Atmos. Chem. Phys. Discuss., 14, C1159–C1162, 2014
www.atmos-chem-phys-discuss.net/14/C1159/2014/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Evolution of the complex refractive index in the near UV spectral region in ageing secondary organic aerosol" *by* J. M. Flores et al.

Anonymous Referee #2

Received and published: 7 April 2014

The manuscript entitled "Evolution of the complex refractive index in the near UV spectral region in ageing secondary organic aerosol" by Flores et al. investigates how the ageing of VOC generates SOA and the evolution of the produced aerosol refractive index, O/C and H/C ratios, and density for three cases. The initial conditions are set to represent biogenic, mixed biogenic and anthropogenic, and biogenic plus a sequential addition of anthropogenic emissions. The ageing was completed at the SAPHIR outdoor photochemical chamber. The new and original results presented here are the optical property/refractive index results as highlighted in the title. Few studies exist of the wavelength dependent optical properties for organic aerosols and those pub-

lished in the literature have been used as a nice comparison in Table 2 and in the text. This work cleanly separates biogenic from mixed (biogenic + anthropogenic) influence in a way ambient measurements cannot always achieve. The results are important for climate change modeling and are especially significant because of organic aerosol loading. Overall, the paper is well written and the new data is important to the community. Further, the work is within the scope of work published by ACP. Therefore, I recommend publication following the author's response to the concerns raised below.

There are two main points that the authors should consider before publications:

1) Using a chamber presents a limitation on the number of trials possible which creates a scenario like a field campaign. So, while control of the initial conditions is possible in the chamber, I assume time limitations prevented repeat experiments. Ideally, repeat experiments would have been completed to allow statistical analysis. Were any repeat experiments performed or are any planned in the future? The use of the chamber also may have contributed to the decision to operate in low/no NOx conditions. Have the authors considered how NOx would change their results? NOx was noted by Jacobson (1999 in JGR) as contributing to the UV light absorption of particles and thus would contribute to the imaginary part of the refractive index. The NOx concentrations could be important in considering anthropogenic cases so it is noted to be limited here and is perhaps not quite representative of anthropogenic cases. The last concern here has to do with wall interaction and this has probably been characterized but I am unfamiliar with SAPHIR literature so perhaps this warrants a comment.

2) With regard to the imaginary refractive index, most organic compounds do not have large absorption as recorded by UV/Vis spectroscopy above about 350 nm (and it could be said above 320 nm). Organic compounds have absorption to longer wavelengths with increased conjugation and with certain functional groups (see Jacobson reference above for example). Based on this, the low imaginary refractive index observed here for the wavelengths from 360-420 nm are to be expected. Are there any plans to extend the wavelength range? Or alter the conditions? As noted by Referee #1, perhaps the

focus should be shifted to the real portion of the refractive index.

Additional note: Referee #1 makes an important point about the use of the RI data at 420 nm to extend into the visible for calculations in RF. The authors and others have seen variable RI at these wavelengths (420 and nearby at 405 nm) and so this assumption may not be valid. There is much less change in RI beyond ∼500 nm.

Detailed comments:

page 4153, and also Table 1 and Figure 1 and 2 - Could the authors clearly list what time of day the experiments began?

page 4155, lines 17-21 - Can the authors comment on the low particle concentrations beyond 15 hr. Is this due to wall losses? Dilution? How are the size selected optical property measurements made under these conditions?

page 4157, line 22 - The sizes selected for the refractive index retrievals is somewhat narrow (only D=175-300 nm) and some of these sizes were only used at the end of the experiment. Can the authors comment on how the narrow size range impacts retrievals, if at all? Do they obtain the same results at the end of the experiment if they use 175-230 versus 175-300 nm? Have they done work where a wider range of size selected particles are possible (to 500 or 600 nm) and compared to results when size range limitations were placed?

page 4157-4158 - How much fluctuation is seen in the light intensity of the particle free cavity over a retrieval experiment? Does this impact the retrieval results? If so, is a correction applied? Is the intensity monitored?

page 4159, line 12 - Are the spectra smoothed before retrieval or are the RI averaged after retrieval? If the later, how much does noise across the spectrum impact the retrievals?

page 4159, line 17 - The BVOC data is limited because of the lack of data beyond 5 hours so the argument with regard to data trends seems weak.

page 4160, literature comparisons -

1) Could the authors give a bit more information for comparison to the literature? It would be useful to know how comparable this data is with their own with regard to oxidant concentration and exposure time. Perhaps such data could be included in Table 2? This is also relevant for the later comparison for oxidation level and RI on page 4162.

2) The trends noted in several of the cases presented are within the uncertainties making conclusions challenging.

page 4161 and Figure 4 - The lack of data between 7-22 hrs is concerning. Can the authors comment on this? Were particle concentrations too low? Also, can some of the "rates" discussed be reinforced with fits so the slopes can be compared? Finally, what are the uncertainties on the RI and O/C or H/C ratios? Are the trends within these values?

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 4149, 2014.