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Atmospheric Chemistry and Physics Discussions

Interactive comment on "On the roles of sulphuric acid and low-volatility organic vapours in the initial steps of atmospheric new particle formation" *by* P. Paasonen et al.

P. Paasonen et al.

pauli.paasonen@helsinki.fi

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Referee #1: This manuscript aimed to investigate the influences of sulphuric acid and organic vapors on atmospheric new particle formation rate. Though this is an important and fascinating topic, the reviewer feels that this work adds limited contribution to the field. The correlation between new particle formation rate and sulphuric acid has been systematically examined before (e.g., Weber et al., 1997, Riipinen et al., 2007; Kuang et al., 2008). Elucidating the role of organic compounds in atmospheric nucleation would be a significant development; however, the scientific approach and applied method in this manuscript need further justification. Rather than directly mea-

suring concentrations of low-volatility organic vapors, empirical methods were used to estimate them. Among many assumptions made while estimating organic compound concentration, using equation (1) implies that the uptake of organics by new formed particles is purelya physical mass transfer process, i.e., condensation. Though it has been observed that the uptake of H2SO4 by new formed particles can be modeled as the condensation process (e.g., Sipila et al., 2010), the uptake of organics are most likely limited by surface reactions rather than by mass transfer. Accordingly, equation (1) would underestimate the concentration of organic compounds. The estimated organics concentrations for four sites are 10ËĘ7 molecules/cm3 (Table 1), which are not surprisingly several orders below the concentrations directly measured during a recent campaign. Therefore, the proposed correlations between new particle formation rate and organic compounds, which are based on those estimated organics concentrations, are highly questionable.

Response: We do agree that all the organic vapour molecules colliding with the particle are not necessarily attached into it. The fact that the concentration of this/these organics determined with Eq. (1) is a minimum concentration required for the observed growth is mentioned in the text (page 12, lines 19-21). This subject could change the estimated concentrations of the organic vapours participating in the initial growth of the particles and the values of the nucleation coefficients related to organic involving models. However, it does not neglect the difference between the sites in terms of the coupling between H2SO4 and nucleation rate, nor that this difference is significantly reduced if the organic vapours are assumed to nucleate with or without sulphuric acid simultaneously with kinetic H2SO4-nucleation. Furthermore, the most recent studies on this subject seem to point out that the surface processes involved in uptake of organic vapours do play a significant role only in particle sizes larger than 4 nm (Wang et al., Nature Geoscience, vol 3, 2010). This result and the reference are going to be added to the manuscript.

Referee #1: The proposed homomolecular organic vapor nucleation, K[org]2, is primarily motivated by the data from Hohenpeissenberg site. It implies that organics alone (without H2SO4) can trigger atmospheric new particle formation events. The time dependent H2SO4 concentration along with particle size distributions should be included to justify this argument. In addition, only two nucleation events from this site were studied in this manuscript. The authors mentioned that "measurements at HPB are continuously running and corresponding data should become available soon". More nucleation events will certainly help to further evaluate the proposed mechanism.

Response: We used altogether 15 nucleation events from Hohenpeissenberg in the analysis, as shown in Table 1. Only two of these occurred during the late spring and summer months, these being the months when the data from the other sites was gathered. The data of these events is separated in some of the figures and discussed shortly corresponding to these figures. Nucleation rate on every data point is also compared with time dependent H2SO4 concentration, but in Hohenpeissenberg these quantities are not strongly coupled (Fig. 5, upper right, both red and black data points).

Referee #1: The authors assumed that the same organics responsible for particle growth are also responsible for atmospheric nucleation. This needs further justifications. In summary, additional work are required before the manuscript can be considered for publication at Atmospheric Chemistry and Physics.

Response: We do not claim that all the vapours growing the particles would participate in nucleation, even less that they alone would be responsible for it. Instead, we assume that those non-sulphuric acid vapours that are participating in nucleation (if any) could also be able to participate in the very initial growth of the particles. Whether this assumption holds or not, and can this be analysed with the growth rate closure method used in this manuscript, was the initial idea of this study. Our results seem to be more in favour than against this assumption, as nucleation at all the sites can be described with quite a simple and reasonable parameterization. However, as stated in the conclusions, more research from several perspectives needs to be made in order to gain more knowledge of the nucleation processes.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 11795, 2010.