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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Variability of air ion concentrations in urban Paris" *by* V. N. Dos Santos et al.

Anonymous Referee #2

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This paper describes a year of measurements of air ions and particle number concentrations in Paris and shows seasonality, diurnal variation and contrast between weekdays vs. weekends on air ions and particle concentrations. NPF occurs most frequently in summer, due to higher sun flux and cleaner air quality. But ions in either positive or negative polarity and in different size bins each show different time variations as NPF. There are some general correlations between intermediate size ions and NPF, but somehow small ions do not show any correlations with NPF. The manuscript also contains useful comparison of ions and NPF reported from different mega-cities. How ions contribute to particle formation at the ground level (or in lower troposphere) is still controversial, in part due to the lack of comprehensive measurements and analysis and also in part due to usage of inconsistent terminologies regarding to ion-induced nu-

cleation (IIN) and ion-mediated nucleation (IMN) and ion-ion recombination in neutral nucleation. So this paper provides useful information on this scientific topic.

General comments:

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.

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).

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

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 dis-

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crepancy? 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.

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.

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.

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.

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

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SO2 concentrations (ppb level constantly).

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.

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 re-word appropriately.

References:

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Kirkby, J., et al. (2011), Role of sulphuric acid, ammonia and galactic cosmic rays in atmospheric aerosol nucleation, Nature, 476(7361), 429-433.

Lee, S.-H., J. M. Reeves, J. C. Wilson, D. E. Hunton, A. A. Viggiano, T. M. Miller, J. O. Ballenthin, and L. R. Lait (2003), Particle formation by ion nucleation in the upper troposphere and lower stratosphere, Science, 301, 1886-1889.

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Yu, H., et al. (2013), Sub-3nm particles observed at the coastal and continental sites in the United States, J. Geophys. Res., Doi:10.1029/2013JD020841.

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Interactive comment on Atmos. Chem. Phys. Discuss., 15, 10629, 2015.