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Interactive comment on “Atmospheric sulphuric acid and aerosol formation: implications from atmospheric measurements for nucleation and early growth mechanisms” by S.-L. Sihto et al.

S.-L. Sihto et al.

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Response to Referee #1's comments

We would like to thank the referee for the constructive comments to our manuscript.

The main question pointed out by the referee was, how we can be sure that the nucleation takes place close to the ground based measurements. In fact, we do not say that nucleation and subsequent growth takes place at the measurement station. Particle formation process is expected to be a large scale phenomenon that extends over several hundreds of kilometers where meteorological conditions are more or less uniform. Small, freshly nucleated particles (~ 3 nm) are formed near the measurement site, but bigger particles are advected from a longer distance depending on the wind speed. For

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example, 10 nm particles may have formed about 5 h ago (assuming a growth rate of 2 nm/h from 1 to 10 nm), which implies that with a wind speed 5 m/s they must have formed about 90 km away from the station. Similarly, 3 nm particles would have been formed about 18 km upwind the station. If meteorological conditions remain sufficiently steady during the day, so that measurements at the station are made in the same air mass, we can assume that particles advected to the station belong to the same large scale nucleation event. Most events are observed on clear, sunny days when this condition is fulfilled. One evidence of the validity of this assumption is the quality of the particle formation event "banana plot": good, continuous "banana plot" with steady growth implies steady meteorological conditions while change in air mass results in rapid changes in concentrations and a fuzzy "banana plot". Dal Maso et al. (2005) have presented a scheme to classify particle formation events to different classes according to event characteristics. During QUEST II campaign there were exceptionally many good quality (class 1) events.

The referee discussed about the possibility of upper troposphere to be a potential place of new particle formation. Correlation of sulphuric acid and freshly nucleated particles (3-6 nm) with sometimes a fairly short time delay (about 1 hour) points to that particle formation probably takes place everywhere in the boundary layer when there is sufficiently sulphuric acid present. However, we can't definitely rule out the upper troposphere as a source of tiny clusters.

The main source for sulphuric acid (H_2SO_4) in the lower boundary layer is the gas phase oxidation of SO_2 . First SO_2 is oxidized by OH: $\text{SO}_2 + \text{OH} \rightarrow \text{HOSO}_2$, after which two reactions involving O_2 and H_2O lead to the formation of H_2SO_4 (see e.g. Finlayson-Pitts and Pitts, 2000). The formation rate of sulphuric acid is determined by the reaction of SO_2 and OH, the subsequent reactions are in normal conditions so fast that they do not limit the H_2SO_4 production. OH is a short lived radical that is produced by UV light. In Hyytiälä, SO_2 does not usually have strong variation during the day, and therefore H_2SO_4 production varies according to OH concentration that peaks at

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midday. The main sink for H_2SO_4 is condensation to particle surfaces. Because H_2SO_4 has a low saturation vapour pressure, it condenses easily and it is not expected to be transported in gas phase over long distances. H_2SO_4 concentration is thus governed by local OH concentration (production term) and condensation sink CS (loss term). Because condensation sink varies during the day much less than OH concentration, the diurnal profile of H_2SO_4 is set mostly by OH. During QUEST II campaign also OH measurements were performed, which lets us to investigate this connection. H_2SO_4 and OH correlated strongly: average of the daily correlation coefficients was 0.78.

Boy et al. (2005) have investigated this sulphuric acid production scheme with a chemical box model in connection with QUEST II campaign. The correspondence between calculated and measured H_2SO_4 concentrations was reasonably good: typically the estimated concentrations were within 20 % of the measured values and almost always within 50 %.

Detailed comments:

$CoagS_{3-6}$ is the average coagulation sink for the particles in size range 3-6 nm. To be exact, the coagulation loss term should be calculated:

$$\text{Coag. loss in 3-6 nm range} = \sum_{3\text{nm} \leq d_{p,i} \leq 6\text{nm}} CoagS_{d_{p,i}} N_i,$$

where $CoagS_{d_{p,i}}$ is the coagulation sink for particles of diameter $d_{p,i}$, N_i is their number concentration, and summation goes over DMPS size classes with diameter in range 3-6 nm. We approximate this summation by one term: $CoagS_{3-6} N_{3-6}$. For $CoagS_{3-6}$ we use the coagulation sink for 4 nm particles, $CoagS_{d_p=4\text{nm}}$: 4 nm is approximately the geometric mean of 3 and 6 nm (corresponding the mean value in logarithmic scale). This approximation for the coagulation sink gives reasonably accurate results in these calculations. The coagulation sink for $d_p = 4$ nm particles is calculated as follows:

$$\text{Coag}S_{d_p=4\text{nm}} = \sum_{d_{p,i} \geq 4\text{ nm}} K(d_p, d_{p,i}) N_i,$$

where $K(d_p, d_{p,i})$ is the coagulation coefficient (collision frequency function) between particles of diameter $d_p = 4\text{ nm}$ and $d_{p,i}$ (see e.g. Seinfeld and Pandis, 1998).

In Equation 3 "2 nm" means difference in diameter: $\Delta d_p = 3\text{ nm} - 1\text{ nm} = 2\text{ nm}$. We add this to the article to make the equation clearer.

We didn't estimate the contribution of sulphuric acid to the growth of 3-6 nm particles. Boy et al. (2005) estimated that on 11 nucleation events during QUEST II campaign the sulphuric acid contribution in 3-25 nm size range was 5-17 % and on average about 9 %. Previous study of Hyytiälä data by Boy et al. (2003) gave sulphuric acid contribution of 4-31 %. These values imply that other compounds (most probably organic vapours) have a considerable effect on particle growth. In this study, the contribution of sulphuric acid to the growth between 1 and 3 nm was estimated to be on average about 50 %, and it was increasing with increasing sulphuric acid concentration (see Fig. 3). This contribution is much greater than that estimated for 3-25 nm particles in previous studies. The results however do not contradict each other: it is expected that the contribution of sulphuric acid is greatest in small particles, because organic vapours most probably have greater saturation vapour pressures than sulphuric acid, and thus they don't condense as easily to small particles. In 3-6 nm size range the contribution of sulphuric acid to the growth is presumably close to or slightly less than that in 1-3 nm range.

We observed that the nucleation coefficients A and K had some correlation with terpene oxidation products. Whether the correlation is related to nucleation process or growth to detectable size of 3 nm, is still an open question. To be able to draw conclusions from this correlation, more experimental and theoretical knowledge on the nucleation process and analysis of bigger data sets are needed.

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We agree with the referee that the analysed data set, 15 days, is fairly short time period and certainly more data analysis is required. The analysed particle formation events are typical for that time of the year in Hyytiälä. The maximum number of events is observed in spring, when new particle formation occurs about 48 % of all days (Dal Maso et al., 2005). During QUEST II campaign events were observed even more frequently due to favourable meteorological conditions. In their characteristics the analysed 15 events are typical springtime events, and thus they form a representative set of particle formation events in Hyytiälä.

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