2.4 | 4.3 |
| SD[e] | 1.9 | 0.4 | 1.9 | 2.1 | 1.8 | 3.6 |
| Min | 1.9 | 0.4 | 0.7 | 0.6 | 1.0 | 0.6 |
| Median | 3.6 | 1.2 | 2.4 | 1.8 | 1.8 | 3.2 |
| Max | 14.5 | 2.1 | 13.0 | 10.3 | 10.1 | 22.8 |

a. The maximum number concentration of ultrafine particles (0.01–0.1 μm).
b. The minimum number concentration of ultrafine particles (0.01–0.1 μm).
c. $\Delta N = N_{UFP[MAX]} - N_{UFP[MIN]}$.
d. $\Delta t = t_{MAX} - t_{MIN}$.
e. Standard deviation.

Fig. 5 shows the temporal variation of the average nucleation mode, Aitken mode, and UFP number concentrations during (a) non-event days, (b) Aitken mode event days, and (c) nucleation mode event days. The particle number concentrations on non-event days were considerably lower than on event days and showed no distinct features. On the other hand, the Aitken and nucleation mode event days each had two peak UFP number concentrations during the daytime. The first peak at 0830 EDT, appearing on both the Aitken and nucleation mode event days, shows that there is a common source responsible for the elevated concentrations. The second peak, however, occurred at a different time of day; at 1600 EDT for the Aiken mode events and at 1330 EDT for the nucleation mode events. This indicates the sources and/or meteorological conditions responsible for the respective particle events were likely different.

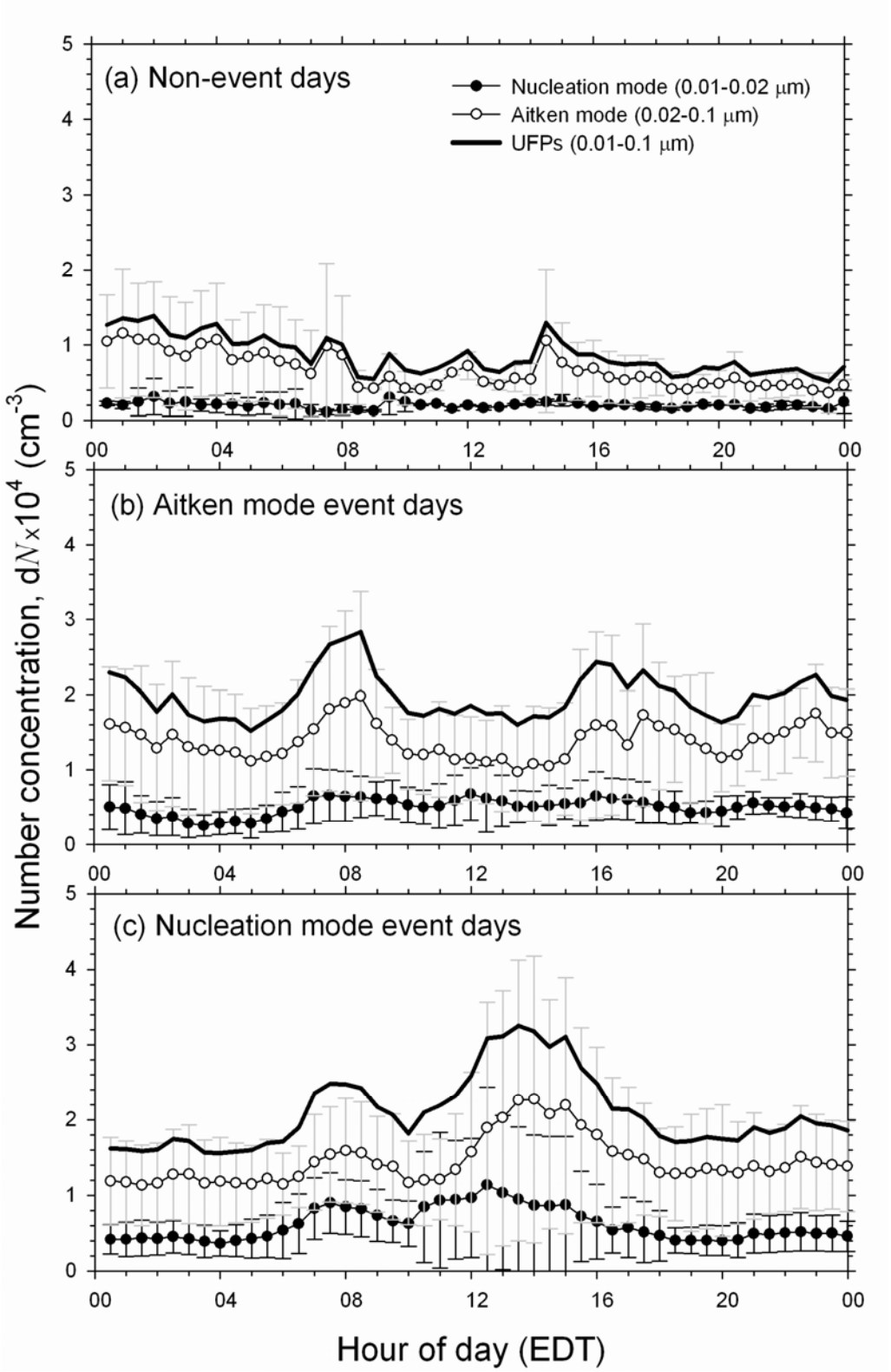


**Fig. 5.** The temporal variation of nucleation and Aitken mode particles on (a) non-event days, (b) Aitken mode event days, and (c) nucleation mode event days.

***Aitken mode particle events***

The Aitken mode particle events in southwest Detroit are characterized by a significantly higher fraction (> 0.57) of 0.02–0.1 μm particles in the UFP size range, as expected from the present identification and classification scheme. Fig. 6 shows the time series plots of the size-resolved particle number concentrations, gas pollutants, $PM_{2.5}$, total particle surface area ($S_{Total}$), wind direction, and the number size distributions during two typical Aitken mode particle events on August 31, 2004. In the first event at 0800 EDT the particle number concentrations coincided with high levels of CO (3.4 ppm), NO (194 ppb), $PM_{2.5}$ (39 μg $m^3$), and $S_{Total}$ (990 $\mu m^2/cm^3$). In addition, it closely followed the morning rush-hour traffic pattern. These correlations suggest those UFPs were resulted from morning traffic emissions. The combination of increased traffic volume and stable surface meteorological conditions in the early morning (Fig. 4) favors the buildup of pollutant concentrations. In the second event at 1600 EDT the particle number concentrations coincided with not only CO, NO, $PM_{2.5}$, and $S_{Total}$, but also with a high level of $SO_2$. The maximum $SO_2$ concentration was about 45 ppb, which is considerably higher than that from traffic-related events (< 10 ppb) (e.g., see the 0800 EDT event). The prevailing south-southwesterly winds during that period come directly from where the major $SO_2$ point sources are located. Also noted is the anti-correlation between $O_3$ and all other pollutants; a common feature of fresh plumes of local origin, where the $O_3$ is consumed by the primary pollutants in the plume (e.g., NO). All these observations suggest that industrial plumes were the main contributor to the UFPs. The traffic contribution to the 1600 EDT Aitken mode particle event was considered minor because of the higher wind speed and mixing height in the late afternoon (see Fig. 4). Advection of industrial $SO_2$-enriched plumes to the sampling site is common during the summers because of the prevailing southwesterly winds (Fig. 1). At the same sampling site, Keeler *et al.* (2005) showed a strong association between elevated $SO_2$ and southwesterly winds.

In both events, the simultaneous increase of $N_{UFP}$ and $S_{Total}$ suggests a substantial presence of particles larger than 0.1 μm. Recall that the accumulation mode particles on average account for approximately 60% of the total particle surface (Table 2) and are typically attributed to long-range transport because of their long atmospheric lifetimes. In this case, however, it is indicative that the measured Aitken mode particles were part of local polluted (particle-laden) plumes, such as traffic emissions and industrial plumes.

Without exception, all the identified Aitken mode particle events in this study coincided with elevated particle surface area and at least one of the primary gas pollutants (i.e., CO, NO, or $SO_2$) from combustion sources. This highlights the strong association between the Aitken mode particle events and fossil fuel combustion. Here we illustrated that with the aid of $SO_2$ and wind direction data it is possible to differentiate $SO_2$-enriched industrial plumes from traffic emissions.

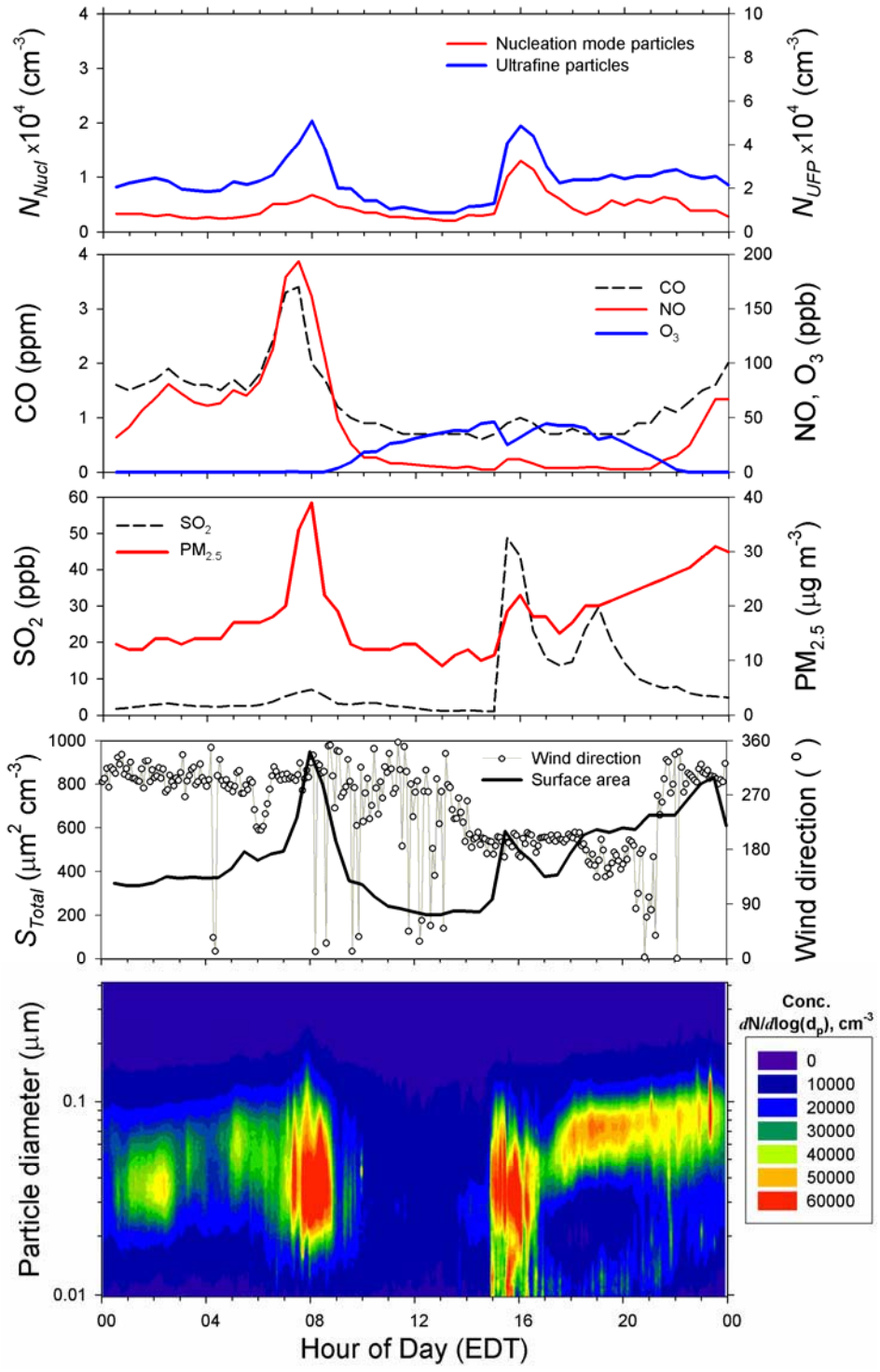


**Fig. 6.** Time series plots of the pollutant concentrations, wind direction, and particle number size distributions during two Aitken mode particle events on 8/31/04. The event at 0800 EDT is associated with morning rush-hour traffic and the one at 1600 EDT is associated with $SO_2$-plume.

***Nucleation mode particle events***

The nucleation mode particle events are characterized by a significantly higher fraction (> 0.34) of 0.01–0.02 μm particles in the UFP size range. An analysis for correlations with co-pollutants showed that there are in fact two distinct types of nucleation mode particle event. One type shows characteristics similar to the Aitken mode particle events, i.e., fresh plumes from fossil fuel combustion. Therefore, these events are referred to as "in-plume" nucleation mode particle event. Conversely, the other type shows no such correlation with CO, NO, and $S_{total}$ but occasionally $SO_2$. These events are referred to as "secondary" nucleation mode particle event. Of the 34 nucleation mode particle events, 25 were classified as in-plume events and 9 as secondary events.

***In-plume nucleation mode particle event***

A pronounced nucleation mode particle event on July 31, 2005 is shown in Fig. 7 (a). A burst of $N_{Nucl}$ ($6.0 \times 10^4$ 1/cm$^3$) at 1230 EDT was accompanied by a sharp increase of $SO_2$ (106 ppb), $PM_{2.5}$, and $S_{Total}$. The NO increased as well but to a lesser extent. A decrease of $O_3$ concentration and prevailing southerly winds were observed during the event. These features are very similar to one of the Aitken mode event discussed previously. Therefore, the nucleation mode event was likely a result of $SO_2$-enriched industrial plumes. The elevated $S_{Total}$ suggests the nucleation mode particles co-existed with a large number of larger (i.e., Aitken and accumulation mode) particles despite the high surface area that can act upon these small particles as a sink. The evolution of the number size distributions shows an intense and continuous burst of particles smaller than 0.07 μm over a period of ~ 4 hr. An inspection on the individual size distributions reveals that the newly formed particles were growing to larger sizes. The particle growth is not visible from the present contour plot because the concentrations of the new particles and larger particles were of similar magnitude.

Motor vehicles also emit nucleation mode particles. Fig. 7 (b) shows another in-plume nucleation mode particle event on August 30, 2004. The elevated $N_{Nucl}$ at 0800 EDT coincided with high levels of CO, NO, $PM_{2.5}$, $S_{Total}$ and morning rush-hour traffic. Noted is the considerably low $S_{Total}$ prior to the morning rush hour, in which favors the survival of nucleation mode particles. The low $S_{Total}$ was largely due to the two rainy days earlier and the prevailing northwesterly winds as a result of a passing cold front. Air masses from the north (Canada and the Arctic) are typically cleaner and cooler. The number size distributions reveals that particles initially in the nucleation mode size range grew into the Aitken mode range over the course of 4 hr, from a mode diameter of 0.017 to 0.031 μm (0.004 μm/hr). This shows the number size distribution of UFPs is not a static property, but evolves with time. It also implies the number size distribution alone cannot be used as a source signature.

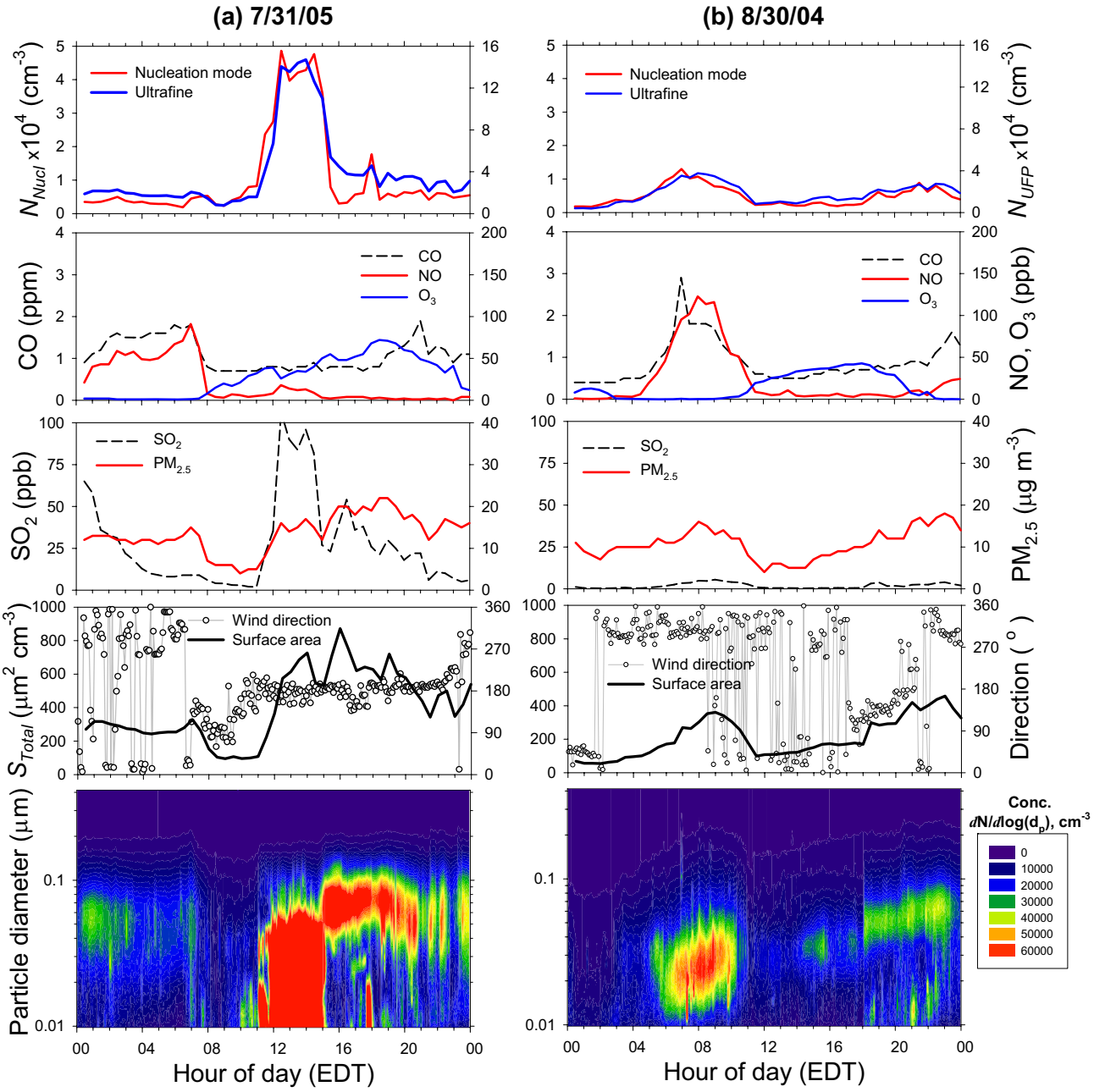


**Fig. 7.** Time series plots of the pollutant concentrations, wind direction, and particle number size distributions during an "in-plume" nucleation mode particle event on (a) 7/31/05: $SO_2$-plume and (b) 8/30/04: morning rush-hour traffic.

### *Secondary nucleation mode particle event*

Here we present another type of nucleation mode particle event that exhibits characteristics distinctly different from the in-plume (or combustion-related) events described previously. A pronounced secondary nucleation mode particle event on September 1, 2004 is shown in Fig. 8 (a). The burst of $N_{Nucl}$ at 1100 EDT was not correlated with elevated CO, NO, and $S_{Total}$ but only

$SO_2$. This suggests the nucleation mode particles were not directly emitted from local combustion sources and the potential involvement of $H_2SO_4$ in the nucleation processes. The low initial $S_{Total}$ and its subsequent *gradual* increase from 0930 to 1630 EDT imply that the nucleation event was not associated with polluted plumes. The number size distributions show the growth of the nucleation mode particles from 0.01 μm to 0.07 μm over a 6 hr period (0.01 μm/hr) was responsible for the gradual increase of the $S_{Total}$.

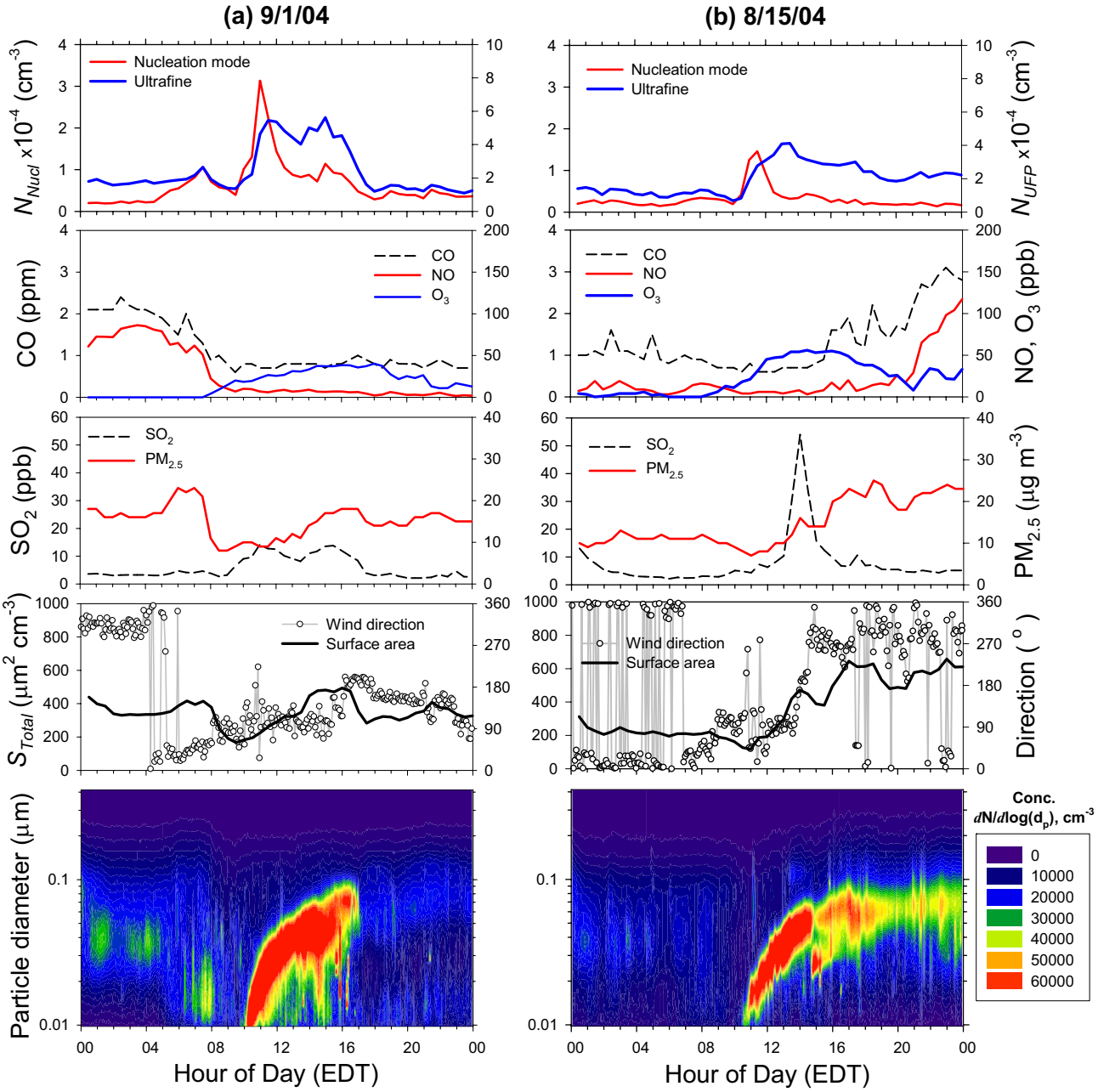


**Fig. 8.** Time series plots of the pollutant concentrations, wind direction, and particle number size distributions during a "secondary" nucleation mode particle event on (a) 9/1/04 and (b) 8/15/04.

Another secondary nucleation mode event on August 15, 2004 is shown in Fig. 8 (b). The burst of $N_{Nucl}$ at 1100 EDT was not accompanied with simultaneous increases of any gas pollutants, including $SO_2$. The $S_{Total}$ again was at a minimum at the start of the event and increased gradually over the event period. A $SO_2$ peak concentration was observed 3-hr after the onset of the event, suggesting the event probably took place at the outskirt of a $SO_2$-enriched plume. The number size distributions show the particles grew from 0.013 to 0.05 μm in 3.5-hr (0.01 μm/hr). Unlike the previous secondary event, the peak concentration in the size distributions at the start of the event was at a size slightly above the smallest measurable size, resulting in a "closed" contour plot. This implies that the actual nucleation did not take place locally but some distance away from the sampling site or the growth of nucleation mode particles is non-linear (Birmili *et al.*, 2003). During transport toward the sampling site the particles therefore had grown to larger sizes. After the particles grew into the Aitken mode size range they maintained there throughout the evening, from 1500–2400 EDT, regardless of changing wind directions. This indicates that the spatial extent of the event was likely on the order of regional scale.

Two noticeable features among the secondary nucleation events are (1) all of them took place shortly after the breakup of the nocturnal inversion or near solar noon and (2) the drop of $S_{Total}$ to a minimum prior to the events. These two features are in fact coupled as atmospheric dilution due to the breakup of the inversion layer lowers the $S_{Total}$ as well as other ambient pollutants (e.g., Fig. 6, 7, and 8). The majority of nucleation events observed globally took place between sunrise and noon (Kulmala *et al.*, 2004), suggesting a connection between nucleation and photochemistry. Fig. 9 shows the time series plot of the solar radiation and RH on non-event, primary and secondary nucleation event days. As shown, the secondary nucleation event days were associated with stronger solar radiation and lower RH. Also noticeable is the higher RH before sunrise and sharper drop of RH after sunrise on secondary nucleation event days. Fig. 10 shows the ranges of the $S_{Total}$ for Aitken, in-plume and secondary nucleation mode event days. Nucleation events, especially secondary ones, showed clear preference for low particle surface area conditions. Strong solar radiation and low pre-existing particle surface area together, however, did not always warrant secondary nucleation mode particle events, and therefore they are necessary but not sufficient factors. These findings are consistent with the classical nucleation theory; stronger solar radiation results in stronger photochemical activities, hence more condensable species (e.g., $H_2SO_4$), and lower particle surface represents conditions of weaker competition from vapor condensation, both of which favor nucleation.

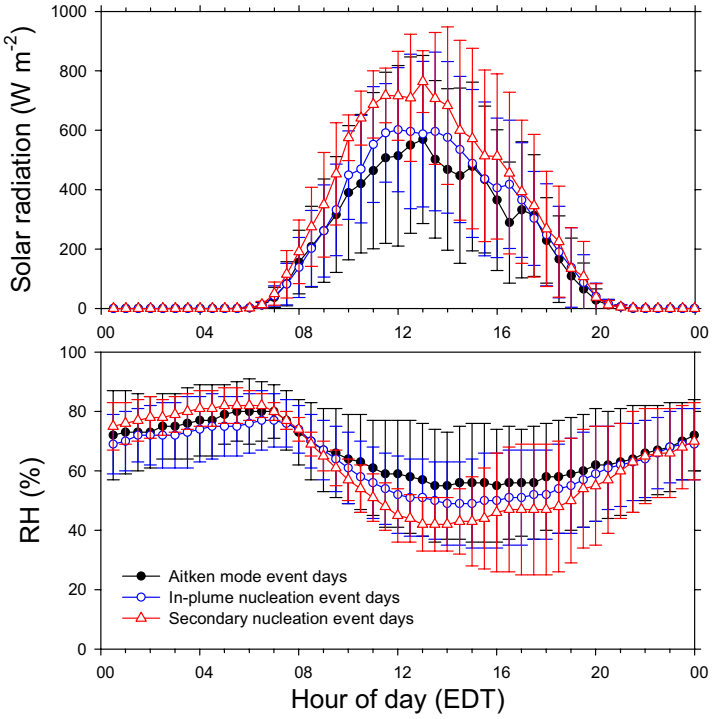


**Fig. 9.** The diurnal patterns of the mean solar radiation and RH during Aitken, in-plume nucleation, and secondary nucleation mode particle event days.

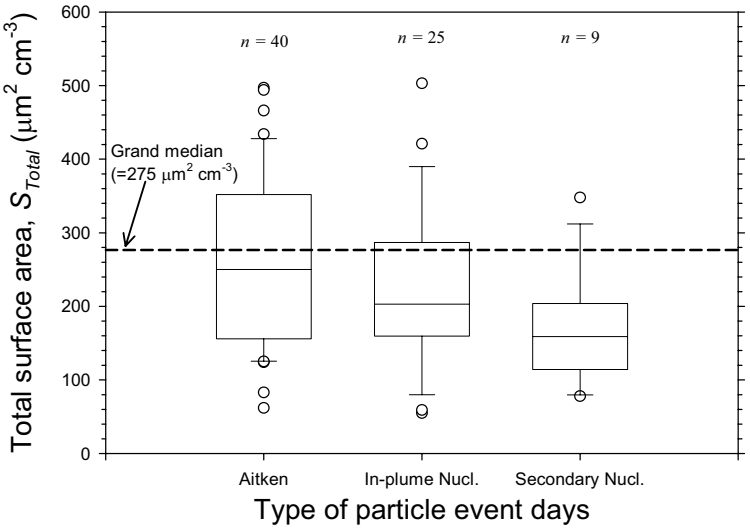


**Fig. 10.** Box plots of total particle surface area for Aitken, in-plume nucleation, and secondary nucleation mode particle event days. The lower and upper boundary of the box represents the 25$^{th}$ and 75$^{th}$ percentiles, respectively. The line inside the box is the 50$^{th}$ percentile. The whiskers indicate the 10$^{th}$ and 90$^{th}$ percentiles. The circles are outliers below the 10$^{th}$ and above the 90$^{th}$ percentiles.

## CONCLUSION

A total of 74 ambient ultrafine particle (UFP) events were identified and classified during the summer months of 2003, 2004, and 2005 in southwest Detroit. These events were analyzed for source and meteorological implications. According the characteristics of the particle size distributions, 40 (54%) were classified as Aitken mode particle events and 34 (46%) as nucleation mode particle events. Sixty-five out of the 74 events were classified as "in-plume" particle events due to their strong associations with elevated CO, NO, and total particle surface area. This implies that fossil fuel combustion, such as traffic emissions and industrial plumes, is the dominant source of elevated UFPs in southwest Detroit. The remaining 9 UFP events, on the other hand, showed no correlation with the CO, NO, $PM_{2.5}$, and total particle surface area, hence are referred to as "secondary" events. These events are characterized by the gradual, not simultaneous, increase in the particle surface area due to the ensuing particle growth. On occasion these events were correlated with $SO_2$, suggesting the potential involvement of $H_2SO_4$ in the nucleation processes. Furthermore, all the secondary events took place several hours after the breakup of the inversion layer or near solar noon. It is indicative that atmospheric mixing/dilution and photochemistry play an important role in the nucleation processes. The former reduces the pre-existing particle concentration whereas the latter results in the formation of condensable species (e.g., $H_2SO_4$). It is noted that the in-plume nucleation mode particle events could also take place at noon time. Without the aid of co-pollutant measurements one could easily mistake the in-plume events as secondary nucleation events. Such misclassification can lead to the mischaracterization of exposure because the physical and chemical properties are likely different between the in-plume and secondary UFPs.

## ACKNOWLEDGMENTS

The authors thank the members of the UM Air Quality Lab for their efforts and contributions to the sampling campaigns. This study was supported by the Michigan Life Science Corridor Award AIBS1558 and the UM Rackham Graduate School One-term Dissertation Fellowship.

## REFERENCES

Aalto, P., H.ameri, K., Becker, E., Weber, R., Salm, J., Mäkelä, J. M., Hoell, C., O'Dowd, C.D., Karlsson, H., Hansson, H.-C., Väkevä, M., Koponen, I.K., Buzorius, G. and Kulmala, M. (2001). Physical characterization of aerosol particles in boreal forests. *Tellus B* 53: 344–358.

Alam, A., Shi, J.P. and Harrison, R.M. (2003). Observations of New Particle Formation in Urban Air. *J. Geophys. Res.* 108: doi:10.1029/2001JD001417.

Baron, P.A. and Willeke, K. (2001). *Aerosol Measurement: Principles, Techniques, and Applications*. Wiley, New York.

Bellouin, N., Boucher, O., Haywood, J. and Reddy, M.S. (2005). Global Estimate of Aerosol Direct Radiative Forcing from Satellite Measurements. *Nature.* 438: 1138-1141.

Birmili, W., Berresheim, H., Plass-Dülmer, C., Elste, T., Gilge, S., Wiedensohler, A. and Uhrner, U. (2003). The Hohenpeissenberg Aerosol Formation Experiment (HAFEX): A Long-term Study Including Size-resolved Aerosol, $H_2SO_4$, OH, and Monoterpenes Measurements. *Atmos. Chem. Phys.* 3: 361-376.

Boy, M. and Kulmala, M. (2002). Nucleation Events in the Continental Boundary Layer: Influence of Physical and Meteorological Parameters. *Atmos. Chem. Phys.* 2: 1-16.

Brock, C.A., Trainer, M., Ryerson, T.B., Neuman, J.A., Parrish, D.D., Holloway, J.S., Nicks, D.K., Frost, G.J., Hubler, G., Fehsenfeld, F.C., Wilson, J.C., Reeves, J.M., Lafleur, B.G., Hilbert, H., Atlas, E.L., Donnelly, S.G., Schauffler, S.M., Stroud, V.R. and Wiedinmyer, C. (2003). Particle Growth in Urban and Industrial Plumes in Texas. *J Geophys. Res.* 108: doi: 10.1029/2002JD002746.

Chang, M.C.O., Chow, J.C., Watson, J.G., Hopke, P.K., Yi, S.M. and England, G.C. (2004). Measurement of Ultrafine Particle Size Distributions from Coal-, Oil-, and Gas-fired Stationary Combustion Sources. *J. Air Waste Manage. Assoc.* 54: 1494-1506.

Curtius, J. (2006). Nucleation of Atmospheric Aerosol Particles. *C. R. Physique.* 7: 1027-1045.

Harrison, R.M. and Jones, A.M. (2005). Multisite Study of Particle Number Concentrations in Urban Air. *Environ. Sci. Technol.* 39: 6063-6070.

Hussein, T., Karppinen, A., Kukkonen, J., Härkönen, J., Aalto, P.P., Hämeri, K., Kerminen, V.M. and Kulmala, M. (2006). Meteorological Dependence of Size-fractionated Number Concentrations of Urban Aerosol Particles. *Atmos. Environ.* 40: 1427-1440.

Jeong, C.H., Hopke, P.K., Chalupa, D. and Utell, M. (2004). Characteristics of Nucleation and Growth Events of Ultrafine Particles Measured in Rochester, NY. *Environ. Sci. Tech. 3*8: 1933-1940.

Keeler, G.J., Morishita, M. and Young, L.H. (2005). Characterization of Complex Mixtures in Urban Atmospheres for Inhalation Exposure Studies. *Exp. Toxicol. Pathol.* 57: 19-29.

Kittelson, D.B., Watts, W.F. and Johnson, J.P. (2006). On-road and Laboratory Evaluation of Combustion Aerosols – Part 1: Summary of Diesel Engine Results. *J. Aerosol Sci.* 37: 913-930.

Kulmala, M., Vehkamäki, H., Petäjä, T., Dal Maso, M., Lauri, A., Kerminen, V.M., Birmili, W. and McMurry, P.H. (2004). Formation and Growth Rates of Ultrafine Atmospheric Particles: A Review of Observations. *J. Aerosol Sci.* 35: 143-176.

Lee, S.H., Reeves, J.M., Wilson, J.C., Hunton, D.E., Viggiano, A.A., Miller, T.M., Ballenthin, J.O. and Lait, L.R. (2003). Particle Formation by Ion Nucleation in the Upper Troposphere and Lower Stratosphere. *Science.* 301: 1886-1889.

Lohmann, U. and Feichter, J. (2005). Global Indirect Aerosol Effects: A Review. *Atmos. Chem. Phys.* 5: 715-737.

Maguhn, J., Karg, E., Kettrup, A. and Zimmermann, R. (2003). On-line Analysis of the Size Distribution of Fine and Ultrafine Aerosol Particles in Flue and Stack Gas of a Municipal Waste Incineration Plant: Effects of Dynamical Process Control Measures and Emission Reduction Devices. *Environ. Sci. Technol.* 37: 4761-4770.

Mäkelä, J.M., Dal Maso, M., Pirjola, L., Keronen, P., Laakso, L., Kulmala, M. and Laaksonen, A. (2000). Characteristics of the Atmospheric Particle Formation Events Observed at a Boreal Forest Site in Southern Finland. *Boreal Enviro. Res.* 5: 299-313.

Maricq, M.M., Chase, R.E., Xu, N. and Laing, P.M. (2002). The Effects of the Catalytic Converter and Fuel Sulfur Level on Motor Vehicles Particulate Matter Emissions: Light Duty Diesel Vehicles. *Environ. Sci. Technol.* 36: 283-289.

Michigan Department of Transportation (MDOT) (2005). Average Daily Traffic (ADT) Map, http://www.michigan.gov/mdot/0,1607,7-151-9622_11033-22141--,00.html.

Nel, A. (2005). Air Pollution-related Illness: Effects of Particles. *Science.* 308: 804-806.

Nel, A., Xia, T., Mädler, L. and Li, N. (2006). Toxic Potential of Materials at the Nanolevel. *Science.* 311: 622-627.

O'Dowd, C.D., Hämeri, K., Mäkelä, J., Väkeva, M., Aalto, P., de Leeuw, G., Kunz, G.J., Becker, E., Hansson, H.C., Allen, A.G., Harrison, R.M., Berresheim, H., Kleefeld, C., Geever, M., Jennings, G. and Kulmala, M. (2002). Coastal New Particle Formation: Environmental Conditions and Aerosol Physicochemical Characteristics During Nucleation Bursts. *J. Geophys. Res.* 107: doi: 10.1029/2000JD000206.

Sardar, S.B., Fine, F.M., Yoon, H. and Sioutas, C. (2004). Associations Between Particle Number and Gaseous Co-pollutant Concentrations in the Los Angeles Basin. *J. Air Waste Manage. Assoc.* 54: 992-1005.

Stanier, C.O., Khlystov, A.Y. and Pandis, S.N. (2004a). Ambient Aerosol Size Distributions and Number Concentrations Measured During the Pittsburg Air Quality Study (PAQS). *Atmos. Environ.* 38: 3275–3284.

Stanier, C.O., Khlystov, A.Y. and Pandis, S.N. (2004b). Nucleation Events During the Pittsburgh Air Quality Study: Description and Relation to the Key Meteorological, Gas Phase, and Aerosol Parameters. *Aerosol Sci. Technol.* 38(S1): 253-264.

Vehkamäki, H., Dal Maso, M., Hussein, T., Flanagan, R., Hyvärinen, A., Lauros, J., Merikanto, J., Mönkkönen, P., Pihlatie, M., Salminen, K., Sogacheva, L., Thum, T., Ruuskanen, T.M., Keronen, P., Aalto, P.P., Hari, P., Lehtinen, K.E.J., Rannik, Ü. and Kulmala, M. (2004). Atmospheric Particle Formation Events at Värriö Measurement Station in Finnish Lapland 1998–2002. *Atmos. Chem. Physics.* 4: 2015-2023.

Virtanen, A., Rönkkö, T., Kannosto, J., Ristimäki, J., Mäkelä, J.M., Keskinen, J., Hillamo, R., Pirjola, L. and Mämeri, K. (2006). Winter and Summer Time Size Distributions and Densities of Traffic-related Aerosol Particles at a Busy Highway in Helsinki. *Atmos. Chem. Phys.* 6: 2411-2421.

Woo, K.S., Chen, D.R., Pui, D.Y.H. and McMurry, P.H. (2001). Measurement of Atlanta Aerosol Size Distributions: Observations of Ultrafine Particle Events. *Aerosol Sci. Technol.* 34: 75-87.

Young, L.H. and Keeler, G.J. (2004). Characterization of Ultrafine Particle Number Concentration and Size Distribution During a Summer Campaign in Southwest Detroit. *J. Air Waste Manage. Assoc.* 54: 1079-1090.

Young, L.H., Benson, D.R., Montanaro, W.M., Lee, S.H., Pan, L.L., Rogers, D.C., Jensen, J., Stith, J.L., Davis, C.A., Campos, T.L., Bowman, K.P., Cooper, W.A. and Lait, L.R. (2007). Enhanced New Particle Formation Observed in the Northern Midlatitude Tropopause Region. *J. Geophys. Res.* 112: doi:10.1029/2006JD008109.

Zhu, Y., Kuhn, T., Mayo, P. and Hinds, W.C. (2006). Comparison of Daytime and Nighttime Concentration Profiles and Size Distributions of Ultrafine Particles near a Major Highway. *Environ. Sci. Technol.* 40: 2531-2536.

*Received for review, February 28, 2007*
*Accepted, April 6, 2007*