

Final response to the referee comments

MS No.: acp-2013-277

We thank the reviewer for the helpful remarks on our manuscript. Please find our point-by-point responses below.

Referee 2:

1. In this manuscript the authors conclude that oxidized organics are not important to the formation and growth of new particles (e.g. page 16302, lines 11-13). However, it is not always clear exactly what organics the authors are referring to. Are they referring only to first generation oxidation products? A fair amount of evidence now suggests that oxidized organic matter is crucial to the formation and growth of new particles, although most of these species may be the result of several generations of oxidation. If the authors are referring in this manuscript only to first generation oxidation products, then why are they invoking the presence of highly oxidized products as possible candidates to explain the observations from the PHA-UCPC (page 16311, lines 5-14)? It seems that these are two opposed possibilities. If the only first generation oxidation products are formed, then one should not expect highly oxidized products to contribute to nanoparticle growth. In short, the explanation of what organics are/are not contributing to growth and their respective oxidation levels is not very clear and needs to be made more precise.

Reply:

We did not give a precise definition of oxidized organics in the manuscript and will include a respective definition into the next version of the paper. Thereto we'll adopt the following line of thought: Due to the short residence times and under the conditions prevailing in our flow tube experiments, we have to expect that nearly exclusively oxidation products of the first generation are formed. These first generation oxidation products comprise of a series of organic acids as low vapour-pressure products, see for example Yu et al., *J. Atmos. Chem.*, 34, 207-258, 1999. However, there are some indications from different recent experiments by various groups that highly oxidized products maybe formed very rapidly as stable first generation products as well. These products have been found in course of atmospheric observations (Ehn et al. (*Atmos. Chem. Phys.*, 12, 5113-5127, 2012), and at this stage we cannot rule out their existence in our experiments. In fact, some PHA-UCPC measurements are indicative for large molecules or clusters (maybe the highly oxidized organics) formed from terpene ozonolysis for conditions of very low H<sub>2</sub>SO<sub>4</sub> concentrations. Consequently we define first generation oxidized organics as the "classic" organic acids plus the potentially present highly oxidized products. It should be noted, that we are not able to give any statements regarding the "oxidation level" of the oxidation products as a result of this study and the analytical techniques applied here.

2. The amine background levels (107 – 108 molecule/cm<sup>3</sup>, page 16302, line 5) seem to be comparable to typical ambient levels (page 16304, lines 10-13). Was any effort made to reduce the amine contamination? Additionally, it is not clear in the manuscript if or how amine concentrations were measured (e.g. page 16316, lines 10-14). If no reliable way of measuring the concentration was available, how were the amine concentrations approximated?

Reply:

As a result of the extrapolation of measured particle numbers to zero amine addition we had to conclude that there were possible amine contaminations equivalent to the presence of  $10^7$  molecule  $\text{cm}^{-3}$  of trimethylamine or  $10^8$  molecule  $\text{cm}^{-3}$  of aniline. A possible source is the water used in the humidifier. We tested different water qualities and also the acidification of the humidifier water as described by Ball et al. (*J. Geophys. Res.*, 104, 23709-23718, 1999), but without a change or “improvement” regarding the possible amine background. As the carrier gas we used commercial synthetic air (99.999 vol%, Air Products) with further purification using GateKeeper. The feed air from Air Products was also substituted by air from a commercial PSA (pressure swing adsorption), further purified in columns with highly activated molecular sieve and activated charcoal, and then in a next step by GateKeeper. Also here, no clear change was observed.

We didn't measure the amine concentrations directly. However, we are able to produce well defined, diluted amine samples using a gas metering unit based on absolute pressure measurements. These amine samples are further diluted with the carrier gas at the entrance of the flow tube to establish the final tube concentration. The same procedure has been done with  $\text{NH}_3$ . In the case of  $\text{NH}_3$  we were able to measure the resulting  $\text{NH}_3$  concentration after final dilution at the flow-tube inlet and outlet by means of a sensitive  $\text{NH}_3$  detector OMNISENS TGA310, see Berndt et al., *Atmos. Chem. Phys.*, 10, 7101-7116, 2010. After an equilibration time of about one hour stable  $\text{NH}_3$  concentration were measured at the inlet and outlet being close to the expected concentration as calculated from the diluted gas sample. For the amines we assumed the same behaviour as measured for  $\text{NH}_3$ . The measurements showed that also in the case of amine additions about one hour was needed to adjust stable nucleation conditions (constant particle numbers) in the tube. The given amine concentrations are the calculated values at the tube entrance. In the beginning of paragraph 4.4, p.16316, this procedure is described shortly. Obviously, that was not explained clearly enough and will be treated more comprehensively.

3. The authors conclude that in the first set of experiments (where no amine was added) about half of the growth was due to sulfuric acid condensation (e.g. page 16320, line 5) and imply that the rest of the growth (by volume?) was due to amines, despite no amines being intentionally added to the setup. It seems a bit unreasonable that ammonia and amines make up the other 50% of the growth, since they would be much smaller in volume (and mass) than sulfuric acid. The authors should explain in more detail why it is reasonable to assume amines and ammonia are responsible for 50% of the growth.

Reply:

We have to clarify that it's not stated in the manuscript that 50% of the growth is caused by any amines. It is stated that  $\text{H}_2\text{SO}_4$  accounted for roughly half of the growth observed. Possible substances, also involved in early growth, are amines, water vapour,  $\text{H}_2\text{SO}_4$ (amine) dimers or larger cluster. In the first set of experiments no amines were added. But nevertheless, we have to assume an amine background of  $10^7 - 10^8$  molecule  $\text{cm}^{-3}$ . A possible contribution of organic oxidation products to particle growth under our conditions can be not totally ruled out, but is expected to be very small due to the growth rates by organics reported in the literature, cf. Riccobono et al. (*Atmos. Chem. Phys.*, 12, 9427-9439, 2012). An upper limit estimate yields a diameter increase of only 0.028 nm for our growth time of 50 sec (0.4 - 0.6 nm due to  $\text{H}_2\text{SO}_4$ ).

We are not able to distinguish between the possible participants (amines, water vapour,  $\text{H}_2\text{SO}_4$ (amine) dimers or larger cluster) probably involved in the growth. It's simply a list to show what substances can be responsible for the remaining growth beside  $\text{H}_2\text{SO}_4$ .

Minor Comments:

4. Figure 3: It was not clear to this reviewer what the different lines refer to in this

figure. Particularly, what does the dotted line represent?

Reply:

The dashed line in Fig.3 should help to separate the data from the PHA-UCPC and the TSI 3025 because the data from both counters started to merge for relatively high  $\text{H}_2\text{SO}_4$  concentrations. The full lines connect the particle data measured from photolysis experiments.

5. Page 16304, line 5, and page 16318, line 12: Wikipedia should not be used as a source. The authors should find an appropriate reference, perhaps from the CRC Handbook.

Reply:

The referee is right. We will use a more appropriate reference.

6. Page 16304, lines 2-4, and page 16318, lines 17-20: The authors should search and reference appropriate literature studies of effects of gas phase basicity and molecular structure of amines in sulfuric acid clusters.

Reply:

In the manuscript we argued only with the amine basicity for simplicity. We will follow the referee's suggestion.

7. Page 16305, line 17: "form" should be "from".

8. Page 16313, line 13: "dominate" should be "dominant".

Reply:

Required changes will be done.