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An approach to investigate new particle formation in the vertical direction on the basis of high time-resolution measurements at ground level and sea level

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HIGHLIGHTS

- CV metric can be adopted to study NPF in the vertical direction.
- Formation and growth rates of new particle were different in the vertical direction.
- New particle was predominantly from horizontal transport in inland atmospheres.
- New particle was generally from vertical transport in marine atmospheres.

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ABSTRACT

In this study, we investigated new particle formation (NPF) in the vertical direction using high time-resolution (1 s) measurements made by Fast Mobility Particle Sizers at ground level and at sea level. The coefficient of variation (CV), i.e., the ratio of standard deviation to mean value for <100-nm particle number concentration (N_{100}) in every 30 s, is introduced as a metric to distinguish horizontal and vertical transport of atmospheric particles. We first examined the CV metric using the data collected at a semi-urban site in Toronto during the summer of 2007. The 50th and 95th percentiles of CVs associated with horizontal transport were 1–13 times smaller than those during strong vertical transport. We then compared the N_{100}, GMD_{55} (geometric mean diameter of <55-nm particles) and GMD_{100} corresponding to the 0–5th percentiles of CVs with those corresponding to the 95–100th percentiles of CVs in five NPF events. The comparative results are discussed in terms of different formation and growth rates in the vertical direction. The similar analysis was also conducted in various marine atmospheres. We found that the CV metric can improve our understanding of NPF in the vertical direction.

1. Introduction

New particle formation (NPF) events have been reported to occur over a large spatial scale with both horizontal and vertical extensions (Kulmala et al., 2004; Boulon et al., 2011; Zhang et al., 2011; Crippa and Pryor, 2013; Dall'Osto et al., 2013; Matsui et al., 2013). In the horizontal direction, NPF events can occur over tens to hundreds of kilometers, and new particle formation and growth rates are generally heterogeneous between sites (Wehner et al., 2007; Jeong et al., 2010; Crippa and Pryor, 2013). However, the two rates are usually homogeneous at small scales of a few hundred meters because of homogeneous atmospheric composition and similar local meteorological conditions (Hussein et al., 2009). In the vertical direction, most NPF events have been reported to initiate at a certain altitude and then extend to other altitudes (Siebert et al., 2004; Olofson et al., 2009; Wehner et al., 2010; Boulon et al., 2011; Pryor et al., 2011). For example, some studies have proposed that new particles were initially formed at the residual layer, and then transported downwards to ground level along with the break-up of the nocturnal inversion and development of the mixed layer, thereby resulting in peaks of particle number concentration at ground level (Siebert et al., 2004; Olofson et al., 2009; Wehner et al., 2010). Crippa et al. (2012) simulated NPF events observed in

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southern Indiana and their results supported the above-mentioned mechanism. Overall, these studies are an effort to localize the altitude of NPF events. However, there is still a limited understanding of new particle formation and growth rates in the vertical direction.

Recently, several fast-response particle sizers have been developed for measuring the number concentrations of different sized particles (Yao et al., 2005; Pryor et al., 2011). A combination of fast-response particle sizers and an eddy covariance system have been used to study vertical transport of atmospheric particles (Gordon et al., 2011). The calculated vertical exchange fluxes of atmospheric particles of different sizes are always positive; however, this is practically impossible in the atmosphere. Our previous study found that many noisy signals exist in the eddy covariance system at frequencies <0.8 Hz (Duan et al., 2013). Noisy signals can lead to calculation fluxes that deviate far from the real value. To minimize interference from the low frequency noises and the high frequency noise (conventionally referred to as white noise), frequencies between 0.8 and 1.5 Hz should be used to calculate the vertical flux (Duan et al., 2013). Unfortunately, the highest sampling frequency of particle sizers reported in the literature is just 1 Hz. The combination technology seemingly faces a big challenge. Thus, we attempt to use particle measurements with fine temporal resolution at ground level alone to study NPF in the vertical direction.

In the summer of 2007, a Fast Mobility Particle Sizer (FMPS) operating at a 1 s time resolution was used to measure the number concentration of particles ranging from 5.6 nm to 560 nm at a semi-urban site in Toronto. During the study, a black carbon (BC) monitor, a Gas Particle Ion Chromatograph (GP-IC), a $PM_{2.5}$ monitor and NO_x, SO_2 and O_3 gas analyzers collected data every 1–15 min time resolution to measure the mixing ratios of pollutant gases and the chemical composition of atmospheric particles. Using this dataset, we developed an approach to interpret the variation in number concentrations or the geometric mean diameters (GMD) of <100-nm particles (N_{100}, GMD_{100}) in relation to the horizontal and vertical transport of atmospheric particles. We found that the coefficient of variation (CV), i.e., the ratio of standard deviation to mean value for N_{100}, can be used as an indicator to identify horizontal and vertical transport of these particles. Using the indicator, we further evaluate new particle formation and growth rates in the vertical direction during five NPF events. To further examine CV metric, we conducted the similar analysis in the marine atmosphere using the data published in literature.

2. Experimental

In this study, two datasets were used to examine the CV metric. One dataset was related to an intensive campaign performed to measure gas and particle concentrations in a mixed zoning urban area of Toronto, Canada (43°42′33″N, 79°32′36″W) from 17 to 28 August, 2007 (Yao et al., 2011, 2013). The sampling site is located at approximately 190 m south of 401 Highway which is one of the busiest highways in North America. All instruments were deployed on two mobile labs that were parked side by side ~5 m apart. In one mobile lab, an FMPS (TSI Instruments) and a GP-IC (Dionex Corporation) were used to measure particle number size distributions in 1 s time resolution and gas and particulate species concentrations every 15 min. In the GP-IC, a continuous particle collector was used to collect and extract particles downstream of a denuder. The extract was then sequentially passed through cation and anion concentrator columns. During the 15-min analysis period, 15 nm NaOH was used to elute anions captured by the anion concentrator column, and the anions including SO_4^{2-}, NO_3^-, etc., were analyzed directly online using a Dionex ICS-2000 (Yao et al., 2009). In the other lab, a complementary suite of gas and particle analyzers were used to measure BC (multi-angle absorption photometer, MAAP, Thermos 5012), $PM_{2.5}$ mass concentration (Thermos tapered element oscillating microbalance, TEOM 1400AB), NO_x (TECO 42C), SO_2 (TECO 43CTL) and O_3 (TECO 49C) at a 1–5 min resolution. At the same time, meteorological data including solar radiation (SR), ambient temperature (T), relative humidity (RH), wind speed (WS) and wind direction (WD) were obtained from a rooftop approximately 100 m from the mobile labs.

The other dataset was collected on two cruises from 16 October to 5 November 2011 and from 2 to 11 November 2012 across marginal seas of China (Liu et al., 2014). An identical FMPS was deployed on the front board of a research vessel *Dongfanghong 2* to measure particle number concentrations. The sampling location was approximately 15 m above the sea level.

Formation rates (J_{30}) and growth rates (GR) of new particles were estimated based on Dal Maso et al. (2005) and Yao et al. (2010).

$$J_{30} = \mathrm{d}N_{30}/\mathrm{d}t + F_{\mathrm{growth}} + F_{\mathrm{coag}}, \quad (1)$$

where N_{30} is the number concentration of the 5.6–30-nm particles during the initial 1–2 h of the new particle burst; F_{growth} is the flux of particles growing out of 30 nm; it is conventionally assumed to be zero because particles rarely grew out of 30 nm in the initial 1–2 h (Dal Maso et al., 2005); and F_{coag} is the sum of the particle–particle inter- and heterocoagulation rates.

$$\mathrm{GR} = \Delta D_p/\Delta t, \quad (2)$$

where D_p and t represent the GMD of new particles and the time slot for the particle growth, respectively.

Moreover, a time period of 30 s was used to calculate CVs. Compared to 10 s, 20 s and 60 s time periods, the choice of 30 s is an effort to maximize the relative difference between the 5th percentile of CVs and the 95th percentile of CVs and minimize the system noise. The statistical significance of variables was assessed by the F test and the t test ($p < 0.05$).

Air mass back trajectories were obtained using the National Oceanic and Atmospheric Administration (NOAA) HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model with the Eta Data Assimilation System (EDAS) 40 km meteorological data (Jeong et al., 2010). The trajectories were used to facilitate our analysis of NPF events. The US EPA Community Multi-scale Air Quality Model (CMAQ v4.7.1) was used to simulate the concentrations of gases and particulate species during the two cruise campaigns, and the results were analyzed in terms of origins of new particle precursors (Liu et al., 2014).

3. Results and discussion

3.1. Characteristics of UFP during the summer campaign in Toronto

In the summer campaign in Toronto, 227 h of size distribution data of particle number concentrations were obtained, excluding the occasional instrument malfunction and short-term regular maintenance. The N_{100} varied over two orders of magnitude, i.e., from <1.0×10^3 to 3.2×10^5 cm^{-3} with an average of 1.5×10^4 cm^{-3}. The GMD_{100} varied by a factor of six, i.e., from 12 to 83 nm with an average of 32 nm (Fig. 1). The averaged value of N_{100} almost doubled the value observed in downtown Toronto (on average, 8010 cm^{-3}) during 20 June to 8 July, 2007 (Jeong et al., 2010). Traffic emissions from 401 Highway were likely the major cause for the higher particle number concentrations in this study. For example, a few spikes of N_{100}, NO_x and BC occurred simultaneously for minutes or tens of minutes when the WS was less than 1.5 m s^{-1} and the