

Response to Referee's (#2, acpd-14-C2886-2014-supplement) 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:**

As requested, some attempts have been made to streamline the paper and make the results section less repetitious.

#### **Regarding Submission to special issue**

As pointed out by the referee BC (black carbon) is believed to affect the radiation balance in the Arctic region. However, it is not clear to what degree BC or aged BC influences this region as absorbing or reflecting particles, and the contribution to the cloud condensation nuclei (CCN) or ice nuclei (IN) populations. This study addresses the role of BC and of photochemically processed BC as CCN. The laboratory work performed here is part of the work accomplished within the CRAICC (Cryosphere-atmosphere interactions in a changing Arctic climate) community (Workpackage 5: *Cryosphere-aerosol-cloud-climate interactions*). Although, the results in this study are not directly linked to the Cryosphere, it is of importance to understand the role of BC as CCN at micro scale in the Atmosphere. Part of the results in this paper has been presented at workshops and meetings within the CRAICC community.

In the overall aim it is stated that short-lived climate pollutants (soot being one of the most important) is a focus of CRAICC:

*"We will focus our attention on the role played by short-lived pollutants (recently also called short-lived climate forcers, SLCF) and clouds and their linkages with cryospheric changes".*

In the program for CRAICC WP5 *Cryosphere-aerosol-cloud-climate interactions* it is stated:

*"The aim is to gain detailed understanding of the relation between the cryosphere, aerosols and clouds, as well as their climate feedbacks in the Arctic, with a combination of field and lab studies and modelling. The objectives are to analyze:*

- the contributions of natural and anthropogenic aerosol types in the North (primary, secondary, BC and their combinations) to different cloud types*

*This is done by a combination of 1.....3) laboratory studies on ice nucleating properties of aerosols and cloud droplet formation ability"*

*"In particular it will provide information of the processes that control concentrations of soot, other inorganic and organic particles and ozone in the atmosphere and how these species interact with climate and cryosphere."*

(For more information please see the CRAICC homepage:  
<http://www.atm.helsinki.fi/craicc/index.php/wp-5>)

The paragraph regarding the Arctic in the introduction have been moved and changed somewhat to better fit the context in the introduction.

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### **Answers to Specific comments:**

The Experimental and Instrumentation sections (4 and 4.1) have been moved, as suggested by the referee (#2), before the Theory and Modelling sections (2 and 3). Hence, **Experimental** is now Sect.2, **Instrumentation** is Sect.2.1, **Theory** is Sect.3, **Modelling** is 4, **CCN activation modelling** is Sect.4.1 and **Modelling of gas-phase chemistry, organic aerosol formation and composition: ADCHAM** is Sect.4.2. Also, the figure order has been changed.

#### Distinguishing between POA and BC

pg.8861, Line 22 (MS: pg.14, line 11): States how POA has been approximated. The APM measures a small mass fraction of organics before the photochemical processes have started. This organic mass has been considered as POA. The AMS measurements support this assumption.

pg.8867, Line 1 (MS: pg.8, lines 23 and 24): increase/decrease: 120 s, constant max/min: 20 s. This has been included in the manuscript.

#### SP-AMS

pg.8868, lines 9-15 (MS: pg.9, line 30 to pg.10, line 7): That is correct, the conventional Tungsten vaporizer was retained during these experiments, and kept at the standard 600 °C (initially, we tried turning off the Tungsten vaporizer, however, the heat from the filament was enough to heat the vaporizer sufficiently for vaporization of the organic PM we sampled). The manuscript has been updated to indicate this.

The filament was also continuously engaged (the ions we studied here all origin from 70 eV electron ionization: hence, there is no signal without the filament current). The reason why we chose to operate the laser in hourly five minute intervals was that at the time of these experiments (late 2010, early 2011) we did not understand how the SP-AMS works well enough to sacrifice more of the (non-SP) AMS sampling, which we employed in an overlapping campaign (Nordin et al., 2013) and had previous experience with.

We used a HEPA filter to quantify the gas phase CO<sub>2</sub> interferences, and made sure the fragmentation table adequately described the gas phase contribution to CO<sub>2</sub><sup>+</sup>. Interestingly the gas phase interferences were utterly negligible compared with the CO<sub>2</sub><sup>+</sup> signal originating from the rBC as illustrated in Fig. A below:

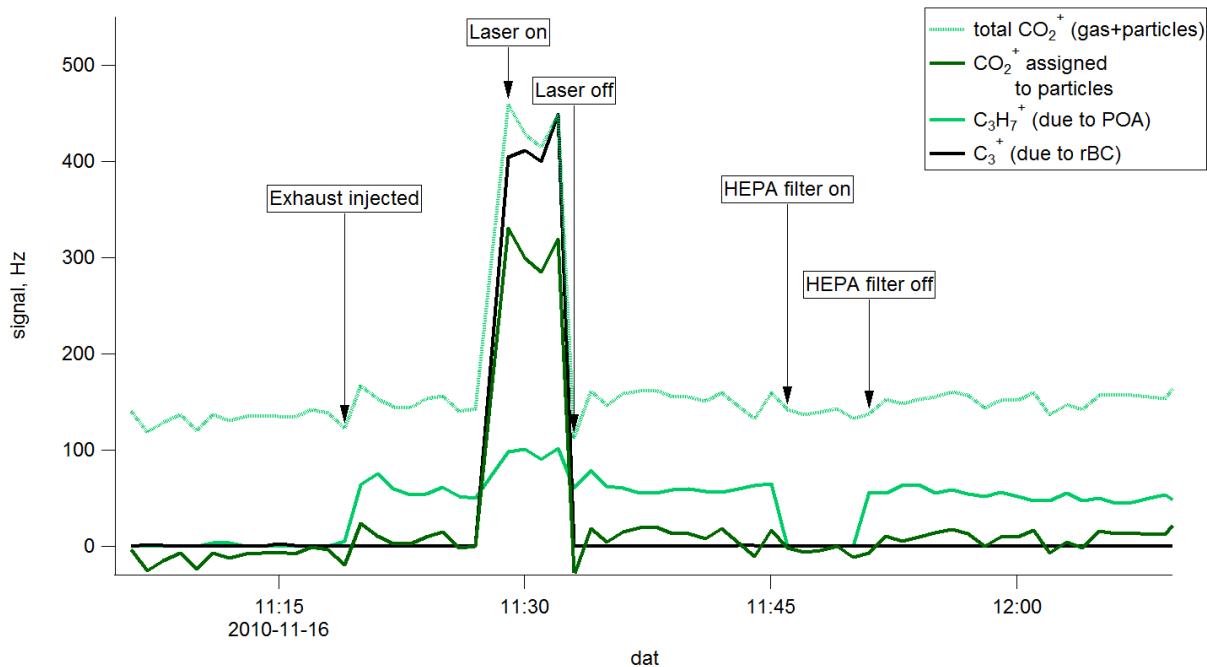


Figure A. Selected ions after exhaust injection in experiment DEP2.

The data with HEPA filter in line after 1145 was one of three sets used to determine the correct fragmentation table in this experiment (we used a constant value based on the average). For reference, the  $\text{CO}_2^+$  signal due to aged organics sampled with the laser disengaged at the end of the experiment (which impacts the estimated mean carbon oxidation state) was about 400 Hz.

We used the sampling with laser engaged (which in our experiments caused vaporization but not ionization) to estimate the relative amount of organic coatings and BC. As detailed in the Supplement (because it is a technical point which mainly interests specialists) “Determining  $\text{mf}_{\text{OA}}$  from the SP-AMS data” we assumed a collection efficiency of 1 for the laser vaporizer for both organics and BC. Note however that our results are not sensitive to that number, as we report the relative amounts and not absolute concentrations. The relative ionization efficiencies used were 0.2 for BC and 1.4 for organic PM, default estimates due to lack of calibration experiments. For the conventional vaporizer we made no assumptions about the collection efficiencies: that data was used to investigate the chemical evolution of the organic PM we sampled. Given internal mixtures, collection efficiencies have no impact on that analysis.

#### DMA-TD-APM

A small addition regarding the volume equivalent diameter has been made as well as the operational details have been added in a Table to the Supplement (with a reference in the MS), MS: pg.9, lines 21-24 and Supplement Table S1.

#### 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. B below.

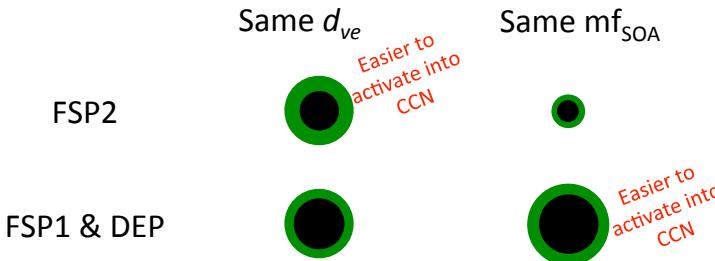


Figure B. Conceptual picture of how particles with the same volume equivalent diameter or the same mass fraction SOA activate at different critical supersaturation, depending on primary particle diameter. NOTE, the illustration is only conceptual and therefore shows spherical particles instead of the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

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

#### BC and organic masses from SP-AMS

pg.8871, lines 2-3 (MS: pg.18, lines 29-31): the text is still in the Supplement. We don't want to extend the paper further and change the focus of the paper. The text is still in the results section to make it easier for the reader to understand the context and don't mix up the instrument used (the SP-AMS mass fractions are only used for one experiment). However, a change/addition has been made in the Instrumentation section (pg.8868, line 13 (MS: pg.10, lines 3-7)) to give some information early on.

Figure 1. has been updated as suggested by the referee (#2).

#### Figure 9 and in the text:

The TEM pictures are not used to distinguish between hygroscopic and hydrophobic parts, only the soot is visible. The TEM pics are used for (a) showing the structure of the soot particles at different stages of coating/ageing (pg.8875, line 24; MS: pg.23, line 5), and (b) for visualising the theory of activation sites (pg.8875, lines 28 to pg.8876, line 6; MS: pg.23, lines 8-16). For the freshly emitted soot particles or the slightly coated soot particles an untypical behaviour is seen. From calculations using Köhler theory a lower critical supersaturation should be required than are actually measured. The deviation between modelled and measured results show that the overall soluble volume fraction is not the only important parameter for the CCN activation. Therefore, we suggest other possibilities and discuss them (activation sites is one possibility). In the conclusion (Sect. 6) we summarize what we believe is of importance. NOTE, this is only of importance for the freshly emitted/slightly coated soot particles.

Some linguistic changes have been made to clarify this. pg.8875, line 29 to pg.8876, line 4 (MS: 23, lines 10-23).

**Minor Comments:**

The minor comments are corrected and the yellow colour has been changed to pink or darkened when adequate.

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