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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Aging fingerprints in combustion particles" *by* V. Zelenay et al.

Anonymous Referee #1

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The manuscript by Zelenay et al. presents an investigation of the chemical and physical properties of combustion particles, originating from two different diesel vehicles and a wood stove, before and after photochemical aging in a smog chamber. Measurements were performed using a number of complementary instrumental techniques on both airborne and individual collected particles, and include particle number size distributions, hygroscopicity, morphology, fractal dimension, and the functional group content.

It is found that the aging slightly increases the size of combustion particles, but has little impact on their morphology, as judged from the nearly constant values of fractal dimensions before and after aging. A substantial increase in the signatures of unsaturated, phenolic, and carboxylic carbon occurs for particles from diesel vehicles, but for particles from wood combustion the chemical signatures before and after aging are similar. The hygroscopic behavior of particles is found to relate well with their chem-

ical signatures, i.e. higher amount of carboxylic and penolic carbon leads to higher water uptake by aggregated particles, resulting in their noticeable restructuring upon humidification.

Aging of combustion aerosols is of significant interest to the atmospheric science and aerosol communities, as recent experimental and theoretical evidence indicates that the development of coatings on aged particles may significantly change their optical and hygroscopic properties, altering the lifetime and direct and indirect impacts of aerosols on climate. One of the important features of this study is the direct measurements of the chemical signatures of particles before and after aging, on a single particle basis, providing a better understanding of the relation between the coating chemical makeup and climate-related properties of combustion particles.

Although the results of this study are significant and novel, the manuscript in the present form contains considerable deficiencies that need to be addressed before a decision can be made on whether the manuscript can be accepted for publication. Specifically, because of the limited information about the conditions of smog chamber experiments, it is impossible to reach substantial conclusions regarding the extent of processing of similar combustion particles in the real atmosphere. Major critical points followed by minor technical comments are provided below.

The conditions of aging experiments in the smog chamber are neither defined nor constrained. No measurements of the gases crucial to photochemical aging, such as volatile organic compounds (VOC), nitrogen oxides (NOx), and sulfur dioxide (SO2), are reported in the manuscript. This is a major deficiency as the coating thickness and associated properties of particles may depend on the concentration and chemical nature of VOCs and other species generated upon combustion. For instance, photochemical oxidation of VOCs requires NOx to generate the hydroxyl radical. The concentration of NOx in the chamber may vary widely, depending on the combustion source. Wood combustion may produce little NOx because of the relatively low combustion temperature. The inefficient OH generation may explain the small change

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in particle size and morphology observed for the wood combustion particles in this study. Sulfuric acid from photochemical oxidation of SO2 upon aging not only may condense efficiently on the particles, forming hygroscopic coatings, but may also promote particle-phase reactions as suggested in the manuscript. For a vehicle equipped with the exhaust post-treatment system, the particles may be coated by sulfuric acid already when leaving the tailpipe. The extent of SOA formation and particle-phase reactions may depend on the relative humidity (RH), but no measurements of RH in the smog chamber experiments are provided. To summarize, comparison between aging behaviors of combustion particles from different sources is pointless unless the concentrations of major gas-phase species associated with aging are known.

Do “EURO 2” and “EURO 3” refer to different fuels, different vehicles, or the presence of an exhaust post-treatment device? This is an important point to be clarified in order to understand the observed/expected differences in combustion particle properties and aging behaviors.

An AMS instrument has been utilized in this study to measure the composition of the volatilizable fraction of combustion particles. However, the presentation of the AMS data is very brief and the data is not used fully to support some of the conclusions made in the manuscript. For instance, measurements of the mass concentrations of sulfate and ammonium in combustion particles following aging could have been used to support the statement regarding the carbonate ion/sulfuric acid/ammonium ion-catalyzed particle-phase aldol condensation. Also, aerodynamic diameter measurements by AMS for nascent and thermally denuded combustion aerosol from the smog chamber could have been used to determine the mass fraction of the coating material on particles and also their fractal dimension.

Presently, the discussion of particle-phase reactions in EURO 2 combustion aerosol particles raises many questions. Carbonate is not a typical constituent of diesel particles and hence is irrelevant (on the other hand, high levels of carbonate are often found in wood combustion particles, but no particle-phase reactions seem to occur in those

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particles, as shown by this study). Is diesel exhaust a significant source of ammonia to form sufficient ammonium concentration in the particles to catalyze aldol condensation reactions? Evidence of ammonia generation by diesel vehicles needs to be provided. Finally, sulfuric acid may catalyze aldol condensation, but its content in the particles also has not been measured. It is not clear how much sulfuric acid could potentially form because neither SO2 concentrations in the smog chamber nor the information about the sulfur content of the diesel fuel is provided.

I believe that the statement in the Conclusions section about the role of particle-phase reactions in aging of particles is not supported by direct observations and needs to be either removed or made less strong.

For the diesel exhaust samples, ozone added to the smog chamber to convert NO to NO2 prior to irradiation will also react with alkenes from combustion, initiating OH radical generation and dark oxidation of the alkane/alkene mixture.

In the discussion of the AMS measurements, particularly on pages 14467-14468, in some places it is difficult to distinguish between the present findings and findings obtained in previous studies.

What was the surface coverage of membrane substrates by particles at the end of the sample collection? The appearance of a large-size fraction in Figure 3 obtained from SEM images, in disagreement with SMPS measurements, may have been caused by particle collisions and coagulation on the membrane.

Other minor and technical issues are identified below:

Add “A fractal dimension of 1.81” instead of “1.81” in line 5 on page 14464

Replace “the Figure” with “Figure 2” in line 17 on page 14464

Describe exactly how the “spectrum strongly resembles that of liquid water” (line 21, page 14470) or provide a spectrum of liquid water in Figure 8.

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Replace “restructuring” with “partial restructuring” in line 15 on page 14473.

In the discussion of the dependence of morphology and optical properties of combustion aggregates on the coating mass (page 14474) refer to the following papers: (1) Pagels, J., A. F. Khalizov, P. H. McMurry, and R. Y. Zhang (2009), Processing of Soot by Controlled Sulphuric Acid and Water Condensation-Mass and Mobility Relationship, Aerosol Sci. Technol., 43(7), 629 – 640; (2) Khalizov, A. F., R. Zhang, D. Zhang, H. Xue, J. Pagels, and P. H. McMurry (2009), Formation of highly hygroscopic soot aerosols upon internal mixing with sulfuric acid vapor, J. Geophys. Res., 114, D05208. (3) Gysel, M., S. Nyeki, E. Weingartner, U. Baltensperger, H. Giebl, R. Hitzenberger, A. Petzold, and C. W. Wilson (2003), Properties of jet engine combustion particles during the PartEmis experiment: Hygroscopicity at subsaturated conditions, Geophys. Res. Letts., 30(11), 1566. (4) Khalizov, A. F., Xue, H., Wang, L., Zheng, J. and Zhang, R. (2009). Enhanced Light Absorption and Scattering by Carbon Soot Aerosol Internally Mixed with Sulfuric Acid. J. Phys. Chem. A 113:1066-1074.

In line 7 on page 14474, specify between which samples “For the wood combustion particles, no substantial differences in the absorption spectra were observed”

In line 13 on page 14474, replace “fresh diesel cars without any treatment” with “fresh particles from diesel cars without exhaust post-treatment”. Also, the conclusion that soot particles from diesel engine with an exhaust post-treatment device do not take up water is only applicable to low-sulfur fuels. For sulfur-containing fuels, on the contrary, the post-treatment device will oxidize SO2 to sulfuric acid already in the exhaust system, resulting in restructured particles that are thickly coated with sulfuric acid (see for instance, Olfert, J. S., J. P. R. Symonds, and N. Collings (2007), The effective density and fractal dimension of particles emitted from a light-duty diesel vehicle with a diesel oxidation catalyst, J. Aerosol Sci, 38(1), 69-82)

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 14455, 2011.