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Atmospheric
Chemistry
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Discussions

Interactive comment on "Atmospheric nucleation: highlights of the EUCAARI project and future directions" *by* V.-M. Kerminen et al.

V.-M. Kerminen et al.

veli-matti.kerminen@fmi.fi

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I would like to thank Jan Kazil for his comments which were very helpful in improving the quality of this manuscript. Our detailed response to each of these comments is given below.

Comment: 1) Generalization of findings

"All the results obtained during EUCAARI indicate that sulphuric acid plays a central role in atmospheric nucleation, in addition to which other vapours, especially organic ones, are needed to explain the nucleation and the subsequent growth processes." (16499/12-15) Would this also hold in regions of the atmosphere where organic vapors, or e.g. ammonia, are not plentiful? An example would be the Pacific Ocean, and in

particular its upper troposphere, where concentrations of organics and ammonia are arguably much lower than over Europe.

We agree with the reviewer. The text in the abstract was modified as follows:

"All the results obtained during EUCAARI indicate that sulphuric acid plays a central role in atmospheric nucleation. However, also vapours other than sulphuric acid are needed to explain the nucleation and the subsequent growth particle processes, at least in continental boundary layers. Candidate vapours in this respect are some organic compounds, ammonia, and especially amines"

Comment: "Overall, our observations are indicative of frequent, yet moderate, ion-induced nucleation usually outweighed by much stronger neutral nucleation events in the lower troposphere." (16499/21) I do not object the finding, but a bit of caution may not hurt: Since the strong neutral nucleation events in the lower troposphere of the EUCAARI domain are likely caused by compounds such as organics, ammonia, amines, etc., it cannot be excluded that in the lower troposphere of regions where these compounds are less plentiful, say over the Southern Ocean, ion-induced nucleation may play a more important role.

We agree here as well. The text in the abstract and concluding remarks was modified into the following form:

"Overall, our observations are indicative of frequent, yet moderate, ion-induced nucleation usually outweighed by much stronger neutral nucleation events in the continental lower troposphere". Also the sentence on page 16527 (lines 28-29) was slightly modified:

"Finally, although ion-induced nucleation appears to be of minor significance in continental boundary layers, this is not necessarily the case in the free troposphere or above the oceans."

Comment: 2) Nucleation parametrizations The same argument on generalizing the validity of the results can be made for the nucleation parametrizations (16522/18-25) that have been derived from the EUCAARI field data: Do these work (or should they be expected to work) in environments that are very different (temperature, gas phase composition) from those at the field sites, such as over the open oceans, or in the upper troposphere?

This is a valid point. We added the following paragraph on page 16523 (after line 20, see also the comment 5 by the other reviewer):

“There are two issues worth mentioning here. First of all, the derivation of semi-empirical parameterizations, like Eqs. 4-11, is always subject to uncertainties in measured quantities. For example, there is up to 50% uncertainty in measured H2SO4 concentrations and even a slightly larger one in [NucOrg] due to uncertainties related to determining the growth rate of 2-4 nm particles (Paasonen et al., 2010). Likewise, formation rates of 2-nm particles (J2) may be up to a factor two lower or higher than the estimated ones due to uncertainties in measurements and data analysis (Manninen et al., 2010). Second, it is clear that Eqs. 4-11 are oversimplifications of the physical and chemical factors influencing the nucleation rate. These include the ambient temperature and relative humidity and the stabilizing effect of vapors other than H2SO4 and NucOrg, causing additional scatter in measured data points. Such factors need to be investigated more thoroughly in the future, along with the applicability of the current parameterizations outside the continental boundary layers.”

Note further that in the concluding remarks we have already stated that these parameterizations require theoretical improvements.

Comment: 3) Binary sulfuric acid-water nucleation "The new H2SO4–H2O nucleation experiments are in line with EUCAARI field observations" (16509/25)

The laboratory experiments treat nucleation of H2SO4 and H2O, and yet they are in line with the field observations? That sounds not right. It would mean that either the lab experiments have a problem with impurities (organics ?), which lead to a similar

nucleation process as observed in the field, or that the nucleation in the field is due to homogeneous nucleation of H2SO4 and H2O.

"Roughly the same number of H2SO4 molecules in a critical cluster and similar H2SO4 concentration levels needed for a given nucleation rate in both the laboratory and the ambient atmosphere suggests strongly that particles are formed via a similar H2SO4-driven nucleation mechanism in these two environments." (16510/7) Same thing: The laboratory experiments investigate binary H2SO4/H2O nucleation, but the nucleation process responsible for the nucleation observed in the field is likely a different one, for instance cluster activation. How can the two produce similar nucleation rates at comparable H2SO4 concentrations?

The reviewer is definitely correct here. The most plausible explanation for the agreement between lab and field data are impurities in binary nucleation experiments. This would concern practically all lab experiments conducted so far. We modified the last paragraph in section 3.2 into the following form:

“The new H2SO4–H2O nucleation experiments are in line with EUCAARI field observations (Figure 1). They both predict a slope between about 1 and 2 in a plot of the nucleation rate versus gaseous H2SO4 concentration, and require roughly the same amount of H2SO4 to initiate the nucleation process. These findings indicate 1) that particles are very likely formed via a similar H2SO4-driven nucleation mechanism in both the laboratory and the ambient atmosphere, and 2) that according to the nucleation theorem, critical clusters formed in the nucleation process contain only one or two H2SO4 molecules. Both laboratory and field measurements could be explained by either activation-type (Kulmala et al., 2006) or kinetic (McMurry and Friedlander, 1979) nucleation, but not by the thermodynamic binary H2SO4–H2O nucleation which predicts more than five H2SO4 molecules in a critical cluster under typical ambient conditions (e.g. Yue, 2008). This does not necessarily mean that existing binary H2SO4–H2O nucleation theories are wrong by themselves: it is possible that H2SO4–H2O nucleation is affected by the presence of impurities like ammonia, amines and various organic compounds. Such compounds are practically always present in the atmosphere, and low level of these compounds (impurities) cannot be excluded from current laboratory experiments."

Comment: 4) Nucleation probability In equation 3, the exponent in exp(-I*t) seems not to be unitless, as one would expect, is that correct? Also, please give a few more details on the nucleation time t.

The quantity I is the heterogeneous nucleation rate per particle, which has a unit of one over time. This has been clarified in the revised manuscript.

Comment: 5) Coagulation sink "... is their coagulation sink ..." (16525/1) Please give a few more details on the coagulation sink (= sink for coagulation on pre-existing aerosol?).

The text was modified into the following form: "...CoagS(dnuc) is their coagulation sink, i.e. the rate at which they coagulate with larger pre-existing aerosol particles,..."

Comment: 6) Manuscripts in preparation In several places, manuscripts that are in preparation are cited. I understand the difficulty of timing the publication of the results in a project of the size of EUCAARI, but still, it would be a more robust approach to cite only works that have progressed farther in the publication process. Maybe this is the case by now.

We updated the references and removed those which still are "in preparation".

Comment: 7) Ideology (16505/7) Maybe there is a better word than ideology.

The word ideology was replaced with the word approach.

Comment: 8) Bipolar ions (16506/3) This may be just my personal ignorance, but I don't know what bipolar ions are.

Admittedly, the used term may be misleading. We rewrote the sentence as: "...provides an excess amount of both negative and positive ions that..."

Comment: 9) References Missing umlaut in the reference Kulmala et al. 2009 (Pöschl) (16532/23)

Corrected.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 16497, 2010.