

Answer to Reviewer 2

We copied the referee comments and set it in italic and our answers are in normal font.

This work describes chamber studies of secondary organic aerosol (SOA) generated from both aromatic (anthropogenic) and monoterpene (biogenic) precursors. The focus is on mixed anthropogenic-biogenic SOA ("ABSOA"), with the goal of understanding how the anthropogenic fraction influences the properties of the aerosol as a whole. The topic is certainly of interest to the ACP readership. The dataset, which includes measurements of particle loading, composition, and volatility - is extensive and quite impressive. However, the interpretation of results in terms of how aromatic SOA influences monoterpene SOA is not very clear; additionally, some of the data analysis needs to be explained in more detail. These need to be addressed prior to publication in ACP.

Ans: We kindly thank the reviewer for his helpful comments and changed the manuscript considering his major and minor points.

Major points:

***Rev.:** The authors provide an excellent, extensive dataset on mixed aromatic-terpene SOA, and then attempt to describe how one component affects the other. However, at no point is the mixed aerosol ("ABSOA") ever described in terms of simple additivity – how well are the key SOA parameters (yield, O/C, VFR) described by a combination of the pure aromatic and biogenic components? For example, how much of the decrease in volatility when ASOA is added to BSOA is just a result of the mixing in of lower-volatility ASOA, and how much is from some additional synergistic effect? This is a crucial question in understanding anthropogenic-biogenic interactions. This question of additivity needs to be in the manuscript (probably starting in section 4.2) if any conclusions about aromatic influences on biogenic SOA are to be made.*

Ans.: The referee addressed a very interesting point. We first would like to mention that at no point in the manuscript we claim that the presence of aromatic components increases the SOA yield. It is also not clear to us why O/C or f44 should change in a synergetic way in a mixture. The molecules would be the same in the mixtures but more of them. But we tried to realize the suggestions by the reviewer in the following way. Section 3: It looks that a linear combination of f44bsoa for pure BSOA and f44asoa for pure ASOA is able to describe the anthropogenic fraction as predicted by the simple model at the end of the experiments. This is now more clearly stated in the text section 3. We Section 4.1 we added BSOA yield to Table 1 and discuss relation to ASOA yields. We added data points for BSOA 18/19, a-pinene SOA experiment. New Section 4.5 and Figure 7 discussing linear mixing and enhancement: O/C can be predicted by a linear combination at e.g. 50-60 mc-3 s OH Dose, from exp in Table 2. We analyzed our SOA yields (now shown in Table 1), but considering the variation of OH/O3 as oxidants and the different ways the experiments were performed, the data matrix is to

small and the yields are too much error afflicted that we can't say too much about an synergetic effect on the yields. For 22/6 It seems to be linear dependent on the ASOA and BSOA contributions. In Figure 7 VFR is plotted and analyzed as a function of the ASOA fraction. It is now clearer that the presence of the aromatic components decreases the volatility more than the stoichiometric occurrence in the particulate phase. There is the strongest hint in the red curve (10/6) in Figure 6 and 7, where the VFR increases faster with OH dose as soon as toluene was added. Another indication is exp 22/6, violett curve in Fig. 6 and 7, where the pure aromatic VFRs are reached at an estimated ASOA fraction of 50% or less. We thank the reviewer for encouraging this analysis. We changed Conclusions accordingly.

Rev.: *Throughout the paper, "aromatic" and "anthropogenic" are taken to be synonymous, as are "monoterpene" and "biogenic". However there are many more anthropogenic SOA precursors than just aromatic species, and many more biogenic ones than just monoterpenes. The language throughout should be altered to reflect this.*

Ans.: We use now the notations aromatic/anthropogenic and monoterpene/biogenic in stricter sense throughout the manuscript. We refer now to "aromatic" instead to "anthropogenic" and to "monoterpenes" or the "mix of α -pinene and limonene" instead of "biogenic", especially when referring to the specific chemistry.

We added one sentence already in the abstract:

"In this study aromatic compounds served as examples of anthropogenic VOC and a mixture of α -pinene and limonene as an example for biogenic VOC."

We underlined stronger the aspect that aromatics and MT are considered as *examples* for anthropogenic and biogenic precursors. For example we changed in the introduction the wording "representative" to "example of".

We kept the terms anthropogenic and biogenic when referring to SOA, since SOA from aromatics can be considered as anthropogenic SOA and likewise monoterpene SOA as biogenic SOA.

Rev.: *Also throughout the manuscript, volatility is described in terms of "persistency", with low-volatility particles referred to as "persistent". I'm not sure I understand this nonstandard use of the word "persistent". The particles are indeed longer-lasting upon dilution or heating, but in general that won't greatly affect their lifetime in the atmosphere – the main sink of SOA is usually deposition. Thus I would recommend the VFR data be interpreted in terms of volatility rather than persistence.*

Ans.: We are using now only the notations volatile, less-volatile, and non-volatile to prevent mixing of general persistence and thermal persistence.

Other points

Rev.: *P. 20315, Line 15: "Low NOx" (1 ppb) and "High NOx" (10 ppb) conditions are described, but not explained. Whether conditions are considered low or high NOx usually*

refers to the fate of RO₂ radicals – high NO_x refers to when RO₂ radicals react with NO. Was this definitely the case here?

Ans.: The quotations are not quite correct. We did not use capital letters, thus referred simply to two different concentrations one lower, the other higher. This was well defined in line 15f on page 20315. Also in the header of Table 1 clearly defined what we mean with low and high NO_x. A connection to atmospheric High NO_x and Low NO_x regimes was not intended. We see no need to change this.

Rev.: Additionally, there is little discussion of NO_x concentrations later in the paper (Results, Discussion). Did NO_x levels have any bearing on results?

Ans.: In our context NO_x did not have a significant impact and this therefore not further discussed.

Rev.: Section 2: Much more information needs to be provided as to how yields are calculated. What value is used for density? How are losses particle wall loss treated? Vapor wall losses? How is dilution (which affects both dHC and Coa) accounted for?

Ans.: Section 3 deals with the yield determination. As described there, we derived the chemical turnover of the precursor by two methods considering either the flush out (dilution) or directly the reaction with OH. Vapor losses were not considered. The particle losses were derived under assumption that the final particle mass must be finite. We did not take into account interaction of the particles lost with the remaining vapors. In Figure 2 and section 4.1 we compare our yields under neglect of vapor wall loss and vapor particle interactions on the walls to Hildebrandt's results which included such phenomena for their smaller chamber. And we discussed the impact of vapor loss in our chamber. Although we think all other information requested was already given in the submitted manuscript we added the flush out rate and gas and particle lifetime to section 3. Moreover, we added this sentence to section 3:
"The loss of vapors to the wall and interaction of particles deposited wall with the vapors was not considered."

As a density to convert SMPS volume to mass data we used 1.4 g/cm³. This information was indeed missing and is now given in the manuscript. Thank you.

Rev.: Table 1 and Figure 2: Extremely low aerosol loadings (<0.02 ug/m³) and yields (<0.0001) are reported. At such low loadings, background aerosol formation, which can be of this level (or higher), needs to be considered. Were blank runs (irradiation of NO_x in the absence of VOC) carried out?

Ans.: Blank experiments were performed as we expected low particulate mass concentrations in the experiments dealing with pure aromatic SOA. The roof of the chamber was opened before AVOC addition for some hours, since we wanted to learn about the background reactivity and chamber induced aerosol formation. The background reactivity of the chamber produced particulate matter in the range of 0.004-0.015 ug m⁻³, depending on

the individual experiment. The according value was subtracted from the AVOC induced ASOA formation. If BVOC was involved we added O₃ to the BVOC mix in the dark just before roof opening. In these cases background reactivity is unimportant.

We added the following sentences in the experimental section:

“In the ASOA studies we opened the roof of the chamber and exposed it to sun light before AVOC addition in order to learn about the chamber induced particle formation. The background reactivity in the chamber produced particulate mass < 0.015 μg m⁻³ and typically 0.005 μg m⁻³ - a negligible contribution in most cases. The ASOA yields only consider AVOC induced ASOA mass and the background particulate mass was treated as an offset.”

Rev.: *Tables 1 and 2: both the initial HC and the amount of HC reacted away should be given.*

Ans: *Done*

In Table 2 we added the reacted fraction at time of the filter sample.

Rev.: *Fig 3: What are the sources of OH in the chamber? Are the fluctuations in [OH] real (from changing amounts of sunlight), or a function of noise in the LIF?*

Ans.: We added the following sentences to the experimental section:

“The OH radicals inside SAPHIR are predominantly formed by the photolysis of HONO coming off the walls and to a minor fraction by ozone photolysis (c.f. Rohrer et al., 2005).”

The variation of the LIF signal is caused by passing clouds and related variations in JHONO and JO₃ modulating the OH source strength. This is now noted in the Figure caption of Figure 3.

Rev.: *P 20320: the calculation of ASOA fraction needs to be described in more detail. I assume “P” refers to semivolatile products only? A major assumption here is that partitioning is not only instantaneous but also ideal: aromatic oxidation products mix in with BSOA as well as they do ASOA. A second assumption is that the extent of oxidation of a given precursor is independent of the presence of other species. The validity and implications of these assumptions should be discussed.*

Ans.: Yes, it is a very simple one product model. We assume instantaneous partitioning and discussed implications with respect of loss. Hildebrandt showed that aromatic mix with itself as they mix with MT-SOA. The extent of oxidation of the precursors is treated using the observed OH concentration, therefore the existence of a second precursor is considered in form of lower OH concentrations. We regard this as a rough estimate and did not intend to predict quantitatively, instead we wanted to classify the experiments. Actually, without turning any knobs, we overpredict the mass in pure aromatic cases by only a factor of 1.4 and if this correction is applied for the mixed ABSOA cases the model estimates match the AMS observations using f44. We mentioned this comparison now already at the end of section 3 and refer more clearly that the results are shown in the last column of Table 2.

Rev.: P 20320, Line 22: A reference is made to experimental determination of ASOA fraction, in order to validate the model, but as far as I can tell there is no description of how the experimental value is determined. This needs to be discussed. Additionally, Table 3 includes ASOA fractions determined by AMS data; how these are determined is also not explained (other than a very vague statement in the table caption). The model measurement discrepancies in this table are very different from those discussed in the text (p 20320) – why is this?

Ans.: Table 2, last column contains the estimates of the ASOA fraction in ABSOA as delivered by the simple model and corrected by the factor of 1.4. The factor 1.4 was derived from the comparison of the model output of particulate mass for pure aromatic systems to observations by SMPS/AMS. The values in parenthesis were derived from f44 of AMS measurements now described more clearly in section 3. This use of f44 served us to constrain the model prediction experimentally.

Moreover, we added as foot note 1

“¹⁾ Values estimated from simple model, section 3, values in () from AMS measurements, section 4.4”

Rev.: P 20321: Comparison with other yield results other than just Hildebrandt et al would be useful.

Ans.: Hildebrandts is the latest comprehensive study containing a detailed comparison with and discussions of older studies. Moreover, Hildebrandt provides an interesting approach to consider interaction with particles deposited on the walls.

We added more references to ASOA now in the introduction section.

Rev.: P 20322, Line 13: “remains in the condensed phase” is more accurate than “is nonvolatile”.

Section 4.4 (and Figure 6): It seems the strongest correlation is between VFR and ASOA fraction, but this is never plotted directly. It probably deserves its own panel in Figure 6.

Ans.: The wording was fixed. We added a new panel and discuss VFR as f(ASOA fraction)

Rev.: P 20329, L7: I don't understand this sentence. For a smaller carbon backbone, more oxidation steps are NOT necessary for a given increase in O/C. In fact, aromatic oxidation mechanisms involve relatively large increases in O/C per reaction step, since multiple O₂ molecules can be added.

Ans.: Here we did not discuss reaching a given O/C ratio but that smaller C-backbones need higher O/C ratios to reach a low enough vapor pressure to form particulate matter.

“... more oxidation steps are needed and that AVOC vapours are more oxidized before they form particulate matter, probably because they have smaller C-backbones.”

This would explain why ASOA has higher O/C and f44 than BSOA from monoterpenes. We will not change this.

Rev.: P 20331, L 5-19 (and P 20333, L 15): Here the results are described in terms of previous work showing “anthropogenically influenced biogenic SOA”. However, the authors have not clearly shown that the aromatic SOA is truly changing the biogenic SOA – rather, it just appears that when aromatic SOA mixes in, it alters the properties of the overall SOA, on account of its high O/C and low volatility. To show the biogenic fraction is truly being influenced by the aromatic fraction, the additivity calculations (described above) would seem to be necessary.

Ans.: Typos: 20321, L21: principal; 20325, L28: disentangle; 20331, L28: (units)
Thank you, typos fixed.