Atmos. Chem. Phys., 6, 4801–4807, 2006
www.atmos-chem-phys.net/6/4801/2006/

Atmospheric Chemistry and Physics

On the time-averaging of ultrafine particle number size spectra in vehicular plumes

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Received: 17 May 2006 – Published in Atmos. Chem. Phys. Discuss.: 24 July 2006
Revised: 11 October 2006 – Accepted: 17 October 2006 – Published: 24 October 2006

Abstract. Ultrafine vehicular particle (<100 nm) number size distributions presented in the literature are mostly averages of long scan-time (~30 s or more) spectra mainly due to the non-availability of commercial instruments that can measure particle distributions in the <10 nm to 100 nm range faster than 30 s even though individual researchers have built faster (1–2.5 s) scanning instruments. With the introduction of the Engine Exhaust Particle Sizer (EEPS) in 2004, high time-resolution (1 full 32-channel spectrum per second) particle size distribution data become possible and allow atmospheric researchers to study the characteristics of ultrafine vehicular particles in rapidly and perhaps randomly varying high concentration environments such as roadside, on-road and tunnel. In this study, particle size distributions in these environments were found to vary as rapidly as one second frequently. This poses the question on the generality of using averages of long scan-time spectra for dynamic and/or mechanistic studies in rapidly and perhaps randomly varying high concentration environments. One-second EEPS data taken at roadside, on roads and in tunnels by a mobile platform are time-averaged to yield 5, 10, 30 and 120 s distributions to answer this question.

1 Introduction

Size distributions of on-road ultrafine (<100 nm) vehicular particle number concentrations are important to the study of particle formation and evolution processes, and they can be used as signatures for source identification (Zhu et al., 2002a, b; Bukowiecki et al., 2003; Gidhagen et al., 2003; Jacobson and Seinfeld, 2004; Vouitsis et al., 2005; Morawska et al., 2006). Averages of long scan-time (~30 s or more) spectra of vehicular particles are usually reported in the literature (Zhu et al., 2002a, b; Bukowiecki et al., 2003; Gidhagen et al., 2003; Sturm et al., 2003; Kittelson et al., 2004; Burtscher, 2005; Morawska et al., 2006) and several mathematical models have been developed to explain the formation and evolution processes of these particles (Kim et al., 2002; Gidhagen et al., 2003; Jacobson and Seinfeld, 2004; Zhang and Wexler et al., 2004; Zhang et al., 2004; Vouitsis et al., 2005). Commercially available ultrafine particle sizers such as Scanning Mobility Particle Sizer (SMPS) take as long as 30 s to yield a full 3–560 nm particle size spectrum although individual researchers have custom-improved the scanning speed of SMPS to 1–2.5 s (Shah and Cocker, 2002; Wang et al., 2002). Faster scanning speed data are deemed to be more favorable for mechanistic studies. However, none of these fast instruments are commercially available, and most of the literature reports are still based on 30-s SMPS spectra. In addition, other fast particle sizers such as the Electrical Aerosol Spectrometer (Tammet et al., 2002), and the Differential Mobility Spectrometer (Biskos et al., 2005) are also developed by individual researchers. Upon the introduction of the Engine Exhaust Particle Sizer (EEPS, TSI, Inc.) in 2004, size (5.6–560 nm) distribution measurements as fast as 32-channel per second can be obtained (Johnson et al., 2004; Jacobson et al., 2005; Yao et al., 2005), and the results showed that particle number concentration frequently varied at least as rapidly as 1 s in concentrated particle environments such as roadside, on roads and in tunnels. This poses the question on the generality of using averages of long scan-time spectra for dynamic and/or mechanistic studies in rapidly and perhaps randomly varying high concentration environments. Conceivably, in slow or relatively non-varying environments, time-averaging of particle size distributions for mechanistic studies would not be a problem.

The objective of this study is to address the question raised above, by comparing 1-s EEPS ultrafine vehicular particle number size distributions with those obtained by time-averaging (5, 10, 30 and 120 s) the same 1-s EEPS

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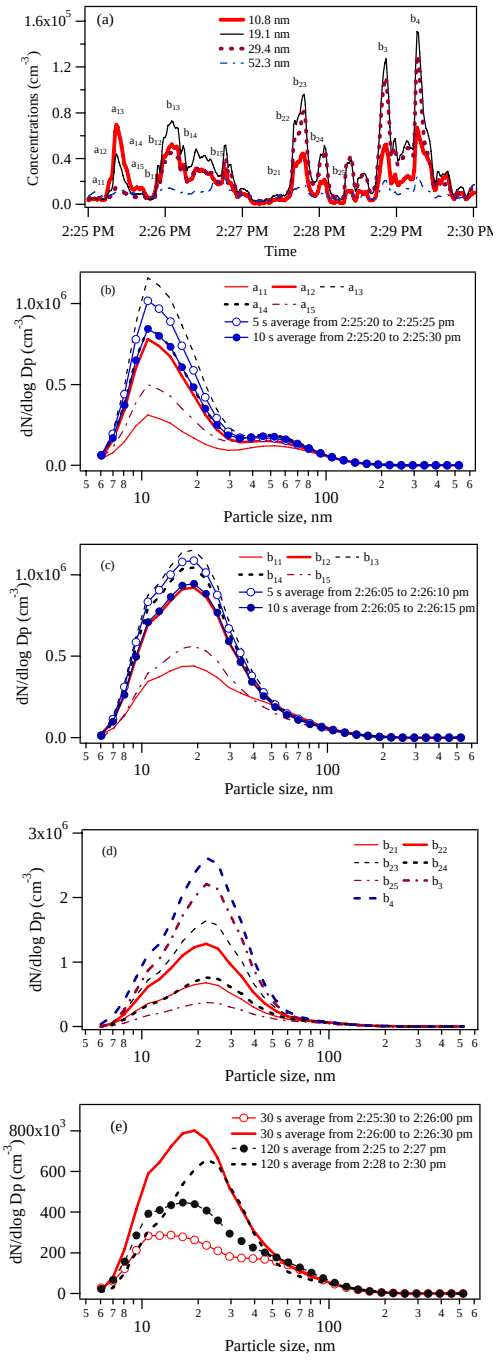

Fig. 1. Light traffic roadside ultrafine particle concentrations and size distributions, 02:30 p.m., 7 October 2004. **(a)** Concentrations of 10.8, 19.1, 29.4 and 52.3 nm particles, **(b)** Size distributions and 5 s and 10 s time-averaged spectra at a_{11}–a_{15}, **(c)** Size distributions and 5 s and 10 s time-averaged spectra at b_{11}–b_{15}, **(d)** Size distributions at b_{21}–b_{25}, b_{3-4}, **(e)** 30 s and 120 s time-averaged spectra. Note: a_{1n} are bi-modal size distributions at ∼10 nm and ∼50 nm, b_m and b_{mn} are bi-modal size distributions at ∼10 nm and ∼20 nm; the subscripts reflect different times.

dataset. The implication of numerically averaging these rapidly changing data is discussed.

2 Experimental

The Mobile Real-time Air Monitoring Platform (MAP) has been used since 2002 to obtain temporal and spatial size distributions of ultrafine particles as it traveled or parked at roadsides as a stationary station to obtain time-series air pollutant data. Detail specifications of MAP are reported in Yao et al. (2005). There are two state-of-art fast response particle counters onboard: Engine Exhaust Particle Sizer (5.6–560 nm, 1 s per 32-cut scan), and Electrical Low Pressure Impactor (ELPI, 12 cuts ranging 0.03–20 μm at a scan rate of 1 s) (Dekati, Ltd.). Stand-alone gas analyzers for SO_2, NO_x, CO and O_3 (API, Inc., response time from 10 s to 20 s) and an aethalometer (Magee Scientific, response time is 5 s) for black carbon (BC, total particles) yields real-time data for these species. A composite global positioning system (GPS)/digital compass/speedometer navigation system and an automatic weather station are also used. MAP has a forward-pointing isokinetic, unidirectional sampling probe for taking aerosol samples at a vehicle speed of 50–70 km hr^{-1}. The nominal vehicle speed is 60 km hr^{-1}. It can be deployed as a conventional stationary monitoring facility with an omni-directional PM10 inlet (R&P, Corporation). The probe is on the top of the front of the vehicle and is ∼4 m above ground level. The exhaust is at the tail end of the vehicle, a distance of ∼2 m from the probe in horizontal direction. In the normal driving mode, any self-contamination is thus circumvented. Depending on the distance between MAP and the vehicles ahead, the samples can either be localized plumes directly from the vehicles in front or a dispersed mixture.

On 23 and 27–28 September and 7–8, 11–14 October 2004, ∼50 h of air pollutant measurements were made and, in particular, ultrafine particle number concentrations using EEPS. The measurements started daily at 10:00 and ended at 16:00. The data taken on 7 and 8 October are analyzed and used in this discussion as examples to demonstrate some of the problems associated with time-averaging ultrafine particles for size distribution studies.

3 Results and discussion

In the afternoon of 7 October 2004, MAP was parked on the roadside to collect high time resolution ultrafine particle data. In Figs. 1a–e are the concentrations (all concentrations are number concentrations unless otherwise specified) of the 10.8, 19.1, 29.4 and 52.3 nm particles and particle size distributions as measured by EEPS for a period of five minutes. No gaseous pollutant data were measured. The traffic was light (<100 vehicles per hour). Several peaks can be seen in the particle concentration (Fig. 1a); they were plumes

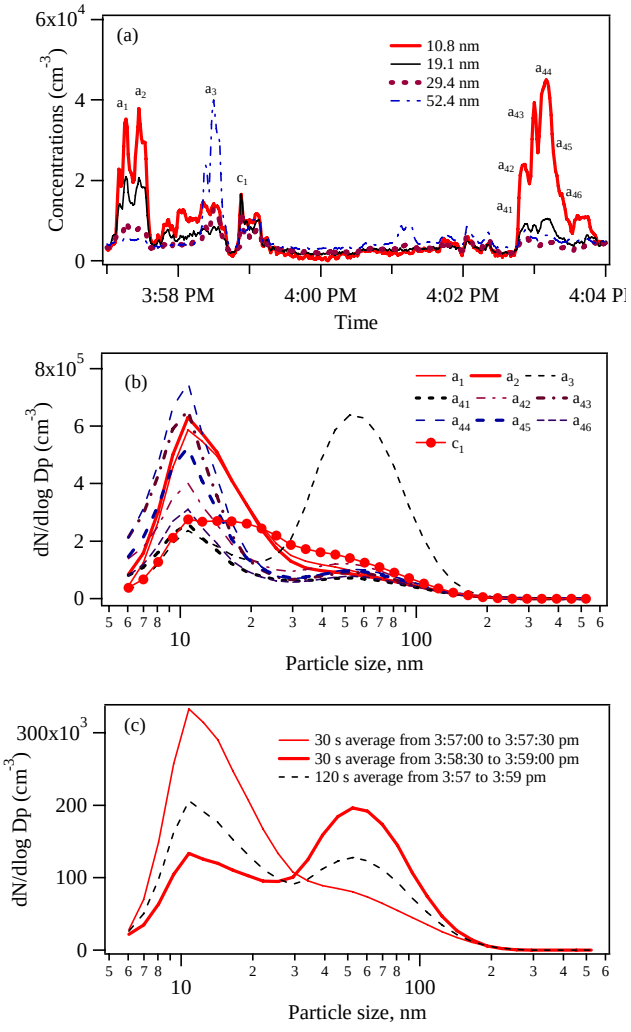

Fig. 2. Light traffic roadside ultrafine particle concentrations and size distributions, ~04:00 p.m. on 7 October 2004. **(a)** Concentrations of 10.8, 19.1, 29.4 and 52.3 nm particles, **(b)** Size distributions at a_1, a_2, a_3, a_{41}, a_{42}, a_{43}, a_{44}, a_{45}, a_{46} and c_1, **(c)** 30 s and 120 s time-averaging spectra. Note: a_m and a_{mn} are bi-modal size distributions at ~10 nm and ~50 nm, c_1 is a tri-modal size distribution at ~10 nm, ~20 nm and ~50 nm; the subscripts reflect different times.

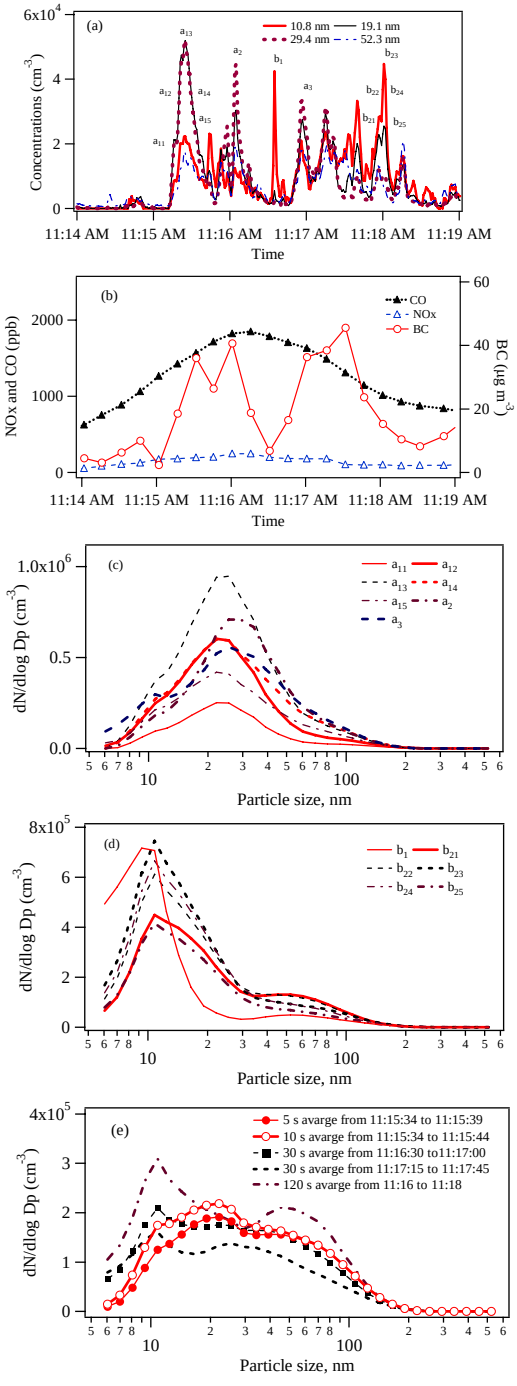

Fig. 3. On road ultrafine particle concentrations and size distributions, 7 October 2004. **(a)** Concentrations of 10.8, 19.1, 29.4 and 52.3 nm particles, **(b)** CO (ppb), NO_x (ppb) and BC ($\mu g\,m^{-3}$), **(c)** Size distributions at a_{11}–a_{15}, a_2 and a_3, **(d)** Size distributions at b_1, b_{21}–b_{25}, **(e)** 5 s, 10 s, 30 s and 120 s time-averaging spectra. Note: a_{1n} and a_n are bi-modal size distributions at ~10 nm and ~20 nm; b_n and b_{mn} are bi-modal size distributions at ~10 nm and ~50 nm; the subscripts reflect different times.

from vehicles passing by MAP. For these peaks, there are two types of bi-modal distributions: one characterized by the dominant ~10 nm mode and a minor ~50 nm mode, and the other by the dominant mode at ~20 nm and a minor ~10 nm mode (Figs. 1b–d). Time-averaging these size distribution data for relatively short times (5 and 10 s) yielded distributions that are similar to the original 1 s distributions, however, for relatively long times (30 and 120 s), the resulting distributions can sometimes be distorted and tri-modal size distributions are obtained (Fig. 1e).

In the case when only one type of size distribution dominated such as the light traffic roadside data in Figs. 2a–c, there is no significant change of the particle mode number

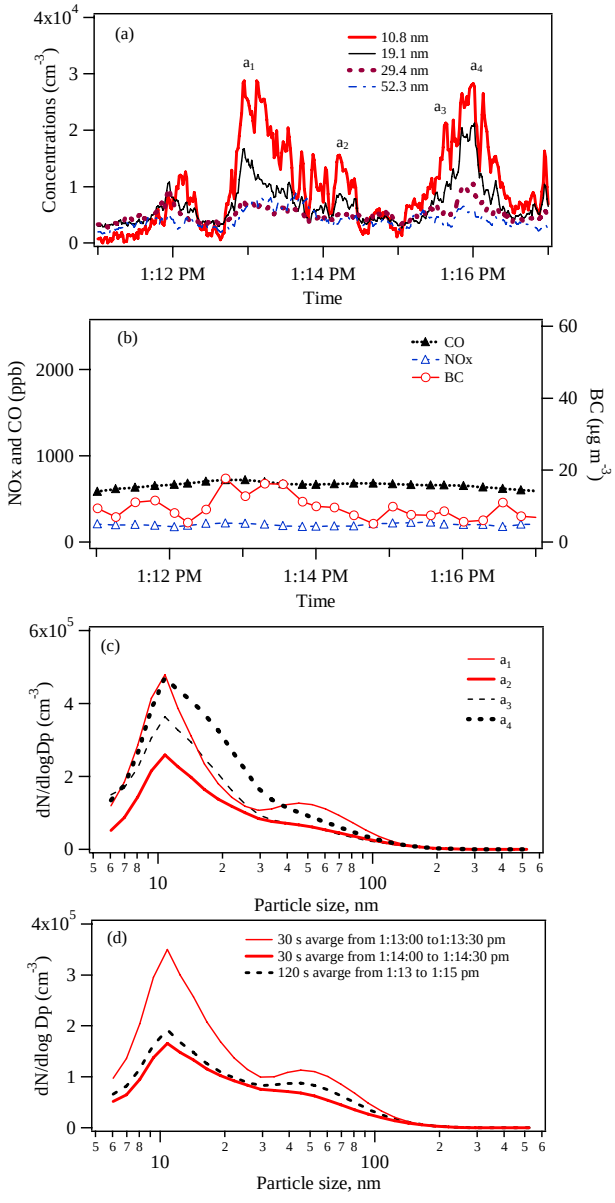

Fig. 4. On road ultrafine particle number concentrations and size distributions, 8 October 2004. **(a)** Concentrations of 10.8, 19.1, 29.4 and 52.3 nm particles, **(b)** CO (ppb), NO−x (ppb) and BC ($\mu g\,m^{-3}$), **(c)** Size distributions at a_1, a_2, a_3 and a_4, **(d)** 30 s and 120 s time-averaging spectra. Note: a_n are bi-modal size distributions at ∼10 nm and ∼50 nm and the subscripts reflects different times.

and diameter between the original and time-averaged distributions.

For on-road data (Figs. 3a–e), particle concentration peaks existed (Fig. 3a) and they were due to plumes from either the vehicles ahead of MAP and/or the vehicles passing by in the opposite lane. The particle peaks $a_{11}-a_{15}$, a_2 and a_3, bi-modal size distributions (∼10 nm and ∼20 nm) at different times, coincided with the black carbon (BC) peaks (Fig. 3b) suggesting that they were probably due to emissions from heavy-duty diesel vehicles. On the other hand, low BC concentrations were detected at b_1 and $b_{21}-b_{25}$, also bi-modal size distributions (∼10 nm and ∼50 nm) at different times, suggesting emissions from light-duty vehicles such as gasoline-powered cars. Due to longer instrument response times (∼20 s), CO and NOx concentrations are less sensitive than the particle and BC concentration changes.

In Figs. 3c–d, at $a_{11}-a_{15}$, a_2 and a_3, bi-modal particle size distributions with a dominant mode at ∼20 nm and a minor mode at ∼10 nm are detected. A different bi-modal distribution is observed at b_1 and $b_{21}-b_{25}$ with a dominant mode at ∼10 nm and a minor mode at ∼50 nm. This difference in the size distribution is attributed to the different evolution of particles in the respective vehicle plumes, including the growth of nucleated particles by gas-condensation and particle-particle coagulation (Zhang and Wexler, 2004; Zhang et al., 2004; Jacobson et al., 2005; Yao et al., 2005). Details of the characteristics of vehicular particles in Hong Kong are reported by Yao et al. (2005). The nucleated particles are believed to be smaller than 3 nm and primary soot particles are usually reported to have a particle mode at about 100 nm in the literature (Harris and Maricq, 2001; Bukowiecki et al., 2003; Kittelson et al., 2004).

Time-averaging (5, 10, 30 and 120 s) the bi-modal distributions resulted in tri-modal patterns with ∼10, ∼20 and ∼50 nm modes or bi-modal distributions with modes at ∼20 and ∼50 nm (Fig. 3e). What happened is particle size distributions from different sources measured at different times are numerically mixed, and, in particular, the 50 nm mode is significantly enhanced. In the literature, these time-averaged size distributions are often attributed to particle evolutions and/or to engine operating conditions (Zhu et al., 2002a, b; Bukowiecki et al., 2003; Gidhagen et al., 2003; Ketzel et al., 2003; Sturm et al., 2003; Morawska et al., 2006). It becomes obvious that numerically mixing physically meaningful particle modes from different sources could and would yield complicated particle spectra, and trying to explain them from an evolutionary point of view may not be valid.

Similar gas and particle data measured for a period of 6 min by MAP traveling on roads on 8 October are in Figs. 4a–d. In this dataset, only one particle size distribution dominated: a bi-modal pattern with a dominant mode at ∼10 nm and a minor mode at ∼50 nm. Time-averaged (30 s and 120 s) particle size distributions (Figs. 4c and d) are similar to the original size distribution (1 s) and no significant difference on the particle mode number and diameter is detected.

Additional MAP EEPS data collected inside tunnels where particles from multiple sources with much higher concentrations are in Figs. 5 and 6 to further substantiate this discussion. When only one particle size distribution dominated, time-averaged (30 s and 120 s) particle size distributions (Fig. 5d) are similar to the original size distribution (1 s).

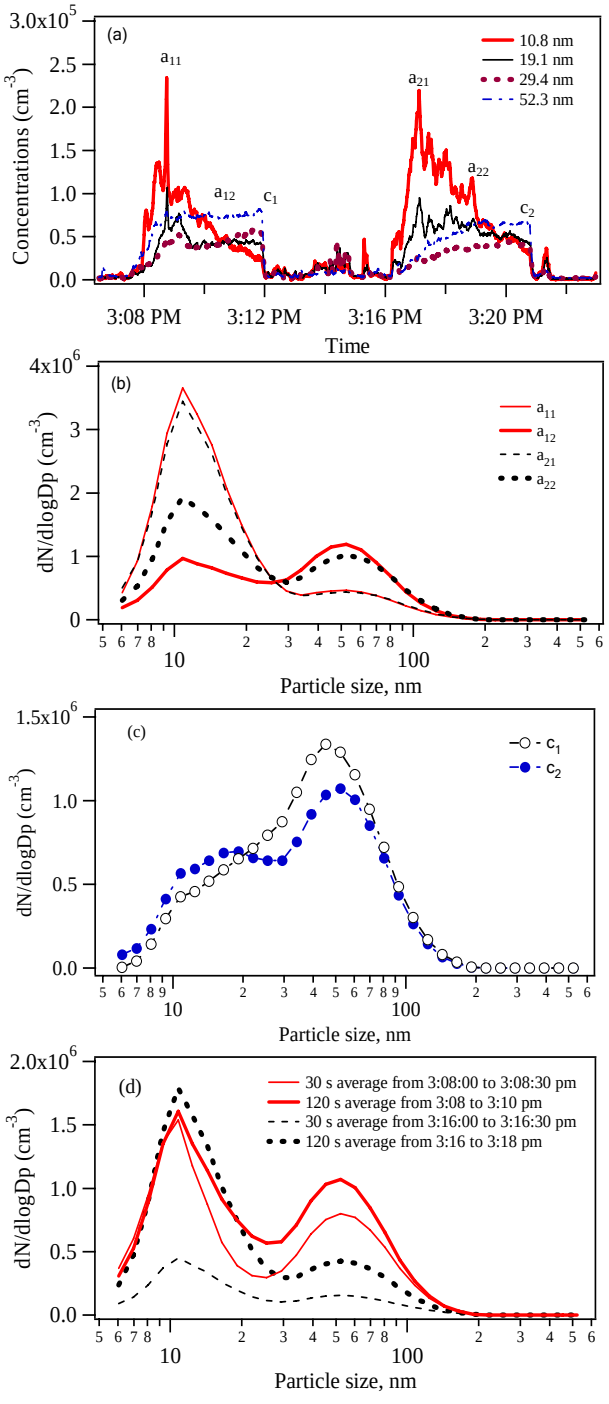

Fig. 5. Ultrafine particle number concentrations and size distributions in Tate Cairn's Tunnel, 7 October 2004. Concentrations of **(a)** 10.8, 19.1, 29.4 and 52.3 nm particles, **(b)** Size distributions at a_{11}, a_{12}, a_{21} and a_{22}, **(c)** Size distribution at c_1, c_2, **(d)** 30 s and 120 s time-averaging spectra. Note: a_{mn} are bi-modal size distributions at ~10 nm and ~50 nm; c_n are tri-modal size distributions at ~10 nm, ~20 nm and ~50 nm; the subscripts reflects different times.

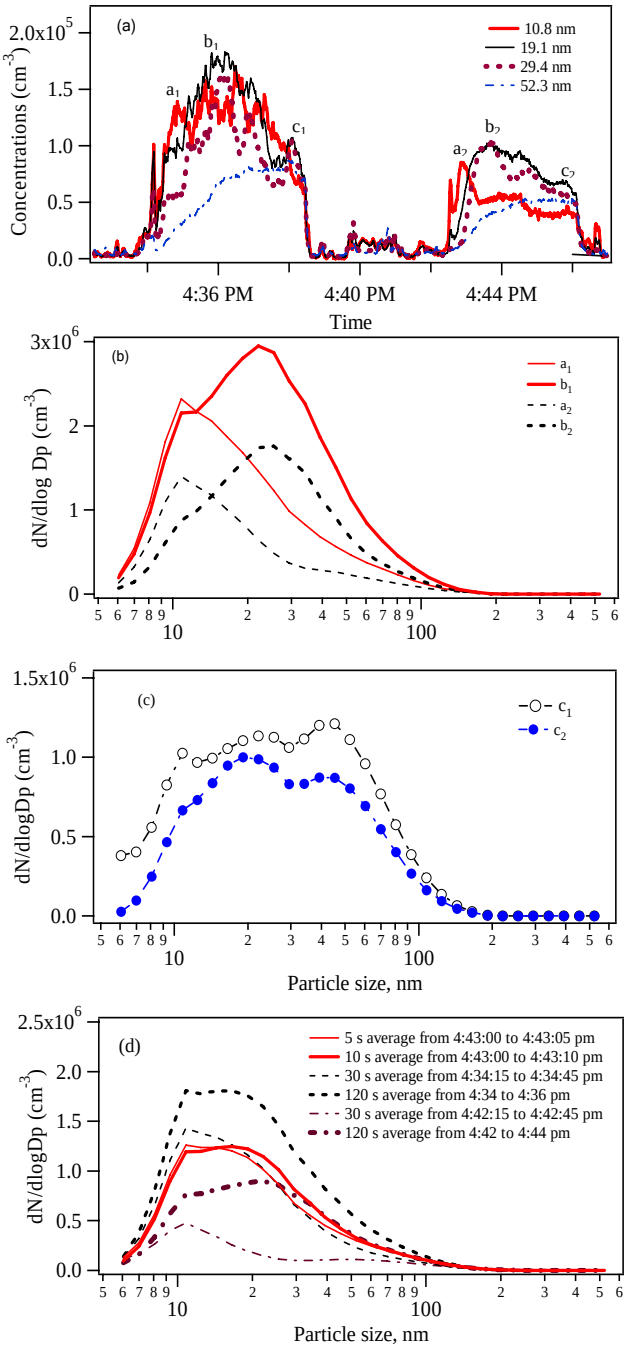

Fig. 6. Ultrafine particle number concentrations and size distributions in Tseung Kwan O Tunnel, 7 October 2004. Concentrations of **(a)** 10.8, 19.1, 29.4 and 52.3 nm particles, **(b)** Size distributions at a_1, b_1, c_1, a_2 and b_2 and c_2, **(c)** Size distributions at c_1, c_2, **(d)** 5 s, 10 s, 30 s and 120 s time-averaging spectra. Note: a_n are bi-modal size distributions at ~10 nm and ~50 nm; b_n are bi-modal size distributions at ~10 nm and ~20 nm; c_n are tri-modal size distributions at ~10 nm, ~20 nm and ~50 nm; the subscripts reflects different times.

When size distribution varies rapidly (in seconds), time-averaged (5, 10, 30 s and 120 s) particle size distributions display distortions (Fig. 6d) due to the numerical mixing of particles from two types of sources.

What has been demonstrated is time-averaging (5–120 s) 1-s size distribution data of two different types of particle size distributions can numerically yield a large variety of complicated size distributions, depending on the relative strengths of the respective sources, and in particular, tri-modal size distributions can be obtained. By the same token, a fast particle sizer could also measure particle size distributions that are physically mixed. In Figs. 5b and 6b, in the mid-section of the tunnel when only one dominant mode exists, tri-modal distribution is not detected due to the overwhelmingly high concentrations of the smaller particles ($\sim$10 nm). At the end section when no one mode dominates, tri-modal particle size distributions (1 s) are measured in Figs. 5c and 6c. It is possible that these tri-modal size distributions are due to physically mixing particles from different sources and not a true tri-modal distribution from a particular source. Tri-modal distributions were occasionally detected in well-dispersed vehicle plumes outside tunnels as shown in Fig. 2b.

4 Summary and conclusion

High time resolution ultrafine particle concentration data in vehicular plumes at roadside, on roads and in tunnels show that they can vary rapidly in the second scale. Time-averaging of particle size distributions collected in such environments can yield misleading and/or meaningless evolutionary interpretations in that the time-averaged spectra can be vastly different from the real ones. In this case, time-averaging amounts to numerically mixing particles from different sources. However, in a slow varying atmosphere, time-averaging may still be justified. To be fair, fast sizers can also measure physically mixed particles.

Acknowledgements. This project is sponsored by the Hong Kong Jockey Club Charities Fund for which the team is grateful. TSI, Inc., USA generously loaned the EEPS (Model 3090) to the team without which this study would not have been possible.

Edited by: R. Vautard

References

Biskos, G., Reavell, K., and Collings, N.: Description and theoretical analysis of a differential mobility spectrometer. Aerosol. Sci. Technol., 39, 527–541, 2005.

Bukowiecki, N., Dommen, J., Prévôt, A. S. H., Richter, R., Weingartner, E., and Baltensperger, U.: Fine and ultrafine particles in the Zürich (Switzerland) area measured with a mobile laboratory: an assessment of the seasonal and regional through a year, Atmos. Chem. Phys., 3, 1477–1494, 2003, http://www.atmos-chem-phys.net/3/1477/2003/.

Burtscher, H.: Physical characterization of particulate emissions from diesel engines: a review, J. Aerosol Sci., 36, 896–932, 2005.

Gidhagen, L., Johansson, C., Ström, J., Kristensson, A., Swietlicki, E., Pirjola, L., and Hansson, H. C.: Model simulation of ultrafine particles inside a road tunnel, Atmos. Environ., 37, 2023–2036, 2003.

Harris, S. J. and Maricq, M. M.: Signature size distribution for diesel and gasoline engine exhaust particulate matter, J. Aerosol Sci., 32, 749–764, 2001.

Jacobson, M. K. and Seinfeld, J. H.: Evolution of nanoparticle size and mixing state near the point of emission, Atmos. Environ., 38, 1839–1850, 2004.

Jacobson, M. Z., Kittelson, D. B., and Watts, W. F.: Enhanced coagulation due to evaporation and its effect on nanoparticle evolution, Environ. Sci. Technol., 39, 9486–9492, 2005.

Johnson, T., Caldow, R., Pocher, A., Mirme, A., and Kittelson, D. B.: A new electrical mobility particle sizer spectrometer for engine exhaust particle measurements, SAE-2004-01-1341, 2004.

Ketzel, M., Wåhlin, P., Berkowicz, R., and Palmgren, F.: Particle and trace gas emission factors under urban driving conditions in Copenhagen based on street and roof-level observations, Atmos. Environ., 37, 2735–2749, 2003.

Kim, D., Gautam, M., and Gera, D.: Parametric studies on the formation of diesel particulate matter via nucleation and coagulation modes, J. Aerosol Sci., 33, 1609–1621, 2002.

Kittelson, D. B., Watts, W. F., and Johnson, J. P.: Nanoparticle emissions on Minnesota highways, Atmos. Environ., 38, 9–19, 2004.

Morawska, L., Johnson, G. R., He, C., Ayoko, G. A., Lim, M. C. H., Swanson, C., Ristovski, Z. D., and Moore, M.: Particle number emissions and source signatures of an Industrial Facility, Environ. Sci. Technol., 40, 803–814, 2006.

Shah, S. D. and Cocker, D. R.: A fast scanning mobility particle spectrometer for monitoring transient particle size distributions, Aerosol Sci. Technol., 39, 519–526, 2005.

Sturm, P. J., Baltensperger, U., Bacher, M., Lechner, B. Hausberger, S., Heiden, B., Imhof, D., Weingartner, E., Prevot, A. S. H., Kurtenbach, R., and Wiesen, P.: Roadside measurements of particulate matter size distribution, Atmos. Environ., 37, 5273–5281, 2003.

Tammet, H., Mire, A., and Tamm, E.: Electrical aerosol spectrometer of Tartu University, Atmos. Res., 62, 315–324, 2002.

Vouitsis, E., Ntziachristos, L., and Samaras, Z.: Modelling of diesel exhaust aerosol during laboratory sampling, Atmos. Environ., 39, 1335–1345, 2005.

Wang, J., McNeill, V. F., Collins, D. R., and Flagan, R. C.: Fast mixing condensation nucleus counter: application to rapid scanning differential mobility analyzer measurements, Aero. Sci. Technol., 36, 678–689, 2002.

Yao, X. H., Lau, N. T., Fang, M., and Chan, C. K.: Real-time observation of the transformation of ultrafine atmospheric particle modes, Aerosol Sci. Technol., 39, 831–841, 2005.

Zhang, K. M. and Wexler A. S.: Evolution of particle number distribution near roadways, Part I: analysis of aerosol dynamics and its implications for engine emission measurement, Atmos. Environ., 38, 6643–6653, 2004.

Zhang, K. M., Wexler, A. S., Zhu, Y. F., Hinds W. C., and Sioutas, C.: Evolution of particle number distribution near roadways. Part II: the Road-to-Ambient process, Atmos. Environ., 38, 6655–

6665, 2004.

Zhu, Y., Hinds, W. C., Kim, S., Shen, S., and Sioutas, C.: Study of ultrafine particles near a major highway with heavy-duty diesel traffic, Atmos. Environ., 36, 4323–4335, 2002a.

Zhu, Y., Hinds, W. C., Kim, S., and Sioutas, C.: Concentration and size distributions of ultrafine particles near a major highway, J. Air Waste Manage. Assoc., 52, 1032–1042, 2002b.