**Atmospheric
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Comment

Interactive comment on "Volatility of secondary organic aerosol during OH radical induced ageing" *by* K. Salo et al.

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1. Page 19510, lines 8-14: Is this paragraph correct? Don't radicals diffuse to a particle faster than they do to a molecule since a particle is larger? I thought the reason reactions of radicals with molecules in particles were slower was that the radicals reaching the particle surface only see a small fraction of the molecules, and that once they penetrate into the particle diffusion is slower. Perhaps it would help to be more precise about whether you are talking about the rate of removal of an organic molecule or a radical.

Answer: We agree that the paragraph might be confusing and will modify it by moving and rephrasing the statement based on the Lambe et al. 2009 reference. (it is now found after gas phase discussion and before descriptions on the bulk phase limita-

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tions). The modified paragraphs, with the changed statements within **statement** will be:

"In the atmosphere, during daytime, the subsequent oxidation of ozonolysis products will most likely occur via reaction with the OH radical. The OH radical reacts with saturated VOCs by hydrogen abstraction, which forms a water molecule and an alkyl radical. This is followed by the fast addition of O2 to form peroxy radicals. The radicals formed in these reactions will take part in further reactions to form a wide array of products in the atmosphere. The OH radical reaction with organic compounds in the gas phase often occurs within an order of magnitude of the diffusion limit. **As outlined by Lambe et al., 2009 (see supplement) the heterogeneous reaction of OH radicals with the SOA particles should be slower by more than an order of magnitude than the homogeneous reactions with the gas phase of the aerosol.** It is not fully clear how fast OH reactions proceed in the SOA condensed phase (George et al., 2010); however, recent laboratory studies indicate the possibility of oxidation, accelerated by photo-sensitized reactions (D'Anna et al., 2009). In the condensed phase the reaction may be mass-transport limited. For example, SOA may form a viscous liquid or an amorphous solid state that significantly reduces the liquid phase diffusion (Zobrist, Marcolli et al. 2008; Buchholz 2010; Virtanen, Joutsensaari et al. 2010). That would probably confine OH reactions to an outer shell of the particles."

2. Page 19514, line 20: What values of densities were used?

Answer: The density used were (1.25 ± 0.10) g cm-3 for α-pinene and (1.3 ± 0.2) g cm-3 for limonene (Saathoff, Naumann et al. 2009). These values will be written out in the text in order to avoid confusions.

3. Page 19514, lines 22-25: Since semi-volatile compounds are of interest, what was done to evaluate possible evaporation in the sampling lines and adsorption to tube walls? At these low aerosol concentrations I would expect that the tube walls have the capacity to adsorb a large fraction of the semi-volatile compounds for a long time.

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Answer: It is true that SVOCs can be lost in the sampling lines. This can cause loss of information especially when sampling volatile particles e.g. during the low temperature experiments in the AIDA chamber. In this specific study only metal (copper or stainless steel) tubing were used during the experiments to minimize uptake of SVOCs. In addition, the measured final particle diameters after evaporation (Df) were normalised to the initial diameters (Di) measured after passing through the reference oven at 298 K. This implicates that all VFRs (VFR= (Df/Di)3) reflects the difference in particle material evaporated in the heated zone of the ovens. Still in this and similar studies one might be concerned about pre-conditioning of the aerosols in the reaction line, as pointed out by the reviewer. The magnitude of this pre-conditioning is reflected by the stability of the reference diameter (i.e. caused by evaporation in the lines, the first DMA and the ovens held at the reference temperature). The stability of the reference diameter was better than 0.5% for most of the experiments and up to 2 % in extreme cases. For the general reproducibility of this type of volatility measurements one can refer to a previous study by Jonsson et al. 2007.

To clarify the raised issue of evaporation in the lines, the experimental section in the manuscript was modified:

"The final particle mode diameter (Df) after evaporation was monitored for a number of temperature settings and normalised to the initial particle mode diameter (Di) determined after the aerosol passed the oven while hold at the reference temperature (298 K). The Volume Fraction Remaining (VFR) was determined as VFR = ((Df)/(Di))3, assuming spherical particles. This procedure was applied to ensure that any changes in Dp was a result of evaporation in the oven unit and to reduce any artefacts from possible evaporation in the sampling lines. The general reproducibility of the method is described in Jonsson et al, 2007. (Jonsson, Hallquist et al. 2007)"

4. Page 19515, lines 2-11: Since NH4NO3 particles are also rigid, don't they bounce? How can one correct for bouncing loss of rigid particles by using other rigid particles?

Answer: The reviewer addresses correctly a problematic issue. For the conclusions of the paper this is fortunately not relevant, since SMPS –volume and AMS-mass where highly correlated as soon as the modal maximum was larger than 85 nm. In this sense we have an in-situ calibration using the effective density which was derived from the modal positions in volume and mass assuming spherical particles. Besides of that there is a small error in the manuscript: with ammonium nitrate we determine the ionization efficiency of nitrate and not the relative ionization efficiency. This will be corrected. (All procedures regarding the AMS were standard procedures. In principle we determine the effect of both CE and IE, which cannot be separated so easily, but this is not an issue for this manuscript). We don't really understand why the CE for the organics is so low. We applied the usual RIE = 1.4 for organics. Using RIE= 1.4 we found in previous studies for BSOA generated from precursor mixtures agreement between AMS and SMPS better than 20% (e.g. Kiendler - Scharr et al, 2009). Matthew et al. 2008 investigated CE relative to NH4NO3 and stated: The higher CEs for liquid particles compared with solid particles were attributed to wet or coated particles tending to stick upon impact with the AMS vaporizer, while a significant fraction of solid particles bounced prior to vaporization/detection. We tried to offer bouncing of rigid organic particles as a rationale for our low CE. We have indication that the particles generated from α-pinene were solid as they shrunk with increasing RH before they grow again in HTDMA measurements (Buchholz 2010). The BSOA generated from precursor mixtures do not show such behavior. Solid SOA particles would be in agreement with the findings of Virtanen (2010).

Regarding the questions of bouncing of ammonium nitrate, we would argue that ammonium nitrate is a very hygroscopic substance with low tendency to crystallize when dried in a diffusion dryer. The particles could be solid but "soft". According to Matthew et al. 2008 ammonium sulphate has a lower CE than ammonium nitrate (both solid salts). The issue of bouncing cannot be resolved within this manuscript and it distracts from the relevant findings.

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Consequently, we will skip the bouncing argument as it seems to be misleading (page 19515, row 8-10). In addition we will be more specific regarding the AMS sampling set up. The new parts of the manuscript now read (with changed sentences within ** sentence **):

"In the SAPHIR chamber the number size distribution was measured by a TSI SMPS3080 system equipped with a TSI UWCPC3786. The SMPS system was connected to the chamber by a 3m long vertical and 50cm long horizontal stainless steel line. **The HR-TOF-AMS sampled from the same vertical line with a 130 cm horizontal line, which was pumped with a total flow of 380ml /min.** The analysis of the particle data in SAPHIR was based on the combination of AMS and SMPS data. First, the effective density rho_eff was calculated from the modal positions of the volume respective the mass size distribution as observed by SMPS and AMS (Bahreini et al., 2005) yielding an average _eff of **1.3 ± 0.1 g cm-3,** in good agreement with values reported previously by Saathoff et al. (2009). The SMPS data were converted to particle mass by applying rho_eff. **In the evaluation of AMS data we applied a relative ionization efficiency of 1.4 (relative to ammonium nitrate) for the SOA.** The organic mass observed by AMS was highly correlated with the SMPS derived mass (R = 0.9997); however, the absolute values were significantly lower by a factor of 0.38 ± 0.01.Herein only data with mass modal positions >85nm were considered to ensure that all particles were well within the working window of the aerodynamic lens. The slope indicates a reduced AMS collection efficiency of about 40% compared to NH_4NO_3 particles that were used for calibration **of the ionization efficiency. At the moment we cannot explain why this is the case, however, reduced collection efficiency has been observed before in lab and field studies (Matthews et al.2008).** "

5. Page 19517, line 29- page 19518, line 2: How is it known that only acidic vapours deposit on the walls? Please provide a reference for this.

Answer: Independent AIDA experiments with non acidic substances like acetone, pentanol, pinonaldehyde, and terpenes showed very small wall losses. In contrast, acidic

compounds like nitric acid, pininc acid, or pinonic acid are rapidly and irreversibly lost to the walls of the well stirred ADIA on time scales in the order of 1000-10000 s. Therefore, we will modify our statement to:

"SOA losses in AIDA are dominated by irreversible deposition of acidic vapours to the chamber walls with a time constant of_$\sim(1.8–3.8)\times10-4$ s-1 as determined from the COSIMA simulations also in experiments with pure acids in the AIDA chamber (Müller et al., ACPD, 2011) and in agreement with previous studies (Saathoff et al., ACP 2009)."

6. Page 19518, lines 6-7: Might use of a fan in SAPHIR but not AIDA lead to differences in results, for example by enhancing transport of particles and vapours to walls?

Answer: Yes, the use of fans influences the wall effect and there was a difference between the two chambers. In the paper we explicitly provide loss rates for both chambers and for the conditions used. In AIDA the fans were always on while in the SAPHIR conditions both with and without fans were applied. We think this is clearly stated in the paper in its current form.

7. Page 19520, lines 19-27: How was it determined that SOA losses in SAPHIR are dominated by dilution and particle deposition on walls, and that vapour loss was not important? How does one separate the effects of dilution on the evaporation of vapours from particles from the evaporation of vapours from Teflon walls? Are the timescales for these processes known? It might help to show a figure of the results for SAPHIR comparable to Figure 3 for AIDA. This would make a nice comparison.

Answer: In this context the main statements compares VFR in AIDA and SAPHIR and uses the argument that AIDA walls are a stronger sink for acidic gases than the SAPHIR walls. It is not intended to make statements of importance of vapor wall losses in SAPHIR. The SAPHIR chamber has a compensating flow of 9 m3 h-1 for sample taking and to keep up 50 Pa over pressure. This dilution is significantly larger than in the AIDA chamber. The magnitude of the dilution in the two chambers is quantified by direct measurements. The additional losses can be parameterized as first order

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loss of the aerosol volume, as explained in the paper. The detailed mechanism behind these losses is not clear. Since the observed losses are higher when the ventilator is switched on and higher during the daytime it is likely that they a related mainly to transport of particles to the walls. If the main loss would be vapour deposition we would expect larger losses in the colder nights. It may be noted that the Pinonaldehyde loss has been quantified in SAPHIR and it is dominated by flush out.

Regarding Figure 3: This type of experiment was not done in the SAPHIR experiments. However, Figure 4 (AIDA) and 5 (SAPHIR) can be compared. Figure 4 includes the detailed COSIMA model results that are only applicable to the AIDA chamber.

We prefer to not speculate further on the detailed mechanism and think that the information provided are sufficient for the current paper.

8. Were there any surprises or new insights from these experiments? One can get the feeling from the clear and confident interpretations that the authors almost knew ahead of time what they would see, and that the results fit a little too neatly into their conceptual model.

Answer: We are happy that the reviewer appreciates our clear and confident interpretations. However, there has been a lot of hard work in achieving this. From a starting point in 2008 when the first AIDA measurements were done we were very surprised about the dip in VFR when exposing the mixture to additional OH radicals. We expected that the oxidation by the OH radical should lead to a less volatile aerosol. We can now by using the evaluated results from the experiments and corresponding modeling demonstrate that gas-phase oxidation of secondary products leads to a more volatile aerosol which is clearly a new insight into the field of SOA.

Technical Comments Page 19508, lines 6 and 7: Are KIT and FZJ acronyms? Please define.

Answer: Yes, Karlsruhe Institute of Technology (KIT) and Forschungszentrum Jülich,

Research Centre Jülich (FZJ). Explanations for these acronyms are added in the text when they first appear.

References: Buchholz, A. (2010). Secondary Organic Aerosols: Chemical Aging, Hygroscopicity, and Cloud Droplet Activation. Köln, Mathematisch-Naturwissenschaftliche Fakultät, Universität zu Köln

Jonsson, Å. M., M. Hallquist, et al. (2007). "Volatility of secondary organic aerosols from the ozone initiated oxidation of a-pinene and limonene." Journal of Aerosol Science 38(8): 843-852

Kiendler-Scharr, et al. "Aerosol Mass Spectrometric Features of Biogenic SOA: Observations from a Plant Chamber and in Rural Atmospheric Environments" Environ Sci Technol 43(21):8166-8172 (2009)

Müller et al, "Formation of 3-methyl-1,2,3-butanetricarboxylic acid via gas phase oxidation of pinonic acid – a mass spectrometric study of SOA aging", Atmos. Chem. Phys. Discuss., 11, 19443–19476, 2011

Saathoff, H., K. H. Naumann, et al. (2009). "Temperature dependence of yields of secondary organic aerosols from the ozonolysis of alpha-pinene and limonene." Atmospheric Chemistry and Physics 9(5): 1551-1577

Virtanen, A., J. Joutsensaari, et al. (2010). "An amorphous solid state of biogenic secondary organic aerosol particles." Nature 467(7317): 824-827

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