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Comment

Interactive comment on “Physico-chemical

characterization of secondary organic aerosol derived from catechol and guaiacol as a model substance for atmospheric humic-like substances” by J. Ofner et al.

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Answer to Referee #3:

We thank referee #3 for the careful consideration of our manuscript and the very detailed and helpful comments.

The authors report on the ozone oxidation of two phenols - catechol and guaiacol –

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under several conditions of light/dark and dry/"wet". They then analyze the characteristics of the resulting SOA using a large suite of complementary analytical tools. Overall this is an interesting paper that should be published after addressing the points made below.

Major Comments

A. The authors make a major point of saying that the SOA produced in their experiments is very similar to atmospheric HULIS. But there are several important differences between their product and the very broadly defined HULIS: e.g., their SOA has too low an H/C ratio and contains no N; furthermore, the hygroscopic properties have not been explored. It is interesting that the phenol-derived SOA is very similar in some ways to HULIS, but I don't see this as a requirement of the paper. It's interesting to see the phenol-derived SOA in its own right, without being tethered to HULIS. I suggest the authors point out these similarities, but don't make it a major point of the work.

Answer: The title was changed to "Physico-chemical characterization of SOA derived from catechol and guaiacol – a model substance for the aromatic fraction of atmospheric HULIS". The main focus is now on the characterization of the SOA and an intensive discussion about the suitability as a model for HULIS and comparison to other model compounds.

B. The authors have coined a new term (HULI-SOA) to refer to the humic-like SOA produced in their experiments. Do we really need this term? Does this term (presumably meaning Humic-Like SOA) accurately describe the products? My suggestion is to drop the term and replace it with a clearer, more accurate phrase such as "phenol-derived SOA".

Answer: The terms "HULI-SOA" and "HULIS-SOA" are skipped throughout the manuscript.

C. There are a number of parts of the manuscript that could be shortened. For example:

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p. 17374, main paragraph (it's a bit rambling); p. 17375, paragraph under "2 Methods" repeats points made in the Introduction and could be deleted.

Answer: The introduction has been shortened. Also the paragraph mentioned above.

Revised p. 17373, 21 – 17374, 29: *"SOA from catechol and guaiacol has been chosen as a model system and has been analysed in time dependence under defined photochemical conditions in an aerosol smog-chamber. Different relative humidities have been simulated playing an important role in aerosol formation and/or processing (Vesna et al., 2009). While a variety of methods is available to study atmospheric surfaces and their interaction with atmospheric trace gases (Zellner et al., 2009), surface functional groups play an important role for heterogeneous aerosol chemistry (Lary et al., 1999). For studying the formation and processing of those functional groups Fourier transform infrared spectroscopy is most suitable (Najera et al., 2009). Time resolved FTIR spectroscopy of the formation of organic aerosol particles was applied by Sax et al. (2005). Coury and Dillner (2008) used ATR-FTIR spectroscopy to quantify organic functional groups in ambient aerosols. Furthermore, light-absorption of organic materials plays an important role for the radiative forcing (Shapiro et al., 2009). To complete and confirm spectroscopic results ultrahigh resolution mass spectroscopy (ICR-FT/MS) and imaging by electron microscopy are used in the present study."*

The repetition was deleted.

D. The IR data (both LP and ATR) is very interesting but the description in the text is very long and difficult to read because it requires flipping back and forth between the text and figures.

(1) Is there a way to graphically highlight the main points? What about including the functional group assignments on the figures? (Some of this information is on the figures, but not nearly to the level of detail as found in the text.) It would be worthwhile as a reader to see a figure with the suggested assignments in the text.

Answer: Unfortunately, graphically highlighting of the main points in the figures is rather impossible, because of the many possible assignments. We now relegate the reader at figures 6, 7, and 8 to table 1, which contains the main assignments. We don't want to confuse the reader with too much information within the figures, since there is already plenty of information inside.

(2) It would be useful if the results could be put in some order of importance, whether abundance or some other criterion.

Answer: Subsection 4.3 was restructured to group functionalities which are belonging together. Subsection 4.2 consists of two main descriptions – the overall formation (Fig 6) and the comparison at different simulated environmental situations (Fig 7)

(3) Have the authors tried to make their assignments quantitative? (As in the Coury and Dillner paper cited.) This would be very interesting.

Answer: There are many difficulties measuring ATR-bands quantitatively. First, the ESP allows us to precipitate particles directly onto the ATR crystal without the need of any further substrate (see Teflon problem at Coury and Dillner). But a handicap is, that the total deposited mass might vary – caused by different charging situations depending on the particle concentration. Further, this method is coupled to an intensive calibration using a huge variety of standard compounds. While the described method is very successful in qualitative analysis and should be used for further aerosol characterization, it was not applied to the quantitative analysis of SOA from catechol and guaiacol.

E. The authors have very little to say about Figure 11 (section 4.6). Are there other important points to make from this figure? If not, why not put it in Supplemental material?

Answer: Fig. 11a and Fig. 12 were merged into Fig. 11a and 11b. 11a is important because it's the only statement according the masses (although these are only m/z ratios).

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F. Fig. 8. UV-Vis spectra were obtained from samples deposited on quartz filters. But presumably each sample had a different mass. Thus presenting the spectra as in Fig. 8 is misleading because the results are not normalized to sample mass (or sample OC or some other parameter).

Answer: The sample mass on the filters was kept constant by applying the same sampling time and flow at comparable particle number concentrations. The UV/VIS-spectra were not interpreted according to the overall absorption, only to the appearance of significant transitions below 300 nm, indicating formation of conjugated systems with high molecular weights. Quantifying diffuse reflectance spectra and calculating the absorption coefficients is a very difficult task and goes beyond the scope of this paper.

Minor and Technical Comments

a. The proper names of catechol and guaiacol should be included.

Answer: The IUPAC-conform names were added to the figure (see answer to referee # 2, question 3a).

b. p.17372, lines 22-23, “: : from other precursors: : ”: What other precursors.

Answer: This paragraph of the introduction was totally rewritten, summarizing now different studied aromatic precursors (see answer to referee #1, comment 2).

c. p. 17373, last sentence. It's not clear what this means.

Answer: This unclear sentence was deleted. The overall paragraph was totally rewritten (see answer to question C).

d. p.17377, lines 14-16. How were the standards used? Were they applied to the UV-Vis data in any way?

Answer: Spectralon standards are used, which are white standards, defining an albedo of 1, i.e. the maximum diffuse reflectance that can be achieved. This was then also crosschecked with the quartz filters, causing no significant loss of diffuse reflectance.

Hence, any absorption occurring, measured by the “Ulbricht” sphere is caused by the aerosol sample. The Spectralon standards are applied to the data in an indirect way, by defining the baseline.

e. p. 17379, line 6. What was the RH under the “dry” conditions? Was this variable between experiments? If so, in what range?

Answer: Experiments were done at 0% and 25% relative humidity. 25% was the upper limit because of the use of long-path FTIR spectroscopy.

The relative humidity was described in more detail,

Revised, p 17379, line 5: *“For each precursor three experiments were carried out: 1. formation of SOA in the dark with O₃ only (0% relative humidity), 2. formation of SOA at simulated sunlight with O₃ only (0% relative humidity) and 3. formation of SOA at simulated sunlight with O₃ and 25% relative humidity. No particle formation could be observed from the reaction of guaiacol with O₃ in the dark – hence no data is presented.”*

f. p. 17380, line 5: “: : yields are observed to increase significantly.” Compared to what? The low RH case?

Answer: Page 17380, line 5: The sentence was clarified: “At a relative humidity of 25% these yields are observed to increase significantly compared to the yields at dry conditions or without simulated sunlight.”

g. p. 17381, line 22. In discussing the IR C=O groups, the list mistakenly contains peroxides (which does not contain a carbonyl).

Answer: Peroxides were deleted from the discussion of carbonyl vibrations.

h. p. 17382. Is there any evidence from either the LP or ATR FTIR analyses for dimers, as recently reported for the aqueous oxidation of phenols by Sun et al. (ACP, 2010). Could dimers or higher oligomers be determined by their IR methods?

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Answer: ATR spectra exhibit some hints on carboxylic acid dimer formation below 3000 cm^{-1} . This aspect was added to the discussion of the ATR-FTIR spectra: Page 17383, line 14: “The $\nu(\text{O-H})$ absorption below 3000 cm^{-1} coupled to the carbonyl stretch at low wavenumbers observed for all samples gives also hints on carboxylic acid dimer formation (Excoffon and Marechal, 1972; Florio et al., 2003).”

The suggested literature was added to the introduction: Page 17372, line 14: “Sun et al. (2010) report dimer formation in aqueous-phase reactions of different phenols, including guaiacol.”

Finally this was mentioned in the new Conclusions (chapter 5): “While Sun et al. (2010) report dimer formation based on C-O or C-C, ATR-FTIR spectra from catechol and guaiacol give also hints on formation of carboxylic acid dimers.”

i. p. 17386, line 10. What is an ortho-benzene? Simply any benzene ring with ortho substituents? If so, this would be more accurately described as “ortho-substituted benzene”.

Answer: Page 17386, line 10: The description was wrong and was changed to “...indicating the presence of highly-oxidized benzenes or conjugated olefins.”

j. p. 17387, lines 1-2. How does spherical morphology indicate atmospheric origin? (e.g., primary soot spherules are also spherical but not from atmospheric origins.) For the current study, what other origin would be possible for the particles?

Answer: Page 17387, lines 1-2; The sentence was changed to chapter 4.1

Revised, p 17380, 17-18: “*The particles with diameters between 100 and 250 nm are of nearly perfect spherical morphology, indicating their airborne formation by gas-to-particle conversion (Pöschl et al., 2010).*”

k. Table 2. The line “where guaiacol SOA dark does not exist...” appears in the table heading and as a footnote.

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Answer: Now, the line only exists in the footnote.

The completed references will be supplied in the revised manuscript.

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/10/C8594/2010/acpd-10-C8594-2010-supplement.pdf>

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 17369, 2010.

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