Anthropogenic pollution elevates the peak height of new particle formation from planetary boundary layer to lower free troposphere

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Abstract

New particle formation (NPF) and subsequent growth are primary sources of atmospheric aerosol particles and cloud condensation nuclei. Previous studies have been conducted in relatively clean environments; investigation of NPF events over highly polluted megacities is still lacking. Here we show, based on a recent yearlong aircraft campaign conducted over Beijing, China, from April 2011 to June 2012, that NPF occurrence peaks in the lower free troposphere (LT), instead of planetary boundary layer (PBL), as most previous studies have found and that the distance of NPF peak to PBL top increases with increasing aerosol loading. Further analysis reveals that increased aerosols suppress NPF in PBL, but enhance NPF in LT due to a complex chain of aerosol-radiation-photochemistry interactions that affect both NPF sources and sinks. These findings shed new light on our understanding of NPF occurrence, NPF vertical distribution, and thus their effects on atmospheric photochemistry, clouds, and climate.

Plain Language Summary

Comparing with planetary boundary layer (PBL) and upper free troposphere (UT), the lower free troposphere (LT) is thought as weak new particle formation (NPF) region, where particles are thus thought to be either uptransported from PBL or downtransported from UT. Whereas, such distribution seems to be changed under highly aerosol-polluted regions. Our observations collected during a yearlong (April 2011 to June 2012) aircraft field campaign over Beijing, China, show that NPF peak region has been elevated from PBL to LT. Further analysis reveals that increased aerosols suppress NPF in PBL but enhance NPF in LT due to a complex chain of aerosol-radiation-photochemistry interactions that affect both NPF sources and sinks. These findings shed new light on our understanding of NPF occurrence, NPF vertical distribution, and thus their effects on atmospheric photochemistry, clouds, and climate.

1. Introduction

As primary sources of atmospheric aerosol particles and cloud condensation nuclei, new particle formation (NPF) and its subsequent growth have drawn increasing attention [Kulmala et al., 2004; Yu and Luo, 2009; Merikanto et al., 2009; Venzac et al., 2008; Zhang et al., 2012]. Previous studies have identified two main regions of NPF occurrence: (1) well-mixed planetary boundary layer (PBL) where most anthropogenic pollutants and natural gas precursors are emitted and located [Väisänen et al., 2016; Wehner et al., 2007; Laakso et al., 2007; Siebert et al., 2004; Stratmann et al., 2003; O'Dowd et al., 2009; Pyyrälä et al., 2011; Crumeyrolle et al., 2010; Dunne et al., 2016] and (2) the upper free troposphere (UT) where NPF may be related to low temperature and cloud processes [Dunne et al., 2016; Krejci et al., 2003; Clarke et al., 2013; Young et al., 2007; Miehe et al., 2010; Weigel et al., 2011; Wang et al., 2016; Lee et al., 2003; Weigelt et al., 2009]. Rare NPF events in lower free troposphere (LT) have been reported and are thought to be related to the upward transport of PBL-originated air rising along valleys [Venzac et al., 2008; Bianchi et al., 2016] or convective movement [Rose et al., 2015]. LT particles are thus thought to be either uptransported from PBL or downtransported from UT [Merikanto et al., 2009; Wang et al., 2016]. However, previous studies have been conducted in relatively clean environments; investigation of NPF events in LT over highly polluted megacities is limited. Also poorly understood is the quantitative relationship of NPF occurrence to aerosol loading. Furthermore, developing countries, such as China and India, are experiencing serious air pollution and high aerosol loading accompanied with rapid economic development, with the observed PM2.5 mass concentration reaching up to 600 μg m⁻³ [Quan et al., 2014]. In addition to harmful health effects, there is also a pressing need to understand the...
physical and chemical mechanisms underlying such high aerosol loading that can drastically affect Earth’s energy balance, atmospheric photochemistry, clouds, and climate. To fill the gap and need, a comprehensive, yearlong (April 2011 to June 2012) aircraft field campaign was conducted over Beijing, China, one of the most aerosol-polluted regions in the world. Analysis of this unique data set uncovers new NPF phenomena and provides a new understanding of NPF in highly polluted megacities like Beijing.

2. Field Campaign and Data

A total of 42 flights (118 flight hours) with an instrumented Y-12 aircraft was conducted during the field campaign. A fixed flight pattern was utilized with quasi-circular horizontal legs over the inner Beijing city, spiraling down around the rectangle of the fourth ring road from 2.1 km to 0.6 km (above sea level), with a vertical interval of 300 m and vertical sounding flights at the Shahe airport (up to 3.6 km) after departure and before landing (Figure S1 in the supporting information). Aerosol properties, gas pollutants, and meteorological parameters were measured. The details about the instruments and data processing are described in the supporting information (SI). A total of 28 NPF events during the campaign was identified according to the measurements of a Scanning Mobility Particle Sizer (SMPS, TSI-3936, USA), which measures particles from 14 to 661 nm in diameter with 107 size bins and a temporal resolution of 3 min. An NPF event is defined if the following two criteria are both satisfied: (1) the concentration of SMPS-measured ultrafine condensation nuclei (UCN) (diameter ≤ 25 nm) exceeds 103 cm−3; (2) the ratio of UCN concentration to the total SMPS aerosol (CN) concentration (hereafter UCN-CN ratio) is larger than 20%. The aerosol size distributions were bimodal for the NPF events, as opposed to the monomodal for the non-NPF events (Figure S2).

3. Results and Discussion

To examine the effects of aerosol loading on NPF, the NPF occurrence data are partitioned into two groups of high (HA) and low (LA) aerosol loading according to the SMPS-measured aerosol surface area concentrations (SA) at ground level. The HA and LA groups represent the averages of all samples with the ground SA ≥ 500 μm2 cm−3 and SA < 500 μm2 cm−3, respectively. A comparison of the vertical profiles of NPF events reveals striking differences between the HA and LA groups (Figure 1). Under LA, NPF events tend to occur within PBL (10 out of 13 cases, Figure 1a) whereas NPF events tend to appear near the PBL top and LT under HA (12 out of 15 cases, Figure 1b). On average, the height with peak NPF frequency elevated from 0.9 km under LA to 2.1 km under HA (Figure 1c). This contrast between LA and HA can be further seen from Figure 1d, which shows the relationship between peak NPF height and PBL top height. The peak NPF height (H_{PF}) is determined from the vertical profile of UCN-CN ratio as the height where the maximum UCN-CN ratio occurs. The PBL top height is determined at the altitude where there is an inversion or abrupt large change in dew point [Wilczak et al., 1996; Quan et al., 2013] and is calculated from the aircraft measurements of temperature and relative humidity.

The LA results are consistent with the previous studies [Vääränen et al., 2016; Wehner et al., 2007; O’Dowd et al., 2009; Laakso et al., 2007; Siebert et al., 2004; Stratmann et al., 2003; Pryor et al., 2011; Crumeyrolle et al., 2010; Dunne et al., 2016]; however, the HA results are new and worthy of further investigation. Figure 2 shows the dependence on the aerosol surface area concentration of PBL top height (Figure 2a), peak NPF height (Figure 2b), and the difference between the two heights (Figure 2c). The results not only confirm Figure 1 but also further suggest a clear functional dependence of NPF occurrence on aerosol loading. The position of NPF occurrence relative to PBL top results from the combined effects of decreased PBL (Figure 2a) and increased NPF height (Figure 2b) as aerosol loading increases.

The relationships of peak UCN height (H_{UCN}), determined from the vertical profile of UCN as the height where the maximum UCN occurs, with PBL top height and aerosol concentration exhibit similar behaviors (Figure S3). The vertical distributions of UCN and CN concentrations provide more detailed information (Figure 3). Under LA, high UCN (>2000 cm−3) concentration generally appears at 0–1.5 km (inside PBL), with the peak UCN at 0.6 km. Under HA, UCN first increases with altitude and reaches its peak at 2.1 km (above PBL), then decreases with altitude. The maximum UCN-CN ratios appear at 1.2 km and 2.1 km for LA and HA, respectively, which is consistent with the vertical NPF frequency (Figure 1c). The height of minimum median diameter (D_m) is also consistent with the peak UCN height, further supporting that NPF occurred in LT, rather than PBL under HA. Under HA, D_m in LT (60 nm) is much smaller than in PBL (84 nm), whereas D_m in LT...
(47 nm) is slightly larger than that in PBL (42 nm) under LA. These results collectively suggest that increased aerosol loading suppresses the NPF occurrence near ground and in PBL, and delays the occurrence of NPF peak to a higher altitude.

A key process that determines NPF occurrence is the conversion of gaseous SO$_2$ molecules into sulfate particles [Kulmala et al., 2004; Kulmala et al., 2001]. To understand the role of aerosols on photochemical capacity and hence SO$_2$-to-sulfate conversion, the concentration of OH ([OH]), a key atmospheric oxidant, and the sulfuric acid concentration ([H$_2$SO$_4$]) under two aerosol conditions (HA, LA) are calculated. The detailed methodology can be found in SI [Madronich, 1989; Nenes et al., 1998; Li et al., 2011; Petäjä et al., 2009; Tie et al., 2005]. Evidently, [OH] drops considerably under HA (Figure 4a). For example, the averaged [OH] is 2.3 × 10$^6$ molec cm$^{-3}$ in height of 0–1 km under LA, and decreased to 1.2 × 10$^6$ molec cm$^{-3}$ under HA. The vertical profile of [OH] also indicates that its concentration in LT (higher than 0.96 km in HA and 2.35 km in LA) is much higher than in PBL. Therefore, the decreased [OH] under HA decreases the SO$_2$-to-sulfate conversion, especially at surface and in PBL where aerosols are mainly located. The suppressed photochemical reaction and thus SO$_2$-to-sulfate conversion in PBL permit more SO$_2$ molecules to be transported to LT. The calculated [H$_2$SO$_4$] profile substantiates these analyses (Figure 4b): its value is suppressed under HA at surface and in PBL, and increases with altitude, reaching its peak at a height of 1.2–2.4 km.

The balance may enhance NPF events in LA in view of the crucial role of SO$_2$-to-sulfate conversion in NPF [Kulmala et al., 2004; Kulmala et al., 2001]. The above analysis is further corroborated by the vertical distributions of SO$_2$ and CO under HA and LA (Figure S4). The SO$_2$ concentration between 0 and 1 km height increases from 3.5 ppb under LA to 14.1 ppb under HA, with an increase rate of 300%, much higher than the CO increase (from 1.7 to 2.2 ppm, with an increase rate of 27%). According to Parrington et al. [2013] and Vakkari et al. [2014], the difference ratio, $\Delta$SO$_2$/$\Delta$CO, can be used as an indicator of the intensity of SO$_2$-to-sulfate conversion; a lower $\Delta$SO$_2$/$\Delta$CO indicates a higher photochemical activity and relatively more
gaseous SO₂ is transferred to aerosol particles. The difference △ is defined as the local measurement minus the corresponding background value represented by the averaged value in free troposphere under LA (i.e., SO₂ = 0.72 ppb and CO = 1.55 ppm). This is confirmed by our results, which indicates that the mean

Figure 2. Dependence on the aerosol surface area concentration (SA) at ground of (a) PBL top height, (b) peak NPF height, and (c) the difference between the two heights. Dependence on the dimensionless parameter \( L_Γ \) at ground of (a) PBL top height, (b) peak NPF height, and (c) the difference between the two heights. The green and red dots represent data under LA and HA, respectively.

Figure 3. Vertical profiles of (a) total condensation nuclei (CN) concentration, (b) ultrafine condensation nuclei (UCN) (diameter ≤ 25 nm) concentration, (c) UCN-CN ratio, and (d) effective diameter \( (D_m) \) under HA (red) and LA (green) in cases of NPF events.
△SO₂/△CO between 0–1 km heights was 14.7 ppb/ppm under LA and increased to 20.1 ppb/ppm under HA. These results suggest that increased aerosols suppress the SO₂-to-sulfate conversion especially at surface and in PBL and that more SO₂ molecules are transported to the free troposphere. It is noteworthy that the SO₂ concentration of 3–5 ppb above 2 km altitudes is even higher than those observed at ground in Europe [Stehr et al., 2000; Denby et al., 2010].

In addition to its effects on photochemical capacity and SO₂-to-sulfate conversion, increased aerosols can also affect NPF by altering sinks from condensation (CS) and coagulation (CoagS) [Maso et al., 2002; Kulmala et al., 2000]. The detailed methodology can be found in the SI [Kulmala et al., 2001; Fuchs and Sutugin, 1971; Fuchs, 1964; Allen and Raobe, 1985]. The profiles of calculated CS (Figure 4c) and CoagS (Figure S5) illustrate that both increase sharply under HA, especially inside PBL. For example, the mean CS is $9.2 \times 10^{-2}$ s⁻¹ at a height of 0–1 km and sharply decreases to $1.5 \times 10^{-2}$ s⁻¹ at a height of 2–3.6 km under HA, while under LA, the mean CS is only $1.7 \times 10^{-2}$ s⁻¹ and $0.7 \times 10^{-2}$ s⁻¹. The concurrent increases of CS and CoagS with increasing aerosol loading further reinforce the role of high aerosols in suppressing NPF in PBL through enhancing NPF sinks. McMurry and Friedlander [1979] proposed a dimensionless parameter $L$, that describes the ratio between scavenging of newly formed particles by the preexisting aerosol to the growth rate of newly formed particles. Kuang et al. [2010] revised this parameter $L$, and identified that NPF is suppressed when $L$ is beyond a threshold (0.7). The detailed methodology can be found in the SI [McMurry et al., 2005; Kuang et al., 2010]. Our calculation shows that the mean $L$ between 0 and 1 km heights was 0.15 under LA and increased to 1.57 under HA (Figure 4d), suggesting that NPF in the low layer (0–1 km) is significantly suppressed under high aerosols. The suppressed NPF under high aerosols is caused by increased condensation sink of preexisting aerosols and decreased atmospheric oxidation. The former appears to play a more important role. For example, the CS between 0 and 1 km heights increases from $1.7 \times 10^{-3}$ s⁻¹ under LA to $9.2 \times 10^{-3}$ s⁻¹ under HA, with an increase rate of 450%, about 11 times higher than the H₂SO₄ decrease (from $8.5 \times 10^6$ moles cm⁻³ to $5.2 \times 10^6$ moles cm⁻³, with a decrease rate of 40%). Dependence on the ground $L$ of PBL top height, peak NPF height, and the difference between the two heights is further analyzed (Figures 2d–2f) to understand the complex relationships of aerosol, PBL, and NPF. Under HA, ground NPF is suppressed (Figure 2d), and the height NPF occurrence is elevated (Figure 2e). Hence, NPF tends to occur in FT rather than in PBL under HA, which is clearly different with LA (Figure 2f). It is noteworthy that

Figure 4. Vertical profiles of (a) derived OH concentration, (b) H₂SO₄ concentration, (c) condensation sink (CS), and (d) dimensionless parameter $L$ under HA (red) and LA (green).
In summary, our collective analyses show that high concentration of aerosols (mainly located in PBL) decreases the NPF occurrence in PBL by simultaneously reducing the source (represented by $[\text{H}_2\text{SO}_4]$) and increasing their sink (represented by CS and CoagS) of new particles. Atmospheric oxidation is lowered by high aerosols, which suppresses the $\text{SO}_2$-to-sulfate conversion in PBL and enables more $\text{SO}_2$ transported to the free troposphere. The combined higher $\text{SO}_2$ and higher oxidation rate in the free atmosphere due to lower aerosol concentration enhance NPF in the free atmosphere, leading to a unique vertical distribution of NPF occurrence that peaks in LT instead of PBL, as most previous studies have found. These findings shed new light on our understanding of NPF in highly polluted environments. The dramatic differences in NPF occurrence and vertical distribution suggest potentially different NPF effects on clouds, precipitation, and thus climate in highly polluted environments. It should be noted that the freshly formed particles (a few nanometers) were not directly measured in this work. Although similar approaches have been successfully used to identify NPF events by others [Venzac et al., 2008; Wang et al., 2016], a direct measurement of such particles is desirable. Also noteworthy is that this study is based on the data collected in Beijing, and whether the findings can be generalized to other megacities warrants further investigation.

References


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