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Interactive comment on "Model for acid-base chemistry in nanoparticle growth (MABNAG)" *by* T. Yli-Juuti et al.

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Reply to the comments from Anonymous Referee 2. Comments from the referee are written on italics and our reply on normal font.

In the manuscript, the authors presented a "Model for Acid-Base chemistry in Nanoparticle growth (MABNAG)" to inveatigate the dynamics of condensational growth and its coupling with the particle phase chemistry. The systems with sulfuric acid, one kind of organic acid, ammonia, one kind of amine, and water were studied. In the MABNAG model, it was assumed that the growth rate is limited by condensation of sulfuric acid and organic acid, with a fast (instantaneous) equilibrium between the particle and the gaseous water, ammonia, and amine. Because of this assumption, their derived *growth rate of nanoparticles corresponded to the upper limit of the actual growth rate. In reality, the assumption is only reasonable for water but not for ammonia and amine, since in the atmosphere the concentration of water is typically 108-9 times higher than those of ammonia and amine. A more accurate model also needs to treat the condensation of ammonia/amine dynamically. In the current study, the assumption is accurate enough for an upper limit estimation. Based on the assumption, at each step, (1) the equilibrium of water, ammonia, and amine with the particle is maintained, while the equilibrium saturation vapors of sulfuric acid and organic acid are calculated (Peq,i). (2) Using equation (1), a new composition is obtained, which is used for calculating the new equilibrium. Performing (1) and (2) iteratively, the growth rate of nanoparticles can be obtained. According to their simulations, the authors claimed that the amine concentration affected the growth rate less than organic acid concentration, which is obvious according to their assumption. Overall, the material presented in the manuscript is interesting and may be publishable, pending revisions as outlined below.*

We would like to thank Anonymous Referee 2 for his/her comments that helped improving the manuscript. While we agree with the referee in that the equilibrium assumption may overestimate the condensation of amine, we disagree with the referee's statement about the reasonability of the equilibrium assumption for ammonia. As stated also in the manuscript, ammonia is a small molecule, like water, and is expected to equilibrate in similar times scales with water and clearly faster than sulfuric acid and the organic acid. Therefore, we consider the equilibrium assumption between gas and particle phase to be very reasonable for ammonia. On the other hand, like also the referee pointed out, our aim was to make an upper limit estimate for the salt formation and therefore the equilibrium assumption is well justified also for the amine.

We do not think that the result of organic acid concentration affecting GR more than amine concentration is obvious as in such a system with multiple compounds the processes may be non-linear. Further, that result is not caused by our assumption of equilibrium gas-particle partitioning for amine. As the equilibrium assumption is an upper limit estimation for the condensation of amine, one expects that dynamic calculation of condensation of amine would decrease the effect of amine making the importance of the organic acid over amine clearer for the growth. While including dynamic mass flux calculations for amine in the model is an important addition in the model in the future, the current version serves well the purpose of this study (upper limit estimation for the effect of salt formation). This model is also unique in that, for the first time, it represents nanoparticle growth with detailed particle phase thermodynamics for acid-base chemistry in an atmospherically relevant mixture of compounds and is thus a necessary step towards comprehensive understanding of the atmospheric nanoparticle growth.

Please see our detailed response for the comments by Referee 2 below.

(1) On page 7190 line 27, the authors claimed that "the mass fractions of the bases decreased simultaneously with the mass fraction of sulfuric acid during particle growth suggesting that the condensation of the bases on the particle was driven by the neutralization of sulfuric acid instead of organic acid". This statement was wrong. The decrease of basic species percentage was because of the basic species was limited (Figure 4 panel d->e->f). If the basic species were not limited, the mass percentage of basic species would not decrease (Figure 4 panel g->h->i). Figure 4 panel i clearly shows that the basic species also react with organic acid in the particle phase. Also, the topic of the base-organic acid reaction on nanoparticle growth has been suggested previously (Chem. Rev. 112, 1957, 2012; Phys. Chem. Chem. Phys. 15, 5738, 2013), but those relevant literatures were largely ignored here.

We agree that organic acid also reacts with the bases and we did not intent to state otherwise. However, unless base concentrations are elevated, most of the bases go into neutralization of sulfuric acid, leaving most of the organic acid in its non-dissociated form. To clarify this we have revise the text in the following way:

'In most cases, the fraction of bases in the particle dry mass decreased as the particle size increased (Fig. 4) and therefore the contribution of bases on the particle mass is highest for the smallest particles. In these cases, most of the particle phase bases were used for neutralizing sulfuric acid, and as a result the mass fractions of the bases decreased simultaneously with the mass fraction of sulfuric acid during the particle growth.'

In the revised manuscript we have also added references to the papers that the referee mentioned.

(2) For Figure 4, it would be better if the mass percentage was presented in mole percentage, which would make it easier to compare the relative abundance of basic to acidic species. For example, in Figure 4 panel i, it appears that basic species are less than acidic species. However, if the mole percentage is used, the percentage of basic and acidic species may be equal.

We chose to present mass fractions because they are more easily comparable to particle composition measurements (which are often reported as mass fractions) than mole fractions and because from mass fractions one can easily see the direct contribution of each of the compounds on the particle GR. However, we agree that mole fractions may be practical when looking at the acid-base interactions and in the revised manuscript we have added Fig. 5 which is the same as Fig. 4 but presents the molar fractions and we have also added molar fractions in the Fig. 7 (=old Fig. 6).

(3) From Figure 7(c), it is even evident that organic acid reacts with ammonia. At size of 40 nm, the mole fraction of organic acid2- is close to the half of NH4+. This half coefficient is a result of charge conservation. I suggest that the authors replot all the mass percentage in mole percentage or at least present both.

Yes, this is correct, and we do state also in the text (at the end of the sect. 4.5) that 18-40 % (depending on the particle size) of the organic acid was predicted to dissociate on the case study day. The dissociated fraction of organic acid is neutralized mostly by ammonia. We have added molar fractions in the figures (see reply to the above comment (2)).

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 7175, 2013.