

## ***Interactive comment on “Atmospheric ions and nucleation: a review of observations” by A. Hirsikko et al.***

**Anonymous Referee #2**

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This is a review paper on the measurements of atmospheric ions and possible role of ions in new particle formation. The topic is important and appropriate for ACP. The manuscript is clearly written and easy to follow. I have a couple of comments which should be properly addressed before the final publication of the manuscript in ACP.

Main comments:

1. The relative importance of ion versus neutral nucleation pathways in the atmosphere is controversial. This manuscript reviewed in detail a number of previous measurements of air ions and analysis (most by co-authors of this paper) that concluded the dominance of neutral nucleation (>~90%). However, the work of opposite opin-

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ion (i.e., the dominance of ion mediated nucleation over neutral nucleation) was only mentioned very briefly. As a review paper, I think that it is useful and necessary to give more in-depth discussion about the possible reasons of difference in the interpretations with regard to the importance of ion versus neutral nucleation. Are there any uncertainties/limitations in both sides of arguments? Such insights derived from a comprehensive review of related works will be useful to the readers.

Yu (JGR, 2010, section 2.2) discussed the possible causes of the controversy and argued that Kulmala and colleagues might have underestimated the importance of ion-mediated nucleation, and the results of Laakso et al. (ACP, 2007) may actually support the significance of ion-mediated nucleation. The main argument of Yu (2010) is that Kulmala and colleagues assume that all neutral particles ~ 2 nm or growing into 2 nm are from neutral nucleation, which may lead to significant underestimation of the ion-mediated nucleation contribution because a significant fraction of neutral particles ~ 2 nm and smaller may be formed from the ion-mediated nucleation. The authors should comment on these arguments.

2. Equations 10 and 11. Based on Yu (2010)'s argument, many neutral particles smaller than 2 nm may form as a result of ion-ion recombination and thus should be considered as ion-mediated nucleation rather than neutral nucleation. It is apparent from Equation 11 that the ion-ion recombination contribution in authors' analysis only includes the recombination of charged particles between 2-3 nm with ions of opposite charge. It appears that the conclusions about the <10% contribution of ion-mediated nucleation are based on the assumption that all neutral clusters smaller than 2 nm are formed via neutral nucleation pathway. I don't think that this assumption is justified. If the authors consider the contribution of ion-mediated nucleation to sub-2 nm particles (including those neutral), their conclusion about the importance of ion-mediated nucleation may change significantly. At least, this implied assumption should be explicitly pointed out and possible effect on the conclusion (with regard to the importance of ion mediated nucleation) should be discussed and reflected in the summary and abstract.

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3. Page 24279, lines 21-25. Based on Yu (2010), the conditions for ion-mediated nucleation to be important can also be encountered in the lower troposphere (including boundary layer), especially at relatively high latitudes during the spring and fall seasons. This should be pointed out and discussed.

Other comments:

4. Page 24279, lines 11-18. It will be good to list those references suggesting the role of ammonia and other bases and those references pointing to ions separately.

5. Page 24291, lines 19-22. Please give some details about “the opposite has been observed”. Does it refer to the growth rate of particles larger than 3 nm? It is well known that the effect of ion in enhancing growth is generally very small for particles larger than  $\sim 3$  nm. What message do the authors want to convey in this sentence?

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