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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Triplet State Formation of Chromophoric Dissolved Organic Matter in Atmospheric Aerosols: Characteristics and Implications" *by* Qingcai Chen et al.

Anonymous Referee #2

Received and published: 24 February 2020

General comments:

In this manuscript, the authors describe the formation of triplet state chromophoric dissolved organic matter (3CDOM*) from a variety of aerosol samples, including laboratory generated primary organic aerosol and secondary organic aerosol, and ambient particulate matter, under simulated sunlight. Using trimethylphenol as a probe for 3CDOM*, all aerosol samples investigated formed 3CDOM* to a greater extent than the experimental control. The rate of formation of 3CDOM* in the aerosol samples was correlated with chemical and optical properties of the sample including fluorescence and UV-visible absorbance. The contribution of the 3CDOM* to form reactive oxygen

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species such as singlet molecular oxygen and hydroxyl radical was also quantified.

The experiments described in this manuscript were thoughtfully designed and executed rigorously. However, the communication of these results should be improved before publication, as indicated in my comments below. The writing style used in this manuscript makes it challenging to read at times. For example, the authors often state a conclusion before giving context or discussing the data. This requires the reader to read through the paragraph more than once to be sure of the meaning. In addition, there are grammatical issues such as in the materials and methods section which switches between past and present tense. Better clarity in the writing would greatly improve this manuscript and better communicate these interesting results. Furthermore, some of the data was presented without sufficient discussion of its meaning and its larger scientific context. For example, discussion is lacking about why the correlation of AAE and kTMP differs between laboratory generated aerosol and ambient aerosol samples; why there is a lack of linear correlation between kTMP and contribution of C1 for the SOA samples; and the meaning of the data shown in Figures 5 and 6.

Specific comments:

Lines 10 – 13: It is not clear what the two types of identified CDOM were and how that relates to nitrogen-containing chromophores.

Line 50: The topic of the reference “You et al. 2012” does not match with the text.

Lines 78 – 80: This section of text is very repetitive and uses vague terms “types and compositions” multiple times. Please clarify what you mean by CDOM “types and compositions”.

Lines 140 – 147: How long are the VOCs exposed to the low-oxidation and moderate oxidation conditions? The reaction time is only mentioned for the high-oxidation condition.

Lines 203 – 204: State what you used as the “high-concentration” and “low-

concentration" for TMP.

Lines 205 – 207: The reaction rate constant should not be expected to change with TMP concentration, but the rate of the reaction will change. The calculated k value on Figure S3 shows that the rate constant does remain essentially the same between the different concentration conditions.

Figure 1: Legend for A (ii) does not match terminology in figure caption of "LO, MO, and HO". And the caption for graph C does not explain what data is presented.

Lines 305 – 307: The first two sentences of section 3.2 seem to be contradicting each other. It is stated that the 3CDOM* formation rate is different for each aerosol source, but then the data is presented to show that the average formation rate is the same for all aerosol sources.

Lines 312 – 314: The TMP rate constants should be state for both the straw and wood burning samples.

Lines 314 – 316: Phenolic compounds would be expected to be present in both the wood burning samples and straw burning samples. How do you explain the difference in kTMP for these two samples?

Lines 324 – 330: Its surprising to me that the 3CDOM* does not depend strongly on the SOA precursor. Especially since these SOA materials will have different light absorbance properties. Do you have any further insight into why the 3CDOM* formation is so similar between these samples?

Lines 353 – 355: The strength of the correlations should be state in the text. In most cases there is only a moderate correlation between MAE or E2/E3 and kTMP.

Lines 369 – 372: Why would the correlation of kTMP and AAE be opposite between POA, SOA, and ambient PM? This result should be discussed further.

Line 377: "The 3CDOM* formation ability depends on the CDOM type." The data to

support this claim is not presented until the following paragraph and it does not fit the topic of the paragraph it is in.

Line 382: The comparison of the excitation-emission peaks to tryptophan and products from the Maillard reaction should have a reference.

Lines 383 – 384: The content of C3 in the samples is quite variable and seems to be a significant fraction in the moderate-oxidation and low-oxidation SOA samples. Could this tell you more about the SOA composition under different oxidation conditions?

Figures S7 – S10 should be referenced directly in the main text.

Lines 417 – 418: It would be helpful to refer back to the reaction pathways in Scheme 1 during this discussion.

Lines 420 – 422: The lack of correlation of C1 in the SOA samples with kTMP should be discussed as well.

Line 430: It is not clear what is meant by “external mixing state of photochemical aging level”.

Lines 431 – 432: The relative contribution of 3CDOM* to overall oxidation is not shown in Table S1. I could not find this data in the paper or the supporting information.

Lines 445 – 464: This section with the data on ROS production would be better suited in the Results & Discussion section of the paper.

Lines 446 – 450: The meaning of the signals and the type of sample shown in Figures 5 and 6 should be explained. As well, parts (a) and (b) should be explained in the text.

Supporting information:

Table S3: categories of oxidation should match text in main paper, with “low, moderate, and high oxidation”.

Figure S3: The label for the concentration of TMP shows 4×102 μM, but this does not

match with the main text description that the TMP concentration is 4 mM (4×103 μM).

Figure S4: Legend has incorrect spelling of ‘ammonium’.

Technical corrections:

Line 1: “chromophore” -> “chromophoric”

Line 3: “driving” -> “drive”

Lines 6 – 8: The wording of this sentence is unclear: “Biomass combustion has the strongest 3CDOM* generation capacity and the weakest vehicle emission capacity.” Is this trying to say that vehicle emissions have the weakest 3CDOM* generation?

Line 11: “structural-activity” -> “structure-activity”

Line 85: “expected” -> “well-suited”

Line 128: “is collected” -> “was collected”

Line 266: “were selected” -> “was selected”

Line 420: “Figure 3D” -> “Figure 4D”

Line 428: “has” -> “have”

Line 646: Incorrect spelling of author’s name: “Canonica”

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