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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Secondary organic aerosol formation and composition from the photo-oxidation of methyl chavicol (estragole)" *by* K. L. Pereira et al.

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We would like to thank the referees for their detailed comments, suggestions and guidance with this manuscript. We have addressed all the comments below.

Referee 1. Comments:

The three main comments are discussed here and the manuscript.

Aerosol loadings, products and partitioning theory: Aerosol loadings in areas where methyl chavicol emissions are significant, such as northern Borneo, have been found to range from 5 μg m-3 (800 meters above an oil palm plantation), to 100 μg m-3

(in a chimney plume of an near-source oil palm processing plant) (MacKenzie et al., 2011). The aerosol loadings in the experiments performed here start well below these levels, and then increase through each run to reach levels considerably higher than the loadings in northern Borneo. Thus, it is likely that we observe more higher volatility species in the aerosol phase than we would at atmospherically relevant loadings; due to more higher volatility species partitioning into the aerosol phase at higher mass loadings (Pankow, 1994a, b; Odum et al., 1996). However, the structurally identified compounds were characterised as semi- to low-volatility oxygenated organic aerosol, and so at atmospherically relevant conditions a sizable fraction of these compounds would be expected to exist in the aerosol phase (e.g. Donahue et al. (2012)).

Chosen VOC:NOx ratio: The chosen VOC/NOx ratio represents the lower MC/NOx ratio of an agro-industrialised oil palm plantation site in northern Borneo (Hewitt et al., 2009; MacKenzie et al., 2011); where the boundary layer (500-800 m) NOx concentration (75th percentile) was $\sim$ 0.6 ppbv (Hewitt et al., 2009), with a methyl chavicol abundance of $\sim$ 3 ppbv at midday (MacKenzie et al., 2011), corresponding to a MC/NOx ratio of 5. The typical mixing ratio of NOx above the oil palm plantation site was 0.35 ppbv, corresponding to a MC/NOx ratio of $\sim$ 9 (MacKenzie et al., 2011). The high concentrations of NOx observed at the Borneo site was the result of on-site oil palm processing and nitrogen fertilizer (MacKenzie et al., 2011). As mentioned in the manuscript, oil palm agriculture is expanding and as a result it is very likely that more on-site oil palm processing sites will open and more fertilizer will be used; increasing NOx emissions and making the chosen MC:NOx ratio investigated even more relevant in the future as industrialisation continues to increase.

Fate of the RO2 radicals, chamber vs. ambient: At the start of the chamber experiments, the high NO concentrations will be representative of methyl chavicol emissions directly next to a high NO source, such as a processing plant (MacKenzie et al., 2011). Here, the peroxy radicals (RO2) will preferentially react with NO forming alkoxy radicals (RO) and NO2 (leading to O3 formation). As a relatively low NO environment in the chamber is entered (i.e. the majority of NO has been converted to NO2), the RO2 radicals will increasingly react with RO2 or (primarily) HO2; instead of NO. At the end of an experiment, ca. 68 % of the RO2 radicals react with HO2, 32 % with NO and <1 % with other RO2, based on preliminary modelling. The oxidation products formed whilst the NO concentration is relatively low but the NO2 concentration is approximately at maximum will be representative of the methyl chavicol oxidation products formed in polluted environments, i.e. agro-industrialised oil palm plantation site (MacKenzie et al., 2011). As the chamber experiment progresses, the NO2 concentration decreases, approaching zero (as the NOx is not replenished in the chamber) and although the O3 concentration increases, OH remains the dominant methyl chavicol oxidation pathway. This chamber scenario then corresponds to an environment representative of the products formed downwind of an agro-industrialised oil palm plantation; where there is less pollution (low NOx), but O3 is present.

Specific comments:

1. Changed. 2. “Classical” photo-oxidation experiments were performed where no additional OH source was added into the chamber. This is now discussed in the manuscript. We have shown that the methyl chavicol + OH reaction dominates over the reaction with O3 in both experiments; see SI, Figures 2 and 3, and the discussion in the manuscript. 3. Changed. 4. Please note that 56 of the 59 compounds were observed in MClow, not 57. The manuscript now addresses possible reasons why less compounds were observed in MClow. 5. Discussed below in Referee 2. Specific comments: 3. 6. Amended.

7. The amendment of the HC:NOx ratio of Lee et al. (2006) means in this study, the HC:NOx ratio is greater. For the vast majority of VOC precursors, SOA yields are observed to increase with decreasing NOx (c.f Kroll and Seinfeld. (2008). The SOA yields of only a minority of VOCs have been found to increase with increasing NOx (Ng et al., 2007; Cappa et al., 2013; Chacon-Madrid and Donahue, 2011; Chacon-Madrid et al., 2013). Here, we have not shown the effect of the NOx level on the SOA yield of

methyl chavicol and thus, it would not be appropriate to suggest methyl chavicol follows a trend only observed for a minority of VOCs (increasing SOA yields with increasing NOx). We have therefore removed this discussion.

8. Changed.

9. The four gas phase compounds, MW 122, 136, 150 and 166 g mol-1 are formed as a result of decomposition, leading to higher volatility species. Our focus in this manuscript is SOA formation and particularly in Figure 4, justifying how the structurally identified SOA compounds could have formed. We have mentioned these compounds in the manuscript to support the identification of these species in the literature. It is possible that compounds MW 136 and 151 g mol-1 could of formed the two identified acids, 4-methoxybenzoic acid and (4-methoxyphenyl)acetic acid, respectively, through the further reaction with OH as suggested in Gai et al. (2013). However, as mentioned in the manuscript the detailed reaction pathways for the formation of acids from OH oxidation is currently unknown and as such, we have not included these compounds in the mechanism. We have referred the readers to Gai et al. (2013) for the gas phase mechanism of these species.

Referee 2. Specific comments:

1. The PILS samples were evaporated to dryness for a variety reasons. Firstly, the PILS dilutes the sampled particles during collection. This occurs from the transfer of the grown water soluble particles into the sealed vials (sample flow), condensation of steam and uptake during particle growth; see Orsini et al. (2003) for further information. The amount of the sample diluted is usually determined from spiking the transport flow with a known concentration of lithium fluoride. However, we were uncertain if lithium fluoride would affect the SOA composition and/or analytical method (e.g. sensitivity, adduct formation). For this reason, we avoided spiking the transport flow and evaporated the PILS samples to dryness to eliminate the unknown sample dilution amount. Secondly, evaporation and re-suspension of the samples into a smaller volume allowed

us to concentrate the samples; which almost certainly allowed us to observe more SOA species. Finally, as the reviewer mentions, the re-suspension of the samples into 50:50 methanol:water was performed to be more compatible with the HPLC separation (suspending the sample in 100 % water can affect the compound retention time and distort peak shape) and to increase the electrospray ionisation efficiency (c.f. Kebarle and Verkerk. (2009)). We have added this into the manuscript.

2. The detailed structural characterization of compounds 1 and 5 were only shown as an example of methodology used for determining the structures of the identified compounds. We focused on compounds 1 and 5 to show the affect of a nitro- functional group on fragmentation (where unusual fragmentations are observed) and also because these compounds are the subject of a manuscript in preparation. Whilst we are happy to provide the detailed structural characterization of the other compounds, we feel this would be excessive in the manuscript, considering this is not a mass spectrometry focused journal.

3. We have added the reaction time of compound 1 to support its identification in the first PILS sample. However, we have purposively avoided adding this detail into the manuscript as it is the subject of a manuscript in preparation.

4. “The majority of the compounds” has been changed to “the majority of the structurally identified SOA species”. The concentrations of 4-methoxybenzoic acid and (4-methoxyphenyl)acetic and the total percentage SOA mass these compounds represent have been added into the manuscript. We have changed the manuscript in line with the specific comments 5, 6 and 7. 8. We have spilt Figure 4 in to two parts to make it bigger, see revised Figures 4a and b.

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