

We would like to thank the referees for the constructive comments to help us to improve the manuscript. Below are our answers to the comments by the referee.

Answers to the referee comments by Anonymous Referee #1 on our manuscript “Variability of air ion concentrations in urban Paris” by V. N. Dos Santos et al.

General comments:

It will be very good if you put graph of $dN/d\log D$ for ion and particle combined hourly for event days (one day only), I wanted to see how the variation looks like. Characterization of ions should be follow on some old paper, in general for all the AIS measurement and see Mirme and Mirme also paper all are followed by Horrak's and Tammet's, even though Helsinki groups they all are following the same, Characterization of ion by Prof. Tammet. It will good if follow the same pattern and will be easy for comparison.

We have plotted $dN/d\log D$ for ions on selected NPF event days in Fig. 6. We don't want to combine ion (measured with AIS) and particle number size distribution (measured with TDMPS) here as ions are only charged fraction of the total aerosol particle. Thus, combining ion and particle plot might be physically misleading and technically challenging as we should use two different color scale in one surface plot. We hope referee understands our criterion.

In this study we will use the following mobility diameter ranges: small or cluster ions ($1.3 - 0.5 \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}$), intermediate ($0.5 - 0.034 \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}$) and large ions ($0.034 - 0.0042 \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}$), which correspond to mobility diameters of 0.8 – 2 nm, 2 – 7 nm and 7 – 20 nm, respectively. These size ranges correspond better our current understanding of cluster and particle formation dynamics, as transformation from cluster activation to new particle formation occurs at 1.5-2 nm range (Kulmala et al., *Science* 2013).

I also find many places cited only the Hirsikko et al., 2011- Review paper, that is fine, but original paper may also be cited.

Yes, modified the text and replaced the Hirsikko et al 2011 review paper citations when not needed. We have now added citations to original work throughout the manuscript. See the replies below for more details.

You have data for longer period- data collected at different seasons-right, how much temperature variations you have been noticed, it may be some time negative value of temperature. We may ware that mobility of ions depends on temperature- please comments.

The median monthly temperature in Paris varies from 20 °C (July) to 5 °C (January). Thus, temperature will go below zero Celsius degree during winter months, as referee pointed out. We have been converting the ion electrical mobilities to Millikan-Stokes diameters using Eq. 1 in Mäkelä et al., 1996 (more details by Kulmala et al. *Nature Protocols* 2012). We have done these conversions in NPT conditions: 20°C (293.15 K) and 1 atm (101.325 kPa). We tested that the effect of the ambient temperature changes to the ion mobilities, and the influence was minor. E.g. an ion with a physical size of 1.0 nm (20°C, 1 atm) would be

detected at ambient temperatures of 20 °C, 0°C and -20 °C, as 1.0000, 1.0010, and 1.013 nm, respectively, when using NTP condition assumption in the mobility to diameter conversion. Thus, we neglected it in further analysis, as the instrument particle sizing accuracy is much less sensitive than the mobility change caused by ambient temperature.

Some recent reference may be cited here e.g. Garcia et al., 2014, ACP; Kecorius, S. et al., 2015. Nocturnal aerosol particle formation in the north China plain. Lithuanian J. Phys. 55: 44-53; Kolarz P, Gaisberger M, Madl P, Hofmann W, Ritter M, Hartl A. 2012. Characterization of ions at Alpine waterfalls. Atmos. Chem. Phys. 12: 3687-3697. doi:10.5194/acp-12-3687-2012.

We added a reference to paper by Kolarz et al. ACP 2012. As it is slightly related to a possible ion source at urban locations. We didn't see relevance to add other citations as they were not related to urban studies and our Introduction has in general more recent and updated citations now added (see replies below, Revised manuscript, Page 3, lines 7-12).

I have one strong feeling that your results should be compare with model work also.

We agree that atmospheric model including all necessary sources and sinks to support the diurnal cycle of ambient ions would be good. Nevertheless, it is out of scope of this study which focuses on reporting our field observations.

It will be very good if the author calculate the formation rate (J5), because we can say something about the formation of particle and compare with other worker's results.

We didn't calculate the ion formation rates as we didn't have all the nucleation parameters needed for the calculations (e.g. number concentration of the neutral aerosol particle to estimates ion losses due to charging of neutral particles). We have the TDMPS measurements from only two month - July 2009 and 15 Jan/15 Feb 2010 - but we only used July 2009 (summer) which was the intensive observation period of the Megapoli campaign.

Appendix E and F is not essential, not getting any significant, author can remove it- if they wish.

We decided to keep the Appendix E and F (Figures A5-6) to show all data points used in this study. Especially to show the variation number concentration.

Minor comments

Page 2, lines 2: Define here the types of ions.....Author defined the air ions lines 7-8, page 2- I think atmospheric ion or only ion you can say...This line may be shifted in line 2 along with mobility ranges (also diameter).

We agree the ions should have been defined earlier in the manuscript. We modified the introduction of the manuscript accordingly.

Revised manuscript, Page 3, Lines 1-3: “The air ions were mobility-classified as small or cluster ions ($1.3 - 0.5 \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}$), intermediate ($0.5 - 0.034 \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}$) and large ions ($0.034 - 0.0042 \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}$), which correspond to mobility diameters of 0.8 – 2 nm, 2 – 7 nm and 7 – 20 nm, respectively.”

In the abstract please mentioned the name of instruments. Also abstract may be shortening, give only whatever essential.

We added the instrument names to the abstract.

Revised manuscript, Abstract, lines 1-3: “We measured air ion number size distributions (0.8–42 nm) with an Air Ion Spectrometer and fine particle number concentrations ($> 6 \text{ nm}$) with Twin Differential Mobility Particle Sizer in an urban site of Paris between 26 June 2009 and 4 October 2010.”

Page 3, lines 5-7; With some condition secondary aerosol particle can grow? Or all aerosols can grow upto CCN, I do not think. As our knowledge they can grow up to CCN or even beyond with the suitable condition.

We clarified the text that it is clearer that not all newly formed particle activate as CCN's.

Revised manuscript, Page 2, lines 5-7: “Freshly formed secondary aerosol particles may grow within a day or two up to sizes where they can act as cloud condensation nuclei (CCN) and affect the radiation budget of the Earth (Makkonen et al., 2012; Kerminen et al., 2012; Wiedensohler et al., 2009).”

Page 3 lines 26-32; Some original work may be cited here.

We revised manuscript accordingly. We added citations to the text and papers to reference list.

Revised manuscript, Page 3, lines 7-12: “Small ions are always present in the air and are responsible for the atmospheric electrical conductivity (e.g. Harrison and Carslaw, 2003; Hirsikko et al., 2011). They are mainly formed from ionizing radiation of decaying radon, gamma radiation and galactic cosmic radiation. Thunderstorms, water splashing, rain and snow storms also contribute to the formation of air ions in the atmosphere (Virkkula et al., 2007; D'Alessandro, 2009; Tammet et al., 2009; Kolarž et al., 2012). Increased small ion concentrations have been observed in the vicinity of power lines (Jayaratne et al., 2008). Small ion emissions in fuel burning processes in engines or via nucleation from exhaust gas have been studied theoretically and experimentally (e.g. Yu and Turco, 1997; Haverkamp et al., 2004; Gopalakrishnan et al., 2005; Lähde et al., 2009; Jayatane et al., 2010; Ling et al., 2013).”

Page 3, lines 31; Kamsali et al., 2011 delete—this not dealing the ion-ion-recombination- Please see work done by Prof. Hoppel and suitable reference may be cited here.

We revised the manuscript accordingly and deleted Kamsali et al. (2011) citation. We added citations to Hoppel (1985) and Hoppel and Frick (1986).

Revised manuscript, Page 3, lines 12-14: “The most important sinks for ions are ion-ion recombination to form neutral particles, and attachment to pre-existing aerosol particles (Hoppel, 1985; Hoppel and Frick, 1986).”

Page 3, lines 27-30. Sources of ion are mentioned limited. May be add more sources—for example- combustion, raindrop splashing, braking ocean waves, corona discharge and tree branches below the thunderstorm. For the combustion please see Gopalakrishnan et al., 2015 (GRL) or any other, on the waterfall some paper by Helsinki group etc.

This is true. We revised manuscript accordingly. We added citations to the text and papers to reference list. Unfortunately we didn't find a paper corresponding to search “Gopalakrishnan” at *Geophysical Research Letters*. We assume the referee points to this paper: Gopalakrishnan, V and Pawar, SD and Siingh, D and Kamra, AK (2005) Intermediate ion formation in the ship's exhaust. *Geophysical Research Letters*, 32 (11). pp. 1-4.

Revised manuscript, Page 3, lines 7-12: “Small ions are always present in the air and are responsible for the atmospheric electrical conductivity (e.g. Harrison and Carslaw, 2003; Hirsikko et al., 2011). They are mainly formed from ionizing radiation of decaying radon, gamma radiation and galactic cosmic radiation. Thunderstorms, water splashing, rain and snow storms also contribute to the formation of air ions in the atmosphere (Virkkula et al., 2007; D'Alessandro, 2009; Tammet et al., 2009; Kolarz et al., 2012). Increased small ion concentrations have been observed in the vicinity of power lines (Jayaratne et al., 2008). Small ion emissions in fuel burning processes in engines or via nucleation from exhaust gas have been studied theoretically and experimentally (e.g. Yu and Turco, 1997; Haverkamp et al., 2004; Gopalakrishnan et al., 2005; Lähde et al., 2009; Jayatane et al., 2010; Ling et al., 2013).”

Page 4, line 10: As mentioned in abstract also, study period was 26 June 2009-4 OCT Oct, 2010 (16 months)- how you are going to address climatic related issues with limited period of data. Comment?

The small and intermediate ions will have climatic effect if they manage to grow into CCN sizes. Typically a small fraction will grow into sizes where they can act as cloud condensation seeds and therefore have climatic relevance via cloud formation. Nevertheless, typically a large number of urban studies are based on considerably smaller data sizes. Thus, we are confident on our data set.

Objection of the manuscript is clear to me- Pleases clarify.

We have tried to write the objective of the manuscript clearly. In the original manuscript (Online published ACPD paper: Page 10632, lines: 21-22) is says: “The main aim of this study was to determine the frequency and seasonal variations of NPF events in a megacity based on ion number size distribution measurements.” Later this study and our NPF

frequency can be used to estimate the contribution of anthropogenic and biogenic secondary aerosol formation to clouds and climate.

Section 2.1- Description of the site.

More site description is required around the measurements site- it will be very good if author can put closed view of the site in figure 1 (In the legend author are mentioned "estimated location, what is meaning of estimation?). Inlet photograph of both the instrument is more useful. Some information of met parameter is more useful to understand about the source of the particles- as author mentioned that anthropogenic sources of the particle.

We modified Fig. 1 to describe and visualize the measurement location better. And we revised the figure caption.

Revised manuscript, Page 30, lines 21-22: Figure 1: Location of the LHVP site in Paris (rooftop of Laboratoire d'Hygiène de la Ville de Paris, Paris 13 arrondissement, 11 Rue George Eastman, 75013 Paris).

New Fig. 1 below:



Page 5, lines 24-25. How you convert the mobilities to diameter of ion? Are you consider during conversion single charge or multiple charge ions- Please see the Tammet, 1995 or Horrak et al., 2003. Asmi et al., 2009 is not appropriate here.

Throughout the manuscript we apply the mobility diameter, i.e. Millikan-Stokes diameter, when converting the measured mobility to particle diameter (see Mäkelä et al., 1996).

We added following sentence to manuscript when electrical mobility diameters mentioned for the first time:

Revised manuscript, Page 6, Lines 21-26: “The air ions were mobility-classified as small or cluster ions ($1.3 - 0.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), intermediate ($0.5 - 0.034 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and large ions ($0.034 - 0.0042 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), which correspond to mobility diameters of 0.8 – 2 nm, 2 – 7 nm and 7 – 20 nm, respectively. In these size ranges charged particles are assumed to be single charged. In this study, we apply the mobility diameter, i.e. Millikan diameter, when converting the measured mobility to particle diameter (see Mäkelä et al., 1996).”

Section 2.2.1 and 2.2.2

Please shorten this section. Detailed is not required. Put the website or refer.

We shortened the instrument descriptions as requested by the referee. We removed all information which is not needed to evaluate the accuracy of the number concentration measurements of ions and particles. See revised manuscript pages 5-6.

Section 2.3

Page 7, lines 5-8; Please correct the diameter range of respective mobility, Please see the Horrak et al., 2003, also you can find in Siingh et al., 2013. Intermediate ion size range up to 7.4 not 7. Similar mistake in Small and light large also. Similar changed may be made in table 1 also.

As replied in general comments: In this study we will use the following mobility diameter ranges: small or cluster ions ($1.3 - 0.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), intermediate ($0.5 - 0.034 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and large ions ($0.034 - 0.0042 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), which correspond to mobility diameters of 0.8 – 2 nm, 2 – 7 nm and 7 – 20 nm, respectively. These size ranges correspond better the current understanding of cluster and particle formation dynamics, as new particle formation occurs at 1.5-2 nm range (Kulmala et al., Science 2013).

Page 8 lines 1-3; Please write name of the Months. Not short.

We modified the manuscript accordingly, and we didn't not use the abbreviation of the months within the manuscript.

Revised manuscript, Page 7, Lines 17-19: “Months were classified into seasons as follows: winter: December, January and February; spring: March, April and May; summer: June, July and August; autumn: September, October and November.”

Section 3; Results and discussion

Page 8, lines 27-28; Why you are getting more negative number concentration, it is because of electrode effect? Or something else.

An electrode effect should lead into observing slightly more positive ions when sampled close to ground level (Hoppel, 1967). In addition, we were sampling at rooftop. Thus, the electrode effect will not explain it. We cannot speculate what causes this small difference in small ion concentrations.

Page 9, line 23-26; I agree but more concentration for large particles not for intermediate ion, generation of intermediate ion are different.

There are several studies which are cited in manuscript. In addition, we added citations to give sources for intermediate ions as requested already earlier by the referee. These citations show that intermediate ions can form via vehicle emissions e.g. Yu and Turco, 1997; Haverkamp et al., 2004; Gopalakrishnan et al., 2005; Lähde et al., 2009; Jayatane et al., 2010; Ling et al., 2013). Therefore, traffic can cause emissions to both intermediate and large ions (10-40 nm), when comparing to Hirsikko et al. (2007b).

Page 10, lines 9-17; What is significant of correlation- please clarify.

We assume the comment refers to Appendix A (and Fig. A1). As was indicated already in the original manuscript (Online published ACPD paper: Page 10640, lines: 10-19), the p-value for the correlation coefficient for large ions and particle numbers was smaller than 0.01, indicating statistically significant correlation.

Page 10, lines 20-21, Morning peak may be some other region- like solar activity? Please investigate the possible sources, If possible- only traffic I am not agrees. Is any change in wind direction? May be one of the factor- if not then leave these comments. Please also explore the nocturnal activities and give some suitable reference.

Very interesting point. All this supplementary analysis would be a topic for a new publication. Meteorological analysis were unfortunately not included into this study. We had issues with a time format in the supplementary meteorological data and the data archive for Megapoli campaign at this LHVP measurement site. Thus, we needed to leave this out of the scope of this study and rely on the published literature.

Page 11, line 14; at your place sunrise time different at different months. Please comments- That why I want more and detailed information about observation site- then we can say some local source or not.

We added more detail description of the measurement site as requested earlier. More detailed analysis of the sunrise time and sunset times connecting the photochemistry and boundary layer development are not needed as we didn't include the meteorological data analysis to this study.

Page 12, line 20; how you can say? Do you have any measurement?

Unfortunately, we can't respond to this comment, as we have difficulties to follow referee's page and line numbers. We cannot locate which statement he/she is commenting.

Page 13, lines 3-4, it is obvious, environmental condition are different at Puy de Dôme mountain and your site.

Yes, we were trying to indicate the altitude difference (different environment) by writing to original manuscript (Online published ACPD paper: Page 10643, lines: 24-25): “Despite the differences in altitude, Rose et al. (2013) also observed the lowest concentrations of small ions in spring in Puy de Dôme, a mountain in central France (1465 m above sea level).” No modifications done.

Page 14, lines 2-17, In India other than Pune and Kanpur e.g. Himalayas region also getting NPF is more in spring/summer.

In the original manuscript, we wanted to cite studies done at urban areas to report NPF event frequency. Thus, we will not add citation to Himalayas region study.

Page 15, lines 12-13, Agree! Horrak et al., 1998 already suggested that during the NPF burst of intermediate ions. This finding is not new.

Very good.

Page 16, lines 23-26, Do you have any support- like air mass back trajectory – please show from air-mass back trajectory analysis.

We do not have air mass trajectory analysis included in this study. Pikridas et al. (ACP 2015) studied in more detail the connection between NPF and air mass origin in Paris during Megapoli campaign. Their results are summarized in the manuscript.

Page 18, lines 3-4, What is Kelvin effect and Nano-Köhler effect? Please define in short, general reader may not be knowing.

We assume that expert readers who will be interested in this detail will know or find this information from the citations provided. No modification, to not to lose the focus of the paper.

Summary and conclusion: Heading should be “conclusion” Conclusion should be focused based on the study only and compact. Please rewrite the main conclusion only.

We changed the heading into “Conclusions” as suggested by the referee. And we modified the text accordingly to shorten the conclusions. We removed the repetition from the Conclusions to shorten it and highlight the main results.

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