P1.21 OBSERVATIONS OF RECENT NEW PARTICLE FORMATION IN HOUSTON DURING TEXAQS-2000

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1. INTRODUCTION

Continuous particle number size distribution measurements (5-600nm diameter) were conducted at a tall building site (Williams Tower, 254m AGL) near downtown Houston, and on-board the DOE G-1 aircraft during the TEXAQS-2000 study between August 21 and September 13. In this study we examine the conditions under which recent new particles were formed, with particular attention to periods when air was sampled near the top of the developing boundary layer.

2. EXPERIMENTAL SYSTEM

2.1 Size distribution measurements.

The building and aircraft measurement systems are built around two commercially available differential mobility analyzers (DMA), one short DMA for selecting particles in the 5-85nm diameter size range (TSI Model 3085) and one long DMA for particles in the 35-800nm size range (TSI Model 3081). The DMA selects particles based on their electrical mobility, which depends on the particle size, the mean free path of air, and the number of elementary charges carried by the particle. For a given voltage setting of the DMA a relatively monodisperse particle population is selected from the polydisperse ambient aerosol sampled at the DMA inlet. The inlet sample flow is passed through a charge neutralizer so that a Boltzmann equilibrium distribution of charge is imparted to the incoming particles. Only between 1 and 28% of the polydisperse aerosol entering the DMA have a single elementary charge, depending upon the particle size, and the DMA only selects charged particles. Therefore, corrections must be applied to the observed concentrations exiting the DMA for singly and multiply charged fractions of the sampled particles. Once the particles exit the DMA, commercial condensation particle counters (TSI Model 3010) are used to determine their concentration. For the monodisperse sample leaving the short DMA, the CPC is operated with an increased temperature difference (22^{o}C compared to 17 ^{o}C) between the saturator and condenser so that the diameter at which 50% of the particles are detected is decreased from 12 to 7nm. The voltages in each DMA are scanned simultaneously over a 60s period so that an entire size distribution is obtained with 1 minute time resolution. Particle size can change with relative humidity (RH), therefore the RH inside each DMA is controlled to values below 10% and the ambient aerosol sample flow into each DMA is dried using an in-line dryer (Permapure Inc.).

2.2 Estimates of the boundary layer height.

Daytime boundary layer heights were derived from reflectivities measured by the 915 MHz boundary layer radar wind profilers at the Houston Southwest and Wharton sites. The Williams Tower is located between the profiler sites and the boundary layer height estimates from the two profilers were generally similar. Therefore, we assume that the data may be applied to our downtown site location. The humidity gradient at the top of the mixed layer causes a peak in radar reflectivity. The time-height patterns of reflectivity were examined manually to determine the BL height each half-hour during the day. It is not always possible to determine the BL height, for example if the capping inversion is too weak. Clouds also complicate the interpretation. For further information on the technique, see Grimsdell and Angevine (1998).

3. MEASUREMENT RESULTS

Measurements at the building site showed that on about one-half of the days, recent aerosol formation near the sampling site occurred and that the freshly formed particles grew from the nucleation to Aitken mode. Superimposed on this formation were emissions of primary aerosols from traffic.

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3.1 Total number concentration in Houston downtown.

Total number concentrations (5-600 nm) exhibited a distinct diurnal trend with a minimum at night and maximum values in the morning (Figure 1). Measured total concentrations ranged from 100 to 100000 particles cm^{-3}. In Figure 1 dots represent the entire data set of integrated total number concentrations from the building size distribution data.

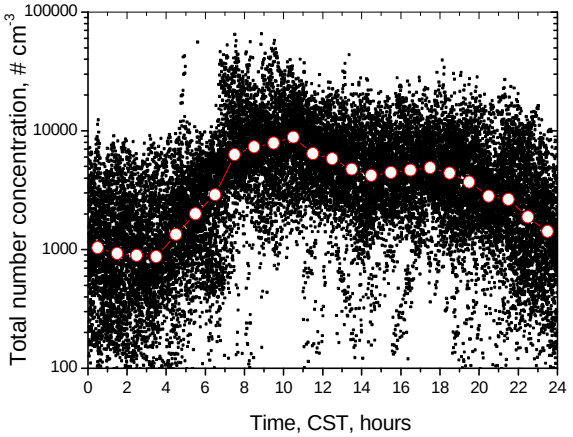

Figure 1. Diurnal trend in total number concentration at building site for entire study.

Circles show median value of all data points within the given hour. During many nights, the boundary layer top was below the measurement altitude at the building site and low total number concentrations were observed. Traffic emissions were occasionally transported to the building site a few hours before the rising boundary layer top passed the measurement altitude (about 6 am, CST). In each instance when the top of the convective boundary layer passed the sampling point at 254 m, total particle number concentrations increased dramatically.

3.2 Total particle volume

Size distributions revealed that the observed morning increases in total number concentrations were due to high concentrations of nucleation and Aitken mode particles. Although these are relatively small particles, this increase is seen to affect volume concentrations (Figure2). The symbols in Figure 2 are defined as in Figure 1. Diesel and gasoline engine exhausts are known to contain high number concentrations of 10-200 nm diameter aerosols (Harris and Matti-Maricq, 2001). Thus traffic emissions can help explain the diurnal trend in the number concentration.

Typical particulate mass concentration values derived from the total volume data assuming a density of 1 g cm^{-3} are around 10 μg m^{-3}. However, occasional order of magnitude increases were observed.

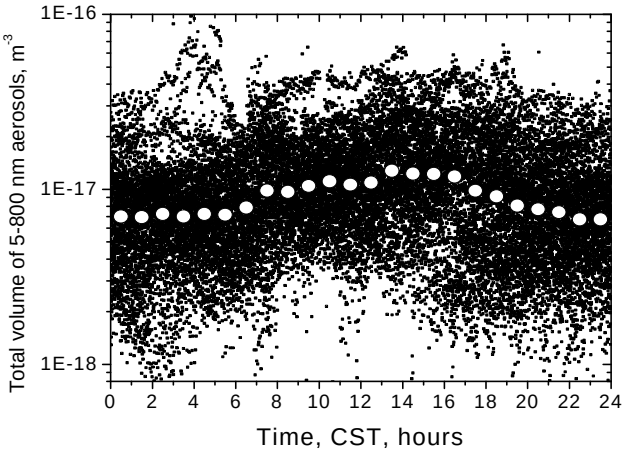

Figure 2. Diurnal trend of total aerosol volume, for particles with 5-800 nm sizes (building site).

3.3 Case study of a high nanoparticle concentration event

Nanoparticles in the 5-15 nm diameter size range can originate from primary traffic emissions as well as from secondary formation processes through heterogeneous and homogenous gas-to-particle conversion. Our ambient aerosol size distributions sometimes show a dominant number size mode that gradually increases with time. This suggests that nucleation mode particles (smaller than 10 nm) grow by condensation and/or coagulation into the Aitken mode (roughly 10-50 nm). Often this growth is associated with secondary aerosol formation. In order to identify the relative importance of primary emissions and secondary formation processes toward nanoparticle production, additional measurements would be required, including simultaneous gas-phase precursor concentrations, nanoparticle composition, and size distributions of particles smaller than 5 nm. Primary traffic emissions are believed to represent a significant component of high nanoparticle concentration events. Vakeva et al. (1999) also found that number concentrations were dominated by traffic emissions, but showed that in some instances nucleation would be favored, and may have been observed, at an elevated site in their study. Figure 3 shows particle concentrations for sizes between 5 and 15 nm on August 29 at the Williams Tower sampling site. Observations of size distributions during two aircraft flights on this day also showed high concentrations of particles in this size range. Boundary layer height is also shown in

the figure, with squares (Wharton) and triangles (Southwest).

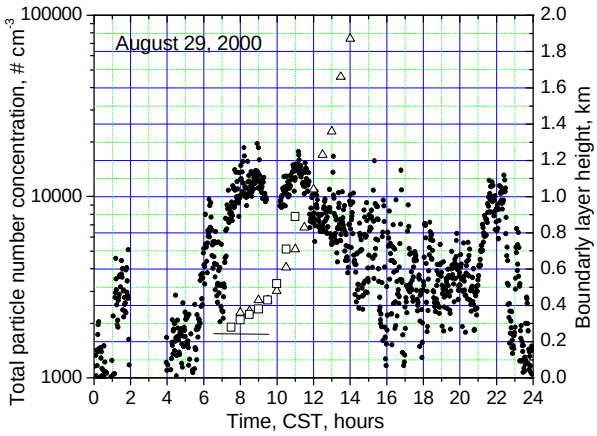

Figure 3. 5-15 nm aerosol number concentration in small circles, with boundary layer heights from two sites are plotted against right ordinate scale and marked as squares and triangles. A horizontal line marks altitude of the sampling point.

Between 6 and 7am the peak in particle number may be due to an overshooting thermal which penetrated the boundary layer top and reached the sampling altitude bringing high particulate number concentration. Around 7am the boundary layer top reached the measurement altitude and the number concentration increased simultaneously by an order of magnitude. It is likely that the majority of these particles were primary aerosols from traffic emissions. Later in the morning, around 10 am, distinct particle growth was observed until 3 pm. During that time the particle size dominating the number concentration gradually moved from the nucleation mode to much larger 70-90 nm diameter particles.

3.4 Aerosol growth.

Similar growth events were observed on a number of days during the campaign. These events are believed to represent secondary aerosol formation and subsequent growth that increased the total particle number and resulted in the observed diurnal cycle of the aerosol size distribution shown in Figure 4.

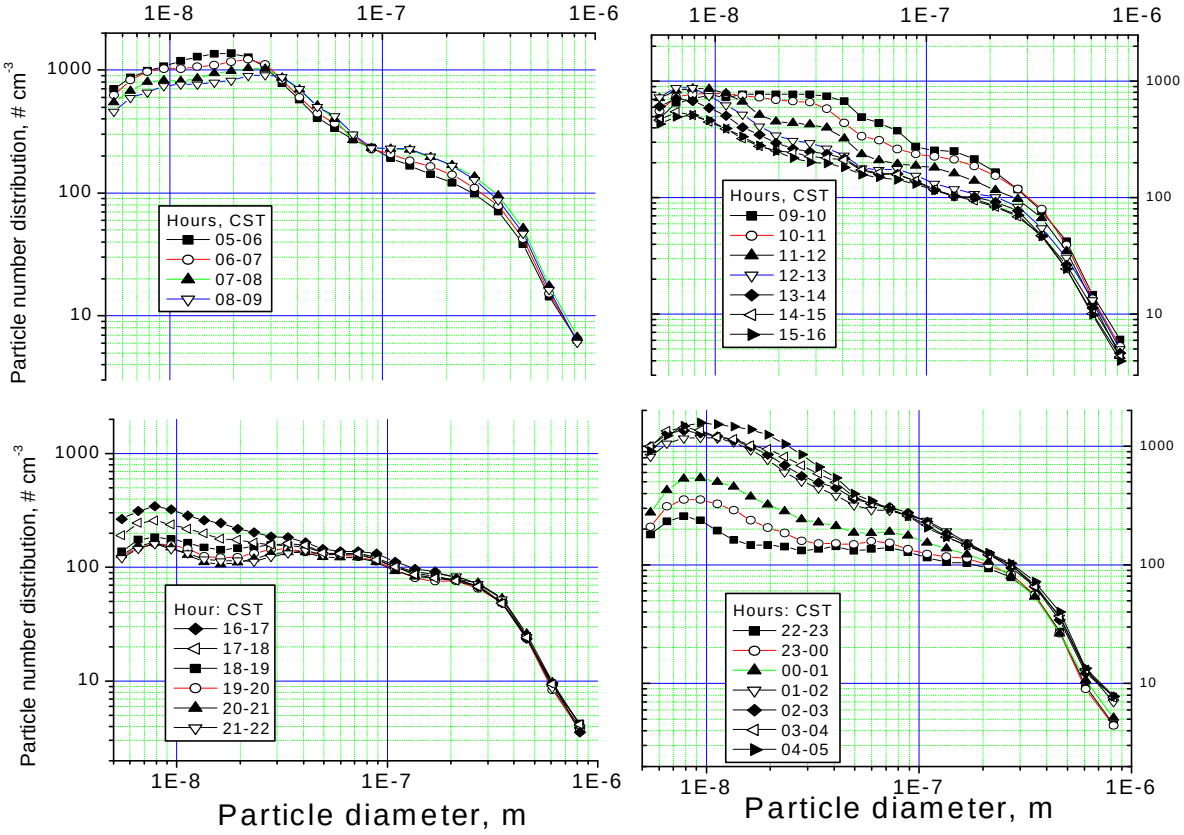

Figure 4. Diurnal variation of aerosol size distribution. Various size distributions represent a median concentration for a given hour.

Figure 4 shows the diurnal trend in ambient aerosol size distributions over the entire study. Changes in concentrations of particles larger 300 nm are very small. The lowest concentrations of particles of all sizes were during the night hours from 6 pm to midnight when the tall building site was often located in a residual layer aloft that was decoupled from surface particle sources.

Concentrations of nucleation and Aitken mode particles were highest during early morning hours. Growth from the nucleation to Aitken mode particles started after the sunrise. During this growth, the concentration of nucleation mode particles declined. During the late morning hours, concentrations of 10-30 nm diameter particles also decreased. This picture is representative of the averaged diurnal variation over the entire study, and is not necessarily representative of the variability on any single day.

4. Conclusions

Particle number size distribution measurements were conducted at a tall building site and on a research aircraft during the TexAQS-2000 study. High concentrations of nucleation mode particles were observed during the early morning hours at the same time as the top of the developing boundary layer reached the sampling altitude. Transport of primary emissions from traffic and other local sources, as well as secondary formation processes, was observed. Growth of particles from the nucleation to Aitken modes appears to significantly impact the observed diurnal variation in the number size distribution. As these particles grow to larger sizes they may become more effective at scattering radiation and could act as cloud condensation nuclei, resulting in visibility and climate effects.

5. References

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