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Discussions

Interactive comment on "Characterization of fresh and aged organic aerosol emissions from meat charbroiling" *by* Christos Kaltsonoudis et al.

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Kaltsonoudis et al. presents a series of smog chamber experiments to study the aging of primary emissions from meat charbroiling. They found that the initial and aged AMS spectra of meat charbroiling differed considerably. The derived fresh and aged cooking factors in laboratory were compared with ambient COA factors during Fat Thursday in Patras, Greece. The experiments are novel and performed with an extensive suite of instrumentation to systematically study the chemical aging of emissions from a very important anthropogenic source, namely meat charbroiling.

The paper potentially has significant implications to the formation of SOA and control of PM in many urban environments. While the datasets are interesting, the manuscript can be improved by providing more detailed interpretation of the data. The paper can be recommended for publications after the following questions are addressed.

General comments:

(1) *The experiments were not conducted at atmospheric relevant conditions, which could bias the conclusions and implications. As shown in Table 1, the mass concentration of PM1 ranged from 130 to 540 micrograms per cubic meter, much higher than typical concentrations of PM1 in ambient air. The chemistry occurred at higher mass loadings of OA may be different from that at lower mass loadings. Did the authors conduct experiments at lower mass loadings of OA? If not, some discussions to relate the current findings to atmospheric implications at more realistic PM concentrations would be needed.*

This is a good point. The experiments were conducted at concentrations higher than atmospheric and this could be a potential limitation of the aging experiments. However, the concentration in Experiment 1 when aging began was only a factor of 4 higher than the ambient COA levels shown in Figure 9, so these levels are by no means unreasonable at least initially. The fact that we did not observed significant differences in behavior with initial concentration (the investigated variation was also a factor of 4) and the relatively good agreement of the aged laboratory COA AMS spectra with the ambient spectra suggests that the effect of the COA levels was probably not a serious problem. This point and the corresponding limitation of the present work is now discussed in the end of the Conclusions section of the revised paper.

(2) *In Line 1-3, Page 6, the authors mentioned that "For the same sampling time the AMS mass concentration (CE=1) was 600 μg m^{-3}, the SMPS (assuming density 1 g cm^{-3}) was 100 μg m^{-3}, and the filter-based concentration was 500 μg m^{-3}." Was a CE value of 1 applied to the entire study of POA and SOA in laboratory and ambient measurements? As CE values are dependent on chemical composition of PM1 (Middlebrook et al., 2012), a fixed CE value may be not suitable. In addition, gas-phase*

CO2 will contribute to the CO_2^+ signal and thus influence the mass spectra (Aiken et al., 2007; Aiken et al., 2008). Was the contribution of gas-phase CO2 to CO_2^+ signal corrected in this study? This information was missed in the manuscript. Furthermore, the authors attributed the difference of SMPS and AMS measurements to shape of the particles. It is unlikely that alone can explain the difference of 5-8 times in concentrations.

A CE=1 was applied for both fresh and aged OA for the laboratory experiments. The composition-dependent collection efficiency of Middlebrook et al. (2012) is based on the mass fractions of ammonium, nitrate and sulfate in the total PM_1. In our case, the COA was almost entirely composed of organics, thus the above method is not directly applicable to our laboratory results. The ambient measurements have been corrected for the CE, applying the algorithm of Kostenidou et al. (2007), comparing the AMS mass distributions to the SMPS volume distributions. The CE for these multicomponent particles was 0.76±0.07. This information has been added to the corresponding section.

We have corrected for the gas phase CO_2 contribution to the CO_2^+ signal by sampling through a HEPA filter during the experiments. The CO_2 levels were in the 395-435 ppm range and did not change significantly during the course of each experiment. This information has been added in the revised manuscript.

We agree that the shape of the particles is only one factor that leads to the apparent discrepancies between these SMPS and AMS-based OA concentrations. Other factors include the CE, the particle density, the different size ranges of the two instruments, etc. This is now explained in the text.

(3) *The authors should give a more detailed discussion of the wall loss corrections of particles. SOA formation and wall loss are competition processes that a significant wall loss would bias the measurements of the SOA in mass loading, composition, and elemental ratios etc. How would the conclusion of high POA/SOA ratio be affected*

by wall loss? In addition, the exhaust was transferred through copper tubing and a metal bellows pump (not clear if the system was heated). Did the authors characterize the losses of PM and VOC of this setup? Also, will the metal bellows pump generate particles or VOC? Any data of blank experiments with purified air?

Wall loses in the chamber were calculated assuming a first order loss rate for the mass concentration of the total OA. The loss rate constant was established during the characterization period of each experiment prior to the beginning of chemical aging. The wall rate constants obtained for the experiments were in the range of 0.14 - 0.28 h^{-1} and the corresponding linear fits had very high correlation coefficients.

Losses of particles to the walls do remove part of the OA from the air in the chamber and make it “invisible” for our measurements. However, the observed chemical changes were relatively fast taking place mostly within a couple of hours. The corresponding time scales for losses were 4-6 hours so our conclusions are quite robust. This can be clearly seen, for example, in the dark ozonolysis experiment where fresh COA is decreasing following the ozone addition significantly faster than it is lost to the walls before aging begun (see Figure 7a). However, the fact that we could not observe the corresponding potential changes to the COA particles deposited on the walls introduces some uncertainty in the results. While one would expect similar changes in these deposited particles if mass transfer of oxidants and condensable material was rapid enough, we cannot confirm this. However, the effect of wall losses of particles on the observed SOA/POA ratio is expected to be small modest to small. A summary of this discussion with a reference to the work of Hildebrandt et al. (2009) who discussed the extremes of the potential fate of particles deposited on smog chamber walls has been added to the revised paper.

The copper tubing used for the sampling was insulated and was therefore heated by the exhaust vapors. Its length was less than 2 m. We have confirmed that the metal bellows pump, as expected based on its design, does not generate particles or VOCs. The PM_1 losses in the Metal Belows pump have been characterized previously (Kostenidou et al. 2013) using 2 SMPS systems for both ammonium sulfate and ambient particles. The losses were less than 10 percent for particles larger than 150 nm, increasing to 30 percent for 100 nm particles. This additional information has been added to the manuscript.

Specific comments:

(4) *Line 5, page 2: A recent study in HK suggests that COA can be 35 percent of OA (Lee et al., 2015).*

The proposed reference has been added to the revised manuscript.

(5) *Line 19-20, page 1: "after a few hours of chemical aging" is not clear. Can the authors provide information on the OH or ozone exposures?*

We now clarify that the corresponding exposures were of the order of 10^{10} molecules cm^{-3} s for OH and 100 ppb hr for ozone.

(6) *Line 6-7, page 3: What is the meaning that the cooking particles are the same? Does it mean emission rate of cooking particles?*

This sentence refers to the cooking practices in Greece during winter and summer. Due to the mild climate there is no significant change in what is cooked during the different seasons (as opposed for example to cities in much colder climates). We have rephrased the sentence to avoid confusion.

(7) *Line 17-18, page 3: A brief introduction of the chamber facility should be given.*

A short description of the chamber facility has been added in the revised manuscript.

(8) *Line 24-27, page 3: What was the flow rate in the transfer line? Line 28-29, page 3: The RH and T during the experiments should be provided.*

The flow rate for the transfer line was approximately 170 L min^{-1}. The T and RH were in the range of 20-25^{o}C and 15-35 percent respectively. The above information has been added to the revised manuscript.

(9) *Line 32-34, page 3: What is the size range of the SMPS? As suggested by the manual of SMPS 3080, the sheath flow should be set to a 10:1 ratio with the aerosol flow. Will the ratio of 5:1 set here influence the measurement of size distribution?*

The size range of the SMPS under this configuration is from 10 to 500 nm. The 10:1 ratio provides more accurate size distribution measurements as the instrument has a sharper transfer function but it reduces the measurement range to 10-300 nm. Given the modest size accuracy requirements in this study (a few percent), we selected to cover a larger size range instead.

(10) *Line 17, page 5: How was BC measured in this study? This information was missed in the manuscript.*

A Multiple-Angle Absorption Photometer (MAAP, Thermo Scientific Inc.) with a PM$_1$ cyclone was used for the BC measurements (please see lines 34-35 in page 3 of the original manuscript).

(11) *Line 27-28, page 5: The angle θ was used for the comparison between different AMS spectra throughout the entire manuscript. It would be useful to explicitly introduce the relationships between θ and spectra similarities.*

A short discussion of the various similarity measures (e.g., the coefficient of determination) and the angle θ has been added to the revised manuscript.

(12) *Section 3.2: The authors mentioned that COA emission rates varied due to the different types of meat and cooking procedures. What are the experimental conditions* *for the studies of Hildemann et al. (1991) and McDonald et al. (2003)? Any suggestions on the influence of meat types and cooking procedures on COA emission rates?*

Hildemann et al. (1991) studied the emissions from hamburger cooking of regular and lean meet either by frying or charbroiling. McDonald et al. (2003) determined the emission ratios of meat cooking (hamburger, steak and chicken) due to charbroiling or grilling. Generally charbroiling emits more particles than frying and also the emissions increase with increasing fat content of the meat cooked. There is also additional variability related to where the meat is placed with the respect to the very hot surfaces (e.g., charcoal). In the present study we tried to duplicate the cooking conditions/practices used in Greece.

(13) *Line 5, page 6: Any evidence that the particles from charbroiling are non-spherical?*

We have SEM pictures of fresh COA particles that suggest that the particles are not spherical. However, particles evaporate in the SEM so the proof is not conclusive. The second piece of evidence is the disagreement between the SMPS and AMS measurements, while the AMS results are consistent with the filter measurements.

(14) *Section 3.3: Emissions factors of VOCs were listed here. Any comparison or conclusions? To what extent are they related with the formation of new OA?*

To the best of our knowledge there is little information about VOC emissions from cooking. For example, Schauer et al. (1999) has reported the emission factors from meat charbroiling over a natural gas fired grill. So our major objective was to add to this limited literature. Based on the emissions measured the SOA formation potential of cooking would be limited compared to the primary emissions. This is consistent with the limited additional SOA that we have observed experimentally. This discussion has been added to the revised paper.

(15) *Line 26, page 6: What was the reaction time for experiment 3?*

It took two hours for the O:C ratio to reach 0.21 in this experiment. The experiment lasted 7 hours after the ozone addition. This is now mentioned in the paper.

(16) *Line 32-36, page 6: It is not convincing that the increase of O:C ratios in experiment 3 was due to the initial presence of ozone. If the increase of O:C ratios are due to the reactions of particles with ozone, the concentration of ozone should have decreased prior to the addition of ozone, which is not reflected in Figure 5b. In addition, as shown in Figure 5a, similar concentration of ozone prior to the addition of ozone was also observed for experiment 2, but no increase of O:C ratios was observed for experiment 2 prior to the addition of ozone. Experiment 2 seems unique with both O:C and H:C increased prior to the addition of ozone. Are there any other explanations for this phenomenon?*

This is an interesting observation. We have updated Figure 5b in the paper to show better what happened before the beginning of the aging phase. Ozone concentrations decreased from approximately 10 ppb to 6 ppb in this phase within one hour so this is consistent with our hypothesis. In experiment 2 in which the initial ozone was 5 ppb, there was little change during the characterization phase. Of course, there are other differences in Experiment 3 (e.g., the highest initial OA concentration) that could have played a role in the results.

(17) *Line 21-22, page 7: This sentence should be mentioned prior to the description of variations of ozone and OH concentration. The authors mentioned that similar results were obtained for the rest of the UV illumination experiments. Do the authors mean similar levels or trends of OH concentrations? It is suggested to provide the OH concentrations for all UV experiments.*

The OH and ozone concentrations for Experiments 2, 4, and 5 in which UV illumination was used were quite similar. Table 1 has been updated to include the average OH radical concentration for the chamber experiments. For Experiment 1 the OH radical concentration was not measured (no d-butanol was added).

(18) *Line 25-28, page 7: What is the definition of new OA here? As the chemical composition of OA changed during aging, should the aged OA be regarded as new OA? This will largely influence the split of POA and SOA. This needs to be clarified. In addition, is there an evidence for the heterogeneous reactions?*

Given that there are both homogeneous and heterogeneous reactions taking place in the system we have rephrased this deleting the characterization "new" referring instead to "net OA production". Also given the complexity of the situation we have avoided the use of the term SOA, as based on the traditional definition SOA formation requires gas-to-particle conversion. The evidence for heterogeneous reaction is indirect and is based on the significant changes in composition (e.g., O:C) that cannot be explained by the small additional OA formation in these experiments. This important point is clarified in the revised paper.

(19) *Line 29-32, page 7: The formation of carbonyls was listed. What is the implication?*

The increase of the concentration of these relatively small compounds suggests the fragmentation of the mostly larger organic molecules emitted during meat charbroiling. It is not clear if these molecules are products of the organics in the particulate phase (that is products of the heterogeneous reactions) or if they were produced in the gas phase. This point has been added to the paper.

(20) *Line 33-35, page 7: What are the WSOC to OC ratios for the other experiments? The conclusion seems to be based on only one experiment.*

The WSOC/OC ratio for the fresh emissions was measured in each experiment and was always low with values in the 0.05 to 0.13 range. The WSOC/OC ratio was measured in three experiments, two after UV illumination (Experiments 1 and 2) and one

after dark ozonolysis (Experiment 3). In all these three experiments the WSOC/OC ratio increased dramatically to 0.7 for Exp. 1, 0.85 for Exp. 2, and 0.55 for Exp. 3. This information has been added to the paper.

(21) *Line 1-8, page 8: Though detailed PMF analysis was provided in the SI, a brief introduction should be provided here. Please give some explanations on the variations of 2 factors. Did the aged COA factor show some time delay from meal hours?*

A brief summary of the PMF analysis has been added. The two COA factors from the PMF analysis of the chamber experiments were quite similar to the spectra obtained from the PMF analysis of ambient air. Given that the preparation of the food often starts before meal hours and atmospheric dispersion mixes the emissions from different parts of the city, it was difficult to conclude something about any potential time delay.

(22) *Section 3.5: This section should be discussed together with the comparison of mass concentrations measured by AMS and SMPS. Also, for comparison, it is better to present the volume mode mobility diameter of particles measured by SMPS. A table that compares the COA characteristics of this study and those reported in the literature would be useful to readers.*

The material of this section has been moved to Section 3.1 which is now called "Size distribution and chemical composition of the fresh COA". We have added the information about the volume mode mobility diameter of the particles as measured by the SMPS. We would prefer not to add the recommended table because of the many differences of the various studies.

Technical comments:

(23) *Line 3, page 3: BC and NOx are not primary organic aerosol components.*

We have rephrased this sentence.

(24) *Line 13, page 7: “tents” should be “tends”.*

We have corrected the typo.

References:

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