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

Anonymous Referee #2

Received and published: 15 February 2014

Overall Comment and Recommendation:

As the authors well state, SOA formation from the oxidation of methyl chavicol has only been investigated in very few studies, and thus, the details of this chemistry remain unclear. Considering the importance of new oil palm plantations in Malaysia and Indonesia, methyl chavicol emissions could be important to the local SOA budgets in these developing countries. Further, methyl chavicol has been linked to some SOA in the western U.S. The aim of this study was to characterize SOA constituents produced from photochemical oxidation of methyl chavicol in a few experiments performed in the EUPHORE smog chamber facility. A battery of ESI-MS techniques were used

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to characterize the SOA constituents collected into PILS vials. HPLC-ITMS was used to first screen for "real" SOA constituents from methyl chavicol oxidation. Then to aid in structural elucidation, the authors used FTICR-MS since accurate masses could be obtained for 49 out of the 59 compounds observed. Errors for the accurate mass fittings were within publishable ranges. Since not enough signal was available in the FTICR-MS for MS/MS analyses, the authors also used HPLC-QTOFMS2 to obtain accurate masses on fragment ions to further aid in structural elucidation. Also, the use of HPLC-Q-TOFMS allowed for 10 additional compounds to be identified, likely owing to the fact these compounds were low in concentration and were likely not ionizing through direct infusion of the entire sample matrix in the FTICR-MS (i.e., matrix and ion suppression effects). Overall, the analytical approach is quite solid here. The manuscript is well-written and the results are interesting and important to the literature. The main weaknesses of this manuscript lie in the fact that only 3 experiments were conducted and no atmospheric samples were analyzed to confirm the importance of the identified compounds. It would have been very helpful (although I know chamber time and funding can always be the limiting factor) if the authors could have explored this chemistry more systematically. For example, explore this as a function of RH, seed aerosol composition and NOx. This kind of investigation would have certainly provided more insights into the chemical mechanism. Although the number of experiments are limited, I should state here to the Editor that the analytical work is quite good and extensive. I think the Editor should consider this manuscript for publication, especially once the authors address the specific comments below. Even though there is no field samples to show the atmospheric relevance of these compounds, I do think this would be a useful paper to have in the literature. This paper would aid future field studies conducted in methyl chavicol dominant regions (e.g., Malaysia and Indonesia).

Specific Comments:

1.) PILS Experimental:

It is unclear to me why there is a need to evaporate the solvent from the original PILS

vials? Is this to make the samples more compatible with LC separations? I wonder if the authors considered injecting the original samples collected into the PILS onto their various mass spectrometers? These would certainly be compatible with the HPLC techniques. I'm guessing the authors evaporated off the original water and redissolved into 50:50 methanol-water solutions to help with ionization into the FTICR-MS. The authors should clarify this in the experimental section.

2.) Structural Characterization:

Except for compounds 2 and 6 (which the authors have authentic standards for), why do the authors only focus their detailed structural characterization efforts on compounds 1 and 5? Why not do a similar exercise for the remaining compounds in the Table 2?

3.) Page 33122, Lines 12-16:

Since the PILS collects samples every 30 minutes, couldn't the authors show or confirm timing of different products? Specifically, I think it would be very useful and helpful to show the time traces of the 10 compounds focused on in Table 2 in a new figure. This exercise would either support the proposed mechanism or provide new insights.

4.) Page 33124, Lines 19-21:

Be careful! You say majority but without quantification of the compounds you identify here, you really don't know how much of the SOA mass you identify. I'm curious, for the compounds in which you have authentic standards, how much of the SOA mass do they account for in each experiment? I'm surprised the authors didn't do this since this would tell readers how important they are.

5.) Page 33124, Line 28:

Revise this to:

Only structures for 8 of 59 compounds detected could be tentatively identified; however, 2 structures were confirmed with authentic standards.

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6.) Page 33125, Last two lines of main text:

I would include that further work should also investigate SOA formation from methyl chavicol at different RHs, seed aerosol compositions, and NOx levels.

7.) Table 2:

Could the authors add a footnote to compounds 2 and 6 in Table 2 designating these were confirmed with authentic compounds?

8.) Mechanism 2:

This is VERY hard to read. Please make bigger.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 13, 33105, 2013.

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