

## ***Interactive comment on “Studies of propane flame soot acting as heterogeneous ice nuclei in conjunction with single particle soot photometer measurements” by I. Crawford et al.***

**I. Crawford et al.**

i.crawford@manchester.ac.uk

Received and published: 15 August 2011

We thank the referee for his comments and suggestions. Our responses to the comments are given below.

The study described in this paper is quite interesting and scientifically relevant. It is well written and should be published; however, there are several loose ends that I think need tying up, or at least tidied up. The one that puzzles me the most concerns the characterization of the particles produced by the CAST generator. In this paper, it is stated that “By varying the propane-air ratio, a range of soot containing of the order of a few percent organic carbon content to organic carbon contents of up to 80% can

C7769

be generated in a repeatable fashion (Schnaiter et al., 2006).” So I went to read what Schnaiter et al. had done to characterize the properties of the CAST generator and in looking at their Fig. 1, it seems that by varying the C/O ratios they get a very nice relationship of EC and OC to TC ratio but nowhere could I find where these EC and OC values came from so I don't really know how to interpret the 5% versus 30% OC discussed in the current paper. A number of questions arise 1) Does OC5 and OC30 mean 5% and 30% by mass or by number? 2) Does 5% OC mean that 95% of the particles contain EC?

Response: OC5 and OC30 mean 5% and 30%, respectively, of organic carbon content by mass. An OC of 5% means that 95% of the carbon mass is classified as EC as detected as CO<sub>2</sub> by the thermographic method detailed in Schnaiter et al. 2006 in section 3, page 2984. We accept that the definition of OC is not sufficiently discussed in the section detailing the soot production and this section will be expanded to include a description of the thermographic method.

Inserted text: “The organic carbon (OC) content of the soot was determined using an off-line thermographic technique. Combustion aerosol samples were deposited onto quartz fibre filters which were then analysed over three temperature stages; in the first stage low volatility OC compounds were volatilised in 350°C helium flow and then catalytically oxidised. The carbon fraction was determined as CO<sub>2</sub> by NDIR spectrometry; in the second stage, the remaining less volatile OC compounds were volatilised in a 650°C helium flow; in the final stage the remainder of the sample was burned in a 650°C oxygen flow and the detected carbon fraction was classified as Elemental Carbon (EC), allowing the EC/OC ratio to be calculated. Organic carbon amounts given in this paper always refer to the sum of both the volatile and less volatile fractions analysed thermographically. Further details can be found in Schnaiter et al. 2006.”

3) Were the OC5 and OC30 left in the coagulation chamber the same amount of time? If so, given the higher concentrations of OC5 with respect to OC30 and OC70, would that lead to a higher relative fraction of coagulated particles and hence more active as

C7770

IN is related to size?

Response: The aim of the study was not to investigate size effects but to ascertain the effect of coating on IN efficiency. Residence times in the NAUA chamber were dictated by experimental protocol such as; sampling time for filters; SMPS measurements and the preparation of the AIDA chamber for the transfer of aerosol from the NAUA to the AIDA. The residence time of the OC5 soot was approximately 40 minutes and for the OC30 and OC70 soot it was approximately 20. However, the important feature is that the resulting aerosol size distributions are similar. Within the 20 min more residence time of the OC5 soot, coagulation decreased the particle number by less than a factor of two. So, when assuming that the number and nature of IN sites on the soot particles were not affected by coagulation (which we did not prove, but is an interesting question to be addressed in a follow-up study), the fraction of IN sites per total particle number should be enhanced by less than a factor of two due to the additional coagulation time. However, when comparing experiments IN09\_08 and IN09\_18, the fraction of ice active soot particles at a temperature of about 227 K and Si of about 1.21 is a factor of 10 higher for the OC5 soot (1 % activation data) compared to the OC30 soot (0.1 % activation data). Therefore we believe the results from different experiments can mainly be compared to each other in terms of different particle composition and not different size.

4) Evaluating the change in the aerosol population in the chamber involves six types of particles: pre-cloud no rBC (pcNBC), pre-cloud rBC (pcBC), cloud residual no BC (crNBC), cloud residual rBC (crBC), interstitial no BC (iNBC) and interstitial rBC (iBC). In order to compare the relative properties of the different types of OC with and without sulfate coating, these six types of particles need to be compared with respect to the OC content in order to assess what fraction of particles are being removed by nucleation and which ones are removed by inertial impact.

Response: We accept that the scavenging of interstitial aerosol by growing ice crystals could affect the ice residual analysis but the focus of the experiments was the IN

C7771

efficiency of the test aerosol and not scavenging effects. We did not aim to analyse scavenging effects and we are not able to quantify them.

5) The size distributions should be shown, not only as normalized percent as a function of rBC mass, but also the concentrations normalized as a function of optical diameter measured with the SP-2, for particles with and without rBC.

Response: The retrieval of optical size for rBC-containing particles requires information about the position of the particle in the laser beam to obtain accurate leading-edge only fits (Gao et al., 2007), which is measured by a multiple-element APD in newer versions of the instrument. The SP2 instrument operating during this study did not have the special APD detector, so unfortunately we could not determine the optical size of rBC-containing particles. We have followed the reviewers suggestion and included normalized number distributions of the non-rBC containing particles for which we could obtain accurate sizing information with standard APD detectors because these particles are not destroyed by laser-induced incandescence.

Page 11010, line 6: What is the relevance here of mentioning the Baumgardner et al (2008) studies, other than that a CVI (not PCVI) was used? The analysis that was done in that study is somewhat different than done in the study described here.

Response: The reviewer is correct that the studies are quite different and that the reference is not relevant and it will be removed from the manuscript.

Page 11012, line 17: “. . . left to coagulate. . .”, There should be SMPS size distributions that show the before and after coagulation properties. Were all samples left for the same time period?

Response: The initial size distributions are somewhat meaningless because of the fast dynamical changes experienced by the soot particles during the initial coagulation phase. We waited for the aerosol system to relax to a state with slower dynamic evolution before characterizing the aerosol and starting procedures for transferal to the AIDA

C7772

chamber. The second part of the question was answered earlier in the response.

Page 11013, line 15. It is never explained why two different CAST generators were used and the difference between the two is never quantified with size distributions from the two units.

Response: The mini-CAST generator was simply a new replacement for the old CAST generator. We will include a figure of the size distributions from the two generators for comparison in the revised manuscript (attached to bottom of document, fig.1). The following text will be inserted at the end of sentence starting on page 11012, line 13: "A comparison of the aerosol size distributions for each of the soots generated with the CAST and mini-CAST generator is given in fig.x. Note that the coagulation times of the soot in the NAUA chamber before injection into the AIDA chamber were longer for the IN09 case, which explains the difference in modal diameters."

The mini-CAST generator has just recently been characterised in a similar fashion to the CAST generator. A figure of the OC/EC ratios for different C/O burning conditions will be included in the discussion of the generator (fig.2). It was found that the OC/EC ratio changes more rapidly with changing C/O for the mini-CAST and the following revisions are made to the reported OC contents for the mini-CAST soot for the C/O used:

OC5 > OC30

OC30 > OC80

OC70 > OC90

The following text from page 11012 is modified from:

"A mini-CAST (Jing-CAST Technologies) propane burner was used for a subset of experiments which may exhibit a slight change in the composition of the flame soot for the same gas flows."

C7773

To: "A mini-CAST (Jing-CAST Technologies) propane burner was used for a subset of experiments which exhibit a slight change in the composition of the flame soot for the same gas flows. Fig.xx shows the OC/EC ratios for a given C/O burning ratio as detailed in Schnaiter et al. 2006."

Page 11014, line 8: "Aerosol residuals were analysed using a number of instruments but for this work we focus on measurements of the soot core mass and associated coating thickness made by a Single Particle Soot Photometer (SP2; DMT, Boulder, Colorado, USA, which was available for the first series of experiments examining the uncoated soot only)". This sentence doesn't seem to make any sense, i.e. the SP-2 was used for looking at coating thickness, but in parentheses it says it was used in experiments examining uncoated soot?

Response: We are referring to the SP2 being unavailable for the sulphuric acid coated soot experiments, but realize the wording is unclear. The text in the revised version has been changed to:

"Aerosol residuals were analysed using a number of instruments but for this work we focus on measurements of rBC core mass and associated coatings made by a Single Particle Soot Photometer (SP2; DMT, Boulder, Colorado, USA). The SP2 was available for the first series of experiments examining soot (rBC plus any associated organics), but not the second series of experiments when soot particles were also coated with sulphuric acid."

Page 11017, line 8, Shouldn't the BC core size be rBC core size? Also, in previous papers using SP2 data, this diameter is often referred to as mass equivalent diameter, or MED. I think the same units should be used throughout for size, either nm or  $\mu\text{m}$ .

Response: The reviewer is correct. BC core size should be rBC core size and we have also clarified that the diameters reported are mass equivalent diameters. We have changed any diameters reported in nm to  $\mu\text{m}$  throughout the revised manuscript. The revised text is now: "...at an rBC core mass equivalent diameter (DBC) of 0.25  $\mu\text{m}$ ."

C7774

Page 11017, line 19. The interpretation of the fraction of rBC to scattering only particles has to be done cautiously as this ratio is affected by the different size ranges of light scattering detection versus incandescent detection. I think that these ratios should be constrained within the same size range of light scattering and incandescence for the different conditions.

Response: The reviewer is correct that the different size ranges detected by incandescence and light scattering can affect the ratios. Unlike newer versions of the instrument, the SP2 as configured during these experiments had a relatively large lower rBC limit (7 fg or 0.19  $\mu\text{m}$  for rBC density of 1.8 g cm<sup>-3</sup>), meaning the nominal size range for incandescence and scattering detection were actually quite similar (0.19-0.73  $\mu\text{m}$  for incandescence; 0.15-0.6  $\mu\text{m}$  for scattering, reported on page 11015 lines 12-18 of the discussion paper). The exact values for the lower and upper limits are affected by assumptions regarding density of rBC (incandescence) and refractive index (scattering), so rather than pick a fixed size range we reported ratios for the entire detected populations. We have revised the text to stress this issue as follows but have not adjusted the reported ratios. "Analysis of the scattering and incandescence detected particles of the pre-expansion soot found that for the OC5 soot 1 in every 420 particles exhibited no incandescence. For the OC30 soot this was found to be approximately 1 in 21 particles. These ratios describe the entire detectable populations of particles sampled but do not necessarily represent to total population of particles outside either the incandescence (DBC = 0.19-0.73  $\mu\text{m}$ ) or scattering (D = 0.15-0.6  $\mu\text{m}$ ) detection limits of the instrument."

Page 11023, final sentence of the summary: ". . . however this poor IN behaviour may be compensated for if they exceed concentrations >10 L<sup>-1</sup>." This seems an odd note to end the paper and I found it also rather cryptic as I didn't know what it means

Response: We accept that the final sentence is not clear and will be removed such that the paper now ends with: "Given the findings of this paper, such coatings would act to reduce the efficiency of OC5 soot as an ice nuclei such that they may not activate at

C7775

RHi  $\leq$  130."

Cited references: Schnaiter, M., Gimmler, M., Llamas, I., Linke, C., Jäger, C., and Mutschke, H.: Strong spectral dependence of light absorption by organic carbon particles formed by propane combustion, *Atmos. Chem. Phys.*, 6, 2981-2990, doi:10.5194/acp-6-2981-2006

Gao, R. S., J. P. Schwarz, K. K. Kelly, D. W. Fahey, L. A. Watts, T. L. Thompson, J. R. Spackman, J. G. Slowik, E. S. Cross, J. -H. Han, P. Davidovits, T. B. Onasch, and D. R. Worsnop, A novel method for estimating light-scattering properties of soot aerosols using a modified single-particle soot photometer, *Aerosol Science and Technology*, 41, 125-135, 2007

Caption to fig. 1: "Comparison of size distributions of mini-CAST and CAST soot as measured with an SMPS; 30%/5% (top), 80%/30% (middle) and 90%/70% (bottom) organic carbon (OC) content after growth in the NAUA aerosol chamber prior to injection into the AIDA aerosol chamber. Note: the coagulation times of the soot in the NAUA chamber before injection into the AIDA chamber were longer for the IN09 case, which explains the difference in modal diameters."

Caption to fig.2: "Dependence of the particle composition (OC and EC content) on the C/O atomic ratio in the burner. Full symbols indicate measurements on samples from the NAUA chamber, open symbols indicate samples taken directly behind the CAST burner. For further details see Schnaiter et al. 2006."

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 11, 11007, 2011.

C7776

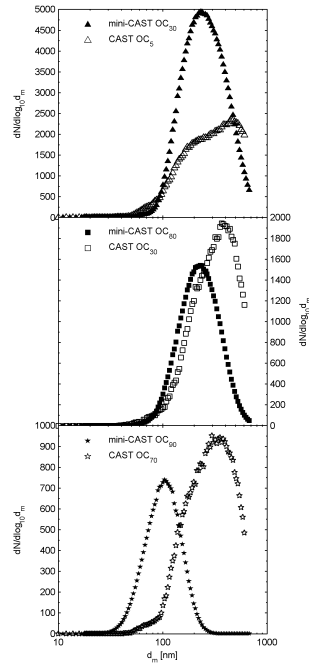


Fig. 1.

C7777

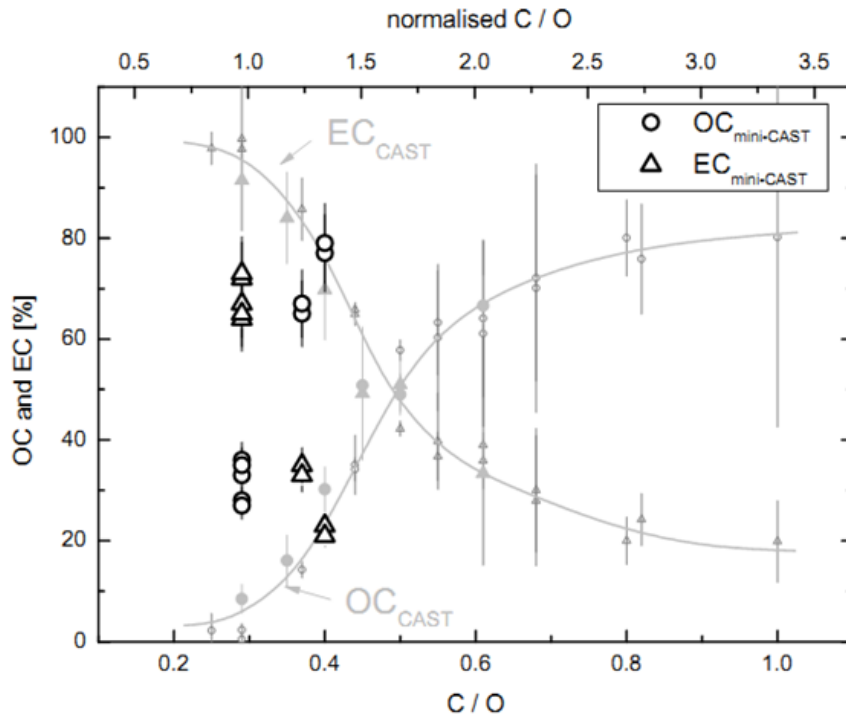


Fig. 2.

C7778