

Author response

Dear editor,

Thank you so much for handling our paper. We are grateful to both referees for their comments and suggestions. We have submitted our point-by-point responses and improved our manuscript according to the referee's suggestions. Below are (1) our responses to referees, (2) list of changes made in the manuscript, and (3) revised manuscript with a supplement.

Sincerely,

Xiaobin Xu

Response to Anonymous Referee #1

The authors present measurements of vertical profiles of O₃ and aerosol by unmanned aerial vehicle, balloon, and LIDAR over a rural site in the North China Plain (NCP) region. The distributions of O₃, aerosol number density, and aerosol scattering property in the mixed layer and residual layer are examined. This new vertical profile data is compared against the previous MOZIAC measurements over the Beijing area to assess the increase in the boundary layer O₃ over the NCP region. Overall, the observations are valuable and the interpretation is convincing. The manuscript is clearly organized and well written. I would like to recommend that the paper can be accepted for publication after the following specific comments being addressed.

Response: Thank you very much for taking time to review our paper and give valuable comments and suggestions. Please find below our point-by-point responses (in blue).

Specific comments:

1. Page 1, Line 17: change “still quite limited” to “still limited”.

Response: Yes, we have deleted the word “quite”.

2. Page 1, Line 30: In-Service. . .

Response: We have corrected the word.

3. Page 2, Line 5: impacts on human health. . .

Response: We have changed “impacts to human health” to “impacts on human health”.

4. Page 2, Lines 9-10: “actual vertical distribution of O₃ is fundamental. . .” is strange. Please rephrase this sentence.

Response: We have reworded the text as “The vertical distribution of O₃ is influenced by chemical and meteorological processes and varies with time and location (Kleinman et al., 1994; Fast et al., 1996; Lin et al., 2007; Ma et al., 2011). Therefore, direct measurements are needed to

acquire the knowledge about the vertical distribution of O₃, which is important to understanding atmospheric chemistry and O₃ radiative forcing”.

5. Page 2, Line 18: the authors use “Atmospheric boundary layer (ABL)” throughout the manuscript. In the reviewer’s opinion, “planetary boundary layer (PBL)” should be more familiar for the community and readers. The authors should consider to replace the “ABL” by “PBL”.

Response: We have replaced “atmospheric boundary layer” with “planetary boundary layer” and “ABL” with “PBL”.

6. Page 4, Line 17, “some other reactive gases”: please state what species were measured.

Response: Other measured reactive gases include NO/NO₂/NO_x, NO_y, HCHO, PAN, SO₂, CO, NH₃, etc. We have changed “some other reactive gases” to “some other reactive gases (NO/NO₂/NO_x, NO_y, HCHO, PAN, SO₂, CO, NH₃, etc.)”.

7. Section 2: the authors used a set of miniature analyzers including O₃ and aerosol number size distribution monitors for the UAV measurements. Did the authors inter-compare these equipment against the more reliable instruments deployed for the ground-based observations? What’s the design of the sampling inlet of the UAV to avoid interference? It would be better if the authors could provide such information, maybe in the supporting materials.

Response: A newly delivered personal ozone monitor (POM, 2B Technologies, USA) was used in our UAV measurements of O₃ vertical profiles. The POM was calibrated in the factory just before delivery using a working standard (Model 205), which was calibrated against a transfer standard (TE 49i-PS, Thermo Electron, USA) traceable to the standard reference photometer #0 (SRP 0) at the US National Institute of Standards and Technology (NIST). We did not calibrate the POM again. However, we confirmed its proper working at the site using an O₃ calibrator (TE 49i-PS, Thermo Electron, USA).

The optical particle counters (OPC) used in our UAV flights were calibrated by the manufacturer Lighthouse following the procedures in accordance with key standards for particle counters including ISO 21501 (<https://www.golighthouse.com/en/calibration-and-repairs>). The calibration is NIST-traceable. We did not compare the OPC with other instruments at the site.

The sampling inlet that we used in the UAV measurements of aerosol is a stainless steel tube (300 mm, ID 5 mm) with a bullet-shaped head, which has a taper gas way (Figure R1). The sampling inlet was fixed at the front of the UAV nose, parallel to the inlet for airspeed measurement. The tip of the head has an ID of 2.1 mm. The OPC works at a flow rate of 2.83 l/min. These conditions cause an air velocity of about 14 m/s at the tip of the inlet head, which is close to the cruising speed of the UAV (22 m/s). This design of sampling inlet made sure that the aerosol number concentrations were measured under a nearly isokinetic condition. Since a battery-powered UAV was used, there was no interference from engine.

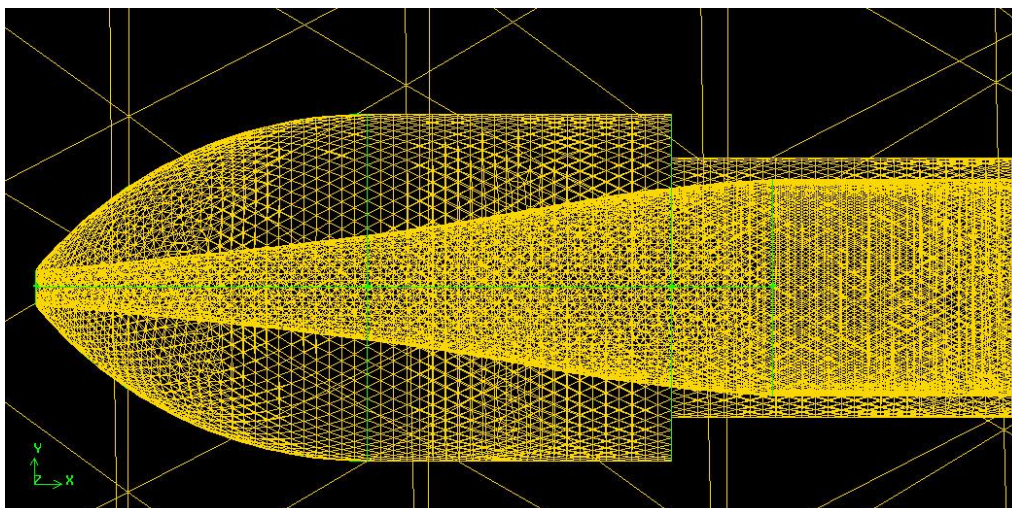


Figure R1. Schematic of the head of the sampling inlet used in the UAV measurements of aerosol.

We have included the above details in the supplement (section S1) and added "More details are given in the supplement (section S1)." at the end of the 3rd paragraph of section 2.2.

8. Page 5, Line 15 and elsewhere: "vertical profile" instead of "profile".

Response: We use now "vertical profile" instead of "profile" in the whole paper.

9. Page 6, Section 3.1: this section consists of only one paragraph which just documents the measurement data with little interpretation. This seems to be not enough as a section. The authors may need to consider either strengthen the discussion of data or combine this paragraph with other sections.

Response: Indeed, the original section 3.1 lacks some scientific materials. However, we think it is better to give an overview of our vertical profile measurements in the first section in "Results and discussion". We have decided to add some analysis and discussion to this section instead of combining this with the next one. Some vertical profiles show special features (Figs. 1(b1), 1(b2) and 1(a2)), which we discussed in section 3.3 in the previous version. Since Referee #2 suggests to move some of the materials in section 3.3 to the supplement, we have decided to move a part of the text to this section. The following text is added to section 3.1:

"It is noteworthy in Fig. 1 that aerosol number concentrations during late morning of June 29 (Flights 1) and early morning of July 1 (Flight 3) and the O₃ mixing ratio during late morning of June 29 (Flight 1) were significantly lower than those during other flights, and their vertical profiles were slightly different from others. This indicates that some factors might have impacted the levels and vertical profiles of O₃ and aerosol. To understand those phenomena, we display the airflow fields at 1000 hPa and 850 hPa over the area surrounding RMS in Fig. S2 in the supplement and 48-h backward trajectories of air parcels arriving at 100 m, 500 m, 1000 m, 1500 m and 2000m over RMS in Fig. S3 in the supplement for 8:00 local time of June 29, July 1, July 29 and July 31, 2014, calculated using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Draxler and Rolph,

2003).

Figures S2(a) and S2(b) indicate that the 1000 hPa and 850 hPa levels on early morning of June 29 were dominated by different air circulations. Figure S3(a) shows that the air parcels arriving at 100 m and 500 m over RMS were from the boundary layer over the nearby areas and mainly from south of the site, while those arriving at 1000 m and above originated far from the north (northern Heilongjiang) and travelled rapidly over 2000 m for most of the time. The disparate airflows in the bottom and upper layers made a large negative gradient in the vertical distributions of O₃ and aerosol number concentration during Flight 1, as can be seen in the vertical profiles shown in Figs. 1(b1) and 1(b2).

In the early morning of July 1 (Flight 3), the aerosol number concentration was significantly low in the whole layer. Figures S2(c) and S2(d) in the supplement show that the airflow at the 1000 hPa and 850 hPa levels over RMS was mostly from the south-southwest. Figure S3(b) in the supplement indicates that air parcels arriving at different heights over RMS originated either from south or from west or east bending to south. Using the Meteorological Information Comprehensive Analysis and Process System (MICAPS, <http://www.cma.gov.cn/en2014/20150311/20160615/index.html>) we found that there was rainfall within the 48 hours prior to 5:00 LT of July 1 over the north, south by southwest and the southeast of RMS. It can be inferred that in the early morning of July 1 air transported to the lower troposphere over RMS had been mixed with cleaner air during the rainy conditions so that the aerosol number concentration declined substantially. Therefore, synoptic situations are important factors influencing the concentrations of air pollutants and their vertical distributions. Another important factor is the PBL evolution, as discussed in the next section.”

10. Page 7, Line 23: after sunrise. . .

Response: We have changed “after the sunrise” to “after sunrise”.

11. Page 10, Line 20: Heilongjiang

Response: Corrected.

12. Section 3.5: the authors discussed the increasing trend of O₃ concentrations over the NCP region, especially in the northern part. A recent study reported a significant increase of O₃ at a mountain site (Mt. Tai) in the central part of the NCP region. Moreover, this study presents another non-surface measurement effort in this region, and is hence relevant to the present study. The authors may consider to compare their results with this previous effort. Sun, L., Xue, L. K., Wang, T., Gao, J., Ding, A. J., Cooper, O. R., Lin, M. Y., Xu, P. J., Wang, Z., Wang, X. F., Wen, L., Zhu, Y. H., Chen, T. S., Yang, L. X., Wang, Y., Chen, J.M., and Wang, W. X. Significant increase of summertime ozone at Mount.Tai in Central Eastern China, Atmos. Chem. Phys., 16, 10637-10650, 2016.

Response: We have compared our results with the relevant results reported in other papers including Sun et al. (2016). Changes have been made in the last two paragraphs of this section.

Please see details in our response to comment #13.

13. Page 13, Line 11: the enhancement of 20-41.6ppbv in O₃ concentrations from 2004-2014 points to the rate of 2.0-4.1 ppbv/year of O₃ increase. It would be helpful if the authors compare this magnitude of O₃ increase with other previous results.

Response: Thank you for your suggestion. So far, only a few papers reported rates of change in O₃ at sites in the NCP. To compare our results with those from different papers, we have rewritten the fourth paragraph and revised the fifth paragraph in section 3.5 as follows:

“Figure 8(c) shows that the O₃ level over the NCP had experienced a strong positive increase, indicating strengthening photochemical pollution in about two decades. The average mixing ratio of O₃ near the ground level had a relatively small increase (8.9 ppb) during 2004-2014, corresponding to an increase rate of about 0.9 ppb/yr. This increase rate is close to the average increase rate (1.1 ppb/yr) reported by Tang et al. (2009) of surface O₃ at six urban/suburban sites in Beijing in July-September during 2001-2006, but only about one third of what Zhang et al. (2014) found for August daytime surface O₃ at an urban site in Beijing during 2005-2011 (2.6 ppb/yr). However, the high-end value of O₃ near the ground level had a larger increase, as suggested by the right end of the error bars (Fig. 8(c)). This larger increase in the high-end value of O₃ is consistent with the large increase of the maximum daily average 8 h (MDA8) mixing ratio of O₃ at the Shangdianzi background station (Ma et al., 2016). Compared with the increase of O₃ near the ground-level, much larger increases were found in O₃ at higher altitudes in the lower troposphere over Raoyang during 2004-2014, with the maximum increase (41.6 ± 15.5 ppb) being found at 1.5 km. Assuming that the O₃ level increased linearly over the ten years, the increase rate would be about 4.2 ± 1.6 ppb/yr. Sun et al. (2016) compiled and analyzed the O₃, and NO_x and CO data collected at the Mt. Tai site (36.25°N, 117.10°E; 1534m asl) during a few campaigns from 2003 to 2015. They reported that O₃ at Mt. Tai increased at 1.7 ± 1.0 ppb/yr in June and 2.1 ± 0.9 ppb/yr in July-August during 2003-2015. These rates of increase in summer O₃ at Mt. Tai and that we obtained for 1.5 km over Raoyang agree within the uncertainties though both sites are about 240 km apart. Based on the MOZAIC measurements over Beijing in summer afternoons (at 15:00–16:00 LT in MJJ) during 1995-2005, Ding et al. (2008) reported an increase rate of about 3 ppb/yr for O₃ in 0-2 km. From the data shown in Fig. 8(c), we can obtain an increase rate of 3.3 ppb/yr for summer O₃ in 0-2 km over Raoyang for the period 2004-2014, which agrees well with that reported by Ding et al. (2008). Note that the average O₃ vertical profile for summer 2014 (Fig. 8(c)) contains measurements from the morning flights so that our estimated increase rate may be significantly lower than that for summer afternoon.”

“The above comparisons confirm that the abundance of O₃ in the lower troposphere over the north part of the NCP has largely increased since about two decades. The increase of the O₃ level in summer afternoon period seems to speed up after 2004. Network observations indicate that surface O₃ pollution in China’s polluted regions, including the NCP, has become more severe in recent years in contrast with the apparent decreases of PM_{2.5} and primary gaseous pollutants (http://www.cnemc.cn/publish/totalWebSite/0492/newList_1.html). Such trend in surface O₃ may

exert significant impacts on human health and vegetation. The increase of O₃ in the lower troposphere may influence atmospheric chemistry, i.e., increase the oxidation capacity (Ma et al., 2012), and add radiation forcing over the region.”

14. Table 1: I presume all the time given here is local time. Please specify.

Response: We specify that the time given in Table 1 is local time (LT), and point out that the period in the whole paper is local time.

References

- Ding, A. J., Wang, T., Thouret, V., Cammas, J.-P., and Nédélec, P.: Tropospheric ozone climatology over Beijing: analysis of aircraft data from the MOZAIC program, *Atmos. Chem. Phys.*, 8, 1–13, doi:10.5194/acp-8-1-2008, 2008.
- Draxler, R. R. and Rolph, G. D.: HYSPLIT (HYbrid SingleParticle Lagrangian Integrated Trajectory). Model access via NOAA ARL READY Website: <http://www.arl.noaa.gov/ready/hysplit4.html>, NOAA Air Resources Laboratory, Silver Spring, MD, 2003.
- Ma, Z.Q., Xu, J., Quan, W.J., Zhang, Z.Y., Lin, W.L., and Xu, X.B.: Significant increase of surface ozone at a rural site, north of eastern China, *Atmos. Chem. Phys.*, 16, 3969–3977, 2016.
- Sun, L., Xue, L.K., Wang, T., Gao, J., Ding, A.J., Cooper, O.R., Lin, M.Y., Xu, P.J., Wang, Z., Wang, X.F., Wen, L., Zhu, Y.H., Chen, T.S., Yang, L.X., Wang, Y., Chen, J.M., and Wang, W.X.: Significant increase of summertime ozone at Mount Tai in Central Eastern China, *Atmos. Chem. Phys.*, 16, 10637–10650, 2016.
- Tang, G., Li, X., Wang, Y., Xin, J., and Ren, X.: Surface ozone trend details and interpretations in Beijing, 2001–2006, *Atmos. Chem. Phys.*, 9, 8813–8823, 2009.
- Zhang, Q., Yuan, B., Shao, M., Wang, X., Lu, S., Lu, K., Wang, M., Chen, L., Chang, C.-C., and Liu, S. C.: Variations of ground-level O₃ and its precursors in Beijing in summertime between 2005 and 2011, *Atmos. Chem. Phys.*, 14, 6089–6101, doi:10.5194/acp-14-6089-2014, 2014.

Response to Anonymous Referee #2

This manuscript could benefit from some organization and focusing on key findings. The manuscript would be much more focused if the evaluation of the differences between the flights and the HYSPLIT modeling could be moved to supplementary material and simply referenced in the manuscript and focus the manuscript on the ozone and aerosols in the mixed and residual layers and the comparison to MOZAIC observations and trends.

Response: Thank you for your comments and suggestions. We have moved the figures about airflow fields and air mass trajectories to the supplement. The related text has been modified and moved section 3.1 to strengthen the discussion there as suggested by Referee #1.

Specific Comments

1. Abstract lines 21-22: What methods were used to determine the mixed and residual layers? Simply stating that potential temperature profiles and aerosol number concentration should suffice.

Response: The depths of the mixed layer and residual layer were determined using two methods. One is the vertical gradient of LIDAR particle extinction (dE/dz), the other is the vertical gradient of aerosol number concentration (dN/dz). Based on individual dE/dz profiles of particle extinction, we were able to determine the tops of the mixed layer and residual layer for the periods with UAV flights by identifying the minima below 2000 m in the dE/dz profiles if there were no obviously unreasonable values in the vertical profiles due to interferences or noises. In order to select the minima that were really resulted from a strong decrease of aerosol burden for a small height change rather than abnormal variation, we compared the minima in the dE/dz profiles during the flights with those before and after the flights. Finally, the MLD and RLD were obtained according to the heights at which the minima were considered to be the most reasonable ones. Similar to the vertical gradient of particle extinction, the vertical gradient of aerosol number concentration were also used for the determination of mixed and residual layer depths. To find out the key inflection points in the vertical profiles, which indicate the tops of the mixed layer and residual layer, we paid attention to the major structures in vertical profiles and gradients of aerosol number concentration during the ascent and descent flights. Due to the slight differences in time and space in the flight, there were some differences in particle number concentrations measured at the same height between the ascent and descent of a flight. Even though, the t-test ($\alpha=0.05$) helped to judge whether or not the results are accordant.

We have changed the sentence to “The depths of the mixed layer and residual layer were determined according the vertical gradients of LIDAR particle extinction and aerosol number concentration.”

2. Page 2 Line 19: The atmospheric boundary layer (ABL) acronym used later in the manuscript should be defined here. Additionally, the introduction of the friction layer as equivalent to the ABL complicates the sentence and the term friction layer is not used elsewhere and should be removed.

Response: Because “planetary boundary layer (PBL)” is more familiar for the community and readers, we have replaced the “ABL” with “PBL” as suggested by Referee #1. According to your suggestion, we have removed the term friction layer.

3. Page 2 Line 22: The sentence “The ABL with vigorous turbulence is often called the mixed layer (or mixing layer)” is not needed because it is discussed in more detail and clarity on page 3 line 1.

Response: We have removed the sentence “The ABL with vigorous turbulence is often called the mixed layer (or mixing layer)”.

4. Page 3 line 8: “deserves attention and studies” is redundant. “deserves attention.”Should suffice.

Response: We have removed “and studies”.

5. Page 10 line 24: What exactly does “significantly low” mean? Compared to the other profiles? How was significance determined?

Response: By “significantly low” we meant that the aerosol number concentration in the early morning of July 1 (Flight 3) was much lower than that in the other two flights (Flight 4 and 5) in the early morning of July 29 and July 31. The original expression was not clear enough. Therefore, we have changed the sentence to “In the whole layer, the aerosol number concentration in the early morning of July 1 (Flight 3) was much lower than those in the other two flights (Flight 4 and 5) in the early morning of July 29 and July 31 (Fig. 1(a2)).”. Note that the modified text has been moved to section 3.1.

6. Page 13 line 17: While “severer” is technically correct, “more severe” is more commonly used.

Response: We have replaced “severer” with “more severe”.

7. Figure 3: The caption does not state what figures (a), (b) or (c) designate. I assume that they are the same as in Figure 1 but this should be explicitly stated.

Response: Figure 3 shows vertical profiles of particle extinction averaged every two hours. We divided the whole day into three periods, (a) 0:00-7:00, (b) 8:00-15:00 and (c) 16:00-23:00 in order to clearly show the average PBL diurnal cycle of vertical distribution of particle extinction. We have changed the figure caption to “Vertical profiles of particle extinction averaged every two hours for (a) 0:00-7:00 LT, (b) 8:00-15:00 LT, and (c) 16:00-23:00 LT”.

List of changes made in the manuscript

(All page and line numbers refer to the ACPD version.)

1. Added a supplement with three sections. Section S1 gives some technical details of the UAV measurements. Section S2 contains two figures moved from manuscript to here (original Figures 7 and 8). Section S3 contains a newly added plot showing the average diurnal variations of surface O₃ and NO at Raoyang during the campaign.
2. P1, L17: deleted "quite".
3. P1, L21-22: changed "using two methods" to "according the vertical gradients of LIDAR particle extinction and aerosol number concentration".
4. P1, L30 and elsewhere: changed "profiles" or "profile" to "vertical profiles" or "vertical profile".
5. P1, L20: changed "In-Serves" to "In-Service".
6. P2, L5: changed "impacts to" to "impacts on".
7. P2, L9-11: changed "Therefore, actual2011)" to "The vertical distribution of O₃ is influenced by chemical and meteorological processes and varies with time and location (Kleinman et al., 1994; Fast et al., 1996; Lin et al., 2007; Ma et al., 2011). Therefore, direct measurements are needed to acquire the knowledge about the vertical distribution of O₃, which is important to understanding atmospheric chemistry and O₃ radiative forcing".
8. P2, L18: changed "atmospheric boundary layer" to "planetary boundary layer", "ABL" (also elsewhere) changed to "PBL".
9. P2, L19: deleted "and also called the planetary boundary layer and the friction layer".
10. P2, L22: deleted "The ABL with vigorous turbulence is often called the mixed layer (or mixing layer)".
11. P3, L8: deleted "and studies".
12. P4, L17: added "(NO/NO₂/NO_x, NO_y, HCHO, PAN, SO₂, CO, NH₃, etc.)" after "reactive gases".
13. P5, L7: changed "with a TE 49C O₃ analyzer" to "using an O₃ calibrator (TE 49i-PS, Thermo Electron, USA)."
14. P6, L1: changed "with a TE 49C O₃ analyzer" to "with the TE 49i-PS O₃ calibrator".
15. P6, L8: added "More details are given in the supplement (section S1)".
16. P6, Section 3.1: added three paragraphs:

"It is noteworthy in Fig. 1 that aerosol number concentrations during late morning of June 29 (Flights 1) and early morning of July 1 (Flight 3) and the O₃ mixing ratio during late morning of June 29 (Flight 1) were significantly lower than those during other flights, and their vertical profiles were slightly different from others. This indicates that some factors might have impacted the levels and vertical profiles of O₃ and aerosol. To understand those phenomena, we display the airflow fields at 1000 hPa and 850 hPa over the area surrounding RMS in Fig. S2 in the supplement and 48-h backward trajectories of air parcels arriving at 100 m, 500 m, 1000 m, 1500 m and 2000m over RMS in Fig. S3 in the supplement for 8:00 local time of June 29, July 1, July 29 and July 31, 2014, calculated using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Draxler and Rolph, 2003).

Figures S2(a) and S2(b) indicate that the 1000 hPa and 850 hPa levels on early morning of June 29 were dominated by different air circulations. Figure S3(a) shows that the air parcels arriving at 100 m and 500 m over RMS were from the boundary layer over the nearby areas and mainly from south of the site, while those arriving at 1000 m and above originated far from the north (northern Heilongjiang) and travelled rapidly over 2000 m for most of the time. The disparate airflows in the bottom and upper layers made a large negative gradient in

the vertical distributions of O₃ and aerosol number concentration during Flight 1, as can be seen in the vertical profiles shown in Figs. 1(b1) and 1(b2).

In the early morning of July 1 (Flight 3), the aerosol number concentration was significantly low in the whole layer. Figures S2(c) and S2(d) in the supplement show that the airflow at the 1000 hPa and 850 hPa levels over RMS was mostly from the south-southwest. Figure S3(b) in the supplement indicates that air parcels arriving at different heights over RMS originated either from south or from west or east bending to south. Using the Meteorological Information Comprehensive Analysis and Process System (MICAPS, <http://www.cma.gov.cn/en2014/20150311/20160615/index.html>) we found that there was rainfall within the 48 hours prior to 5:00 LT of July 1 over the north, south by southwest and the southeast of RMS. It can be inferred that in the early morning of July 1 air transported to the lower troposphere over RMS had been mixed with cleaner air during the rainy conditions so that the aerosol number concentration declined substantially. Therefore, synoptic situations are important factors influencing the concentrations of air pollutants and their vertical distributions. Another important factor is the PBL evolution, as discussed in the next section.”

17. P6, L18 and elsewhere: added “LT” to indicate local time.
18. P9, L22: added “(see Fig. S4 in the supplement)” after “is shallower”.
19. P10, L9-31: deleted “It is noteworthy in Table 2 and Fig. 1 that declined substantially” and added “With the PBL development during the daytime aerosol particles are mixed within a deeper layer as can be seen in Fig. 2”.
20. Renumbered Figure 9/Fig. 9 to Figure 7/Fig. 7 and Figure 10/Fig. 10 to Figure 8/Fig. 8.
21. P11, L32: changed “Fig. 8” to “Fig. S3 in the supplement”.
22. P13, L8-14: changed this paragraph to “Figure 8(c) shows that the O₃ level over the NCP had experienced a strong positive increase, indicating strengthening photochemical pollution in about two decades. The average mixing ratio of O₃ near the ground level had a relatively small increase (8.9 ppb) during 2004-2014, corresponding to an increase rate of about 0.9 ppb/yr. This increase rate is close to the average increase rate (1.1 ppb/yr) reported by Tang et al. (2009) of surface O₃ at six urban/suburban sites in Beijing in July-September during 2001-2006, but only about one third of what Zhang et al. (2014) found for August daytime surface O₃ at an urban site in Beijing during 2005-2011 (2.6 ppb/yr). However, the high-end value of O₃ near the ground level had a larger increase, as suggested by the right end of the error bars (Fig. 8(c)). This larger increase in the high-end value of O₃ is consistent with the large increase of the maximum daily average 8 h (MDA8) mixing ratio of O₃ at the Shangdianzi background station (Ma et al., 2016). Compared with the increase of O₃ near the ground-level, much larger increases were found in O₃ at higher altitudes in the lower troposphere over Raoyang during 2004-2014, with the maximum increase (41.6 ± 15.5 ppb) being found at 1.5 km. Assuming that the O₃ level increased linearly over the ten years, the increase rate would be about 4.2 ± 1.6 ppb/yr. Sun et al. (2016) compiled and analyzed the O₃, and NO_x and CO data collected at the Mt. Tai site (36.25°N, 117.10°E; 1534m asl) during a few campaigns from 2003 to 2015. They reported that O₃ at Mt. Tai increased at 1.7 ± 1.0 ppb/yr in June and 2.1 ± 0.9 ppb/yr in July-August during 2003-2015. These rates of increase in summer O₃ at Mt. Tai and that we obtained for 1.5 km over Raoyang agree within the uncertainties though both sites are about 240 km apart. Based on the MOZAIC measurements over Beijing in summer afternoons (at 15:00–16:00 LT in MJJ) during 1995-2005, Ding et al. (2008) reported an increase rate of about 3 ppb/yr for O₃ in 0-2 km. From the data shown in Fig. 8(c), we can obtain an increase rate of 3.3 ppb/yr for summer O₃ in 0-2 km over Raoyang for the period 2004-2014, which agrees well with that reported by Ding et al. (2008). Note that the average O₃ vertical profile for summer 2014 (Fig. 8(c)) contains measurements from the morning flights so that our estimated increase rate may be significantly lower than that for summer afternoon.”
23. P13, L15: changed “the abundance of O3 over...” to “the abundance of O3 in the lower troposphere over...”.

24. P13, L16: changed “the O3 level seems” to “the O3 level in summer afternoon period seems”.
25. P13, L17 and P14, L4: changed “severer” to “more severe”.
26. P16-17: inserted three references:
Sun, L., Xue, L.K., Wang, T., Gao, J., Ding, A.J., Cooper, O.R., Lin, M.Y., Xu, P.J., Wang, Z., Wang, X.F., Wen, L., Zhu, Y.H., Chen, T.S., Yang, L.X., Wang, Y., Chen, J.M., and Wang, W.X.: Significant increase of summertime ozone at Mount Tai in Central Eastern China, *Atmos. Chem. Phys.*, 16, 10637-10650, 2016.
Tang, G., Li, X., Wang, Y., Xin, J., and Ren, X.: Surface ozone trend details and interpretations in Beijing, 2001–2006, *Atmos. Chem. Phys.*, 9, 8813–8823, 2009.
Zhang, Q., Yuan, B., Shao, M., Wang, X., Lu, S., Lu, K., Wang, M., Chen, L., Chang, C.-C., and Liu, S. C.: Variations of ground-level O3 and its precursors in Beijing in summertime between 2005 and 2011, *Atmos. Chem. Phys.*, 14, 6089–6101, doi:10.5194/acp-14-6089-2014, 2014.
27. Figure 3: changed the caption to “Vertical profiles of particle extinction averaged every two hours for (a) 0:00-7:00 LT, (b) 8:00-15:00 LT, and (c) 16:00-23:00 LT”.
28. Figure 7 and Figure 8: moved to the supplement.

Lower tropospheric distributions of O₃ and aerosol over Raoyang, a rural site in the North China Plain

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Abstract. The North China Plain (NCP) has become one of the most polluted regions in China, with the rapid increasing economic growth in the past decades. High concentrations of ambient O₃ and aerosol have been observed at urban as well as rural sites in the NCP. Most of the in situ observations of air pollutants have been conducted near the ground so that current knowledge about the vertical distributions of tropospheric O₃ and aerosol over the NCP region is still ~~quite~~ limited. In this study, vertical profiles of O₃ and size-resolved aerosol concentrations below 2.5 km were measured in summer 2014 over a rural site in the NCP using an unmanned aerial vehicle (UAV) equipped with miniature analyzers. In addition, vertical profiles of aerosol scattering property in the lower troposphere and vertical profiles of O₃ below 1 km were also observed at the site using a LIDAR and tethered balloon, respectively. The depths of the mixed layer and residual layer were determined according the vertical gradients of LIDAR particle extinction and aerosol number concentration using two methods. Average O₃ and size-resolved aerosol number concentration in both the mixed and residual layer were obtained from the data observed in seven UAV flights. The results show that during most of the flights the O₃ levels above the top of mixed layer were higher than those below. Such positive gradient in vertical distribution of O₃ makes the residual layer an important source of O₃ in the mixed layer, particularly during morning when the top of mixed layer is rapidly elevated. In contrast to O₃, aerosol number concentration was normally higher in the mixed layer than in the residual layer, particularly in early morning. Aerosol particles were overwhelmingly distributed in the size range <1 μm, showing slight differences between the mixed and residual layers. Our measurements confirm that in the lower troposphere over the rural area of the NCP is largely impacted by anthropogenic pollutants locally emitted or transported from urban areas. Compared with the historic O₃ ~~profile~~ vertical profiles over Beijing from the Measurement of Ozone and Water Vapor by Airbus In-~~Serves-Service~~ Aircraft (MOZAIC), a strong increase in O₃

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can be found at all heights below 2.5 km in the decade from 2004 to 2014, with a largest enhancement of about 41.6 ppb. This indicates that the lower troposphere over the north part of the NCP has experienced rapid worsening photochemical pollution. This worsening trend in photochemical pollution deserves more attention in the future.

1 Introduction

- 5 Ozone (O_3) is a key trace gas and oxidant in the troposphere, which can generate hydroxyl radical (OH) that affects the oxidizing capacity of the atmosphere. Ground-level O_3 causes deleterious impacts ~~to-on~~ human health and vegetation (Anenberg et al., 2009; Mckee, 1994; Yue et al., 2014; Feng et al., 2008). Meanwhile, tropospheric O_3 is an effective greenhouse gas. The fifth IPCC assessment report points out that the increase of O_3 in the troposphere has caused $+0.40 (\pm 0.20)$ $W m^{-2}$ of radiative forcing (Myhre et al., 2013). The vertical distribution of O_3 can influence the accumulation of O_3 in the
- 10 surface layer and chemical reactions as well as radiation budget at different altitudes. ~~Therefore, actual vertical distribution of O_3 is fundamental to atmospheric chemistry and radiative transport model~~ The vertical distribution of O_3 is influenced by chemical and meteorological processes and varies with time and location (Kleinman et al., 1994; Fast et al., 1996; Lin et al., 2007; Ma et al., 2011). Therefore, direct measurements are needed to acquire the knowledge about the vertical distribution of O_3 , which is important to understanding atmospheric chemistry and O_3 radiative forcing.
- 15 Atmospheric aerosols influence the climate by direct effect and indirect effect (Schwartz, 1996; Coakley et al., 1983; Kiehl and Briegleb, 1993; Charlson, et al., 1997; Tegen et al., 2000). High loading of aerosols causes poor visibility and air quality. The diameters of aerosol particles span over four orders of magnitude, from a few nanometers to around 100 μm (Seinfeld and Pandis, 2006). Aerosol size distribution is one of the most critical factors determining light scattering property, health effects, and lifetime of aerosols. Observations of aerosol size distribution and its spatiotemporal variations have been one of the
- 20 important aspects in the study of atmospheric aerosols.

The ~~atmospheric-planetary~~ boundary layer (~~ABL-PBL~~) is the lowest part of the troposphere, which is influenced to a large extent by the friction of earth's surface and objects on it ~~and also called the planetary boundary layer and the friction layer~~ (Ahrens, 2011). The ~~ABL-PBL~~ is directly impacted by most of anthropogenic and natural sources of trace gases and aerosols. In the ~~ABL-PBL~~, the air turbulence can be so strong that it drives the rapid exchange of heat, water vapor, trace gases and aerosols

between the atmosphere and earth's surface. ~~The ABL with vigorous turbulence is often called the mixed layer (or mixing layer).~~ The structure of the ABL/PBL is critical to the vertical diffusion and transport of air pollutants so that the changes of vertical distributions of many trace gases (such as O₃) and aerosols are closely related to the evolution of the ABL/PBL.

The diurnal evolution of the ABL/PBL usually leads to a well-developed mixed layer in the daytime (He and Mao, 2005) and a stable layer overlaid by a residual layer in the nighttime. The formation of nocturnal stable layer may exert significant impacts on the concentrations of species in the surface layer. For example, surface O₃ is substantially removed during night by reactions with NO and some other species, and by dry deposition, particularly in urban areas during cold seasons (Lin et al., 2011). Following the development of the mixed layer on the next day, O₃ in the residual layer can be downward mixed, making a contribution to the enhancement of ground-level O₃ and even driving the photochemical processes (Aneja et al., 2000; Kleinman et al., 1994; Neu et al., 1994; Zhang et al., 1999). Therefore, the O₃ distribution in both mixed layer and residual layer deserves attention ~~and studies~~. Similarly, chemical compositions and physical properties including size distribution of aerosols may also be impacted by the evolution of ABL/PBL. Knowledge of this aspect is important for atmospheric chemistry and physics studies.

In recent decades, with the rapid economic development and the urbanization in China, ground-level and tropospheric O₃ and aerosol have increased significantly, especially in the North China Plain (NCP) (Ding et al., 2008; Xu and Lin, 2011; Ma et al., 2016; Chen et al., 2015; Ding and Liu, 2014). So far, observational studies on O₃ and aerosol in the NCP have been mainly conducted in the surface layer. There is only limited knowledge of the vertical distributions of tropospheric O₃ and aerosol over the NCP region, gained in some sporadic observational studies (Chen et al., 2009; Chen et al., 2013; Ma et al., 2011; Wang et al., 2012; Zheng et al., 2005). This hinders extensive validations of atmospheric chemistry models as well as the assessment of climate effects of O₃ and aerosols over this important region.

The detection of vertical distributions of O₃ and aerosol can be made using balloon sounding, aircraft, and tethered balloon. Each of the techniques has its advantages and disadvantages. Balloon sounding is a good way of obtaining O₃ and aerosol ~~profile~~ vertical profiles below about 30 km, but the sondes for O₃ and aerosol are usually expensive and not reusable, not to mention ground facilities needed for the sounding. Tethered balloon attached with O₃ and aerosol devices can be used for many times of observations under stable weather conditions, but it is usually not suitable to be operated above 1 km and needs

manpower to run it carefully. Aircraft equipped with analyzers for O₃, other trace gases and aerosol instruments can be used to simultaneously obtain distributions of these species along the flight tracks, but such observation is normally expensive and needs strong logistic supports of airport.

Typically, most aircraft measurements are made using manned aircrafts. However, unmanned aerial vehicles (UAVs) can also be used as research platforms. In the last decade, UAVs have been successfully used in the fields of atmosphere science and environment monitoring in order to understand the three-dimensional distribution of atmospheric species (Altstädter, et al., 2015; Illingworth et al., 2014; Watai et al., 2006; Rauneker and Lischeid, 2012; Gao et al., 2016). In comparison with manned aircrafts, UAVs have a few advantages, such as no need for airport, lower costs, higher flexibility, the possibility to investigate atmospheric parameters at small scales and low altitudes and the potential for application in regions dangerous for manned aircraft (Altstädter, et al., 2015). Above all, measurements with high spatial resolutions can be obtained using UAVs. For example, in a city center with a diameter of approximately 2 km, a typical instrument with 1 Hz resolution would only be able to make approximately 20 measurements during an overpass of the city when a normal atmospheric research aircraft was used. In contrast, more measurements would be obtained by an UAV so that the measurement uncertainty can be effectively reduced.

In this paper, we present UAV measurements of vertical distributions of O₃ and size-resolved aerosol number concentrations obtained over a site in the NCP during a field campaign. Data of surface O₃ and LIDAR observations of aerosol extinction from a nearby site are included in the analysis to facilitate interpretations and discussions of the measurements. To the best of our knowledge, there has been no similar published study from China.

2 Experimental

2.1 Ground-based measurements

Ground-based measurements, including measurements of surface O₃ and some other reactive gases (NO/NO₂/NO_x, NO_y, HCHO, PAN, SO₂, CO, NH₃, etc.), tethered balloon measurements of O₃ and black carbon (BC) profilevertical profiles, LIDAR observation of aerosol profilevertical profiles, etc., were conducted from 7 June to 18 August 2014 at the Raoyang Meteorological Station (RMS, 115°44'N, 38°14'N, 20m, a semirural site) in the NCP. RMS is located in Raoyang County, an

agriculture county in the middle of Heibei Province. There are no large industrial sources in Raoyang. However, some influences on the RMS site from the residence and traffic sources in the surrounding areas cannot be excluded. More details about the RMS site are given in Ran et al. (2016).

Surface O₃ was measured using a photometric O₃ analyzer (TE 49C, Thermo Electron, USA). The detection limit and precision of the O₃ analyzer are 1 ppb and 1 ppb, respectively. The analyzer was calibrated on 17 June, 16 July and 18 August, 2014 and showed no significant drifts. Details about the calibration and maintenance are described in Lin et al. (2009). A dual beam ozone monitor (Model-205, 2B Technologies, USA) was used for the tethered balloon observations of O₃ ~~profile~~vertical profiles. The ozone monitor has dimensions of 9 × 21 × 29 cm and weighs only 2.3 kg. It works based on the UV absorption at 254 nm at a maximum frequency of 0.5 Hz. It measures O₃ with a precision of 1 ppb or 2% of reading and has a limit of detection of 1 ppb. The ozone monitor was calibrated at the site ~~with using an TE 49C O₃ analyzer~~calibrator (TE 49i-PS, Thermo Electron, USA).

Vertical profiles of aerosol were observed using a LIDAR (Leosphere, France). The LIDAR principle is based on the scattering phenomenon of light. A laser pulse is sent into the atmosphere and scattered by the target molecules or particles (clouds, dust, soot particles etc.). The backscattered light is collected by an optical system and its intensity is measured by a photo-detector, converted into an electronics signal and stored onto a computer. The wavelength of the laser sent is 355 nm. The vertical resolution of the LIDAR measurements is 15m and data below 200 m are discarded (EZ Aerosol and cloud LIDAR user manual).

2.2 Flight information

An UAV platform was used for the ~~profile~~vertical profile measurements. The body of the UAV is made of glass fiber reinforced plastics, with a wingspan of 3.2 m. The UAV is battery-powered so that there is no contaminant from the engine exhaust of the UAV. The cruising speed and maximum cruising altitude of the UAV are 25 m/s and 5.5 km, respectively. As we were more interested in the vertical distributions of O₃ and aerosol in the lower troposphere, the UAV was programmed to fly below 3 km over an area within 5 km in diameter.

A miniature ozone monitor, personal ozone monitor (POM, 2B Technologies, USA) and handheld optical particle counter (OPC) (Handheld 2016 or 3016, Lighthouse, USA) were installed in the small cabinet of the UAV to measure the O_3 and aerosol number concentrations on the flight. The POM has dimensions of 10.2 x 7.6 x 3.8 cm and weighs only 0.34 kg. It works based on the UV absorption at 254 nm at a maximum frequency of 0.1 Hz. It measures O_3 with a precision of 2 ppb or 2% and has a limit of detection of 4 ppb, well below the normal O_3 level over the Raoyang site. The POM was calibrated in the factory against a NIST-traceable standard instrument and compared at the site with ~~a the~~ TE 49Ci-PS O_3 ~~analyzer~~ calibrator. The handheld OPC has dimensions of 22.23 x 12.7 x 6.35 cm and weighs about 1 kg. The Handheld 2016 counts aerosol numbers in the size-bins 0.2-0.3 μ m, 0.3-0.5 μ m, 0.5-0.7 μ m, 0.7 -1.0 μ m, 1.0-2.0 μ m and >2 μ m, while the Handheld 3016 (used only in the flight during 5:53-6:18 of July 31) records aerosol numbers in the size-bins 0.3-0.5 μ m, 0.5-1.0 μ m, 1.0-3.0 μ m, 3.0-5.0 μ m, 5.0-10.0 μ m and >10 μ m in differential or accumulation method. The OPC devices were set to collect data at 1 Hz. An isokinetic tube was mounted on the nose of the UAV to introduce ambient air into the OPC. In addition, a temperature/humidity sensor was attached to the OPC so that the sampling flow rate was converted to standard condition. Both OPC devices were calibrated against a NIST-traceable source. More details are given in the supplement (section S1).

Limited mainly by the availability of airspace, only seven successful UAV measurements were conducted several kilometers west of the RMS during the observation period. More detailed flight information is summarized in Table 1.

3 Results and discussion

3.1 ~~Profile~~ Vertical profiles of O_3 , aerosol number concentration and extinction

The ~~profile~~ vertical profiles of O_3 were acquired during seven UAV flights as listed in Table 1, while aerosol number concentrations in six size-bins were observed during five of the seven flights (Flights 1-5). The observed aerosols particles were predominately distributed in the accumulation mode since it is not possible to count the aerosol numbers in the Atkin mode using the handheld OPC. Figure 1 shows the ~~profile~~ vertical profiles of O_3 and aerosol number concentration observed during all flights. To study how the evolution of ABLPBL influences O_3 and aerosol concentration at different altitudes, the ~~profile~~ vertical profiles in Fig.1 are grouped in early morning (5:40-8:00 LT), late morning (10:00-12:00 LT) and afternoon

(15:00-19:00 LT) periods and shown in Figs. 1(a), 1(b) and 1(c), respectively. In addition, average particle extinction profile vertical profiles simultaneously obtained by the LIDAR are presented, with data points less than or equal to zero being excluded. All the profile vertical profiles shown in Fig. 1 include averages over 50 m vertical layers, regardless of the spatial resolutions of actual observations. Although the site over which the flights were conducted is several kilometers away from the RMS, both sites were influenced by the same synoptic system. Therefore, the results (Fig.1) from both sites should be comparable within the observation uncertainties. In the early morning of July 29, 2014, particle extinction of more than 3000 Mm^{-1} was observed at around 1600 m (Fig. 1(a3)), indicating the presence of cloud there (Huang et al., 2011).

It is noteworthy in Fig. 1 that aerosol number concentrations during late morning of June 29 (Flights 1) and early morning of July 1 (Flight 3) and the O_3 mixing ratio during late morning of June 29 (Flight 1) were significantly lower than those during other flights, and their vertical profiles were slightly different from others. This indicates that some factors might have impacted the levels and vertical profiles of O_3 and aerosol. To understand those phenomena, we display the airflow fields at 1000 hPa and 850 hPa over the area surrounding RMS in Fig. S2 in the supplement and 48-h backward trajectories of air parcels arriving at 100 m, 500 m, 1000 m, 1500 m and 2000m over RMS in Fig. S3 in the supplement for 8:00 local time of June 29, July 1, July 29 and July 31, 2014, calculated using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Draxler and Rolph, 2003).

Figures S2(a) and S2(b) indicate that the 1000 hPa and 850 hPa levels on early morning of June 29 were dominated by different air circulations. Figure S3(a) shows that the air parcels arriving at 100 m and 500 m over RMS were from the boundary layer over the nearby areas and mainly from south of the site, while those arriving at 1000 m and above originated far from the north (northern Heilongjiang) and travelled rapidly over 2000 m for most of the time. The disparate airflows in the bottom and upper layers made a large negative gradient in the vertical distributions of O_3 and aerosol number concentration during Flight 1, as can be seen in the vertical profiles shown in Figs. 1(b1) and 1(b2).

In the whole layer, the aerosol number concentration in the early morning of July 1 (Flight 3) was much lower than those in the other two flights (Flight 4 and 5) in the early morning of July 29 and July 31 (Fig. 1(a2)). Figures S2(c) and S2(d) in the supplement show that the airflow at the 1000 hPa and 850 hPa levels over RMS was mostly from the south-southwest. Figure S3(b) in the supplement indicates that air parcels arriving at different heights over RMS originated either from south or from

west or east bending to south. Using the Meteorological Information Comprehensive Analysis and Process System (MICAPS, <http://www.cma.gov.cn/en2014/20150311/20160615/index.html>) we found that there was rainfall within the 48 hours prior to 5:00 LT of July 1 over the north, south by southwest and the southeast of RMS. It can be inferred that in the early morning of July 1 air transported to the lower troposphere over RMS had been mixed with cleaner air during the rainy conditions so that the aerosol number concentration declined substantially. Therefore, synoptic situations are important factors influencing the concentrations of air pollutants and their vertical distributions. Another important factor is the PBL evolution, as discussed in the next section.

3.2 Determination of the mixed and residual layer depth

The ABL/PBL development can, in principle, be determined by measurement of profile/vertical profile of a variety of atmospheric properties, with potential temperature being the most common one (Lenschow, 1986). Vertical aerosol number concentration profile/vertical profile allow the determination of the ABL/PBL, as aerosol acts as a tracer of atmospheric turbulent forces along height (Ferrero et al., 2011, 2014). One powerful way to probe the ABL/PBL is based on profile/vertical profile of particle extinction detected using LIDAR. There are several methods to explore the structure of ABL/PBL from profile/vertical profile of particle extinction, such as the calculation of vertical gradient of particle extinction (He and Mao, 2005; Huang et al, 2011; Hayden et al., 1994; Hoff et al., 1996; Melfi et al., 1985), wavelet analysis (Cohn et al., 1997; Brooks et al., 2003), and parameterization (Steyn et al., 1999). In this study, calculations of the vertical gradient of LIDAR particle extinction (dE/dz) and particle number concentration (dN/dz) are adopted to identify the mixed layer depth (MLD) and residual layer depth (RLD).

To obtain a general picture of the diurnal ABL/PBL evolution, particle extinction values at different heights in the lower troposphere (0-3 km) were averaged for different time intervals on all sunny days during the campaign. The average profile/vertical profile in a half hour and two hour intervals are displayed in Figs. 2 and 3, respectively. The zero and negative values in the LIDAR measurements were excluded, which may lead to averages slightly overestimated. Averages with less than 75% data availability were rejected to avoid the impact of under-sampling on the average profile/vertical profiles. As mentioned in section 1, the ABL/PBL experiences a diurnal cycle. The mixed layer develops after the sunrise. Its top rises

continually up and may exceed the top of the residual layer formed on the previous day. After the sunset, the mixed layer collapses gradually, forming the nocturnal stable layer and residual layer.

Figures 2 and 3 clearly show the average ~~ABL~~PBL diurnal cycle of vertical distribution of particle extinction. According to the solar elevation angles, the sunrise and sunset time is estimated to be 5:00-6:00 LT and 19:00-20:00 LT, respectively. In Fig. 3, the maximum of particle extinction was 0.53 km⁻¹ at 660 m after the sunset and the top of residual layer was about 705 m. Moreover, the nocturnal stable layer started forming, reaching a depth of about 300 m at 0:00-1:00 LT on the next day (Fig. 3(a)). During the night, the top of average residual layer fluctuated slightly around 700 m. After ~~the~~ sunrise on the next day, the nocturnal stable layer disappeared gradually, and the mixed layer developed. The top of mixed layer reached about 840 m at around 11:00 LT and stayed until 13:00 LT, when it started declining. The particle extinction in the mixed layer increased during the morning period, presumably because of the increasing aerosol emissions, downward mixing from the residual layer, and photochemical production from precursor gases.

The data shown in Figs. 2 and 3 are consistent with our understanding of the diurnal ~~ABL~~PBL evolution, suggesting that LIDAR data captured the structure of ~~ABL~~PBL and can be used in the determination of the MLD and RLD. Based on individual dE/dz ~~profile~~vertical profiles of particle extinction, we can determine the tops of the mixed layer and residual layer for the periods with UAV flights by identifying the minima below 2000 m in the dE/dz ~~profile~~vertical profiles if there were no obviously unreasonable values in the ~~profile~~vertical profiles due to interferences or noise. In order to select the minima that were really resulted from a strong decrease of aerosol burden for a small height change rather than abnormal variation, we compared the minima before and after the flights with those during the flights. Finally, the MLD and RLD were obtained according to the heights at which the minima were considered to be the most reasonable ones. However, this method was not applicable when the MLD was in the blind zone of LIDAR (lower than 200m) or there was cloud near the top of residual layer.

The ~~profile~~vertical profile of particle extinction and its gradient for the flight (10:18-10:47 LT) in the late morning of June 29 (Flight 1) are displayed in Fig. 4 to show how to determine the MLD and RLD. To facilitate the identification of the mixed layer and residual layer, the ~~profile~~vertical profile of particle extinction before and after the flight are also shown in Fig. 4(a). With the consideration of turbulent time scale in the atmosphere, the particle extinction ~~profile~~vertical profiles at 8:00 LT and 12:00 LT were calculated from the LIDAR observations in the periods 7:30-8:30 LT and 11:30-12:30 LT, respectively. As can

be seen in Fig. 4(b), there are a few minima in the calculated gradient, two of which (marked with filled black circles) may represent the tops of the mixed layer and residual layer. Comparing the profilevertical profile of particle extinction during the flight with those before and after the flight, we can see gradual changes in heights of the inflection points in the lower parts of the profilevertical profiles (0-1500 m) with the evolution of the ABLPBL. This makes us more certain that the filled black circles in the gradient curve in Fig. 4(b) indicate the tops of the mixed layer and residual layer.

Similar to the vertical gradient of particle extinction, the vertical gradient of aerosol number concentration can also be used to probe the ABLPBL. To find out the key inflection points in the vertical profiles, which indicate the tops of the mixed layer and residual layer, we paid attention to the major structures in vertical profiles and gradients of aerosol number concentration during the ascent and descent flights. Due to the slight differences in time and space in the flight, there were some differences in particle number concentrations measured at the same height between the ascent and descent of a flight. Even though, the t-test ($\alpha=0.05$) may help to judge whether or not the results are accordant. As an example, Fig. 5 shows the aerosol number concentration data from a flight in the early morning of July 29 (Flight 4). The two minima at 275 m and 1770 m (marked with red solid circles) in the gradient curve (Fig. 5(b)) corresponds obviously the major inflection points in the vertical profile of ascent flight (Fig. 5(a)). In the gradient curve from the descent flight, there are also two minima below 2000 m. These two minima do not overlay those from the ascent flight, but there are no significant ($\alpha=0.05$) differences in the minimum positions between ascent and descent. Therefore, the marked heights 275 m and 1770 m are considered to be the tops of mixed layer and residual layer, respectively.

Determining the MLD and RLD facilitates the calculations of average O_3 and aerosol number concentrations in the mixed layer and the residual layer. Table 2 summarizes the mixed and residual layer heights, determined using the methods discussed above, and the calculated O_3 and aerosol number concentrations for the two layers during the flights. The MLD or RLD during some flights cannot be determined in the case that the MLD was in the blind zone of LIDAR (lower than 200m) or there was cloud near the top of residual layer. Ideally, the mixed and residual layer heights determined using the two methods were the same, so would be the average O_3 and aerosol number concentrations. However, the real conditions were not idealized. As can be seen in Table 2, the two methods produced different results of the MLD and RLD, and the average O_3 and aerosol number concentrations.

To see how the results from the two methods are different from each other, we conducted correlation analyses. In Fig. 6, average O_3 and aerosol number concentrations obtained using the method of particle extinction gradient (Method 1) are compared with those obtained using the method of particle number concentration gradient (Method 2). As can be seen in the figure, the averages obtained using the two methods are highly significantly correlated. Linear regressions suggest that the slopes of correlation lines for average O_3 and aerosol number concentrations in the mixed layer and residual layer are all close to 1.0. In other words, the two methods used for the determination of the MLD and RLD are reliable and can produce comparable results.

3.3 Average O_3 and aerosol number concentrations in the mixed and residual layers

Data in Table 2 indicate that the mixed layer height increased from early morning to late morning and to afternoon. The top of residual layer did not show such tendency. The mixing ratio of O_3 in the surface layer and mixed layer was lowest in the early morning and highest in the afternoon. This can be readily explained by the changes in photochemical production, NO titration, and dry deposition of O_3 in the course of the day. Photochemical reactions often produce much more O_3 around noon than in the other period, while NO titration and dry deposition remove O_3 more effective during the night and early morning, when the NO level is higher and the mixed layer is shallower (see Fig. S4 in the supplement). In most cases, the diurnal cycle of surface O_3 can be well explained by these factors, if advection is negligible. However, there may be additional factors that contribute significantly to the diurnal variations of O_3 in the mixed layers, at least in our cases. Table 2 shows that the level of O_3 in the surface and mixed layers were lower than that in the residual layer during all early morning flights (Flights 3-5). Data from the flight in late morning of June 29 (Flight 1) indicate that the O_3 level in the residual layer was slightly lower than those in the surface and mixed layers. Fig. 1(c1) shows that O_3 ~~profile~~vertical profile were relatively straight and the O_3 levels in the surface and mixed layers were close to or slightly lower than those at the heights above the mixed layer. These suggest that during most of our flights the O_3 levels above the top of mixed layer were higher than those below. Similar vertical O_3 profiles were also observed over a site in Beijing by Ma et al. (2011).

~~Such~~The positive gradient in vertical distribution of O_3 makes the residual layer an important source of O_3 in the mixed layer, particularly during morning when the top of mixed layer is rapidly elevated. Therefore, downward mixing of O_3 in the

residual layer over our site may play an important role in the diurnal cycle of O_3 at ground-level and in the mixed layer. Previous studies show that O_3 in the free troposphere over the NCP can be rapidly downward transported to the surface layer, driven by high wind speed in winter (Lin et al., 2011; Zhang et al., 2014a) or nighttime convection processes in summer (Jia et al., 2015). Our data show that even under normal meteorological conditions in summer, downward mixing of O_3 at higher altitudes over the NCP can be a significant contributor to the O_3 level in the mixed layer. The physical processes that influence surface O_3 are normally considered in modern air quality models. It is of interest to test how well the models can simulate the impacts of these processes on surface O_3 . Our measurements provide valuable experimental data for validating model results and satellite retrievals, which is out of scope of this paper.

In contrast to the O_3 level, aerosol number concentration in early morning was higher in the mixed layer than in the residual layer. This can be attributed to the fact that the major sources of primary and secondary aerosols are in the mixed layer. With the PBL development during the daytime aerosol particles are mixed within a deeper layer as can be seen in Fig. 2. ~~It is noteworthy in Table 2 and Fig. 1 that aerosol number concentrations during Flights 1 and 3 and the O_3 mixing ratio during Flight 1 were significantly lower than those during other flights, and their profiles were slightly different from others. This indicates that some factors other than the ABL evolution might have exerted impacts on the levels and profiles of O_3 and aerosol.~~

~~To understand those phenomena, we display the airflow fields at 1000 hPa and 850 hPa over the area surrounding RMS in Fig. 7 and 48 h backward trajectories of air parcels arriving at 100 m, 500 m, 1000 m, 1500 m and 2000m over RMS in Fig. 8 for 8:00 local time of June 29, July 1, July 29 and July 31, 2014, calculated using the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPPLIT) model (Draxler and Rolph, 2003). Figures 7(a) and 7(b) indicate that the 1000 hPa and 850 hPa levels on early morning of June 29 were dominated by different air circulations. Figure 8(a) shows that the air parcels arriving at 100 m and 500 m over RMS were from the boundary layer over the nearby areas and mainly from south of the site, while those arriving at 1000 m and above originated far from the north (northern Helongjiang) and travelled rapidly over 2000 m for most of the time. The disparate airflows in the bottom and upper layers made a large negative gradient in the vertical distributions of O_3 and aerosol number concentration during Flight 1, as can be seen in the profiles shown in Figs. 1(b1) and 1(b2).~~

~~In the early morning of July 1 (Flight 3), the aerosol number concentration was significantly low in the whole layer. Figures 7(c) and 7(d) show that the airflow at the 1000 hPa and 850 hPa levels over RMS was mostly from the south-southwest. Figure 8(b) indicates that air parcels arriving at different heights over RMS originated either from south or from west or east bending~~

to south. Using the Meteorological Information Comprehensive Analysis and Process System (MICAPS, <http://www.cma.gov.cn/en2014/20150311/20160615/index.html>) we found that there was rainfall during the 48 hours prior to 5:00 of July 1 over the north, south by southwest and the southeast of RMS. It can be inferred that in the early morning of July 1 air transported to the lower troposphere over RMS had been cleaned by wet deposition so that the aerosol number concentration declined substantially.

3.4 Aerosol number size distributions in the mixed layer and residual layer

The mass concentration, size distribution, and chemical composition of aerosol are closely related with emissions, atmospheric chemistry, and meteorological conditions. The formation of the mixed layer and residual layer reduces the vertical mixing and may cause some differences in the physico-chemical properties of aerosols between both layers. Here, we investigate the difference in aerosol number-size distribution between the mixed and residual layers, taking the advantage of clear separation of both layers. Aerosol number concentrations in different size-bins were averaged for the mixed and the residual layers determined using aerosol number concentration gradients. Figure 9-7 shows the aerosol number and volume size distributions in the mixed layer and residual layer during early morning of July 1 (Flight 3), early morning of July 29 (Flight 4), late morning of June 29 (Flight 1) and afternoon of June 29 (Flight 2). The aerosol volume concentrations were calculated from the measured number size distributions under the assumption that all particles were spherical.

Obviously, the particle number concentration in the mixed layer was higher than that in the residual layer. This is expected as the mixed layer is normally more impacted by emission sources, which are mainly within the mixed layer. On the other hand, the differences of aerosol number and volume concentration between the mixed layer and the residual layer were more significant in the size range $>2 \mu\text{m}$ in comparison with the other size ranges. This can be well explained by the fact that the mixed layer is much more influenced than residual layer by the ground-level emission of aerosol in coarse mode. Moreover, aerosol particles were overwhelmingly distributed in the size range $<1 \mu\text{m}$, independent of observation time. Such aerosol size distribution and ranges of aerosol number concentrations unsurprisingly resembled urban aerosol (Baron et al., 2011). Although some coarse particles may be released by the farm over which our UAV observations were conducted, their contribution to our measurements of aerosol number concentration should be limited within the surface layer, considering the wind conditions during the UAV flights. In other word, the aerosol size distributions at higher altitudes of the ABLPBL were

nearly not influenced by local coarse particle emissions. In recent decades, the NCP region has been found to be one of the most polluted regions of the world, suffering severe haze pollution (Fu et al., 2014). Even in the rural areas of the NCP, air quality is largely impacted by anthropogenic pollutants locally emitted or transported from urban areas (Lin et al., 2008; Lin et al., 2009; Liu et al., 2010). Therefore, aerosol size distributions shown in Fig. 9–7 should represent well mixed aerosol over a rural area in the NCP, which is dominated by fine particles.

It is interesting to see that the patterns of aerosol number and volume size distributions in Flight 4 (early morning in July 29) are different from those in Flights 1 (late morning in June 29), 2 (afternoon in June 29) and 3 (early morning in July 1). The number size distributions in Flights 1, 2 and 3 show monotonic decreasing with increasing aerosol size (Figs. 97(a), 97(c) and 97(d)), while those in Flight 4 peak in the range of 0.3–0.5 μ m (Fig. 97(b)). The aerosol size distribution in the early morning of July 29 (Flight 4) was unique in that a larger portion of aerosol particles was found in the range 0.3–0.5 μ m. It may be caused by different synoptic conditions. Figure 1 indicates that among all the ~~profile~~vertical profiles, the ~~profile~~vertical profiles from July 1 (Flight 3) and July 29 (Flight 4) represent most clean and most polluted cases, respectively. Backward trajectories (Fig. 8S3 in the supplement) indicate that in early morning of July 29, air masses were from the southeast sector. Studies at other NCP sites also show that air masses from southeast are associated with higher particle number concentration (Shen et al., 2011) and contain aerosols of relatively larger mean medium diameter (Zhang et al., 2014c), which coincide with our results.

3.5 Comparison with historic O₃ ~~profile~~vertical profiles

The increase in emissions of air pollutants in the NCP region has caused haze and O₃ pollution in recent decades. Emission control measures that have been introduced in this region have led to a decrease trend after 2003 in the annual number of haze days (Fu et al., 2014). However, the O₃ air quality has not been improved yet. In contrast, the maximum daily average 8-h (MDA8) mixing ratios of O₃ at a background site in the NCP increased at a rate of 1.13 ppb/yr from 2003 to 2015 (Ma et al., 2016). The increase of O₃ level has taken place not only at ground-level, but also at other altitudes in the troposphere, particularly in the ABLPBL. Ding et al. (2008) revealed a strong positive trend of the O₃ level in the boundary layer over

Beijing from 1995 to 2005 using the Measurements of Ozone and Water Vapor by Airbus In-Service Aircraft (MOZAIC). Multi-year ozonesonde measurements over Beijing also indicate a significant increase of tropospheric O₃ during the period 2002-2010 (Wang et al., 2012).

It is of great interest to see how lower tropospheric O₃ has changed over the NCP region. Many locations in the NCP region are controlled by similar prevailing winds (southwesterly and northeasterly), particularly in summer (Lin et al., 2008; Lin et al., 2009). Although the MOZAIC measurements and our UAV observations of O₃ were conducted over two sites about 200 km apart from each other, O₃ [profilevertical profiles](#) in the lower troposphere over both sites may represent the situations over the north part of the NCP. Therefore, it is assumed that the O₃ [profilevertical profile](#)s over both sites might be comparable. Under this assumption, we can try to obtain an idea about the change of summer O₃ in the lower troposphere over the NCP between the first MOZAIC measurements and our measurements.

Figure [40-8](#) displays average O₃ [profilevertical profiles](#) for different time period of the day in the lower troposphere obtained at RMS during our tethered balloon (Fig. [408\(a\)](#)) and UAV observations (Fig. [408\(b\)](#)) and summer daytime (5:00-19:00 [LT](#)) average O₃ [profilevertical profiles](#) from MOZAIC observations and our observations (Fig. [408\(c\)](#)). The MOZAIC O₃ data have an estimated accuracy of $\pm[2 \text{ ppb}+2\%]$ for individual 4 s measurements and is suitable for building reliable O₃ climatologies (Thouret et al., 1998; Zbinden et al., 2013). MOZAIC O₃ [profilevertical profile](#) data for the greater Beijing area are available only for 1994-2005 with varying monthly [profilevertical profile](#) numbers and most of the [profilevertical profiles](#) were obtained during 5:00-18:00 [LT](#) period (Ding et al., 2008). To enhance the representativeness of average [profilevertical profiles](#), all average MOZAIC O₃ [profilevertical profiles](#) were calculated from at least 7 individual [profilevertical profiles](#). For some years, no average MOZAIC O₃ [profilevertical profiles](#) were available due to inadequate MOZAIC measurements in summer. O₃ measurements from 52 tethered balloon experiments (TBE) over Raoyang were grouped and averaged for the early morning (5:00-10:00 [LT](#)), late morning (10:00-12:00 [LT](#)) and afternoon (12:00-19:00 [LT](#)) periods (Fig. [408\(a\)](#)). Only 7 UAV experiments (UAVE) could be made during our campaign at Raoyang. Nevertheless, average O₃ [profilevertical profiles](#) were calculated for early morning, late morning and afternoon (Fig. [408\(b\)](#)), respectively. It is noted that only one UAV flight was made in late morning (Flight 1; 10:28-10:50 [LT](#) on June 29, 2014). Therefore, the late morning average O₃ [profilevertical profile](#) in Fig. [408\(b\)](#) is less representative. If this [profilevertical profile](#) is not considered, we can see in Figs. [408\(a\)](#) and [408\(b\)](#)

a clear development of vertical O_3 distribution in the lower troposphere, with a substantial increase of the O_3 level in the mixed layer and a slight increase above the mixed layer in the course from the early morning to the afternoon. Although the mixing ratios of O_3 over Raoyang were mostly higher than 100 ppb in the afternoon, the overall average values were about 100 ppb as shown in the bottom-right plot of Fig. 10(c). Both our measurements and the MOZAIC measurements indicate high O_3 pollution in the lower troposphere over the NCP in summer.

~~Figure 10(c) shows that the O_3 level over the NCP had experienced a strong positive increase, indicating strengthening photochemical pollution in about two decades. The O_3 profiles in Fig. 10(c) suggest that the variations of O_3 before 2004 were small and the major increases occurred during 2004–2014. The average mixing ratios of O_3 between 400 m and 2400 m were enhanced nearly by 33.8 ppb (20.0–41.6 ppb) during 2004–2014. In contrast, the average mixing ratio of O_3 near the ground level increased only slightly in the same period. However, the high-end value of O_3 near the ground level had a large increase, too, as suggested by the right end of the error bars. This finding is consistent with the large increase of the maximum daily average 8 h (MDA8) mixing ratio of O_3 at the Shangdianzi background station (Ma et al., 2016). Figure 8(c) shows that the O_3 level over the NCP had experienced a strong positive increase, indicating strengthening photochemical pollution in about two decades. The average mixing ratio of O_3 near the ground level had a relatively small increase (8.9 ppb) during 2004–2014, corresponding to an increase rate of about 0.9 ppb/yr. This increase rate is close to the average increase rate (1.1 ppb/yr) reported by Tang et al. (2009) of surface O_3 at six urban/suburban sites in Beijing in July–September during 2001–2006, but only about one third of what Zhang et al. (2014b) found for August daytime surface O_3 at an urban site in Beijing during 2005–2011 (2.6 ppb/yr). However, the high-end value of O_3 near the ground level had a larger increase, as suggested by the right end of the error bars (Fig. 8(c)). This larger increase in the high-end value of O_3 is consistent with the large increase of the maximum daily average 8 h (MDA8) mixing ratio of O_3 at the Shangdianzi background station (Ma et al., 2016). Compared with the increase of O_3 near the ground-level, much larger increases were found in O_3 at higher altitudes in the lower troposphere over Raoyang during 2004–2014, with the maximum increase (41.6 ± 15.5 ppb) being found at 1.5 km. Assuming that the O_3 level increased linearly over the ten years, the increase rate would be about 4.2 ± 1.6 ppb/yr. Sun et al. (2016) compiled and analyzed the O_3 , and NO_x and CO data collected at the Mt. Tai site (36.25°N, 117.10°E; 1534 m asl) during a few campaigns from 2003 to 2015. They reported that O_3 at Mt. Tai increased at 1.7 ± 1.0 ppb/yr in June~~

and 2.1 ± 0.9 ppb/yr in July-August during 2003-2015. These rates of increase in summer O_3 at Mt. Tai and that we obtained for 1.5 km over Raoyang agree within the uncertainties though both sites are about 240 km apart. Based on the MOZAIC measurements over Beijing in summer afternoons (at 15:00–16:00 LT in MJJ) during 1995-2005, Ding et al. (2008) reported an increase rate of about 3 ppb/yr for O_3 in 0-2 km. From the data shown in Fig. 8(c), we can obtain an increase rate of 3.3 ppb/yr for summer O_3 in 0-2 km over Raoyang for the period 2004-2014, which agrees well with that reported by Ding et al. (2008). Note that the average O_3 vertical profile for summer 2014 (Fig. 8(c)) contains measurements from the morning flights so that our estimated increase rate may be significantly lower than that for summer afternoon.

The above comparisons confirm that the abundance of O_3 in the lower troposphere over the north part of the NCP has largely increased since about two decades. The increase of the O_3 level in summer afternoon period seems to speed up after 2004. Network observations indicate that surface O_3 pollution in China's polluted regions, including the NCP, has become ~~severer~~ more severe in recent years in contrast with the apparent decreases of $PM_{2.5}$ and primary gaseous pollutants (http://www.cnemc.cn/publish/totalWebSite/0492/newList_1.html). Such trend in surface O_3 may exert significant impacts on human health and vegetation. The increase of O_3 in the lower troposphere may influence atmospheric chemistry, i.e., increase the oxidation capacity (Ma et al., 2012), and add radiation forcing over the region.

4 Conclusion

In this study, vertical profiles of particle extinction property, O_3 and size-resolved aerosol concentration were simultaneously measured using miniature devices installed in an UAV over a rural site in the NCP during 2014 summer, allowing the characterization of diurnal O_3 and aerosol concentration in mixing layer and residual layer over a small area. Seven vertical profiles were successfully obtained in this campaign.

We found a positive gradient in the vertical distribution of O_3 , higher above the top of mixed layer than those below, making the residual layer an important source of O_3 in the mixed layer, particularly during morning when the top of mixed layer is rapidly elevated. However, aerosol number concentration in early morning was higher in the mixed layer than in the residual layer. The aerosol particles were abundant and overwhelmingly distributed in the size range $<1 \mu m$, consistent with urban aerosol. The historic O_3 data from the MOZAIC project, together with our measurements, were used to investigate the

long-term changes in O₃ ~~profile~~vertical profiles in the lower troposphere over the NCP. The comparison of data from the 2014 summer campaign with those from MOZAIC suggests that the O₃ level over the north part of the NCP has experienced a strong positive increase, and the increase of the O₃ level seems to speed up after 2004, indicating rapidly strengthening photochemical pollution particularly in the last decade. Observations show that surface O₃ pollution in China's polluted regions, including the NCP, has become more severe ~~severer~~ in recent years in contrast with the apparent decreases of PM_{2.5} and primary gaseous pollutants. In view of this, more attention should be paid to O₃ concentration under the control of PM.

Data availability

The entire data set can be made available for scientific purposes upon request to the corresponding author.

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- 30

Table 1. The ascent and descent flight time (local time LT) and the max height.

Flight	Date	Ascent period	Hmax (m)	Descent period
1	June 29	10:18-10:36	1316	10:36-10:47
2	June 29	17:58-18:24	2498	18:24-18:38
3	July 1	6:34-6:55	2021	6:55-7:07
4	July 29	7:35-7:51	2430	7:51-8:04
5	July 31	5:53-6:18	2468	6:18-6:33
6	July 31	17:26-17:44	2676	17:44-18:02
7	August 2	15:17-15:29	2410	15:29-15:45

Table. 2. O₃ and aerosol number concentration calculated in method of particle extinction gradient (left of “”) and method of aerosol number concentration gradient (right of “”). O₃ concentration on the surface is obtained in the surface measurement program.

		<u>Early morning</u>		<u>Late morning</u>		<u>Afternoon</u>	
Surface	O ₃ (ppb)	Jul.1 (Flight 3)	Jul.29 (Flight 4)	Jul.31 (Flight 5)	Jun.29 (Flight 1)	Jun.29 (Flight 2)	Jul.31 (Flight 6) Aug.2 (Flight 7)
		6:34-7:07	7:35-8:04	5:53-6:33	10:18-10:47	17:58-18:38	15:17-15:45
Mixed layer	O ₃ (ppb)	20.8±0.7	39.7±0.81	29.6±2.5	73.7±1.7	97.8±0.98	87.1±1.43
	Height(m)	::/200	255/275	255/267	360/281	795/525	795/::
	O ₃ (ppb)	::/37.4±20.8	44.3±8.5/44.3±8.5	70.5±38.6/72.4±38.2	71.2±9.0/69.1±9.6	106.7±7.9/103.2±9.2	99.1±5.4/::
	N (10 ³ p/cm ³)	::/1.99±0.36	8.7±0.12/8.69±0.13	5.73±2.00/5.73±2.00	4.17±0.75/4.54±0.75	6.28±0.17/6.39±0.10	::/::
Residual layer	Height(m)	1215/1331	::/1770	1110/1577	840/974	::/::	::/::
	O ₃ (ppb)	103.4±12.4/105.1±8.24	::/111±10.7	97±9.23/99.6±8.9	66.5±6.1/65.8±8.5	::/::	::/::
	N (10 ³ p/cm ³)	1.17±0.18/1.12±0.16	::/6.77±0.52	5.45±0.48/5.38±0.47	2.57±0.08/2.64±0.25	::/::	::/::

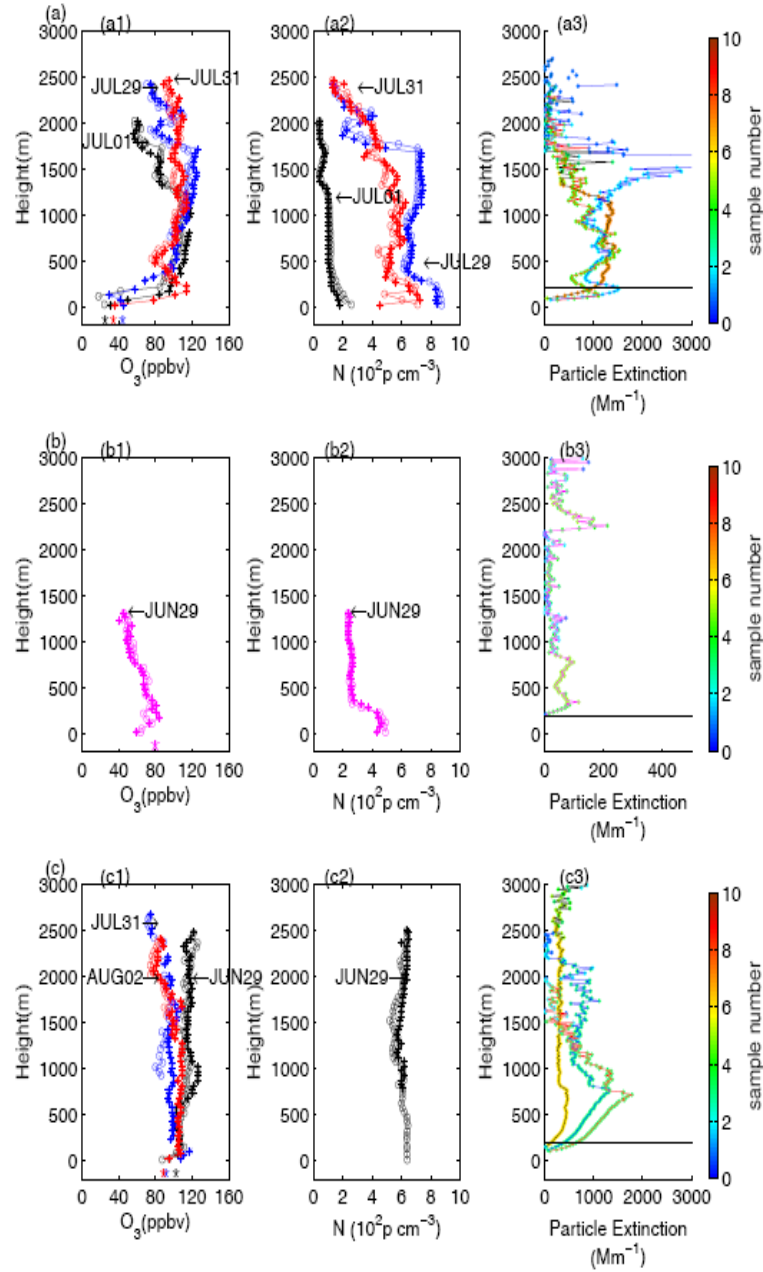


Figure 1. ProfileVertical profiles of O_3 (a1,b1,c1), aerosol number concentration (a2,b2,c2) and particle extinction (a3,b3,c3) obtained in (a) early morning, (b) late morning, and (c) the afternoon, respectively. The O_3 and aerosol profilevertical profiles obtained during the ascent and descent of the UAV are indicated with circles and asterisks, respectively. Ground-level O_3 mixing ratios during the flights are also shown together with the O_3 profilevertical profiles (bigger asterisks with a negative offset in altitude). The color scales attached to particle extinction graphs (c1, c2, c3) show the sample numbers of individual particle extinctions, from which the averages of particle extinctions were calculated. The black lines indicate the altitude of 200 m above ground, under which the particle extinction data should

not be used.

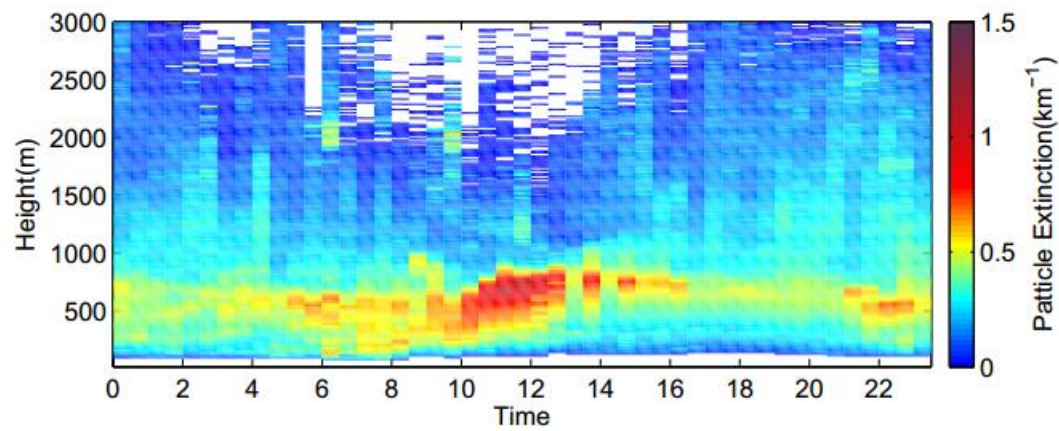


Figure 2. Average diurnal patterns of vertical distribution of particle extinction.

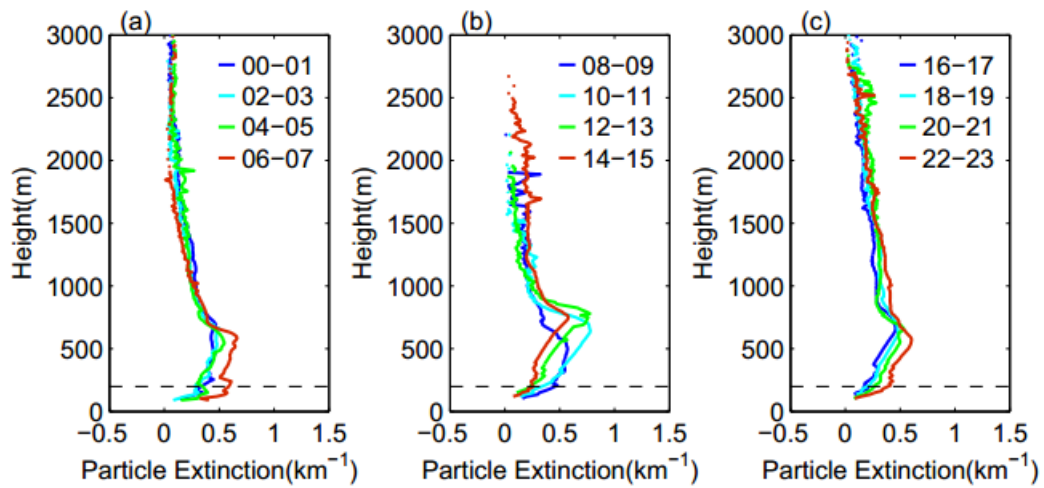


Figure 3. ~~Profile~~Vertical profiles of particle extinction averaged every two hours for (a) 0:00-7:00 LT, (b) 8:00-15:00 LT, and (c) 16:00-23:00 LT.

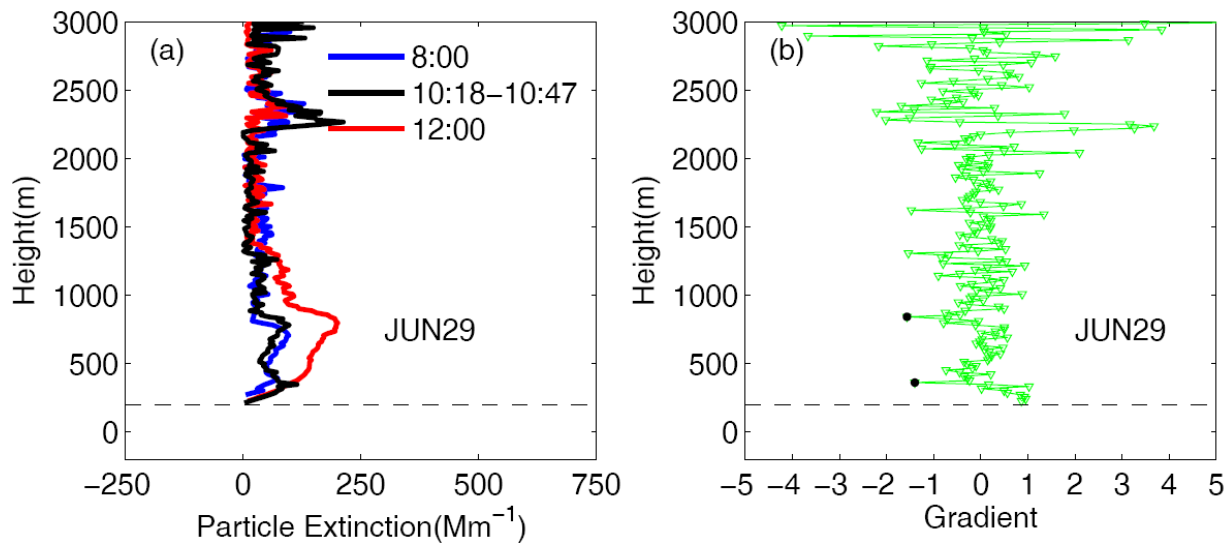


Figure 4. The ~~profile~~vertical profile of particle extinction observed during the flight in the late morning of June 29 (a) and its gradient (b) and the ~~profile~~vertical profiles of particle extinction before (blue) and after (red) the flight. The dashed lines indicate the lower limit of LIDAR.

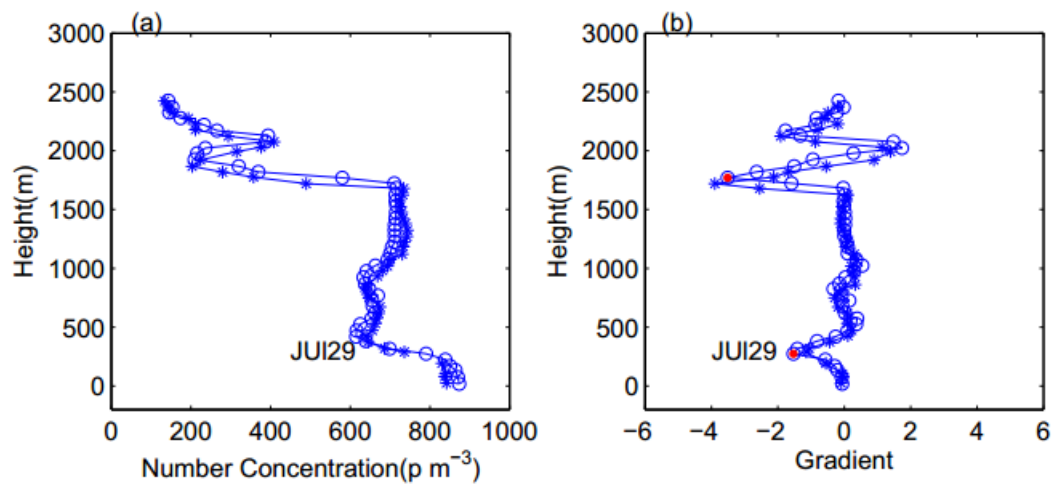


Figure 5. ~~Profile~~Vertical profiles of aerosol number concentration (a) and their gradients (b) from the ascent (open circles) and descent (asterisks) flight in the early morning of July 29 (Flight 4). The red solid circles indicate the tops of mixed layer and residual layer.

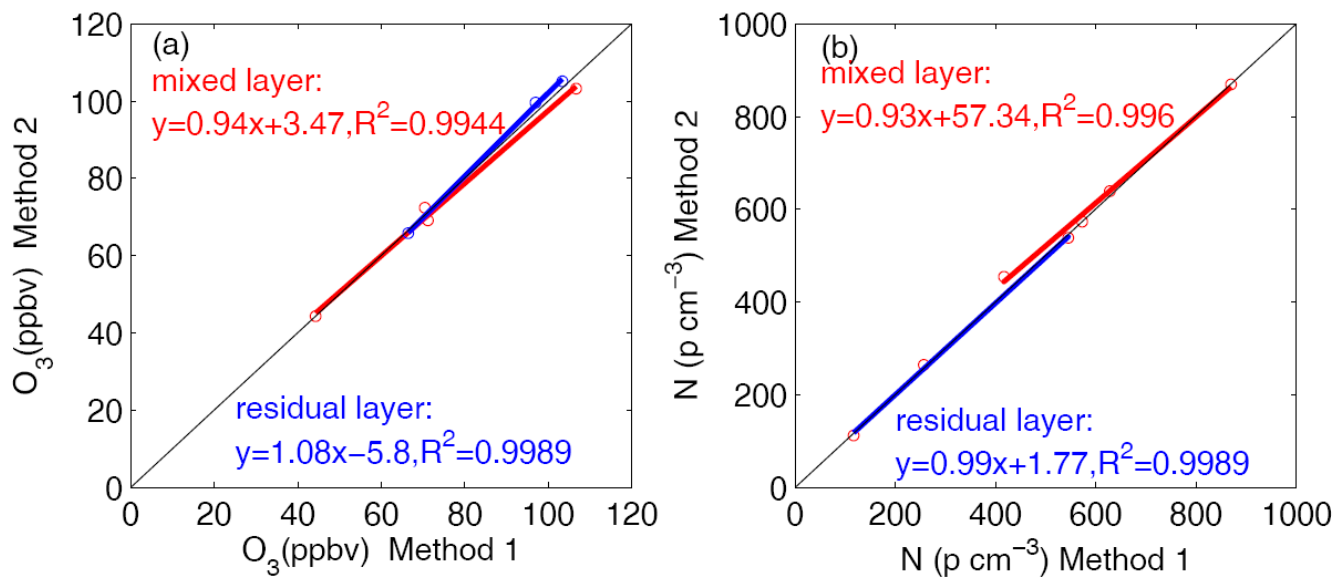


Figure 6. Average O_3 mixing ratios (a) and aerosol number concentrations (b) in the mixed layer and residual layer obtained using the method of particle extinction gradient (Method 1) in comparison with those obtained using the method of particle number concentration gradient (Method 2).

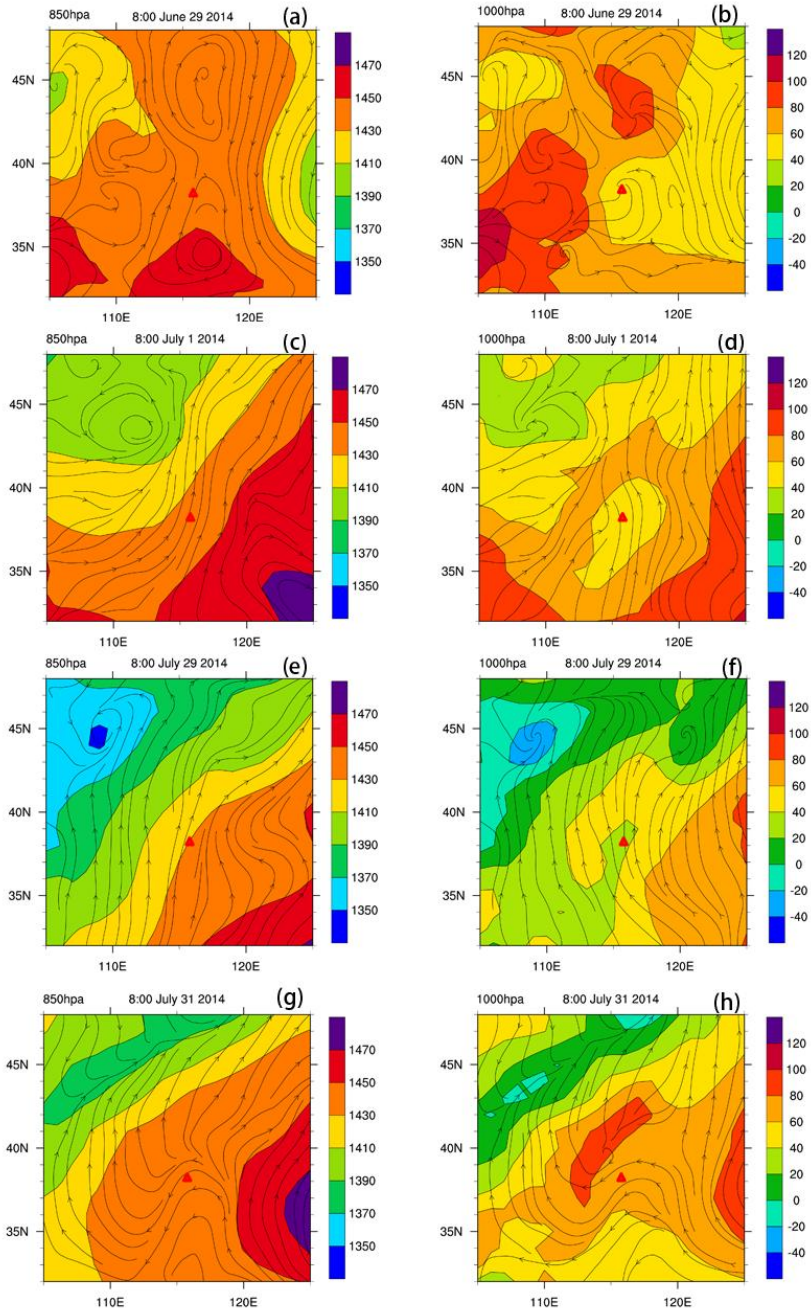


Figure 7. Geopotential heights (see color scale) and streamlines over the area surrounding RMS at 8:00 of June 29, 2014 at 850 hPa (a) and 1000 hPa (b); at 8:00 of July 1, 2014 at 850 hPa (c) and 1000 hPa (d); at 8:00 of July 29, 2014 at 850 hPa (e) and 1000 hPa (f); at 8:00 of July 31, 2014 at 850 hPa (g) and 1000 hPa (h). The reanalysis data from ECWME were used to make these plots.

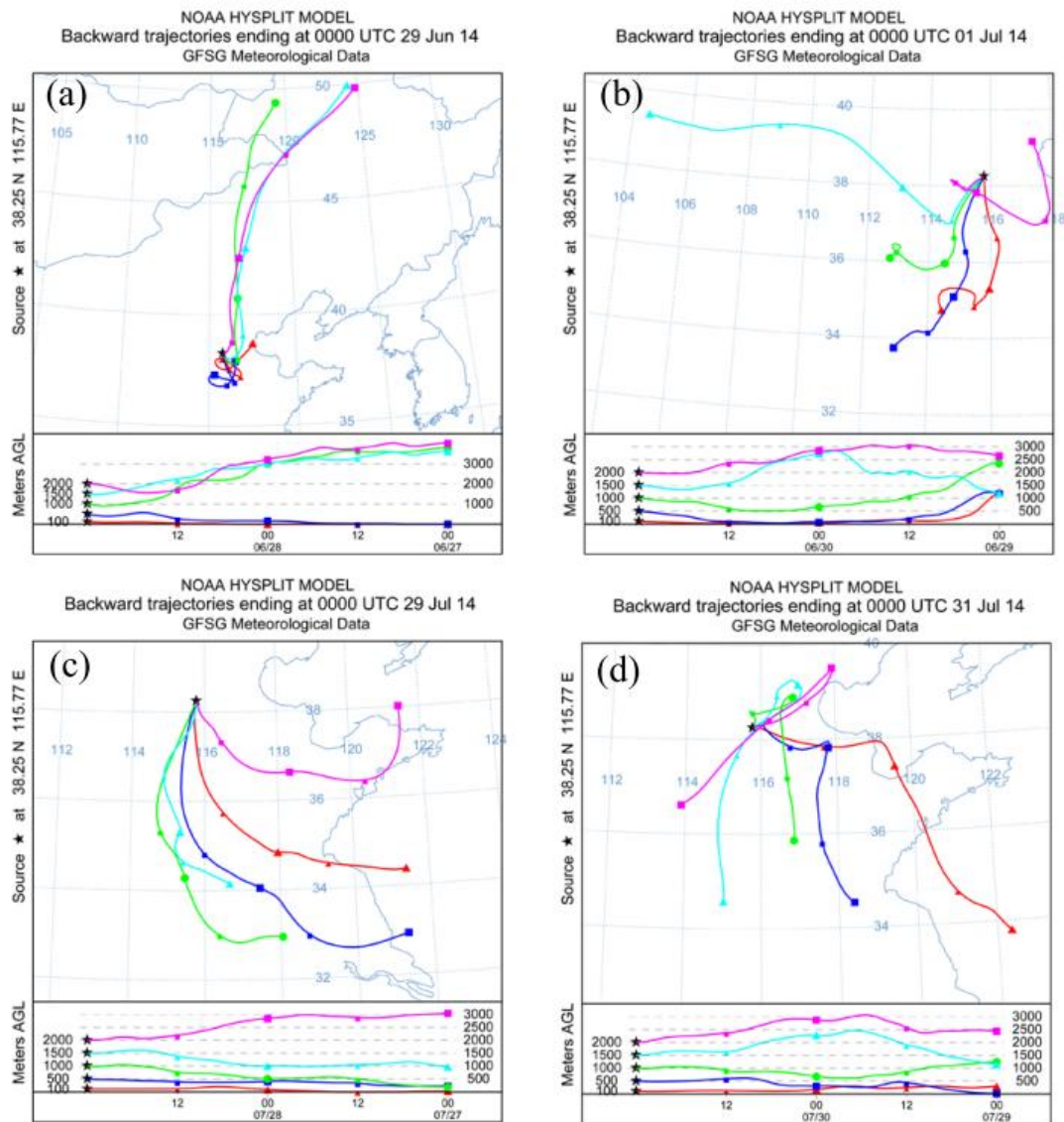


Figure 8. 48-h backward trajectories ending at 100 m, 500 m, 1000 m, 1500 m and 2000 m over RMS at 8:00 of June 29 (a), July 1 (b), July 29 (c) and July 31 (d), 2014.

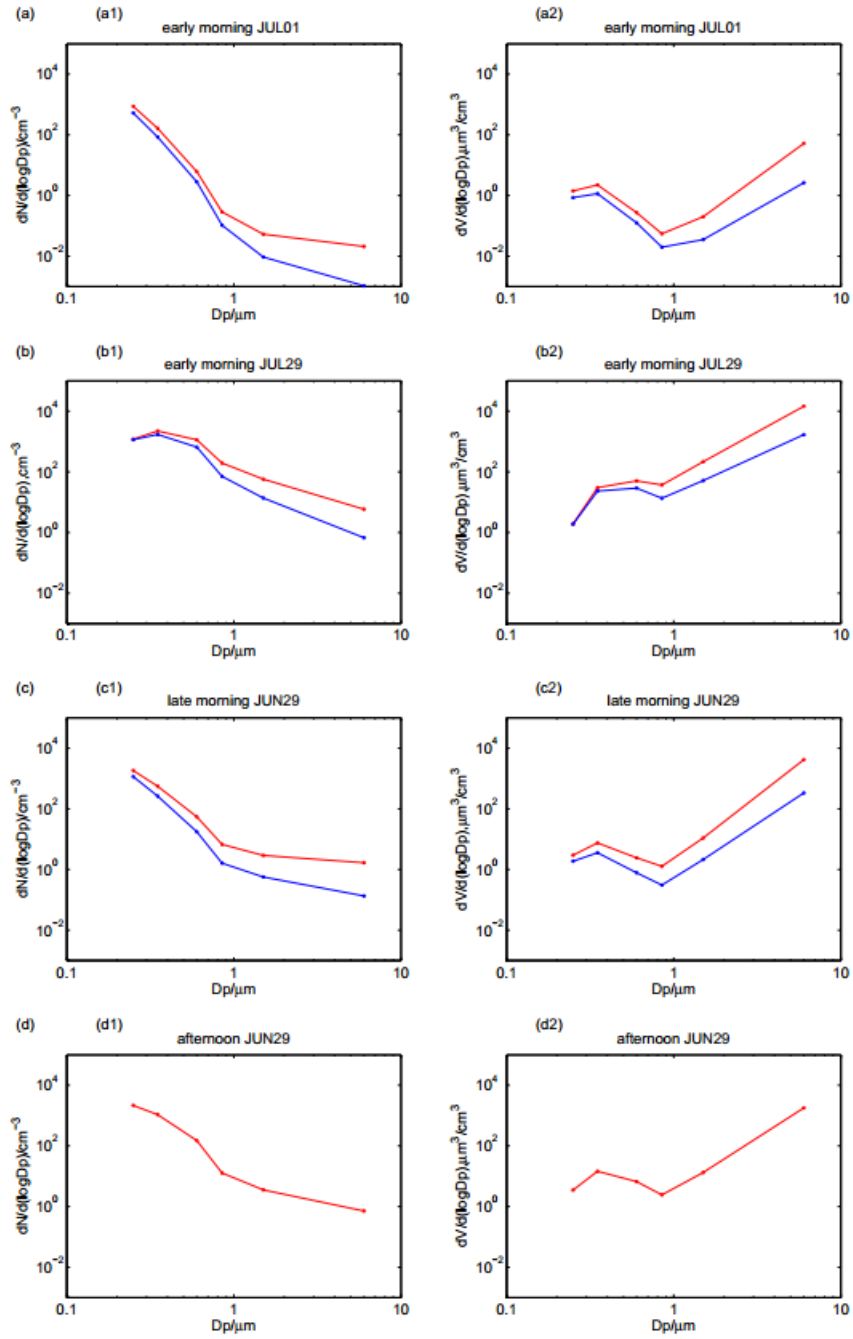


Figure 97. Aerosol number and volume size distributions in the mixed layer (red) and residual layer (blue), in the early morning of July 1 (a) and July 29 (b), late morning of June 29 (c) and afternoon of June 29 (d) flights. The mixed layer and residual layer heights are determined using the method of aerosol number concentration gradient.

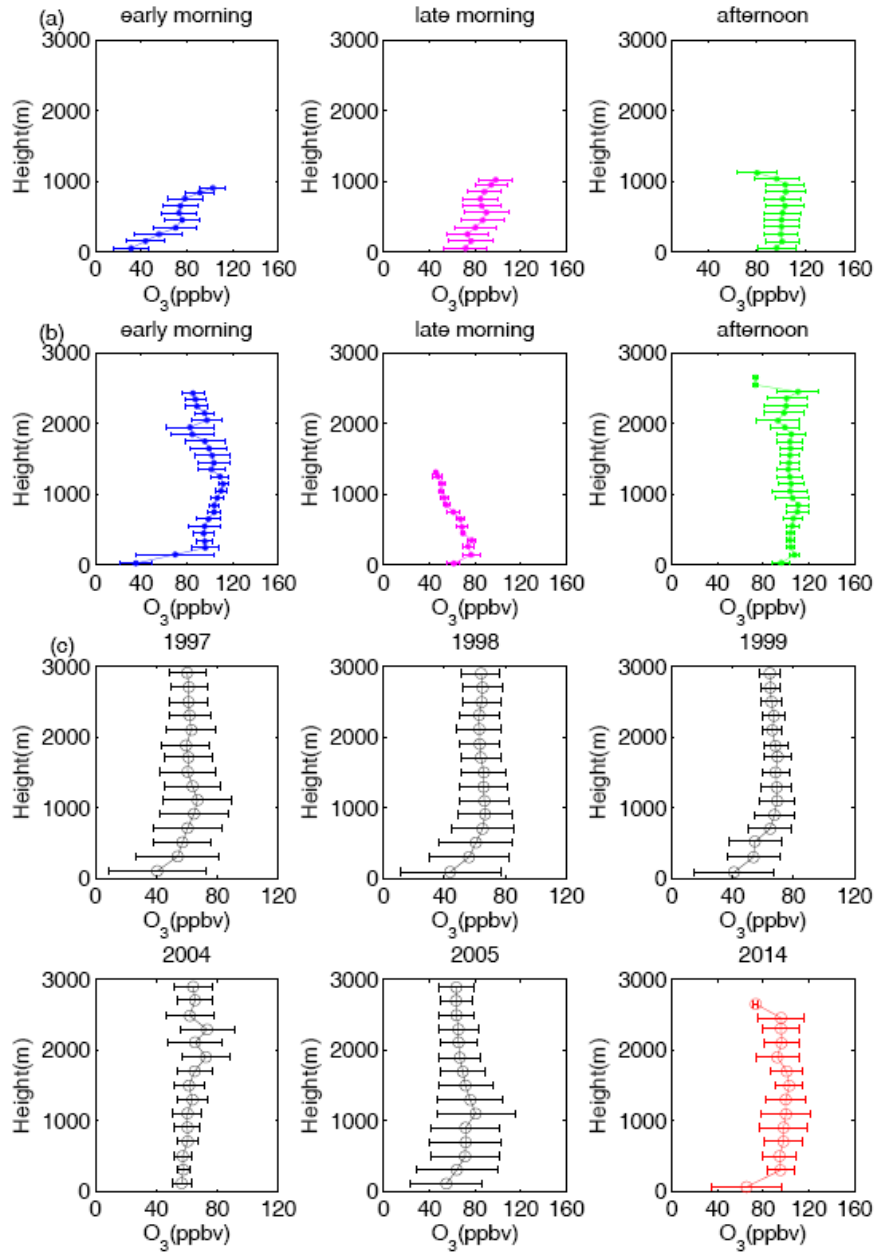


Figure 108. Comparison of average O_3 profilevertical profiles observed in the lower troposphere during summer of different years. (a) shows O_3 profilevertical profiles from the tethered balloon experiments during summer of 2014 averaged over early morning (5:00-8:00 LT), late morning (8:00-12:00 LT) and afternoon (12:00-19:00 LT). (b) presents O_3 profilevertical profiles from the UAV experiments during summer of 2014 averaged over early morning (Flights 3, 4 and 5), late morning (Flight 1) and afternoon (Flights 2, 6 and 7). (c) shows O_3 profilevertical profiles averaged over daytime (5:00-19:00 LT) MOZAIC measurements in summer of 1997, 1998, 1999, 2004, 2005 and our Raoyang measurement in summer of 2014. The error bars indicate one standard error of the mean.

Supplement of

Lower tropospheric distributions of O₃ and aerosol over Raoyang, a rural site in the North China Plain

Rui Wang et al.

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S1 Technical details of the UAV measurements

A newly delivered personal ozone monitor (POM, 2B Technologies, USA) was used in our UAV measurements of O₃ vertical profiles. The POM was calibrated in the factory just before delivery using a working standard (Model 205), which was calibrated against a transfer standard (TE 49i-PS, Thermo Electron, USA) traceable to the standard reference photometer
10 #0 (SRP 0) at the US National Institute of Standards and Technology (NIST). We did not calibrate the POM again. However, we confirmed its proper working at the site using an O₃ calibrator (TE 49i-PS, Thermo Electron, USA).

The optical particle counters (OPC) used in our UAV flights were calibrated by the manufacturer Lighthouse following the procedures in accordance with key standards for particle counters including ISO 21501 (<https://www.golighthouse.com/en/calibration-and-repairs>). The calibration is NIST-traceable. We did not compare the OPC
15 with other instruments at the site.

The sampling inlet that we used in the UAV measurements of aerosol is a stainless steel tube (300 mm, ID 5 mm) with a bullet-shaped head, which has a taper gas way (Figure S1). The sampling inlet was fixed at the front of the UAV nose, parallel to the inlet for airspeed measurement. The tip of the head has an ID of 2.1 mm. The OPC works at a flow rate of 2.83 l/min. These conditions cause an air velocity of about 14 m/s at the tip of the inlet head, which is close to the cruising speed
20 of the UAV (22 m/s). This design of sampling inlet made sure that the aerosol number concentrations were measured under a nearly isokinetic condition. Since a battery-powered UAV was used, there was no interference from engine.

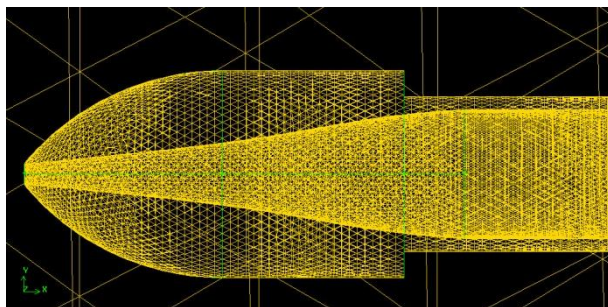


Figure S1. Schematic of the head of the sampling inlet used in the UAV measurements of aerosol.

S2 Airflow fields and air-mass backward trajectories

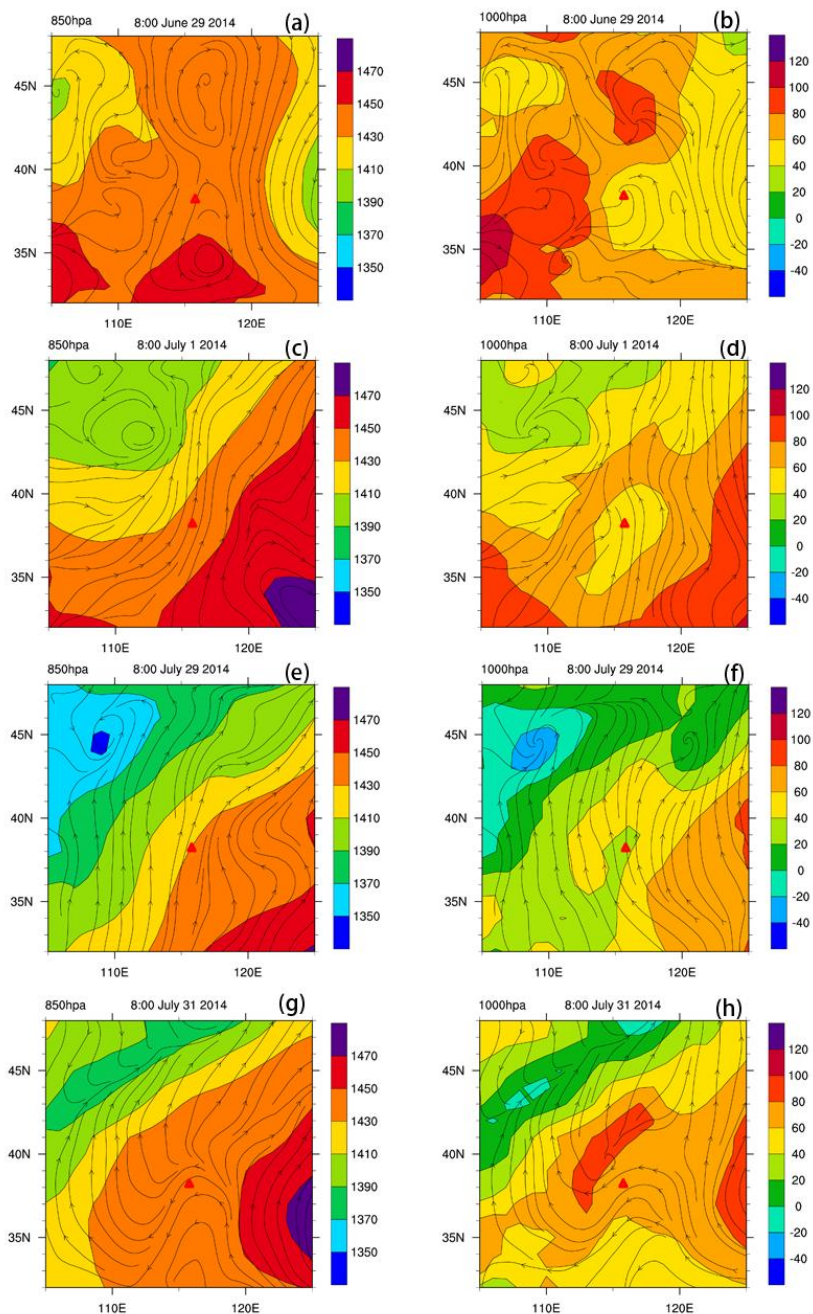


Figure S2. Geopotential heights (see color scale) and streamlines over the area surrounding Raoyang at 8:00 of June 29, 2014 at 850 hPa (a) and 1000 hPa (b); at 8:00 of July 1, 2014 at 850 hPa (c) and 1000 hPa (d); at 8:00 of July 29, 2014 at 850 hPa (e) and 1000 hPa (f); at 8:00 of July 31, 2014 at 850 hPa (g) and 1000 hPa (h). The reanalysis data from ECWMF were used to make these plots.

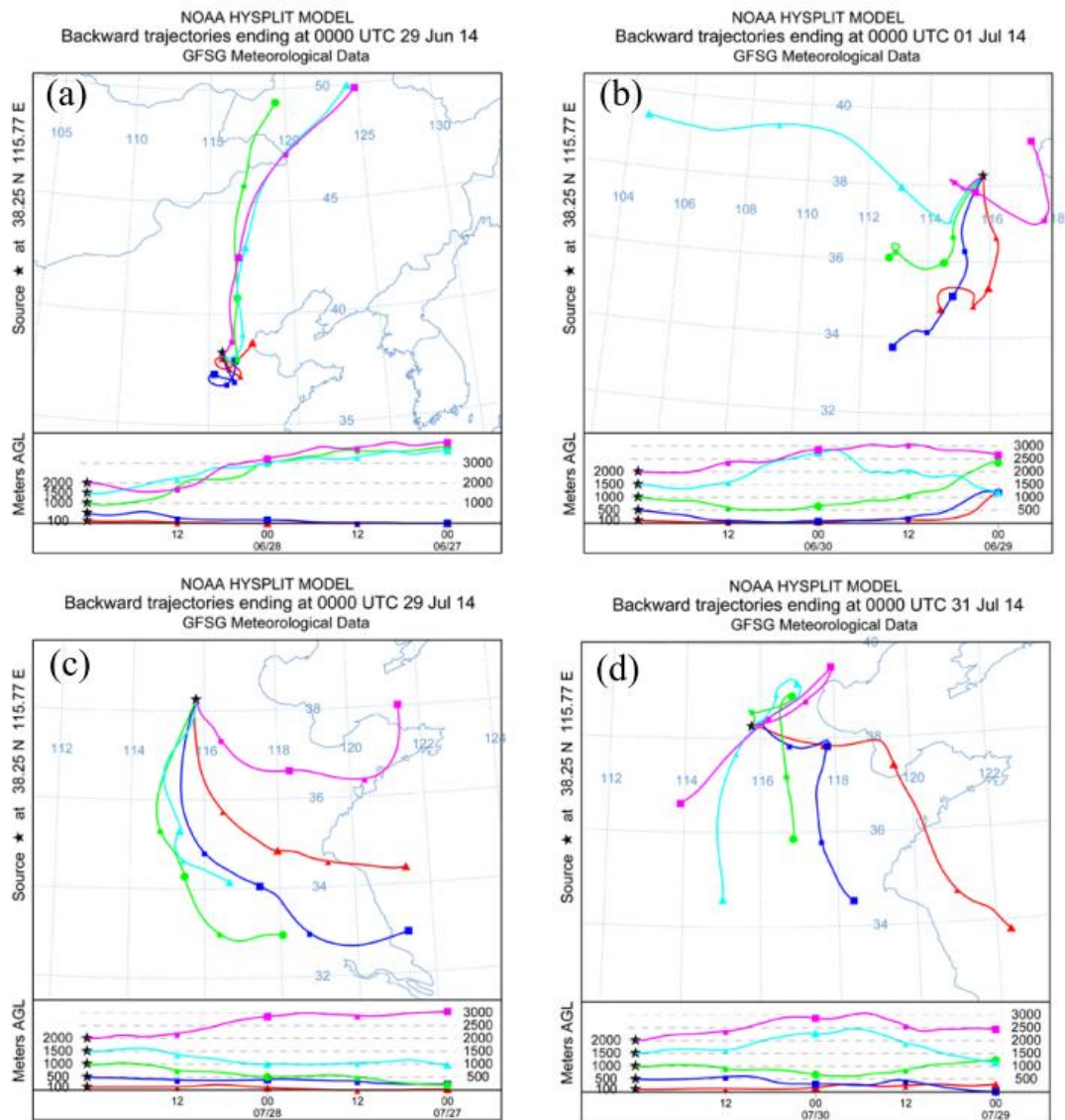


Figure S3. 48-h backward trajectories ending at 100 m, 500 m, 1000 m, 1500 m and 2000 m over Raoyang at 8:00 of June 29 (a), July 1 (b), July 29 (c) and July 31 (d), 2014.

S3 Average diurnal variations of O₃ and NO

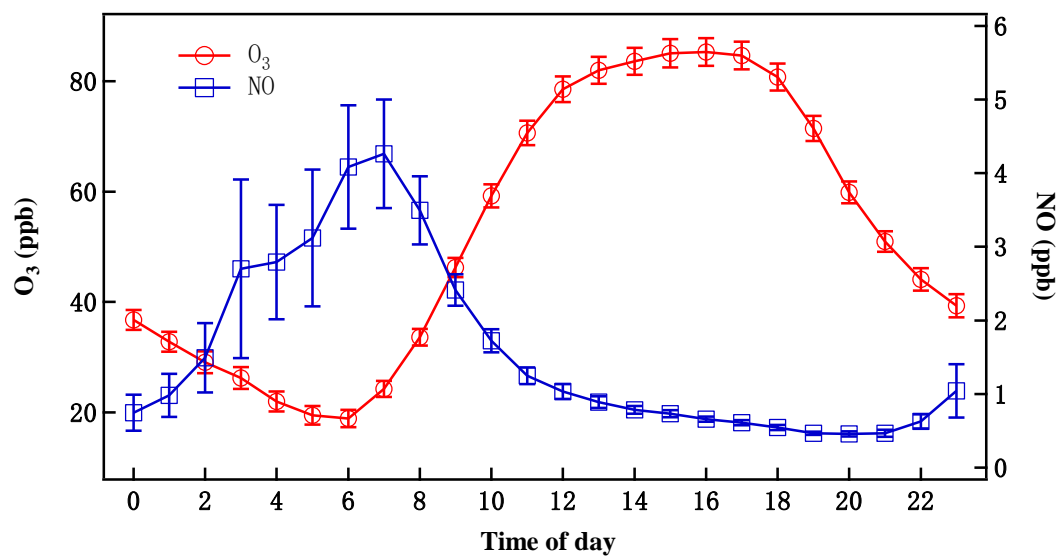


Figure S4. Average diurnal variations of surface O₃ and NO at Raoyang during the campaign in June-August 2014. The error bars represent one standard error of the mean.

Lower tropospheric distributions of O₃ and aerosol over Raoyang, a rural site in the North China Plain

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Abstract. The North China Plain (NCP) has become one of the most polluted regions in China, with the rapid increasing economic growth in the past decades. High concentrations of ambient O₃ and aerosol have been observed at urban as well as rural sites in the NCP. Most of the in situ observations of air pollutants have been conducted near the ground so that current knowledge about the vertical distributions of tropospheric O₃ and aerosol over the NCP region is still limited. In this study, vertical profiles of O₃ and size-resolved aerosol concentrations below 2.5 km were measured in summer 2014 over a rural site in the NCP using an unmanned aerial vehicle (UAV) equipped with miniature analyzers. In addition, vertical profiles of aerosol scattering property in the lower troposphere and vertical profiles of O₃ below 1 km were also observed at the site using a LIDAR and tethered balloon, respectively. The depths of the mixed layer and residual layer were determined according the vertical gradients of LIDAR particle extinction and aerosol number concentration. Average O₃ and size-resolved aerosol number concentration in both the mixed and residual layer were obtained from the data observed in seven UAV flights. The results show that during most of the flights the O₃ levels above the top of mixed layer were higher than those below. Such positive gradient in vertical distribution of O₃ makes the residual layer an important source of O₃ in the mixed layer, particularly during morning when the top of mixed layer is rapidly elevated. In contrast to O₃, aerosol number concentration was normally higher in the mixed layer than in the residual layer, particularly in early morning. Aerosol particles were overwhelmingly distributed in the size range <1 μm, showing slight differences between the mixed and residual layers. Our measurements confirm that in the lower troposphere over the rural area of the NCP is largely impacted by anthropogenic pollutants locally emitted or transported from urban areas. Compared with the historic O₃ vertical profiles over Beijing from the Measurement of Ozone and Water Vapor by Airbus In-Service Aircraft (MOZAIC), a strong increase in O₃ can be found at

all heights below 2.5 km in the decade from 2004 to 2014, with a largest enhancement of about 41.6 ppb. This indicates that the lower troposphere over the north part of the NCP has experienced rapid worsening photochemical pollution. This worsening trend in photochemical pollution deserves more attention in the future.

1 Introduction

5 Ozone (O_3) is a key trace gas and oxidant in the troposphere, which can generate hydroxyl radical (OH) that affects the oxidizing capacity of the atmosphere. Ground-level O_3 causes deleterious impacts on human health and vegetation (Anenberg et al., 2009; Mckee, 1994; Yue et al., 2014; Feng et al., 2008). Meanwhile, tropospheric O_3 is an effective greenhouse gas. The fifth IPCC assessment report points out that the increase of O_3 in the troposphere has caused $+0.40 (\pm 0.20) \text{ W m}^{-2}$ of radiative forcing (Myhre et al., 2013). The vertical distribution of O_3 can influence the accumulation of O_3 in the surface layer and
10 chemical reactions as well as radiation budget at different altitudes. The vertical distribution of O_3 is influenced by chemical and meteorological processes and varies with time and location (Kleinman et al., 1994; Fast et al., 1996; Lin et al., 2007; Ma et al., 2011). Therefore, direct measurements are needed to acquire the knowledge about the vertical distribution of O_3 , which is important to understanding atmospheric chemistry and O_3 radiative forcing.

Atmospheric aerosols influence the climate by direct effect and indirect effect (Schwartz, 1996; Coakley et al., 1983; Kiehl
15 and Briegleb, 1993; Charlson, et al., 1997; Tegen et al., 2000). High loading of aerosols causes poor visibility and air quality. The diameters of aerosol particles span over four orders of magnitude, from a few nanometers to around $100 \mu\text{m}$ (Seinfeld and Pandis, 2006). Aerosol size distribution is one of the most critical factors determining light scattering property, health effects, and lifetime of aerosols. Observations of aerosol size distribution and its spatiotemporal variations have been one of the important aspects in the study of atmospheric aerosols.

20 The planetary boundary layer (PBL) is the lowest part of the troposphere, which is influenced to a large extent by the friction of earth's surface and objects on it (Ahrens, 2011). The PBL is directly impacted by most of anthropogenic and natural sources of trace gases and aerosols. In the PBL, the air turbulence can be so strong that it drives the rapid exchange of heat, water vapor, trace gases and aerosols between the atmosphere and earth's surface. The structure of the PBL is critical to the vertical

diffusion and transport of air pollutants so that the changes of vertical distributions of many trace gases (such as O₃) and aerosols are closely related to the evolution of the PBL.

The diurnal evolution of the PBL usually leads to a well-developed mixed layer in the daytime (He and Mao, 2005) and a stable layer overlaid by a residual layer in the nighttime. The formation of nocturnal stable layer may exert significant impacts on the concentrations of species in the surface layer. For example, surface O₃ is substantially removed during night by reactions with NO and some other species, and by dry deposition, particularly in urban areas during cold seasons (Lin et al., 2011). Following the development of the mixed layer on the next day, O₃ in the residual layer can be downward mixed, making a contribution to the enhancement of ground-level O₃ and even driving the photochemical processes (Aneja et al., 2000; Kleinman et al., 1994; Neu et al., 1994; Zhang et al., 1999). Therefore, the O₃ distribution in both mixed layer and residual layer deserves attention. Similarly, chemical compositions and physical properties including size distribution of aerosols may also be impacted by the evolution of PBL. Knowledge of this aspect is important for atmospheric chemistry and physics studies.

In recent decades, with the rapid economic development and the urbanization in China, ground-level and tropospheric O₃ and aerosol have increased significantly, especially in the North China Plain (NCP) (Ding et al., 2008; Xu and Lin, 2011; Ma et al., 2016; Chen et al., 2015; Ding and Liu, 2014). So far, observational studies on O₃ and aerosol in the NCP have been mainly conducted in the surface layer. There is only limited knowledge of the vertical distributions of tropospheric O₃ and aerosol over the NCP region, gained in some sporadic observational studies (Chen et al., 2009; Chen et al., 2013; Ma et al., 2011; Wang et al., 2012; Zheng et al., 2005). This hinders extensive validations of atmospheric chemistry models as well as the assessment of climate effects of O₃ and aerosols over this important region.

The detection of vertical distributions of O₃ and aerosol can be made using balloon sounding, aircraft, and tethered balloon. Each of the techniques has its advantages and disadvantages. Balloon sounding is a good way of obtaining O₃ and aerosol vertical profiles below about 30 km, but the sondes for O₃ and aerosol are usually expensive and not reusable, not to mention ground facilities needed for the sounding. Tethered balloon attached with O₃ and aerosol devices can be used for many times of observations under stable weather conditions, but it is usually not suitable to be operated above 1 km and needs manpower to run it carefully. Aircraft equipped with analyzers for O₃, other trace gases and aerosol instruments can be used to

simultaneously obtain distributions of these species along the flight tracks, but such observation is normally expensive and needs strong logistic supports of airport.

Typically, most aircraft measurements are made using manned aircrafts. However, unmanned aerial vehicles (UAVs) can also be used as research platforms. In the last decade, UAVs have been successfully used in the fields of atmosphere science and environment monitoring in order to understand the three-dimensional distribution of atmospheric species (Altstdter, et al., 2015; Illingworth et al., 2014; Watai et al., 2006; Rauneker and Lischeid, 2012; Gao et al., 2016). In comparison with manned aircrafts, UAVs have a few advantages, such as no need for airport, lower costs, higher flexibility, the possibility to investigate atmospheric parameters at small scales and low altitudes and the potential for application in regions dangerous for manned aircraft (Altstdter, et al., 2015). Above all, measurements with high spatial resolutions can be obtained using UAVs. For example, in a city center with a diameter of approximately 2 km, a typical instrument with 1 Hz resolution would only be able to make approximately 20 measurements during an overpass of the city when a normal atmospheric research aircraft was used. In contrast, more measurements would be obtained by an UAV so that the measurement uncertainty can be effectively reduced.

In this paper, we present UAV measurements of vertical distributions of O_3 and size-resolved aerosol number concentrations obtained over a site in the NCP during a field campaign. Data of surface O_3 and LIDAR observations of aerosol extinction from a nearby site are included in the analysis to facilitate interpretations and discussions of the measurements. To the best of our knowledge, there has been no similar published study from China.

2 Experimental

2.1 Ground-based measurements

Ground-based measurements, including measurements of surface O_3 and some other reactive gases ($NO/NO_2/NO_x$, NO_y , $HCHO$, PAN , SO_2 , CO , NH_3 , etc.), tethered balloon measurements of O_3 and black carbon (BC) vertical profiles, LIDAR observation of aerosol vertical profiles, etc., were conducted from 7 June to 18 August 2014 at the Raoyang Meteorological Station (RMS, $115^\circ44'N$, $38^\circ14'N$, 20m, a semirural site) in the NCP. RMS is located in Raoyang County, an agriculture county in the middle of Heibei Province. There are no large industrial sources in Raoyang. However, some influences on the

RMS site from the residence and traffic sources in the surrounding areas cannot be excluded. More details about the RMS site are given in Ran et al. (2016).

Surface O₃ was measured using a photometric O₃ analyzer (TE 49C, Thermo Electron, USA). The detection limit and precision of the O₃ analyzer are 1 ppb and 1 ppb, respectively. The analyzer was calibrated on 17 June, 16 July and 18 August, 2014 and showed no significant drifts. Details about the calibration and maintenance are described in Lin et al. (2009). A dual beam ozone monitor (Model-205, 2B Technologies, USA) was used for the tethered balloon observations of O₃ vertical profiles. The ozone monitor has dimensions of 9 × 21 × 29 cm and weighs only 2.3 kg. It works based on the UV absorption at 254 nm at a maximum frequency of 0.5 Hz. It measures O₃ with a precision of 1 ppb or 2% of reading and has a limit of detection of 1 ppb. The ozone monitor was calibrated at the site using an O₃ calibrator (TE 49i-PS, Thermo Electron, USA).

Vertical profiles of aerosol were observed using a LIDAR (Leosphere, France). The LIDAR principle is based on the scattering phenomenon of light. A laser pulse is sent into the atmosphere and scattered by the target molecules or particles (clouds, dust, soot particles etc.). The backscattered light is collected by an optical system and its intensity is measured by a photo-detector, converted into an electronics signal and stored onto a computer. The wavelength of the laser sent is 355 nm. The vertical resolution of the LIDAR measurements is 15m and data below 200 m are discarded (EZ Aerosol and cloud LIDAR user manual).

2.2 Flight information

An UAV platform was used for the vertical profile measurements. The body of the UAV is made of glass fiber reinforced plastics, with a wingspan of 3.2 m. The UAV is battery-powered so that there is no contaminant from the engine exhaust of the UAV. The cruising speed and maximum cruising altitude of the UAV are 25 m/s and 5.5 km, respectively. As we were more interested in the vertical distributions of O₃ and aerosol in the lower troposphere, the UAV was programmed to fly below 3 km over an area within 5 km in diameter.

A miniature ozone monitor, personal ozone monitor (POM, 2B Technologies, USA) and handheld optical particle counter (OPC) (Handheld 2016 or 3016, Lighthouse, USA) were installed in the small cabinet of the UAV to measure the O₃ and aerosol number concentrations on the flight. The POM has dimensions of 10.2 x 7.6 x 3.8 cm and weighs only 0.34 kg. It works

based on the UV absorption at 254 nm at a maximum frequency of 0.1 Hz. It measures O_3 with a precision of 2 ppb or 2% and has a limit of detection of 4 ppb, well below the normal O_3 level over the Raoyang site. The POM was calibrated in the factory against a NIST-traceable standard instrument and compared at the site with the TE 49i-PS O_3 calibrator. The handheld OPC has dimensions of 22.23 x 12.7 x 6.35 cm and weighs about 1 kg. The Handheld 2016 counts aerosol numbers in the size-bins 0.2-0.3 μ m, 0.3-0.5 μ m, 0.5-0.7 μ m, 0.7-1.0 μ m, 1.0-2.0 μ m and >2 μ m, while the Handheld 3016 (used only in the flight during 5:53-6:18 of July 31) records aerosol numbers in the size-bins 0.3-0.5 μ m, 0.5-1.0 μ m, 1.0-3.0 μ m, 3.0-5.0 μ m, 5.0-10.0 μ m and >10 μ m in differential or accumulation method. The OPC devices were set to collect data at 1 Hz. An isokinetic tube was mounted on the nose of the UAV to introduce ambient air into the OPC. In addition, a temperature/humidity sensor was attached to the OPC so that the sampling flow rate was converted to standard condition. Both OPC devices were calibrated against a NIST-traceable source. More details are given in the supplement (section S1).

Limited mainly by the availability of airspace, only seven successful UAV measurements were conducted several kilometers west of the RMS during the observation period. More detailed flight information is summarized in Table 1.

3 Results and discussion

3.1 Vertical profiles of O_3 , aerosol number concentration and extinction

The vertical profiles of O_3 were acquired during seven UAV flights as listed in Table 1, while aerosol number concentrations in six size-bins were observed during five of the seven flights (Flights 1-5). The observed aerosols particles were predominately distributed in the accumulation mode since it is not possible to count the aerosol numbers in the Atkin mode using the handheld OPC. Figure 1 shows the vertical profiles of O_3 and aerosol number concentration observed during all flights. To study how the evolution of PBL influences O_3 and aerosol concentration at different altitudes, the vertical profiles in Fig.1 are grouped in early morning (5:40-8:00 LT), late morning (10:00-12:00 LT) and afternoon (15:00-19:00 LT) periods and shown in Figs. 1(a), 1(b) and 1(c), respectively. In addition, average particle extinction vertical profiles simultaneously obtained by the LIDAR are presented, with data points less than or equal to zero being excluded. All the vertical profiles shown in Fig. 1 include averages over 50 m vertical layers, regardless of the spatial resolutions of actual observations. Although the site over which the flights

were conducted is several kilometers away from the RMS, both sites were influenced by the same synoptic system. Therefore, the results (Fig.1) from both sites should be comparable within the observation uncertainties. In the early morning of July 29, 2014, particle extinction of more than 3000 Mm^{-1} was observed at around 1600 m (Fig. 1(a3)), indicating the presence of cloud there (Huang et al., 2011).

5 It is noteworthy in Fig. 1 that aerosol number concentrations during late morning of June 29 (Flights 1) and early morning of July 1 (Flight 3) and the O_3 mixing ratio during late morning of June 29 (Flight 1) were significantly lower than those during other flights, and their vertical profiles were slightly different from others. This indicates that some factors might have impacted the levels and vertical profiles of O_3 and aerosol. To understand those phenomena, we display the airflow fields at 1000 hPa and 850 hPa over the area surrounding RMS in Fig. S2 in the supplement and 48-h backward trajectories of air parcels arriving at 100 m, 500 m, 1000 m, 1500 m and 2000m over RMS in Fig. S3 in the supplement for 8:00 local
10 time of June 29, July 1, July 29 and July 31, 2014, calculated using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Draxler and Rolph, 2003).

Figures S2(a) and S2(b) indicate that the 1000 hPa and 850 hPa levels on early morning of June 29 were dominated by different air circulations. Figure S3(a) shows that the air parcels arriving at 100 m and 500 m over RMS were from the
15 boundary layer over the nearby areas and mainly from south of the site, while those arriving at 1000 m and above originated far from the north (northern Heilongjiang) and travelled rapidly over 2000 m for most of the time. The disparate airflows in the bottom and upper layers made a large negative gradient in the vertical distributions of O_3 and aerosol number concentration during Flight 1, as can be seen in the vertical profiles shown in Figs. 1(b1) and 1(b2).

In the whole layer, the aerosol number concentration in the early morning of July 1 (Flight 3) was much lower than those in
20 the other two flights (Flight 4 and 5) in the early morning of July 29 and July 31 (Fig. 1(a2)). Figures S2(c) and S2(d) in the supplement show that the airflow at the 1000 hPa and 850 hPa levels over RMS was mostly from the south-southwest. Figure S3(b) in the supplement indicates that air parcels arriving at different heights over RMS originated either from south or from west or east bending to south. Using the Meteorological Information Comprehensive Analysis and Process System (MICAPS, <http://www.cma.gov.cn/en2014/20150311/20160615/index.html>) we found that there was rainfall within the 48 hours prior to
25 5:00 LT of July 1 over the north, south by southwest and the southeast of RMS. It can be inferred that in the early morning of

July 1 air transported to the lower troposphere over RMS had been mixed with cleaner air during the rainy conditions so that the aerosol number concentration declined substantially. Therefore, synoptic situations are important factors influencing the concentrations of air pollutants and their vertical distributions. Another important factor is the PBL evolution, as discussed in the next section.

5 3.2 Determination of the mixed and residual layer depth

The PBL development can, in principle, be determined by measurement of vertical profiles of a variety of atmospheric properties, with potential temperature being the most common one (Lenschow, 1986). Vertical aerosol number concentration vertical profiles allow the determination of the PBL, as aerosol acts as a tracer of atmospheric turbulent forces along height (Ferrero et al., 2011, 2014). One powerful way to probe the PBL is based on vertical profiles of particle extinction detected using LIDAR. There are several methods to explore the structure of PBL from vertical profiles of particle extinction, such as the calculation of vertical gradient of particle extinction (He and Mao, 2005; Huang et al, 2011; Hayden et al., 1994; Hoff et al., 1996; Melfi et al., 1985), wavelet analysis (Cohn et al., 1997; Brooks et al., 2003), and parameterization (Steyn et al., 1999). In this study, calculations of the vertical gradient of LIDAR particle extinction (dE/dz) and particle number concentration (dN/dz) are adopted to identify the mixed layer depth (MLD) and residual layer depth (RLD).

To obtain a general picture of the diurnal PBL evolution, particle extinction values at different heights in the lower troposphere (0-3 km) were averaged for different time intervals on all sunny days during the campaign. The average vertical profiles in a half hour and two hour intervals are displayed in Figs. 2 and 3, respectively. The zero and negative values in the LIDAR measurements were excluded, which may lead to averages slightly overestimated. Averages with less than 75% data availability were rejected to avoid the impact of under-sampling on the average vertical profiles. As mentioned in section 1, the PBL experiences a diurnal cycle. The mixed layer develops after the sunrise. Its top rises continually up and may exceed the top of the residual layer formed on the previous day. After the sunset, the mixed layer collapses gradually, forming the nocturnal stable layer and residual layer.

Figures 2 and 3 clearly show the average PBL diurnal cycle of vertical distribution of particle extinction. According to the solar elevation angles, the sunrise and sunset time is estimated to be 5:00-6:00 LT and 19:00-20:00 LT, respectively. In Fig. 3,

the maximum of particle extinction was 0.53 km^{-1} at 660 m after the sunset and the top of residual layer was about 705 m. Moreover, the nocturnal stable layer started forming, reaching a depth of about 300 m at 0:00-1:00 LT on the next day (Fig. 3(a)). During the night, the top of average residual layer fluctuated slightly around 700 m. After sunrise on the next day, the nocturnal stable layer disappeared gradually, and the mixed layer developed. The top of mixed layer reached about 840 m at around 11:00 LT and stayed until 13:00 LT, when it started declining. The particle extinction in the mixed layer increased during the morning period, presumably because of the increasing aerosol emissions, downward mixing from the residual layer, and photochemical production from precursor gases.

The data shown in Figs. 2 and 3 are consistent with our understanding of the diurnal PBL evolution, suggesting that LIDAR data captured the structure of PBL and can be used in the determination of the MLD and RLD. Based on individual dE/dz vertical profiles of particle extinction, we can determine the tops of the mixed layer and residual layer for the periods with UAV flights by identifying the minima below 2000 m in the dE/dz vertical profiles if there were no obviously unreasonable values in the vertical profiles due to interferences or noise. In order to select the minima that were really resulted from a strong decrease of aerosol burden for a small height change rather than abnormal variation, we compared the minima before and after the flights with those during the flights. Finally, the MLD and RLD were obtained according to the heights at which the minima were considered to be the most reasonable ones. However, this method was not applicable when the MLD was in the blind zone of LIDAR (lower than 200m) or there was cloud near the top of residual layer.

The vertical profile of particle extinction and its gradient for the flight (10:18-10:47 LT) in the late morning of June 29 (Flight 1) are displayed in Fig. 4 to show how to determine the MLD and RLD. To facilitate the identification of the mixed layer and residual layer, the vertical profiles of particle extinction before and after the flight are also shown in Fig. 4(a). With the consideration of turbulent time scale in the atmosphere, the particle extinction vertical profiles at 8:00 LT and 12:00 LT were calculated from the LIDAR observations in the periods 7:30-8:30 LT and 11:30-12:30 LT, respectively. As can be seen in Fig. 4(b), there are a few minima in the calculated gradient, two of which (marked with filled black circles) may represent the tops of the mixed layer and residual layer. Comparing the vertical profile of particle extinction during the flight with those before and after the flight, we can see gradual changes in heights of the inflection points in the lower parts of the vertical

profiles (0-1500 m) with the evolution of the PBL. This makes us more certain that the filled black circles in the gradient curve in Fig. 4(b) indicate the tops of the mixed layer and residual layer.

Similar to the vertical gradient of particle extinction, the vertical gradient of aerosol number concentration can also be used to probe the PBL. To find out the key inflection points in the vertical profiles, which indicate the tops of the mixed layer and residual layer, we paid attention to the major structures in vertical profiles and gradients of aerosol number concentration during the ascent and descent flights. Due to the slight differences in time and space in the flight, there were some differences in particle number concentrations measured at the same height between the ascent and descent of a flight. Even though, the t-test ($\alpha=0.05$) may help to judge whether or not the results are accordant. As an example, Fig. 5 shows the aerosol number concentration data from a flight in the early morning of July 29 (Flight 4). The two minima at 275 m and 1770 m (marked with red solid circles) in the gradient curve (Fig. 5(b)) corresponds obviously the major inflection points in the vertical profile of ascent flight (Fig. 5(a)). In the gradient curve from the descent flight, there are also two minima below 2000 m. These two minima do not overlay those from the ascent flight, but there are no significant ($\alpha=0.05$) differences in the minimum positions between ascent and descent. Therefore, the marked heights 275 m and 1770 m are considered to be the tops of mixed layer and residual layer, respectively.

Determining the MLD and RLD facilitates the calculations of average O_3 and aerosol number concentrations in the mixed layer and the residual layer. Table 2 summarizes the mixed and residual layer heights, determined using the methods discussed above, and the calculated O_3 and aerosol number concentrations for the two layers during the flights. The MLD or RLD during some flights cannot be determined in the case that the MLD was in the blind zone of LIDAR (lower than 200m) or there was cloud near the top of residual layer. Ideally, the mixed and residual layer heights determined using the two methods were the same, so would be the average O_3 and aerosol number concentrations. However, the real conditions were not idealized. As can be seen in Table 2, the two methods produced different results of the MLD and RLD, and the average O_3 and aerosol number concentrations.

To see how the results from the two methods are different from each other, we conducted correlation analyses. In Fig. 6, average O_3 and aerosol number concentrations obtained using the method of particle extinction gradient (Method 1) are compared with those obtained using the method of particle number concentration gradient (Method 2). As can be seen in the

figure, the averages obtained using the two methods are highly significantly correlated. Linear regressions suggest that the slopes of correlation lines for average O_3 and aerosol number concentrations in the mixed layer and residual layer are all close to 1.0. In other words, the two methods used for the determination of the MLD and RLD are reliable and can produce comparable results.

5 3.3 Average O_3 and aerosol number concentrations in the mixed and residual layers

Data in Table 2 indicate that the mixed layer height increased from early morning to late morning and to afternoon. The top of residual layer did not show such tendency. The mixing ratio of O_3 in the surface layer and mixed layer was lowest in the early morning and highest in the afternoon. This can be readily explained by the changes in photochemical production, NO titration, and dry deposition of O_3 in the course of the day. Photochemical reactions often produce much more O_3 around noon than in the other period, while NO titration and dry deposition remove O_3 more effective during the night and early morning, when the NO level is higher and the mixed layer is shallower (see Fig. S4 in the supplement). In most cases, the diurnal cycle of surface O_3 can be well explained by these factors, if advection is negligible. However, there may be additional factors that contribute significantly to the diurnal variations of O_3 in the mixed layers, at least in our cases. Table 2 shows that the level of O_3 in the surface and mixed layers were lower than that in the residual layer during all early morning flights (Flights 3-5). Data from the flight in late morning of June 29 (Flight 1) indicate that the O_3 level in the residual layer was slightly lower than those in the surface and mixed layers. Fig. 1(c1) shows that O_3 vertical profiles were relatively straight and the O_3 levels in the surface and mixed layers were close to or slightly lower than those at the heights above the mixed layer. These suggest that during most of our flights the O_3 levels above the top of mixed layer were higher than those below. Similar vertical O_3 profiles were also observed over a site in Beijing by Ma et al. (2011).

20 The positive gradient in vertical distribution of O_3 makes the residual layer an important source of O_3 in the mixed layer, particularly during morning when the top of mixed layer is rapidly elevated. Therefore, downward mixing of O_3 in the residual layer over our site may play an important role in the diurnal cycle of O_3 at ground-level and in the mixed layer. Previous studies show that O_3 in the free troposphere over the NCP can be rapidly downward transported to the surface layer, driven by high wind speed in winter (Lin et al., 2011; Zhang et al., 2014a) or nighttime convection processes in summer (Jia et al., 2015). Our

data show that even under normal meteorological conditions in summer, downward mixing of O_3 at higher altitudes over the NCP can be a significant contributor to the O_3 level in the mixed layer. The physical processes that influence surface O_3 are normally considered in modern air quality models. It is of interest to test how well the models can simulate the impacts of these processes on surface O_3 . Our measurements provide valuable experimental data for validating model results and satellite

5 retrievals, which is out of scope of this paper.

In contrast to the O_3 level, aerosol number concentration in early morning was higher in the mixed layer than in the residual layer. This can be attributed to the fact that the major sources of primary and secondary aerosols are in the mixed layer. With the PBL development during the daytime aerosol particles are mixed within a deeper layer as can be seen in Fig. 2.

3.4 Aerosol number size distributions in the mixed layer and residual layer

10 The mass concentration, size distribution, and chemical composition of aerosol are closely related with emissions, atmospheric chemistry, and meteorological conditions. The formation of the mixed layer and residual layer reduces the vertical mixing and may cause some differences in the physico-chemical properties of aerosols between both layers. Here, we investigate the difference in aerosol number-size distribution between the mixed and residual layers, taking the advantage of clear separation of both layers. Aerosol number concentrations in different size-bins were averaged for the mixed and the residual layers

15 determined using aerosol number concentration gradients. Figure 7 shows the aerosol number and volume size distributions in the mixed layer and residual layer during early morning of July 1 (Flight 3), early morning of July 29 (Flight 4), late morning of June 29 (Flight 1) and afternoon of June 29 (Flight 2). The aerosol volume concentrations were calculated from the measured number size distributions under the assumption that all particles were spherical.

Obviously, the particle number concentration in the mixed layer was higher than that in the residual layer. This is expected

20 as the mixed layer is normally more impacted by emission sources, which are mainly within the mixed layer. On the other hand, the differences of aerosol number and volume concentration between the mixed layer and the residual layer were more significant in the size range $>2 \mu m$ in comparison with the other size ranges. This can be well explained by the fact that the mixed layer is much more influenced than residual layer by the ground-level emission of aerosol in coarse mode. Moreover, aerosol particles were overwhelmingly distributed in the size range $<1 \mu m$, independent of observation time. Such aerosol size

25 distribution and ranges of aerosol number concentrations unsurprisingly resembled urban aerosol (Baron et al., 2011).

Although some coarse particles may be released by the farm over which our UAV observations were conducted, their contribution to our measurements of aerosol number concentration should be limited within the surface layer, considering the wind conditions during the UAV flights. In other word, the aerosol size distributions at higher altitudes of the PBL were nearly not influenced by local coarse particle emissions. In recent decades, the NCP region has been found to be one of the most polluted regions of the world, suffering severe haze pollution (Fu et al., 2014). Even in the rural areas of the NCP, air quality is largely impacted by anthropogenic pollutants locally emitted or transported from urban areas (Lin et al., 2008; Lin et al., 2009; Liu et al., 2010). Therefore, aerosol size distributions shown in Fig. 7 should represent well mixed aerosol over a rural area in the NCP, which is dominated by fine particles.

It is interesting to see that the patterns of aerosol number and volume size distributions in Flight 4 (early morning in July 29) are different from those in Flights 1 (late morning in June 29), 2 (afternoon in June 29) and 3 (early morning in July 1). The number size distributions in Flights 1, 2 and 3 show monotonic decreasing with increasing aerosol size (Figs. 7(a), 7(c) and 7(d)), while those in Flight 4 peak in the range of 0.3-0.5 μm (Fig. 7(b)). The aerosol size distribution in the early morning of July 29 (Flight 4) was unique in that a larger portion of aerosol particles was found in the range 0.3-0.5 μm . It may be caused by different synoptic conditions. Figure 1 indicates that among all the vertical profiles, the vertical profiles from July 1 (Flight 3) and July 29 (Flight 4) represent most clean and most polluted cases, respectively. Backward trajectories (Fig. S3 in the supplement) indicate that in early morning of July 29, air masses were from the southeast sector. Studies at other NCP sites also show that air masses from southeast are associated with higher particle number concentration (Shen et al., 2011) and contain aerosols of relatively larger mean medium diameter (Zhang et al., 2014c), which coincide with our results.

3.5 Comparison with historic O₃ vertical profiles

The increase in emissions of air pollutants in the NCP region has caused haze and O₃ pollution in recent decades. Emission control measures that have been introduced in this region have led to a decrease trend after 2003 in the annual number of haze days (Fu et al., 2014). However, the O₃ air quality has not been improved yet. In contrast, the maximum daily average 8-h (MDA8) mixing ratios of O₃ at a background site in the NCP increased at a rate of 1.13 ppb/yr from 2003 to 2015 (Ma et al.,

2016). The increase of O_3 level has taken place not only at ground-level, but also at other altitudes in the troposphere, particularly in the PBL. Ding et al. (2008) revealed a strong positive trend of the O_3 level in the boundary layer over Beijing from 1995 to 2005 using the Measurements of Ozone and Water Vapor by Airbus In-Service Aircraft (MOZAIC). Multi-year ozonesonde measurements over Beijing also indicate a significant increase of tropospheric O_3 during the period 2002-2010 (Wang et al., 2012).

It is of great interest to see how lower tropospheric O_3 has changed over the NCP region. Many locations in the NCP region are controlled by similar prevailing winds (southwesterly and northeasterly), particularly in summer (Lin et al., 2008; Lin et al., 2009). Although the MOZAIC measurements and our UAV observations of O_3 were conducted over two sites about 200 km apart from each other, O_3 vertical profiles in the lower troposphere over both sites may represent the situations over the north part of the NCP. Therefore, it is assumed that the O_3 vertical profiles over both sites might be comparable. Under this assumption, we can try to obtain an idea about the change of summer O_3 in the lower troposphere over the NCP between the first MOZAIC measurements and our measurements.

Figure 8 displays average O_3 vertical profiles for different time period of the day in the lower troposphere obtained at RMS during our tethered balloon (Fig. 8(a)) and UAV observations (Fig. 8(b)) and summer daytime (5:00-19:00 LT) average O_3 vertical profiles from MOZAIC observations and our observations (Fig. 8(c)). The MOZAIC O_3 data have an estimated accuracy of $\pm[2 \text{ ppb}+2\%]$ for individual 4 s measurements and is suitable for building reliable O_3 climatologies (Thouret et al., 1998; Zbinden et al., 2013). MOZAIC O_3 vertical profile data for the greater Beijing area are available only for 1994-2005 with varying monthly vertical profile numbers and most of the vertical profiles were obtained during 5:00-18:00 LT period (Ding et al., 2008). To enhance the representativeness of average vertical profiles, all average MOZAIC O_3 vertical profiles were calculated from at least 7 individual vertical profiles. For some years, no average MOZAIC O_3 vertical profiles were available due to inadequate MOZAIC measurements in summer. O_3 measurements from 52 tethered balloon experiments (TBE) over Raoyang were grouped and averaged for the early morning (5:00-10:00 LT), late morning (10:00-12:00 LT) and afternoon (12:00-19:00 LT) periods (Fig. 8(a)). Only 7 UAV experiments (UAVE) could be made during our campaign at Raoyang. Nevertheless, average O_3 vertical profiles were calculated for early morning, late morning and afternoon (Fig. 8(b)), respectively. It is noted that only one UAV flight was made in late morning (Flight 1; 10:28-10:50 LT on June 29, 2014).

Therefore, the late morning average O_3 vertical profile in Fig. 8(b) is less representative. If this vertical profile is not considered, we can see in Figs. 8(a) and 8(b) a clear development of vertical O_3 distribution in the lower troposphere, with a substantial increase of the O_3 level in the mixed layer and a slight increase above the mixed layer in the course from the early morning to the afternoon. Although the mixing ratios of O_3 over Raoyang were mostly higher than 100 ppb in the afternoon, the overall average values were about 100 ppb as shown in the bottom-right plot of Fig. 8(c). Both our measurements and the MOZAIC measurements indicate high O_3 pollution in the lower troposphere over the NCP in summer.

Figure 8(c) shows that the O_3 level over the NCP had experienced a strong positive increase, indicating strengthening photochemical pollution in about two decades. The average mixing ratio of O_3 near the ground level had a relatively small increase (8.9 ppb) during 2004-2014, corresponding to an increase rate of about 0.9 ppb/yr. This increase rate is close to the average increase rate (1.1 ppb/yr) reported by Tang et al. (2009) of surface O_3 at six urban/suburban sites in Beijing in July-September during 2001-2006, but only about one third of what Zhang et al. (2014b) found for August daytime surface O_3 at an urban site in Beijing during 2005-2011 (2.6 ppb/yr). However, the high-end value of O_3 near the ground level had a larger increase, as suggested by the right end of the error bars (Fig. 8(c)). This larger increase in the high-end value of O_3 is consistent with the large increase of the maximum daily average 8 h (MDA8) mixing ratio of O_3 at the Shangdianzi background station (Ma et al., 2016). Compared with the increase of O_3 near the ground-level, much larger increases were found in O_3 at higher altitudes in the lower troposphere over Raoyang during 2004-2014, with the maximum increase (41.6 ± 15.5 ppb) being found at 1.5 km. Assuming that the O_3 level increased linearly over the ten years, the increase rate would be about 4.2 ± 1.6 ppb/yr. Sun et al. (2016) compiled and analyzed the O_3 , and NO_x and CO data collected at the Mt. Tai site ($36.25^\circ N$, $117.10^\circ E$; 1534m asl) during a few campaigns from 2003 to 2015. They reported that O_3 at Mt. Tai increased at 1.7 ± 1.0 ppb/yr in June and 2.1 ± 0.9 ppb/yr in July-August during 2003-2015. These rates of increase in summer O_3 at Mt. Tai and that we obtained for 1.5 km over Raoyang agree within the uncertainties though both sites are about 240 km apart. Based on the MOZAIC measurements over Beijing in summer afternoons (at 15:00–16:00 LT in MJJ) during 1995-2005, Ding et al. (2008) reported an increase rate of about 3 ppb/yr for O_3 in 0-2 km. From the data shown in Fig. 8(c), we can obtain an increase rate of 3.3 ppb/yr for summer O_3 in 0-2 km over Raoyang for the period 2004-2014, which agrees well with that reported by Ding et al. (2008). Note that the average O_3 vertical profile for summer 2014 (Fig. 8(c)) contains

measurements from the morning flights so that our estimated increase rate may be significantly lower than that for summer afternoon.

The above comparisons confirm that the abundance of O_3 in the lower troposphere over the north part of the NCP has largely increased since about two decades. The increase of the O_3 level in summer afternoon period seems to speed up after 2004.

- 5 Network observations indicate that surface O_3 pollution in China's polluted regions, including the NCP, has become more severe in recent years in contrast with the apparent decreases of $PM_{2.5}$ and primary gaseous pollutants (http://www.cnemc.cn/publish/totalWebSite/0492/newList_1.html). Such trend in surface O_3 may exert significant impacts on human health and vegetation. The increase of O_3 in the lower troposphere may influence atmospheric chemistry, i.e., increase the oxidation capacity (Ma et al., 2012), and add radiation forcing over the region.

10 4 Conclusion

In this study, vertical profiles of particle extinction property, O_3 and size-resolved aerosol concentration were simultaneously measured using miniature devices installed in an UAV over a rural site in the NCP during 2014 summer, allowing the characterization of diurnal O_3 and aerosol concentration in mixing layer and residual layer over a small area. Seven vertical profiles were successfully obtained in this campaign.

- 15 We found a positive gradient in the vertical distribution of O_3 , higher above the top of mixed layer than those below, making the residual layer an important source of O_3 in the mixed layer, particularly during morning when the top of mixed layer is rapidly elevated. However, aerosol number concentration in early morning was higher in the mixed layer than in the residual layer. The aerosol particles were abundant and overwhelmingly distributed in the size range $<1 \mu m$, consistent with urban aerosol. The historic O_3 data from the MOZAIC project, together with our measurements, were used to investigate the
- 20 long-term changes in O_3 vertical profiles in the lower troposphere over the NCP. The comparison of data from the 2014 summer campaign with those from MOZAIC suggests that the O_3 level over the north part of the NCP has experienced a strong positive increase, and the increase of the O_3 level seems to speed up after 2004, indicating rapidly strengthening photochemical pollution particularly in the last decade. Observations show that surface O_3 pollution in China's polluted regions, including the

NCP, has become more severe in recent years in contrast with the apparent decreases of PM_{2.5} and primary gaseous pollutants.

In view of this, more attention should be paid to O₃ concentration under the control of PM.

Data availability

The entire data set can be made available for scientific purposes upon request to the corresponding author.

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Table 1. The ascent and descent flight time (local time LT) and the max height.

Flight	Date	Ascent period	Hmax (m)	Descent period
1	June 29	10:18-10:36	1316	10:36-10:47
2	June 29	17:58-18:24	2498	18:24-18:38
3	July 1	6:34-6:55	2021	6:55-7:07
4	July 29	7:35-7:51	2430	7:51-8:04
5	July 31	5:53-6:18	2468	6:18-6:33
6	July 31	17:26-17:44	2676	17:44-18:02
7	August 2	15:17-15:29	2410	15:29-15:45

Table. 2. O₃ and aerosol number concentration calculated in method of particle extinction gradient (left of “”) and method of aerosol number concentration gradient (right of “”). O₃ concentration on the surface is obtained in the surface measurement program.

		<u>Early morning</u>		<u>Late morning</u>		<u>Afternoon</u>	
Surface	O ₃ (ppb)	Jul.1 (Flight 3)	Jul.29 (Flight 4)	Jul.31 (Flight 5)	Jun.29 (Flight 2)	Jul.31 (Flight 6)	Aug.2 (Flight 7)
		6:34-7:07	7:35-8:04	5:53-6:33	17:58-18:38	17:26-18:02	15:17-15:45
Mixed layer	O ₃ (ppb)	20.8±0.7	39.7±0.81	29.6±2.5	73.7±1.7	97.8±0.98	87.1±1.43
	Height(m)	::/200	255/275	255/267	360/281	795/525	795/::
	O ₃ (ppb)	::/37.4±20.8	44.3±8.5/44.3±8.5	70.5±38.6/72.4±38.2	71.2±9.0/69.1±9.6	106.7±7.9/103.2±9.2	99.1±5.4/::
	N (10 ³ p/cm ³)	::/1.99±0.36	8.7±0.12/8.69±0.13	5.73±2.00/5.73±2.00	4.17±0.75/4.54±0.75	6.28±0.17/6.39±0.10	::/::
Residual layer	Height(m)	1215/1331	::/1770	1110/1577	840/974	::/::	::/::
	O ₃ (ppb)	103.4±12.4/105.1±8.24	::/111±10.7	97±9.23/99.6±8.9	66.5±6.1/65.8±8.5	::/::	::/::
	N (10 ³ p/cm ³)	1.17±0.18/1.12±0.16	::/6.77±0.52	5.45±0.48/5.38±0.47	2.57±0.08/2.64±0.25	::/::	::/::

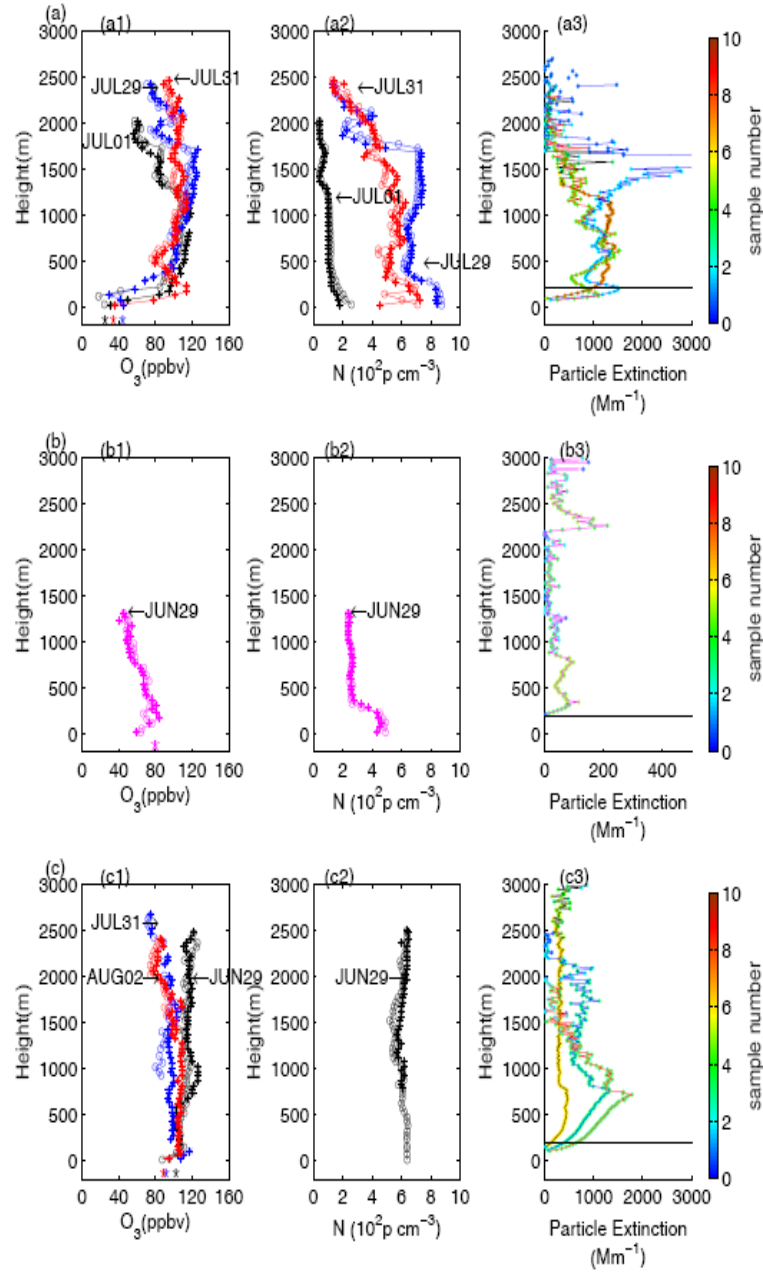


Figure 1. Vertical profiles of O_3 (a1,b1,c1), aerosol number concentration (a2,b2,c2) and particle extinction (a3,b3,c3) obtained in (a) early morning, (b) late morning, and (c) the afternoon, respectively. The O_3 and aerosol vertical profiles obtained during the ascent and descent of the UAV are indicated with circles and asterisks, respectively. Ground-level O_3 mixing ratios during the flights are also shown together with the O_3 vertical profiles (bigger asterisks with a negative offset in altitude). The color scales attached to particle extinction graphs (c1, c2, c3) show the sample numbers of individual particle extinctions, from which the averages of particle extinctions were calculated. The black lines indicate the altitude of 200 m above ground, under which the particle extinction data should not be used.

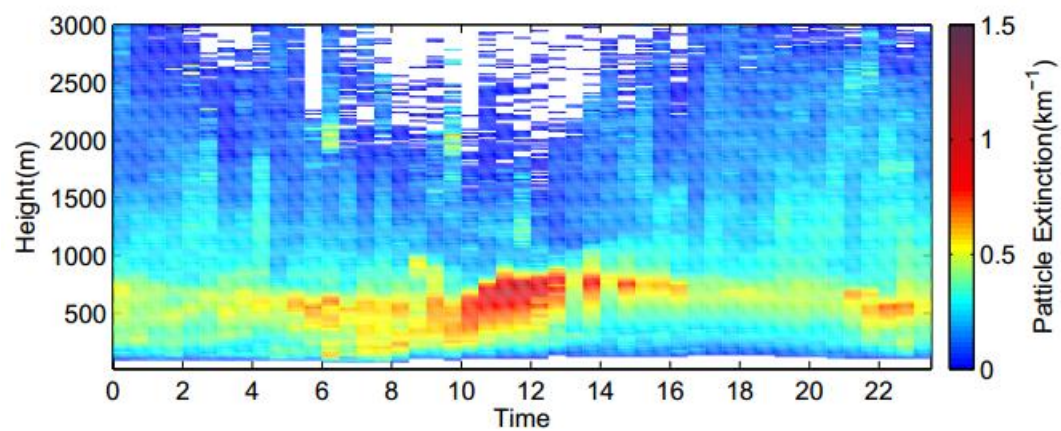


Figure 2. Average diurnal patterns of vertical distribution of particle extinction.

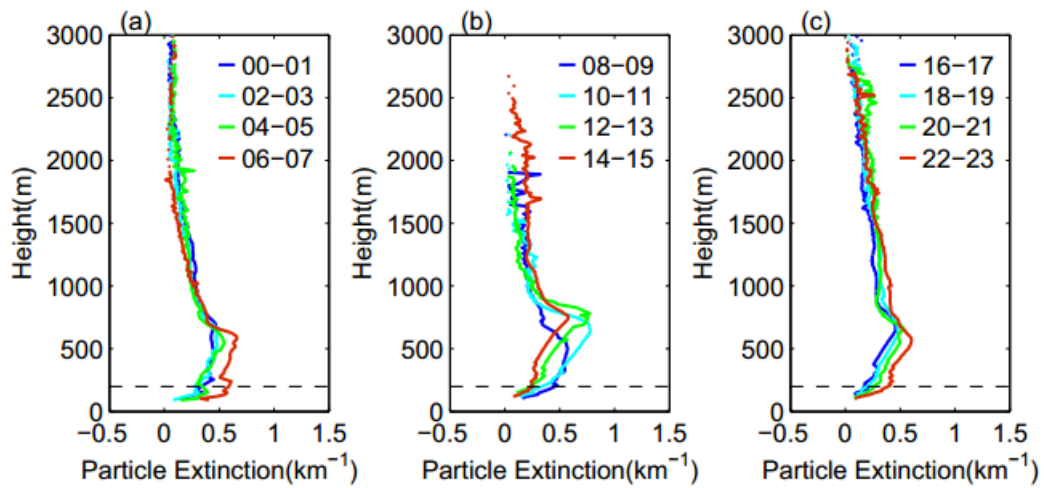


Figure 3. Vertical profiles of particle extinction averaged every two hours for (a) 0:00-7:00 LT, (b) 8:00-15:00 LT, and (c) 16:00-23:00 LT.

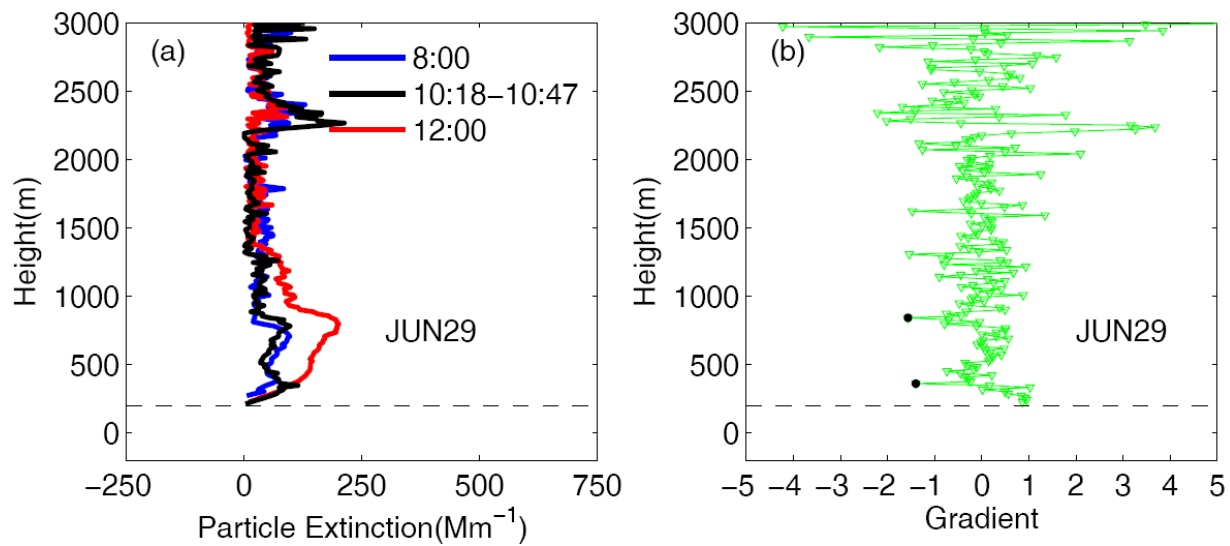


Figure 4. The vertical profile of particle extinction observed during the flight in the late morning of June 29 (a) and its gradient (b) and the vertical profiles of particle extinction before (blue) and after (red) the flight. The dashed lines indicate the lower limit of LIDAR.

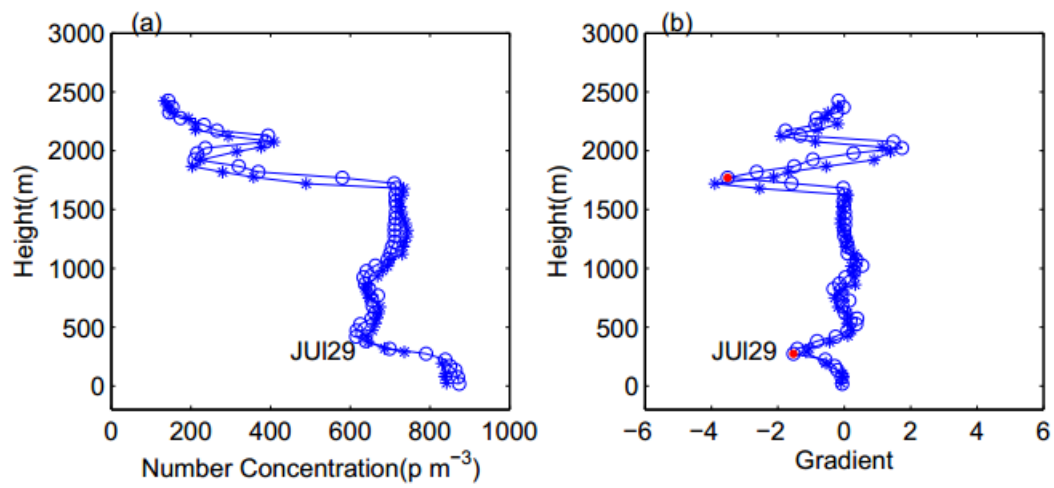


Figure 5. Vertical profiles of aerosol number concentration (a) and their gradients (b) from the ascent (open circles) and descent (asterisks) flight in the early morning of July 29 (Flight 4). The red solid circles indicate the tops of mixed layer and residual layer.

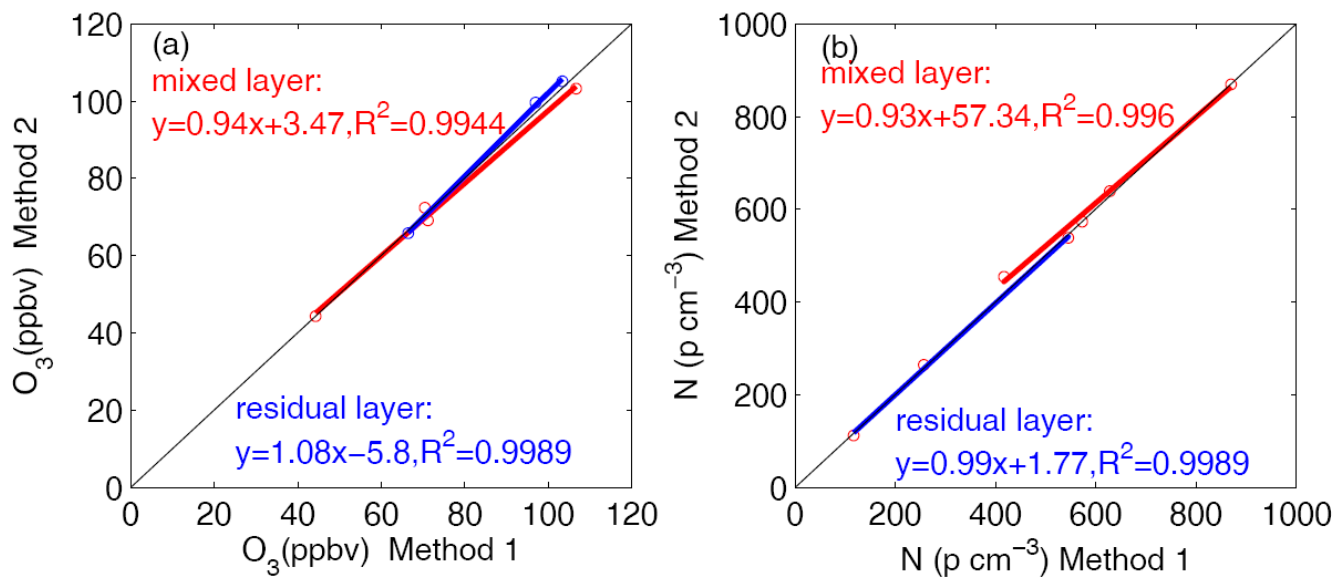


Figure 6. Average O_3 mixing ratios (a) and aerosol number concentrations (b) in the mixed layer and residual layer obtained using the method of particle extinction gradient (Method 1) in comparison with those obtained using the method of particle number concentration gradient (Method 2).

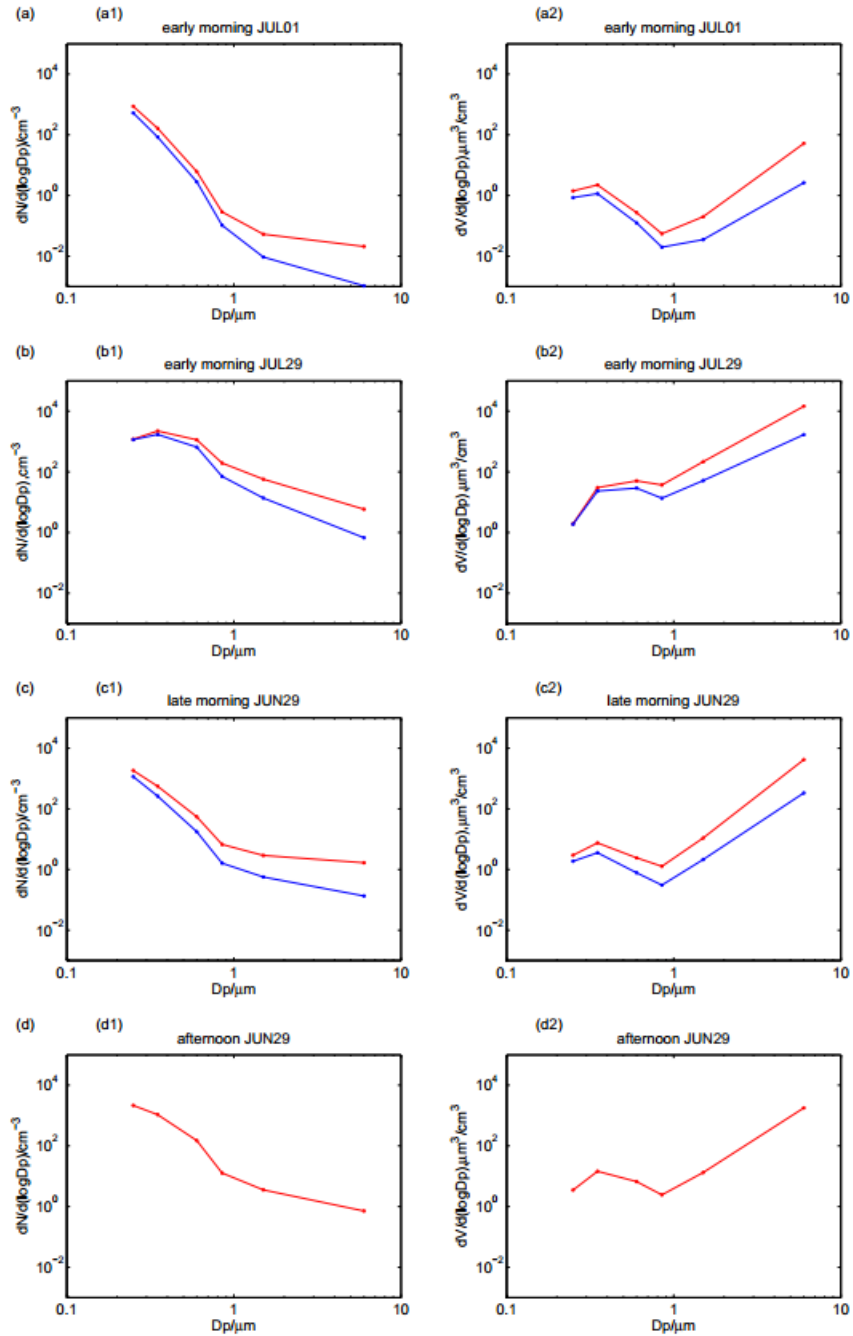


Figure 7. Aerosol number and volume size distributions in the mixed layer (red) and residual layer (blue), in the early morning of July 1 (a) and July 29 (b), late morning of June 29 (c) and afternoon of June 29 (d) flights. The mixed layer and residual layer heights are determined using the method of aerosol number concentration gradient.

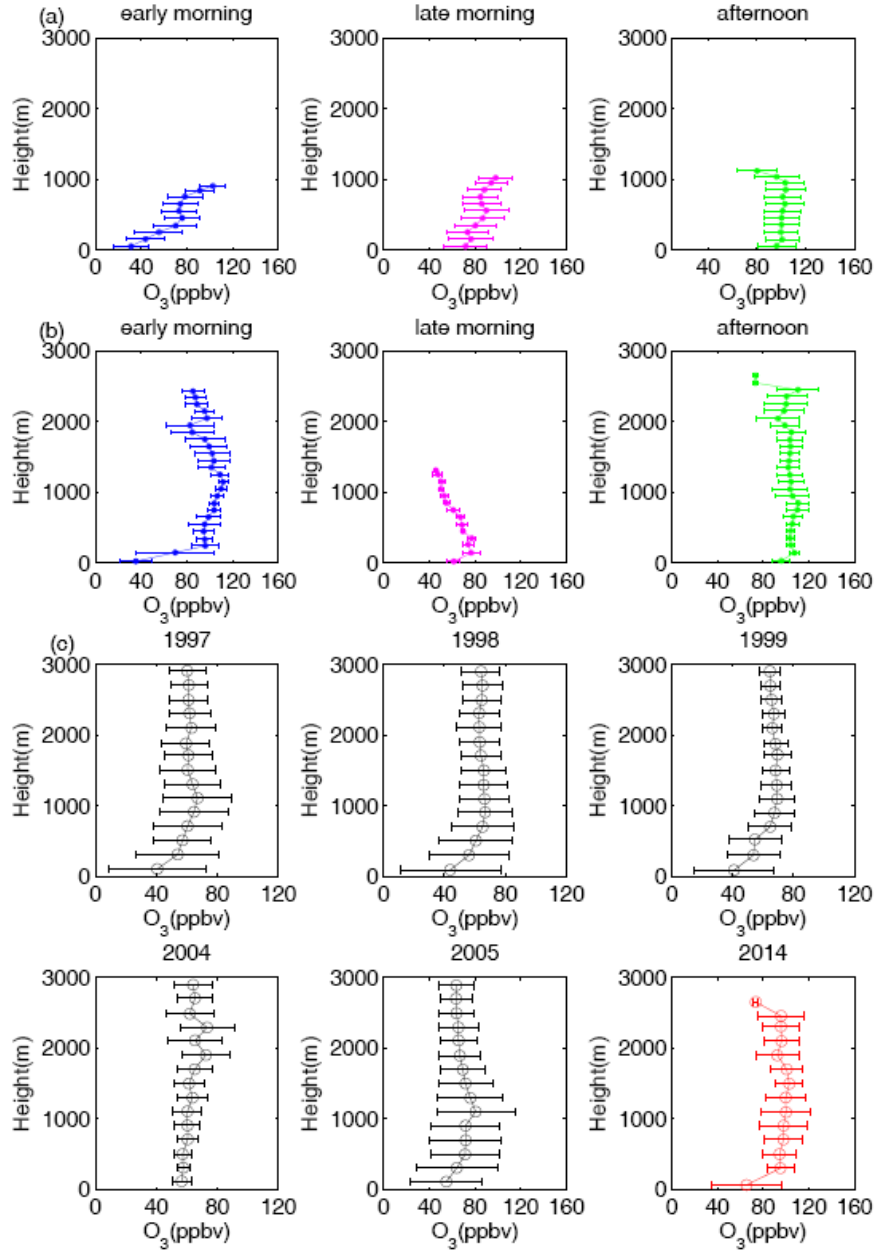


Figure 8. Comparison of average O_3 vertical profiles observed in the lower troposphere during summer of different years. (a) shows O_3 vertical profiles from the tethered balloon experiments during summer of 2014 averaged over early morning (5:00-8:00 LT), late morning (8:00-12:00 LT) and afternoon (12:00-19:00 LT). (b) presents O_3 vertical profiles from the UAV experiments during summer of 2014 averaged over early morning (Flights 3, 4 and 5), late morning (Flight 1) and afternoon (Flights 2, 6 and 7). (c) shows O_3 vertical profiles averaged over daytime (5:00-19:00 LT) MOZAIC measurements in summer of 1997, 1998, 1999, 2004, 2005 and our Raoyang measurement in summer of 2014. The error bars indicate one standard error of the mean.