

Interactive comment on “Aging fingerprints in combustion particles” by V. Zelenay et al.

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General response:

We would like to thank the two referees for their thorough reading, the overall positive response and the many constructive comments on this manuscript. In response to the general comments made by the two referees, we would like to make following general comment: this manuscript presents a case study around samples taken during smog chamber experiments dedicated to investigating the properties of primary combustion particles and their evolution during formation of secondary organic material upon photooxidation of the diluted exhaust. Complete accounts of the HTDMA/CCN and AMS measurements are given elsewhere (Tritscher et al., 2011; Chirico et al., 2010; Heringa et al., 2011). This manuscript captures some of the more general features of soot aging, which became apparent using the STXM/NEXAFS technique. The novel aspect

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is that this technique is employed for the first time to SOA formation / smog chamber studies. The technique by its nature is constrained to a limited number of samples and thus remains somewhat restricted to the analysis of special cases. Where appropriate, we have included data from the other analysis methods (discussed in more detail in the publications cited) for comparison with our results. This aspect will be clarified in the revised introduction, discussion and conclusion sections. It is clear (and it was not the purpose of the first version) that the conclusions must remain within the constraints of the samples investigated. However, we believe as also pointed out explicitly by the two referees that STXM/NEXAFS can provide additional combined information about chemical composition and the ability to interact with water for such aging experiments. We will carefully check wording throughout the text to make this clear. Below, we respond to each comment made by the referees. For the sake of brevity, the referee comments are reproduced in short only.

Referee #1

Comment: 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 (NO_x), 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 NO_x to generate the hydroxyl radical. The concentration of NO_x in the chamber may vary widely, depending on the combustion source. Wood combustion may produce little NO_x because of the relatively low combustion temperature.

Response: This is a valid point. We will provide a summary of the general conditions of gas and particle phases in the revised manuscript and also directly refer to the individual experiments described in more detail in Heringa et al. (2011), during which the samples have been taken. This will include initial NO_x, O₃ at the time of sampling,

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relative humidity, and particulate mass for POA and SOA.

Comment: The inefficient OH generation may explain the small change in particle size and morphology observed for the wood combustion particles in this study.

Response: The OH budget cannot be assessed in detail for these experiments. But indeed the photochemical conditions (light intensity corresponded to middle European winter afternoon) may not have been vigorous enough to lead to more substantial oxidation in the wood burning experiments. We will discuss this point in the revised text where the aged wood particle samples are discussed.

Comment: 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.

Response: Nitrate did not show an increase (1.3 -> 1.4 ug/m³), sulfate increased from 0.3 -> 1.0 ug/m³, ammonium increased but was very low during the whole exp: <0.05 ug/m³ Therefore, one might expect excess acidity. This will be added to the revised text, where the potential particle phase, acid catalyzed processes are mentioned.

Comment: 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.

Response: The relative humidity of 50% will be added to the experimental section and at other relevant places in the text.

Comment: 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.

Response: We would like to thank the reviewer for pointing out these deficiencies. We

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hope that with the amendments and additions mentioned above, we can appropriately deal with these.

Comment: 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.

Response: We will add a more complete description of the vehicles to the experimental part to make clear that EURO 2 refers to a Volkswagen Transporter TDI Syncro from December 2000, with a mileage of 109 000 km not equipped with emission abatement devices, while EURO 3 refers to a EURO 3 Opel Astra 2.0 DTI from February 2002, with a mileage of 45 000 km equipped with a DOC. We will also reiterate presence or absence of the DOC when discussing the results, since, as already pointed out by Tritscher et al.

Comment: 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.

Response: As mentioned above in our general response, this manuscript focuses on the cases where STXM data are available and AMS data from Chirico et al. (2010) and Response: Heringa et al. (2011) are only mentioned where comparisons in the sense of trends are made. Statistically sound correlations are not possible in view of the small number of STXM samples.

Comment: 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.

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Response: As mentioned above, the mass concentrations of acid species will be added where available to substantiate this point. Comment: 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.

Response: We have not run the AMS behind a DMA in either configuration to allow for an independent density measurement.

Comment: 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 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.

Response: As mentioned above some information about sulfate, nitrate and ammonium is available to be added to this discussion; actually, with the numbers given above, aldol is more likely than speculated in the original manuscript.

Comment: 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.

Response: As mentioned above some information about sulfate, nitrate and ammonium is available to be added to this discussion. The information about the fuel sulfur

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content (10 ppm) will be added in the experimental part. Our intention for the original manuscript was to remain extremely cautious about particle phase processes, but only to mention them, since we agree that they may occur. However, we cannot entirely separate particle phase processes well enough from the standard route based on the information available.

Comment: 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.

Response: Since the O/C ratio did not change during titration of NO (see Chirico et al., 2010), we assume that the main fate of O₃ added was to oxidize NO and that the dark OH production from alkene oxidation was not substantial enough. This information will be added to the revised text, where the addition of ozone is described.

Comment: 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.

Response: As mentioned upfront we will make the distinction of results around these STXM experiments more clear from those described in Heringa et al., Chirico et al. and Tritscher et al..

Comment: 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.

Response: The text mentions two potential biases from sampling: the preference for smaller particles due to the electric field applied; and post-depositional coagulation. We will check wording to make this clearer and also to mention that the SMPS measurements cut off above 800 nm.

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Comment: 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

Response: ok

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

Response: ok

Comment: 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.

Response: We will add the spectrum of liquid water on top as spectrum (e) to make the comparison clear.

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

Response: ok

Comment: 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; etc.

Response: We will check out these references and include the most relevant ones. However, our estimate is only of exemplary character to mention the issue, and not a detailed discussion of this.

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

Response: Ok, will be rephrased to make clear that it is the difference between primary and aged particles.

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Comment: In line 13 on page 14474, replace “fresh diesel cars without any treatment” with “fresh particles from diesel cars without exhaust post-treatment”.

Response: ok

Comment: 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)

Response: Ok, we will make clear that our conclusions only hold within the constraints of the vehicles used, the operating conditions, the low fuel sulfur content etc..

Referee 2

Comment: My main concern is with the authors’ message that “we show that the soot particles take up water in humid environments and that their water uptake capacity increases with photochemical aging”. Although this might be true for some datasets, I strongly do not believe that the provided data in this manuscript can be generalised to support this conclusion. Using the offline technique, water uptake was only clearly shown for the wood sample and not much uptake was shown for the two cars.

Response: Apart from the general response made in the beginning above (case study character of results), we would like to mention that the STXM technique used here is sensitive to an increase in water mass, even if it is not associated with an increase in diameter as necessary to for the HTDMA experiments (in terms of the equivalent mobility diameter). Therefore, the expression ‘take up water’ may already apply to the situation of a hydrophilic interaction, with no uptake that would be detected as hygroscopic growth. To some degree the restructuring of the larger particles and the

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fact that only small particles do exhibit hygroscopic growth observed in the HTDMA experiment (Tritscher et al., 2011) reflects this. We will make this point more clear and reiterate in the conclusions.

Comment: On the other hand, the HTDMA data indicated that the photochemical aging had hardly any influence on hygroscopic growth factors of all three soot samples (wood, EURO2 and EURO3). The authors should discuss the resolution of the GF measured by the HTDMA? The largest reported change was between 1.02 to 1.04 (or 1.06) in the EURO2 case. In my experience, the resolution of the GF reported by most HTDMAs is about 0.05, which makes the reported changes insignificant. The authors should quantify the errors associated with this data and show if there was really any water uptake as a function of photochemical aging. References to this should be revised accordingly throughout the manuscript.

Response: There are different ways to access the uncertainty and accuracy of an HTDMA. In terms of absolute GF uncertainty including the accuracy of the RH measurement the instruments might be in the range of 0.05 (depending of the GF and RH). In the smog chamber experiments to study aging processes the focus is on the temporal evolution at one constant high RH. For this the precision of the measurement is more important than the accuracy. Based on dry measurements, so called D zero measurements to calibrate the sizing, the variation of GF is smaller than 1%. At the very low GF values (for soot) with little growth the overall uncertainty is about +/- 0.01. Other effects like restructuring or swelling of the soot have a larger influence on the measurement. As mentioned above, this study presents a case study around the available STXM samples, but does not provide a full account of HTDMA results from all combustion exhaust aging studies (Tritscher et al., 2011). However, to make the case of the HTDMA more clear, we will also add GF data for a smaller particle size to this figure, where growth is more apparent. Furthermore, as mentioned in the response to the previous comment, it is mainly the different sensitivity to water mass vs. diameter growth that leads to more cases with 'water uptake' than based on the HTDMA

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results alone. This is especially true for the wood combustion samples, which exhibit strong restructuring of the larger particles, which masks water uptake by hygroscopic material contained in them.

Comment: Other Comments: Title: the manuscript does not really provide aging "fingerprints". It does, however, provide characterisation or investigation of aging effects on the properties of soot particles.

Response: Indeed, in its present form the title probably refers to a more general character of results than we can actually provide. The term 'Fingerprints' slipped in since NEXAFS is a technique providing functional groups, not individual compounds, thus 'chemical fingerprints'. This study looks at changes in these fingerprints due to aging. Therefore, we will change the title to 'Aging induced changes on NEXAFS fingerprints in individual combustion particles'.

Comment: Abstract: It is mostly qualitative in nature and I suggest that it should include the appropriate quantitative results as discussed in the manuscript. The final statement of the manuscript should be revised in accordance with the outcome of the main comments above.

Response: Ok, the abstract has not been well reflecting the conclusions; we will extend it and make it compliant with the guidelines for ACP. Comment: Page 14459, L12 – 13: O3 was added to the mix before lights on. Was this before or after the collection of the fresh soot sample for the offline analysis? If before, could ozonolysis reactions have altered the chemical composition of the collected fresh samples?

Response: Samples referred to as 'primary' were always taken before O3 was added; this will be clarified in the experimental section.

Comment: Page 14460, L1: Figure 10 does not really show changes in GF after 2 hours. The "definition" of aged sample should be revised.

Response: Considering the uncertainty mentioned above, the changes in GF are sig-

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nificant for EURO 2 and EURO 3, but the changes for EURO 2 are more obvious, and for wood, the assessment is complicated by the restructuring effects. For EURO 3 and wood combustion, there are clear differences between humidity pretreated particles and not. As discussed in detail by Tritscher et al. (2011), these differences are depending on the particle size selected for the measurement. In general, the smaller particles (≤ 100 nm) did not show restructuring but only significant hygroscopic growth. In the larger particles, this hygroscopic growth was buried under the restructuring effect. The restructuring, a collapsing of the fractal soot agglomerate structure under the influence of high humidity, decreases the particle diameter. The particle was interacting with water indicating the presence of hygroscopic or at least hydrophilic material in the agglomerate structure. We will include a more detailed discussion and reference to the Tritscher et al. results in the revised version.

Comment: Page 14463, L16 -18: I disagree with this statement. On their own, SEM size distributions do not really show an obvious change with aging. This might be due to evaporation of semi-volatile material in the high vacuum of the SEM? Based on the provided results, I doubt that the technique is suitable for probing the size evolution, unlike the SMPS.

Response: The main aim of the SEM/SMPS comparison was to demonstrate that the samples taken for STXM reasonably represent the size distributed as seen from SMPS. On top of that the analysis indicates no significant changes in fractal character. We do not conclude that the chemical changes induced by aging result in significant structure changes beyond the physical coagulation during the time in the chamber. Overall we clearly leave caveats for sampling biases (due to electric field and on-substrate coagulation) as well as due to vacuum conditions. The text will be clarified to make this clearer. Note: we would not expect the primary particles having more vaporizable material than the SOA, rather the other way round.

Comment: Page 14464, L 29 – Page 14465, L1: If that was the case, why did it not feature in the other samples?

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Response: This caveat applies to all samples – will be clarified in revised text.

Comment: Page 14465, L12 – 13: I am not sure how does this rule out any potential size dependant composition? Please explain.

Response: Meant here was that they physically represent the same population. Yes, we cannot exclude size dependent chemical composition. A caveat will be added.

Comment: Page 14467, L2: is it possible to provide an error estimates associated with these numbers? Is the change from 0.84 to 0.80 significant?

Response: We will provide error bars for the two numbers in the revised version. Comment: Similarly on line 6: provide an error estimate of the m/z 44 fraction to show whether the change from 10.1 to 10.3% is meaningful or not.

Response: A fit over 5 hours shows that there is a real increase in the percentage Org44 (0.12 +/- 0.03 per hour) during the experiment period considering a 95% confidence interval. Numbers will be added.

Comment: Page 14467: Relating m/z 44 fraction to the offline carboxyl measurements deserves a brief discussion. Note that the wood sample showed the highest fraction of m/z 44 at 10% and yet the EURO2 sample appeared to have the biggest change in the carboxyl measurement despite being much lower.

Response: Duplissy et al. (2011) demonstrated the link of acids (both mono and diacids) to m/z 44. Other functional groups like carbonyls and alcohols present in SOA do not contribute much to m/z 44. Primary organics like sugars like e.g. levoglucosan in wood burning contain some m/z 44 (Alfarra et al., 2007). This information will be added. As mentioned in response to a comment of referee 1, the photochemical oxidation conditions were relatively mild, so that the difference between primary particle chemistry and that of the first generation oxidation products of gas phase precursors appearing upon aging is not very large. The primary Euro 2 particles were much more dominated by EC so that already small amounts of SOA material containing carboxylic

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acids condensing on the primary particles lead to apparently more substantial changes. Reference to the paragraph, where this is discussed, will be added here.

Comment: Page 14469, L16: the errors associate with the AMS O:C ratios should be provided.

Response: A detailed discussion of the error associated with O:C ratios derived from AMS data has been given by Aiken et al. (2008). They state “The uncertainty, based on single compound measurements is 31%. Precision is much better than accuracy for individual compounds at 3%, indicating that the variability in the bias from molecule to molecule is the dominant contribution to the uncertainty. Because this uncertainty is an average of single standards, we expect that it should be an upper limit for the uncertainty when measuring complex mixtures, such as ambient OA, because of compensating effects from different compounds”.

Comment: Page 14471, L2 -5: Could the authors provide any explanation of the lack of potassium signal, where it was expected to feature?

Response: Potassium cannot be quantified by the AMS. However, potassium emissions for log wood burners are generally low compared to carbonaceous PM. McDonald et al. (2000) report 200 times higher emissions for OC+EC compared to soluble potassium. Fine et al. (2001) reported 1% potassium for fireplace combustion emissions for different types of hardwood. The resulting K:C ratios are far below levels detectable in the NEXAFS spectra. The sentence will be amended to reflect this.

Comment: Page 14473, L12 -13: Based on the discussion above, I think the phrase “in agreement with the HTDMA measurements” should be omitted.

Response: As mentioned in response to the comments around the difference of GF measurements by HTDMA and water uptake as detected by NEXAFS, we will clarify the conclusions and make a clear differentiation between hygroscopic volume growth and water uptake into the interior of agglomerate particles.

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Comment: Page 14473, L19 -21: The increase was observed in the SMPS data and only for the EURO3 SEM data. The statement should be revised.

Response: Ok, this is indeed true. However, the aim of this part is only to demonstrate how scattering albedo responds to size change. As suggested by referee 1, we will add more references specifically addressing the effects of complex morphologies in such estimates.

Comment: Page 14474, L4 – 5: I am not sure where this conclusion came from. Please provide the appropriate discussion in the relevant section.

Response: We will tune down the generality of the statement to say that for the case considered here, the car with aftertreatment device has smaller SOA material condensing on primary particles and also refer to Chirico et al. (2010) and Tritscher et al. (2011), where this is discussed in more detail.

Comment: Page 14474, L13 – 15: I do not believe that this conclusion is supported by the presented results. This should be revised.

Response: We will omit these last sentences of this paragraph and make clear conclusions in the subsequent section.

Comment: Minor comments: Comment: Page 14459, L17: The acronym STXM-NEXAFS has not been introduced in the manuscript and should be.

Response: We will make sure that it is explained upon first mentioning in the introduction part.

Comment: Page 14459, L20: should be organic ‘loading’ not ‘compounds’.

Response: Ok

Comment: Page 14459, L28 – 29: how long was the fresh sample collected for?

Response: These samples were always collected during one hour. This will be clarified

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in the experimental part.

Comment: Page 14465, L15 – 17: Figure 4 is introduced but not explained. A brief introduction of absorption maps and how they are utilised in this manuscript is appropriate here.

Response: Ok, this will be done. Reference will be given to the experimental section, where the procedure to obtain absorption maps is described.

Comment: Page 14467, L21: 'shows' not 'show'

Response: ok

Comment: I suggest the x-axis of figures 1 -3 are shown with the same size range for ease of visual comparison.

Response: Ok, will be done.

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