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Atmospheric Chemistry and Physics Discussions

# *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 #2:**

We thank referee #2 for the careful consideration of our manuscript and the very detailed and helpful comments.

Comment: This manuscript presents a fairly detailed characterization of secondary

organic aerosol (SOA) derived from the oxygenated aromatic precursors catechol and guaiacol. The authors propose that SOA derived from catechol and guaiacol has physical and chemical characteristics similar to atmospheric humic-like substances (HULIS) and therefore may serve as a model for atmospheric HULIS in future experiments. While the topic of the paper is in accord with the theme of ACP, there exist significant deficiencies that must be addressed prior reconsideration for publication in ACP. Comments below are categorized into technical and scientific points.

I) **Technical Points**: The following section addresses technical deficiencies of the written document. The summary below represents a sample of the typical problems and is by no means a comprehensive listing.

1) Use of abbreviations and acronyms:

a) Abstract: CNC-DMPS is used before it is defined.

Answer: page 17371, line 17: "condensation-nucleus-counter and differential-mobility-particle-sizer (CNC/DMPS)" has been added

1. The acronym HULI-SOA is presented (page 17372, line 29) without being previously defined. It is probably more accurate to define humic-like substances secondary organic aerosol as HULIS-SOA than HULI-SOA.

Answer: Page 17371, line 2 and 5: „Secondary organic aerosol (SOA)" and "HUmic-LIke Substances (HULIS)" has been added.

***Revised, p. 17372, 28:*** *"Thus, for performing aerosol smog-chamber studies, the representative precursors are needed as in-situ model substances to generate SOA with HULIS qualities (Cowen and Al-Abadleh, 2009)."*

On suggestion of referee #3 the terms "HULI-SOA" or "HULIS-SOA" are skipped throughout the whole document.

1. TPP-MS is presented (page 17377, line 26) before being defined. The term "temperature programmed-pyrolysis mass spectroscopy" is stated in the abstract and the authors could introduce the acronym there. The authors should also use either "temperature programmed" or the unhyphenated analogue consistently throughout the document.

Answer: page 17371, line 15: "Temperature-programmed-pyrolysis mass spectroscopy (TPP-MS)". The term has been explained and has been used throughout the whole manuscript.

d) Field-emission-gun scanning electron microscopy should be consistently hyphenated as FEG-SEM or FEGSEM throughout the document.

Answer: page 17371, line 18: the term "field-emission-gun scanning electron microscopy (FEG-SEM)" is defined and has consistently been used throughout the document.

2) References: There are many statements in the submission that need to be referenced:

a) Page 17384, beginning on line 25. "Very important functional groups in the aerosol particles are carboxylic acids and lactones." The levels of carboxylic acids in SOA have been determined in several publications including by Fisseha et al. [*Fisseha et al.*, 2004], wherein the high-levels of carboxylic acids in SOA derived from an aromatic precursor (i.e. 1,3,5-trimethylbenzene) are discussed. Other recent works that quantify carboxylic acid levels in SOA, especially when derived from aromatic precursors should also be cited. I am less familiar with the quantification of lactones in SOA, but if this has been quantified or estimated in prior works these publications should be also cited.

Answer: This paragraph was deleted. A new paragraph was added, discussing the relevance of carboxylic acids citing relevant literature. Further the presence of lactones in natural samples has been discussed, documented by literature.

Deleted, p. 17384, 25 – 26.

***Added, p.17384, 3:*** *"Most important functional groups of SOA from catechol and guaiacol seem to be carboxylic acids, carboxylic anhydrides and lactones or esters, shown by ATR absorptions at 1317 and 1295 cm$^{-1}$ and TPP-MS. Those groups are reported for an ambient aerosol at a rural site with aromatic content of 17% (Coury and Dillner, 2009). Samburova et al. (2007) found high carboxylic and arylic fractions in HULIS samples. Aromatic acids with high-molecular weights were well correlated with HULIS by Stone et al. (2009). Carboxylic acids and their modifications are highly reported for natural HULIS, biomass burning aerosol and water-soluble organic carbon (WSOC) (Salma and Láng, 2008; Kundu et al., 2010; Limbeck and Puxbaum, 1999; Kumagai et al., 2010). 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."*

b) The authors should cite a paper that presents the details of the characterization of the Bayreuth aerosol smog chamber. The authors should also use one convention of hyphenation of "smog chamber" and similar terms.

*Answer: The term "(Aerosol) smog-chamber" has been used as a standard term. The characterization of the aerosol smog-chamber was added to the manuscript.*

***Added, p. 17375, 15:*** *"The principal setup of the aerosol smog-chamber has been described previously (Nolting et al., 1988). The current setup of the smog-chamber varies from the described one by increasing the volume by an additional 60-cm section to 700 L and thus changing the surface to volume ratio down to 8.7 m$^{-1}$. Further, the solar simulator is placed below the smog-chamber. Residence times of 105$\pm$15 minutes were measured for particles with diameters of 50$\pm$5 nm at simulated sunlight and 5-10 Pa overpressure."*

c) Page 17372, beginning on line 1: "Mass fluxes of 30–270 Tg year$^{-1}$ are estimated to be emitted per year by tropospheric oxidation of biogenic and anthropogenic volatile organic compounds (Andreae and Crutzen, 1997)." While this may be the seminal paper in this area, a great deal has been learned about the sources and global flux of aerosols, including SOA, in the last decade. The authors may want to revise their mass flux estimates for SOA in accord with recent reviews on this subject [*Hallquist et al.*, 2009; *Kanakidou et al.*, 2005; *Kroll and Seinfeld*, 2008], and also specify if they are citing bottom-up or top-down (inverse) estimates because there is often significant disparity between these types of estimates.

Answer: We thank the referee for the recommended literature and have updated our introduction discussing those mass fluxes. We kept this section short, because this paper is neither a review nor based on flux measurements or field studies.

***Revised, 17371, 24 – 17372, 5:*** *"Atmospheric aerosol particles strongly influence the global atmosphere, and their contribution to climate change is versatile (Forster et al., 2007). Especially SOA play a major role in the impact of atmospheric chemistry on climate. Mass fluxes of 30-270 Tg year$^{-1}$ have been estimated to be emitted per year by tropospheric oxidation of biogenic and anthropogenic volatile organic compounds (Andreae and Crutzen, 1997). Contributions to the fine aerosol of organic materials between 20-50% at mid-latitudes and up to 90% in tropical forested areas are reported and reviewed by Kanakidou et al. (2005). According to aromatic SOA precursors they report anthropogenic emissions of 6.7 Tg y$^{-1}$ toluene, 4.5 Tg y$^{-1}$ xylene, 0.8 Tg y$^{-1}$ trimethylbenzene and 3.8 Tg y$^{-1}$ of other aromatic compounds. Hallquist et al. (2009) report total biogenic SOA fluxes of 12-70 Tg y$^{-1}$ from bottom-up estimates. Fluxes of 17 TgC y$^{-1}$ for SOA from biomass burning and 10 TgC y$^{-1}$ for SOA from anthropogenic sources are reported by them based on a top-down approach."*

d) Page 17373, beginning on line 21: "In the recent past several field studies of SOA have been performed using aerosol mass spectroscopy as a powerful tool identifying a myriad of compounds." The authors should reference the use of aerosol mass spectrometry (AMS) for identifying compounds in SOA, including recent reviews and other comprehensive works that address this important application of AMS [*Canagaratna et al.*, 2007; *Hallquist et al.*, 2009; *Jimenez et al.*, 2009; *Sullivan and Prather*, 2005; *Zhang et al.*, 2007].

Answer: The whole section has been shorted by suggestion of referee #1. Although, AMS is currently a hot topic and is very interesting, our experimental approach in ESI-MS is rather different and is not directly comparable.

e) Page 17387, beginning on line 10: "Especially ATR-FTIR spectra of synthetic HULI-SOA from catechol and guaiacol show many common features with reported natural HULIS according to structural elements and functional groups." This sentence needs to have references for "many common features with reported natural HULIS". Also, the construction of this sentence is awkward.

Answer: page 17387, line 10: The sentence has been deleted. Comparison to natural HULIS or other models was added to the discussion and the conclusions.

***Revised, p. 17383, 14 – 25:*** *"Aromatic or $\alpha$,$\beta$-unsaturated esters in the dark-formed SOA might be indicated by the bands at 1716, 1295, 1196 and 1118 cm$^{-1}$. Carboxylic acids are represented by the $\nu$(C=O) at 1740 cm$^{-1}$, the $\nu$(C-O) and $\delta$(O-H) at 1416, 1317 and 1295 cm$^{-1}$ and the broad $\nu$(O-H) from 3100 to 2500 cm$^{-1}$. The $\nu$(O-H) absorption below 3000 cm$^{-1}$ coupled to the carbonyl stretch at low wavenumbers observed for all samples gives also hints at carboxylic acid dimer formation (Excoffon and Marechal, 1972; Florio et al., 2003).*

*Absorptions in the range of 3200-2500 cm$^{-1}$ might belong to intramolecular-bonded ortho-phenols and the O-H stretch vibration of carboxylic acids. The broad structured absorption between 1400 and 1000 cm$^{-1}$ implies O-H deformation and C-O stretch vibration combinations of aliphatic and aromatic alcohols. The band at 1196 cm$^{-1}$ might – apart from structural features – also belong to the C-O stretch vibration in aromatic ethers or phenols, shown by all SOA samples. Hence, the absorption at 1045 cm$^{-1}$, which is masked by ozone in the gas phase spectra in the long-path absorption spectra, might belong to the C-O aliphatic stretch vibration of aliphatic-aromatic ethers.*

*Same absorptions of carbonyls and aromatic rings were found for photodegradated tannic acid as a model for HULIS (Cowen and Al-Abadleh, 2009) or for SRFA (Hatch et al., 2009)."*

***Added, p. 17384, 3:*** *"ATR-FTIR spectra of SOA from catechol and guaiacol exhibit absorptions reported for natural HULIS and used proxys like SRFA. The carbonyl and aromatic stretching region between 1600 and 1800 cm$^{-1}$ is dominated by two bands at 1620 and 1716 or 1740 cm$^{-1}$. Those absorptions are reported for SRFA and for natural HULIS (Salma et al., 2010). Especially the $\nu$(C=O) at 1716 cm$^{-1}$ of SOA catechol formed in the dark was found in BBOA (Salma et al., 2010). Most important functional groups of SOA from catechol and guaiacol seem to be carboxylic acids, carboxylic anhydrides and lactones or esters, shown by ATR absorptions at 1317 and 1295 cm$^{-1}$ and TPP-MS. Those groups are reported for an ambient aerosol at a rural site with aromatic content of 17% (Coury and Dillner, 2009). Samburova et al. (2007) found high carboxylic and arylic fractions in HULIS samples. Aromatic acids with high-molecular weights were well correlated with HULIS by Stone et al. (2009). Carboxylic acids and their modifications are highly reported for natural HULIS, biomass burning aerosol and water-soluble organic carbon (WSOC) (Salma and Láng, 2008; Kundu et al., 2010; Limbeck and Puxbaum, 1999; Kumagai et al., 2010). 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."*

***Added, p. 17384, 15:*** *"The UV/VIS spectra are in good agreement with other aromatic precursor oxidation studies (Gelencsér et al., 2003; Hoffer et al., 2004). Especially the $\pi \rightarrow \pi^*$ electronic transition at about 260 nm is similar to natural HULIS samples (Baduel et al., 2009)."*

f) Page 17387, beginning on line 22: "But the measured medium H/C ratio of 1 is too low for atmospheric HULIS. The reported values are between 1.6 and 1.7." The second sentence needs to be referenced. This referencing and associated discussion should be fairly comprehensive because the comparison of the H/C ratio presented in

this work with other reported values is of importance for establishing the veracity of employing catechol and guaiacol derived SOA as a model for atmospheric HULIS. (I address scientific aspects of this and related sections below in "Scientific Points.")

Answer: The second sentence (page 17387, line 23) is based on the review of Graber and Rudich, 2006, where those values are reported to be significant for atmospheric HULIS. The too low ratio of 1 H/C is related to the precursors. Absence of any saturated aliphatic groups (except the methyl-ether-group) determines the final H/C ratio, although the ratio is slightly enhanced by addition of hydroxyl groups to the conjugated system.

***Added, p. 17386, 12:*** *"The O/C ratio between 0.3 and 1 is in good agreement with the reported O/C ratios for LV-OOA (low-volatile oxidized organic aerosol) and SV-OOA (semi-volatile OOA) (Jimenez et al., 2009). Further, the medium value of 0.6-0.7 fits the described oxidation state of atmospheric HULIS very well, although the measured H/C ratio of about 1 is lower than the reported 1.6-1.7 (Graber and Rudich, 2006). The H/C ratio is in good agreement with the widely used proxy SRFA (Dinar et al., 2006)."*

g) Page 17378, beginning on line 28: "The medium mass of organic molecules in the particles of 300–450 Da is close to natural HULIS samples." Similar comments as presented in point (f) are applicable for this statement.

Answer: The respective sentence has been changed.

***Revised, p. 17385, 22 – 25:*** *"The main m/z ratio of organic molecules in the particles of 200-450 is closer to natural HULIS samples than SRFA (Graber and Rudich, 2006) and is comparable to other SOA samples from photooxidation (Kalberer et al., 2004).*

*The distribution of the m/z signal in ICR-FT/MS is very similar between the catechol- and guaiacol-aerosol extracts. A detailed description on the elementary composition level shows signals that are typical of the catechol or guaiacol origin."*

a) Page 17372, beginning on line 7: "Aerosol chamber studies have been applied to investigate particle formation and processing (Iinuma et al., 2004)." I believe the authors are specifically referring to $\alpha$-pinene derived SOA. In that case a single reference (that is not a review on SOA or $\alpha$-pinene derived SOA) is inadequate because there are numerous papers on the SOA particle formation and processing from this important biogenic precursor. The authors can either give several specific references (preceded by an "e.g.") or refer the readers to some of the recent reviews on SOA that discuss $\alpha$-pinene derived SOA [*Hallquist et al.*, 2009; *Kroll and Seinfeld*, 2008].

Answer: This section has been revised.

***Revised, p. 17372, 6-14:*** *"While the formation of SOA from different terpenes (e.g. Jonsson et al., 2007; Jonsson et al., 2008; Iinuma et al., 2004) has been studied in detail and summarized in recent reviews (Yu et al., 2008; Kroll and Seinfeld, 2008), there is still a lack of knowledge of SOA formation from aromatic precursors (Johnson et al., 2005). The atmospheric oxidation of benzene has been studied in detail (e.g. Lay et al., 1996). Forstner et al. (1997) studied the formation of SOA from toluene- and xylene-type precursors, discussing ring-opening mechanisms based on reactions with hydroxyl radicals. Studies on formation and processing of those precursors according to SOA formation at* $NO_x$ *conditions have been performed by Ng et al. (2007) and Jang and Kamens (2001). Fisseha et al. (2004) used 1,3,5-trimethylbenzene as precursor and determined a contribution of 20-45% of organic acids to the overall aerosol mass. Formation of airborne polymers from photooxidation of aromatic precursors by reaction of carbonyls and their hydrates is reported by Kalberer et al. (2004). Sun et al. (2010) report dimer formation in aqueous-phase reactions of different phenols, including guaiacol. Physico-chemical properties of those aerosols according to optical properties and functional groups are hardly reported."*

3) Other Technical Problems:

a) The chemical structures of catechol and guaiacol are not shown and should be presented as a figure or as an inset on an extant figure. The molecular weight of these

compounds should be stated.

Answer: A figure with the chemical structures has been added as Fig 1.

***Added p. 17373, 5:*** *"Catechol is also known as pyrocatechol, 1,2-dihydroxybenzene or benzene-1,2-diol. It is the ortho isomer of the three isomeric benzenediols (Fig. 1). Catechol is also used as a model compound for soils (Huber et al., 2010). Fahimi et al. (2003) used different derivatives of benzene, including catechol to study the formation of chloroacetic acids. The transformation of catechol to humic polymers with the context of humus formation was studied by Ahn et al. (2006)."*

***Added p. 17373, 20:*** *"Also the methyl-ether modification of catechol, guaiacol could be used to study aerosol formation. It is also known as o-methoxyphenol, 2-methoxyphenol or methylcatechol (Fig. 1). "*

***Revised, p 17379, 2-4:*** *" The precursors for the SOA were catechol (Riedel-de Haën, 32101, pro analysis grade, >99% HPLC) and guaiacol (Sigma Aldrich, G5502, pro analysis grade, >99% GC) (Fig. 1). Catechol has a molecular weight of 110,11 g* $mol^{-1}$*, guaiacol of 124,14 g* $mol^{-1}$*."*

1. The purity of catechol and guaiacol should be stated if known. This is especially important because of the impurities noted by the authors as determined by ultrahigh resolution mass spectrometry (page 17378, beginning on line 19).

Answer: page 17378, line 19: The impurities determined by ICR/FT-MS are caused by the quartz filters. The sentence in parenthesis was changed into "(only few formulae corresponding to impurities were found as CHNO, CHOS and CHNOS, which are caused by the quartz filters)";

1. If "Labsphere" is the name of a corporation it should be capitalized throughout the document.

Answer: page 17377, line 15-17: “Labsphere” has been capitalized.

d) Table 2: The term “catechol dark” is italicized while the rest of the terms in that column are not.

Answer: Table 2: This row in table 2 is italicized on purpose, in order to clarify that all changes in intensity of the other samples are related to the catechol dark spectrum.

e) Figure 2: The abbreviation for “CAe” for particle mass concentration should be replaced by the more commonly used abbreviation *COA*. If the authors want to retain the abbreviation CAe they should define it in text.

Answer: page 17396, new figure 3 and new figure caption 3: The abbreviation $C_{OA}$ has been added and has been used throughout the document.

f) Page 17374, beginning on line 2: “Organic matter is semi-volatile and thus readily exchanges between gas and aerosol phase.” This statement is incorrect. Organic matter observed in particles has a range of volatilities that includes nonvolatile, semivolatile, and intermediate volatility compounds. An excellent discussion of the volatility distribution of organic compounds in particles under atmospheric conditions is given by Robinson and coworkers [*Robinson et al.*, 2007].

Answer: page 17374, line 2: The sentence “Organic matter is semi-volatile and thus readily exchanges between gas and aerosol phase” has been taken from Jimenez et al 2009. However, the overall paragraph has been deleted upon the suggestion of referee #1 to shorten the introduction.

II) **Scientific Points**: The following section addresses scientific deficiencies in the reported work.

1) Aromatic SOA: I do not understand why the authors discuss $\alpha$-pinene derived SOA and abnegate any explicit discussion of SOA derived from other aromatic precursors, including benzene, toluene, xylene, and 1,3,5-trimethylbenzene.

Answer: We have added more discussion about other precursors to the introduction and have discussed their results related to SOA from catechol or guaiacol. The conclusions will also be extended focusing on comparison of SOA from catechol and guaiacol and other precursors.

***Added P 17372, 14:*** *“The atmospheric oxidation of benzene has been studied in detail (e.g. Lay et al., 1996). Forstner et al. (1997) studied the formation of SOA from toluene- and xylene-type precursors, discussing ring-opening mechanisms based on reactions with hydroxyl radicals. Studies on formation and processing of those precursors according to SOA formation at* $NO_x$ *conditions have been performed by Ng et al. (2007) and Jang and Kamens (2001). Fisseha et al. (2004) used 1,3,5-trimethylbenzene as precursor and determined a contribution of 20-45% of organic acids to the overall aerosol mass. Formation of airborne polymers from photooxidation of aromatic precursors by reaction of carbonyls and their hydrates is reported by Kalberer et al. (2004). Sun et al. (2010) report dimer formation in aqueous-phase reactions of different phenols, including guaiacol. Physico-chemical properties of those aerosols according to optical properties and functional groups are hardly reported.”*

a. These compounds are more structurally similar to the featured analytes (i.e. catechol and guaiacol) compared to $\alpha$-pinene, and have been the focus of many chamber-based SOA studies (e.g. [*Fisseha et al.*, 2004; *Jang and Kamens*, 2001; *Kalberer et al.*, 2004; *Ng et al.*, 2007])

b. Has SOA derived from any of these or other aromatic precursors been shown to have any of the physical or chemical characteristics similar to atmospheric HULIS? This is an important point to address in the discussion because the aforementioned aromatics are more frequently employed in chamber-based SOA studies than catechol and guaiacol and are also more important anthropogenic volatile organic compound (VOC) emissions.

Answer: A comparison to HULIS-properties of those compounds has been added to the introduction. Catechol and guaiacol are used as model compounds in soil science [Fahimi et al., Chemosphere, 2003; Ahn et al., Soil Biology & Biochemistry, 2006; Huber et al., Enivron. Sci. Technol., 2010]. A detailed discussion about their use in soil science and as a model for atmospheric science has been added.

***Revised, p 17372, 6-14:*** *"While the formation of SOA from different terpenes (e.g. Jonsson et al., 2007; Jonsson et al., 2008; Iinuma et al., 2004) has been studied in detail and summarized in recent reviews (Yu et al., 2008; Kroll and Seinfeld, 2008), there is still a lack of knowledge according to SOA formation from aromatic precursors (Johnson et al., 2005)."*

***Added p 17372, 14*** *see above.*

***Revised, 17372, 15- 17373, 20:*** *"The state-of-the-art model of atmospheric HULIS, since 20 years in use, is based on selected macromolecular structures with an aromatic or olefinic core (Mukai and Ambe, 1986). The large aromatic content of HULIS may origin from oxidative and non-oxidative particle-phase reactions of different precursors including aromatics (Kroll and Seinfeld, 2008). Gelencsér et al. (2003) report formation of light-absorbing organic matter from aromatic hydroxy-acids with hydroxyl radicals and suggest those products as HULIS. Hoffer et al. (2004) characterized the Fenton-reaction products of 3,5-dihydroxybenzoic acid with OH radicals as synthetic HULIS. Humic substances, especially commercial humic and fulvic acids (e.g. Suwannee River fulvic acid (SRFA)) seem to differ significantly from atmospheric HULIS, as reported by a detailed and critical review about the humic-like character of atmospheric HULIS (Graber and Rudich, 2006). Further, their preparation as aerosols inside an aerosol smog-chamber is rather difficult. Thus, precursors are needed as in-situ model substances to generate SOA with HULIS qualities (Cowen and Al-Abadleh, 2009).*

*An appropriate candidate for SOA with HULIS-properties is catechol, which is also reported as a strong emission from open biomass burning (Hays et al., 2005) and fireplace combustion (Fine et al., 2002) leading to so-called biomass-burning organic*

*aerosols (BBOA). Catechol is also known as pyrocatechol, 1,2-dihydroxybenzene or benzene-1,2-diol. It is the ortho isomer of the three isomeric benzenediols (Fig. 1). Catechol is also used as a model compound for soils (Huber et al., 2010). Fahimi et al. (2003) used different derivatives of benzene, including catechol to study the formation of chloroacetic acids. The transformation of catechol to humic polymers with the context of humus formation was studied by Ahn et al. (2006). Aerosol formation from catechol has been studied very recently (Coeur-Tourneur et al., 2009), obtaining large mass yields ranging from 17 to 86wt.% in a smog-chamber in the presence of ozone with only minor influence of self-produced OH, which is known from scavenger experiments to enhance the consumption of catechol by 30% (Tomas et al., 2003). The rate constant for the reaction of catechol with* $O_3$ *has been determined to be 9.6x10*$^{-18}$ *cm*$^3 s^{-1}$ *at 298K, and the vicinal OH groups have been suggested as a potential cause of the high reactivity of catechol towards ozone (Tomas et al., 2003). The gas-phase reaction of dihydroxybenzenes with OH radicals has been studied in detail (Olariu et al., 2000). Furthermore, infrared spectroscopy of the oxidation of catechol has been performed in aqueous phase (Khovratovich et al., 1998). Aerosol flow reactor studies demonstrate ring-opening processes and formation of carboxylic acids located at aromatic or olefinic sites (Ofner et al., 2010). Nieto-Gligorovski et al. (2008, 2010) studied oxidation reactions of 4-carboxybenzophenone/catechol films using UV/VIS and FTIR spectroscopy. They report a photosensitized oxidation of the phenolic precursor by ozone in the presence of simulated sunlight to form products with properties similar to HULIS. Processing of catechol aerosol has been studied recently (Broeske et al., 2003). Also the methyl-ether modification of catechol, guaiacol could be used to study aerosol formation. It is also known as o-methoxyphenol, 2-methoxyphenol or methylcatechol (Fig. 1)."*

2) Humidity: How was the relative humidity (RH) regulated in the smog chamber? How was RH determined? How accurate is the RH? Why was a RH of 25% the highest RH value employed in these studies?

Answer: The relative humidity, used in the experiments, is limited by the absorption of infrared radiation by water. Useful infrared spectra using the long-path absorption optics could only be obtained at RHs up to 25%.

***Added p 17375, 17:*** *"The relative humidity was regulated at the beginning of the smog-chamber experiments by vaporizing a calculated amount of water. The Magnus equation (Sonntag, 1990) was used to calculate the saturated vapour pressure. The saturation gave access to the absolute amount of water, which was achieved based on a given relative humidity. The relative humidity was monitored using a Steinecker hydrometer (Type 49076D). The upper level of relative humidity was limited by the interference of water absorption in the long-path infrared absorption spectra."*

3) H/C ratio: On page 17387, beginning on line 22, the authors state: "But the measured medium H/C ratio of 1 is too low for atmospheric HULIS. The reported values are between 1.6 and 1.7." As stated above, the authors must reference the reported H/C range. The H/C range of approximately 1 is similar to those reported for Suwannee River fulvic acid (e.g. see Table 3 in Dinar et al.[*Dinar et al.*, 2006]), which is not discussed or noted in the report and should be included because it is often used as a proxy to atmospheric HULIS in many recent studies (e.g. [*Baduel et al.*, 2009; *Dinar et al.*, 2006; *Hatch et al.*, 2009]). The authors need to establish through a meaningful discussion that SOA derived from catechol and guaiacol is a better proxy to atmospheric HULIS than commercially available Suwannee River fulvic acid and humic acid.

Answer: The discussion of H/C ratios has been clarified and referenced. We may state that this model compounds represent the aromatic part of HULIS. Some features of SOA from catechol and guaiacol are closer to natural HULIS than from SRFA, as we added to the conclusions. Further, catechol and guaiacol allow organic aerosol formation in aerosol smog-chambers without the need of nebulising or vaporizing a dilution of SRFA.

***Added, p 17385, 22:*** *"The main m/z ratio of organic molecules in the particles of 200-450 is closer to natural HULIS samples than SRFA (Graber and Rudich, 2006) and is comparable to other SOA samples from photooxidation (Kalberer et al., 2004)."*

***Added, p 17386, 12:*** *"The O/C ratio between 0.3 and 1 is in good agreement with the reported O/C ratios for LV-OOA (low-volatile oxidized organic aerosol) and SV-OOA (semi-volatile OOA) (Jimenez et al., 2009). Further, the medium value of 0.6-0.7 fits the described oxidation state of atmospheric HULIS very well, although the measured H/C ratio of about 1 is lower than the reported 1.6-1.7 (Graber and Rudich, 2006). The H/C ratio is in good agreement with the widely used proxy SRFA (Dinar et al., 2006)."*

***Revised chapter conclusions, paragraph 6-7:*** *"SOA from catechol and guaiacol provides several features according to natural and synthetic HULIS and commercial proxies as discussed above. Especially the high molecular weight caused by the aromatic system and the polycarboxylic acidic functionality matches those properties.*

*Due to the easy preparation it is applicable for lab-scale measurements of organic aerosol processing in aerosol smog-chambers or aerosol flow reactors. Commercial HULIS proxies like SRFA need special and complex preparation techniques like ultrasonic nebulising or atomizing of solutions. The easy formation even in the dark or at different simulated environmental situations using only one precursor allows aerosol preparation with comparable properties. SOA could perform like SV- and LV-OOA using aerosol-smog-chamber experiments close to natural conditions. Different stable aged modifications of SOA from catechol and guaiacol could be obtained. Synthetic SOA from catechol and guaiacol produced in aerosol smog-chamber experiments fulfil the physical chemical characteristics of HULIS better than SRFA due to their analytical properties and can be used as atmospheric model substances for HULIS in laboratory experiments to study heterogeneous reactions with aromatic or olefinic cores."*

4) Molecular weight: In the abstract the authors state: "Ultrahigh resolved mass spectroscopy (ICRFT/MS) determined O/C-ratios between 0.3 and 1 and main molecular weights between 200 and 500 Da." However, in the conclusion (Page 17387, begin-

ning on line 28) the authors state: “The medium mass of organic molecules in the particles of 300–450 Da is close to natural HULIS samples.” The authors should clarify what the term “main molecular weight” means. I think the term “medium mass” is vague and the appropriate terminology should be employed. As noted above, this statement needs to be referenced. The authors also need to develop the discussion that compares their results for the molecular mass of compounds in catechol and guaiacol derived SOA with the molecular mass of compounds in atmospheric HULIS samples. This includes addressing problems with HULIS associated with the water soluble organic compound fraction of atmospheric aerosols that may be either high molecular weight macromolecules or a complex mixture of poorly separable compounds (see the review on HULIS by Graber and Rudich [*Graber and Rudich*, 2006] for further discussion). In summary, the authors have presented a vague description of the molecular weight of compounds in catechol and guaiacol derived SOA particles and also have not formulated a convincing argument that this class of SOA is a good representation of atmospheric HULIS.

Answer: The term “main molecular weight” has been replaced by “main observed m/z ratio”. Since we have no obvious correlation of molecular weights with the data we see in FTMS. We only detect the molecules in the gas phase ionisable in ESI(-) within the frame of the experimental conditions of FT/MS. . . .the masses are in the same range. A discussion on comparability of those derived values to the review of Graber and Rudich has been added.

***Added, p 17385, 22:*** *“The main m/z ratio of organic molecules in the particles of 200-450 is closer to natural HULIS samples than SRFA (Graber and Rudich, 2006) and is comparable to other SOA samples from photooxidation (Kalberer et al., 2004).”*

***Revised chapter conclusions, paragraph 1-5:*** *“SOA from catechol and guaiacol typically exhibits small particles with diameters between 40 and 90 nm, built up by a very fast formation process. Those particles have a nearly perfect spherical morphology, indicating their airborne formation by gas-to-particle conversion. Environmental conditions like solar radiation or relative humidity influence not only physical properties like aerosol size distributions or formation yields but also chemical properties like the total amount of oxidized sites and amount and types of functional groups.*

*The difference between the H/C values is explained by the absence of aliphatic side chains in the SOA from catechol and guaiacol. Hence, SOA from those precursors represents the aromatic and olefinic oxidized core structure of atmospheric HULIS very well. Only saturated aliphatic parts of atmospheric HULIS are not represented.*

*Light absorption of those organic particles ranges from less than 200 nm up to 600 nm into the visible region and declines very smoothly. Thus, derived SOA samples are light brown coloured. This optical feature indicates absorption processes according to aromatic or olefinic structures with a large variety of chemically bound oxygen.*

*The chemical transformation from the gaseous precursor to the final aerosol particle is distinguished by the formation of different functional groups and disappearance of well defined structural elements of the entire benzene ring. The aromatic or olefinic structural element, an important attribute for atmospheric HULIS, still persists in the aerosol particle.*

*The variation of simulated sunlight or relative humidity results in various degrading structural elements like aromatic $\nu$(C=C) and $\nu$(C-H) stretch vibrations and pronounced oxygen containing functional groups, shifting $\nu$(C=O) vibrations.”*

5) The authors provide no meaningful discussion that compares the optical properties of catechol and guaiacol derived SOA particles to atmospheric HULIS or other laboratory generated materials that have been suggested to be a model for atmospheric HULIS. For example, Gelencsér et al. [*Gelencsér et al.*, 2003] formed a brownish material by reacting 3,5-dihydroxybenzoic acid with OH radicals, which was subsequently shown to have properties similar to naturally occurring HULIS[*Hoffer et al.*, 2004]. The optical properties of the products derived from 3,5-dihydroxy-benzoic acid and any other aromatic precursors that have been proposed to be models or proxies for at-

mospheric HULIS should be compared to those properties for catechol and guaiacol derived SOA.

Answer: A comparison of optical properties was added to chapter 4.4 and to the conclusions (see above). We have added and discussed the suggested and new available literature. Further, we will focus more on other model compounds and atmospheric samples related to our compounds. The used precursors have been discussed according to their model features for soil science. According to investigating formation and changes of functional groups, we have discussed now the absence of any saturated aliphatic compound (normally shown by atmospheric HULIS). This absence helps to assign changes, triggered by heterogeneous processing with atmospheric trace gases, to the aromatic core structure. Hence, SOA from catechol and guaiacol only represents structural elements related to the HULIS core structure, without aliphatic side chains.

***Added p 17384, 15:*** *"The UV/VIS spectra are in good agreement with other aromatic precursor oxidation studies (Gelencsér et al., 2003; Hoffer et al., 2004). Especially the* $\pi \rightarrow \pi^*$ *electronic transition at about 260 nm is similar to natural HULIS samples (Baduel et al., 2009)."*

**Conclusion**: While the topic of the submission of Ofner et al. is in accord with the theme of ACP, this work has extensive technical concerns that must be corrected prior to resubmission. More importantly, this work also lacks a meaningful discussion of how the results obtained by Ofner et al. compare to other important studies. After reading this paper I was not convinced by the authors that catechol and guaiacol derived SOA is an appropriate model for atmospheric HULIS.

Answer: We have addressed the technical concerns properly and we do hope that we have convinced the referees and the readers of ACP that SOA derived from catechol and guaiacol is a model substance that exhibits interesting and unique features, which can not be simulated with other model systems, and therefore is suited for more detailed investigations also by other groups working in this field. We state that our model compound "only" represents a structural element of the overall complex system "HULIS". Hence, this model compound may serve as a proxy for the aromatic/olefinic core structure of atmospheric HULIS.

**The title was changed based on this statement to "Physico-chemical characterization of SOA derived from catechol and guaiacol – a model substance for the aromatic fraction of atmospheric HULIS"**

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/C8574/2010/acpd-10-C8574-2010-supplement.pdf

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