

Response to Referee's (#1, acpd-14-c2874-2014) comments for  
"Cloud droplet activity changes of soot aerosol upon smog chamber ageing"  
doi:10.5194/acpd-14-8851-2014

We would first and foremost thank the editor and referees for the helpful comments and remarks. By highlighting the weak spots we have been able to improve the paper.

NOTE! The first page no. refers to the published MS in ACPD, the second page no. (inside the brackets) refers to the revised MS that is sent to the Editor. Also, a detailed list of the changes made has been sent to the Editor.

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Answer to General Comments:

In an attempt to meet the request from the referee of been sent back and forth the Experimental and Instrumentation sections (4 and 4.1) have been moved before the Theory and Modelling sections (2 and 3). Also, the figure order has been changed. Also some changes have been made in an attempt to streamline and straighten the MS, listed below.

The focus of the paper is the cloud droplet activity and how the hygroscopicity of the soot particles changes with organic coating or ageing. Therefore the introduction of the ADCHAM model has been kept short, although a small addition is made, not to mislead the reader of the focus. ADCHAM has been used (as stated in Sec. 3.2) "in order to better understand the mechanisms responsible for the observed changes in SOA coating, chemical composition and hygroscopic properties". Hence, the model is merely for support and to bring the discussion further.

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Answer to Specific Comments:

**Introduction:**

This section have been changed somewhat in an attempt to meet the request of straightening and strengthen the introduction.

**IVOCs**

IVOCs have been changed to "Intermediate volatility organic compound" and a reference (Donahue et al., 2009) has been added to the MS at pg.8874, line 17 (MS: pg.22, lines 1-2) The division of VOCs according to Donahue et al. (2009) is generally accepted in the literature as described below:

"Low Volatility Organic Compounds (LVOCs):  $C^* \cdot \{0.01, 0.1\} \mu\text{g m}^{-3}$ . These compounds are mostly in the condensed phase in all but the most remote (and warm) parts of the atmosphere. Semi-Volatile Organic Compounds (SVOCs):  $C^* \cdot \{1, 10, 100\} \mu\text{g m}^{-3}$ . Significant fractions of these compounds will be found in both phases under typical conditions.

**Intermediate Volatility Organic Compounds (IVOCs):**  $C^* \cdot \{10^3, 10^4, 10^5, 10^6\} \mu\text{g m}^{-3}$ . These compounds are almost entirely in the gas phase, but they comprise an enormous number of difficult to measure compounds and (probably) a small but important fraction of the total atmospheric burden,..."

### “Soot in the Arctic”

The paragraph on “soot in the Arctic” has been moved to an earlier and more general part of the introduction and somewhat changed to meet the request of the referee (#1).

### Köhler theory

Köhler theory is introduced briefly in the Introduction (Sect.1) to get some background and motivation to why it is important to use the Köhler theory in this study. However, the Köhler equation is more thoroughly described in the Theory section (an addition has been made in the manuscript with reference to this section). In this paragraph the most common biogenic organic aerosol studies are listed to show the wider amount of studies performed in the field. The latter paragraph lists other kinds of studies as well as the studies regarding biogenic SOA above (gas phase and diesel soot particle SOA - anthropogenic, biogenic SOA, and ambient air) using the parameter  $\kappa$ . Hence, the two paragraphs have different foci.

Regarding the hygroscopicity of soot in general:

pg.8855, lines 4-5 (MS: pg.4, lines 12-14) in the Introduction states: “Freshly emitted soot particles are hydrophobic or limited in hygroscopicity and unlikely to contribute to the CCN population in the atmosphere (Weingartner et al., 1997; Meyer and Ristovski, 2007; Zhang et al., 2008; Tritscher et al., 2011).”. Furthermore, it is stated that “non- or slightly hygroscopic compounds have a  $\kappa$  equal or close to zero” at pg.8857, line 13 (MS: pg.5, lines 29-30). Followed by the examples of  $\kappa$  for diesel exhaust. Due to the hydrophobicity of soot,  $\kappa$  is equal to zero for an uncoated soot particle (as defined at pg.8857, lines 12-13; MS: pg.5, lines 29-30). Many particles in the ambient air contain soot (e.g. Liu et al., 2013), but the soot fraction in the particle does not always reflect the obtained  $\kappa$  of these particles. Therefore, only the chamber experiment of Trischer et al. has been referenced. An addition on untreated soot particles has been made (pg.8857, line 14; MS: pg.5, line 30). Pure soot in the ambient air is hard to measure (if existing), therefore are  $\kappa$  values of ambient air listed (see answer above).

### Rissler’s $\kappa$

pg.8857, lines 4-9 (MS: pg.5-6, lines 31-32 and 1-3): The two different  $\kappa$  has been introduced to acknowledge that the  $\kappa$  was first suggested by Rissler. The definitions of the different  $\kappa$  are similar (as described in the paper) and easy to translate. It doesn’t matter which one to use. However, the  $\kappa$  introduced by Petters and Kreidenweis is more commonly and broadly used and therefore we have decided to use that one. But to clarify to the readers, both  $\kappa$  are introduced.

### Shape and morphology

The diameter of the agglomerated soot particles will be different depending on measurement techniques. For example, the non-spherical shape of a fresh soot aggregate will have a larger mobility diameter (measured by the DMA) than the volume equivalent diameter, as discussed in the paper. Knowledge of the structure is thus needed to relate mobility diameter to particle volume and mass. Additionally, the agglomerated shape of the freshly emitted soot particle might be able to hinder the water uptake (according to what is stated in the literature). The branches, made of soot primary particles, are unfavourably both changing the curvature of the surface area and there is also a possibility of unevenly distributed organic material, which “hide” in cavities and voids (discussed in the result section). An addition is made (pg.8855, line 6; MS: pg.4, line 14-16) to highlight the difficulties when using different measurement techniques.

### **Sect. 3.2 (now 4.2) ADCHAM:**

The gas- and particle- phase chemistry is complex and hard to understand and the partitioning is not known. The kappa-Köhler theory deviates from measured results in the early ageing process (when the amount of organic material is small) and to support our assumptions and bring the discussions further the Aerosol Dynamics, gas- and particle- phase chemistry model for laboratory CHAMber studies (ADCHAM) was used. The results from the model are used for the molar mass of SOA (pg.8862, lines 19-21; MS: pg.15, lines 4-5). Otherwise, the general behaviour of the model results is used in the discussion. A clarifying addition is made in the text (pg.8864, lines 4 and 8; MS: pg.16, lines 11-13 and 15-21): “ADCHAM is a model primarily intended to be used to recreate laboratory chamber experiments on SOA. The model explicitly simulates the deposition and re-evaporation of organic compounds from the chamber walls, all fundamental aerosol dynamics processes, detailed gas- and particle- phase chemistry and the mass transfer limited mixing of compounds in the particle phase.”

### DEP2

pg.8864, line 6. After changing the order of the section the abbreviation is now introduced, as well as a clarification is made in the MS.

### DMA-TD-APM

The same labelling is now used throughout the whole MS.

### **Sect. 5**

#### Carbon mean oxidation state

pg.8869, line 1 (MS: pg. 17, line 8): The term “carbon mean oxidation state” is introduced here the first time in the manuscript, together with the equation used for the estimation of it and a reference. The carbon mean oxidation state is a useful parameter for understanding oxidation-reduction (redox) and combustion reactions. The term is commonly used to determine the changes in redox reactions. The oxidation state of a molecule describes the transfer of electrons. Using the AMS, we are able to measure this term. The oxidation state term is commonly used in the chemistry community (and other fields) and therefore it is of interest to present these results here. The reference used in the paper (Kroll et al., 2011) gives a good presentation of the carbon mean oxidation state, calculated from AMS measurements. An addition is made in the MS to clarify (MS:pg.17, lines 6-12).

#### CCN and primary particle diameter

pg.8870, line 1 (MS: pg.17, line 28 to pg.18, line 2)(same answer to both referees): As pointed out by the referee the volume equivalent diameter ( $d_{ve}$ ) is used as input in the Köhler theory. The  $d_{ve}$  in turn is affected by the structure and size of the primary soot spherules. The smaller primary spherules (FSP2) make up particles with higher agglomeration than when larger primary particles are present (FSP1 and DEP), according to previous studies (see pg.8876, lines 13 to 19; MS: pg.23, lines 24 to 29). Results from the DMA-TD-APM measurements show that the  $d_{ve}$  for FSP1 is closer to  $d_{ve}$  for DEP, than  $d_{ve}$  for FSP2 (Supplement, Fig. S 2). The primary particle diameters are calculated from the mass-mobility relationship. We assume that the particle diameters for FSP1 and all DEP experiments are more similar than FSP1 and FSP2.

To strengthen this assumption are the results from CCN measurements (a linguistic change is made in the MS). In Figure 10, the results show that the FSP1 and DEP particles need a higher critical supersaturation ( $s_c$ ) for activation than the FSP2 particles, i.e. the FSP2 particles have more organic material for a given  $d_{ve}$  than FSP1 and DEP and are therefore easier to activate into cloud droplets. While in Figure 12, it is the opposite. The FSP2 particles

are harder to activate for a certain  $mf_{SOA}$ , due to smaller  $d_{ve}$ . This is summarised in a conceptual way in Fig.A below.

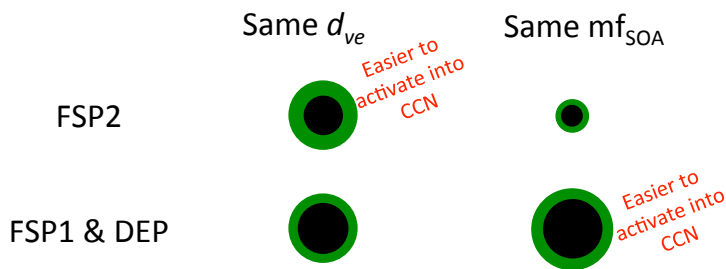


Figure A. Conceptual picture of how particles with the same volume equivalent diameter or the same mass fraction SOA activate at different critical supersaturation, depending on primary particle diameter. NOTE, the illustration is only conceptual and therefore shows spherical particles instead of the agglomerated soot structure.

This issue is discussed in Sect. 5.2 (pg.8877, lines 2-16 MS: pg.24, lines 9 to 20).

The 4 factors

The 4 factors are the outcome of our investigation. A linguistic change has been made in the MS to clarify this (pg.8872, line 8; MS: pg.19, line 30 to pg.20, line 4).

## Sect. 6

The change in hygroscopicity and morphology of the ageing soot particles will affect the deposition of the particles in the human respiratory tract according to Londahl et al., 2009 (described in the introduction of the paper, pg.8854, line 11). Changes made in the manuscript (pg.8888, line 7, MS: pg.33, line 22).

## Technical notes

These are corrected/added/changed if not commented below.

pg.8853, line 11 (MS: pg.2, line 22): “ERFari” is “...the effective radiative forcing from aerosol-cloud interactions (ERFaci...” as stated in the paper

pg. 8853, line 22-23 (MS: pg.3, line 2): “RFari” is “...radiative forcing from aerosol-radiation interactions (RFari...” as stated in the paper

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