

Interactive comment on “Transformation of logwood combustion emissions in a smog chamber: formation of secondary organic aerosol and changes in the primary organic aerosol upon daytime and nighttime aging” by P. Tiitta et al.

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We thank the referee for a thorough review of our manuscript. The referee comments were very valuable and we believe that addressing the issues raised by the referee will considerably improve the manuscript.

Major comments:

Comment 1, Given that a substantial amount of discussion in the manuscript is made within the context of fast vs slow ignition, the authors should dedicate a paragraph in the results section to discuss the main differences between the two methods in terms

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of emission profiles in order to help and guide the reader throughout the discussion.

Answer 1: We extended the discussion about fast vs slow ignitions (lines 16-21, page 9) as referee suggested including an additional figure to Supplements (Fig. S7).

”Furthermore, it was observed in the slow ignition cases that the emissions of non-methane VOCs (NMVOC) show a distinct peak at about 8 – 10 minutes after ignition (Fig. S7), whereas fast ignition produced substantially lower peak at around 5 minutes after ignition. The ignition method had also a strong effect on the combustion rate of the whole batch. In the experiments 2B and 5B there were still yellow flames after 35 minutes (considered as a length of the batch), while in the experiments 1B and 4B the flaming phase ended already at around 28 minutes from ignition and the rest of the combustion process included only char burning without visible flames.” The whole chapter 3 (lines 12-16 + new text) without potassium results were moved in the beginning of Chapter 3.1 (Primary emissions).

Comment 2: PMF Factors: The SOA2 factor suggested to be a result of NO₃ chemistry should only be important during dark ageing experiment. The fact that the concentration of this factor remain high (or even slightly increase) in Figure 5 suggest that other oxidation sources are important to its formation or that the light source in the chamber does fully represent day time chemistry in the troposphere. This should be discussed and clarified in the revised manuscript. On a related note, the correlation between SOA2 and NO₃ mass in Figure S5 should be supplemented by more information showing (perhaps a lack of) relationship between nitrate and SOA1 and SOA3 in order to confirm the argument suggested by the authors.

Answer 2: We thank for the relevant comment. The formation of organic nitrate factor (SOA2) is through two channels: One is the one as the reviewer suggested through the NO₃ radical oxidation in case of excessive NO_x and O₃ in dark:

NO₂+O₃->NO₃ (radical) NO₃+VOC->ON The other channel is though photo-chemistry via reactions of peroxy radical (RO₂) with NO (Atkinson et al., 2000).

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RO₂+NO→RONO₂ (ON) This most likely explains why we are seeing the formation of SOA₂ after UV was switched on. We added new chapter in page 23 right after Chapter 3 with the following text:

“The formation of secondary organic nitrate factor is through two channels: One is through the NO₃ radical oxidation in case of excessive NO_x and O₃ in dark experiments (described in previous chapter) and the another channel is through photochemistry via reactions of peroxy radical (RO₂) with NO (Atkinson et al., 2000). This most likely explains why we are seeing the formation of SOA₂ after UV was switched on in presence of high NO in experiments 4B (Figs.5d).” New figure S8 was added to clarify the good correlation between nitrate and SOA₂ during dark aging in which correlations between SOA₁, SOA₂ and SOA₃ vs. NO₃ are now presented (updated Fig. S5i).

Here are the referee minor comments followed by replies:

Comment 1: Page 1, line 21-22: statement about substantial contribution from SOA from small scale wood combustion to global atmospheric PM matter needs to be supported and referenced in the introduction. This issue is more likely to have local/regional impact. In either case, references should be added to support a correct statement.

Answer 1: The reviewer is correct that contribution of small-scale combustion emitted SOA to global atmospheric PM is not well-defined. We modified Abstract (Page1, line 20-22) as follows

“Organic aerosols (OA) derived from small-scale wood combustion emissions are not well represented by current emissions inventories and models, although they contribute substantially to the atmospheric particulate matter (PM) levels. The secondary organic aerosol (SOA) fraction of the organic emissions is formed via. . .”

Also new references were added to add information about the impact of residential

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combustion emissions (Butt et al., 2016) (Introduction, Page 4, line 12).

“Small-scale combustion emissions have received insufficient attention until today, although this type of emission is known to be among the largest sources of OM (organic mass) and climate-active BC (e.g., Bond et al., 2004; Denier van der Gon et al., 2015; Butt et al., 2016).”

Comment 2: Page 1, line 24: replace “deployed” with “used”, “employed” or “utilised”

Answer 2: “deployed” was replaced with “utilized” in Page 1, line 24.

Comment 3: Page 2, line 21: the phrase “and internally mixed” should be removed from this sentence. The mixing state of these components is not universal and it is known to change depending on source and conditions.

Answer 3: The phrase “internally mixed” was removed (Page 2, lines 20-22).

“The main properties of soot particles, which are mixtures of elemental carbon, organic matter and inorganic species (ash), may change significantly due to coatings formed by atmospheric aging of emissions.”

Comment 4: Page 3, line 13: change “generateproducts” to “generate products”

Answer 4: “generateproducts” is changed to “generate products (Page 3, line 13)

Comment 5: Page 6, line 3-4: What is the relevance of the extra statement on OH concentrations in China to this study?

Answer 5: Extra statement is not necessary so lines 2-4 (Page 6) are modified as follows

“The hydroxyl (OH) radical is one of the main reactive species in the atmospheric boundary layer; peak daytime OH radical concentrations are in the range of (1-10) $\times 10^6$ molec. cm^{-3} (e.g., Atkinson et al., 2000; Huang et al. 2014).”

Comment 6: Page 7, line 15: References should be made to two very recent and

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studies in this area by (Ye et al., 2016 and Krechmer et al., 2016).

Answer 6: New references were added as referee suggested (Page 7, line 15).

“Particle wall losses (WL correction) have been characterized for decades (e.g., McMurry and Rader, 1985), although the estimation of losses of semi-volatile species remains challenging (e.g., Zhang et al., 2014; Kokkola et al., 2014; Krechmer et al., 2016; Ye et al., 2016).”

Comment 7: Page 10, line 21-22: The authors should comment on whether or not the small increase in SO₂ from 1.5ppb to 2.5ppb from HONO addition is sufficient to explain the increase in SO₄ particle mass from about 1 to 5 μg/m³ shown in Figure 2b?. A comment about the nature of the sulphate particles should be made given the remark made in the manuscript about a “lack of base such as NH₃” (page 13, line 21).

Answer 7: When 1 ppb of SO₂ is oxidized about 4 μg m⁻³ sulfuric acid is formed, assuming a full conversion, so relatively small changes in gas phase SO₂ can explain the observed sulfate increase. The SO₄ mass increase after HONO addition was an artefact and was caused because a small amount of SO₂ ended up in the chamber together with the HONO addition.

Logwood emitted primary sulfate appears mainly in form of K₂SO₄ (Torvela et al., 2014) (Page 9, line 21). Secondary sulfate exists most likely as sulphuric acid due to the absence of base such as NH₃.

Following modification was added in text (Page 10, lines 21-23)

“The SO₄ mass increased because a small amount (from 1.5 ppb to 2.5 ppb) of SO₂ ended up in the chamber together with the HONO addition. This secondary sulfate existed probably as sulphuric acid due to the absence of base such as NH₃. This was indicated by the very low ammonium ion concentrations.”

Comment 8: Page 13, line 16-18: The direct connection made by the authors between the “level of oxidation” and “volatility” of the different types of SOA is not really sup-

ported by any volatility measurements in this work. Although it is true that other papers in the literature have made such association for other types of particles (e.g. ambient), it is advised that these statements are either supported directly by measurements or to be appropriately toned down.

Answer 8: We fully agree with the referee that “volatility” of the different types of SOA are not supported by any measurements in this work and we modified text as follows (page 13, lines 15-18) “The oxidation level of SOA1 was clearly lower than SOA2 and SOA3 (Table 6), suggesting that the oxidation products of ozonolysis from logwood combustion are less oxidized than the oxidation products of NO₃ or OH radicals, which agrees with earlier findings (e.g., Chhabra et al., 2010).

Comment 11: Page 14, line 9-10: The comment regarding a sharp decrease in POA1 after the UV lights were switched on is not consistent with data shown in Figure 5; none of the plots in this figure show a sharp decrease in POA1. This should be clarified and revised.

We agree that sharp decrease of POA1 is not visually evident based on the Fig.5. However, Fig.S5 shows the decrease of POA1 in the UV-aging phase (Supplement information). Nevertheless, to clarify the POA chapter (age 14, line 9-10) we modified the text regarding POA1 (page 14) as follows:

“Both POA1 (BBOA factor including PAH) and POA2 (HOA factor) were higher during the slow ignition than the fast ignition experiments. POA1 decreased mainly after the UV lights were switched on while POA2 was found to decline also via dark aging. The decrease of primary organic matter upon aging can be induced by partitioning of semi-volatile compounds combined with chemical reactions both in vapor and particulate phases. The PAH compounds (Dzepina et al., 2007) included in the POA1 were observed in low concentrations. Total PAH ranged from 0.1 to 0.5 $\mu\text{g m}^{-3}$ (Fig. S5a) which is about 1 % of total OA.

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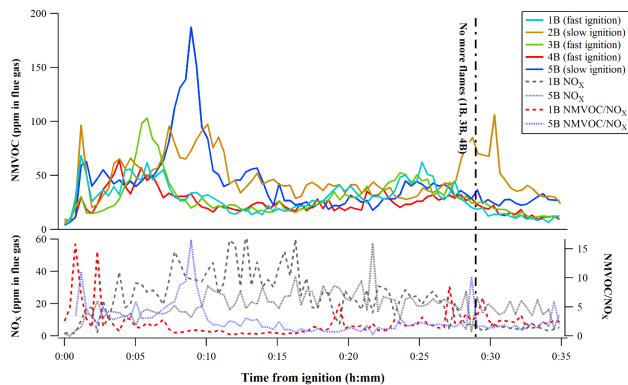


Figure S7. Time series from emissions of non-methane VOC and nitrogen oxides and their ratio measured with FTIR from raw flue gas. Dash line indicates a point at fast ignition experiments when visible flames extinguished and only char burning continued.

Fig. 1.

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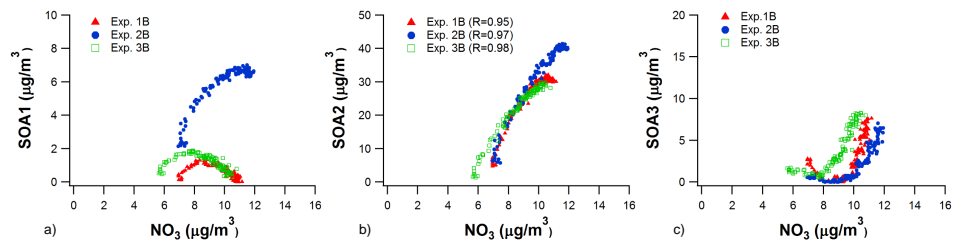


Figure S8. PMF factors (a) SOA1, (b) SOA2 and (c) SOA3 vs. particulate nitrate during dark aging and corresponding correlation coefficients (R^2) for SOA2.

Fig. 2.

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