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

Comments on the manuscript entitled “Chemical characterization of the main secondary organic aerosol (SOA) products formed through aqueous-phase photonitration of guaiacol” by Z. Kitanovski, A. Cusak, I. Grgic, and M. Claeys

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/(-)ESI-MS-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.

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”
- **Introduction:**
 - p. 3995 line 13: add a reference
 - p. 3995 line 20: can the authors add a sentence about the water solubilities of the target compounds?
 - 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).

- 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.
 - 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.
 - p. 3997 line 9: “The main goal...” this is the real goal of the paper!!
- **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
 - 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.
- **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).
 - Pp. 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.
 - 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 (N₂ 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 H₂O₂: they showed no significant reactivity of H₂O₂ with phenol in the dark).

- 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 H₂O₂, 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(?)
- 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.
- P. 4008 lines 4-5: specify in the text that 4NG, 6NG and 4,6DNG are standards at this point.
- 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.
- P.4008 line 22: 4NG was isolated from the experiments described in section 2.1.2?
- **Conclusions**
 - P. 4015 line 10: “SOA-low volatility products”: nothing is mentioned in the paper concerning the volatility of the products formed.
- **Tables and Figures**
 - **Table 1:** in each column write the appropriate numbers on the same line as the compounds’ chemical structures
 - **Tables 5 and 6:** what does the last column stand for?
 - **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?
 - **Fig 4, 5, 6 and 7:** these figures are very interesting but the numbers are too small.

References:

- Chou P. T. and Khan A.U.: l-ascorbic acid quenching of singlet delta molecular oxygen in aqueous media: generalized antioxidant property of vitamin C. *Biochemical and biophysical research communications*, 115, 932-937, 1983.
- Ervens, B., Turpin, B. J., and Weber, R. J.: Secondary organic aerosol formation in cloud droplets and aqueous particles (aqSOA): a review of laboratory, field and model studies, *Atmos. Chem. Phys.*, 11, 11069–11102, doi:10.5194/acp-11-11069-2011, 2011.
- Fischer M., Warneck P. (1996): Photodecomposition of Nitrite and Undissociated Nitrous Acid in Aqueous Solution. *J Phys Chem* 100, 18749-18756.
- Sun, Y. L., Zhang, Q., Anastasio, C., and Sun, J.: Insights into secondary organic aerosol formed via aqueous-phase reactions of phenolic compounds based on high resolution mass spectrometry, *Atmos. Chem. Phys.*, 10, 4809–4822, doi:10.5194/acp-10-4809-2010, 2010.
- Jung M.Y., Kim S.K. and Kim S.Y.: Riboflavin-sensitized photooxidation of ascorbic acid: kinetics and amino acid effect. *Food chemistry* 53, 397-403, 1995.