Response to Reviewers
Manuscript Number: acp-2014-34
Manuscript Title: Evolution of the complex refractive index in the UV spectral region in ageing secondary organic aerosol

We would like to thank the anonymous referee for having thoroughly read the paper and giving us useful comments. Following are the response to his/her comments.

Response to Reviewer #1 Comments:

Major Comments:
1) The author proposed that "The increase in the real part points to the fact that it can be associated with an increase in the aerosol density". As suggested by the authors it is a possible explanation for the results that the real part of RI slightly increased from 4.5 to 7 h when O/C ratio did not increase but not from 7 to 29.5 h when O/C ratio increased in case of sequential experiment. In contrast, Lambe et al. (2013) reported the decrease in real part of RI with aging, they also reported the positive correlation between O/C ratio and density of alpha-pinene SOA in their supplemental material. How do you explain the difference between your results with their results?

We do not have a clear explanation for the differences with the Lambe et al. (2013) study. It is puzzling that Lambe et al. observed a decrease in the real part when the density of the α-pinene SOA increased. There seems to be inconsistencies in the existing literature that actually call for further research on the topic. For example, Liu and Daum (2008), Cappa et al. (2011) and Nakayama et al. (2013) also observed an increase in the real part with an increase in the O/C ratio, consistent with the results of the current study. All these results are discussed and cited in the manuscript.
A possible explanation for the difference might come from Figure 6 in the Lambe et al. (2013) study. In this figure Lambe et al. show a small increase in the imaginary part (k) of the RI as the O/C ratio increases and a decrease in the real part of the refractive index. Since the real and imaginary parts of the RI are not independent of each other by the nature of the retrieval, the increase in the imaginary component could have decreased the amount of scattering. However, the reported k values are very small ($k<0.005$), for alpha-pinene they are even smaller ($k<0.001$), so they will most likely not have a substantial effect on the real part.

I recommend adding some possible reasons to cause the increase in the density from 4.5 to 7 h (if possible).

The idea of the sequential experiments was to see the influence of p-xylene-d_{10} oxidation products on the properties of BSOA. It is possible that at 4.7h, where the sun insolation was extremely low (Fig.2 j(NO_2) values), photochemistry and oxidation of p-xylene-d_{10} ceased. However, some ozone and monoterpenes were still present in the chamber. A close inspection shows that the O/C ratio was practically constant, even slightly decreasing in the 4.7 – 7h period. This indicates that either ozonolysis products with lower O/C values than the products from photo-chemistry condensed onto the SOA, or that at the same time non-oxidative liquid phase processes of glyoxal-like structures (oligomerization) took place; for example, condensation reactions that may lower the O/C, but still compact the particles. O/C

during the dark period is thus a complex overlap of both processes, in addition to the evaporation of more volatile material due to the dilution by the replenishment flow.
We added the following explanation at the end of the Discussion section: "The increase in the density from 4.5 h to 7 h after the beginning of the experiment seen in the sequential experiment occurred practically under dark conditions (see Fig. 2 j(NO2) values). This might be attributed to a combination of a few processes: condensation of ozonolysis products, oligomerization and evaporation of more volatile material from the particles. Between 4.5 h and 7 h the photochemistry and oxidation of p-xylene-d$_{10}$ stopped due to the lack of sunlight, but O$_3$ and some monoterpenes were still present. Furthermore, the O/C ratio slightly decreased in that period. This indicates that either ozonolysis products with smaller O/C ratios than the products from photo-chemistry condensed onto the SOA, or that non-oxidative liquid phase processes of glyoxal-like structures (i.e., oligomerization) took place at the same time, such as condensation reactions that can lower the O/C ratio, but still compact the particles."

2) I think the discussion on the assessment of the change in the radiative forcing (RF) is not adequate. First, the assumption that the real part of RI between 420 and 950 nm are same with that of 420 nm seems to be unrealistic. Second, the main suggestion that negative RF values are obtained for all calculations conducted seems to be obvious (especially for first two cases when k is assumed to be 0.0001). Third, although I think that the difference in the wavelength dependence of SFE between 1.5 and 29.25 h data is mainly due to the difference in the assumed diameters of SOAs. It might be better to use same diameter if the influence of the change in RI to SFE are examined.

The reviewers are correct and we have removed this section.

Minor Comments:
1) Title I think it is better to replace the "complex refractive index" to "real part of refractive index", because this paper focused on real part.

We respectfully disagree with the reviewer. Although the focus of the paper is the real part of the complex refractive index, it will be inaccurate to say that we only derived the real part. To obtain the retrievals we did not constrain the imaginary part to zero and only allowed the real part to vary. We allowed the real part to vary for n > 1 and the imaginary part for k ≥ 0.

2) Page 4159, line 4: "the imaginary part reached zero at all wavelength". => I think the upper limit of the imaginary part of RI should be given.

The phrase now reads: "the imaginary part reached zero $\left(^{+0.03}_{-0.00}\right)$ at all wavelengths"

3) Page 4159, lines 11-14: "the errors for each wavelength were averaged and the average of the errors is shown on the left side of each panel (red symbols)" => What do the absolute values of the red symbols in Fig.3 indicate? These values do not seem average values for all measured wavelength.

There is no meaning to the absolute values of the red symbols. The position in the graph is for clarity purpose only. To clarify a possible confusion we rephrased lines 12 – 15 on page 4159 to read the following: "For clarity, the shown retrieved real parts are averaged every 1.5 nm and their individual errors not shown, and, for the mixture experiment, only three out of six retrievals are shown. The averaged errors for the retrievals for each experiment are shown on the left side of each panel (red symbols; their value has no meaning)."

4) Page 4159, lines 11-14: "Due to technical problems only two retrievals could be obtained for this experiment." => What are the technical problems?

Often the mirrors of the cavities become dirty due to deposition of aerosols or gases. Consequently, we had to remove the mirrors, clean them, re-align, take reflectivity measurements, a zero air measurement, and a sample measurement to make sure the overlap region of the cavities is consistent. As a result of the long procedure we unfortunately missed several runs.

5) Figure 4: => The authors reported "Size selection measurements were done, if possible, approximately every two hours: : :" in Page 4158 lines 6-7. Why could the authors determine the n values for 1.5h and 2h aging time (within 0.5h)?

There are two reasons for that. First, the mixture experiment was the last run of the campaign. This allowed us to fix some of the problems we encountered before. By the time of this experiment we had a 'standardized' procedure to conduct the size-selection measurements efficiently. Second, on that day we decided to take two consecutive retrievals instead of one. It took us approximately 20 min to conduct the size-selection measurements.

6) Figure 2, caption (in Interactive comment by Flores et al.): => ": : :NOx levels were below 1 pptv" may be ": : :NOx levels were below 1 ppbv"

The reviewer is correct, thank you. The caption has been changed to "…NOx levels were below 1 ppbv…"