

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 #1

This paper presents results from trying to chemically characterize the products formed from the aqueous-phase photonitration of guaiacol. Aqueous-phase reactions of guaiacol were performed in the lab. The products formed were purified, collected, and then analyzed by various types of nuclear magnetic resonance (NMR) spectroscopy and electrospray ionization tandem mass spectrometry (ESI-MS/MS). The three main products formed from the aqueous-phase photonitration are discussed. The presence of these products is investigated in PM10 filter samples collected during the winter in Ljubljana, Slovenia.

This work is showing that guaiacol can contribute to secondary organic aerosol (SOA) formation, a process that is still not well understood. Given that this SOA formation can occur in the aqueous-phase and yield brown carbon it is even more significant since these are two very hot topics currently in aerosol science. Therefore, many in the atmospheric community would be interested in this work. Overall, this is a very good paper. The authors have clearly done a lot of really great analytical work. In addition, they provide the details of each step very clearly so readers can easily follow their work. The only weakness is that they really do not show ambient data even though filter samples were analyzed by the methods presented. This makes it harder for the reader to get a feel of the atmospheric concentrations of the aqueous-phase products studied in the guaiacol experiments. I might suggest adding a time series for these compounds from the filter samples analyzed. Given that guaiacol comes from biomass burning, then maybe a correlation between the compounds identified from its photonitration vs. levoglucosan or other biomass burning tracers could be shown. Otherwise, I have just a handful of minor comments outlined below that need to be addressed before this paper can be considered for publication.

Re: We thank Reviewer #1 for useful comments, which improved the manuscript. We also believe that time series using the ambient data for 4NG and 4,6DNG can promote further discussions on the origin of the nitroguaiacols in the atmospheric aerosol. In our previous work we described a novel HPLC/MS method for determination of several groups of nitroaromatics, including 4NG (Kitanovski et al., 2012). However, the measured concentration of 4NG in the winter samples was either below LOD or between LOD and LOQ of the method (Kitanovski et al., 2012). Therefore, we cannot supply additional information about 4NG (except for those already published), including time series. We also cannot provide time series for 4,6DNG for two main reasons. First, we already spent the entire PM samples for the analyses in previous (for HPLC/MS, GC/MS and EC/OC analysis) and present work. And secondly, the HPLC/MS method used for estimation of the concentration of 4,6DNG was not fully validated for 4,6DNG determination. That is why (as we stressed in the text) the 4,6DNG concentrations are only estimated, since we did not test the accuracy and precision of the method for its determination. The HPLC/MS methods described in the manuscript were used only for unambiguous identification of the nitroguaiacols in real samples.

Specific Comments: Abstract Page 3994, Line 5 – Suggest changing distributed in the atmospheric to distributed atmospherically in the

Re: The wording was changed accordingly.

Page 3994, Line 11 – The chemical formula used is not defined

Re: The chemical formula was defined accordingly.

Page 3994, Line 15 – The abbreviations 1H, 13C, and 2D are not defined

Re: The abbreviations were defined accordingly.

Page 3994, Line 22 – The abbreviation UV is not defined

Re: The abbreviation was defined accordingly.

Introduction Page 3995, Line 2 – Suggest removing the the before plant

Re: The change was made accordingly.

Page 3996, Lines 2 and 3 – The abbreviations H₂O₂, UV, and IR are not defined

Re: The abbreviations were defined accordingly.

Page 3996, Line 6 – The chemical formula used is not defined

Re: The chemical formula was defined accordingly.

Page 3996, Line 24 – The chemical formula used is not defined

Re: The chemical formula was defined accordingly.

Page 3997, Line 4 – Suggest changing nor its nitro-products have been to nor have its nitro-products been

Re: The change was made accordingly.

Page 3997, Line 8 – The chemical formulas used are not defined

Re: The chemical formulas were defined accordingly.

2.1.2. Solutions for the aqueous-phase photonitration of guaiacol at a larger scale Page 3998, Line 15 and 24 – Suggest changing under dark to in the dark

Re: The corrections were made accordingly.

2.2. Experimental setup for studying aqueous-phase reactions Page 3999, Line 13 – I am not sure I understand the phrase minimum 1 sun

Re: 1 sun is equivalent to irradiance of one solar constant i.e. 1367 W m⁻² (according to the World Metrological Organization). It was defined in the text accordingly.

2.3. Semi-preparative HPLC purification of the reaction product extract Page 4000, Line 6 – The chemical formulas used are not defined

Re: The chemical formulas were defined accordingly.

Page 4000, Line 14 – The abbreviation MW is not defined

Re: The abbreviation was defined accordingly.

2.4.NMR Analysis Page 4001, Line 3 – The chemical formula used is not defined

Re: The chemical formula was defined accordingly.

3.2.3.NMR spectra of the nitroguaiacols Page 4010, Line 5 – Suggest changing splitted to split

Re: The correction was made accordingly.

3.3.Identification of guaiacol SOA compounds in atmospheric particulate matter Page 4014, Lines 8-10 – These are the only ambient concentrations mentioned for the compounds identified from the aqueous-phase reaction of guaiacol. I think to make this more tangible to the reader it would be useful to supply a time series of 4NG and 4,6DNG in the PM10 filter samples analyzed from Ljubljana. If possible, since these two compounds are likely coming from biomass burning, having a correlation of them with levoglucosan or other biomass burning tracers would also provide useful information to assess their importance in ambient air.

Re: Unfortunately, at this stage we cannot provide more information about 4NG and 4,6DNG as explained above (general comments).

Supplemental Information S1.Chemicals Page 2 – I don't believe that section S1 is every referenced in the main text of the paper

Re: The section S1 is now referenced in the main text.

S2.Extraction and concentration of products from guaiacol photonitration Page 3, Line 3 – higher is misspelled

Re: The correction was made accordingly.

Page 3, Line 9 – Suggest adding an a before HLB

Re: The correction was made accordingly.

Page 3, Line 24 - Page 4, Line 1- Suggest changing compounds, such as: to compounds. These other solvents included

Re: The sentence was corrected accordingly.

S3.Product isolation after semi-preparative HPLC purification Page 5, Line 24 – Suggest changing weighted to weighed Page 6, Line 3 – Suggest changing weighting to weighing

Re: The corrections were made accordingly.

S4.Preparation of the standard solutions Page 7, Lines 2, 6, 9 – It should be 4,6DNG instead of 4.6DNG

Re: The corrections were made accordingly.

Page 7, Line 6 – Suggest adding an a before methanol

Re: The correction was made accordingly.

Table S1 Page 14, Line 3 – What is the note about re-equilibration time referring to? There is no star in the Table. Is it additional time after the 22 minute method outlined in the Table?

Re: The note about re-equilibration time is referring to the additional time (after the gradient) needed for complete column re-equilibration with the initial mobile phase composition before the next sample injection/analysis.

In Table S1, the star was removed and an explanation is given about the additional re-equilibration time.

References:

Kitanovski, Z., Grgić, I., Vermeylen, R., Claeys, M., Maenhaut, W.: Liquid chromatography tandem mass spectrometry method for characterization of monoaromatic nitro-compounds in atmospheric particulate matter, J. Chromatogr. A, 1268, 35-43, 2012.