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 #2 on our manuscript "Variability of air ion concentrations in urban Paris" by V. N. Dos Santos et al.

General comments by Anonymous Referee #2:

> *It would be helpful if the authors discuss more whether actually ions contribute to NPF or not. It is not clear to me what is exact relationship between ions and NPF in this case at this location? This discussion was made in some parts of the manuscript. Authors are encouraged to provide a clearer statement on this.*

As we write in the abstract of the manuscript: "Because the median concentrations of intermediate ions were considerably higher on NPF event days in comparison to NPF non-event days, the results indicate that intermediate ion (2-7 nm) concentrations could be used as an indication for NPF in Paris." Due to earlier studies in urban environment, we assume that in Paris the observed ions are only the naturally charged fraction of the total aerosol number concentration. Thus, the intermediate ions can be used an indicator whether or not NPF occur. We had no other sub-3 nm aerosol instrumentation available during Megapoli project at Paris. The original hypothesis was whether there could be some other source for intermediate ions in addition to natural secondary aerosol formation (NPF events).

As we didn't have supporting instrumentation to measure the total particle concentration in 2-3 nm range, e.g. Particle Size Magnifier (PSM), Differential Mobility Particle Sizer or Neutral Cluster and Air Ion Spectrometer (NAIS), we cannot calculate the fraction of ion-induced or ion-mediated nucleation following procedures by Kulmala et al. 2012 *Nature Protocols*. We added following sentence to the Introduction section to clarify the issue:

Revised manuscript, Page 2, Lines 31-33: "Based on earlier urban studies by Gagné et al. (2012), Iida et al. (2006) and Herrmann et al. (2014), we assume that ions and charged particles detected in Paris are the naturally charged fraction of total aerosol particles."

> *There are always sub-2 nm ions measured by AIS. Why? Is this because these ions are actually present all the time at this size range or because AIS always detects these sub-2 nm ions wherever and whenever? Do you know any examples that an AIS instrument did not detect any sub-2 nm particle for a substantial period in the atmosphere, at any other locations? If so, please mention this. I am raising this, because when we measured sub-2 nm particles with PSM (particle sizing magnifier) at several sites in US, we found that sub-2 nm particles are present only when sulfuric acid is sufficient and definitely not during the nighttime (e.g., [Huan Yu et al., 2013; Huan Yu et al., 2014]), in contrast to what shown in your present manuscript and many other publications of AIS measurements. For example, in an Alabama forest, when PSM did not show sub-2 nm particles, a co-located AIS actually showed this constant band of small ions day and night all the time during SOAS 2013 campaign at the ground site (I am mentioning this solely based on my initial observations at the site without comprehensive data analysis since then).*

Yes, we have detected the cluster ions (so-called small ions) in all environmental conditions we have measured with the ion spectrometer varying from extremely polluted areas (e.g. Backman et al., 2012; Herrmann et al., 2014) to extremely clean environments (Virkkula et al., 2007) as well as from lower troposphere to free troposphere (e.g. Mirme et al., 2010; Manninen et al., 2010). An ion review by Hirsikko et al. (ACP 2011) confirms this with inquiry of ca. 260 publications, 93 of which included data on the temporal and spatial variation of the concentration of small ions. The only exception where no cluster ion is observed is inside a cloud, as cloud droplets work as a strong sink for cluster ions (Lihavainen et al., 2007).

It is very important note that small ions are not formed via NPF, whereas activation of these small ions may lead to NPF (Online published ACPD paper: Page 10631, lines: 21-24). In sub-2 nm small ions are formed via natural terrestrial radioactivity and cosmic ray ionization like listed in the Introduction (Published ACPD paper: Page 10632, lines: 6-8). To clarify more, we revised following sentence in the Introduction:

Revised manuscript, Page 3, Lines 3-5: ”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.”

> *What is your rough estimation of fractions of positive and negative ions in total particles (those including neutral particles together)?*

Unfortunately, based on our ion measurements at sub-3 nm alone which is only the charged fraction of total aerosol particles, we cannot calculate the charged fraction as requested above.

> *The overall impression is that positive and negative ions show similar concentrations (with positive ions slightly higher than negative ions) as well as similar time variations. Laboratory studies by [K Froyd, D. and Lovejoy, 2004; K D Froyd and Lovejoy, 2003] show that negative ions are more important for IIN, so how do you explain this discrepancy? And what is the implication of this difference on the role of ions in NPF? It is an important point that CERN CLOUD chamber studies often assumed, and lately showed, that ion clusters (showed negative mostly in papers) and neutral clusters have similar chemical compositions and from these assumption they proposed different nucleation mechanisms for neutral nucleation. So differences or similarities of positive and negative ions, and differences of ions and neutral particles, would be an interesting point for understanding the role of ions in NPF at the ground level.*

The number concentration of positive and negative ions should show similar concentrations as the atmospheric ions are in a charge equilibrium as expected in most environments. Estimating the importance of IIN nucleation is out of scope of this study. We assume that neutral nucleation pathways dominate in polluted environments like Paris. This is in agreement with a manuscript very recently submitted to ACP by Kontkanen et al. which is unfortunately not yet published in ACPD. Kontkanen et al. study shows results from measurements with a PSM and a NAIS that in polluted environment at Po Valley, Italy,

where the neutral pathways dominate. This is in agreement with field observations by Lin Wang's group in Fudan University.

Minor comments:

The authors stress that NPF produces intermediate ions in Paris, but rather I believe because of the presence of substantial intermediate ions, NPF takes place. This is a minor point though, but different wording would be more appropriate and consistent with the description in the field.

We disagree. According to the current knowledge, within the atmospheric new particle formation (NPF) aerosol particles nucleate and growth. The particle goes through a phase transition from gas phase to liquid or solid phase, i.e. the nucleation of stable liquid or solid phase clusters from gas phase pre-cursors. Atmospheric nucleation can happen via molecular clustering, and it is followed by cluster activation for enhanced growth (Kulmala et al., 2013). Thus, intermediate ions are formed due to NPF, not vice versa.

Page 10631 Line 24 to Page 10632 Line 5: These statements are incorrect. The chamber studies actually are mostly consistent with field observations and IIN modeling studies. For example, Kirkby 2011 [Kirkby et al., 2011] and subsequent CERN CLOUD chamber studies showed the temperature dependence of IIN, and they reproduced the conclusion of [Lee et al., 2003] and [Lovejoy et al., 2004] studies. What is really controversial is that different models show different predictions, mostly between IMN vs. IIN. As mentioned above, this is also due to different usages of terminology and depends on whether ion-ion recombination is considered in neutral cluster processes or solely in IMN.

To clarify, we modified the text by adding following sentence:

Revised manuscript, Page 2, Lines 22-27: "On the other hand, some models and chamber studies suggest that ion-mediated nucleation (which considers ion-ion recombination) may be a significant path for NPF (Yu and Turco, 2011; Yu, 2010; Svensmark et al., 2007; Nagato and Nakauchi, 2014). Chamber studies in the CLOUD project have shown that in low temperatures and at low precursor species concentrations ion-induced nucleation can have a significant contribution to the total nucleation rates (Kirkby et al., 2011; Riccobono et al., 2014)."

Page 10369 last paragraph and similar statements in other places: As the authors stress in Conclusion, comparison of ions and particles in different sites require careful consideration of seasons and ion polarities.

We agree and have followed this principle throughout the manuscript whenever possible (by mentioning size range and season when ions were measured in the reference study).

Page 10645 last paragraph: Recent studies by Lin Wang's group in Fudan University show much high frequencies of NPF in Shanghai, similar to those reported from Beijing. This makes sense, because the Eastern China regions are heavily influenced by high SO2 concentrations (ppb level constantly).

We added citations to the new studies by Wang et al. Most of these studies are from shorter campaigns (few months maximum). Thus, we need to be careful when doing conclusions about an annual NPF event frequency. We added also two year NPF study by Wu et al. (2008) in Beijing, China.

We modified the text accordingly.

Revised manuscript, Page 14, Lines 3-10: "In cities such as Nanjing (China), São Paulo (Brazil), Helsinki (Finland), Shanghai (China), Pune and Kanpur (India), Birmingham (UK) and Budapest (Hungary) the frequency of NPF events was between 5 – 27% (Herrmann et al., 2014; Backman et al., 2012; Hussein et al., 2008; Du et al., 2012; Leng et al., 2014; Xiao et al., 2015; Kanawade et al., 2014; Zhang et al., 2004; Salma et al., 2011) which is within range of the observations in Paris (13%). However, NPF frequencies as high as 40 – 55% were observed in Beijing (China), Pittsburgh (USA), and Brisbane (Australia), and Nanjing (Wu et al., 2007, 2008; Stanier et al., 2004; Crilley et al., 2014; Yu et al., 2015), although not all the studies comprised an entire year of measurements."

These new citations added to Reference list in revised manuscript:

Wu, Z. J., Hu, M., Lin, P.,Liu, S., Wehner, B., and Wiedensohler, A.: Particle number size distribution in the urban atmosphere of Beijing, China. *Atmos. Environ.*, 42: 7967–7980, 2008.

Xiao, S., Wang, M. Y., Yao, L., Kulmala, M., Zhou, B., Yang, X., Chen, J. M., Wang, D. F., Fu, Q. Y., Worsnop, D. R., and Wang, L.: Strong atmospheric new particle formation in winter in urban Shanghai, China, *Atmos. Chem. Phys.*, 15, 1769-1781, doi:10.5194/acp-15-1769-2015, 2015.

Leng, C., Zhang, Q., Tao, J., Zhang, H., Zhang, D., Xu, C., Li, X., Kong, L., Cheng, T., Zhang, R., Yang, X., Chen, J., Qiao, L., Lou, S., Wang, H., and Chen, C.: Impacts of new particle formation on aerosol cloud condensation nuclei (CCN) activity in Shanghai: case study, *Atmos. Chem. Phys.*, 14, 11353-11365, doi:10.5194/acp-14-11353-2014, 2014.

Yu, H., Zhou, L. Y., Dai, L., Shen, W. C., Zheng, J., Ma, Y., and Chen, M. D.: Nucleation and growth of sub-3 nm particles in the polluted urban atmosphere of a megacity in China, *Atmos. Chem. Phys. Discuss.*, 15, 18653-18690, doi:10.5194/acpd-15-18653-2015, 2015.

> *Page 10647 2nd paragraph on the role of air mixing. Since the current study does not have measurements of air mixing, this discussion does not add to the quality of science of the paper. I suggest remove this.*

We wish to keep the text as it is. We have cited other studies published within the Megapoli project (Cimini et al. 2013 and Pikridas et al. 2015; Published ACPD paper: Page 10641, lines 1-5) to estimate the atmospheric vertical mixing in Paris. It is clear that strong vertical mixing is connected to the onset of NPF. Thus, this is not a speculation.

Page 10648 1st paragraph on regional NPF. Do you have any indication that the NPF events occur at the regional scale? Otherwise, I would remove this discussion or reword appropriately.

The NPF events presented in our 4 case studies are regional as we are able to follow the homogeneous growth until the late afternoon (this requires uniform air masses to last for at least few hours) (see Published ACPD paper: Page 10670, Fig. 6a-d). The simple fact that we observe the so-called "banana" shape in number size distributions is an indication that the NPF is regional scale. In local scale events, we would not observe homogeneous growth.

References

Backman, J., Rizzo, L. V., Hakala, J., Nieminen, T., Manninen, H. E., Morais, F., Aalto, P. P., Siivola, E., Carbone, S., Hillamo, R., Artaxo, P., Virkkula, A., Petäjä, T., and Kulmala, M.: On the diurnal cycle of urban aerosols, black carbon and the occurrence of new particle formation events in springtime São Paulo, Brazil, Atmos. Chem. Phys., 12, 11733–11751, doi:10.5194/acp-12-11733-2012, 2012.

Harrison, R.G. and Carslaw, K.S.: Ion-aerosol-cloud processes in the lower atmosphere, Reviews of Geophysics, 41:3, doi:10.1029/2002RG000114, 2003.

Herrmann, E., Ding, A. J., Kerminen, 5 V.-M., Petäjä, T., Yang, X. Q., Sun, J. N., Qi, X. M., Manninen, H., Hakala, J., Nieminen, T., Aalto, P. P., Kulmala, M., and Fu, C. B.: Aerosols and nucleation in eastern China: first insights from the new SORPES-NJU station, Atmos. Chem. Phys., 14, 2169–2183, doi:10.5194/acp-14-2169-2014, 2014.

Lihavainen, H., Komppula, M., Kerminen, V.-M., Järvinen, H., Viisanen, Y., Lehtinen, K., Vana, M. and Kulmala, M.: Size distributions of atmospheric ions inside clouds and in cloud-free air at a remote continental site. Boreal Env. Res. 12: 337–344, 2007.

Kulmala, M., Petäjä, T., Nieminen, T., Sipilä, M., Manninen, H.E., Lehtipalo, K., DalMaso, M., Aalto, P.P., Junninen, H., Paasonen, P., Riipinen, I., Lehtinen, K.E.J., Laaksonen, A. and Kulmala, M.: Measurement of the nucleation of atmospheric aerosol particles, Nature Protocols 7, 1651-1667, doi:10.1038/nprot.2012.091, 2012.

Kulmala, M., Kontkanen, J., Junninen, H., Lehtipalo, K., Manninen, H. E., Nieminen, T., Petäjä, T., Sipilä, M., Schobesberger, S., Rantala, P., Franchin, A., Jokinen, T., Järvinen, E., Äijälä, M., Kangasluoma, J., Hakala, J., Aalto, P. P., Paasonen, P., Mikkilä, J., Vanhanen, J., Aalto, J., Hakola, H., Makkonen, U., Ruuskanen, T., Mauldin III, R. L., Duplissy, J., Vehkamäki, H., Bäck, J., Kortelainen, A., Riipinen, I., Kurtén, T., Johnston, M. V., Smith, J. N., Ehn, M., Mentel, T. F., Lehtinen, K. E. J., Laaksonen, A., Kerminen, V.-M., and Worsnop, D. R.: Direct observations of atmospheric aerosol nucleation, *Science*, 339, 943–946, 2013.

Manninen, H. E., Nieminen, T., Asmi, E., Gagné, S., Häkkinen, S., Lehtipalo, K., Aalto, P., Vana, M., Mirme, A., Mirme, S., Hõrrak, U., Plass-Dülmer, C., Stange, G., Kiss, G., Hoffer, A., Törõ, N., Moerman, M., Henzing, B., de Leeuw, G., Brinkenberg, M., Kouvarakis, G. N., Bougiatioti, A., Mihalopoulos, N., O'Dowd, C., Ceburnis, D., Arneth, A., Svenningsson, B., Swietlicki, E., Tarozzi, L., Decesari, S., Facchini, M. C., Birmili, W., Sonntag, A.,

Wiedensohler, A., Boulon, J., Sellegri, K., Laj, P., Gysel, M., Bukowiecki, N., Weingartner, E., Wehrle, G., Laaksonen, A., Hamed, A., Joutsensaari, J., Petäjä, T., Kerminen, V.-M., and Kulmala, M.: EUCAARI ion spectrometer measurements at 12 European sites – analysis of new particle formation events, Atmos. Chem. Phys., 10, 7907–7927, doi:10.5194/acp-10-7907-2010, 2010.

Mirme, S., Mirme, A., Minikin, A., Petzold, A., Hõrrak, U., Kerminen, V. -M., and Kulmala, M.: Atmospheric sub-3 nm particles at high altitudes, *Atmos. Chem. Phys.*, 10, 437–451, doi:10.5194/acp-10-437-2010, 2010.

Pikridas, M., Sciare, J., Freutel, F., Crumeyrolle, S., von der Weiden-Reinmüller, S.-L., Borbon, A., Schwarzenboeck, A., Merkel, M., Crippa, M., Kostenidou, E., Psichoudaki, M., Hildebrandt, L., Engelhart, G. J., Petäjä, T., Prévôt, A. S. H., Drewnick, F., Baltensperger, U., Wiedensohler, A., Kulmala, M., Beekmann, M., and Pandis, S. N.: In situ formation and spatial variability of particle number concentration in a European megacity, Atmos. Chem. Phys., 15, 10219-10237, doi:10.5194/acp-15-10219-2015, 2015.

Virkkula, A., Hirsikko, A., Vana, M., Aalto, P. P., Hillamo, R. and Kulmala, M.: Charged particle size distributions and analysis of particle formation events at the Finnish Antarctic research station Aboa. Boreal Env. Res. 12: 397–408, 2007.