

Chemical characterization of the main secondary organic aerosol (SOA) products formed through aqueous-phase photonitration of guaiacol

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Response to comments from Anonymous Referee #2

General comments:

This paper is of high interest, as it provides a thorough chemical analysis of atmospherically relevant compounds, i.e. nitroguaiacols that are formed secondarily in the atmosphere after biomass burning emissions, and may contribute a significant role in the light absorption properties of Secondary Organic Aerosol (SOA). The chemical analysis determination is very well done with suitable different and complementary analytical devices (NMR and HPLC/(-)ESIMS-MS), after isolating the target compounds. This systematic approach is very important and useful for the characterization of ambient and smog chamber organic matrices which are highly complex and require deep investigation to avoid misinterpretations as shown at the end of the paper.

My two main concerns deal with 1) the lack of description and discussion on the aqueous phase photooxidation processes (which are claimed to be the goal of the paper); and 2) the inappropriate use of the SOA term: there is no discussion on the volatility of the target nitroguaiacols as compared to their precursor (guaiacol), and their potential partitioning between the gas and the particle phases in the atmosphere (see detailed comments).

The results are significant and fully appropriate for the journal, the paper is well written, and I recommend its publication after revisions.

Re: We thank Reviewer #2 for useful comments and suggestions, which helped improving the quality of the manuscript. We agree that the text lacks an insightful discussion on the aqueous photooxidation processes and volatilities of the nitroguaiacol products. However, the main goal of the work described in the manuscript was the chemical characterization of formed photonitration products of guaiacol. Hence, we decided to leave the discussion on the photooxidation processes for our future works/papers. In addition, to the best of our knowledge, there is no empirical information about the volatility of the nitroguaiacols and the determination of their volatility was not the goal of the work presented neither. However, we accept the Reviewer's comment on the use of the SOA term and made appropriate corrections in the manuscript.

Detailed comments:

Title: the title is not appropriate in the current state of the paper: it suggests a study of aqueous phase mechanisms of photonitration of guaiacol, producing SOA after water evaporation, but neither these issues are discussed in the paper. In order to maintain the actual main goal of the paper, I suggest a more general title such as "Chemical characterization of atmospheric nitroguaiacols"

Re: The title of the manuscript was changed accordingly to reflect the main goal of the work presented.

Introduction:

p. 3995 line 13: add a reference

Re: A reference was added accordingly.

p. 3995 line 20: can the authors add a sentence about the water solubilities of the target compounds?

Re: The water solubilities of guaiacol, 4-methylguaiacol and syringol are 2.41×10^4 , 1.03×10^4 and 1.82×10^4 g/m³, respectively (Sagebiel and Seiber, 1993). These numbers, however, were not included in the revised text since it was corrected and rewritten from another point of view.

p. 3995 line 20: for the air/water partitioning: the reference cited (Sagebiel and Seiber, 1993) shows an aqueous phase enrichment of pesticides but not that of wood markers, which are the target compounds of the present paper. This issue needs to be revised, together with the overall justification of the aqueous phase study (see next comments).

Re: The text was corrected and rewritten. In the reference cited (Sagebiel and Seiber, 1993), there is a visible, approximately linear aqueous-phase enrichment of pesticides, which at first sight, cannot be clearly observed for the methoxyphenols. This does not mean that the authors did not observe and report any enrichment of the wood markers (studied methoxyphenols) in the aqueous-phase. On the contrary, they reported enrichment factors (EF) ≥ 1 (usually between 3 and 4; Table 5 in the reference), but with lower values compared to those for the pesticides.

p. 3995 lines 23-26: this last sentence is not clear at all. The link with the prior sentence is not obvious at all. This part should be more developed to justify the study performed in the aqueous phase.

Re: The text was corrected and rewritten accordingly.

p. 3997 lines 6-7: This is not the real goal of the paper as the aqueous phase processes implicated are not mentioned and not discussed, and also the formation of SOA is not even experimented. The study in the aqueous phase looks rather a way to produce nitroguaiacols from guaiacol, and not a full study of the aqueous phase processes, which would require a much more thorough description and discussion on the complex mixture of reactants (see for example Fischer and Warneck, 1996) and a discussion of the relative importance of direct photolysis of guaiacol as compared to its reaction towards the different reactants.

Re: We agree with Reviewer #2. This study was focused solely on the chemical characterization of the main guaiacol products formed by photonitration in the aqueous-phase. The guaiacol aqueous-phase processes, which are currently studied in our lab, were not discussed in this work. The text was rewritten taking into account the Reviewer's comment.

p. 3997 line 9: "The main goal..." this is the real goal of the paper!!

Re: We agree with Reviewer #2.

Experimental

Paragraph organization: the titles of paragraphs 2.1.1 and 2.1.2 are redundant, I suggest rather to suppress the title of paragraph 2.1.1, and leave its text as an introduction to the part 2.1

Re: The title of the paragraph 2.1.1 was removed, as suggested, but that of paragraph 2.1.2 was left (now renamed as paragraph 2.1.1 in the revised version) since it describes separate procedures for production of nitroguaiacols at a larger scale (which precede nitroguaiacols' isolation and identification).

p. 3998 lines 12-14 and lines 21-23: can the authors justify the reason why they used different initial reactant concentrations as well as different reaction times to prepare the solutions of 4NG and 6NG? Is it related to the kinetics of formation of these products? If yes, it should be very interesting to show these kinetics after quantification of these compounds, this would give some arguments in the study of their aqueous phase mechanisms of formation.

Re: The reaction conditions used for production of 4NG and 6NG are different, since 6NG is more reactive than 4NG towards additional nitration in the aqueous-phase, resulting in 4,6DNG. Therefore, a shorter reaction time, a higher concentration of guaiacol, and a lower one of nitrite and peroxide, were used for the production of sufficient amounts of 6NG (for semi-preparative purification). The kinetics and mechanisms of the aqueous-phase formation of 4NG and 6NG are beyond the scope of this manuscript. However, kinetic studies on their aqueous-phase photoproduction are currently undergoing in our lab.

Results and discussions

P. 4003 lines 15-16: it is true that the concentration of guaiacol employed is higher than those measured in fog water, but it should be on the order of what should be encountered in wet aerosol (see Ervens et al., 2011), also it is of the order of the upper values of the total methoxyphenols concentrations measured in fog samples (Sagebiel and Seiber, 1993).

Re: We agree. The text was corrected accordingly.

p. 4004 and 4005: the results shown for the quenching methods are very interesting, and convincing but again, prior these results, there is a lack of determination of what reactants need to be quenched. There is only a general statement (p. 4004 lines 5-7) mentioning reactants such as OH, NO₂ and H₂O₂. For OH radicals: the aqueous life time of OH radicals is lower than 1 second, so this reactant should not last in the dark, after sampling, and it does not need to be quenched. For NO₂ radicals: the authors should discuss how NO₂ radicals are formed in the reaction, and their role in the formation of nitroguaiacols. They should also discuss NO₂ life time in the aqueous phase in the dark. For H₂O₂: is this compound reactive towards guaiacol? If not, it does not need to be quenched.

Re: The aqueous-phase reactions of nitrite and hydrogen peroxide in the presence of sunlight and in the dark are complex and involve different reactive species (radicals, etc). In the presence of sunlight, the photolysis of hydrogen peroxide and nitrite serves as an important source of OH and other radicals (Vione et al., 2006): $H_2O_2 + hv \rightarrow 2 \cdot OH$; $NO_2^- + hv + H^+ \rightarrow \cdot NO + \cdot OH$. The nitrite can react with OH radicals and give nitro radicals: $NO_2^- + \cdot OH \rightarrow \cdot NO_2 + OH$. These reactive species (NO₂ and OH radicals) can react with electron-rich aromatics (such as guaiacol) and form different oxidation products, such as nitro-aromatics (Vione et al., 2005).

After quenching the reactions in the reaction mixture, it is reasonable to believe (which was also confirmed by additional experiments) that there are still some amounts of unreacted nitrite and hydrogen peroxide. Since the pH of the medium is acidic, it is also reasonable to state that part of the nitrite will be in the form of nitrous acid: $\text{NO}_2^- + \text{H}^+ \rightarrow \text{HNO}_2$. These unreacted species, i.e., H_2O_2 and HNO_2 can further react (also in the dark) resulting in a powerful nitrating agent, i.e., peroxyntrous acid (HOONO): $\text{H}_2\text{O}_2 + \text{HNO}_2 \rightarrow \text{HOONO} + \text{H}_2\text{O}$, which can generate NO_2 and OH radicals or other reactive species in acidic solutions, such as NO^+ and NO_2^+ , promoting electrophilic nitration reactions (Vione et al., 2003). Therefore, it is clear that a suitable quencher must be used to stop the reactions involving radical species, to enable the study of the reaction kinetics of guaiacol photonitration. The effective quencher should have the ability among others (previously stated) to destroy the remaining H_2O_2 to prevent unwanted nitration in the dark. The experiments show (as shown in the manuscript) that ascorbic acid is a suitable candidate for this purpose. We found that it can meet these requirements, since it is already known that it is an effective radical and H_2O_2 scavenger (Wang and Jiao, 2000). In conclusion, we unambiguously have shown that using ascorbic acid as quencher efficiently stops the reactions and is superior than reaction quenching by addition of catalase or by simple drying out of a reaction mixture aliquot.

Since the detailed elaboration on the radical reactions in the aqueous-phase during the photonitration of guaiacol is beyond the scope of the present manuscript (and more suitable for our future work), we did not make any changes in the text.

P. 4005 line 5: the reference to Sun et al. (2010) misrepresents what was actually published: these authors did not use the drying method as a quenching method, but rather as a method to produce SOA after water evaporation. Even though this method is somewhat drastic for SOA production (N_2 blow down does not represent the atmospheric gas-particle equilibrium), it has not been used to quench the reaction of phenol with OH radicals (and not with H_2O_2 : they showed no significant reactivity of H_2O_2 with phenol in the dark).

Re: We agree with the Reviewer. The text was corrected accordingly.

P. 4005 lines 10-16: here again, the authors forgot to justify why they used ascorbic acid as a quencher. They mention later (p. 4006, line 6-7) that it is an effective scavenger for superoxide radicals and H_2O_2 , but they forget to mention its effectiveness to quench singlet oxygen (Jung et al. 1995; Chou and Khan, 1983) which may be formed in their complex reactant mixture (?)

Re: The text was corrected accordingly.

P. 4006 line 17: the title of section 3.2 should be replaced by “characterization of the formed nitroguaiacol” as nothing is performed to produce SOA.

Re: The title was corrected accordingly.

P. 4008 lines 4-5: specify in the text that 4NG, 6NG and 4,6DNG are standards at this point.

Re: The change was made accordingly.

P. 4008 line 19: explain how the deprotonated molecule at m/z 213 is very stable as compared to those arising from 4NG and 6NG.

Re: The deprotonated molecule at m/z 213 is more stable than corresponding ions of 4NG and 6NG, due to the electron-withdrawing effect of the second nitro group in the structure of 4,6DNG. The

second nitro group further decreases the electron density of the aromatic ring and allows formation of a more stable anion (in negative ion ESI) in which the charge is delocalized within the aromatic ring. The delocalization of the charge lowers the ion's internal energy and thus increases its stability (Odum et al., 1994; Schmidt et al., 2006). The stabilization is also pronounced for the demethylated product ion at m/z 198 (phenoxy radical anion), which can form a rearranged ortho-quinone radical anion. As can be seen from the 4,6DNG spectrum in Fig. 5C, the lower m/z product ions have a lower relative abundance compared to corresponding ions in the MS/MS spectra of 4NG and 6NG, which additionally supports our claim.

P.4008 line 22: 4NG was isolated from the experiments described in section 2.1.2?

Re: That is correct.

Conclusions

P. 4015 line 10: "SOA-low volatility products": nothing is mentioned in the paper concerning the volatility of the products formed.

Re: The text was corrected accordingly.

Tables and Figures

Table 1: in each column write the appropriate numbers on the same line as the compounds' chemical structures

Re: We believe it is impractical to add the MS/MS parameters of the two SRM transitions separately for every nitroguaiacol (4NG, 5N, and 6NG), since the parameter values are the same for all of them.

Tables 5 and 6: what does the last column stand for?

Re: The last column is redundant; therefore, it was removed from the tables.

Fig. 2: do the authors have an explanation for the contrast between {4NG + 6NG} and 4,6DNG formation kinetics using catalase or ascorbic acid as quenchers?

Re: As already outlined in the manuscript, when catalase was used as quencher a non-zero value was obtained for the nitro-products (4NG, 6NG and 4,6DNG) at $t = 0$, indicating inefficient quenching of the aqueous-phase reactions. In contrast, when ascorbic acid was used as quencher, all products were absent from the reaction mixture at $t = 0$. Thus, the difference in the product formation curves (Fig 2A vs. 2B) is solely due to the difference in the efficiency of reaction quenching provided by the quenchers. The use of a quencher was indicated in our case since guaiacol and its products in the reaction mixture were measured off-line (by using a HPLC-UV method). Therefore, reaction quenching was required to ensure "conservation" of the reaction mixture at the point of sampling (at defined reaction times). Since the ascorbic acid provided the desired, efficient and instant quenching of the aqueous-phase reactions, it was proposed as a suitable quencher for the study of the guaiacol photonitration kinetics.

Fig 4, 5, 6 and 7: these figures are very interesting but the numbers are too small.

Re: The quality of the figures is high (600 dpi) and the size of the numbers and letters are adequate to their original dimensions. When the manuscript was published in AMTD, we noticed that the resolution of the figures was lowered (probably due to the limited byte size of the PDF manuscript), as well as their dimensions. For publication of the manuscript in the final AMT form, we hope that the original figures of full quality (resolution) will be used.

References:

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