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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 #1

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General feedback:

The authors sampled three different types of atmospheric aerosols onto quartz filters: (1) ambient PM2.5 in Xi'an, China, (2) primary organic aerosols from biomass burning, coal combustion and vehicle exhaust, as well as (3) laboratory-generated secondary organic aerosols from smog chamber experiments using a-pinene, limonene, naphthalene and toluene in a mixture of different yet unspecified concentrations. The list of all these samples are presented in Tables S1, S2, and S3. However, the data presented in the paper seems to have regrouped these samples in different and again unspecified ways with unsupported conclusions. All raw data of the experiments are unfortu-

nately missing. Nevertheless, the TMP probe is an appropriate method for quantifying 3CDOM*, yet further controls need to be presented. For example, TMP kinetics with the blank filter and in water (two negative controls), TMP kinetics for triplicate of one sample and TMP kinetics with a known 3CDOM* as a positive control. As it stands, experiments couldn't be reproduced due to lack of details and the authors should address this issue. Furthermore, the reported TOC measurements are appropriate, yet an emphasis on the importance of concentration for the measured kinetics should be added.

A serious revamp of the manuscript writing is also recommended to present a logical sequence of events/results. For example, a discussion of the method and why the method is appropriate using logical sequencing (for example reorganizing the logic presented in lines 61-76 where the last sentence of the paragraph remains unsubstantiated and the reader is left wondering that "TMP has a higher reactivity" than what & why "TMP is not easily affected by these substances" and). I encourage the authors to aim to be precise and concise throughout their text.

There is a missing discussion on how this study builds upon past work. For example, are the authors' results consistent (or not) with what other have observed so far? I would encourage the authors to state clearly what their hypothesis was and why they specifically chose the aerosol samples listed to support their hypothesis. Furthermore, was the starting hypothesis validated? The authors should clearly state their scientific approach.

Therefore, as it stands the paper has too little technical details, making it difficult to understand and interpret the results and thus difficult to recommend for publication in its current state.

Specific feedback:

For example, the data in Figures 1, 2, 3, 4 are incongruent with the samples described in Tables S1, S2, S3 and so clear explanations are required to follow the authors'

logic. A description of how the samples were grouped for experiments and how many experiments were conducted in total should also be added. The column for kTMP in the SI tables suggests that data was collected for each one of the samples, and so the data needs to be shown (at least in the SI). The authors should add a description of error bars/standard deviations/uncertainty of the measurement.

Acronyms: Avoid LO, MO, HO and avoid acronyms for chemical names, particularly since Atmos. Chem. Phys. does not have a word limit. Describe all acronyms in each figure caption. As it stands it is difficult to understand what is being plotted in most figures.

Title:

The title is misleading, as no “implications” of the work is mentioned.

Abstract:

Lines 4-5: the statement of 3CDOM* contributing significantly to aerosol photochemistry is a conclusion of the work, and not an introductory statement. There has yet to be studies demonstrating the impact of 3CDOM* to aging in the context of aerosol-cloud interactions.

Line 5: “the ability” of what?

Between lines 4-8: please add information on the types of aerosols investigated as well as the method used.

Line 6: be specific when mentioning primary, secondary and ambient aerosols. To some extent all these qualifies could indicate identical samples.

Line 11: The structure-activity relationship description should be made clear that it was developed in this work.

Line 16: be precise as to *how* the study verified that 3CDOM* drives 1O2. At the end: add a sentence relating to the implications of the work for aerosol photochemistry.

TOC art:

What is the meaning of the different colors/shades?

Introduction:

Lines 24-26: unsubstantiated sentence and unsupported by the chosen references. Best to use reviews on brown carbon (or even better, modeling studies) to support a claim on climate impacts, since the current references deal with laboratory studies.

Line 32: the Kaur et al. 2019 reference is only valid for the 1O2 claim in this sentence. Best to include accurate references for the other oxidants.

Lines 35-54: I encourage the authors to be more specific when referencing earlier studies. The authors should add and specify the mechanisms at play, the specific atmospheric environment (line 37), the explanation of how Corral Arroyo et al 2018 proved that the triplet state affected aerosol aging (lines 41-42), the explanation of how 3CDOM* contributes to SOA formation (line 45), the specific “certain chemical reactivity” (line 46), the specific “important role” (line 49).

Line 55: low concentrations compared to what?

Lines 58-59: consider rewriting this sentence. A method “becoming an early analysis method” appears to be an oxymoron, especially when a 1969 reference is used.

Line 61: specific the chemical probe method

Line 75: Why isn’t TMP not easily affected by “these substances”. Add more specific information.

Lines 84-85: specifically mention what (Korak et al., 2014; Ma et al., 2010; McKnight et al., 2001; Rosario-Ortiz & Canonica, 2016; Wenk et al., 2015) observed.

Lines 88-95: what is the study’s scientific hypothesis? Why were Xi’an samples studied? How do these samples help support the hypothesis?

Material and methods:

All raw data should be included. Enough detail must be included for any scientist to be able to reproduce the data presented and be able to compare future work with this work. As the manuscript stands, these details are missing.

All details on the vehicles and buses used for exhaust PM need to be indicated. Even adding pictures of the set up could be useful for future comparisons.

Lines 103-104: a 1000 L/min flow rate for a 24 h sample appears to be very high. The PM2.5 samplers I've worked with don't typically exceed 50 L/min. The authors should comment on this high flow rate and specify the instrument used for collection.

Line 114: why is the flow rate here only 16.7 L/min? why is different than previously mentioned?

How were the quartz filters pre-conditioned before sampling?

Lines 120-133: verbs should be in the past tense. A further lack of detail, which is rather frustrating for the reader.

Line 122: specific which alcohol.

Line 136: no need for acronyms here.

Line 141: what was the concentration of cyclohexane added?

Line 142: how was ozone produced? Which high voltage? Which instrument?

Line 150: discuss why the filters were ultrasonically extracted in light of the paper, "To Sonicate or Not to Sonicate PM Filters: Reactive Oxygen Species Generation Upon Ultrasonic Irradiation"(Miljevic et al., 2014)

Lines 152-153: the filter was made of what material?

Lines 153-154: add this background extraction data to the tables in the SI.

Line 159: The Sievers M9 TOC analyzer, as far as I know is from Suez Technologies, not from General Electric. . .

Lines 159-161: why was sample exposure to air and time a problem. Please show this data.

Line 162: specific which background samples

Line 165: describe in detail the offline analysis method.

Line 166: why was the background subtracted? Please show the data.

Line 174: define the background samples

Lines 176-177: define the "inner filter effect" and show the data

Line 180: show dimensions of the customized reactor in Figure S1

Line 186: why are the 25 oC and 50% RH conditions chosen? Are they relevant to Xi'an?

Line 195: show the calculation (in the SI) to arrive at a factor 1.2-1.3.

Line 203: specific the "previous study" as there are no references.

Lines 208-209: support this claim with references

Lines 209-219: this paragraph is vague and lacks details. Please specific which salts were investigated and why would the authors expect a salt effect on 3CDOM*? Which literature are they building upon?

Line 159 & 221: America is a continent not a country, and should be corrected.

Lines 220-221: add information on the column used in the UPLC.

Lines 226-227: show the data for this statement in the SI.

Lines 233-234: $^1O_2$ was quantified using EPR, how do these values compare with the

FFA method (Appiani et al., 2017)? How was the signal quantified? Which positive control was used?

Line 244: which probe was used?

Line 254: specify which types of CDOM and give examples.

Results and discussion:

I did not find any evidence to support scheme 1 in the paper. The authors should clarify how their own experiments rule out or support a particular pathway. I am rather sceptical that the measurements done in this study can differentiate between a chemical reaction and an energy transfer. How do the authors know whether the product is directly from 3CDOM* or from 1O2 + DOM? Also why did the authors chose to use the acronym BrC in this scheme when throughout the text, they use 3CDOM*? The scheme should also be made much larger and should have at least font size 12.

All figures should be separated into individual panels. For example, Figure 1 should be 3 separate figures. Why do only a few of the panels in figure 1B have error bars? Where is the error in Figure 1A? Why are there so many significant figures reported in Figure 1A; I doubt they are all meaningful. The acronyms in the figures should all be described in the caption.

Line 288: what is means by "more 3CDOM* is formed in the initial stage?

The average values reported in lines 307-308 represent which samples? What does the standard deviation represent? The authors should use IUPAC units and should report their values in seconds, rather than in minutes.

Line 308 contradicts line 307. The authors state no difference and then the authors state a significant difference. These statements need to be clarified that the seasonality of the ambient aerosols is now being discussed.

Line 312: what is the chemical difference between straw and wood burning?

Line 318: the authors claim that N-alkyl, carboxylic acids and alkanols do not produce 3CDOM*. Where is this evidence and/or this data?

Line 323: explain why aliphatic compounds cannot from 3CDOM* and why these specific compounds are attributed to the authors' result for vehicle exhaust.

Line 345: which "types" of 3CDOM* are the authors referring to? Be specific.

Figure 2: avoid all the acronyms in the middle of the figure. What do the error bars signify and why are the + values shown but not the – values?

Lines 366-367: show the data.

Figure 3: for optimal comparison, best to have all the same values for all the axes.

Figure 4 should be split into 4 or 5 individual figures. Why were SOA values not included in the fit and which mechanism explains their deviation from the fit?

Environmental implication:

Figures 5 & 6: why do the signals' noise look different in each figure?

Where and how did the authors identify C1 and C3 chromophores in the study? And how did they measure N-containing substances. None of these experiments appear in this study.

Line 472-473: this sentence is confusing. The hypothesis should be reiterated here and the results stated with the implications of the work. The authors should be comparing their work with previous work on 3CDOM* in the atmosphere in this section.

References: Appiani, E., Ossola, R., Latch, D. E., Erickson, P. R. and McNeill, K.: Aqueous singlet oxygen reaction kinetics of furfuryl alcohol: effect of temperature, pH, and salt content, Environ. Sci. Process. Impacts, 19(4), 507–516, doi:10.1039/C6EM00646A, 2017.

Miljevic, B., Hedayat, F., Stevanovic, S., Fairfull-Smith, K. E., Bottle, S. E. and Ris-

tovski, Z. D.: To Sonicate or Not to Sonicate PM Filters: Reactive Oxygen Species Generation Upon Ultrasonic Irradiation, Aerosol Sci. Technol., 48(12), 1276–1284, doi:10.1080/02786826.2014.981330, 2014.

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