

Atmos. Chem. Phys. Discuss., referee comment RC2  
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## Comment on acp-2021-842

Anonymous Referee #2

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Referee comment on "Characterization of aerosol triplet state in the separated components with different polarity" by Dongjie Guan et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-842-RC2>, 2021

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### Overview

The authors examine the photogeneration of triplet excited states ( $3C^*$ ) in extracts of fine particles collected from the atmosphere and from several emissions sources (e.g., wood burning). The novel aspect of the work is examining triplet generation in three different polarity fractions of the PM: high-polar water soluble material (HP-WSM), water-soluble humic-like substances (HULIS), and lower polarity methanol soluble material (MSM). They also measure the formation of singlet molecular oxygen ( $^1O_2^*$ ) and hydroxyl radical (OH) in some of their samples.

The broad idea of examining the photoreactivity of chromophores as a function of polarity is interesting. There are also some interesting results in the manuscript. But it's not clear that the results can be trusted since there are several important experimental errors, described below. The manuscript also suffers from a frustrating lack of care in the writing, which makes the work very difficult to read and understand. Based on these important and widespread problems, I recommend that the manuscript be rejected.

### Major Issues

1. Quenching. The quenching experiments used to distinguish between high and low

energy triplets (Section 3.3) are problematic. The authors examine the difference in  $1O_2^*$  formation with and without 1 mM sorbic alcohol (SA), which they believe will quench the high energy triplet states. But this concentration of SA is not high enough to completely prevent high-energy triplet states from reacting with dissolved  $O_2$  to make  $1O_2^*$ . This leads to an incorrect assessment of high and low energy triplets. The authors need to use the kinetics of the  $3C^* + SA$  and  $3C^* + O_2(aq)$  reactions, along with the SA and dissolved  $O_2$  concentrations, to understand what fraction of high-energy triplet states were actually quenched. They can then use this information to revise their estimate of high- and low-energy triplets.

Worse, the quenching experiments used to determine the contribution of triplets to OH generation (Section 3.4) are unusable. Sorbic alcohol, which they use as a triplet quencher, also reacts rapidly with OH to suppress its concentration. Thus examining the decline in OH with SA does not indicate the contribution of triplets to OH generation, as the authors believe, but shows the direct scavenging of OH. This is why the authors find an unreasonably high contribution of triplet states to the generation of OH. The authors should calculate the expected decrease in OH signal based on the competition of OH between the EPR probe DMPO and SA. This likely explains most of the reduction in OH observed, indicating these results are unusable.

Also in Section 3.4, the authors need to dig deeper into their  $1O_2^*$  results with the triplet quencher sorbic alcohol. Of course "... $3C^*$  is an important precursor for the photochemical generation of  $1O_2^*$ ". This is well known. The more interesting question is why doesn't sorbic alcohol completely quench  $1O_2^*$  generation? The authors should examine the competition kinetics of  $3C^*$  reacting with sorbic acid and  $O_2$  to see if their results make sense based on the concentrations of the two reactants.

2. TMP as a Measure of Triplets. The authors have ignored the potential inhibition of TMP decay by sample constituents, especially phenols and dissolved copper (Canonica, Photochem. Photobiol. Sci. 2008; Pan, ES&T, 2018). This inhibition slows the apparent decay of TMP, leading to an underestimate of triplet concentrations (or, here,  $k(TMP)$  and  $f(TMP)$ ). Since both phenols and copper will be most enriched in the HP-WSM fraction, the slow TMP loss seen in this fraction could be a result of inhibition (which is an artifact) and not the result of low triplet concentrations. The authors should measure inhibition factors of TMP loss in different fractions. This inhibition of TMP loss is a more likely explanation of their HP-WSM results than is the theory presented on page 12.

TMP inhibition is probably also a major contributor to the apparent lack of TMP loss in the BB samples (Fig. 2). Previous work has shown that biomass burning PM generate high levels of triplets (e.g., Kaur, ACP, 2019), including the authors' own recent work showing that BB emissions had the highest triplet reactivity (Chen, Atm Env, 2021). I suspect that part/most of this "missing reactivity" is due to inhibition of the TMP probe, which has been seen previously at DOC concentrations of 20 mg-C/L. Essentially, the oxidized TMP probe is reduced back to TMP by phenols in the BB extracts, reducing the apparent loss of TMP. See work by Canonica and others for a description of the inhibition. If this is the reason for the Fig. 2A BB results (which seems likely), it means that they're incorrect and that triplets are generated.

Also, the authors appear to believe that oxidant probes are perfectly specific, i.e., only react with the oxidant of interest, but this is not true. For example, TMP reacts with OH and  $1O_2^*$  as well as triplets. These interferences have often been minor in past studies, but this is not always the case. The authors should quantify OH and  $1O_2^*$  in some samples to see if they make significant contributions to TMP loss.

Finally, for triplets the authors report  $k(\text{TMP})$ , the pseudo-first-order rate constant for TMP loss, and  $f(\text{TMP})$ , the quantum yield coefficient for  $3C^*$ . While these quantities are useful for comparing with past work, they're limited in value otherwise. It would be much better to estimate and report  $3C^*$  production rates and quantum yields, which are more useful. The authors should think about how they could estimate these quantities based on their data.

3. The Writing. The manuscript is often difficult to read, sometimes because there are multiple ideas strung together without a logical flow or transitions, and sometimes because the text doesn't make sense. Examples of the latter include:

line 80, "The cause of the formation of  $3C^*$  is directly related to the chromophore."

lines 170-172, "The sorbic alcohol (1 mM) is used as a high-energy quencher to quench high-energy  $3C^*$  (Zhou et al., 2017a), and combine the  $\Phi(1O_2)$  to quantify the energy distribution of different  $3C^*$ ."

line 371: "For the organic component HULIS, the production of  $\cdot\text{OH}$  is mainly the effect of organic matter."

In addition, portions of the text are incorrect. For example, lines 122-123: "Note that the MSM [methanol-soluble material] here does not actually contain water-soluble substances, thus it represents water-insoluble organic matter." This is almost certainly not true: a significant portion of the compounds in the particles will be soluble in both water and methanol. Another example is lines 264-265: "At the same time, these small molecules are also easy to quench the triplet state." The evidence I have seen – that small molecules do not quench triplet states – contradicts the authors' claim.

Another writing issue is that the authors were not very careful, with numerous instances of typographic errors, incorrect capitalization, noun-verb disagreement, and other issues. The manuscript needs significant attention from a scientific English editor, but it also needs a reworking so that the authors clearly state what they mean. There are also multiple instances of incorrect citations, suggesting little care was taken in citing references. For example, on line 237, the Ervens et al. citation does not discuss any of the issues of the accompanying sentence.

Finally, in terms of writing, much of the discussion about the results is speculative and ignores or glosses over inconsistencies, either within the results or compared to past results. For example, the BB results (no triplet formation) directly contradicts past results showing high triplet reactivity in BB-influenced samples. In addition, it doesn't make any sense that the HULIS + HP-WSM mixture increases  $3C^*$  levels but significantly decreases  $1O2^*$ . I wonder if the mixture makes more OH, which reacts with TMP to make it appear as if more  $3C^*$  is formed.

#### 4. Other Experimental Issues.

There is no discussion of pH, which is an important variable. Were the pH values of the extracts controlled with a buffer? pH values (at least of aqueous extracts) should be listed in the paper. It seems likely that the different polarity extracts had different acidities, which could affect reactivity. This issue should be discussed.

There are no reported daily actinometry (i.e., photon flux) measurements, which make it impossible to extrapolate oxidant rates of formation to ambient conditions. Fig. S5 shows that the experimental light has a much higher photon flux at short wavelengths than actual sunlight, which might affect the chemistry. This should be shown in more detail. I assume that the two curves in this figure are adjusted to have the same peak magnitude, but this should be indicated. Actinometry is needed to relate the two curves.

#### **Minor Issues**

The authors should report  $k(TMP)$  in each polarity fraction of the extracts of the field blanks (that were taken through the entire sample procedure) and compare these to sample values. Also, additional information is needed about how blank corrections were done and the magnitude of these blank corrections.

The authors use the terms "probe" and "quencher" interchangeably, which is confusing. A probe is generally added at a low concentration to measure (but not perturb) the oxidant steady-state concentration, while a quencher is typically added at a high concentration to greatly suppress the oxidant concentration.

Information about the absorbance by each extract needs to be reported, e.g., MAE at 300 nm, Angstrom absorption exponent, and calculated rate of light absorption.

The word "ambient" is usually misspelled in the manuscript (e.g., in figures).

The title is confusing ("Formation characteristics of aerosol triplet state and coupling effect between the separated components with different polarity").

The abstract TOC art shows "Aging" converting ROS to C, but this process seems very unlikely. I recommend they remove this arrow unless there's good evidence this occurs.

line 32. This text is wrong: "Part of the photochemical reaction of aerosol is direct photolysis, and in most cases, it is driven by photochemically generated reactive intermediates..." This is incorrect: in direct photolysis, reactions are initiated directly by light, not by reactive intermediates.

I. 112. What was the flow rate of the sampler?

I. 128. What was the maximum storage time in the refrigerator?

Section 2.3. This OC/EC analysis section is confusing. By "original sample" do the authors mean the sampled filter? Is the "6 mm diameter filter membrane" a 6-mm punch taken out of the sampled filter and analyzed for OC/EC?

I.172.  $k(\text{TMP})$  is a rate constant, not a rate.

I. 187. The rate of light absorption (eq. 3) was determined for a wavelength range of 320 to 600 nm. But there is significant light absorption, and some photons from the solar simulator, at shorter wavelengths, so the lower wavelength range should be extended to 280 nm or shorter. Values of  $R(a)$  should be reported in the supplement.

I. 224-226. Fig. S11 doesn't seem to be correct figure for this point. The fact that the OC from combustion samples is higher than ambient samples is only a result of dilution. This last sentence doesn't add anything to the manuscript and should be deleted.

Fig. 1 (and other figures). (a) It would be helpful to have an explanation of how to read the nested pie (and bar) charts in the caption. (b) In bottom plot of Fig. 1, why isn't the OC bar equal to 100% on the Relative Content axis? Is it because EC or inorganic carbon included in the C budget? Why are the errors so large on the OC bars? The relative

standard deviations are much larger here than on the absolute OC mass concentration bars in the panel above. (c) There is essentially no OC in the HULIS fraction of coal burning PM (Fig. 1), so how can this lead to significant TMP consumption (Fig. 2)? Is this caused by contamination?

Fig. 2. (a) In part A, how did the authors determine an "average" attenuation curve of TMP consumption across the samples? Or are the curves shown in Fig. 2 from the median reactivity sample? (b) Also in part A, the TMP decay order for ambient PM is HULIS > WSOC ~ MSOC. But the corresponding values for  $k(\text{TMP})$  are MSOC ~ HULIS > WSOC. Why is this? Are  $k(\text{TMP})$  values determined based on  $C/C_0$  vs.  $t$  or  $\ln(C/C_0)$  vs  $t$ ? It appears that the authors used the former method, but the latter gives more robust results. (c) In Fig. 2B, there are large error bars for several of the extract conditions, which I assume reflects the intersample variability, but this should be explained. (d) To better show the difference between the measured and calculated HP+HULIS conditions, the authors should make a supplemental figure that shows the ratio of (measured/calculated) for each sample and the overall average; this would reduce the impact of the large differences in absolute reactivity between samples. (e) Examining the interactions of metals with HULIS components, and how it affects triplet concentrations, is interesting. But the description of the process followed is very difficult to understand. (f) For Figure 2C, it's not clear how the "Other" category was calculated and why it is all attributed to WSOC. This should be explained in the text.

l. 301. The addition of nitrate should lead to additional TMP consumption, since nitrate photolysis is a source of OH, which will react with TMP. What nitrate concentration was tested? How does it compare to the maximum ambient sample value?

Figure 4. What sample is this? (The sample ID(s) should be indicated for all figures.)

Fig. 5. The last sentence of the caption should be deleted since it only repeats information from earlier in the caption.

Fig. 6. (a) What samples are included in these regressions? Is it only the ambient PM extracts or does it also include the primary emission sources? If the latter, the points should be marked (e.g., with different symbols or colors) to show the different particle types (ambient, BB, CB). (b) The correlation of  $k(\text{TMP})$  is strongest with light absorption at 400 nm. This plot is labeled WSM, but these "whole extract" experiments were not discussed previously - was TMP loss measured in whole water extracts of the PM? Why not show the HULIS and HP-WSM results on this plot also? And what about the MSM results?

l. 429.  $f(\text{TMP})$  is not a quantum yield.

page 20. This discussion of the correlations does not add much to the manuscript and would be better shortened, without the speculative text about energy and electron transfer.

Section 4. Environmental Implications. This section, which is too long, is mostly just a summary of the results. It should be significantly shortened to focus on the implications.

l. 448. This line might be true, but there is insufficient evidence to say that triplets play an "...important role in the formation and aging process of atmospheric aerosols."

## Supporting Information

The supporting information has some useful components, but it is also filled with errors and text that is difficult to understand. For example: (a) Table S1 – are values averages over the sampling period? If so, give statistics (e.g., mean, standard deviation, range). What are the units for each quantity? (b) Table S3 - It's not clear what most of the column headings mean, e.g., what is "Number of membranes" or "solvent amount"? All of these need to be explained in footnotes. (c) Page S8 – the description of the triplet and singlet oxygen experiments doesn't make sense. Part of the confusion is describing the oxidant probe as "quenching" the oxidant (e.g., TMP for 3C\*). But the probe doesn't quench the oxidant - it is added at a low concentration so as not to perturb the oxidant steady state concentration. Also, the probe concentrations listed here are twice as high as those stated in main text. Which is correct? (d) Page S9 - Why make a standard curve for the oxidant probes? Their loss is first order, so the initial concentration doesn't matter: a plot of  $(Area)_t / (Area)_0$  vs.  $t$  will give a line with a slope equal to the negative of the pseudo-first order rate constant for probe loss, e.g.,  $k(TMP)$ . (e) Page S10 - In Equation 1, "a" needs to be defined. The definition of quantum yield uses the term "quantum" sometimes to refer to "photon", which is confusing. (f) Page S11 – need references for rate constants. (g) Table S4 could be deleted and replaced with a few sentence description. (h) Table S5 only repeats data from Table 1 in the main text and should be deleted. (i) Fig. S12 – Describe what the dashed red boxes represent in the caption. (j) Fig. S16 – Purple symbols should be yellow. (k) Fig. S18 – What do the two middle plots represent? What samples are shown in this figure? All? If so, use different symbols to represent different sample types. (l) The 54 regressions shown in Figures S18 and S19 form the basis of some statistically sketchy work. The authors seem unaware that if you examine dozens of correlations you will get some significant relationships just by chance. Also, they seem unconcerned about the many cases where the correlations are driven by just one or two outliers. They need to deal with these issues in a rigorous statistical way.