

Interactive comment on “Molecular Composition and Photochemical Evolution of Water Soluble Organic Carbon (WSOC) Extracted from Field Biomass Burning Aerosols using High Resolution Mass Spectrometry” by Jing Cai et al.

Anonymous Referee #1

Received and published: 27 October 2019

General comments:

In this paper, the authors use direct high resolution mass spectrometry and liquid chromatography with high resolution mass spectrometry to study the aging of a water soluble organic carbon mixture from biomass burning aerosol. They also study the photochemistry of phenol and guaiacol in the aqueous phase, for comparison to their ambient results. This work provides an interesting combination of experimental methods and laboratory analyses to probe the composition and evolution of water soluble organic compounds at the molecular-level. However, prior to acceptance, I recommend

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the following clarifications in the presentation and discussion of the data, as well as the following grammatical corrections.

Specific comments:

In general, I think the structure of this paper could be improved. It is not immediately clear whether the data discussed in section 3.1 (Mass spectral characteristics of WSOC in biomass burning particulate) are from fresh particles. It seems to be discussing fresh particles, based on the titles of the other sections, but this should be made clearer in the text or in the section title. Section 3.2 (Photochemical oxidation of phenols under laboratory conditions) shows interesting results, but these results could be linked more explicitly to the ambient data presented in the paper. There is a short discussion of a comparison between laboratory and ambient data (lines 379-387) and other discussions in the following section (3.3), but as a reader, I find this information hard to keep track of. Perhaps the paper could benefit from a specific section for lab-ambient intercomparisons. Section 3.3.2 seems to be discussing photochemical stability—consider labeling more clearly as such. Section 3.3.3 seems to be discussing changes in composition as a result of different aging times—consider labeling more clearly as such.

The authors use straw burning aerosol in this study. How representative is straw as a fuel in the particular region the authors are studying? How representative is this fuel more generally? This should be addressed—there are lots of different types of fuel that are burned and the choice of straw should be put into appropriate context.

This study uses negative mode ionization only: how might this skew the types of compounds/compound classes identified? This should be discussed. Negative mode will ionize compounds that can be readily deprotonated, but what about compounds that are not easily deprotonated and may show up preferentially in positive mode ionization (e.g. compounds like amines)? How representative are the data in encapsulating mixture-wide characteristics if positive mode is not used?

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Line 211: CHS compounds do not ionize well with electrospray ionization, which may explain why they are not detected with much prevalence here. This should be discussed.

Are the molecular formulas with the lowest ppm mass difference selected here? Are there any other QC/QA methods you use, like ensuring H/C ratios are reasonable or checking for non-integer DBEs in neutral formulas?

In general, I find the methods a bit challenging to follow. There are lots of interesting sampling and analytical methods used here and the differences between them for accurately interpreting the results are important. Perhaps the authors could include a summary table or flow chart of the different types of sample collection methods and data analysis methods for field and ambient samples.

Line 228-231: Are these percentages by occurrence? By abundance? If weighted by abundance, how is ionization efficiency accounted for?

In Figures 3 and 4, what do the boxes around the data mean? This should be mentioned in the figure caption.

In Figures 2-4, the authors show 1-2 representative samples. How do we know that these samples are truly representative? The authors should consider showing the rest of the data in the SI and highlighting how similar the data are, or perhaps should consider finding a way to show averages across all samples in main text figures.

Line 325-327: I agree that there is an increase in the average O/C of product compounds relative to their precursors, but this is to be expected. There are many products formed during phenol and guaiacol photochemistry, some of which probably have higher O/C than the precursor compounds and some of which may fragment and have lower O/C. While the average O/C of the product mixture increases, it should be acknowledged that this is an average and that many different product compounds are formed.

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Line 343-345: What were the starting pH values and are these changes statistically significant?

Figures 5 and 6 don't show drastically different information, they can probably be combined.

Lines 511-526: It should be clearer which time points you are referring to for these O/C and H/C ratios (t=0? T=4? T=12?).

Line 547: Past work that has discussed the relatively short lifetime of CHON compounds like nitrophenols (order of hours, depending on conditions). In this manuscript, the authors mention that CHON compounds tended to exhibit good stability. What do you estimate the atmospheric lifetime of CHON compounds observed in your analysis to be and how does this compare to past literature?

Technical corrections:

The quality of the writing in this manuscript should be improved upon prior to publication. These are some suggested edits, but in general the authors should carefully review the language in their manuscript.

Abstract

-Line 34: remove comma between “precursor” and “were”

-Line 35: remove comma after “both”

-Line 39: “of” instead of “on”

-Line 41: “extracts” instead of “extract”

-Line 47: “has” instead of “have”

Introduction

- Line 53: space before “WSOC”

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- Line 61: space before “Although”
 - Line 66-67: for clarity, please define functional groups in words first before using abbreviated descriptions
 - Line 68: “carbonyls” instead of “carbonyl”
 - Line 71: could be clarified, what do you mean by “to affect aerosol evolution processes”?
 - Line 82: consider removing the word “emerged”, its meaning is unclear here
 - Line 84: “environments” instead of “environment”
 - Line 109-112: this sentence needs re-structuring for clarity: be more explicit and clear about why LC will help relieve ion suppression and how it will help identify ions (both are possible because of differences in LC retention time between compounds, but this should be made more obvious, for readers who do not frequently use LC techniques)
 - Line 118: “were” instead of “was”
 - Line 120: the word “reference” does not seem to be what you mean to say here, what about changing to “for comparison”?
- Methods - Line 158: What is this ratio in your extraction vs. in actual cloud water?
- Line 160: “In the experimental section of phenol photochemistry” is confusing, perhaps re-phrase to “To study phenol photochemistry”
 - Line 160: “solution” should be “solutions”
 - Line 162: remove comma after “H₂O₂”
 - Line 166-169: should be re-phrased, also I imagine you do not mean that you are looking for “biomarkers” but instead “tracer compounds”?
 - Line 171: define “ESI” the first time you use it

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- Line 176: Orbitrap should be capitalized consistently throughout the text
- Line 185: the plural of “spectrum” is “spectra”
- Line 208: please write out the full name of the “nitrogen rule”

Results and Discussion - Line 215: title seems incomplete, missing the word “matter”

- Line 216: “2.5” should be written as a subscript here and throughout the text (i.e. PM_{2.5})
- Line 224: “spectrum” should be “spectra” if the authors meant it to be plural, also what is meant by “abstracted blank”? I assume this should say “subtracted”
- Line 234-235: this sentence is incomplete
- Line 265: this sentence should be clarified: what is meant by “low content”? Low mass loading?
- Line 290: remove “emerged”
- Line 320: remove comma after “4h”
- Line 328: add “after” before the word “photooxidation”
- Line 321-331: should be clarified, if phenols and methoxyphenols are undergoing photochemical aging, how are they impacting POA?
- Line 351: remove comma after “mechanism”
- Line 357: for clarity, consider using “chromatograms” instead of “diagrams”, and propagate through text
- Line 378: remove “emerged”
- Line 380: remove “stemmed”
- Line 505: “parameter” should be plural

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- Line 520: should be re-phrased for clarity, what is meant by “increased tendency”, what exactly is “consistent with LC observations”?

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