Atmos. Chem. Phys. Discuss., 12, C9909–C9917, 2012
www.atmos-chem-phys-discuss.net/12/C9909/2012/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Effect of photochemical aging on the ice nucleation properties of diesel and wood burning particles" *by* C. Chou et al.

C. Chou et al.

c.chou@herts.ac.uk

Received and published: 28 November 2012

We thank Reviewer 1 for the comments and suggestions on our manuscript. Below are the responses to reviewer 1 comments.

comment) P. 14699, l. 28: I believe it should be "supersaturated" vapour phase?

The term "supersaturated" has been added to the new manuscript

comment) P. 14700: The review by Karcher is mentioned as a reference for ice nucleation experiments performed on soot particles. However, there are more recent publications which also should be mentioned such as Koehler et al., PCCP, 2009 and Friedman et al., JGR, 2011.

The mentioned literature is now included and discussed in the manuscript.

comment) P. 14702, l. 16-20: How does dilution affect the condensed and gas phase species. Here I am referring to studies by the Donahue and Robinson groups showing that dilution can lead to enhanced volatilization. Please discuss these issues.

Low dilution ratios overestimate the emitted fine particle mass at atmospheric relevant conditions because at low dilution ratios less evaporation occurs for some particle-associated organics (Robinson et al., 2007). The mass of particulate matter (PM) with an aerodynamic diameter less than 2.5 μm (PM2.5) emitted by a diesel power generator with no aftertreatment devices can decrease by 50% when the dilution ratio is increased from 20:1 to 350:1 (Lipsky and Robinson, 2006). This mass reduction has been associated with semi-volatile organic compounds (SVOCs) which repartition to the gas phase with increasing dilution to maintain thermodynamic equilibrium (Lipsky and Robinson, 2006). These issues are already discussed in details in Chirico et al., 2011, however prompted by Reviewer 1's comment, we refer to this explanation in the revised version of our manuscript on pages 4-5, line 127 to 132.

comment) P. 14703, l. 7-13: The caveat should be mentioned that actual size and surface areas of sampled particles may deviate significantly from derived mobility diameter due to the fractal geometry of soot particles. Also, more details on how OC to BC ratios have been derived should be given. It should be clearly stated that polydisperse aerosol are introduced into PINC. What are the employed aerosol number concentrations? The caveat has now been mentioned in the revised manuscript as well as a description of the instruments used to derive OC, BC and organic matter (OM) concentrations. The aerosol concentration employed and measured by the Condensation Particle Counter (CPC) was in the order of 1000 to 10000 cm-3 depending on the time and type of experiments. P. 14705, l. 23: Does this indicate that a potential coating was not detected by the SMPS system? Please clarify.

An increase in size of the size distribution was detected by the SMPS system however

we believe that the coating was not totally uniform and did not cover the entire surface of particles. The sentence has now been rephrased for more clarification.

comment) P. 14705, l. 27: It seems odd that suddenly Fig. 7 is mentioned without having discussed Fig. 6. Please change figure numbers according to the sequence as they appear in the text. This affects all remaining figures.

The figure sequence has been modified accordingly in the new manuscript.

comment) P. 14707, section 3.3: I think more is needed to convince the reader that an increase in size is the governing parameter triggering ice nucleation. An increase in particle diameter from 130 to 180 nm enhanced the ice nucleation efficiency shifting the activated fraction at 0.001 from about 113% to 104% RH. Can this be explained by nucleation theory? Showing the actucal change in aerosol size distribution might be beneficial. Does a doubling of the available surface area result in such a decrease in RH? This of course assumes spherical particles which most likely is incorrect. I am not sure what we are learning from derived OC to BC ratios in terms of ice nucleation. I assume these are bulk ratios? For interpretation of ice nucleation it would be beneficial to know the functional groups at the particle surface. What kinds of low volatile gas phase products from oxidation of alpha-pinene are expected that potentially condense on the particles? How might those differ from oxidation products of the combustion generated VOCs? More discussion has to be given to rule out a “chemistry effect” on ice nucleation. How do photochemically aged and organic (due to alpha-pinene oxidation) coated soot particles studied here compare to previously investigated organic coated particles such as in Friedman et al., JGR, 2011, Mohler et al., Env. Res. Lett., 2008, and Knopf et al., GRL, 2010? E.g. the latter study indicates condensation freezing for OC coated particles at similar conditions as for the soot particles coated by oxidation products of alpha-pinene.

We would like to point out that the values above 113% RHw are not directly comparable to the one at 104% RHw as above 113% RHw it is not possible to state if it is ice or

water that our instrument (the OPC) is counting. If we assume that the particles sampled at the two different periods have different contact angles (which is a reasonable assumption due to change in surface material), it is then possible to explain the difference in RH. Considering that ice is forming at RHw = 113% (and not water droplets), more details can be found on the supplement. It is however important to keep in mind, as suggested by Reviewer 1 that this is an approximation as both soot and biomass burning has fractal geometry (we used the surface of a sphere to perform the calculations). The size distribution shows an increase of the particles on almost the entire size range, bringing particles initially smaller than 100 nm to larger than 100 nm. This also can partially explain the better ice nucleation after alpha-pinene. The OC/BC values reported are indeed bulk ratios and we agree with Reviewer 1 that for a deeper interpretation of the data, this information should be for individual particles (whether the particle has nucleated or not). STXM-NEXAFS analysis has been performed and reported in Zelenay et al., 2011, will now in the revised manuscript, refer the interested reader to this information on page 9, lines 291-299. Photochemical aging revealed that for wood burning particles, the carbon functional group are very similar to the untreated particles. For the EURO 2 transporter emissions (which is the vehicle emission used in our experiment with alpha-pinene), a high increase in carboxyl carbon was observed from the oxidized organic compounds. This increase did not have an effect on the ice nucleation efficiency of the EURO 2 emissions. No STXM-NEXAFS analysis has been performed on samples where compounds from oxidized alpha-pinene were present on the particles. The condensed material on the particle can go from alkene to ketones, alcohol or acids. Compounds from oxidized alpha-pinene might favour more hygroscopic behaviour compared to oxidized VOCs from the engine. However it is not certain how these compounds affect the ice nucleation behaviour of the particles. More discussion to reflect this is added to the manuscript on page 9, line 291 to 299. A new section will be added in order to discuss the effect of organic coating from other studies, including Mohler et al, 2008, Friedman et al., 2011 and Knopf et al., 2010.

comment) P. 14708, l. 8: Please provide references for this last statement.

References have been added in the new manuscript.

comment) P. 14708, section 3.4: In general I agree with this discussion. However, the Koop et al. (2000) homogeneous freezing curve depends strongly on particle size. Uncertainties in particle size will shift the curve accordingly (larger droplets shift the curve towards observations). Also, Koop (2004) states an uncertainty of $\pm$2.5% RH for higher temper atures. All this combined would make the occurrence of homogeneous ice nucleation more likely but deposition ice nucleation cannot be ruled out either.

We agree with Reviewer 1 and the information provided has now been added to the discussion.

comment) P. 14709, section 3.5: Comparison of ice nucleation by investigated organic particles with different mineral dust species lacks the information of particle size and number and total particulate surface area available. Some of the authors of this study have previously shown that changes in particle size and available total particle surface area affect ice nucleation. For a fair comparison these information should be provided.

We agree with Reviewer 1 that doing such a comparison would be beneficial; however the main point of section 3.5 is to compare the fresh and aged combustion particles of our study to previous studies with dust and discuss the differences observed for a similar activated fraction value (for instance 0.1%). Furthermore DeMott et al., 2011 and Kanji et al., 2011 are only reporting activated fraction of polydisperse aerosols like in our study and did not investigate monodisperse mineral dust.

comment) P. 14709, l. 25: This sentence implies that photochemical aging also involves the formation of sulfuric acid coatings?

Photochemical ageing does not result in any formation of sulphuric acid in our case and the sentence is revised.

comment) P. 14709, l. 7-11: As mentioned above, I would be more careful in stating that size is the governing factor determining ice nucleation.

The sentences have been modified according to Reviewer 1's suggestions.

Technical corrections:

P. 14702, l. 6: "an" EURO2: : :.

P. 14704, l. 25: I believe a word is missing after "aged" such as "ones"?

P. 14705, l. 18: Delete one occurrence of "in the same".

P. 14705, l. 21: I suggest a hyphen between "non" and "aged".

P. 14708, l. 18: Please add "aqueous" in front of "ammonium".

Figures in general: Titles in figures such as "Ice Nucleation of EURO-2: : :" should be avoided. These titles can be given in caption as first statement, followed by figure description.

P. 14719, Fig. 4: red line should be magenta in color.

P. 14720, figure caption Fig. 4: Definition of magenta line can be taken from Fig. 2. Last sentence should be changed to "The dotted line represents the homogeneous freezing threshold for 200 nm supercooled aqueous ammonium sulphate droplets based on the parameterizations of Koop et al. (2000).

P. 14722, Fig. 6: Dotted line is narrow dotted instead of wide dotted as in previous figures. Common lines can be referred to Fig. 2.

P. 14723, Fig. 7: Panel a: activated fraction is in arbitrary units? Please give panel indicator in figures. Change RHice to RHi as in text. Please change RHi scale to ticks every 5%. Panel b: I assume the blue arrow should be red and vice versa? Mention experiment temperature in figure or caption.

P. 14724, 14725, Fig. 8, 9: OC:BC ratio is in arbitrary units? Use decimal point instead of comma for y-legends. Please give units for "Time".

P. 14726, Fig. 10: Dotted line inconsistent with previous figures. Give exemplary un-

certainties for cited data points. Correct “DeMott”. What does it mean “from a different IN chamber”? Is this an instrument?

All the technical corrections have been made.

References: Chirico, R., DeCarlo, P. F., Heringa, M. F., Tritscher, T., Richter, R., Prevot, A. S. H., Dommen, J., Weingartner, E., Wehrle, G., Gysel, M., Laborde, M., and Baltensperger, U.: Impact of aftertreatment devices on primary emissions and secondary organic aerosol formation potential from in-use diesel vehicles: results from smog chamber experiments, Atmos. Chem. Phys., 10, 11545–11563, doi:10.5194/acp-10-11545-2010, 2010.

Demott, P., Möhler, O., Stetzer, O., Vali, G., Levin, Z., Petters, M., Murakami, M., Leisner, T., Bundke, U., Klein, H., Kanji, Z. A., Cotton, R., Jones, H., Benz, S., Brinkmann, M., Rzesanke, D., Saathoff, H., Nicolet, M., Saito, A., Nillius, B., Bingemer, H., Abbatt, J., Ardon, K., Ganor, E., Georgakopoulos, D. G., and Saunders, C.: Resurgence in ice nuclei measurement research, B. Am. Meteorol. Soc., 92, 1623–1635, 2011. 14726

Friedman, B., Kulkarni, G., Beranek, J., Zelenyuk, A., Thornton, J., and Cziczo, D.: Ice nucleation and droplet formation by bare and coated soot particles, J. Geophys. Res., 116, D17203, doi:10.1029/2011JD015999, 2011. 14708

Kanji, Z. A., DeMott, P. J., Möhler, O., and Abbatt, J. P. D.: Results from the University of Toronto continuous flow diffusion chamber at ICIS 2007: instrument intercomparison and ice onsets for different aerosol types, Atmos. Chem. Phys., 11, 31–41, doi:10.5194/acp-11-31-2011, 2011. 14705, 14706, 14722, 14726

Lipsky, E. M. and Robinson, A. L.: Effects of dilution on fine particle mass and partitioning of semivolatile organics in diesel exhaust and wood smoke, Environ. Sci. Technol., 40, 155–162, 2006. Mohler, O., S. Benz, H. Saathof, M. Schnaiter, R. Wagner, J. Schneider, S. Walter, V. Ebert, and S. Wagner (2008), The effect of organic coating on the heterogeneous ice nucleation efficiency of mineral dust aerosols, Environ. Res.

Lett., 3 (2), 14251435

Robinson, A. L., Donahue, N. M., Shrivastava, M. K., Weitkamp, E. A., Sage, A. M., Grieshop, A. P., Lane, T. E., Pierce, J. R., and Pandis, S. N.: Rethinking organic aerosols: Semivolatile emissions and photochemical aging, Science, 315, 1259–1262, doi:10.1126/science.1133061, 2007.

V. Zelenay, R. Mooser, T. Tritscher, A. Kepelová, M. F. Heringa, R. Chirico, A. S. H. Prévôt, E. Weingartner, U. Baltensperger, J. Dommen, B. Watts, J. Raabe, T. Huthwelker, M. Ammann: Aging induced changes on NEXAFS fingerprints in individual combustion particles, Atmos. Chem. Phys. 11, 11777-11791 (2011), doi :10.5194/acp-11-11777-2011

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/12/C9909/2012/acpd-12-C9909-2012-supplement.pdf

---

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 14697, 2012.

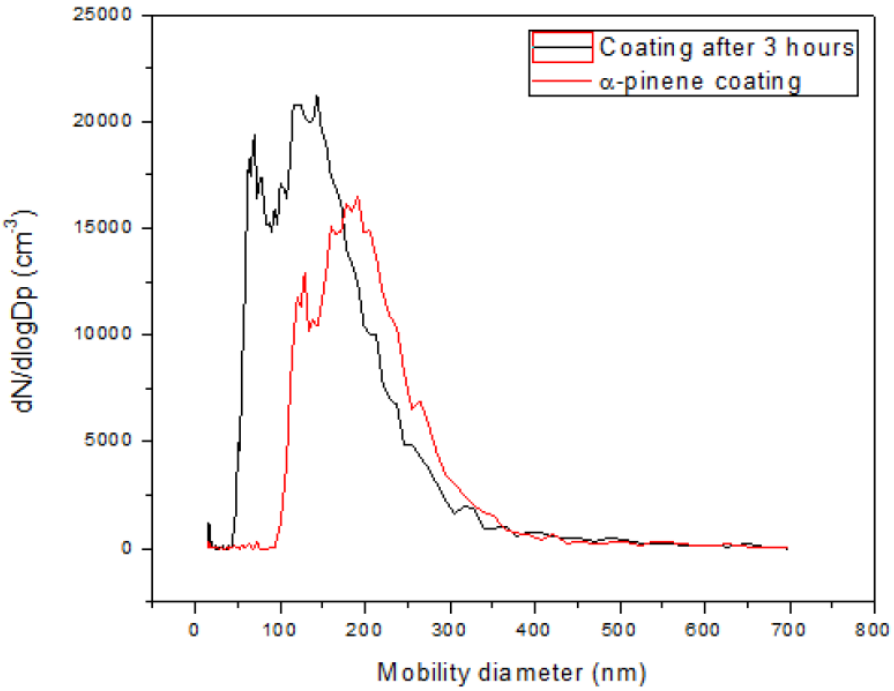

Fig. 1. Figure 1. Size distribution of experiment 15d at 2 different times (before and after alpha-pinene coating)