Response to Reviewers comments for

*Photooxidants from Brown Carbon and Other Chromophores in Illuminated Particle Extracts*
By Richie Kaur et. al.

**Please note:**
Reviewer comment is in black text.
Our response is in blue.

**Please note that line numbers in the revised version are different due to changes in the manuscript.**

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**Anonymous Referee #1**
Received and published: 21 December 2018

This paper reports the results of a study that quantified _OH, 1O2 and triplet states in particulate matter aqueous extracts. As there are few or no studies on the subject, the topic is interesting and deserves publication. However, there are some clarity issues with the present version of the manuscript that should be solved. Moreover, it is not clear whether the procedure to determine the transient species was fully appropriate (in particular, the authors do not specify if and how they dealt with transient scavenging by the probe molecules, which is a confounding factor in this kind of measurements and could possibly explain the inconsistency between the 1O2 and 3C* data). For these reasons, the manuscript should be revised following the recommendations reported below.

We thank this reviewer for their thorough review and the detailed, helpful comments. We have addressed each of them below.

Regarding probe molecules, while we tried to limit probe concentrations so that they were insignificant scavengers of the transient oxidants, we found that we had one condition (MBO used to measure [OH] in the dilution series of sample PME3D) where the probe was a significant sink. As described below (and in the revised manuscript), we corrected these [OH] values for the influence of MBO. For the other oxidant cases – ^1O2* and ^3C*, and [OH] measured in the other samples using benzene – our probe concentrations were low enough that they insignificantly perturbed oxidant kinetics. These determinations are also described below.

1. Page 5, bottom. Please specify the degree (approximate) by which the samples were diluted upon addition of H2SO4. Moreover, measuring pH in a small sample might not be totally trivial: please provide details of the pH measurement device.

The dilution of the samples was always kept below 10%. For each sample, we acidified and measured the pH of a 1 mL aliquot using a pH microelectrode (MI-414 series, protected tip...
We have added this information in Sect. 2.3 (Page 6, top).

2. Line 177. Is the pathlength measured in cm? Please specify.

Yes. Pathlength was measured in cm. We have clarified this (now Page 6, bottom).

3. Page 6, bottom. I suppose that the contributions of nitrate and nitrite to absorption were small. Anyway, that should be specified for completeness (approximately which percentage of absorbance would be accounted for by NO2-/NO3- and which by DOM, of course it varies with wavelength but it is important to have an idea of that).

The contributions of NO2-/NO3- to light absorption were small and vary by wavelength. Integrated across the solar wavelengths, these species accounted for up to 7% of total absorption. We have added this information to Sect. 2.4 (top of page 7).

4. Line 190. Please spell out the “OM” and “OC” acronyms.

We apologize for the oversight. We have spelled out the acronyms OM (organic matter) and OC (organic carbon).

5. Section 2.5 and overall. Scavenging of the reactive species by probes can be a problem, because it decreases the transient steady-state concentration. Because of this, the steady-state concentration in the illuminated sample with the probe can be much different from the steady-state concentration in the sample without probe. If an issue like this occurred in the measurements of 1O2 and the triplet states, that could explain the inconsistency of the results (comparison between 1O2 and 3C* should be carried out in the samples without probes, by means of an extrapolation). Experiments with benzene were carried out at different initial concentrations, and by so doing there is a chance of correcting for probe scavenging (although it was not specified whether such a procedure was followed). In the case of FFA and the triplet probes the used concentration is not provided. This issue should be checked, corrected if necessary, and in any case discussed in the manuscript.

To minimize perturbations in the steady-state concentrations of the oxidants, we used low concentrations of probe compounds for 1O2* and 3C*. The concentrations of FFA and triplet probes (SYR and MeJA) were 10 μM each (Sections 2.5.2 and 2.5.3, respectively). The major sink for 1O2* in our samples is water, with a pseudo-first order rate constant of $2.2 \times 10^5$ s$^{-1}$ (Bilski et al., 1997). In comparison, 10 μM of FFA (with a rate constant $1.2 \times 10^8$ M$^{-1}$ s$^{-1}$; Wilkinson et al. (1995)) has a corresponding rate constant of $1.2 \times 10^3$ s$^{-1}$, indicating that it reduces $[^1\text{O}_2]*$ by less than 1%.

For triplets, there are two major natural sinks: O2, with a pseudo first-order rate constant, $k_{3\text{C}^*+\text{O}_2}[\text{O}_2]$, of $8.0 \times 10^5$ s$^{-1}$ (see Eqn. 8) and dissolved organic compounds, which have an average pseudo-first-order rate constant with triplets of $\sim (9 \times 10^7 \text{ L mol C}^{-1})(3 \times 10^{-3} \text{ mol L}^{-1}) = 3 \times 10^4$ s$^{-1}$ in the standard extracts. Together, these two sinks represent a total background rate
constant for triplet loss of approximately $8.3 \times 10^5$ s$^{-1}$. In contrast, 10 μM of SYR (our most reactive triplet probe) has a pseudo-first-order rate constant of $k_{3C+SYR}[SYR] = (4 \times 10^9$ M$^{-1}$ s$^{-1})(1 \times 10^{-5}$ M) = $4 \times 10^4$ s$^{-1}$. Thus the addition of SYR causes, on average, a decrease in the triplet concentration of only ~ 5%.

The competition kinetics technique, which was used for most measurements of $^\cdot$OH, uses a range of probe (benzene) concentrations so that the parameters $P_{OH}$, $k_{OH}'$ and $[^\cdot OH]$ can be determined under extrapolated conditions of zero added probe. For these cases the probe influence is accounted for in the method.

However, for our final case we found that the probe concentration was indeed too high. This is the dilution series of sample PME3D, where we used 75 μM methylbutenol (MBO) (Section S1). We had to use a high concentration because of analytical limitations: the high background absorbance in the standard extract made it difficult to detect MBO in our samples. However, in hindsight we should have adjusted the MBO concentration so that it was lower in the more dilute PM extracts. MBO has a rate constant with $^\cdot$OH of $7.4 \times 10^9$ M$^{-1}$ s$^{-1}$ (Section S1), thus 75 μM corresponds to a pseudo-first-order rate constant for $^\cdot$OH loss of $5.6 \times 10^5$ s$^{-1}$. With this relatively high value MBO is a significant, and in one case dominant, sink for $^\cdot$OH in the dilution series of PME3D. MBO is significantly suppressing $[^\cdot OH]$ in the more dilute extracts, but not as much in the more concentrated extracts: our originally reported $[^\cdot OH]$ values are too low by factors of 3.3, 1.4, 1.3, 1.2, and 1.1 for samples PME3D10, D2.5, D1.3, D1, and D0.5, respectively. We have added a description of this problem to the manuscript and corrected the $[OH]$ values in the PME3D dilution series. Because we correct our SYR probe results for the contribution of $^\cdot$OH, we have also corrected the corresponding $^{3}C^*$ concentrations for the PME3D dilution samples, as well as our associated Figures and the extrapolations to aerosol liquid water conditions. Because $^\cdot$OH was a minor contributor to SYR loss, the corrections for $^{3}C^*$ are relatively small. We have indicated the problem with MBO determination of $^\cdot$OH, and our correction, in the main text and supplemental material.

6. Lines 199-204. The procedure used here was different from the description of the irradiation experiments provided in section 2.3. Also the irradiated volume is different (5 mL vs. 1 mL), although the same HPLC was used in both cases which required the withdrawal of 100 μL aliquots. The reason for this difference should be provided for clarity.

We thank the reviewer for their attention to detail. At the beginning of Sect. 2.3, we mention that the procedure of using a 1 mL sample volume applies to all measurements except “$P_{OH}$ measurements” when it should have said “$^\cdot$OH measurements using benzene” – this was an error that we have corrected. For all $^\cdot$OH measurements where benzene is used as a probe, we used a larger sample volume (5 mL instead of 1 mL) while withdrawing the same small aliquot for HPLC analysis (100 μL) in order to minimize the headspace in the reaction container. Since benzene is highly volatile, reducing headspace prevents loss of benzene due to volatilization. Since the other probes are less volatile, we were able to use a small volume (1 mL) for those experiments because the additional headspace in the container after a few aliquot withdrawals does not pose a complication, unlike in case of benzene. We have added this clarification in Sect. 2.5.1.
7. Line 201. “illuminated” should read “illumination”.

    Thank you, we have corrected this.

8. Equation (4). Which is the rationale behind this equation? Is it assumed that light screening in ambient particles can be neglected? If so, why (there is a small pathlength there, but concentrations can be very high and compensate)? Please explain for clarity.

    Yes, because of the very small pathlength in ambient particles the screening is negligible for our filtered samples. (Insoluble black carbon might cause screening in airborne particles, but our samples were filtered.) Although the particles are much more concentrated than our solutions (by approximately a factor of $10^3$), the pathlength in the particles (~ 1 μm) is smaller than in our solutions by a larger amount (approximately a factor of $10^4$).

9. Page 8, top. To enable comparison between the two methods, please report reaction yields for benzene => phenol and for MBO.

    The two techniques are not directly comparable. In the benzene technique, we measured the product of the reaction between benzene and •OH, i.e., phenol. The yield for phenol from the benzene + •OH reaction is 73%; we have added this information to Sect. 2.5.1. On the other hand, when MBO was the probe, we measured the loss of MBO in solution, similar to FFA, SYR and MeJA. Because MBO can also react with $^1$O$_2$* and $^3$C*, we corrected the MBO decay to account for these contributions and then calculated [•OH] from the fraction of MBO lost due to •OH alone (see Section S1.1 in the SI). On average, 55 (± 15) % of MBO was lost by reaction with •OH in the PME3D dilution samples where MBO was used.

10. Section 2.5.2. Please specify the FFA concentration and the way 1O2 scavenging by added Ffa was accounted for.

    The concentration of FFA (10 μM) is specified near the beginning of Sect. 2.5.2. As we describe in our response to comment #5 above, this FFA concentration is low enough that it does not significantly affect the singlet oxygen concentration.


    Faster (as we had in the text) is correct. Since $^1$O$_2$* reacts more slowly with D$_2$O than H$_2$O, [$^1$O$_2$*] is higher in the D$_2$O solutions and thus FFA loss is faster.

12. Section 2.5.3. Also in this case, the probe concentration should be specified and its role as 3C* scavenger (or the way scavenging was corrected for) should be discussed, because the presence of the probe alters [3C*].

    The probe concentration of 10 μM is specified near the beginning of Sect. 2.5.3. As we discussed in our response to comment #5 above, our calculations indicate that the addition of SYR (or MeJA) does not significantly affect the triplet concentration. We have added a mention of this to the text.
13. Lines 269-272 and 279. the overall explanation here is not very clear. I imagine that a couple of matching triplets were used and the mole fractions were calculated so that it was possible to exactly match the experimental rate constant ratios. However, this should be explained better because it is definitely not straightforward to derive it from the text.

The reviewer is correct about how our technique works. We have added some text at the top of page 10 to try to clarify our description.

14. Lines 288-289. Canonica estimated 5x10^5 s-1 as the triplet deactivation rate constant. The data provided here suggest a higher value for the estimated rate constant. Which is the reason? Was a different [O2] assumed here in comparison with surface waters? Please explain better.

The triplet deactivation constant (units: s^-1) is the product of the second-order rate constant of triplet quenching by O₂ (k_{3C+O2}; units: M^{-1} s^{-1}) and the molar concentration of O₂. We used Canonica’s estimates for k_{3C+O2} (Canonica et al., 2000) for 3 model triplets, and to mimic natural triplets, we averaged them to get a value of 2.8 × 10^9 M^{-1} s^{-1} (shown in Table S11). We used USGS estimates for dissolved oxygen concentration of 284 μM at our experimental temperature of 20 °C (USGS, 2018), which yields a triplet deactivation constant of 8 × 10^5 s^{-1}. It is possible that some of the surface water studies were done at a different temperatures or used k_{3C+O2} for a single model triplet rather than the average value we used – either or both of those factors could be responsible for that difference. All of these details are given after Equation 8 in the main text.

15. Equation (9) and related discussion. I imagine that also Rabs was normalised to the winter solstice, otherwise there is no consistency. However, I do not understand the reason for using a double normalization. The quantum yield should be independent from the irradiation conditions, thus it should be the same (and better, to my opinion) to use the raw experimental data. If there are additional reasons for using normalized data, that should be explained.

We normalize measured rates of oxidant formation to winter solstice sunlight to correct for daily variations in the output of our lamp; this allows rates in different samples to be directly compared (and averaged). To be consistent, R_{abs}, the rate of light absorption in a sample, is calculated using the winter solstice actinic flux (Equation 2): while we could calculate the rate of light absorption for each experiment, values for different samples couldn’t be properly compared because of variations in light output. So, while we are essentially double normalizing, it allows us to put all values on the same photon flux basis.

16. Line 345. How were the Absorption Angstrom Exponents calculated? Please specify (better by using a formula).
The AAE formula and calculation are described in the footnotes of Table S1 of the SI. In the interest of keeping our main text from getting any larger, we have not added the equation to the main text.

17. Line 362. Do you mean here that absorption declined faster with increasing wavelength? This may have implications for the molecular weight of DOM (higher molecular weight compounds experience a slower decrease of absorption with wavelength).

This is an interesting point. Yes, as shown in Fig. S5 of the SI, the particle extracts had a higher absorbance and mass absorption coefficient at shorter wavelengths. Consequently, the decline of absorbance with wavelength in the extracts was faster than in fog. However, a caveat to this data is that the figure compares the ratios of two specific samples (e.g., median absorbing PM extract with median absorbing fog), so it is unclear how representative each sample is. To better make this comparison we also calculated AAE values for the fog drops: the fog values are generally lower than the PM extract values (consistent with the Fig. S5 result), but the difference is small ($p = 0.56$; Table S1).

18. Lines 378,379. This statement means that PME are not more concentrated than for with respect to NO3- and NO2-. Is there any idea as to the reason for this?

The reviewer is correct, but it’s difficult to interpret this result since the gas-particle partitioning of HNO3 under non-fog conditions is highly dependent upon the availability of ammonia.

19. Line 387. DOC concentration. It would be very useful for the readers to have a range of measured DOC values here.

We have added the range of measured DOC values.

20. Page 14, bottom. It may be interesting to recall that the IO2 formation QY determined here is also not very distant from typical values found in surface waters.

This is a good point. We have added this comparison to the manuscript (on Page 15).

21. Page 15, bottom. Comparing steady-state concentrations in different studies is not very significant because they strongly depend on the irradiation conditions. It would be much better to compare the formation quantum yields.

The reviewer makes a good point. We have added a quantum yield comparison at the end of this section (on Page 16). The concentration comparison we had in the original manuscript (and which we’ve kept) is for the same winter-solstice sunlight conditions.

22. Page 16, top and middle (end of section 3.5). if it is not a consequence of unwanted transient scavenging by probes, this puzzling result might mean that the complicated approach followed here to measure 3C* was not very appropriate. In the context of surface waters, the use of 2,4,6-trimethylphenol as probe usually gives consistent results.
between the 3c* and 1O2 formation quantum yields. That could be discussed to place the used results and methodology into a clearer and more complete framework.

As we described earlier, our calculations indicate that our 1O2* and 3C* probes did not significantly perturb the concentrations of these oxidants, so we do not think there is a problem with our method. It is possible that our PM results for Φ3C*/Φ1O2* are lower than the surface water results described by the reviewer because of differences in OM chemistry between the two types of samples; our result suggests that fΔ is lower in atmospheric waters. But we also note that a recent study by Zhou et al. (2019) shows that the ratio Φ3C*/Φ1O2* for terrestrial NOM is approximately 0.5, similar to our result. The quantum yield for oxidizing triplets probably also depends on the probe used.


Liquid water content for particles in California’s Central Valley during winter were calculated based on particle composition and the component thermodynamics by Parworth et al. (2017). We used their values as an estimate for our samples, as described in Table S14 of the SI.

24. Line 524. In the case of 1O2 production, it is strange that saturation of absorbance was not observed even in the most concentrated samples. In the presence of a very high DOM amount, all or almost all incident radiation should be absorbed and a plateau [1O2] trend should be observed as a consequence. Which was the absorbance in the most concentrated samples that were subject to irradiation?

Our highest absorbing samples had absorption coefficients of less than 0.6 cm\(^{-1}\) at 300 nm (e.g., Fig. 1) but we had a short pathlength (4 mm), so there was no significant screening of light in our experiments. Light screening factors (where a value of 1 indicates no screening) ranged from 0.84 to 0.99 (Table S1) and were accounted for in our calculations.

25. Page 18, 1st half. In the case of surface waters, you need DOC » 20 mgC L\(^{-1}\) to have significant scavenging of 3C* by DOM. What is the situation here? Which were the DOC values of the most concentrated PME samples? It is important to discuss them for comparison.

The DOC values in μM-C for all PME samples are given in Table S2 of the SI. Converted to mg-C L\(^{-1}\), the values for the PME3D samples range from 4.3 to 86 mg-C L\(^{-1}\). Thus, as the concentration. We have added a statement in the main text to indicate this.

26. Line 529. “(Wenk et al., 2011;2013) have shown” should read “Wenk et al. (2011; 2013) have shown”.

Thank you, we have corrected this partially but somehow, we are unable to fix the formatting completely. It now reads “Wenk et al. (2011); (2013)”. We are hoping this can be fixed during typesetting.

27. Lines 577 and 597-599. Role of 1O2 vs. 3C* in PM water. There is a potential
inconsistency here, because 3C* seem to play a minor role with the chosen model compounds but then one has to admit an important 3C* scavenging by DOM. This seems to suggest that the choice of the five model compounds was not fully representative (they might tend to highlight 1O2 reactions). This issue should be discussed better.

This is an interesting point. We don’t think that the duality of our results is because we picked compounds that are not representative, but rather that there are so many compounds (in number and/or quantity) that are reacting with triplets that its steady-state concentration is significantly suppressed in the PM condition (but its formation rate is unaffected). The result is that triplets do not appear to be very significant sinks for individual compounds, but they are significant in aggregate, i.e., when considered over all of the species that react with triplets. We have modified the text to describe this.

28. Line 615. “approximately” should read “approximate”.

Thank you, we have corrected this sentence.

29. Line 622. 600 vs. 3000. According to Fig. 5 one has quite parallel increases of both [1O2] and [3C*] (the latter under the hypothesis of no plateau), while 3000/600 = 5 which is quite a lot as difference. Are these numbers compatible with Figure 5 data? Please add a comment.

This is a good observation from the reviewer: while Fig. 5 considered only an extrapolation of the measured aqueous processes, in the text we also considered gas-phase mass transport and the expected organic sinks for oxidants in highly concentrated particles. To eliminate this confusion, we have modified Fig. 5 to show the expected oxidant concentrations in drops and particles considering both our aqueous measurements and the calculated impacts of organic sinks and mass transport from the gas phase. Under these conditions, the concentration of 1O2* increases by a factor of 2400 from dilute drops to concentrated particles, while the concentration of oxidizing triplets increases by a factor of 30 (best fit) to 2000 (high estimate).

Anonymous Referee #2
Received and published: 2 January 2019

General comments This manuscript presents results of measurements of traditional and novel oxidants in PM extracts of ambient samples and importantly illustrates the potential for brown carbon to increase oxidant concentrations through the formation of triplet states. While many uncertainties exist, this study lays the groundwork for future studies into the role of brown carbon in generating photooxidants. The study presents a novel technique for measuring oxidants that appears to hold even under diluted conditions of aerosol extracts, and the results and conclusions drawn are supported by the available data. The abstract is concise enough, though it may benefit from further shortening and the title reflects the work as presented. The large volume of supplementary information will allow future work to build on this publication.
This work may help address the measurement/model discrepancies between the O/C ratio of ambient SOA and that predicted by chemical models. The manuscript is well presented with clear writing and legible figures. The work is also highly timely, and represents a step forward in our ability to understand the competing reactions taking place in aerosol and aerosol water (oxidant generation and loss). I have only two minor comments to improve the paper and one technical correction.

We thank this reviewer for their thoughtful review, encouraging comments, and specific suggestions for improvement of the manuscript. We had addressed each of the comments below.

Specific comments:

The abstract was a bit hard to get through, and could benefit from further shortening if the authors feel this is possible. For example, lines 34-38 may be omitted without loss of meaning.

We appreciate the reviewer’s comment about the length of the abstract. To make it more concise, we have deleted lines 34-35. We left lines 36-38 as it is to provide an appropriate segue from discussing oxidant concentration measurements in dilute extracts to estimating them in ambient particles.

Lines 448-451: It was difficult to follow the relationship between \( k'_{\text{SYR,3C*}} / k'_{\text{MeJA,3C*}} \), and \( k'_{\text{Probe,3C*}} \) ratio. Are these the same thing, but the latter is a general term? Please clarify.

Yes, the reviewer is correct – these refer to the same thing. The latter \( (k'_{\text{Probe,3C*}} \) ratio) is a general term whereas \( k'_{\text{SYR,3C*}} / k'_{\text{MeJA,3C*}} \) specifically mentions the probes. We have clarified this.

Technical corrections
Line 545: missing “is” between “it also”

We thank the reviewer for their attention to detail. We have made this correction.

Anonymous Referee #3
Received and published: 8 January 2019

This work mainly measured the concentrations of three important photooxidants formed from photoexcitation of brown carbon by collecting ambient particles during heavy residential wood-burning period in winter, extracting them in water, and illuminating the acidified aqueous extracts. The results in aqueous extracts were extrapolated to ambient particle water conditions and compared to the corresponding photooxidants in fog. The main conclusion of this work is that hydroxyl radical in particles had similar levels with fog and cloud drops while singlet oxygen and oxidizing triplet excited sites of organic matters are enhanced in particles. Their results indicate that singlet oxygen
and oxidizing triplet excited sites of organic matters formed from the photoexcitation of brown carbon can be important sinks for organic compounds in atmospheric particles. Although there are large uncertainties in the extrapolation to ambient particle water conditions, especially for oxidizing triplet excited sites of organic matters, this work provides the first measurement of singlet oxygen and oxidizing triplet excited sites of organic matters, which affect the lifetime of organic compounds in particle liquid water. The results are very helpful for the science community to improve our understanding of photooxidants and inspire more works for different seasons and locations, and implementing in current atmospheric models. I think this is an interesting and important work, and recommend for acceptance after comments below are addressed:

We thank this reviewer for their thoughtful review, encouraging comments, and specific suggestions for improvement of the manuscript. We had addressed each of the comments below.

1. Line 154, please explain “air-saturated”.

The term “air-saturated” refers to the fact that the particle extracts are saturated with O$_2$ by exposure to air. This is important because O$_2$ is a sink for triplets, and the lack of oxygen in solutions can artificially enhance the triplet steady-state concentration. During the course of the experiments, we stirred the solutions continuously and exposed the surface of the solution to air each time an aliquot was taken for HPLC analysis.

2. Line 379, the authors mentioned additional source can be photo-Fenton processes, I am wondering if Fe has been/can be measured in the samples. It would be interesting to compare to Fe data.

Unfortunately, we were not able to measure Fe in the solutions due to a lack of sample volumes. However, this is a very valid question that should be addressed in future studies of a similar nature.

3. Line 389-394, suggest adding some literature reviews on the destruction/sinks of OH in this section or in the introduction section.

We have added the references.

4. The authors made a couple comparisons between “standard” and “dilute” extracts throughout the manuscript. From the manuscript, the “standard” extraction was based on extracting particles into 1 mL water and the “dilute” was extracting in 2.5 mL water. It is an effect of dilution. It is not clear to me what is the purpose of comparing “standard” and “dilution” conditions. The authors have already studied extensively the effect of dilution using sample 3 in later experiments, so I don’t understand why repetitive comparison were made here or are there additional purposes of comparing “standard” and “dilute” extracts but were not well presented in the manuscript? The authors need to make it clearer.

We appreciate the reviewer’s comments on this. The comparisons between standard and dilute extracts arise mainly because we started out measuring the oxidant concentrations in the
dilute extracts. After a few samples, we realized that the “dilute” extracts closely resembled fog samples in terms of oxidant concentrations. We then switched to a higher concentration, i.e., extracting the particles in 1 mL water instead of 2.5 mL and we established this as the “standard” condition. The benefits of showing both results in the paper are to illuminate how even this small concentration factor changes oxidant concentrations and how dilute particle extracts essentially mimic fog droplet photochemistry.

5. Method section: sample extracts were mixed with photooxidant probes and then illuminated in light. The authors will need to address whether illumination will affect the probes or the products formed from probes and targeted photooxidants. For example, benzene traps OH radicals and form phenol. How does illumination experiments affect the product phenol. Do the authors concern about the photodegradation or photoenhancement of phenol, therefore, resulting in underestimation or overestimation of the OH concentration? Same concerns will also be needed to address for singlet oxygen and triplets cases.

This is a good question. Briefly, for measuring ’OH, we only illuminated solutions spiked with benzene for time periods where linear increase in phenol concentration was observed (Fig. S1 in the SI). Had there been any secondary chemistry, the concentration of phenol would no longer increase linearly. This is evidence that measuring ’OH from phenol formation within our experimental time frame was not confounded by secondary reactions. Similarly, for \(^1\)O\(_2\)* and \(^3\)C*, the loss of the probes follow first order kinetics (Figs. S2 and S8 in the SI).

6. Line 339, following the last comment, another concern is the effect of illumination on the light absorbance of brown carbon. For example, a recent study by Wong et al. 2017 EST (Changes in Light Absorptivity of Molecular Weight Separated Brown Carbon Due to Photolytic Aging) showed that light Absorptivity of brown carbon changes due to photolytic aging. Please discuss how change of absorptivity affects the conclusions in this work.

This is an interesting question. Part of the photolytic aging of brown carbon are likely the reactions of the dissolved organics with transient oxidants such as ’OH, \(^1\)O\(_2\)* and \(^3\)C*. With respect to photolytic aging affecting the experimental outcomes, since we are measuring photooxidant formation in approximately the same time frame as the Wong et. al. study cited by the reviewer (i.e. about 2 hours), it is possible that some transformation of organics does occur. However, since the loss of probe compounds followed first-order kinetics in all cases and our probes do not undergo direct photolysis, we don’t suspect the aging process to have affected photooxidant formation.
References:


Photooxidants from Brown Carbon and Other Chromophores in Illuminated Particle Extracts

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Abstract

While photooxidants are important in atmospheric condensed phases, there are very few measurements in particulate matter (PM). Here we measure light absorption and the concentrations of three photooxidants – hydroxyl radical (•OH), singlet molecular oxygen (¹O₂*) and oxidizing triplet excited states of organic matter (³C*) – in illuminated aqueous extracts of wintertime particles from Davis, California. ¹O₂* and ³C*, which are formed from photoexcitation of brown carbon (BrC), have not been previously measured in PM. In the extracts, mass absorption coefficients for dissolved organic compounds (MACDOC) at 300 nm range between 13,000–30,000 cm² g⁻¹ and are approximately twice as high as previous values in Davis fogs. The average (± 1σ) •OH steady-state concentration in particle extracts is 4.4 (± 2.3) × 10⁻¹⁶ M, which is very similar to previous values in fog, cloud and rain: although our particle extracts are more concentrated, the resulting enhancement in the rate of •OH photoproduction is essentially cancelled out by a corresponding enhancement in concentrations of natural sinks for •OH. In contrast, concentrations of the two oxidants formed primarily from brown carbon (i.e., ¹O₂* and ³C*) are both enhanced in the particle extracts compared to Davis fogs, a result of higher concentrations of dissolved organic carbon and faster rates of light absorption in the extracts. The average ¹O₂* concentration in the PM extracts is 1.6 (± 0.5) × 10⁻¹² M, seven times higher than past fog measurements, while the average concentration of oxidizing triplets is 1.0 (± 0.4) × 10⁻¹³ M, nearly double the average Davis fog value.
Additionally, the rates of $^{1}O_{2}^{*}$ and $^{3}C^{*}$ photoproduction are both well correlated with the rate of sunlight absorption.

While concentrations of $^{1}O_{2}^{*}$ and $^{3}C^{*}$ are higher in our PM extracts compared to fog, the extracts are approximately 1000 times more dilute than water containing ambient PM. Since we cannot experimentally measure photooxidants under ambient particle water conditions, we measured the effect of PM dilution on oxidant concentrations and then extrapolated to ambient particle conditions. As the particle mass concentration in the extracts increases, measured concentrations of $^{1}OH$ remain relatively unchanged, $^{1}O_{2}^{*}$ increases linearly, and $^{3}C^{*}$ concentrations increase less than linearly, likely due to quenching by dissolved organics. Based on our measurements, and accounting for additional sources and sinks that should be important under PM conditions, we estimate that [$^{1}OH$] in particles is somewhat lower than in dilute cloud/fog drops, while [$^{3}C^{*}$] is 30 to 2000 times higher in PM than in drops, and [$^{1}O_{2}^{*}$] is enhanced by a factor of roughly 2400 in PM compared to drops. Because of these enhancements in $^{1}O_{2}^{*}$ and $^{3}C^{*}$ concentrations, the lifetimes of some highly soluble organics appear to be much shorter in particle liquid water than under foggy/cloudy conditions. Based on extrapolating our measured rates of formation in PM extracts, BrC-derived singlet molecular oxygen and triplet excited states are overall the dominant sinks for organic compounds in particle liquid water, with an aggregate rate of reaction for each oxidant that is approximately 200 – 300 times higher than the aggregate rate of reactions for organics with $^{1}OH$. For individual, highly soluble reactive organic compounds it appears that $^{1}O_{2}^{*}$ is often the major sink in particle water, which is a new finding. Triplet excited states are likely also important in the fate of individual particulate organics, but assessing this requires additional measurements of triplet interactions with dissolved organic carbon in natural samples.

1 Introduction

Photochemically generated oxidants largely drive atmospheric chemistry, both in the gas phase (Thompson, 1992; Finlayson-Pitts and Pitts Jr, 1999; Seinfeld and Pandis, 2012) and in aqueous drops, where they largely govern the reactions and lifetimes of organic compounds (Lim et al., 2005; Lim et al., 2010; Ervens et al., 2011; He et al., 2013; Herrmann et al., 2015; Blando and Turpin, 2000). Similarly, photooxidants can be important for transformations in water-containing particulate matter (PM): they make new PM mass by functionalizing gaseous volatile organics to oxygenated lower-volatility products, and decrease PM mass by fragmenting large
organics into smaller, more volatile species (Jimenez et al., 2009). Oxidants in condensed phases can come from the gas phase (e.g., the mass transport of hydroxyl radical, \(^{\cdot}\)OH) or can be formed photochemically within the particle or drop (Herrmann et al., 2010b). Our focus in this paper is on the latter pathway.

Of the photooxidants formed in airborne particles, hydroxyl radical (\(^{\cdot}\)OH) is the most widely studied. While its concentrations have been measured in cloud/fog drops, rain and dew (Arakaki and Faust, 1998; Arakaki et al., 1999; Anastasio and McGregor, 2001; Kaur and Anastasio, 2017), there are only four known measurements of \(^{\cdot}\)OH photoproduction rates, lifetimes, and steady-state concentrations in ambient particles, all from coastal or marine locations (Anastasio and Jordan, 2004; Arakaki et al., 2006; Anastasio and Newberg, 2007; Arakaki et al., 2013). Based on these and other measurements (e.g., Tong et al. (2017)) and complementary modeling work (Herrmann et al., 2010b; Herrmann et al., 2015), the major sources of \(^{\cdot}\)OH include photolysis of nitrate, nitrite, and hydrogen peroxide (HOOH) as well as reactions of Fe(II) with HOOH or organic peroxides. The major sinks of \(^{\cdot}\)OH are organic molecules since these reactions typically have nearly diffusion-controlled rate constants (Arakaki et al., 2013; Herrmann et al., 2010a; Herrmann et al., 2015). Photoexcitation of organic chromophores, i.e., light-absorbing brown carbon (BrC), can also form oxidants in particles and drops. For example, sunlight absorption by organic chromophores can promote the molecules from their ground states to reactive triplet excited states (McNeill and Canonica, 2016; Kaur and Anastasio, 2018b). Triplets can both directly oxidize organics via electron transfer reactions and form other photooxidants, including singlet molecular oxygen (\(^{1}\)O_2\(^{\ast}\)) (Zepp et al., 1985) and hydrogen peroxide (Anastasio et al., 1997). In this work we examine oxidizing triplets, which we refer to as \(^{3}\)C\(^{\ast}\) or simply “triplets” for simplicity. Such species are important in surface waters, where they rapidly oxidize several classes of compounds including phenols, anilines, phenylurea herbicides, and sulfonamide antibiotics (Canonica et al., 1995; Canonica and Hoigné, 1995; Boreen et al., 2005; Canonica et al., 2006; Bahnmüller et al., 2014).

There has been growing interest in the role and reactivity of triplets formed from particulate brown carbon, especially their role in forming aqueous secondary organic aerosol (SOA(aq))(Smith et al., 2014; 2015; Yu et al., 2014; Yu et al., 2016; Laskin et al., 2015). There is evidence that triplet-forming, light-absorbing species, e.g., imidazoles and pyrazines, are formed in drops and particles (De Haan et al., 2009; 2010; Hawkins et al., 2018) and a few laboratory studies have examined how illuminated imidazole particles can oxidize isoprene or
other alkenes to increase PM mass (Aregahegn et al., 2013; Rossignol et al., 2014). But the formation of SOA(aq) from such reactions appears not to be significant under environmentally relevant conditions where concentrations of triplet precursors are much lower (Tsui et al., 2017). While we recently made the first measurements of triplet concentrations in fog waters (Kaur and Anastasio, 2018b), there are no measurements of $^3$C* in particles, making it difficult to assess their significance. This is doubly difficult because triplets are not a single oxidant, but rather a suite of species with a wide range of reactivities (McNeill and Canonica, 2016).

Another important photooxidant in atmospheric and surface waters is singlet molecular oxygen ($^1$O$_2^*$), which is formed by energy transfer from a triplet excited state to dissolved oxygen, and lost via deactivation by water (Zepp et al., 1977; Haag and Hoigné, 1986; Haag and Gassman, 1984; Faust and Allen, 1992). Similar to triplets, singlet oxygen has been studied widely in surface waters (Zepp et al., 1977; Haag and Gassman, 1984; Haag and Hoigné, 1986; Tratnyek and Hoigné, 1994) and reacts rapidly with electron-rich organics such as phenols, polycyclic aromatic hydrocarbons, amino acids, and reduced sulfur species (Wilkinson et al., 1995). However, there are only four measurements of $^1$O$_2^*$ concentrations in atmospheric waters (Anastasio and McGregor, 2001; Kaur and Anastasio, 2017; Albinet et al., 2010; Faust and Allen, 1992) and none in aqueous particles. To address this gap, we measured $^\cdot$OH, $^1$O$_2^*$, and $^3$C* in illuminated aqueous extracts of fine particles collected from the Central Valley of California during winter, a period of heavy residential wood burning. The goals of this study are to: 1) quantify $^\cdot$OH, $^1$O$_2^*$, and $^3$C* kinetics and concentrations in particle extracts, 2) compare light absorption and photooxidant kinetics with previous measurements made in fog, 3) measure the dependence of oxidant concentrations on particle dilution to predict photooxidant concentrations in ambient particle liquid water, and 4) assess the importance of particle photooxidants in processing organic compounds in the atmosphere.

2 Experimental

2.1 Chemicals

All chemicals were used as received. Furfuryl alcohol (98%), syringol (99%), methyl jasmonate (95%), benzene (≥ 99.9%), 2-methyl-3-buten-2-ol (98%), deuterium oxide (99.9 atom D), and 2-nitrobenzaldehyde (98%) were from Sigma-Aldrich and sulfuric acid (trace metal grade) was from Fisher. All chemical solutions and particulate matter extracts were prepared
using purified water (Milli-Q water) from a Milli-Q Advantage A10 system (Millipore; ≥ 18.2 MΩ cm) with an upstream Barnstead activated carbon cartridge; total organic carbon concentrations were below 10 ppb C.

2.2 Particle collection and extraction

Wintertime particles were collected in a residential neighborhood in Davis, California, (38.5539° N, 121.7381° W, 16 m above sea level) during December 2015 and January 2016, a period with significant wood burning. PM$_{2.5}$ was collected on 8 × 10 inch Teflon-coated quartz filters (Pall Corporation, EmFab™ filters, type TX40HI20-WW) using a high-volume sampler with a PM$_{10}$ inlet (Graseby Anderson) followed by two offset, slotted impactor plates (Tisch Environmental, Inc., 230 series) to remove particles greater than 2.5 μm. Due to technical difficulties, the air flow rate was variable and typically ranged between 1130 and 1560 L min$^{-1}$, corresponding to particle cut points of 2.5 to 1.6 μm. Particles were generally collected over two to three consecutive nights between 5:30 pm and 7:30 am, but one sample (#3) was collected continuously (day and night) for 72 hours (Table S1).

Immediately upon collection, samples were wrapped in aluminum foil (previously baked at 500 °C for 8 h), sealed in Ziplock™ bags and stored at −20 °C. On the day of extraction, several 2 cm × 2 cm pieces were cut (using stainless-steel tools) from the same filter, each was put into a separate pre-cleaned 10 mL amber glass vial, Milli-Q water was added (see below), and the vial was sealed and shaken for 3 hours in the dark. The extracts were filtered (0.22 μm PTFE; Pall), combined, and labeled as Particulate Matter Extract (PME). The standard condition was to use 1.0 mL of Milli-Q to extract each filter square, but in our initial work we used 2.5 mL of Milli-Q per filter square; these latter “dilute extracts” are indicated by an asterisk and footnotes in the figures and tables. We switched from dilute to standard conditions after PME1-3, but we include both results in this work to compare the two types of extracts.

In addition, to study the effect of PM mass concentration, separate portions of filter #3 were extracted using five different extraction volumes between 0.5 and 10 mL (discussed later). Those extracts are labeled as PME3Dx, where “x” is the extraction volume (e.g., PME3D1.3 for filter squares extracted in 1.3 mL of Milli-Q). Upon extraction, each PME was stored in the refrigerator (5 °C) until the day of the illumination experiments. All illumination experiments and analyses on a PME sample were completed within a week of its extraction.
2.3 Sample Illumination and Chemical Analysis

For all illumination experiments except $^1$OH measurements using benzene (discussed in Sect. 2.5.1), on the day of the experiment a 1.0 mL aliquot of an air-saturated particle extract was first acidified to pH 4.2 ± 0.2 using 10 mM sulfuric acid (with sample dilution ≤ 10%) to mimic the particle water acidity in wintertime PM in California’s Central Valley (Parworth et al., 2017).

The pH of the sample was measured using a pH microelectrode (MI-414 series, protected tip, 16 gauge needle, 6 cm length; Microelectrodes, Inc.). The acidified extract was then spiked with a single photooxidant probe and put into a silicone-plugged, fully-filled GE021 quartz tube (4 mm inner diameter, 6 cm length, 1.0 mL volume) and illuminated with a 1000 W xenon arc lamp filtered with a water filter (to reduce sample heating), an AM 1.0 air mass filter (AM1D-3L, Scientech) and 295 nm long-pass filter (20CGA-295, Thorlabs) to mimic tropospheric solar light (Kaur and Anastasio, 2017). Because of the small tube size, samples were not stirred, but the entire sample was illuminated in a chamber held at 20 °C. 100 μL aliquots of illuminated (and parallel dark) samples were periodically removed and analyzed for the concentration of photooxidant probe (see below) using HPLC (Shimadzu LC-10AT pump, ThermoScientific BetaBasic-18 C$\text{_{18}}$ column (250 × 33 mm, 5 μM bead), and Shimadzu-10AT UV-Vis detector).

The photon flux in the sample was measured on each experiment day using a 10 μM solution of 2-nitrobenzaldehyde (2NB) in the same type of quartz tube as the sample (Galbavy et al., 2010).

Major anions and cations in the extracts (Table S2) were quantified using two Metrohm ion chromatographs (881 Compact IC Pro) equipped with conductivity detectors (Ge et al., 2014; Kaur and Anastasio, 2017). Dissolved organic carbon (DOC) in the filtered extracts was measured using a Shimadzu TOC-VCPH analyzer (Yu et al., 2014).

2.4 Light Absorbance

Light absorbance was measured immediately after extraction using a Shimadzu UV-2501PC spectrophotometer with 1-cm quartz cuvettes and a baseline of Milli-Q water.

Absorbance ($A_\lambda$) was converted to light absorption coefficients using

$$\alpha_\lambda = \frac{A_\lambda}{l}$$  \hspace{1cm} (1)

where $l$ is the pathlength in cm. The rate of sunlight absorption ($R_{\text{abs}}, \text{mol-photons L}^{-1} \text{s}^{-1}$) in each extract was calculated as:

$$R_{\text{abs}} = 2.303 \times 10^3 \times \frac{1}{N_A} \times \sum_{450nm}^{300nm} (\alpha_\lambda \times I_\lambda \times \Delta \lambda)$$  \hspace{1cm} (2)
where \(2.303\) is for base conversion, \(10^3\) is for units conversion (\(\text{cm}^3 \text{ L}^{-1}\)), \(N_A\) is Avogadro’s number, \(I_i\) is the Davis winter-solstice actinic flux (photons \(\text{cm}^{-2} \text{s}^{-1} \text{ nm}^{-1}\)) from the Tropospheric Ultraviolet and Visible (TUV) Radiation Model version 4.1 (Madronich et al., 2002), and \(\Delta\lambda\) is the interval between adjacent wavelengths in the TUV output (nm).

Wavelength-dependent mass absorption coefficients for DOC (MAC\(_{\text{DOC}}\); \(\text{cm}^2 \text{ g}^{-1} \text{C}^{-1}\)) were estimated by subtracting the contributions of nitrite and nitrate from the measured absorbance at each wavelength (which were small, \(\leq 7\%\) of the total absorbance) and then dividing the remainder by the DOC concentration:

\[
\text{MAC}_{\text{DOC}, \lambda} = \frac{\alpha_{\text{DOC}, \lambda} \times \ln(10) \times 10^3 \times 10^3}{[\text{DOC}]}
\]  

(3)

where \(\alpha_{\text{DOC}, \lambda}\) (\(\text{cm}^{-1}\)) is the sample absorbance coefficient at wavelength \(\lambda\) due to DOC (Kaur and Anastasio (2017)); \(\ln(10)\) is a base conversion factor; the two \(10^3\) factors are for unit conversion (\(\text{cm}^3 \text{ L}^{-1}\) and \(\text{mg g}^{-1}\)), and the DOC concentration is in \(\text{mg-C L}^{-1}\). Since the average organic matter–to–organic carbon (OM/OC) ratio in California Central Valley particles is approximately 1.7 (Young et al., 2016), the absorption coefficients normalized by OM mass will be approximately 60% of the MAC\(_{\text{DOC}}\) values.

### 2.5 Measurement of photooxidants

#### 2.5.1 Hydroxyl radical (\(\cdot\text{OH}\))

We quantified \(\cdot\text{OH}\) kinetics using a benzene probe (Zhou and Mopper, 1990; Anastasio and McGregor, 2001; Kaur and Anastasio, 2017). Briefly, four aliquots of each extract were spiked with varying concentrations of benzene to trap \(\cdot\text{OH}\) and form phenol (yield: 73\%), which is quantified (Fig. S1). Each benzene stock was made a day before the illumination experiment. Similar to the other photooxidant experiments, all aliquots were air-saturated, acidified to an initial \(\text{pH}\) of 4.2 (± 0.2), capped, and then constantly stirred during illumination in airtight 5.0 mL, 1-cm pathlength, rectangular quartz cuvettes with no initial headspace. For all \(\cdot\text{OH}\) measurements where benzene is used as a probe, we used this larger sample volume (5 mL) instead of 1 mL to minimize the headspace in the cuvette and prevent benzene loss due to volatilization. Throughout the illumination period, 100 \(\mu\text{L}\) aliquots were collected through the cap septum and analyzed for phenol using HPLC-UV (eluent of 30\% acetonitrile: 70\% Milli-Q, flow rate of 0.6 mL/min, detection wavelength of 210 nm and column temperature of 35°C). As described in Kaur and Anastasio (2017), we use these results to determine three experimental
quantities for \(^*\)OH: the rate of photoproduction \((P_{\text{OH,EXP}})\), the rate constant for \(^*\)OH loss due to natural sinks \((k'_{\text{OH}})\), and the steady-state concentration \(([^*\text{OH}]_{\text{EXP}})\). Measured rates of \(^*\)OH formation and steady-state concentrations were normalized to values expected under midday, Davis winter-solstice sunlight and were corrected for the small amount of internal light screening due to light absorption by DOM:

\[
[^*\text{OH}] = \left( \frac{[^*\text{OH}]_{\text{EXP}}}{S_A \times j_{2NB,\text{EXP}}} \right) \times j_{2NB,\text{WIN}} \tag{4}
\]

In this equation, \(S_A\) is the internal light screening factor (Table S1), \(j_{2NB,\text{WIN}}\) is the rate constant for loss of 2-nitrobenzaldehyde at midday near the winter solstice in Davis (solar zenith angle = 62°, \(j_{2NB,\text{WIN}} = 0.0070\ \text{s}^{-1}\); Anastasio and McGregor, 2001), and \(j_{2NB,\text{EXP}}\) is the measured rate constant for loss of 2NB on the day of the experiment. \(^*\)OH results are in Tables S3–S6.

We also measured \(^*\)OH steady-state concentrations in squares of particle filter #3 using five different dilutions with water (discussed later). Because these sample volumes were too small to use the benzene technique, we determined the steady-state concentration of \(^*\)OH by measuring the loss of 2-methyl-3-buten-2-ol (MBO) (Sect. S1). We then measured \(P_{\text{OH}}\) in a 1 cm cuvette using a high benzene concentration (1.5 mM) and determined the rate constant for \(^*\)OH loss due to natural sinks by dividing the rate of photoproduction by the steady-state concentration, \(k'_{\text{OH}} = P_{\text{OH}} / [^*\text{OH}]\) (Sect. S1.3). \(^*\)OH results are in Tables S2–S6. In contrast to the benzene technique, there was some quenching of \(^*\)OH by the probe MBO in our PME3 samples; this quenching was most significant in the most dilute extract, PME3D10. We corrected measured \(^*\)OH concentrations for quenching by MBO in the PME3 samples (Sect. S1) and the final, corrected values are given in the Tables mentioned above.

2.5.2 Singlet molecular oxygen \((^1\text{O}_2^*)\)

Singlet oxygen was quantified by measuring the loss of a furfuryl alcohol (FFA) probe and using heavy water (D\(_2\)O) as a diagnostic tool (Kaur and Anastasio, 2017; Anastasio and McGregor, 2001). Briefly, each extract was divided into two aliquots, acidified to pH 4.2 (± 0.2), and diluted 50:50 using H\(_2\)O or D\(_2\)O. Both aliquots were spiked to 10 \(\mu\)M FFA and illuminated in 1 mL quartz tubes. (At this concentration, FFA should decrease the steady-state concentration of \(^1\text{O}_2^*\) in air-saturated solutions by less than 1\%.) FFA loss was detected using HPLC-UV (eluent of 10% acetonitrile: 90% Milli-Q water, flow rate of 0.6 mL/min, detection wavelength of 210 nm and column temperature of 35°C). The loss of FFA followed pseudo-first-order kinetics and the slope of the plot of \(\ln([\text{FFA}]_t)/[\text{FFA}]_0\) versus time is the negative of the pseudo-
first-order rate constant for loss of FFA (illustrated in Fig. S2). Loss of FFA in the D₂O-diluted aliquot is faster than in H₂O because H₂O is the dominant sink for \(^1\)O₂*, which reacts less quickly with D₂O (Bilski et al., 1997). The differences in the pseudo-first-order rate constants for loss of FFA between the two aliquots were used to calculate the steady-state concentration of \(^1\)O₂* and the rate of singlet oxygen photoproduction (Anastasio and McGregor, 2001). These were normalized to values expected in Davis winter-solstice sunlight (i.e., \([\text{O}_2^*] \) and \(P_{\text{O}_2^*} \) ) and corrected for internal light screening using an equation analogous to Eq. (4). \(^1\)O₂* measurements are in Table S7.

2.5.3 Oxidizing triplet excited states of organic matter (\(^3\)C*)

Triplets were measured using the dual-probe technique we developed recently for fog waters (Kaur and Anastasio, 2018b): two 1.0 mL, pH 4.2 aliquots of each extract were spiked to 10 µM of either syringol (SYR) or methyl jasmonate (MeJA) and the loss of each probe was measured during illumination in plugged quartz tubes (Sect. 2.3). The measured pseudo-first-order rate constant for probe loss (\(k'_{\text{Probe,EXP}} \) ) was determined as the negative of the slope of the plot of ln([Probe]/[Probe]₀) versus illumination time. Values of \(k'_{\text{Probe,EXP}} \) were normalized to Davis winter-solstice sunlight and corrected for internal light screening using an analog of Eq. (4); the resulting rate constants are termed \(k_{\text{Probe}} \) (s⁻¹) (Tables S8, S9 of the SI). This pseudo-first-order rate constant for loss of probe represents the sum of all loss pathways:

\[
k'_{\text{Probe}} = k_{\text{Probe}+\text{OH}} [\text{OH}] + k_{\text{Probe}+\text{O}_2^*} [\text{O}_2^*] + \Sigma (k_{\text{Probe}+3\text{C}^*_i} [\text{C}^*_i]) + j_{\text{Probe}} + \Sigma (k_{\text{Probe}+\text{Other}} [\text{Other}])
\]

(5)

where the first two terms are the contributions of \(^\cdot\text{OH} \) and \(^1\)O₂* to probe loss; \(\Sigma (k_{\text{Probe}+3\text{C}^*_i} [\text{C}^*_i]) \) represents the sum of all triplet contributions to probe loss; \(j_{\text{Probe}} \) is the first-order rate constant for direct photodegradation of the probe, which is negligible for our illumination times (< 4.3 × 10⁻⁶ s⁻¹ and 4.8 × 10⁻⁷ s⁻¹ for SYR and MeJA, respectively, under Davis winter conditions); and \(\Sigma (k_{\text{Probe}+\text{Other}} [\text{Other}]) \) is the sum of contributions from all other oxidants. As described in Sect. S3, we estimate that these other oxidants (hydroperoxyl radical / superoxide radical anion, ozone, carbonate radical, hydrogen ion / aquated electron) contribute 12 % or less of the average measured syringol loss (Sect. S3) and so are ignored. We can then simplify and rearrange Eq. (5) to determine the triplet contribution to probe loss:

\[
k'_{\text{Probe}+3\text{C}^*} = \Sigma (k_{\text{Probe}+3\text{C}^*_i} [\text{C}^*_i]) = k'_{\text{Probe}} - (k_{\text{Probe}+\text{OH}} [\text{OH}] + k_{\text{Probe}+\text{O}_2^*} [\text{O}_2^*])
\]

(6)
In other probe techniques, the equivalent of Eq. 6 is rearranged so that \( \Sigma [^3\text{C}_1^*] \) can be determined based on the measured value of \( k'_{\text{Probe}, 3\text{C}^*} \) and the literature value of the second-order rate constant \( k_{\text{Probe}+3\text{C}_1} \). However, because triplets represent a suite of unidentified compounds, there is no one value of \( k_{\text{Probe}+3\text{C}_3} \). To estimate this second-order rate constant in each sample, we used a combination of rate constants from four model triplets – 2-acetonaphthone (\(^3\text{2AN}^*\)), 3’-methoxyacetophenone (\(^3\text{MAP}^*\)), 3,4-dimethoxybenzaldehye (\(^3\text{DMB}^*\)), and benzophenone (\(^3\text{BP}^*\)) – that roughly span the range of triplet reactivities in natural samples. We first identified the “best match triplets”, i.e., the one or two model triplets that match the triplet reactivity in a given extract. To do this, we determined the model triplets whose mole-fraction-weighted ratio of second-order rate constants (i.e., \( k_{\text{SYR}+3\text{C}^*} / k_{\text{MeJA}+3\text{C}^*} \)) matches the ratio of the measured first-order probe loss rate constants due to triplets (\( k'_{\text{SYR}, 3\text{C}^*} / k'_{\text{MeJA}, 3\text{C}^*} \)) in each extract (for more details, see Kaur and Anastasio (2018b)).

Ratios of the second-order rate constants \( (k_{\text{SYR}+3\text{C}^*} / k_{\text{MeJA}+3\text{C}^*}) \) of the model triplets range from 1.7 for the most reactive species (\(^3\text{BP}^*\)) to 100 for the least reactive, \(^3\text{2AN}^*\) (Table S10). For each extract, we calculated two mole-fraction-weighted second-order rate constants for triplets (one for each probe) and used them to estimate the triplet steady-state concentration:

\[
\Sigma [^3\text{C}_1^*]_{\text{Probe}} = \frac{k'_{\text{Probe}, 3\text{C}^*}}{\chi_{3\text{C}1^*} \times k_{\text{Probe}+3\text{C}1^*} + \chi_{3\text{C}2^*} \times k_{\text{Probe}+3\text{C}2^*}}
\]

(7)

where \( \chi_{3\text{C}1^*} \) and \( \chi_{3\text{C}2^*} \) are the mole fractions of the two best match triplets (\(^3\text{C}_1^* \) and \(^3\text{C}_2^* \)), and \( k_{\text{Probe}+3\text{C}1^*} \) and \( k_{\text{Probe}+3\text{C}2^*} \) are the second-order reaction rate constants of the best model triplet matches. Eq. (7) gives us two estimates of the triplet steady-state concentration, one from each probe, i.e., \( \Sigma [^3\text{C}_1^*]_{\text{SYR}} \) and \( \Sigma [^3\text{C}_1^*]_{\text{MeJA}} \). We averaged the two to obtain the best value for the triplet steady-state concentration in each extract, \( \Sigma [^3\text{C}_1^*] \).

We next estimated the rate of triplet photoformation (\( P_{3\text{C}^*} \)):

\[
P_{3\text{C}^*} = \Sigma [^3\text{C}_1^*] \times (k_{3\text{C}^*+3\text{O}_2} [\text{O}_2] + (k_{\text{rxn}} + k_{\text{Q}}) [\text{DOC}])
\]

(8)

where \( k_{3\text{C}^*+3\text{O}_2} \) is the average bimolecular rate constant for quenching of the model triplets by \( \text{O}_2 \) (\( = 2.8 \times 10^9 \text{M}^{-1} \text{s}^{-1} \); Table S11 and Canonica et al. (2000)), \([\text{O}_2]\) is the dissolved oxygen concentration of 284 \( \mu\text{M} \) at 20 °C (USGS, 2018), \( k_{\text{rxn}} + k_{\text{Q}} \) is the overall reaction and quenching rate constant for triplets by DOC (\( 9.3 \times 10^7 \text{L mol}^{-1} \text{C}^{-1} \text{s}^{-1} \); see below) and [DOC] values are in Table S2. At the concentrations we used (10 \( \mu\text{M} \)), SYR and MeJA are negligible sinks for triplets. Measurements for triplets are in Tables S12 and S13.
For all three photooxidants, the quantum yield of formation was calculated as

$$\Phi_{\text{Ox}} = \frac{P_{\text{Ox}}}{R_{\text{abs}}}$$  \hspace{1cm} (9)

where $P_{\text{Ox}}$ is the Davis winter-solstice-normalized rate of oxidant photoproduction and $R_{\text{abs}}$ is the rate of sunlight absorption by the extract.

2.5.4 PM mass concentration factor (CF)

Due to the volume required for our probe techniques, we extract particles into Milli-Q water, resulting in extracts that are approximately 1000 times more dilute than ambient particles. To examine the impact of dilution on photooxidant concentrations, we extracted sample #3 in five different volumes of Milli-Q water (0.5 to 10 mL) and measured $'\text{OH}$, $^1\text{O}_2^*$ and $^3\text{C}^*$ steady-state concentrations in the five extracts. We define the PM mass concentration factor (CF) as the ratio of (PM mass) / (water mass) in a given extract relative to the most concentrated extract that we can make:

$$\text{CF} = \frac{V_{\text{MIN}}}{V_{\text{EXT}} + V_{\text{P}}}$$  \hspace{1cm} (10)

where $V_{\text{MIN}}$ is the minimum experimentally feasible volume of Milli-Q needed for extraction of one filter square (0.5 mL), $V_{\text{EXT}}$ is the volume of Milli-Q used to extract a given filter square (0.5 to 10 mL), and $V_{\text{P}}$ is the volume of probe stock solution added (typically 20 $\mu$L). Values of CF for the PME3D extracts ranged from 0.05 (least concentrated) to 0.96 (most concentrated) and are listed in Table S14.

2.5.5 Uncertainties

In figures, error bars represent ± 1 standard error (SE) calculated by propagating the uncertainties in each term used to calculate the plotted value.

3 Results and discussion

3.1 General extract characteristics

Similar to Davis fogs collected in 1997-98 (Anastasio and McGregor, 2001) and 2011 (Kaur and Anastasio, 2017), the most abundant ions in the particle extracts are ammonium ($\text{NH}_4^+$, 280–2600 $\mu$M) and nitrate ($\text{NO}_3^-$, 380–3300 $\mu$M) (Table S2). This is expected since
ammonium nitrate is the most significant inorganic component of wintertime particles in the Central Valley (Herner et al., 2006; Heald et al., 2012; Young et al., 2016). The average values of NO$_3^-$ and NH$_4^+$ are not statistically different ($p > 0.5$) between the current particle extracts (PME) and previous fogs, although the ranges are much wider in the particle extracts (Table S2). Similar to nitrate, nitrite is another important source of hydroxyl radical in the aqueous phase (Anastasio and McGregor, 2001), with an average concentration of 6.9 ($\pm$ 2.9) μM in the particle extracts, again statistically similar to the 2011 fog average. On the other hand, the average concentration of potassium – commonly used as a tracer for biomass-burning (Silva et al., 1999; Parworth et al., 2017) – is nearly 40 times higher in the particles than in the 2011 Davis fog samples ($p = 0.019$), suggesting PME enrichment by residential wintertime wood-burning. This is reflected in the dilute PM extracts as well: even though most characteristics in the dilute extracts are similar to fog, the average K$^+$ (38 $\pm$ 7 μM) in the dilute PMEs is 10 times higher than the fog value. Dissolved organic carbon (DOC) in the standard extracts (mean: 3400 ($\pm$ 760) μM-C) is, on average, three times higher than both the dilute extracts and fog.

We employed two field blanks in this study, one each for dilute and standard extraction conditions. Ions and DOC in both field blanks are lower than 10% of the corresponding PME sample averages, with a few exceptions (Table S2).

### 3.2 Light absorption in particle extracts

As shown in Fig. 1a and Table S1, the pathlength-normalized absorbance ($\alpha$, cm$^{-1}$) declines exponentially with wavelength, with values at 300 nm ($\alpha_{300}$) between 0.27 and 0.58 cm$^{-1}$ for the standard extracts PME3–6. The average $\alpha_{300}$ value is nearly five times higher in standard extracts than values in Davis fog samples (Table S1, Fig. S3, data available in Kaur and Anastasio (2018a)), while the “dilute extracts” (PME1*, PME2*, and PME3D2.5*) have absorbances very similar to fog samples. Values of the Absorption Angstrom Exponent (AAE) for all PM extracts range between 6.2 and 7.9 (Table S1), similar to those reported previously for water soluble particulate BrC from biomass burning (Hecobian et al., 2010; Kirchstetter and Thatcher, 2012). For both the fog and PM extracts the calculated rate of sunlight absorption between 300 and 450 nm ($R_{abs}$) is well-correlated with dissolved organic carbon (DOC) ($R^2 = 0.89$ and 0.67, respectively; Fig. S4), suggesting that BrC is mainly responsible for light absorption. The $R_{abs}$ values for the standard extracts are high, with an average value of 9.1 ($\pm$ 4.1) × 10$^{-6}$ mol-photons L$^{-1}$ s$^{-1}$, five times higher than the dilute extracts and past Davis fogs (Table S1). Similar to fog (Kaur and Anastasio, 2018b), the average rate of sunlight absorbance in the
standard particle extracts is 17 times higher than the total formation rates of the three photooxidants (discussed later), indicating that most of the (photo) energy absorbed is either dissipated via non-reactive pathways or leads to formation of other products.

We next calculated mass absorption coefficients for the organics (MAC\textsubscript{DOC}) by subtracting the absorbance contributions by nitrite and nitrate from \( \alpha \) and dividing by the DOC concentration (Eq. (3)). Across both standard and dilute extracts, the average (± \( \sigma \)) MAC\textsubscript{DOC} value at 300 nm is \( 2.2 \pm 0.7 \times 10^{4} \text{ cm}^{2} \text{ g}^{-1} \), 1.7 times higher than the fog sample average (Figs. 1b and S3; data available at Kaur and Anastasio (2018a)). Both \( \alpha \) and MAC\textsubscript{DOC} in the PME are generally higher than in fog, especially at shorter sunlight wavelengths (Fig. S5), although AAE values are similar in the extracts and fog (Table S1). Since MAC\textsubscript{DOC} accounts for dilution (Eq. (3)), the higher values in PM extracts indicates that water-soluble organics in particles are either more strongly light-absorbing (on a per-carbon basis), and/or less diluted with non-absorbing DOC, compared to those in fog. Our PME mass-absorption coefficients at 300 nm are very similar to values reported for the humic–like fraction of biomass-burning aerosols in the Amazon basin (Hoffer et al., 2006) and for the water-soluble organic fractions of rural aerosols (Varga et al., 2001; Sun et al., 2007).

Compared to the samples, light absorption in the field blanks is negligible, representing 0.7% and 3% of the average \( \alpha_{300} \) in the standard and dilute extracts, respectively (Table S1).

### 3.3 Hydroxyl radical

The average Davis winter-solstice-normalized rate of \(^{\cdot}\text{OH}\) photoproduction (\( P_{\text{OH}} \)) in the standard extracts is \( 1.2 \pm 0.5 \times 10^{-9} \text{ M s}^{-1} \) (i.e., \( 4.2 \pm 1.7 \text{ M h}^{-1} \)), 3.3 times faster than the average of previous Davis fogs (Table S3). In Davis fog, the main sources of \(^{\cdot}\text{OH}\) were nitrite and nitrate photolysis, accounting for 70 – 90% of measured \( P_{\text{OH}} \) (Anastasio and McGregor, 2001; Kaur and Anastasio, 2017). However, in the standard PM extracts, nitrite and nitrate together account for an average of only (34 ± 14) % of \( P_{\text{OH}} \) (Table S4), while other, unidentified species account for the remaining (66 ± 14) %. While \( \text{NO}_{2}^{-} \) and \( \text{NO}_{3}^{-} \) concentrations in PME and fog are similar, measured \(^{\cdot}\text{OH}\) photoproduction rates are much higher in the particle extracts. The additional sources of \(^{\cdot}\text{OH}\) likely include photo-Fenton processes (Arakaki and Faust, 1998) and organic peroxides (Tong et al., 2016; Tong et al., 2017; Lim and Turpin, 2015), although there is only a modest correlation between DOC and \( P_{\text{OH}} \) due to unidentified sources (Fig. S6).
While organic compounds are potentially important sources of \(^{\cdot}\)OH in the particle extracts, they are almost certainly the main \(^{\cdot}\)OH sink, as found previously for atmospheric and surface waters (Brezonik and Fulkerson-Brekken, 1998; Dong et al., 2010; Arakaki et al., 2013). The average \((\pm 1\sigma)\) rate constant for \(^{\cdot}\)OH destruction, \(k'_{\text{OH}}\), in the standard extracts is \(2.5 \times 10^6 \text{ s}^{-1}\), three times higher than in dilute extracts and fog (Table S3); DOC concentrations in the standard PM extracts are similarly enhanced, ranging between 2350 and 4090 \(\mu\text{M-C}\) (Table S2). Based on our calculations, inorganic species together account for no more than 10% of \(k'_{\text{OH}}\) in the PM extracts except for PME3D10 which is the most dilute sample and has the largest uncertainty (Tables S5, S6). The rate constant for \(^{\cdot}\)OH destruction due to organics, i.e., \(k'_{\text{OH,org}}\), obtained by subtracting contributions of the inorganic sinks from \(k'_{\text{OH}}\), is well correlated with DOC concentrations \((R^2 = 0.73)\) (Fig. S6). Arakaki et al. (2013) showed that the ratio \(k'_{\text{OH,org}}/\text{[DOC]}\) is relatively constant in atmospheric waters, with an average \((\pm 1\sigma)\) value of \(3.8 \pm 1.9 \times 10^6 \text{ L (mol–C)}^{-1} \text{ s}^{-1}\). Our average \((\pm 1\sigma)\) measured ratio in all particle extracts is nearly twice as high, \(7.1 \pm 2.7 \times 10^6 \text{ L (mol–C)}^{-1} \text{ s}^{-1}\), but not statistically different (Table S3).

Davis winter-solstice-normalized \(^{\cdot}\)OH steady-state concentrations in all extracts are in the range of \((1.7–7.9) \times 10^{-16} \text{ M}\), with an average \((\pm 1\sigma)\) value of \(5.1 \pm 2.4 \times 10^{-16} \text{ M}\) in the standard extracts (Fig. 2a, Table S3). While both the \(^{\cdot}\)OH photoproduction rate and rate constant for \(^{\cdot}\)OH loss are approximately three times higher in the standard PM extracts compared to the dilute extracts and fog, the two enhancements cancel out to give \(^{\cdot}\)OH steady-state concentrations that are similar across all three sample types. This relative consistency of \(^{\cdot}\)OH concentrations has been reported for a wide variety of atmospheric waters (Arakaki et al., 2013); our average concentration is similar to most of these past results (Fig. S7). As we discuss in Sect. 3.6, transport of \(^{\cdot}\)OH from the gas-phase is also an important source to drops and particles, but its importance decreases with decreasing particle size.

We also calculated the quantum yield of hydroxyl radical formation, i.e., the fraction of absorbed photons that result in \(^{\cdot}\)OH formation (Eq. (9)). The average \((\pm 1\sigma)\) value of \(\Phi_{\text{OH}}\) in all particle extracts is \(0.014 \pm 0.010\)%, which is statistically similar to the average fog result (Table S3): while photoformation rates of \(^{\cdot}\)OH increase from fog to standard particle extracts (Table S3), light absorption shows a similar trend (Table S1).

The rate of \(^{\cdot}\)OH photoproduction in the field blanks is negligible, representing 1% and 6% of the average rate in standard and dilute extracts, respectively. The rate constants for \(^{\cdot}\)OH destruction \((k'_{\text{OH}})\) in the standard (FB2) and dilute (FB1) field blanks represent 10% and 43% of the corresponding PME averages. The latter result is puzzling, since the concentrations of \(^{\cdot}\)OH
sinks measured in FB1 (i.e., DOC and NO\textsubscript{2} \textsuperscript{−}; Table S2) are much lower relative to the extract.

We discuss measurements of \( k'_{\text{OH}} \) in the blanks in more detail in Sect. S2. We do not subtract the field blank results for \( k'_{\text{OH}} \) from the corresponding PM extract values and thus our sample results are upper bounds.

### 3.4 Singlet molecular oxygen

The average (± 1\( \sigma \)) Davis winter solstice-normalized \( ^1\text{O}_2^* \) concentration in the dilute extracts (2.4 (± 0.7) × 10\textsuperscript{-13} M) is very similar to the previous fog average (Fig. 2b). This is likely because brown carbon is the source of \( ^1\text{O}_2^* \) (Faust and Allen, 1992; Zepp et al., 1977) and the DOC concentrations in the fog and dilute extracts are very similar (Table S2). On the other hand, the average [\( ^1\text{O}_2^* \)] in the more concentrated, standard PM extracts (PME3–6), is 1.6 (± 0.5) × 10\textsuperscript{-12} M, nearly seven times higher than the averages in Davis fog and dilute extracts (Fig. 2b, Table S7). This is because the standard extracts have higher DOC concentrations but the same major \( ^1\text{O}_2^* \) sink, i.e., water. Across all fog and particle extracts, the rate of singlet oxygen formation \((P_{1\text{O}_2^*})\) is strongly correlated with the rate of sunlight absorption \((R_{\text{abs}})\) \((R^2 = 0.94; \text{Fig. 3a})\), although this correlation is not evident only in the fog samples (Kaur and Anastasio, 2017).

As seen for \(^\text{\textsuperscript{\prime}}\text{OH}\), quantum yields of \( ^1\text{O}_2^* \) are similar in the extracts (standard and dilute) and fog (Table S7); the slope of the \( P_{1\text{O}_2^*} \) versus \( R_{\text{abs}} \) correlation line (Fig. 3a) gives an overall quantum yield of \( ^1\text{O}_2^* \) of (3.8 ± 0.2) %, i.e., across all samples roughly 4% of the photons absorbed lead to the formation of singlet oxygen. This is nearly 260 times higher than the average quantum yield of \(^\text{\textsuperscript{\prime}}\text{OH}\). Our quantum yields for singlet oxygen formation in PM extracts are similar to values previously reported for surface water organics (e.g., 2 – 5% in) Zhou et al. (2019).

### 3.5 Triplet excited states of organic matter (\( ^3\text{C}^* \))

We also determined the kinetics and concentrations of oxidizing “triplets”, by measuring the loss of two probes, syringol (SYR) and methyl jasmonate (MeJA) (Fig. S8). In the standard extracts, the average (± \( \sigma \)) Davis winter-normalized rate constants for loss of SYR and MeJA \((k'_{\text{Probe}})\) are (4.3 ± 1.7) × 10\textsuperscript{-4} s\textsuperscript{-1} and (2.6 ± 0.7) × 10\textsuperscript{-5} s\textsuperscript{-1}, which are equivalent to average lifetimes of 0.70 (± 0.20) and 11 (± 3) h, respectively (Tables S8 and S9). Triplet probe lifetimes in the dilute extracts are approximately three times longer and are very similar to fog values, indicating that the main source of triplet precursors to fog drops is the BrC present in the fog condensation nuclei rather than mass transport from the gas phase.
We correct the loss of triplet probes for oxidation by hydroxyl radical and singlet molecular oxygen (Eq. (6)). In the standard extracts, \(^1\)O\(_2^*\) and \(^1\)OH account for an average of 13 \% and 3 \% of SYR loss, respectively (Table S8, Fig. S9); for methyl jasmonate, the corresponding contributions are 37 \% and 13 \%.

Next we use the ratio of the pseudo-first-order rate constants for probe losses by triplets, i.e., \(k'_{\text{SYR,3C^*}} / k'_{\text{MeJA,3C^*}}\), to characterize the average reactivity of the triplet species in each sample: a ratio close to 1 indicates higher reactivity, while a higher ratio indicates lower reactivity. The \(k'_{\text{probe,3C^*}}\) ratio (i.e., \(k'_{\text{SYR,3C^*}} / k'_{\text{MeJA,3C^*}}\)) in all extracts ranges between 7.9 and 37 (Table S12), which is a narrower range than in Davis fog samples (7.5 to 110) (Kaur and Anastasio, 2018b). Based on the \(k'_{\text{probe,3C^*}}\) ratios, triplets in the PM extracts generally have an average reactivity similar to model aromatic triplets \(^3\)-methoxyacetophenone (\(^3\)MAP*) and 3,4-dimethoxybenzaldehyde (\(^3\)DMB*) (Fig. 2c, Table S12). The average (± σ) triplet steady-state concentration in the standard extracts is 1.0 (± 0.4) \(\times 10^{-13}\) M (Fig. 2c, Table S13), which is nearly twice the fog average, but not statistically significantly different. If we consider only the PM and fog samples that have triplet reactivities similar to \(^3\)MAP* and \(^3\)DMB* (i.e., the green average lines in Fig. 2c), the average triplet concentration in the standard PM extracts is nearly four times greater than in fog (Table S2), similar to the ratio of DOC concentrations.

In the standard extracts the average concentration of oxidizing triplets is 16 times lower than \(^1\)O\(_2^*\) but nearly 290 times higher than \(^1\)OH from \textit{in situ} sources. Our measurements of oxidizing triplet concentrations lie at the higher end of measured and estimated concentrations of total (i.e., oxidizing and energy transfer) triplets in surface waters, \(10^{-15}–10^{-13}\) M (Zepp et al., 1985; Grebel et al., 2011). The average (± 1 σ) rate of triplet photoformation, \(P_{3\text{C^*}}\), is 2.0 (± 1.0) \(\times 10^{-7}\) M s\(^{-1}\) (i.e., 720 (± 360) \(\mu\)M h\(^{-1}\)) in the standard extracts (Table S13). Thus the ratios of the average production rates for \(^1\)O\(_2^*\), \(^3\)C\(*\), and \(^1\)OH are 290 : 170 : 1. There is a fair correlation between \(P_{3\text{C^*}}\) and \(R_{\text{abs}}\) (Fig. 3b), similar to the case for \(P_{102^*}\) (Fig. 3a), consistent with BrC as the source of triplets. Sample-to-sample variability in the fraction of the total triplet pool that can oxidize organics likely causes the \(P_{3\text{C^*}}\) correlation \((R^2 = 0.81)\) to be weaker than that of \(P_{102^*}\) \((R^2 = 0.94)\). The average (± 1σ) oxidizing triplet quantum yield in \textit{standard} extracts is (2.4 ± 1.0) \% (Table S13), approximately two times lower than the value for \(^1\)O\(_2^*\) (Table S7) but 150 times higher than for \(^1\)OH (Table S3). \textbf{Our triplet quantum yields are within the wide range of values that has been reported for surface waters, approximately 0.4 – 7\% (Zepp et al., 1985; Grebel et al., 2011; Zhou et al., 2019).}
Triplet excited states have two main reaction pathways: energy transfer (e.g., to make $^1\text{O}_2^*$) and electron transfer (e.g., to oxidize a phenol) (Zepp et al., 1985; McNeill and Canonica, 2016; Kaur and Anastasio, 2018b). Essentially all triplets possess enough energy to form $^1\text{O}_2^*$ (McNeill and Canonica, 2016), but only a subset of the triplet pool can oxidize organics via electron transfer. Thus the quantum yield of $^1\text{O}_2^*$ can be used to estimate the total triplet quantum yield, while our measurements of $\Phi_{3C^*}$ constrain the smaller subset of oxidizing triplets (assuming energy transfer from triplets is the only source of $^1\text{O}_2^*$). The quantum yield for all triplets can be estimated as $\Phi_{102^*/f_\lambda}$, where $f_\lambda$, the fraction of $^3\text{C}^*$ interactions with dissolved $\text{O}_2$ that yield $^1\text{O}_2^*$, is approximately 0.5 (McNeill and Canonica, 2016; Kaur and Anastasio, 2018b). For our standard extracts, the average value of $\Phi_{102^*/f_\lambda}$ is 0.078 ± 0.019, i.e., approximately 8% of the photons absorbed by brown carbon chromophores make a triplet excited state. Next we use the ratio $\Phi_{3C^*/(\Phi_{102^*/f_\lambda})}$ to estimate the fraction of all triplets that can participate in electron-transfer (oxidation) reactions. The average value of this fraction is 0.35 ± 0.12 for all the PM extracts, i.e., on average, approximately a third of all triplets are oxidizing (range = 18–50% Table S13).

### 3.6 Predicting photooxidant concentrations in ambient particle water

Since our particle extracts are approximately 1000 times more dilute than ambient Davis particles during winter, we want to be able to estimate oxidant concentrations under ambient conditions. To do this we first measured photooxidant concentrations as a function of dilution for the same sample and then extrapolated our results to ambient particle conditions. For the first step, we extracted squares of filter #3 using five different volumes of Milli-Q water, from 10 to 0.50 mL (Sect. 2.5.4), corresponding to aqueous PM mass concentration factors (CF) of 0.05 (most dilute) to 0.96 (most concentrated) (Eq. (10)). For this sample, these are equivalent to PM solute mass / water mass ratios typical for dilute to very concentrated cloud or fog drops, i.e., $(0.35 – 8.4) \times 10^{-4} \mu\text{g-PM} / \mu\text{g}-\text{H}_2\text{O}$ in comparison, ambient particles have ratios of approximately 1 $\mu\text{g-PM} / \mu\text{g}-\text{H}_2\text{O}$ and higher (Table S14). The rate of light absorption increases linearly with CF (Fig. 4a), indicating that BrC and other chromophores are efficiently extracted for all Milli-Q volumes employed.

The change in photooxidant concentration with CF depends on how the ratio of sources and sinks varies with dilution. In the case of hydroxyl radical, $P_{\text{OH}}$ and $k'_{\text{OH}}$ both increase as extracts get more concentrated (i.e., as CF increases), resulting in an $^1\text{OH}$ concentration that is noisy but essentially unchanged over the 20-fold increase in concentration factor (Fig. 4b). This
result is consistent with the relatively constant \[^{[\text{OH}]}\] in our particle extracts relative to fog (Fig. 3a, black dashed lines) and with prior results showing very similar concentrations for rain, cloud, fog, and marine PM extracts (Fig. S7 and Arakaki et al., 2013).

To estimate \[^{[\text{OH}]}\] in particle liquid water, we use the measured linear dependences of the rate of \[^{[\text{OH}]}\] photoproduction \((P_{\text{OH}})\) and loss rate constant \((k'_{\text{OH}})\) on concentration factor, which corresponds to a measured PM mass / water mass ratio (Fig. S10). Under a typical wintertime, Central Valley ambient particle water condition (1 \(\mu\text{g-PM} / \mu\text{g-H}_2\text{O}\)), the \textit{in situ} \(P_{\text{OH}}\) and \(k'_{\text{OH}}\) are estimated to be \(4.2 \times 10^{-6} \text{ M s}^{-1}\) and \(5.5 \times 10^9 \text{ s}^{-1}\), respectively (Fig. S10). This extrapolation of only aqueous processes gives an \[^{[\text{OH}]}\] concentration in particle water of \(7.6 \times 10^{-16} \text{ M}\), which is similar to the average of the measurements in Fig. 4b. However, this estimate does not include the contribution of mass transport of gas-phase \[^{[\text{OH}]}\] to the particles. As detailed in Sect. S4, we estimate that the rate of \[^{[\text{OH}]}\] gas-to-particle transport under particle conditions is \(4.2 \times 10^{-2} \text{ M s}^{-1}\), which is approximately 10% of the \[^{[\text{OH}]}\] photof ormation rate from aqueous sources. Figure 5 shows estimated \[^{[\text{OH}]}\] steady-state concentrations considering both aqueous reactions and gas-phase mass transport across a wide range of drop to particle conditions: \[^{[\text{OH}]}\] decreases from \(5.4 \times 10^{-15} \text{ M}\) under dilute drop conditions \(\left(3 \times 10^{-5} \mu\text{g-PM/\mu g-H}_2\text{O}\right)\) to \(8.4 \times 10^{-16} \text{ M}\) under the much more concentrated particle conditions \(\left(1 \mu\text{g-PM/\mu g-H}_2\text{O}\right)\). The calculated \[^{[\text{OH}]}\] values (orange line in Figure 5) are higher than our measured values (orange points in Figure 5) because of the gas-phase mass transport source. Changes in this source are also responsible for the slow decrease in calculated \[^{[\text{OH}]}\] as conditions become more concentrated \(\left(i.e., as \mu\text{g-PM/\mu g-H}_2\text{O}\right)\) increases). In the case of singlet oxygen, steady-state concentrations increase proportionally with PM mass concentration factor (Fig. 4c). Our interpretation of this result is that the concentration of \(^1\text{O}_2\)\(^*\) sources \(\left(i.e., \text{BrC}\right)\) increase proportionally with concentration factor, while the concentration of the main sink for \(^1\text{O}_2\)\(^*\) \(\left(i.e., \text{water}\right)\) is essentially unchanged. At higher PM mass/water mass ratios, we calculate that organic compounds become a significant sink for singlet oxygen (Sect. S4), leading to a plateau in \(^1\text{O}_2\)\(^*\) under the more concentrated conditions of particles (Fig. 5). This extrapolation for ambient PM conditions \(\left(1 \mu\text{g-PM/\mu g-H}_2\text{O}\right)\) predicts an \(^1\text{O}_2\)\(^*\) concentration in particle water of \(1.6 \times 10^{-10} \text{ M}\) (Table S15, Fig. 5), which is 2400 times higher than our prediction for dilute fog/cloud drops. While there are no other measurements of \(^1\text{O}_2\)\(^*\) in particles, similar enhancements in \(^1\text{O}_2\)\(^*\) concentrations \(\left(up \text{ to } a \text{ factor of roughly } 10^4\right)\) have been found in cases where \(^1\text{O}_2\)\(^*\) precursors become highly concentrated, e.g., in liquid-like regions of ice (Bower and Anastasio, 2013) and in regions of hydrophobic CDOM in solution (Latch and McNeill, 2006).
An increase in extract concentration (i.e., CF) also increases the triplet steady-state concentration (Fig. 4d), but there is greater uncertainty in this trend, in part because there is more uncertainty in measurements of $\Sigma[3C^*]$. As described in Sect. S4, we fit the data in Fig. 4d with a hyperbolic regression under two cases: (1) a best fit, where parameters were adjusted to minimize the regression error, and (2) a high estimate fit, where parameters were adjusted so that the regression line passed near the upper portion of the error bar for the CF 0.96 data point. These are the dashed and dotted lines in Fig. 4d, respectively. In both cases, the triplet concentration initially rises more quickly with CF but then approaches a plateau at higher CF values. Our interpretation of this behavior is that as CF increases, [DOM] and $P_{3C^*}$ increase linearly but the dominant triplet sink switches from dissolved O$_2$ at low CF to DOM at high CF. Wenk et al. (2011); (2013) have shown that surface water DOM can quench triplets when DOM concentrations are greater than 20 mg-C L$^{-1}$; in the PME3D extracts of Fig. 4, DOM ranges from 4.3 to 86 mg-C L$^{-1}$ (Table S2). Based on our previous work, we believe that phenols from wood combustion are reacting with (and physically quenching) triplets in our PM extracts (Smith et al., 2014; 2015). As described in Sect. S5, by fitting a kinetic model to our triplet dilution data we estimate that the total (reaction and quenching) rate constant for triplets with DOC in the PME3 extracts is $9.3 \pm 1.3 \times 10^7$ L mol-C$^{-1}$ s$^{-1}$.

These two extrapolations result in oxidizing triplet concentrations under PM conditions (1 μg-PM / μg-H$_2$O) of $2.3 \times 10^{-13}$ M (best fit) and $1.3 \times 10^{-11}$ M (high estimate). Taken together with the other oxidant measurements, we estimate that the ratio of $^1$O$_2^*$: $^3$C*: 'OH concentrations in ambient particle water is approximately $10^5 : 10^2 : 1$.

4 Implications

Our dilution experiments suggest that 'OH, $^1$O$_2^*$, and $^3$C* behave very differently as the PM/water ratio increases from cloud and fog drop conditions to water-containing particles (Fig. 5). To understand what this implies for the fate of organic compounds, we estimated the gas-aqueous partitioning and lifetimes of five model organic compounds for both fog and aqueous aerosol (Fig. 6). We consider reactions with two gas-phase oxidants ('OH, O$_3$) and four aqueous-phase oxidants ('OH, O$_3$, $^1$O$_2^*$, $^3$C*) (Table S16). Our model organics represent two groups in terms of gas-aqueous partitioning: one group with modest Henry’s law constants ($K_H \sim 10^9$ M atm$^{-1}$) and one with much higher values ($K_H = 10^9 – 10^{11}$ M atm$^{-1}$) (Fig. 6 and Table S17).
Fig. 6a shows the overall lifetimes of the five model organics and the fraction of each present in fog and PM. For the organics with the lowest $K_H$ values, approximately 10–20% is present in the aqueous-phase under fog conditions, but almost none is present in the particle liquid water. Consequently, gas-phase reactions dominate their overall lifetimes, which are approximately 2 to 3 hours for both fog and PM conditions. In contrast, the compounds with high $K_H$ values are partitioned strongly to the aqueous phase for both the fog and PM scenarios (Fig. 6a). But due to the overall higher oxidant concentrations in PM, the lifetimes of these organics are predicted to be shorter – sometimes by large factors – in PM than in fog (Fig. 6a, Table S17).

Additionally, their main sinks change from fog to PM, shifting from aqueous $'$OH, O$_3$, and $^1$O$_2$* in fog to being generally dominated by $^1$O$_2$* in PM water (Fig. 6b). For example, for tyrosine (compound 3), the predominant sink changes from aqueous O$_3$ in fog to $^1$O$_2$* in water-containing particles, while its lifetime decreases from 1.6 h to 0.04 h (Fig. 6b and Table S17).

While triplets are negligible oxidants for individual organics in particles under the conditions of Fig. 6, the picture changes if we move from the Fig. 6 triplet concentration of $2.3 \times 10^{-13}$ M to the high estimate concentration ($1.3 \times 10^{-11}$ M; Fig. 5). Under this condition aqueous oxidation still dominates the loss of the high-$K_H$ compounds, but $^3$C* becomes a much more important oxidant in PM and organic lifetimes get shorter by factors of 3 to 180 compared to fog (Fig. S11). While there is large uncertainty in the triplet concentrations in PM, Figs. 6 and S11 both indicate that aqueous oxidants can control the fate of highly soluble species in aerosols and that organic lifetimes can be shorter in PM because of an enhancement in oxidant concentrations.

Finally, despite the uncertainty in triplet concentration under particle conditions, the formation rate of $^3$C* is fast enough – and the fraction of triplets lost via reaction with organics is high enough – that triplets represent, in aggregate, a significant sink for organic compounds in particles. While these two ideas might seem contradictory, we propose that the suite of reactive organic compounds is suppressing the triplet concentrations enough that $^3$C* are small sinks for individual organic compounds, but are significant sinks when integrated over all of the reactive organics. As described in Sect. 3.5, the formation rates for $^1$O$_2$*, $^3$C*, and $'$OH have a ratio of 290 : 170 : 1, respectively, in the PM extracts; based on our dilution experiments (Fig. 4), we expect similar ratios in ambient particle liquid water. Since organic compounds appear to be the major sinks for all three oxidants under ambient particle conditions, and since each oxidant is at steady-state, the ratio of formation rates is approximately the same as the ratio of total rates of organic compound oxidation by each oxidant. Thus, while the steady-state concentration of $^3$C* might be significantly lower than that of $^1$O$_2$* in particle water, both oxidants appear to be
similarly important in the overall processing of particulate organics. In contrast, the total rate of oxidation of organics by \(^{1}\text{OH}\) appears to be 200–300 times slower, although \(^{1}\text{OH}\) will be relatively more important for less reactive organics. This comparison suggests that both singlet molecular oxygen and triplet excited states are important for the processing of organic compounds in particle liquid water.

### 5 Conclusions and Uncertainties

We have made the first measurements of singlet molecular oxygen and oxidizing triplet states in aqueous extracts of particles, in addition to measuring hydroxyl radical. Under our standard condition, the particle extracts are approximately three times more concentrated than wintertime Davis fog waters. The extracts contain significant amounts of brown carbon, with DOC-normalized mass absorption coefficients between roughly 15,000 and 30,000 cm\(^2\) g\(^{-1}\) and Absorption Angstrom Exponents of 6.2 to 7.9. Upon absorbing light, BrC and other chromophores in the samples form significant amounts of \(^{1}\text{OH}\), \(^{1}\text{O}_2^{*}\), and \(^{3}\text{C}^{*}\). While concentrations of \(^{1}\text{OH}\) in the PM extracts are in the same range as found in fog waters, concentrations of the oxidants derived primarily from BrC – i.e., \(^{1}\text{O}_2^{*}\) and \(^{3}\text{C}^{*}\) – are higher in the extracts compared to in fog by factors of approximately seven and two, respectively.

Dilution experiments indicate that the \(^{1}\text{OH}\) concentration is essentially independent of the PM mass concentration in solution, consistent with previous results, while \(^{1}\text{O}_2^{*}\) and \(^{3}\text{C}^{*}\) increase with increasing aqueous PM concentration. Extrapolating our findings to the much more concentrated conditions expected in ambient particle water suggests that hydroxyl radical concentrations in particles will be somewhat lower than values in fog and cloud drops, a result of size-dependent changes in mass transport from the gas phase. In contrast, oxidants formed from illumination of brown carbon will be enhanced in particles; moving from very dilute drops (3 × 10\(^{-5}\) μg-PM/μg-H\(_2\)O) to concentrated particles (1 μg-PM/μg-H\(_2\)O) we predict that the concentration of \(^{1}\text{O}_2^{*}\) will increase by approximately a factor of 2400, while concentrations of oxidizing triplets will increase between a factor of 30 and 2000. The higher \(^{1}\text{O}_2^{*}\) concentrations predicted in particles lead to a large decrease in the lifetimes of highly water-soluble organic compounds compared to foggy conditions, even though the liquid water content of the particles is roughly 10\(^4\) times lower than the fog. It appears that triplets are also more significant oxidants for individual organic compounds in PM than in fog, but there is too much uncertainty in our data to properly assess this increase. In contrast, \(^{1}\text{OH}\) is important for the oxidation of organics.
that react only slowly with $^1\text{O}_2^*$ and $^3\text{C}^*$, but is otherwise a minor oxidant for the organics we considered since the particulate $^1\text{OH}$ concentration is quite low.

While our results suggest that oxidants derived from brown carbon are very significant in water-containing particles, there are several large uncertainties. Most significantly, because of experimental limitations on the maximum PM concentration in our extracts, we need to extrapolate oxidant measurements over a very large range (approximately a factor of 1000) to predict oxidant levels in ambient water-containing particles. This results in very large uncertainties. As part of this uncertainty, it is difficult to assess how reactions in the particles might suppress concentrations of $^1\text{O}_2^*$ and $^3\text{C}^*$. Secondly, while calculations suggest that unaccounted oxidants are minor sinks for our triplet probes, if these species are important our triplet concentrations would be biased high. Finally, it is unclear how widely our results, which are for one season and one location, can be applied to other particles containing brown carbon.

However, PME3, our one sample collected during both daytime (with little biomass burning) and night (with significant biomass burning) had similar reactivity to the other samples, which were collected only at night. Regardless, since these are the first measurements of $^1\text{O}_2^*$ and $^3\text{C}^*$ in particles, strengthening and improving our findings requires more measurements, especially for other seasons and locations. Measurements under much higher particle mass/water mass ratios, ideally under ambient conditions, are also needed.

Despite the uncertainties, our results indicate that BrC-derived photooxidants such as singlet molecular oxygen and organic triplet excited states can be important oxidants in atmospheric particles. Currently these oxidants are not included in atmospheric models, although our calculations suggest that $^1\text{O}_2^*$ and $^3\text{C}^*$ can dominate the processing of highly soluble organic molecules in aerosol particles.

**Competing Interests**

The authors declare that they have no conflict of interest.

**Author Contribution**

CA and RK developed the research goals and designed the experiments. KB lent and set up the sampler, while RK, CA, and WJ collected samples. RK, JL, and SH performed the photochemistry experiments while WJ analyzed ions and OC. RK analyzed the data and prepared the manuscript with contributions from all co-authors. CA reviewed, wrote portions of, and
edited the manuscript. CA and QZ provided supervision and oversight during the experiments and writing.

**Data Availability**

Light absorption data have been submitted to the data repository Pangaea, cited in the text and are available at [https://doi.pangaea.de/10.1594/PANGAEA.896418](https://doi.pangaea.de/10.1594/PANGAEA.896418). Other data are available upon request.

**Acknowledgments**

We thank Ann Dilnner, Alexandra Boris, and April Chaney (UC Davis, Air Quality Research Center) for use of a microbalance and an anonymous reviewer for extensive and helpful comments. Funding was provided by the National Science Foundation (AGS-1649212), California Agricultural Experiment Station (Project CA-D-LAW-6403-RR), a UC Guru Gobind Singh Fellowship, a Donald G. Crosby Graduate Fellowship, and a James and Rita Seiber International Student Support Award.
Figure 1. (a) Light absorption coefficients, $\alpha_{\lambda}$, in particulate matter extracts (PME) (Eq. (1)) and field blanks (FB). The legend shows the sample identities, arranged from the highest absorbing (top) to lowest absorbing (bottom) at 300 nm. Solid and dotted lines represent standard and dilute extracts, respectively (with the latter indicated with an asterisk; Sect. 2.2). (b) Mass absorption coefficients of DOC in the particle extracts (Eq. (3)).
Figure 2. Measured steady-state concentrations of (a) hydroxyl radical, (b) singlet molecular oxygen and, (c) oxidizing triplet excited states of organic matter in particle extracts, along with previous measurements made in Davis fogs collected between 1997-98 and 2011-12 (Anastasio and McGregor, 2001; Kaur and Anastasio, 2017; Kaur and Anastasio, 2018b). All concentrations are normalized to Davis midday, winter solstice sunlight. Dilute particle extracts are indicated with an asterisk. Dashed lines represent sample averages.
Figure 3. Correlations between (a) the rate of singlet oxygen photoproduction normalized to Davis winter solstice sunlight ($P_{1O2^*}$), (b) the rate of triplet photoproduction normalized to Davis winter solstice sunlight ($P_{3C^*}$) and the rate of light absorption ($R_{abs}$) between 300 to 450 nm. Triplet rates for the fog samples were adjusted to account for the small DOC sink for triplets; Eq. (8). The $P/R_{abs}$ ratios (± 1 SE) listed are unitless and represent the quantum yields.
Figure 4. Effect of change in aqueous particle mass concentration (i.e., sample dilution) for sample PME3 on (a) rate of light absorption and the steady-state concentrations of (b) hydroxyl radical, (c) singlet molecular oxygen and, (d) oxidizing triplet excited states of organic matter. The last panel shows both linear (dotted) and hyperbolic (dashed) fits to the data. In each plot the x-axis is a measure of sample dilution, with higher concentration factors corresponding to more concentrated particle extracts (Eq. (10)).
Figure 5. Dependence of photooxidant concentrations on particle mass/water mass ratio (i.e., aqueous particle concentration) in extracts of sample PME3. Solid diamonds are measured values under experimental dilution conditions (typical for clouds or fogs), while the open circles are values expected in more concentrated particle liquid water based on the dashed line extrapolations. For the solid symbols, error bars (± 1σ) are often smaller than the symbols. Data labels on the diamonds (e.g., D10) represent the water volume used to extract the PME3 filter square (Sect. 2.5.4). The dashed line extrapolations include the contributions from both aqueous processes and interactions with the gas phase (Sect. S4). For oxidizing triplets, two extrapolation scenarios are shown: a best estimate (lower line) and a high estimate (upper line), as described in Sect. S4 and Table S15.
Figure 6. Fate of five model organic compounds – (1) syringol, (2) methyl jasmonate, (3) tyrosine, (4) 1,2,4-butanetriol and (5) 3-hydroxy-2,5-bis(hydroxymethyl)furan – under liquid water content conditions for fog (left of vertical dashed line; 1 g-H₂O/m³-air) and PM (right of line; 20 μg-H₂O/m³-air). Estimated Henry’s law constants for the compounds (in units of M atm⁻¹) are in parentheses beneath each structure. In panel (a) the columns represent overall lifetimes of the organics and the open circles represent the fractions in the aqueous phase. Panel
(b) shows the fraction of each compound lost via various gas and aqueous pathways. The triplet contribution in PM is estimated using the lower-bound triplet concentration extrapolation i.e., $1.3 \times 10^{-13}$ M (Fig. 5). Oxidant concentrations and rate constants are in Tables S16 and S17.
References


Supporting Information for:

**Photooxidants from Brown Carbon and Other Chromophores in Illuminated Particle Extracts**

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Originally Submitted to Atmospheric Chemistry and Physics, 2 December 2018

Revised and Submitted on 23 April 2019
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Figure S6. (Top) Correlation between the rate of \( \cdot \text{OH} \) photoproduction due to sources other than nitrite and nitrate and the concentration of dissolved organic carbon (DOC). (Bottom) Correlation between apparent pseudo-first order rate constant for loss of \( \cdot \text{OH} \) due to organic sinks (obtained by subtracting inorganic contributions from the measured \( k'_\text{OH} \)) and DOC.

Figure S7. Comparison of hydroxyl radical steady-state concentrations formed \textit{in situ} in various atmospheric waters.

Figure S8. Loss of probes for measuring triplet excited states: syringol (SYR) and methyl jasmonate (MeJA) in extract PME5.

Figure S9. Winter-solstice-normalized pseudo-first-order rate constants \( k'_\text{probe} \) for loss of syringol (top panel) and methyl jasmonate.

Figure S10. Dependence of rate of \( \cdot \text{OH} \) photoproduction \( (P_\text{OH}; \text{red circles, left y-axis}) \) and rate constant for loss of \( \cdot \text{OH} \) due to natural sinks \( (k'_\text{OH}; \text{blue squares, right y-axis}) \) with PM mass/water mass ratio in three PME3D samples.

Figure S11. Fate of five model organic compounds – syringol, methyl jasmonate, tyrosine, 1,2,4-butanetriol and 3-hydroxy-2,5-bis(hydroxymethyl)furan – under fog (left of vertical dashed line) and PM (right of dashed line) conditions using an upper-bound estimate for triplet concentrations in PM.

Table S18. Determination of hydroxyl radical steady-state concentrations, \( [\cdot \text{OH}] \), from results of the MBO experiments.

Figure S12. Measured pseudo-first-order rate constant for loss of \( \cdot \text{OH} \) due to natural sinks \( (k'_\text{OH}) \) in various solutions using sodium benzoate/benzoic acid and benzene as \( \cdot \text{OH} \) probes.

Table S 19. Estimates of the organic sink of \( ^{1}O_{2}^* \) in aqueous particles at 1 μg-PM/μg-H₂O.

Figure S13. Change in triplet steady-state concentration with dissolved organic carbon concentration in the PME3D extracts.
### Table S1. Sample collection details and light absorption of particle extracts

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Collection Dates</th>
<th>Collection Times</th>
<th>Concentration of PM&lt;sub&gt;2.5&lt;/sub&gt; (μg/m&lt;sup&gt;3&lt;/sup&gt;)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Average Mass of PM extracted&lt;sup&gt;b&lt;/sup&gt;</th>
<th>&lt;span class=&quot;mathjax&quot; class=&quot;highlight&quot;&gt;R&lt;sub&gt;abs&lt;/sub&gt; (300-450 nm)&lt;/span&gt;&lt;sup&gt;h&lt;/sup&gt; (10&lt;sup&gt;-4&lt;/sup&gt; mol·photons L&lt;sup&gt;-1&lt;/sup&gt; s&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>&lt;span class=&quot;mathjax&quot; class=&quot;highlight&quot;&gt;f&lt;sub&gt;Rabs&lt;/sub&gt; IN&lt;/span&gt;&lt;sup&gt;i&lt;/sup&gt;</th>
<th>MAC&lt;sub&gt;DOC&lt;/sub&gt; (300 nm)&lt;sup&gt;j&lt;/sup&gt; (10&lt;sup&gt;5&lt;/sup&gt; cm&lt;sup&gt;2&lt;/sup&gt; g&lt;sup&gt;-1&lt;/sup&gt;·C&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>AAE&lt;sup&gt;k&lt;/sup&gt;</th>
<th>Light Screening Factor&lt;sup&gt;l&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>PME1&lt;sup&gt;a&lt;/sup&gt;</td>
<td>01/06/16 - 01/08/16</td>
<td>17:30 - 07:30</td>
<td>5.8 (2.1)</td>
<td>0.077</td>
<td>105 (16)</td>
<td>1.7</td>
<td>0.00080</td>
<td>2.6</td>
<td>6.8</td>
</tr>
<tr>
<td>PME2&lt;sup&gt;a&lt;/sup&gt;</td>
<td>12/18/15 - 12/20/15</td>
<td>17:30 - 07:30</td>
<td>15 (10)</td>
<td>0.100</td>
<td>269 (30)</td>
<td>1.8</td>
<td>0.0059</td>
<td>2.0</td>
<td>7.2</td>
</tr>
<tr>
<td>PME3&lt;sup&gt;b&lt;/sup&gt;</td>
<td>01/26/16 - 01/29/16</td>
<td>10:20 - 09:45</td>
<td>16 (11)</td>
<td>0.272</td>
<td>328 (19)</td>
<td>4.2</td>
<td>0.0076</td>
<td>1.3</td>
<td>7.9</td>
</tr>
<tr>
<td>PME4&lt;sup&gt;b&lt;/sup&gt;</td>
<td>12/16/15 - 12/18/15</td>
<td>17:30 - 07:30</td>
<td>20 (8)</td>
<td>0.567</td>
<td>350 (14)</td>
<td>12</td>
<td>0.0031</td>
<td>2.6</td>
<td>6.4</td>
</tr>
<tr>
<td>PME5&lt;sup&gt;b&lt;/sup&gt;</td>
<td>01/10/16 - 01/12/16</td>
<td>17:30 - 07:30</td>
<td>5.9 (3.4)</td>
<td>0.317</td>
<td>132 (11)</td>
<td>7.4</td>
<td>0.00080</td>
<td>2.6</td>
<td>6.2</td>
</tr>
<tr>
<td>PME6&lt;sup&gt;b&lt;/sup&gt;</td>
<td>01/23/16 - 01/26/16</td>
<td>17:30 - 07:30</td>
<td>6.8 (2.9)</td>
<td>0.584</td>
<td>174 (14)</td>
<td>13</td>
<td>0.00058</td>
<td>3.0</td>
<td>6.9</td>
</tr>
</tbody>
</table>

### Particle Extracts Averages (±σ)

| PME3D0.5<sup>c</sup> | | | | | | | | |
|-----------------------|-----------------|-----------------|-----------------------------|------------------------|-----------------------------|-----------------|-----------------------------|-----------------|------------------|
| PME3D1.3<sup>c</sup> | 0.199 | 315 (23) | 3.2 | 0.0071 | 1.3 | 7.6 | 0.95 |
| PME3D2.5<sup>a</sup> | 0.103 | 311 (15) | 1.7 | 0.0092 | 1.3 | 7.6 | 0.97 |
| PME3D10<sup>a</sup> | 0.0263 | 347 | 0.42 | 0.0062 | 1.3 | 7.6 | 0.99 |

### Field Blanks

| FB1<sup>a</sup> | 12/18/15 | 09:38 - 09:40 | 0.0025 | 17.8 (7.6) | 0.024 |
| FB2<sup>b</sup> | 01/20/16 | 10:08 - 10:10 | 0.0037 | 24.9 (9.1) | 0.022 |

---

<sup>a</sup> Samples extracted in 2.5 mL/filter square and referred to as the “dilute” extracts in the main text.

<sup>b</sup> PME3-6 were extracted as 1 mL/filter square and are referred to as “standard” extracts in the main text.

<sup>c</sup> PME3D0.5, PME3D1.3 and PME3D10 are extracts of sample PME3 using varying extraction volumes per filter square, namely 0.5, 1.3 and 10 mL, respectively.

<sup>d</sup> N = Night-time samples, collected from 17:30 on one day until 07:30 AM the next day; this was done for consecutive days on the same filter.

<sup>e</sup> Continuous collection for the indicated number of days.

<sup>g</sup> Average (±1σ) hourly PM<sub>2.5</sub> concentration for each sampling period measured at the UC Davis sampling site by the California Air Resources Board as reported on the iADAM online database (California Air Resources Board, 2018).

<sup>h</sup> Mass absorption coefficient of dissolved organic species at 300 nm for each sample (Eq. (3), main text) in units of 10<sup>4</sup> cm<sup>-2</sup> g<sup>-1</sup>·C<sup>-1</sup>.

<sup>i</sup> Mass absorption coefficient of dissolved organic species at 300 nm for each sample (Eq. (3), main text) in units of 10<sup>4</sup> cm<sup>-2</sup> g<sup>-1</sup>·C<sup>-1</sup>.

<sup>j</sup> Fraction of calculated sunlight absorption due to inorganic nitrogen (nitrite and nitrate) in each sample. Equations are in Kaur and Anastasio (2017).

---

**Notes:**

- **Field Blanks:**
  - FB1: 09:38 - 09:40 (0.0025, 17.8 (7.6), 0.024)
  - FB2: 10:08 - 10:10 (0.0037, 24.9 (9.1), 0.022)

---

**Equations:**

- Equation (1): [Formula]
- Equation (2): [Formula]
- Equation (3): [Formula]
Absorption Angstrom Exponent (AAE), calculated as the negative of the slope of a linear regression of the extract absorbance data between 300 and 450 nm versus the log of the wavelength: \[ \log(\text{Abs}_\lambda) = \log(\text{Abs}_{300}) - \text{AAE} \times \log(\lambda), \] where \( \lambda \) is the wavelength and \( \text{Abs}_\lambda \) and \( \text{Abs}_{300} \) are the absorbance values at \( \lambda \) and 300 nm, respectively.

\[ S_\lambda = \frac{\sum[(1 - 10^{-\alpha_\lambda}) \times I'_\lambda]}{\sum[2.303 \times \alpha_\lambda]}. \] In this equation, \( \alpha_\lambda \) is the pathlength-normalized absorbance of the extract at each wavelength, summed for the wavelength range in which light absorption by the extracts was the highest (280-350 nm); \( l \) is the pathlength of the quartz tube used for illuminating the extracts (0.4 cm); \( I'_\lambda \) is the actinic flux (mol-photons L\(^{-1}\) s\(^{-1}\)) of the illumination system, calculated using the photon count of the illumination system measured using a TIDAS Photo Diode Array Spectrometer and the measured pseudo-first-order rate constant for loss of our chemical actinometer, 2-nitrobenzaldehyde. The numerator represents the actual rate of light absorption by all chromophores in the extract while the denominator is the estimated rate of light absorption in the extract assuming it is low light-absorbing. A value of 1.0 indicates no light screening (Smith et al., 2014; Rehorek and Seidel, 1989).

Average values previously measured in Davis fog samples (n = 4) (Kaur and Anastasio, 2017).

Test statistic for comparison of standard PME and Davis fog averages: \( p \)-value for a two-tailed \( t \)-test for samples of unequal variance. Values below 0.05 are in bold.
Table S2. Chemical characteristics of particle extracts

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<tr>
<th>Sample ID</th>
<th>DOC</th>
<th>[NO$_2^-$]</th>
<th>[NO$_3^-$]</th>
<th>[SO$_4^{2-}$]</th>
<th>[Cl$^-$]</th>
<th>[HCOO$^-$]</th>
<th>[NH$_4^+$]</th>
<th>[Na$^+$]</th>
<th>[K$^+$]</th>
<th>[Ca$^{2+}$]</th>
<th>[Mg$^{2+}$]</th>
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<td>177</td>
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</table>

Averages (±σ)

| “Standard” (PME3-6) | 3440 (760) | 6.9 (2.9) | 1650 (1480) | 120 (124) | 62.6 (17.9) | 12.5 (6.8) | 1290 (1190) | 327 (33) | 136 (58) | 22.2 (15.5) | 6.1 (4.1) |
| “Dilute” (PME1*-2*,3D2.5*) | 953 (419) | 2.4 (1.9) | 749 (580) | 80 (101) | 20.9 (5.9) | 3.8 (1.5) | 541 (420) | 93.2 (21.9) | 38.5 (7.4) | 5.2 (2.9) | 1.2 (1.1) |
| Davis Fog | 1240 (560) | 3.4 (6.1) | 1080 (630) | 120 (84) | 22.9 (13.0) | 5.1 (2.6) | 1070 (550) | - | 3.5 (1.9) | 4.2 (1.1) | 1.4 (0.4) |
| Test statistic e | **0.0042** | 0.35 | 0.51 | 0.98 | **0.013** | 0.11 | 0.75 | - | **0.019** | 0.10 | 0.11 |

Field Blanks

| FB1*     | 78.9 | 0   | 4.5   | 0.8   | 9.0   | 1.1   | 3.1   | 63.8 | 8.3   | 1.4 | 0.0 |
| FB2*     | 244  | 0   | 1.1   | 0.4   | 6.1   | 9.0   | 12.3 | 143.5 | 10.9 | 3.4 | 0.0 |
| MQ       | < DL | < DL | < DL | < DL | < DL | < DL | 1.8  | < DL | < DL | < DL |

a Samples extracted in 2.5 mL/filter square and referred to as the “dilute” extracts in the main text.

b Samples extracted in 1mL/filter square and are referred to as “standard” extracts in the main text.

c DOC and IC values for sample PME3D0.5 were not measured due to a shortage of sample; instead, they were estimated by extrapolating the linear trends between these values and concentration factors for the other PME3 samples, namely, PME3, PME3D1.3, PME3D2.5 and PME3D10.

d Sodium could not be measured in the 2011 Davis fog samples due to high background sodium content.

e Test statistic for comparison of standard PME and Davis fog averages: *p*-value for a two-tailed *t*-test for samples of unequal variance. Values below 0.05 are in bold.
### Table S3. Hydroxyl radical measurements

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$P_{OH}$ $a$ $10^{-10}$ M s$^{-1}$</th>
<th>$P_{OH}$ $a$ μM h$^{-1}$</th>
<th>$k_{OH}^b$ $10^6$ s$^{-1}$</th>
<th>$\tau_{OH}^c$ μs</th>
<th>$[\cdot OH]^d$ $10^{-16}$ M</th>
<th>$10^4 \times \Phi_{OH}^f$</th>
<th>$k_{OH,org} / [DOC]^g$ $10^8$ L (mol-C)$^{-1}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle Extracts</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PME1*</td>
<td>1.0 (0.1)</td>
<td>0.37 (0.04)</td>
<td>0.63 (0.01)</td>
<td>1.6 (0.1)</td>
<td>1.7 (0.2)</td>
<td>0.62 (0.06)</td>
<td>11.1 (0.2)</td>
</tr>
<tr>
<td>PME2*</td>
<td>2.0 (0.2)</td>
<td>0.71 (0.07)</td>
<td>0.44 (0.04)</td>
<td>2.3 (0.2)</td>
<td>4.5 (0.6)</td>
<td>1.1 (0.1)</td>
<td>4.6 (0.4)</td>
</tr>
<tr>
<td>PME3</td>
<td>14.7 (0.3)</td>
<td>5.7 (0.1)</td>
<td>1.9 (0.4)</td>
<td>0.54 (0.13)</td>
<td>7.9 (1.9)</td>
<td>3.5 (0.1)</td>
<td>4.9 (1.2)</td>
</tr>
<tr>
<td>PME4</td>
<td>14 (2)</td>
<td>5.2 (0.6)</td>
<td>2.3 (0.2)</td>
<td>0.43 (0.03)</td>
<td>6.3 (0.6)</td>
<td>1.2 (0.1)</td>
<td>5.4 (0.4)</td>
</tr>
<tr>
<td>PME5</td>
<td>4.6 (0.5)</td>
<td>1.7 (0.2)</td>
<td>1.6 (0.1)</td>
<td>0.62 (0.03)</td>
<td>2.8 (0.3)</td>
<td>0.63 (0.07)</td>
<td>6.8 (0.4)</td>
</tr>
<tr>
<td>PME6</td>
<td>13 (3)</td>
<td>4.8 (1.0)</td>
<td>4.0 (0.8)</td>
<td>0.25 (0.05)</td>
<td>3.3 (0.3)</td>
<td>1.1 (0.2)</td>
<td>11 (2)</td>
</tr>
<tr>
<td>PME3D0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7.3 (1.8) $^c$</td>
<td></td>
</tr>
<tr>
<td>PME3D1.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.0 (0.8) $^c$</td>
<td></td>
</tr>
<tr>
<td>PME3D2.5*</td>
<td>3.1 (0.1)</td>
<td>1.1 (0.2)</td>
<td>0.94 (0.29)</td>
<td>1.1 (0.3)</td>
<td>3.3 (1.0)</td>
<td>1.86 (0.03)</td>
<td>6.4 (2.0)</td>
</tr>
<tr>
<td>PME3D10</td>
<td>0.47 (0.04)</td>
<td>0.17 (0.01)</td>
<td>0.071 (0.03)</td>
<td>14 (6)</td>
<td>6.6 (2.8)</td>
<td>1.1 (0.1)</td>
<td>1.7 (0.7)</td>
</tr>
<tr>
<td>“Standard” (PME3-6)</td>
<td>12 (5)</td>
<td>4.2 (1.7)</td>
<td>2.5 (1.1)</td>
<td>0.46 (0.16)</td>
<td>5.1 (2.4)</td>
<td>1.6 (1.3)</td>
<td>6.9 (2.6)</td>
</tr>
<tr>
<td>“Dilute” (PME1*-2*.3D2.5*)</td>
<td>2.0 (1.0)</td>
<td>0.73 (0.37)</td>
<td>0.67 (0.63)</td>
<td>1.6 (0.6)</td>
<td>3.2 (1.4)</td>
<td>1.2 (0.6)</td>
<td>7.4 (3.4)</td>
</tr>
<tr>
<td>Davis Fog</td>
<td>3.5 (1.0)</td>
<td>1.3 (0.3)</td>
<td>0.87 (0.31)</td>
<td>1.2 (0.4)</td>
<td>4.2 (0.7)</td>
<td>2.4 (1.7)</td>
<td>7.5 (3.2)</td>
</tr>
<tr>
<td>Test statistic $^b$</td>
<td><strong>0.039</strong></td>
<td><strong>0.039</strong></td>
<td><strong>0.058</strong></td>
<td><strong>0.019</strong></td>
<td><strong>0.51</strong></td>
<td>0.47</td>
<td><strong>0.79</strong></td>
</tr>
<tr>
<td>Field Blanks $^i$</td>
<td>≤ 0.012</td>
<td>≤ 0.045</td>
<td>0.34 (0.04)</td>
<td>3.0 (0.4)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FB1 (dilute)</td>
<td>≤ 0.012</td>
<td>≤ 0.045</td>
<td>0.34 (0.04)</td>
<td>3.0 (0.4)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FB2 (standard)</td>
<td>≤ 0.012</td>
<td>≤ 0.042</td>
<td>0.27 (0.01)</td>
<td>3.8 (0.2)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Listed uncertainties (in parentheses) are ± 1 standard error from the errors in inverse plot ($1/R_p^2$ vs. $1/[\text{Benzene}]$) parameters, except for the averages (± 1σ).

All equations used for these calculations are discussed in Kaur and Anastasio (2017) unless otherwise stated.

* Samples extracted in 2.5 mL/filter square and referred to as the “dilute” extracts in the main text.

* Davis winter solstice-normalized rate of OH photoproduction.

* Apparent pseudo-first rate constant for destruction of OH due to natural sinks.

* Lifetime of OH, calculated as $1/k_{OH}$. 

* Winter solstice-normalized steady-state concentration of OH.

* OH concentrations in PME3 and PME3D extracts were measured using MBO as a probe, corrected for loss due to quenching by MBO (discussed in Sect. S1). $k_{OH}$ for these samples was calculated as $P_{OH} / [\cdot OH]$. 

* Apparent quantum yield of OH during simulated sunlight illumination, calculated as $\Phi_{OH} = P_{OH} / R_{abs}$. 

* Ratio of $k'_{OH,org}$ (rate constant for loss of OH due to organics only; Table S6) to the DOC concentration.
Test statistic for comparison of standard PME and Davis fog averages: $p$-value for a two-tailed $t$-test for samples of unequal variance. Values below 0.05 are in bold.

Blanks were analyzed by adding 1.5 mM benzene to an aliquot of the blank. Very little phenol formation was observed after 200 minutes of illumination in both blanks, which was used to calculate the upper limit $P_{OIL}$.
Table S4. Contributions of nitrite, nitrate and other sources to \( ^\cdot \text{OH} \) photoproduction

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>( f_{\text{POH,NO}_2}^a )</th>
<th>( f_{\text{POH,NO}_3}^b )</th>
<th>( f_{\text{POH,Other}}^c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle Extracts</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PME1*</td>
<td>0.072 (0.010)</td>
<td>0.15 (0.02)</td>
<td>0.78 (0.02)</td>
</tr>
<tr>
<td>PME2*</td>
<td>0.36 (0.05)</td>
<td>0.63 (0.09)</td>
<td>0.011 (0.010)</td>
</tr>
<tr>
<td>PME3</td>
<td>0.18 (0.02)</td>
<td>0.24 (0.02)</td>
<td>0.58 (0.03)</td>
</tr>
<tr>
<td>PME4</td>
<td>0.15 (0.02)</td>
<td>0.32 (0.05)</td>
<td>0.53 (0.05)</td>
</tr>
<tr>
<td>PME5</td>
<td>0.21 (0.03)</td>
<td>0.11 (0.02)</td>
<td>0.67 (0.04)</td>
</tr>
<tr>
<td>PME6</td>
<td>0.11 (0.03)</td>
<td>0.046 (0.011)</td>
<td>0.85 (0.03)</td>
</tr>
<tr>
<td>PME3D0.5</td>
<td>0.35 (0.04)</td>
<td>0.57 (0.06)</td>
<td>0.084 (0.068)</td>
</tr>
<tr>
<td>PME3D1.3</td>
<td>0.35 (0.04)</td>
<td>0.57 (0.06)</td>
<td>0.084 (0.068)</td>
</tr>
<tr>
<td>PME3D2.5*</td>
<td>0.35 (0.04)</td>
<td>0.57 (0.06)</td>
<td>0.084 (0.068)</td>
</tr>
<tr>
<td>PME3D10</td>
<td>0.67 (0.08)</td>
<td>0.55 (0.07)</td>
<td>-0.22 (0.11)</td>
</tr>
<tr>
<td>Averages (±σ)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>“Standard” (PME3-6)</td>
<td>0.16 (0.05)</td>
<td>0.18 (0.12)</td>
<td>0.66 (0.14)</td>
</tr>
<tr>
<td>“Dilute” (PME1*-, PME3D2.5*)</td>
<td>0.26 (0.16)</td>
<td>0.45 (0.26)</td>
<td>0.29 (0.42)</td>
</tr>
<tr>
<td>Davis Fog</td>
<td>0.24 (0.40)</td>
<td>0.46 (0.29)</td>
<td>0.41 (0.41)</td>
</tr>
</tbody>
</table>

* Listed uncertainties (in parentheses) are ± 1 standard error calculated from propagating errors in individual terms, except for the averages (± 1σ).

\( f_{\text{POH,NO}_2}^a \) Fraction of \( ^\cdot \text{OH} \) photoproduction rate attributable to nitrite. Calculated as \((j_{\text{NO}_2 \rightarrow \text{OH}} \times [\text{NO}_2^-]) / P_{\text{OH}}\) where the numerator is the rate of \( ^\cdot \text{OH} \) photoproduction due to nitrite \( (P_{\text{OH,NO}_2}) \), and is the product of the aqueous photolysis rate constant under Davis winter-solstice sunlight, \( j_{\text{NO}_2 \rightarrow \text{OH}} = 2.6 \times 10^{-5} \text{ s}^-1 \) (Anastasio and McGregor, 2001), and the molar concentration of \( \text{NO}_2^- \) in each sample.

\( f_{\text{POH,NO}_3}^b \) Fraction \( ^\cdot \text{OH} \) photoproduction rate attributable to nitrate. Calculated using an equation analogous to \( f_{\text{POH,NO}_2}^a \), using aqueous nitrate photolysis rate constant, \( j_{\text{NO}_3^- \rightarrow \text{OH}} = 1.4 \times 10^{-7} \text{ s}^-1 \) (Anastasio and McGregor, 2001) and molar concentration of \( \text{NO}_3^- \) in each sample.

\( f_{\text{POH,Other}}^c \) Fraction of \( ^\cdot \text{OH} \) photoproduction due to non-nitrite and –nitrate sources; calculated as \((P_{\text{OH}} - P_{\text{OH,NO}_2} - P_{\text{OH,NO}_3}) / P_{\text{OH}}\).

\( f_{\text{POH,Other}}^d \) is negative for PME3D10 indicating that the total rate of \( ^\cdot \text{OH} \) photoproduction is over-predicted using the measured molar \( \text{NO}_2^- \) and \( \text{NO}_3^- \) concentrations.
Table S5. Determination of chloride as an ’OH sink, following procedure of Anastasio and Newberg (2007)

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Measured $k'_{\text{OH}}$ s$^{-1}$</th>
<th>[Cl$^{-}$] M</th>
<th>[H$^+$] M</th>
<th>$f_{\text{Cl}^{-}\text{re-formed}}$</th>
<th>$k'_{\text{OH,Cl}^{-}}$ s$^{-1}$</th>
<th>$f_{\text{OH,Cl}^{-}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PME1*</td>
<td>6.3E+05</td>
<td>1.6E-05</td>
<td>6.31E-05</td>
<td>0.9997828</td>
<td>1.5E+01</td>
<td>2.3E-05</td>
</tr>
<tr>
<td>PME2*</td>
<td>4.4E+05</td>
<td>2.0E-05</td>
<td>6.31E-05</td>
<td>0.99978</td>
<td>1.8E+01</td>
<td>4.2E-05</td>
</tr>
<tr>
<td>PME3</td>
<td>1.9E+06</td>
<td>6.6E-05</td>
<td>6.31E-05</td>
<td>0.99978</td>
<td>6.2E+01</td>
<td>3.3E-05</td>
</tr>
<tr>
<td>PME4</td>
<td>2.3E+06</td>
<td>7.0E-05</td>
<td>6.31E-05</td>
<td>0.99978</td>
<td>6.5E+01</td>
<td>2.8E-05</td>
</tr>
<tr>
<td>PME5</td>
<td>1.6E+06</td>
<td>3.7E-05</td>
<td>6.31E-05</td>
<td>0.99978</td>
<td>3.4E+01</td>
<td>2.1E-05</td>
</tr>
<tr>
<td>PME6</td>
<td>4.0E+06</td>
<td>7.8E-05</td>
<td>6.31E-05</td>
<td>0.99978</td>
<td>7.3E+01</td>
<td>1.8E-05</td>
</tr>
<tr>
<td>PME3D2.5*</td>
<td>9.4E+05</td>
<td>2.7E-05</td>
<td>6.31E-05</td>
<td>0.99978</td>
<td>2.5E+01</td>
<td>2.7E-05</td>
</tr>
<tr>
<td>PME3D10*b</td>
<td>7.1E+04</td>
<td>6.9E-06</td>
<td>6.31E-05</td>
<td>0.999783</td>
<td>6.4E+00</td>
<td>9.0E-05</td>
</tr>
</tbody>
</table>

*a Samples PME1*, PME2*, PME3D2.5 were extracted in 2.5 mL Milli-Q per filter square, and are referred to as “dilute extracts” in the main text.
*b PME3D10 was extracted in 10 mL Milli-Q per filter square.
*c Measured pseudo-first order rate constant for loss of ’OH.
*d Measured chloride concentrations in the extracts.
*e Hydrogen ion concentration. Since the extracts were acidified to pH 4.2, this value is constant across all extracts.
*f Fraction of Cl$^{-}$ reacting with ’OH that ends up back as Cl$^{-}$ and ’OH. Values are calculated based on the reactions 1-4 below and the equation $f_{\text{Cl}^{-}\text{re-formed}} = \frac{k_4}{(k_2 \times [\text{Cl}^{-}]) + (k_3 \times [\text{H}^+]) + k_4}$
*g Rate constant for loss of ’OH due to Cl$^{-}$ based on the fraction of reformed Cl$^{-}$, calculated as $k'_{\text{OH,Cl}^{-}} = (1 - f_{\text{Cl}^{-}\text{re-formed}}) \times k_1$
*h Fraction of measured $k'_{\text{OH}}$ due to chloride.

(1) ’OH + Cl$^{-}$ → HOCl$^{-}$, $k_1 = 4.3E+09$ M$^{-1}$s$^{-1}$
(2) HOCl$^{-}$ + Cl$^{-}$ → ’Cl$^{-}$ + OH$^-$, $k_2 = 1.0E+04$ M$^{-1}$s$^{-1}$
(3) HOCl$^{-}$ + H$^+$ → Cl$^{-}$ + H$_2$O, $k_3 = 2.1E+10$ M$^{-1}$s$^{-1}$
(4) HOCl$^{-}$ → Cl$^{-}$ + ’OH, $k_4 = 6.4E+09$ M$^{-1}$s$^{-1}$
Table S6. Contributions of nitrite, chloride and organics to \( k'_{\text{OH}} \)

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Measured ( k'_{\text{OH}} ) ( \text{S}^{-1} )</th>
<th>( k'_{\text{OHNO}_2} ) ( \text{S}^{-1} )</th>
<th>( k'_{\text{OHCl}} ) ( \text{S}^{-1} )</th>
<th>( k'_{\text{OHorg}} ) ( \text{S}^{-1} )</th>
<th>( f_{\text{OHNO}_2} )</th>
<th>( f_{\text{OHorg}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PME1*</td>
<td>6.3E+05</td>
<td>2.9E+03</td>
<td>1.5E+01</td>
<td>6.2E+05</td>
<td>0.0046</td>
<td>1.0</td>
</tr>
<tr>
<td>PME2*</td>
<td>4.4E+05</td>
<td>2.7E+04</td>
<td>1.8E+01</td>
<td>4.1E+05</td>
<td>0.063</td>
<td>0.94</td>
</tr>
<tr>
<td>PME3</td>
<td>1.9E+06</td>
<td>1.0E+05</td>
<td>6.2E+01</td>
<td>1.8E+06</td>
<td>0.055</td>
<td>0.95</td>
</tr>
<tr>
<td>PME4</td>
<td>2.3E+06</td>
<td>8.3E+04</td>
<td>6.5E+01</td>
<td>2.2E+06</td>
<td>0.036</td>
<td>0.96</td>
</tr>
<tr>
<td>PME5</td>
<td>1.6E+06</td>
<td>3.8E+04</td>
<td>3.4E+01</td>
<td>1.6E+06</td>
<td>0.023</td>
<td>0.98</td>
</tr>
<tr>
<td>PME6</td>
<td>4.0E+06</td>
<td>5.4E+04</td>
<td>7.3E+01</td>
<td>4.0E+06</td>
<td>0.013</td>
<td>0.99</td>
</tr>
<tr>
<td>PME3D2.5*</td>
<td>9.4E+05</td>
<td>4.1E+04</td>
<td>2.5E+01</td>
<td>9.0E+05</td>
<td>0.044</td>
<td>0.96</td>
</tr>
<tr>
<td>PME3D10</td>
<td>7.1E+04</td>
<td>1.2E+04</td>
<td>6.4E+00</td>
<td>5.9E+04</td>
<td>0.16</td>
<td>0.83</td>
</tr>
</tbody>
</table>

* Samples PME1*, PME2*, and PME3D2.5* were extracted in 2.5 mL Milli-Q per filter square, and are referred to as “dilute extracts” in the main text.

b PME3D10 was extracted in 10 mL Milli-Q per filter square. All other extracts were extracted in 1.0 mL Milli-Q per filter square (standard extracts).

c Measured pseudo-first order rate constant for loss of \(^*\text{OH}\) (Table S3).

d Pseudo-first order rate constant for loss of \(^*\text{OH}\) due to nitrite. Value is calculated as \( k'_{\text{OHNO}_2} = (k_{\text{OH+NO}_2} \times [\text{NO}_2^-]) \) where \( k_{\text{OH+NO}_2} = 1.1 \times 10^{10} \text{M}^{-1} \text{s}^{-1} \) (Barker et al., 1970).

e Pseudo-first order rate constant for loss of \(^*\text{OH}\) due to chloride. Value is calculated using the reaction between \(^*\text{OH}\) and Cl\(^-\) corrected for the fraction of the initial product HOCl\(^-\) that fragments to reform \(^*\text{OH}\) and Cl\(^-\), as discussed in Table S5 and Anastasio and Newberg (2007).

f Calculated pseudo-first-order rate constant for loss of \(^*\text{OH}\) due to organics, determined by subtracting the contribution of nitrite from the measured \( k'_{\text{OH}} \). Contributions to \( k'_{\text{OH}} \) from common inorganic ions, including sulfate, nitrate, chloride, bicarbonate/carbonate (see footnote h below), and ammonium are negligible.

\( g \) Fraction of measured \( k'_{\text{OH}} \) due to nitrite.

\( h \) Fraction of measured \(^*\text{OH}\) sink due to organic species, estimated by subtracting the contributions due to nitrite from the measured value of \( k'_{\text{OH}} \).

\( i \) The upper bound of the fraction of the measured \( k'_{\text{OH}} \) due to bicarbonate (HCO\(_3^\)) and carbonate (CO\(_3^{2-}\)) was calculated to be \( 1.1 \times 10^{-6} \) based on using the sample pH of 4.2 and assuming equilibrium with 400 ppm of atmospheric CO\(_2\). This fraction was calculated based on the CO\(_2\) equilibria 1-3 below (Seinfeld and Pandis, 2012), \( k_{\text{OH+HCO}_3^-} = 1 \times 10^7 \text{M}^{-1} \text{s}^{-1} \), and \( k_{\text{OH+CO}_3^{2-}} = 4 \times 10^9 \text{M}^{-1} \text{s}^{-1} \) (Buxton et al., 1988b).

(1) \( \text{CO}_2 \leftrightarrow \text{CO}_2\text{H}_2\text{O (aq)}, K_{ht} = 3.4E-02 \text{ M atm}^{-1} \) (Physical Henry’s law constant)

(2) \( \text{CO}_2\text{H}_2\text{O (aq)} \leftrightarrow \text{H}^+ + \text{HCO}_3^-, K_{a1} = 4.3E-07 \text{ M (pKa1 = 6.3)} \)

(3) \( \text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{2-}, K_{a2} = 4.7E-11 \text{ M (pKa2 = 10.3)} \)

Thus, the contributions of HCO\(_3^\) and CO\(_3^{2-}\) to measured \( k'_{\text{OH}} \) in all PME samples should be negligible.
## Table S7. Singlet oxygen measurements

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>( P_{\text{1O}_2}^* ) ( \times 10^{-7} ) M s(^{-1} )</th>
<th>( P_{\text{1O}_2}^* ) ( \mu \text{M h}^{-1} )</th>
<th>( [\text{1O}_2^*] ) ( \times 10^{-12} ) M</th>
<th>( f_{\text{FFA,1O}_2} )</th>
<th>( 10^2 \times \Phi_{\text{1O}_2^*} )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Particle Extracts</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PME1*</td>
<td>0.36 (0.04)</td>
<td>131 (15)</td>
<td>0.16 (0.02)</td>
<td>0.51 (0.08)</td>
<td>2.2 (0.2)</td>
</tr>
<tr>
<td>PME2*</td>
<td>0.68 (0.06)</td>
<td>246 (20)</td>
<td>0.31 (0.03)</td>
<td>0.72 (0.07)</td>
<td>3.8 (0.3)</td>
</tr>
<tr>
<td>PME3</td>
<td>2.4 (0.2)</td>
<td>851 (81)</td>
<td>1.1 (0.1)</td>
<td>1.1 (0.1)</td>
<td>5.7 (0.5)</td>
</tr>
<tr>
<td>PME4</td>
<td>4.2 (0.4)</td>
<td>1515 (135)</td>
<td>1.9 (0.2)</td>
<td>1.0 (0.1)</td>
<td>3.4 (0.3)</td>
</tr>
<tr>
<td>PME5</td>
<td>2.8 (0.2)</td>
<td>1000 (59)</td>
<td>1.3 (0.1)</td>
<td>1.2 (0.1)</td>
<td>3.8 (0.2)</td>
</tr>
<tr>
<td>PME6</td>
<td>4.8 (0.3)</td>
<td>1719 (114)</td>
<td>2.2 (0.1)</td>
<td>1.1 (0.1)</td>
<td>3.8 (0.3)</td>
</tr>
<tr>
<td>PME3D0.5</td>
<td>3.9 (0.4)</td>
<td>1413 (138)</td>
<td>1.8 (0.2)</td>
<td>0.79 (0.10)</td>
<td>4.5 (0.4)</td>
</tr>
<tr>
<td>PME3D1.3</td>
<td>1.1 (0.1)</td>
<td>414 (40)</td>
<td>0.52 (0.05)</td>
<td>0.68 (0.07)</td>
<td>3.6 (0.3)</td>
</tr>
<tr>
<td>PME3D2.5*</td>
<td>0.55 (0.03)</td>
<td>198 (11)</td>
<td>0.25 (0.01)</td>
<td>0.61 (0.04)</td>
<td>3.3 (0.2)</td>
</tr>
<tr>
<td>PME3D10</td>
<td>0.14 (0.02)</td>
<td>50.8 (6.0)</td>
<td>0.064 (0.008)</td>
<td>0.59 (0.09)</td>
<td>3.3 (0.4)</td>
</tr>
<tr>
<td><strong>Average (±σ)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>“Standard” (PME3-6)</td>
<td>3.5 (1.1)</td>
<td>1271 (412)</td>
<td>1.6 (0.5)</td>
<td>1.1 (0.1)</td>
<td>4.2 (1.0)</td>
</tr>
<tr>
<td>“Dilute” (PME1*-2*,3D2.5*)</td>
<td>0.53 (0.16)</td>
<td>192 (58)</td>
<td>0.24 (0.07)</td>
<td>0.61 (0.11)</td>
<td>3.1 (0.8)</td>
</tr>
<tr>
<td>Davis Fog</td>
<td>0.51 (0.14)</td>
<td>183 (49)</td>
<td>0.23 (0.06)</td>
<td>1.4 (0.8)</td>
<td>3.8 (3.1)</td>
</tr>
<tr>
<td>Test statistic</td>
<td><strong>0.0064</strong></td>
<td><strong>0.0064</strong></td>
<td><strong>0.0064</strong></td>
<td></td>
<td>0.98</td>
</tr>
<tr>
<td>Field Blanks</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FB1 (dilute)</td>
<td>≤ 0.076</td>
<td>≤ 27</td>
<td>≤ 0.0034</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FB2 (standard)</td>
<td>≤ 0.069</td>
<td>≤ 25</td>
<td>≤ 0.0031</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Listed uncertainties are ± 1 standard error unless otherwise stated.

* Samples extracted in 2.5 mL/filter square and referred to as the “dilute” extracts in the main text.

\(^a\) Davis winter solstice-normalized rate of \( ^1\text{O}_2^* \) formation.

\(^b\) Davis winter solstice-normalized steady-state concentration of \( ^1\text{O}_2^* \).

\(^c\) Fraction of probe FFA lost due to \( ^1\text{O}_2^* \).

\(^d\) Apparent quantum yield of \( ^1\text{O}_2^* \), calculated as \( \Phi_{\text{1O}_2^*} = P_{\text{1O}_2^*} / R_{\text{abs}} \).

\(^e\) Blanks were analyzed by measuring FFA loss in undiluted blanks. This is an upper bound determined by ascribing all FFA loss to \( ^1\text{O}_2^* \).

\(^f\) Test statistic for comparison of standard PME and Davis fog averages: \( p \)-value for a two-tailed \( t \)-test for samples of unequal variance. Values below 0.05 are in bold.
<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$k'_{\text{SYR}}^{a}$</th>
<th>$\tau_{\text{SYR}}^{b}$</th>
<th>$k'_{\text{SYR,OH}}^{c}$</th>
<th>$k'_{\text{SYR,1O2}}^{d}$</th>
<th>$k'_{\text{SYR,3C}^*}^{e}$</th>
<th>$f_{\text{SYR,3C}^*}^{f}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PME1*</td>
<td>12 (1)</td>
<td>2.3 (0.3)</td>
<td>0.43 (0.04)</td>
<td>0.59 (0.07)</td>
<td>11 (1)</td>
<td>0.92 (0.15)</td>
</tr>
<tr>
<td>PME2*</td>
<td>14 (2)</td>
<td>2.0 (0.3)</td>
<td>1.2 (0.1)</td>
<td>1.1 (0.09)</td>
<td>11 (2)</td>
<td>0.83 (0.17)</td>
</tr>
<tr>
<td>PME3</td>
<td>33 (1)</td>
<td>0.85 (0.03)</td>
<td>2.1 (0.5)</td>
<td>3.9 (0.4)</td>
<td>27 (1)</td>
<td>0.82 (0.06)</td>
</tr>
<tr>
<td>PME4</td>
<td>69 (8)</td>
<td>0.40 (0.04)</td>
<td>1.6 (0.2)</td>
<td>6.9 (0.6)</td>
<td>61 (8)</td>
<td>0.88 (0.15)</td>
</tr>
<tr>
<td>PME5</td>
<td>35 (2)</td>
<td>0.80 (0.04)</td>
<td>0.74 (0.07)</td>
<td>4.5 (0.3)</td>
<td>29 (2)</td>
<td>0.85 (0.06)</td>
</tr>
<tr>
<td>Particle Extracts</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PME3D0.5</td>
<td>48 (3)</td>
<td>0.58 (0.04)</td>
<td>1.9 (0.5)</td>
<td>6.4 (0.6)</td>
<td>40 (3)</td>
<td>0.83 (0.08)</td>
</tr>
<tr>
<td>PME3D1.3</td>
<td>26 (2)</td>
<td>1.1 (0.1)</td>
<td>0.78 (0.21)</td>
<td>1.9 (0.2)</td>
<td>24 (2)</td>
<td>0.90 (0.11)</td>
</tr>
<tr>
<td>PME3D2.5*</td>
<td>15 (2)</td>
<td>1.9 (0.3)</td>
<td>0.86 (0.26)</td>
<td>0.90 (0.05)</td>
<td>13 (2)</td>
<td>0.88 (0.19)</td>
</tr>
<tr>
<td>PME3D10</td>
<td>3.6 (0.4)</td>
<td>7.7 (0.8)</td>
<td>1.7 (0.2)</td>
<td>0.23 (0.03)</td>
<td>1.6 (0.8)</td>
<td>0.46 (0.24)</td>
</tr>
<tr>
<td>Average (±σ)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>“Standard” (PME3-6)</td>
<td>43 (17)</td>
<td>0.70 (0.20)</td>
<td>1.3 (0.2)</td>
<td>5.8 (1.9)</td>
<td>36 (16)</td>
<td>0.83 (0.05)</td>
</tr>
<tr>
<td>“Dilute” (PME1*-2*,3D2.5*)</td>
<td>14 (1)</td>
<td>2.0 (0.2)</td>
<td>0.82 (0.37)</td>
<td>0.87 (0.26)</td>
<td>12 (1)</td>
<td>0.88 (0.04)</td>
</tr>
<tr>
<td>Test statistic $^g$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.040</td>
</tr>
<tr>
<td>Davis Fog</td>
<td>16 (11)</td>
<td>2.4 (1.4)</td>
<td>1.1 (0.2)</td>
<td>0.83 (0.22)</td>
<td>14 (11)</td>
<td>0.85 (0.06)</td>
</tr>
<tr>
<td>Field Blanks</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FB1 (dilute)</td>
<td>1.3 (0.2)</td>
<td>22 (3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FB2 (standard)</td>
<td>0.95 (0.07)</td>
<td>29 (2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Listed uncertainties are ±1 standard error unless otherwise stated.

Bimolecular rate constants are given in Table S10.

* Samples extracted in 2.5 mL/filter square and referred to as the “dilute” extracts in the main text.

$^{a}$ Davis winter-solstice-normalized value of the measured pseudo-first-order rate constant for loss of syringol (SYR).

$^{b}$ Lifetime of syringol, calculated as $1/k'_{\text{SYR}}$.

$^{c}$ Pseudo-first-order rate constant for loss of SYR due to hydroxyl radical, calculated as $k'_{\text{SYR,OH}} = k_{\text{SYR,OH}} \times [\cdot{\text{OH}}]$.

$^{d}$ Pseudo-first-order rate constant for loss of SYR due to singlet oxygen, calculated as $k'_{\text{SYR,1O2}} = k_{\text{SYR,1O2}} \times [^1\text{O}_2^*]$.

$^{e}$ Pseudo-first-order rate constant for loss of SYR due to triplet excited states, calculated as $k'_{\text{SYR,3C}^*} = k'_{\text{SYR}} - (k'_{\text{SYR,OH}} + k'_{\text{SYR,1O2}})$.

$^{f}$ Fraction of SYR loss due to triplets, calculated as $k'_{\text{SYR,3C}^*} / k'_{\text{SYR}}$.

$^{g}$ Test statistic for comparison of standard PME and Davis fog averages: p-value for a two-tailed t-test for samples of unequal variance. Values below 0.05 are in bold.
### Table S9. Methyl jasmonate loss kinetics

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$k_{\text{MeJA}}$ $^a$ $10^{-5}$ s$^{-1}$</th>
<th>$\tau_{\text{MeJA}}$ $^b$ h</th>
<th>$k_{\text{MeJA,OH}}$ $^c$ $10^{-5}$ s$^{-1}$</th>
<th>$k_{\text{MeJA,1O2}}$ $^d$ $10^{-5}$ s$^{-1}$</th>
<th>$k_{\text{MeJA,3C*}}$ $^e$ $10^{-5}$ s$^{-1}$</th>
<th>$f_{\text{MeJA,3C*}}$ $^f$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Particle Extracts</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PME1*</td>
<td>0.98 (0.13)</td>
<td>28 (4)</td>
<td>0.11 (0.01)</td>
<td>0.099 (0.010)</td>
<td>0.77 (0.13)</td>
<td>0.79 (0.17)</td>
</tr>
<tr>
<td>PME2*</td>
<td>1.1 (0.1)</td>
<td>26 (1)</td>
<td>0.30 (0.04)</td>
<td>0.19 (0.02)</td>
<td>0.59 (0.07)</td>
<td>0.55 (0.07)</td>
</tr>
<tr>
<td>PME3</td>
<td>2.4 (0.2)</td>
<td>12 (1)</td>
<td>0.53 (0.13)</td>
<td>0.64 (0.06)</td>
<td>1.2 (0.2)</td>
<td>0.51 (0.10)</td>
</tr>
<tr>
<td>PME4</td>
<td>3.5 (0.4)</td>
<td>7.9 (0.8)</td>
<td>0.42 (0.04)</td>
<td>1.1 (0.1)</td>
<td>2.0 (0.4)</td>
<td>0.56 (0.12)</td>
</tr>
<tr>
<td>PME5</td>
<td>1.7 (0.2)</td>
<td>16 (2)</td>
<td>0.19 (0.02)</td>
<td>0.76 (0.04)</td>
<td>0.79 (0.18)</td>
<td>0.45 (0.11)</td>
</tr>
<tr>
<td>PME6</td>
<td>2.7 (0.2)</td>
<td>10 (1)</td>
<td>0.22 (0.02)</td>
<td>1.3 (0.1)</td>
<td>1.2 (0.2)</td>
<td>0.44 (0.08)</td>
</tr>
<tr>
<td>PME3D0.5</td>
<td>4.7 (0.5)</td>
<td>5.9 (0.7)</td>
<td>0.49 (0.12)</td>
<td>1.1 (0.1)</td>
<td>3.1 (0.6)</td>
<td>0.67 (0.14)</td>
</tr>
<tr>
<td>PME3D1.3</td>
<td>2.6 (0.2)</td>
<td>11 (1)</td>
<td>0.20 (0.05)</td>
<td>0.31 (0.03)</td>
<td>2.1 (0.3)</td>
<td>0.80 (0.12)</td>
</tr>
<tr>
<td>PME3D2.5*</td>
<td>1.8 (0.2)</td>
<td>16 (2)</td>
<td>0.22 (0.07)</td>
<td>0.15 (0.01)</td>
<td>1.4 (0.2)</td>
<td>0.79 (0.15)</td>
</tr>
<tr>
<td>PME3D10</td>
<td>0.67 (0.09)</td>
<td>42 (5)</td>
<td>0.44 (0.19)</td>
<td>0.038 (0.005)</td>
<td>0.19 (0.21)</td>
<td>0.28 (0.31)</td>
</tr>
<tr>
<td><strong>Average (±σ)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>“Standard” (PME3-6)</td>
<td>2.6 (0.7)</td>
<td>11 (3)</td>
<td>0.34 (0.16)</td>
<td>0.96 (0.31)</td>
<td>1.3 (0.5)</td>
<td>0.49 (0.05)</td>
</tr>
<tr>
<td>“Dilute” (PME1*-2*,3D2.5*)</td>
<td>1.3 (0.4)</td>
<td>23 (7)</td>
<td>0.21 (0.10)</td>
<td>0.15 (0.04)</td>
<td>0.92 (0.42)</td>
<td>0.71 (0.14)</td>
</tr>
<tr>
<td>Davis Fog</td>
<td>0.90 (0.12)</td>
<td>31 (4)</td>
<td>0.28 (0.05)</td>
<td>0.14 (0.04)</td>
<td>0.48 (0.17)</td>
<td>0.53 (0.13)</td>
</tr>
<tr>
<td><strong>Test statistic</strong> $^g$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td><strong>0.018</strong></td>
</tr>
</tbody>
</table>

| Field Blanks | 0.17 (0.2) | 160 (18) |
| FB2 (standard) | 0.27 (0.08) | 104 (31) |

---

* Listed uncertainties are ±1 standard error unless otherwise stated.

† Bimolecular rate constants are given in Table S10.

* Samples extracted in 2.5 mL/filter square and referred to as the “dilute” extracts in the main text.

$^a$ Davis winter-solstice-normalized measured pseudo-first-order rate constant for loss of methyl jasmonate (MeJA).

$^b$ Lifetime of methyl jasmonate, calculated as $1/k_{\text{MeJA}}$.

$^c$ Pseudo-first-order rate constant for loss of MeJA due to hydroxyl radical, calculated as $k_{\text{MeJA,OH}} = k_{\text{MeJA,OH}} \times [\cdot \text{OH}]$.

$^d$ Pseudo-first-order rate constant for loss of MeJA due to singlet oxygen, calculated as $k_{\text{MeJA,1O2}} = k_{\text{MeJA,1O2}} \times [\cdot \text{O}_2^*]$.  

$^e$ Pseudo-first-order rate constant for loss of MeJA due to triplet excited states, calculated as $k_{\text{MeJA,3C*}} = k_{\text{MeJA}} - (k_{\text{MeJA,OH}} + k_{\text{MeJA,1O2}})$.  

$^f$ Fraction of MeJA loss due to triplets, calculated as $k_{\text{MeJA,3C*}} / k_{\text{MeJA}}$.

$^g$ Test statistic for comparison of standard PME and Davis fog averages: $p$-value for a two-tailed $t$-test for samples of unequal variance. Values below 0.05 are in bold.
Table S10. Second-order rate constants for reactions of syringol and methyl jasmonate with hydroxyl radical, singlet oxygen, and triplet excited states

<table>
<thead>
<tr>
<th>Oxidants</th>
<th>$k_{\text{SYR} + \text{Oxidant}}$ $10^9$ M$^{-1}$ s$^{-1}$</th>
<th>Reference</th>
<th>$k_{\text{MeJA} + \text{Oxidant}}$ $10^8$ M$^{-1}$ s$^{-1}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>'OH</td>
<td>26</td>
<td>O'Neill and Steenken (1977)</td>
<td>67 (± 3)</td>
<td>Richards-Henderson et al. (2014a)</td>
</tr>
<tr>
<td>$^1\text{O}_2^*$</td>
<td>0.0036</td>
<td>Tratnyek and Hoigne (1991a)</td>
<td>0.0060 (± 0.0007)</td>
<td>Richards-Henderson et al. (2014b)</td>
</tr>
</tbody>
</table>

Model Triplets ($^1\text{C}^*$)

| $^3\text{AN}^*$ | 1.9 (± 0.1) | Kaur and Anastasio (2018) | 0.19 (± 0.07) | Kaur and Anastasio (2018) | 100 (± 37) |
| $^3\text{MAP}^*$ | 3.8 (± 0.6) | Kaur and Anastasio (2018) | 1.2 (± 0.3) | Richards-Henderson et al. (2014b) | 32 (± 9) |
| $^3\text{DMB}^*$ | 3.5 (± 0.8) | Smith et al. (2015) | 4.1 (± 1.6) | Richards-Henderson et al. (2014b) | 8.5 (± 3.8) |
| $^3\text{BP}^*$ | 8.5 (± 1.6) | Kaur and Anastasio (2018) | 51 (± 9) | Kaur and Anastasio (2018) | 1.7 (± 0.4) |

Listed uncertainties are ±1 standard error.

$^a$ Ratio of the bimolecular rate constants for reaction of a given model triplet with syringol (SYR) and methyl jasmonate (MeJA).
### Table S11. Characteristics of model triplet species

<table>
<thead>
<tr>
<th>Model Triplet</th>
<th>$E_T$ (^a) (kJ mol(^{-1}))</th>
<th>$E^0(^{3}C^<em>/C^</em>\cdot)$ (^b) (V)</th>
<th>$k_{O_2+3C^*}$ (^c) (10(^9)) M(^{-1}) s(^{-1})</th>
<th>$f^d_\Delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^32AN^*$</td>
<td>249</td>
<td>1.10</td>
<td>2.5</td>
<td>0.81 (C(_6)H(_6))</td>
</tr>
<tr>
<td>$^33MAP^*$</td>
<td>303</td>
<td>1.64</td>
<td>3.3</td>
<td>0.33 (C(_6)H(_6))</td>
</tr>
<tr>
<td>$^3DMB^*$</td>
<td>298 (estimated)(^e)</td>
<td>-</td>
<td>-</td>
<td>&lt; 0.61 (MeOH) (estimated)(^f)</td>
</tr>
<tr>
<td>$^3BP^*$</td>
<td>288</td>
<td>1.67</td>
<td>2.6</td>
<td>0.35 (C(_6)H(_6))</td>
</tr>
</tbody>
</table>

All values from Canonica et al. (Canonica et al., 2000) and Wilkinson et al. (Wilkinson et al., 1993)

\(^a\) Triplet state energy ($T_1 \rightarrow S_0$).

\(^b\) One-electron reduction potential for the triplet/triplet radical anion pair.

\(^c\) Bimolecular rate constant for quenching of triplet by molecular O\(_2\). To calculate rates of triplet photoformation (described in the main text), an average value of $2.8 \pm 0.4 \times 10^9$ M\(^{-1}\) s\(^{-1}\) is used.

\(^d\) Yield of singlet oxygen from quenching of model triplet species by O\(_2\). The solvent used in the determination is indicated in parentheses. Including the upper-bound value of 0.61 for $^3DMB^*$ (discussed in footnote \(^e\)), the average value of $f_\Delta$ for the model triplets is $0.53 \pm 0.23$.

\(^e\) Since the $E_T$ and $f_\Delta$ values for $^3DMB^*$ are not available, values for benzaldehyde (Hunter, 1970; Wilkinson et al., 1993) are used as estimates. The $f_\Delta$ value is an upper-bound estimate.
### Table S12. Best triplet matches and best estimate triplet steady-state concentrations

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>( k'<em>{\text{SYR,3C}^*} / k'</em>{\text{MeJA,3C}^*} ) (^a)</th>
<th>Mole-fractions of Best Triplet Matches (^b)</th>
<th>Bimolecular rate constants (M(^{-1}) s(^{-1}))</th>
<th>Triplet Steady-State Concentration (10(^{-14}) M)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( 3^2\text{AN}^* )</td>
<td>( 3^3\text{MAP}^* )</td>
<td>( 3^4\text{DMB}^* )</td>
<td>( 3^5\text{BP}^* )</td>
</tr>
<tr>
<td>PME1*</td>
<td>15 (3)</td>
<td>0.55</td>
<td>0.45</td>
<td>3.7E+09</td>
</tr>
<tr>
<td>PME2*</td>
<td>20 (4)</td>
<td>0.76</td>
<td>0.24</td>
<td>3.7E+09</td>
</tr>
<tr>
<td>PME3</td>
<td>20 (4)</td>
<td>0.77</td>
<td>0.23</td>
<td>3.7E+09</td>
</tr>
<tr>
<td>PME4</td>
<td>30 (7)</td>
<td>0.98</td>
<td>0.02</td>
<td>3.8E+09</td>
</tr>
<tr>
<td>PME5</td>
<td>37 (8)</td>
<td>0.34</td>
<td>0.66</td>
<td>3.2E+09</td>
</tr>
<tr>
<td>PME6</td>
<td>24 (4)</td>
<td>0.86</td>
<td>0.14</td>
<td>3.8E+09</td>
</tr>
<tr>
<td>PME3D0.5</td>
<td>12 (2)</td>
<td>0.41</td>
<td>0.59</td>
<td>3.6E+09</td>
</tr>
<tr>
<td>PME3D1.3</td>
<td>12 (2)</td>
<td>0.38</td>
<td>0.62</td>
<td>3.6E+09</td>
</tr>
<tr>
<td>PME3D2.5*</td>
<td>10 (3)</td>
<td>0.22</td>
<td>0.78</td>
<td>3.6E+09</td>
</tr>
<tr>
<td>PME3D10</td>
<td>7.9 (7.6)</td>
<td>0.92</td>
<td>0.01</td>
<td>3.5E+09</td>
</tr>
</tbody>
</table>

Uncertainties in parentheses are ± 1 standard error.

Details of the technique are discussed in Kaur and Anastasio (2018).

* Samples extracted in 2.5 mL/filter square and referred to as the “dilute” extracts in the main text.

\( a \) Ratio of measured values of \( k'_{\text{Probe},3C^*} \) in a given particle extract.

\( b \) Mole fractions of model triplets whose \( k_{\text{Probe},3C^*} \) ratio lies closest to the \( k'_{\text{Probe},3C^*} \) ratio in each sample.

\( c \) Mole-fraction-weighted bimolecular rate constants for both probes.

\( d \) Triplet steady-state concentration calculated from syringol loss as \( k'_{\text{SYR,3C}^*} \times (\chi_{3C1^*} k_{\text{SYR,3C1}^*} + \chi_{3C2^*} k_{\text{SYR,3C2}^*}) \).

\( e \) Triplet steady-state concentration calculated from methyl jasmonate loss as \( k'_{\text{MeJA,3C}^*} \times (\chi_{3C1^*} k_{\text{MeJA,3C1}^*} + \chi_{3C2^*} k_{\text{MeJA,3C2}^*}) \).

\( f \) Best estimate steady-state concentration calculated as the average of the \( \Sigma[3^iC_i]\) \(^d\) and \( \Sigma[3^iC_i]\) \(^e\) values.

\( g \) Uncertainties in parentheses are ± 1 SE propagated from the errors of \( k'_{\text{SYR,3C}^*} \) and \( k'_{\text{MeJA,3C}^*} \) and the mole-fraction-weighted bimolecular rate constants. Values are shown in Tables S8 and S9.
**Table S13. Measurements of triplet excited states of organic matter**

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$\Sigma[^1C_\text{c}]^*$ Best Estimate $^a$</th>
<th>$P_{[^1C_\text{c}]}^b$</th>
<th>$P_{[^1C_\text{c}]}^b$</th>
<th>$10^2 \times \Phi_{[^1C_\text{c}]}^c$</th>
<th>$\Phi_{[^3C_\text{c}]}^d$</th>
<th>$\frac{\Phi_{[^3C_\text{c}]}}{[\Omega_2]}^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Particle Extracts</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PME1*</td>
<td>3.1 (1.2)</td>
<td>0.30 (0.13)</td>
<td>109 (48)</td>
<td>1.8 (0.8)</td>
<td>0.44 (0.20)</td>
<td>0.19 (0.07)</td>
</tr>
<tr>
<td>PME2*</td>
<td>3.1 (1.0)</td>
<td>0.34 (0.13)</td>
<td>122 (47)</td>
<td>1.9 (0.7)</td>
<td>0.26 (0.10)</td>
<td>0.10 (0.03)</td>
</tr>
<tr>
<td>PME3</td>
<td>7.3 (2.3)</td>
<td>1.5 (0.6)</td>
<td>534 (204)</td>
<td>3.6 (1.4)</td>
<td>0.33 (0.13)</td>
<td>0.068 (0.022)</td>
</tr>
<tr>
<td>PME4</td>
<td>16 (5)</td>
<td>3.5 (1.4)</td>
<td>1260 (501)</td>
<td>2.8 (1.1)</td>
<td>0.44 (0.18)</td>
<td>0.083 (0.029)</td>
</tr>
<tr>
<td>PME5</td>
<td>9.3 (3.1)</td>
<td>1.5 (0.6)</td>
<td>534 (211)</td>
<td>2.0 (0.8)</td>
<td>0.28 (0.11)</td>
<td>0.074 (0.025)</td>
</tr>
<tr>
<td>PME6</td>
<td>7.7 (2.2)</td>
<td>1.6 (0.6)</td>
<td>568 (206)</td>
<td>1.3 (0.5)</td>
<td>0.18 (0.06)</td>
<td>0.035 (0.011)</td>
</tr>
<tr>
<td>PME3D0.5</td>
<td>11 (5)</td>
<td>3.6 (1.6)</td>
<td>1286 (593)</td>
<td>4.1 (1.9)</td>
<td>0.48 (0.23)</td>
<td>0.062 (0.026)</td>
</tr>
<tr>
<td>PME3D1.3</td>
<td>6.3 (2.6)</td>
<td>1.1 (0.5)</td>
<td>393 (182)</td>
<td>3.4 (1.6)</td>
<td>0.50 (0.24)</td>
<td>0.12 (0.05)</td>
</tr>
<tr>
<td>PME3D2.5*</td>
<td>3.5 (1.7)</td>
<td>0.44 (0.24)</td>
<td>160 (86)</td>
<td>2.7 (1.5)</td>
<td>0.43 (0.23)</td>
<td>0.14 (0.07)</td>
</tr>
<tr>
<td>PME3D10</td>
<td>0.51 (0.36)</td>
<td>0.0047 (0.0034)</td>
<td>17 (12)</td>
<td>1.1 (0.8)</td>
<td>0.18 (0.13)</td>
<td>0.079 (0.057)</td>
</tr>
<tr>
<td><strong>Averages (±σ)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>“Standard” (PME3-6)</td>
<td>10 (4)</td>
<td>2.0 (1.0)</td>
<td>723 (355)</td>
<td>2.4 (1.0)</td>
<td>0.31 (0.11)</td>
<td>0.065 (0.021)</td>
</tr>
<tr>
<td>“Dilute” (PME1*-2*,3D2.5*)</td>
<td>3.2 (0.2)</td>
<td>0.36 (0.01)</td>
<td>130 (26)</td>
<td>2.1 (0.5)</td>
<td>0.38 (0.10)</td>
<td>0.14 (0.04)</td>
</tr>
<tr>
<td>Davis Fog</td>
<td>5.4 (6.3)</td>
<td>0.59 (0.60)</td>
<td>212 (216)</td>
<td>5.8 (8.6)</td>
<td>0.55 (0.44)</td>
<td>0.21 (0.20)</td>
</tr>
<tr>
<td><strong>Test statistic</strong></td>
<td>0.27</td>
<td>0.059</td>
<td>0.059</td>
<td>0.49</td>
<td>0.35</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Listed uncertainties are ± 1 standard error.

$^a$ Samples extracted in 2.5 mL/filter square and referred to as the “dilute” extracts in the main text.

$^b$ Best estimate of oxidizing triplets steady-state concentration, calculated as the average of the $\Sigma[^1C_\text{c}]^*_{\text{SR}}$ and $\Sigma[^1C_\text{c}]^*_{\text{MeJA}}$ values, as shown in Table S12.

$^c$ Davis winter solstice-normalized rate of triplet photoproduction, calculated as $P_{[^1C_\text{c}]} = \Sigma[^1C_\text{c}]^* \times (k_{[^3C_\text{c}]+[O_2]} + (k_{[^3C_\text{c}]} + k_{[^3C_\text{c}]+[O_2]})$ (Eq. (8), main text).

$^d$ Davis winter solstice-normalized rate of triplet photoproduction, calculated as $P_{[^3C_\text{c}]}^d = P_{[^3C_\text{c}]} / R_{abs}$.

$^e$ quantum yield of formation of oxidizing organic triplet excited states, calculated as $\Phi_{[^3C_\text{c}]} = P_{[^3C_\text{c}]} / R_{abs}$.

$^f$ Fraction of the total triplet pool that can oxidize our probes, i.e., that are “oxidizing triplets”. This is estimated as the ratio of the quantum yields for oxidizing triplets and singlet oxygen (Table S7) divided by the average yield of $[^1O_2]^*$ ($f_s = 0.53$; Table S11) from $[^3C_\text{c}]^*$ via energy transfer. The denominator, $\Phi_{[^1O_2]} / R_{abs}$, is an estimate of the quantum yield for formation of energy-transfer triplets that can make singlet molecular oxygen, a pool that likely includes essentially all organic triplet states.
Ratio of the Davis-winter-normalized steady-state triplet and singlet oxygen concentrations.

Test statistic for comparison of standard PME and Davis fog averages: *p*-value for a two-tailed *t*-test for samples of unequal variance. Values below 0.05 are in bold.
<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Number of filter squares extracted</th>
<th>Volume of Milli-Q water per filter square (mL)</th>
<th>Aqueous PM mass concentration factor (CF)</th>
<th>Average PM mass extracted per filter square (μg)</th>
<th>Total PM mass extracted (μg)</th>
<th>Total volume of extract (mL)</th>
<th>PM mass / water mass (μg-PM / μg-H$_2$O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PME3D10</td>
<td>1</td>
<td>10</td>
<td>0.05</td>
<td>347</td>
<td>347</td>
<td>10</td>
<td>3.5E-05</td>
</tr>
<tr>
<td>PME3D2.5</td>
<td>12</td>
<td>2.5</td>
<td>0.20</td>
<td>331 (15)</td>
<td>3977</td>
<td>30</td>
<td>1.3E-04</td>
</tr>
<tr>
<td>PME3D1.3</td>
<td>8</td>
<td>1.3</td>
<td>0.38</td>
<td>315 (23)</td>
<td>2520</td>
<td>10</td>
<td>2.4E-04</td>
</tr>
<tr>
<td>PME3D1 or “PME3”</td>
<td>12</td>
<td>1.0</td>
<td>0.49</td>
<td>328 (19)</td>
<td>3932</td>
<td>12</td>
<td>3.3E-04</td>
</tr>
<tr>
<td>PME3D0.5</td>
<td>26</td>
<td>0.5</td>
<td>0.96</td>
<td>323 (21)</td>
<td>10979</td>
<td>13</td>
<td>8.4E-04</td>
</tr>
<tr>
<td>Cloud/Fog drop</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(1 – 5)E-04</td>
</tr>
<tr>
<td>Particles</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>≥ 1h</td>
</tr>
</tbody>
</table>

a Volume of water used to extract each 2 × 2 cm square piece of the filter sheet.

b PM mass concentration factor in the extract (Eq. (10), main text).

c Average (± 1σ) mass extracted from the filter squares for each dilution.

d Total mass extracted per extract. For each extract, the filter pieces used in the extraction were weighed pre- and post-extraction using a Mettler Toledo XP2U ultra-microbalance (error ± 2 μg). The PM mass extracted is the difference between pre- and post-extraction weights.

e Total volume of extract = number of filter pieces extracted × water volume per filter square.

f PM mass-to-water mass ratio, calculated as total solute mass extracted / total volume of extract.

g For fog drops, we estimate that PM mass/water mass ratios are in the range of $(1 – 5) \times 10^{-4}$ μg-PM/μg-H$_2$O based on a typical PM mass of 31 μg m$^{-3}$-air in California’s Central Valley, as measured by Young et al. (2016), and assuming a range for the liquid water content (LWC) of 0.06 to 0.3 g-H$_2$O m$^{-3}$-air (Hess et al., 1998).

h Based on measurements of particle mass concentration (Young et al. (2016)) and estimated particle water (Parworth et al., 2017) in California’s Central Valley during winter, the calculated range of PM mass to water mass ratios is 0.79 – 50. From this range, we use a value of 1 to represent typical PM conditions.
### Table S15. Photooxidant concentrations (formed *in situ*) in PME3D extracts and expected values in ambient particles

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Aqueous PM Mass Concentration Factor (CF)</th>
<th>PM Mass /Water Mass (μg-PM/μg-H$_2$O)</th>
<th>[(^{•})OH] (M)</th>
<th>[(^{1})O$_2$•] (M)</th>
<th>∑[(^{3})C•] (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PME3D10</td>
<td>0.05</td>
<td>3.5E-05</td>
<td>6.7E-16</td>
<td>6.4E-14</td>
<td>5.1E-15</td>
</tr>
<tr>
<td>PME3D2.5*</td>
<td>0.20</td>
<td>1.3E-04</td>
<td>3.4E-16</td>
<td>2.5E-13</td>
<td>3.5E-14</td>
</tr>
<tr>
<td>PME3D1.3</td>
<td>0.38</td>
<td>2.4E-04</td>
<td>3.2E-16</td>
<td>5.2E-13</td>
<td>6.3E-14</td>
</tr>
<tr>
<td>PME3D1</td>
<td>0.49</td>
<td>3.3E-04</td>
<td>8.5E-16</td>
<td>1.1E-12</td>
<td>7.3E-14</td>
</tr>
<tr>
<td>PME3D0.5</td>
<td>0.96</td>
<td>8.4E-04</td>
<td>8.3E-16</td>
<td>1.8E-12</td>
<td>1.1E-13</td>
</tr>
<tr>
<td>Ambient Particles</td>
<td></td>
<td>1.0</td>
<td>8.4E-16          1.6E-10</td>
<td>2.3E-13          1.3E-11</td>
<td></td>
</tr>
</tbody>
</table>

* Aqueous PM mass concentration factor (Eq. (10), main text).
* PM mass/water mass ratio (Table S14).
* Expected *in situ* [\(^{•}\)OH] concentration in ambient PM (in the absence of partitioning of \(^{•}\)OH from the gas phase), determined as the average of the five measurements in PME3D extracts and corrected for quenching by probe MBO (Sect. S1.1). Including mass transport of \(^{•}\)OH(g) to the drops will increase the aqueous concentration by approximately 30%, as discussed in the text.
* Best estimate for the ∑[\(^{3}\)C•] concentration in ambient PM; see section S4.
* High estimate for the ∑[\(^{3}\)C•] concentration in ambient PM, obtained by fitting ∑[\(^{3}\)C•] against PM mass/water mass ratio with the equation \(y = ax/(1+bx)\); parameters \(a = 2.26 \times 10^{-10}\) M and \(b = 17.0\) were obtained using Excel. The curve was then extrapolated to a PM mass/water mass ratio of 1.0 μg-PM/μg-H$_2$O.
### Table S16. Gas- and aqueous-phase reaction rate constants for selected organic compounds with the major oxidants

<table>
<thead>
<tr>
<th>#</th>
<th>Organic Compound</th>
<th>Gas-phase rate constant, $k_{\text{ORG}+\text{O}_{2}(g)}$ (cm$^3$ mlc$^{-1}$ s$^{-1}$)</th>
<th>Aqueous-phase rate constants, $k_{\text{ORG}+\text{O}_{2}(aq)}$ (M$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>*OH(g)</td>
<td>Ref.</td>
</tr>
<tr>
<td>1</td>
<td>Syringol</td>
<td>9.6E-11</td>
<td>(Lauraguais et al., 2012)</td>
</tr>
<tr>
<td>2</td>
<td>Methyl jasmonate</td>
<td>7.8E-12</td>
<td>(Meylan and Howard, 1993)</td>
</tr>
<tr>
<td>3</td>
<td>Tyrosine</td>
<td>2.8E-11</td>
<td>(Rinke and Zettsch, 1984)</td>
</tr>
<tr>
<td>4</td>
<td>1,2,4-Butanetriol</td>
<td>8.5E-12</td>
<td>(Atkinson et al., 2006)</td>
</tr>
<tr>
<td>5</td>
<td>3-Hydroxy-2,5-bis(hydroxymethyl) furan</td>
<td>4.0E-11</td>
<td>(Atkinson et al., 1983)</td>
</tr>
</tbody>
</table>

References for the measured rate constants are indicated. Values indicated are at 298 K wherever available. In cases where no measurements were found, rate constants for structurally similar compounds are used as proxies; references for those are provided, and discussed in the following footnotes.

$^a$ For triplets, we use an average of rate constants for $^3$MAP* and $^3$DMB*.

$^b$ Second-order rate constant for the gas-phase reaction of O$_2$ with guaiacol (2-methoxyphenol).

$^c$ Estimated by Richards-Henderson et al. (2014b) using a structurally similar compound.

$^d$ Second-order rate constant for the aqueous reaction of O$_2$ with syringol is used as a proxy, with a ten-fold enhancement based on the measured ratio of phenol and syringol rate constants for reaction with $^3$DMB* (discussed in the SI of Kaur and Anastasio (2018)).

$^e$ Average of cis- and trans-methyl jasmonate rate constants with hydroxyl radical and ozone.

$^f$ Second-order rate constant for the aqueous reaction of O$_2$ with phenol.

$^g$ Second-order rate constant for the aqueous-phase reaction of O$_2$ with 3-methylphenol.

$^h$ Second-order rate constant for the aqueous-phase reaction of tyrosine with 3'-methoxyacetophenone.

$^i$ Second-order rate constant for gas-phase reaction of O$_2$ with 1-butanol.

$^j$ Second-order rate constant for gas-phase reaction of O$_2$ with pinonaldehyde.

$^k$ Second-order rate constant for aqueous-phase reaction of *OH with 1,6-hexanediol.

$^l$ Second-order rate constant for aqueous-phase reaction of $^1$O$_2^*$ with 2-butanol.

$^m$ Second-order rate constant for aqueous-phase reaction of O$_2$ with 2-propanol.

$^n$ Second-order rate constant for aqueous-phase reaction of $^3$DMB* with 2-propanol.

$^o$ Second-order rate constant for gas-phase reaction of *OH and O$_2$ with furan.

$^p$ Second-order rate constant for aqueous-phase reaction of *OH with furan.

$^q$ Second-order rate constant for aqueous-phase reaction of $^1$O$_2^*$ with furan, adjusted by multiplying with 0.5 based on effect of changing substituents.

$^r$ Second-order rate constant for aqueous-phase reaction of O$_2$ with furan in glacial acetic acid.

$^s$ Average of the second-order rate constant for aqueous-phase reaction of $^3$MAP* and $^3$DMB* with methyl jasmonate is used as a proxy, adjusted by multiplying with 0.5 based on effect of changing substituents observed for rate constant of furan with $^1$O$_2^*$.
Table S17. Fate of selected organic compounds in fog and particles

<table>
<thead>
<tr>
<th>#</th>
<th>Organic Compound</th>
<th>$K_{H}$ a (M atm$^{-1}$)</th>
<th>$f_{aq}$ b</th>
<th>Overall</th>
<th>Percent of loss due to each oxidant c</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$k'_{ORG}$ (s$^{-1}$)</td>
<td>$\tau_{ORG}$ (h)</td>
</tr>
<tr>
<td>Fog</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Syringol</td>
<td>5.0E+03</td>
<td>0.11</td>
<td>1.1E-04</td>
<td>2.5</td>
</tr>
<tr>
<td>2</td>
<td>Methyl jasmonate</td>
<td>8.1E+03</td>
<td>0.17</td>
<td>1.2E-04</td>
<td>2.3</td>
</tr>
<tr>
<td>3</td>
<td>Tyrosine</td>
<td>8.0E+10</td>
<td>1.0</td>
<td>1.8E-04</td>
<td>1.6</td>
</tr>
<tr>
<td>4</td>
<td>1,2,4-Butanetriol</td>
<td>4.7E+11</td>
<td>1.0</td>
<td>1.0E-05</td>
<td>28</td>
</tr>
<tr>
<td>5</td>
<td>3-Hydroxy-2,5-bis(hydroxymethyl) furan</td>
<td>1.1E+09</td>
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<td>3.5E-05</td>
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<tr>
<td>PM (Best-fit $[^{2}$C*] scenario)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Syringol</td>
<td>5.0E+03</td>
<td>2.4E-06</td>
<td>9.6E-05</td>
<td>2.9</td>
</tr>
<tr>
<td>2</td>
<td>Methyl jasmonate</td>
<td>8.1E+03</td>
<td>4.0E-06</td>
<td>1.3E-04</td>
<td>2.1</td>
</tr>
<tr>
<td>3</td>
<td>Tyrosine</td>
<td>8.0E+10</td>
<td>0.98</td>
<td>6.3E-03</td>
<td>0.044</td>
</tr>
<tr>
<td>4</td>
<td>1,2,4-Butanetriol</td>
<td>4.7E+11</td>
<td>1.0</td>
<td>1.4E-05</td>
<td>20</td>
</tr>
<tr>
<td>5</td>
<td>3-Hydroxy-2,5-bis(hydroxymethyl) furan</td>
<td>1.1E+09</td>
<td>0.35</td>
<td>5.7E-03</td>
<td>0.049</td>
</tr>
<tr>
<td>PM (High estimate $[^{3}$C*] scenario)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Syringol</td>
<td>5.0E+03</td>
<td>2.4E-06</td>
<td>9.6E-05</td>
<td>2.9</td>
</tr>
<tr>
<td>2</td>
<td>Methyl jasmonate</td>
<td>8.1E+03</td>
<td>4.0E-06</td>
<td>1.3E-04</td>
<td>2.1</td>
</tr>
<tr>
<td>3</td>
<td>Tyrosine</td>
<td>8.0E+10</td>
<td>0.98</td>
<td>1.4E-02</td>
<td>0.020</td>
</tr>
<tr>
<td>4</td>
<td>1,2,4-Butanetriol</td>
<td>4.7E+11</td>
<td>1.0</td>
<td>2.6E-05</td>
<td>10.5</td>
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<tr>
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<td>3-Hydroxy-2,5-bis(hydroxymethyl) furan</td>
<td>1.1E+09</td>
<td>0.35</td>
<td>6.3E-03</td>
<td>0.044</td>
</tr>
</tbody>
</table>

For fog, a liquid water content of $1 \times 10^{-6}$ L-aq / L-air is assumed.
For PM, a liquid water content of $2 \times 10^{-14}$ L-aq / L-air is assumed, based on typical wintertime Central Valley conditions (Parworth et al., 2017).

b Fraction of organic compound present in the aqueous-phase, calculated as $f_{aq} = 1/(1+1/(K_H \times L \times R \times T))$, where $K_H$ is the Henry’s law constant, $L$ is the liquid water content, $R$ is the gas constant (0.082 L atm K$^{-1}$ mol$^{-1}$), and $T = 298$ K.
c Total pseudo-first order rate constant for loss of organic compound, calculated as $k'_{ORG} = \Sigma(f_{aq} \times k'_{ORG,Ox(aq)} + (1-f_{aq}) \times k'_{ORG,Ox(g)})$. $k'_{ORG,Ox(aq)}$ and $k'_{ORG,Ox(g)}$ are by calculated by multiplying the bimolecular reaction rate constant (Table S16) with the corresponding steady-state concentration of oxidant: $[^{*}$OH(g)] = $1 \times 10^{6}$ molecules cm$^{-3}$, $[O_3(g)] = 30$ ppbv = $7.4 \times 10^{11}$ molecules cm$^{-3}$, $[^{*}$OH(aq)] = $2 \times 10^{-15}$ M (includes gas-to-aqueous partitioning; Kaur and Anastasio (2017) and this study), $[O_3(aq)] = 3.3 \times 10^{-10}$ M (based on equilibrium with 30 ppbv O$_3$(g) and $K_H = 1.1 \times 10^{-2}$ M atm$^{-1}$; Seinfeld and Pandis (2012)), $[^{1}$O$_2$(aq)] = $2 \times 10^{-13}$ M in fog (average in Davis fog; Kaur and Anastasio (2017)), and $1.5 \times 10^{-10}$ M in PM (estimate in PM after accounting for evaporative loss and loss due to organic sinks at higher DOC concentrations; Sect. S5). In case of the triplets, in fog $[^{1}$C*(aq)] = $5 \times 10^{-12}$ M (average in Davis fog; Kaur and Anastasio (2018)); in PM both the best-fit and high-estimate concentrations obtained via extrapolation (Table S15) are considered, i.e., $[^{1}$C*(aq)] = $2.3 \times 10^{-13}$ M and $1.3 \times 10^{-14}$ M, respectively.
d Overall lifetime of organic compound, calculated as $1/k'_{ORG}$.
e Percent of organic compound lost due to each pathway, calculated as $(f_{aq} \times k'_{ORG,Ox(aq)})/k'_{ORG}$ for aqueous pathways and $((1-f_{aq}) \times k'_{ORG,Ox(g)})/k'_{ORG}$ for gas-phase processes. The sum of all pathways for a given compound is sometimes not equal to 100% because of rounding.
Figure S1. •OH measurement in extract PME5. Top Panel: Photoformation of phenol in four aliquots of the extract spiked with varying benzene concentrations (0.10 to 1.5 mM). The rates of phenol formation, $R_p$, were determined as the slopes of the linear fits for each of the four data sets. Bottom: “Inverse” plot, i.e., the inverse of $R_p$ vs. the inverse of the benzene concentration. The slope and y-intercept from this plot are used to calculate $P_{\text{OH}}$, [•OH], and $k'_{\text{OH}}$ using equations described in Kaur and Anastasio (2017). •OH results for all particle extracts are tabulated in Table S3.
Figure S2. Singlet oxygen kinetic measurements in extract PME5 diluted 1:1 (volume : volume) with H$_2$O or D$_2$O. Data show the change in probe concentration (furfuryl alcohol, FFA) with illumination time. Closed symbols are illuminated samples while open symbols represent dark controls. Equations for calculating $^1\text{O}_2^*$ steady-state concentrations and rates of photoproduction are described in Kaur and Anastasio (2017).
Figure S3. Top panel: Light absorbance by fog samples collected during 2011-12 in Davis, CA. The legend shows the sample identities, arranged from the highest absorbing (top) to lowest absorbing (bottom) at 300 nm. Bottom panel: Mass absorption coefficient of DOC in the Davis fog samples. All data from Kaur and Anastasio (2017).
Figure S4. Correlation between the rate of sunlight absorption ($R_{\text{abs}}$) in the 300-450 nm wavelength range and dissolved organic carbon (DOC) for the fog samples (data from Kaur and Anastasio (2017)) and particle extracts (PME) (this work). Values for PME in this plot are summarized in Table S1.
Figure S5. (Top) Ratio of pathlength-normalized absorbance for PME and fog samples with highest (black) and median (grey) absorbances. (Bottom): Ratio of mass absorption coefficients of DOC in PME and fog samples with highest (black) and median (grey) absorbances.
Figure S6. (Top) Correlation between the rate of \(^{•} \text{OH}\) photoproduction due to sources other than nitrite and nitrate and the concentration of dissolved organic carbon (DOC). While the \(R^2\) value for this correlation is relatively high, this is largely driven by the highest three points: most of the data are poorly fit by the regression line. (Bottom) Correlation between apparent pseudo-first order rate constant for loss of \(^{•} \text{OH}\) due to organic sinks (obtained by subtracting inorganic contributions from the measured \(k'_{\text{OH}}\)) and DOC. Data include measurements in particle extracts (measured in this work) and in Davis fogs (Kaur and Anastasio, 2017).
Figure S7. Comparison of hydroxyl radical steady-state concentrations formed in situ (i.e., not including mass transport of $^\bullet$OH from the gas phase) measured in various atmospheric waters, as summarized in Arakaki et al. (2013) (blue bars) and including (in yellow bars) our recent data for fog (Kaur and Anastasio, 2017) and current data for PM. Error bars are ± 1σ, calculated from the variability in values used to calculate the mean for a given study.
Figure S8. Loss of probes for measuring triplet excited states: syringol (SYR) and methyl jasmonate (MeJA) in extract PME5. Closed symbols are illuminated samples while open symbols represent dark controls.
Figure S9. Winter-solstice-normalized pseudo-first-order rate constants ($k'_{\text{Probe}}$) for loss of syringol (top panel) and methyl jasmonate (bottom panel). The bar representing each rate constant is colored to represent the contributions of hydroxyl radical (yellow), singlet molecular oxygen (purple) and triplet excited states (green) to probe loss. The Davis winter-solstice lifetime of each probe ($\tau_{\text{Probe}}$, black diamonds) is shown on the right y-axes. The first four bars represent probe data from wintertime fog waters collected in Davis (Kaur and Anastasio, 2018).
**Figure S10.** Dependence of rate of \(^*\)OH photoproduction \((P_{\text{OH}}; \text{red circles, left y-axis})\) and rate constant for loss of \(^*\)OH due to natural sinks \((k'_{\text{OH}}; \text{blue squares, right y-axis})\) with PM mass/water mass ratio in three PME3D samples. \(^*\)OH kinetic measurements were not made in the other two PME3D samples.) Measurements of \(^*\)OH kinetics in the PME3D samples are discussed in Section S1 and shown in Table S3. Using the slopes of the linear relationships to extrapolate \(P_{\text{OH}}\) and \(k'_{\text{OH}}\) to values under ambient particle conditions \((1 \, \mu g/PM/\mu g-H_2O)\) gives \(P_{\text{OH}} = 4.2 \times 10^{-6} \, M \, s^{-1}\) and \(k'_{\text{OH}} = 5.5 \times 10^9 \, s^{-1}\). Error bars represent ± 1 standard error and are too small to be visible for \(P_{\text{OH}}\).
Figure S11. Fate of five model organic compounds – syringol, methyl jasmonate, tyrosine, 1,2,4-butanetriol and 3-hydroxy-2,5-bis(hydroxymethyl)furan – under fog (left of vertical dashed line) and PM (right of dashed line) conditions using an upper-bound estimate for triplet concentrations in PM. Estimated Henry’s law constants for the compounds (in units of M atm$^{-1}$) are in parentheses beneath each structure. Panel (a): the blue columns represent overall lifetimes of the organics via both gas and aqueous-phase loss processes, and the red open circles represent the fractions present in fog or aqueous PM. (b) Fraction of each compound lost via each pathway. The aqueous triplet concentration in PM is $1.5 \times 10^{-10}$ M (Table S15, Fig. 5, main text). All oxidant concentrations and rate constant data are shown in Tables S16 and S17.
S1. Hydroxyl radical measurements in PME3 and PME3D extracts

S1.1: Determining •OH steady-state concentrations ([•OH])

Typically, for •OH measurements we used benzene as the probe. Since benzene is volatile, we performed the illumination in 5 mL sealed quartz cuvettes (instead of quartz tubes) fully filled with extract, only withdrawing 100 µL for analysis at each time point to minimize loss of benzene due to volatilization into the headspace. However, for the PME3D extracts, where we had limited sample volume, we could not fully fill the 5 mL cuvettes. Due to this limitation, for the PME3D samples we monitored the loss of 2-methyl-3-butene-2-ol (MBO) to determine •OH concentrations, then separately measured the production rate of •OH using benzene (for the three dilutions with sufficient volume), and combined these two measures to determine the •OH sink.

There are three main reasons we chose MBO as a probe: 1) it is less volatile than benzene in water, 2) its rate constants with the major photooxidants (i.e. •OH, ^1O2* and ^3C*) are known, and 3) its reaction with •OH is much faster than with ^1O2* and ^3C* (see below). Fresh MBO stock was made one day prior to each experiment. 1.0 mL of acidified (pH 4.2) PME3D extract was spiked to 75 µM MBO, capped and illuminated with simulated sunlight in a quartz tube of 4 mm pathlength. Unfortunately, we later realized that this relatively high concentration of MBO was sometimes a significant sink for •OH in our PME3 extracts, thus suppressing the apparent steady-state concentration of hydroxyl radical. We are able to approximately correct for this error using an MBO Correction Factor, which is described below.

Throughout the illumination period, MBO loss was measured with HPLC-UV (eluent of 20% acetonitrile: 80% Milli-Q water, flow rate of 0.6 mL/min, detection wavelength of 200 nm and column temperature of 35°C). The pseudo-first-order rate constant for loss of MBO (k'_{MBO}; s⁻¹) was obtained as the negative of the slope of the plot of ln([MBO]/[MBO]₀) versus time, then normalized to Davis-winter-solstice light using an analog of Eq. (4) in the main text. Because MBO is not a specific probe for •OH, its loss in each sample is the sum of all its loss pathways:

\[ k'_{MBO} = k_{MBO+OH} [\cdot OH] + k_{MBO+1O2*} [^1O2*] + \Sigma (k_{MBO+3Ci*} [^3Ci*]) + j_{MBO} \] (S1)

where [•OH], [^1O2*] and \( \Sigma [^3Ci*] \) are the steady-state concentrations of the photooxidants. The variables \( k_{MBO+OH} (7.4 (± 0.5) \times 10^9 \text{ M}^{-1} \text{s}^{-1}; \text{(Richards-Henderson et al., 2014b)}) \), \( k_{MBO+1O2*} (7.0 (± 1.0) \times 10^5 \text{ M}^{-1} \text{s}^{-1}; \text{(Richards-Henderson et al., 2014b)}) \) and \( k_{MBO+3Cl*} \) (discussed below) are the
second-order rate constants for reactions of MBO. $j_{MBO}$ is the rate constant for direct photodegradation of the probe and is negligible for our illumination times ($2.7 \times 10^{-7}$ s$^{-1}$).

Eq. (S1) has two unknown quantities: 1) [$\cdot$OH] and 2) the loss of MBO due to triplets, i.e., $\Sigma(k_{MBO+3Cl}[^3C_i^*])$. To get [$\cdot$OH], we first estimated MBO loss due to triplets ($\Sigma(k_{MBO+3Cl}[^3C_i^*])$ by using two assumptions about the triplets. Our first assumption is that all loss of the triplet probe syringol is due to $^3C^*$ and $^1O_2^*$, i.e., $^\cdot$OH is a negligible oxidant for SYR, based on our measurements in the other samples, PME1-6, where the fraction of SYR lost due to $^3C^*$ and $^1O_2^*$ (combined) is 91 to 98% (Table S8). While we did measure the loss of methyl jasmonate in the PME3D samples, we only used syringol loss to determine $^\cdot$OH concentrations since our first assumption listed above is not valid for MeJA, i.e., we cannot assume that all loss of MeJA is due to $^3C^*$ and $^1O_2^*$ since $^\cdot$OH is a significant sink for MeJA (Table S9).

The loss of syringol in the PME3D extracts is the sum of its loss due to $^\cdot$OH, $^1O_2^*$ and $^3C^*$:

$$k'_{SYR} = k_{SYR+OH}[^\cdot$OH] + $k_{SYR+1O2}[^1O_2^*] + \Sigma(k_{SYR+3Cl}[^3C_i^*]) \quad \text{(S2)}$$

Direct photodegradation of syringol is negligible, and the contributions of other oxidants have been previously determined to be small (Section 2.5.3, main text). Based on our first assumption, $k_{SYR+OH}[^\cdot$OH] is much smaller than the sum of the other two terms on the right-hand side of Eq. (S2) and this equation can be simplified to:

$$k'_{SYR} \approx k_{SYR+1O2}[^1O_2^*] + \Sigma(k_{SYR+3Cl}[^3C_i^*]) \quad \text{(S3)}$$

Our second assumption is that the reactivity of the triplet mixture in the PM extracts most closely resembles a binary mixture of the model triplets $^3$3MAP$^*$ and $^3$DMB$^*$—since these are the best triplet matches obtained for majority of the particle extracts (Table S11). For simplicity, we use a 1:1 mixture of the two model triplets. Thus, for $k_{SYR+3Cl}$ we used a triplet-syringol rate constant $(\pm \sigma)$ of $3.7 \pm 0.2) \times 10^9$ M$^{-1}$ s$^{-1}$, which is the average of $k_{SYR+3MAP}$ and $k_{SYR+3DMB}$ (Table S10) in Eq. (S3) to obtain the triplet steady-state concentration:
\[ \Sigma [^3C_i^*] = \frac{k'_{\text{SYR}} - (k_{\text{SYR}} + 1O_2[^1O_2^*])}{k_{\text{SYR}} + 3C_i^*} \]  
\hspace{1cm} \text{(S4)}

Using the measured singlet oxygen concentration, \([^1O_2^*]\), for each PME3 dilution we determine \(\Sigma [^3C_i^*]\) in Eq. (S4), which we then plug into Eq. (S1), along with \(k_{\text{MBO}+3C_i^*} = 3.4 (\pm 0.4) \times 10^7 \text{ M}^{-1} \text{s}^{-1}\), the average of \(k_{\text{MBO}+33\text{MAP}^*}\) and \(k_{\text{MBO}+3\text{DMB}^*}\) (Richards-Henderson et al. (2014b)) to obtain the first iteration of [\(^\cdot\text{OH}\)]:

\[ [^\cdot\text{OH}] = \frac{k'_{\text{MBO}} - k_{\text{MBO}+1O_2[^1O_2^*]} - \Sigma (k_{\text{MBO}+3C_i^*[^3C_i^*]})}{k_{\text{MBO}+3C_i^*}} \]  
\hspace{1cm} \text{(S5)}

We then remove the first assumption and plug these [\(^\cdot\text{OH}\)] values into Eq. (S2) to get a second set of \(\Sigma [^3C_i^*]\) values, which we use in Eq. (S1) to obtain the second iteration of [\(^\cdot\text{OH}\)]. We continue this iterative process until the [\(^\cdot\text{OH}\)] values change by less than 0.01\% (Table S18).

**Table S18.** Determination of hydroxyl radical steady-state concentrations, \([^\cdot\text{OH}]\), from results of the MBO experiments

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Iteration 1</th>
<th>Iteration 2</th>
<th>Iteration 3</th>
<th>Iteration 4</th>
<th>MBO Correction Factor</th>
<th>(1/S_2)</th>
<th>Final [(^\cdot\text{OH})] (10^{-16} \text{ M})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PME3D0.5</td>
<td>5.54 (1.87)</td>
<td>5.72 (1.93)</td>
<td>5.73 (1.93)</td>
<td>5.73 (1.39)</td>
<td>1.10</td>
<td>1.15</td>
<td>7.3 (1.8)</td>
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<tr>
<td>PME3D1</td>
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<td>5.93 (1.97)</td>
<td>5.94 (1.97)</td>
<td>5.94 (1.40)</td>
<td>1.24</td>
<td>1.07</td>
<td>7.9 (1.9)</td>
</tr>
<tr>
<td>PME3D1.3</td>
<td>2.23 (0.76)</td>
<td>2.31 (0.77)</td>
<td>2.31 (0.79)</td>
<td>2.31 (0.57)</td>
<td>1.27</td>
<td>1.05</td>
<td>3.0 (0.8)</td>
</tr>
<tr>
<td>PME3D2.5*</td>
<td>2.19 (0.75)</td>
<td>2.26 (0.77)</td>
<td>2.26 (0.77)</td>
<td>2.26 (0.57)</td>
<td>1.43</td>
<td>1.03</td>
<td>3.3 (1.0)</td>
</tr>
<tr>
<td>PME3D10</td>
<td>1.89 (0.68)</td>
<td>1.95 (0.70)</td>
<td>1.95 (0.70)</td>
<td>1.95 (0.54)</td>
<td>3.31</td>
<td>1.01</td>
<td>6.6 (2.8)</td>
</tr>
</tbody>
</table>

Uncertainties in parentheses are ± 1 standard error.
We then made two corrections to the fourth (and final) iteration values. The first, and largest, correction was to account for the scavenging of \( \cdot \text{OH} \) by MBO by multiplying by an “MBO Correction Factor”. This correction factor is the sum of the pseudo-first-order rate constants for MBO and natural scavengers divided by the pseudo-first-order rate constant for natural scavengers. As shown in Table S18, this correction increases as the sample gets more dilute; values range from a modest 1.10 in the most concentrated extract to a very large 3.31 in the most dilute extract. The second correction was to divide by the light screening factor, \( S_\lambda \) (Table S1 and Sect. 2.5.1 of main text) to account for light absorption in our container; since the light screening factors are close to 1 (i.e., 0.87 – 0.99), these corrections are relatively small. The standard errors on the final \( \cdot \text{OH} \) concentrations account for both the experimental uncertainty as well as the uncertainty associated with the MBO correction factor.

### S1.2: Rate of \( \cdot \text{OH} \) photoproduction \( (P_{\text{OH}}) \)

Similar to the other extracts, in the PME3 samples we used benzene as the probe measure \( \cdot \text{OH} \) photoformation (Kaur and Anastasio, 2017; Anastasio and McGregor, 2001; Zhou and Mopper, 1990). A 5.0 mL aliquot of extract was acidified to pH 4.2 (± 0.2) and spiked with 1500 \( \mu \text{M} \) benzene, which should scavenge essentially all \( \cdot \text{OH} \). The solution was illuminated in a capped, sealed quartz cuvette with a 1 cm pathlength (Sect. 2.5.1 in main text). In all cases, phenol concentration increased linearly with time, and the rate of phenol formation \( (R_p) \) was obtained as the slope of the plot of phenol concentration versus time. We then plotted \( 1/R_p \) versus \( 1/[\text{Benzene}] \) and the intercept of that plot gave the experimentally measured rate of \( \cdot \text{OH} \) photoproduction \( (P_{\text{OH,EXP}}) \) (Zhou and Mopper, 1990). Measured rates of \( \cdot \text{OH} \) formation were normalized to the rate expected under midday Davis, CA winter-solstice sunlight \( (P_{\text{OH}}) \) based on 2-nitrobenzaldehyde (2NB) actinometry:

\[
P_{\text{OH}} = P_{\text{OH,EXP}} \times \frac{j_{2\text{NB,WIN}}}{j_{2\text{NB,EXP}}} \quad (S6)
\]

where \( j_{2\text{NB,WIN}} \) is the rate constant for loss of 2NB measured at midday near the winter solstice in Davis (0.0070 s\(^{-1}\); Anastasio and McGregor, 2001), and \( j_{2\text{NB,EXP}} \) is the measured rate constant for loss of 2NB on the day of the experiment. Due to the volume requirements of this technique, we were only able to measure \( P_{\text{OH}} \) in three extracts – PME3, PME3D2.5* and PME3D10.
**S1.3 Rate constant for loss of \(^{•}\)OH due to natural sinks (\(k'_{\text{OH}}\))**

In the PME3 samples we calculated the pseudo-first-order rate constant for loss of \(^{•}\)OH due to natural sinks by dividing the measured rate of \(^{•}\)OH photoproduction determined with benzene (Sect. S1.2) by the measured \(^{•}\)OH steady-state concentration determined with MBO (Sect. S1.1):

\[
k'_{\text{OH}} = \frac{P_{\text{OH}}}{[^{•}\text{OH}]} \quad (S7)
\]

**S2. \(^{•}\)OH sink measurements (\(k'_{\text{OH}}\)) in field blanks FB1 and FB2**

We also measured the rate constant for loss of \(^{•}\)OH due to natural sinks (\(k'_{\text{OH}}\)) in field blank FB1, which was extracted under the “dilute conditions”, i.e. each 2 \(\times\) 2 cm filter square was extracted in 2.5 mL Milli-Q.

In the early stages of this project, we used benzoate as an \(^{•}\)OH probe (Anastasio and McGregor, 2001), which reacts with \(^{•}\)OH to form m-hydroxybenzoic acid, m-HBA (and other products), which was quantified using UV-HPLC. Four 5.0 mL aliquots of extract were spiked with 100–1500 \(\mu\text{M}\) of sodium benzoate/benzoic acid solution (20 mM) at pH 4.2. Since \(P_{\text{OH}}\) in FB1 was below our detection limit (Table S3), we added 200 \(\mu\text{M}\) hydrogen peroxide as an \(^{•}\)OH source to each aliquot in order to measure the \(^{•}\)OH sinks. Aliquots were illuminated in capped quartz tubes with a 0.4 cm pathlength (Sect. 2.3 main text). The formation of m-HBA was linear in all cases, and the slope of the plot of [m-HBA] versus time in each aliquot is the rate of m-HBA formation (**R** \(P\), \(\mu\text{M} \text{ min}^{-1}\)). Similar to the benzene technique, we then plotted 1/\(R_P\) versus 1/[benzoate], used the slope and y-intercept of the inverse plot to obtain \(P_{\text{OH}}, k'_{\text{OH}}\) and \(^{•}\)OH, which were normalized to Davis midday solstice sunlight conditions. \(k'_{\text{OH}}\) measured using benzoate was 4.4 \((\pm 0.5) \times 10^5 \text{ s}^{-1}\), and represented 56% of the dilute sample average (PME1*, PME2*, PME3D2.5). Because this is high, we ran a number of tests to identify the source of the background \(^{•}\)OH sinks in FB1, starting with measuring \(k'_{\text{OH}}\) in two Milli-Q solutions containing only HOOH and probe stocks to identify whether these were the source of contamination. \(k'_{\text{OH}}\) in Milli-Q was nearly as high as in FB1: even after rigorously cleaning the quartz tubes using a UV+HOOH treatment (Chen et al., 2016), \(k'_{\text{OH}}\) was not lowered appreciably (Fig. S12). Since at this point, it appeared that the probe chemicals (sodium benzoate and benzoic acid) could be contaminated, we decided to switch to benzene as the \(^{•}\)OH probe.
The experimental procedure for the benzene technique is very similar to the benzoate technique, except that the aliquots of FB1 were acidified to pH 4.2 (± 0.2) using 10 mM sulfuric acid. While the $k'_{OH}$ value using benzene was slightly lower than the benzoate case ($3.4 (± 0.4) \times 10^5$ s$^{-1}$), it still represented 43% of the PM sample average. We then performed the benzene technique in Milli-Q water: the resulting $k'_{OH}$ of $1.2 (± 0.1) \times 10^4$ s$^{-1}$ was more than 10 times lower than the other measurements, typical of solutions without any background organic contamination (Chen et al., 2016). This was the lowest $k'_{OH}$ measured in our trials so, we chose to proceed with benzene as the probe for measuring $'OH$ in the particle extracts.

**Figure S12.** Measured pseudo-first-order rate constant for loss of $'OH$ due to natural sinks ($k'_{OH}$) in various solutions using sodium benzoate/benzoic acid and benzene as $'OH$ probes. Samples labeled “Milli-Q” contain only probe and HOOH. Samples labeled “FB1” are measurements in the extract solution of Field Blank 1. “Dilute Sample Average” is the average of the $k'_{OH}$ measurements in PME1*, PME2* and PME3D2.5* (Table S3).

We next determined $k'_{OH}$ in FB2 with benzene under standard extract conditions (1 mL Milli-Q per filter square). However, the resulting value of $2.7 (± 0.1) \times 10^5$ s$^{-1}$ is not much lower than the value in (more dilute) FB1 determined with benzoate and is 20 times higher than the Milli-Q value. But because the $k'_{OH}$ value in the standard extracts (PME3D1-PME6) is high (Table S3),
the corresponding FB2 value is only 11% of the standard sample average. One plausible contributing factor to the high \( k'_{\text{OH}} \) in the field blanks is that organic matter is coming off the filter material during extraction; we see this in the DOC measurements for both field blanks (Table S2). For future studies, we recommend first evaluating a few different types of particle filters by making background \( k'_{\text{OH}} \) measurements and then picking the filters that introduce the least contamination.

We did not adjust values of \( k'_{\text{OH}} \) measured in the particle extracts for the field blank rate constants. If we had adjusted them, \(^{1}\text{OH} \) concentrations would have increased by 50% in the “dilute” extracts and by 10% in the standard extracts. However, the concentrations would still be similar to fog. Additionally, this adjustment would have no effect on the extrapolation to ambient PM conditions, since \([^{1}\text{OH}]\) in all PME3D extracts would go up equally.
S3. Other oxidants in PM extracts

Since the probes we use for triplet determination do not react with only triplets (Eq. (5), main text), we account for the contributions of $^1\text{O}_2^\ast$ and $^\bullet\text{OH}$ to probe loss. However, it is also possible that other oxidants (that we do not measure) are also contributing to triplet probe loss. Here we examine this possibility for triplet probe loss in the PM extracts. In our previous measurements of photooxidants in fog water (Kaur and Anastasio, 2018), we estimated the importance of hydroperoxyl radical/superoxide radical anion ($\text{HO}_2^\ast/\text{O}_2^\ast$-), ozone ($\text{O}_3$), carbonate radical ($\bullet\text{CO}_3^-$) and hydrogen ion/hydrated electron ($\text{H}^\ast$ (aq)/$e^\ast$ (aq)) and found that these species in total contributed less than 7% to the average measured syringol loss. To do this calculation for our PM extracts, we estimate the steady-state concentrations of these oxidants in the illuminated extracts and, using reaction rate constants available in literature, calculate a pseudo-first-order rate constant for their reaction with syringol. We then compare that to the average ($\pm \sigma$) measured syringol loss in the standard extracts, $k'_{\text{SYR}} = 3.9 (\pm 1.3) \times 10^{-4}$ s$^{-1}$. As we noted in our previous paper, there are insufficient rate constants in the literature for reactions of methyl jasmonate in order to estimate its potential loss to other oxidants.

Hydroperoxyl Radical / Superoxide Radical Anion ($\text{O}_2$ (-I))

Hydroperoxyl radical and superoxide radical anion (i.e., $\text{O}_2$(-I)) are a conjugate acid-base pair; the $pK_a$ of $\text{HO}_2^\ast$ is $4.75 \pm 0.08$ (Bielski et al., 1985). Since the pH of our extracts was adjusted to ambient particle pH of 4.2 (Parworth et al., 2017), the mole fractions of $\text{HO}_2^\ast$ and $\text{O}_2^\ast$ - in the extracts are 0.78 and 0.22, respectively. There are no rate constants available for reaction of either species with syringol (2,6-dimethoxyphenol) so we use the fastest reported rate constants for reactions of similar compounds with $\text{O}_2^\ast$ - and $\text{HO}_2^\ast$. For substituted phenols, the rate constant for reaction of $\text{O}_2^\ast$ - with guaiacol (2-methoxyphenol) is $2.5 \times 10^3$ M$^{-1}$s$^{-1}$ (Yasuhisa et al., 1993); for $\text{HO}_2^\ast$, the rate constant with catechol (1,2-benzenediol) is $4.7 \times 10^4$ M$^{-1}$ s$^{-1}$ (Bielski, 1983). At pH 4.2, the mole-fraction weighted rate constant, used as the proxy for $k_{\text{SYR}+\text{O}2\text{(-I)}}$, is $3.7 \times 10^4$ M$^{-1}$s$^{-1}$.

To estimate $\text{O}_2$(-I) concentrations in the extracts, we use previously measured rates of HOOH formation in illuminated fog waters from California’s Central Valley since these two oxidants are intimately connected (Deguillaume et al., 2004; Anastasio, 1994):
\[ \text{O}_2(-I) + \text{Cu}(\text{I}) \rightarrow \text{HOOH} + \text{Cu}(\text{II}) \quad (S8) \]

The maximum measured production rate of HOOH, \( P_{\text{HOOH}} \), in illuminated Central Valley fogs is 3 \( \mu \text{M h}^{-1} \) (8.3 \( \times \) \( 10^{-10} \) \text{ M s}^{-1}; Anastasio (1994)). We expect that \( P_{\text{HOOH}} \) in particle extracts will be higher than fog, so we use an enhancement factor based on the observed increase in singlet oxygen concentrations in the standard extracts, which is a factor of seven higher than Davis fog average (Table S7). The reaction rate constants for \( \cdot \text{O}_2^- \) and \( \cdot \text{HO}_2^- \) reacting with \( \text{Cu}(\text{I}) \) are \( 9.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \) (Piechowski et al., 1993) and \( 3.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \) (Berdnikov, 1973), respectively, which gives an overall, mole-fraction-weighted reaction rate constant, \( k_{\text{O}_2(-I)+\text{Cu}(\text{I})} \), of \( 4.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \).

Solving the rate equation for \( S_8 \) with these inputs gives an \( \text{O}_2(-I) \) steady-state concentration of \( 1.1 \times 10^{-9} \text{ M} \). At this concentration, the estimated loss rate constant for syringol due to \( \text{O}_2(-I) \), \( k'_{\text{SYR},\text{O}_2(-I)} \), is \( 4.1 \times 10^{-5} \text{ s}^{-1} \), which would account for 11% of the average observed syringol loss. This suggests that superoxide is a minor sink for syringol in our samples, although it does appear to be more significant in particle extracts than fog.

**Ozone (O\(_3\))**

Based on the Henry’s law constant for ozone at 25°C (\( K_H = 1.1 \times 10^{-2} \text{ M atm}^{-1} \) (Seinfeld and Pandis, 2012) and assuming a gas-phase mixing ratio for \( \text{O}_3 \) of 30 ppbv, gives an initial aqueous-phase concentration of ozone in our samples of \( 3.3 \times 10^{-10} \text{ M} \). The actual concentration is likely lower since our samples are capped during illumination. The bimolecular rate constant for reaction of ozone with syringol is not available in the literature, so we estimate the rate constant by using the value for phenol (\( k_{\text{PhOH}+\text{O}_3} = 1.3 \times 10^3 \text{ M}^{-1} \text{ s}^{-1} \)) (Hoigné and Bader, 1983) with an enhancement factor of 10 based on the measured ratio of phenol and syringol rate constants for reaction with \(^3\text{DMB}\) (Smith et al., 2015). Under these assumptions, ozone is a very minor sink for syringol in the fog samples (\( k'_{\text{SYR},\text{O}_3} = 4.3 \times 10^{-6} \text{ s}^{-1} \)), accounting for 1% of the average measured syringol loss.

**Carbonate Radical (\( \cdot \text{CO}_3^- \))**

The carbonate radical is formed mainly from the reactions of bicarbonate (\( \text{HCO}_3^- \)) and carbonate (\( \text{CO}_3^{2-} \)) ions with \( \cdot \text{OH} \) and triplet CDOM species. Although DOM components are likely
important sinks for •CO₃−, this quenching is poorly understood (Canonica et al., 2005; Vione et al., 2014; Huang and Mabury, 2000). There are no published measurements of •CO₃− in atmospheric waters, so we use the typical steady-state concentration measured in surface waters of 2 × 10⁻¹⁴ M determined using N,N-dimethylaniline as a probe (Huang and Mabury, 2000; Zeng and Arnold, 2012). There are concerns that aniline probes overestimate •CO₃− since they also react rapidly with triplets (Rosario-Ortiz and Canonica, 2016), so we treat this as an upper-bound estimate. We do not apply an enhancement factor in this case since DOM appears to play the dual role of source and sink. While •CO₃− reacts rapidly with electron-rich phenolates (i.e., a deprotonated phenol), at pH 4.2 syringol is in the neutral, less reactive form. There are no rate constants available for •CO₃− reacting with methoxyphenols, so we assume the value with SYR is 10 times higher than that with phenol (4.9 × 10⁶ M⁻¹s⁻¹; Chen et al. (1975)). This results in a pseudo-first-order rate constant for loss of SYR due to carbonate radical of 1 × 10⁻⁶ s⁻¹, which represents a negligible 0.3% of the average measured syringol loss rate constant in our standard PM extracts.

**Hydrogen Ion / Aquated Electron (H⁺(aq)/e⁻(aq))**

Hydrogen ion (H⁺) and aquated electron (e⁻(aq)) can be formed during irradiation or illumination of dissolved organic matter in natural waters; these exist as a conjugate acid-base pair with a pKₐ of 9.6 (Kozmér et al., 2014; Buxton et al., 1988a). In our extracts at pH 4.2, the predominant species would be H⁺(aq). Zepp et al. (1987) determined an average steady-state concentration of e⁻(aq) in sunlight-illuminated lake waters to be 1.2 × 10⁻¹⁷ M. Similar to ¹O₂*, since DOM is the main source of e⁻(aq), we assume an enhancement factor of seven in the steady-state concentration of e⁻(aq). As an upper bound, we assume the H⁺ concentration to be equal to this. The rate constant for syringol reacting with H⁺ is not known. Using the average rate constant for methoxyphenol, 2.1 × 10⁹ M⁻¹s⁻¹ (O’Neill et al., 1975; Neta and Schuler, 1972), the pseudo-first-order rate constant for loss of SYR due to hydrogen ion is 1.7 × 10⁻⁷ s⁻¹, which would account for only 0.04% of the average observed syringol loss.

**Combined Contributions from Other Oxidants**

Based on our upper-bound estimates, the total rate constant for loss of syringol due to HO₂*/O₂−, O₃, •CO₃− and H⁺(aq)/e-(aq) is ~ 4.6 × 10⁻⁵ s⁻¹, which is only 12% of the average measured
syringol loss rate constant. Since this is small, our assumption that the loss of syringol is mainly due to $^\cdot\text{OH}$, $^1\text{O}_2^*$ and $^3\text{C}^*$ (Eq. (6), main text) seems valid.
S4. Impacts of mass transport and increasing organic concentration on estimates of aqueous photooxidant concentrations in ambient particles

The steady-state concentration of an oxidant reflects the balance between its rate of formation \((P_{\text{OX}})\) and first-order rate constant for loss \(k'_{\text{OX}} = 1 / \tau_{\text{OX}}\):

\[
[\text{OX}] = \frac{P_{\text{OX}}}{k'_{\text{OX}}}
\]

(S9)

where \(k'_{\text{OX}}\) is the sum of all the pseudo-first-order sinks of the oxidant. We can use our oxidant measurements for the dilution series of sample PME3 to estimate how the aqueous formation rate and rate constant for loss vary with solute concentration. But extrapolating these results to particle liquid water conditions requires accounting for additional factors, such as mass transport.

Here we combine our aqueous measurements with estimates of these other factors to better estimate oxidant concentrations from dilute fog or cloud drop conditions (i.e., a PM solute mass/water mass ratio of \(3 \times 10^{-5} \mu g-\text{PM}/\mu g-\text{H}_2\text{O}\)) to a particle liquid water condition (1 µg-PM/µg-H₂O). We roughly estimate the gas-phase influence using a simplified case assuming a temperature of 298 K, total pressure of 1 atm, an aqueous particle radius \(R_p\) of 0.5 µm at a PM mass/water mass ratio of 1 µg-PM/µg-H₂O, and a constant particle/drop density of 1 g cm⁻³.

In the case of hydroxyl radical, based on our current measurements and previous work (Arakaki et al., 2013; Anastasio and Newberg, 2007), the concentrations of the major aqueous sources (nitrate, nitrite, and unknown species) and sinks (organic compounds) both scale linearly with PM aqueous mass concentration, indicating that \(\cdot \text{OH}\) should be independent of dilution. However, this does not consider the influence of the gas phase. The extremely short lifetime of \(\cdot \text{OH}\) in the particles \(1/k'_{\text{OH}} \sim 2 \times 10^{-10} \text{ s}\) indicates that this oxidant will not be at Henry’s law equilibrium and that the gas phase will be a source of \(\cdot \text{OH}\). We estimate the rate of this gas-phase mass transport to the particles \((P_{\text{MT}})\) using the Fuchs-Sutugin transition regime formula (Seinfeld and Pandis, 2012) with an estimated gas-phase \(\cdot \text{OH}\) concentration of \(1 \times 10^6\) molecules cm⁻³ and a mass accommodation coefficient of 1. Under these conditions the drop-volume-normalized rate of \(\cdot \text{OH}\) gas-to-particle transport increases from \(7.7 \times 10^{-10} \text{ M s}^{-1}\) in dilute drops \((3 \times 10^{-5} \mu g-\text{PM}/\mu g-\text{H}_2\text{O})\) to \(4.2 \times 10^{-7} \text{ M s}^{-1}\) under particle conditions \((1 \mu g-\text{PM}/\mu g-\text{H}_2\text{O})\). Over this same range, the aqueous photoformation of \(\cdot \text{OH}\) increases even more strongly, from \(1.3 \times 10^{-10} \text{ M s}^{-1}\) to \(4.2 \times 10^{-6} \text{ M s}^{-1}\), respectively. Thus the contribution of gas-phase mass transport to the overall
\( \cdot \text{OH formation rate decreases as the drops become more concentrated, dropping from 86% in the dilute drops to 9% in the particle condition. Considering both the aqueous- and gas-phase sources of } \cdot \text{OH to the particles, we estimate the steady-state concentration at any dilution using}
\]
\[ [\cdot \text{OH(aq)}] = (P_{\cdot \text{OH}} + P_{\cdot \text{MT}})/k'_{\cdot \text{OH}} \quad (S10) \]

These overall steady-state concentrations range from \( 5.4 \times 10^{-15} \text{ M} \) in the dilute drop condition to \( 8.4 \times 10^{-16} \text{ M} \) in the particle condition, as shown by the solid orange line in Figure 5.

In the case of singlet molecular oxygen, there is little gas-phase data, but past estimates suggested concentrations on the order of \( 1 \times 10^8 \text{ molecules cm}^{-3} \) (Demerjian, 1974). At Henry’s law equilibrium, this gas-phase concentration corresponds to an aqueous concentration of \( 5 \times 10^{-14} \text{ M} \) (using the Henry’s law constant for ground state O\(_2\), 1.3 \times 10^{-3} \text{ M atm}^{-1} \text{ at 298 K}; Seinfeld and Pandis (2012)). This estimated aqueous concentration is somewhat smaller than our measured concentrations in dilute extracts (Table S7), which are approximately as concentrated as fog/cloud drops, and many orders of magnitude lower than our extrapolated particle concentrations. Thus the net effect of mass transport will be to move \( ^1\text{O}_2^* \) from the particles to the gas phase. As an upper bound, the fastest step in evaporation of \( ^1\text{O}_2^* \) is likely liquid-phase diffusion, which has a characteristic time (Seinfeld and Pandis, 2012) of

\[ \tau_{\text{LD}} = R_p^2/(\pi^2\times D_{\text{aq}}) \quad (S11) \]

where \( D_{\text{aq}} \) is the aqueous diffusion coefficient, approximately \( 1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1} \) if we assume an aqueous particle. Calculated liquid-phase diffusion lifetimes range from \( 3 \times 10^{-5} \text{ s} \) for particles (1 \( \mu \text{g-PM/\mu g-\text{H}_2\text{O}} \) and an assumed radius of 0.5 \( \mu \text{m} \)) to 0.02 s for dilute drops (3 \( \times 10^{-5} \mu \text{g-PM/\mu g-\text{H}_2\text{O}} \), which corresponds to a radius of 13 \( \mu \text{m} \)). The inverse of \( \tau_{\text{LD}} \) is the approximate first-order rate constant for liquid-phase diffusion, \( k'_{\text{LD}} \); values range from 60 s in dilute drops to \( 4 \times 10^4 \text{ s}^{-1} \) in particles. These values are low compared to the first-order rate constant for deactivation of \( ^1\text{O}_2^* \) in water (\( k'_{\text{H}_2\text{O}} = 2.2 \times 10^5 \text{ s}^{-1} \); Bilski et al. (1997)), indicating that evaporation is a minor sink.
Under cloud and fog drop conditions (and in our PM extracts) deactivation by water is the major sink for singlet oxygen, but under the more concentrated conditions of aqueous particles, organic compounds might also be important. To very roughly estimate this organic sink, we multiply our average DOC concentration in PM extracts (3.4 mM-C; Table S2) by a factor of 1000 to extrapolate to ambient PM conditions and assume all of this material is soluble, resulting in an aqueous concentration of particulate organics of 3.4 M-C. If each organic molecule has an average of 6 C atoms (i.e., the average is the same as levoglucosan), this corresponds to a water-soluble organic molecule concentration of 0.56 mol-compounds L⁻¹. We apportion this total concentration based on the emissions measurements of Jen et al. (2019), where water-soluble organics in biomass burning emissions are roughly 50% sugars, 25% phenols, and 25% organic nitrogen. Table S19 below shows the resulting estimated particle concentrations, along with an estimated average rate constant for each class based on the compilation by Wilkinson et al. (1995). Summing the contributions from each compound class we estimate a total pseudo-first order rate constant for loss of \(^1\)O₂* by soluble organics in the particles (at 1 μg-PM/μg-H₂O) of \(2.8 \times 10^6 \text{ s}^{-1}\). We linearly scale this sink, \(k_{\text{ORG}}\), by the PM mass/water mass ratio of the drops and particles to address dilution effects; e.g., for particles with 0.1 μg-PM/μg-H₂O, \(k_{\text{ORG}} = 2.8 \times 10^5 \text{ s}^{-1}\).

### Table S19. Estimates of the organic sink of \(^1\)O₂* in aqueous particles at 1 μg-PM/μg-H₂O

<table>
<thead>
<tr>
<th>Compound Class</th>
<th>Dissolved Concentration (M)</th>
<th>2ⁿᵈ-order Rate Constant Range (M⁻¹ s⁻¹)</th>
<th>Assumed 2ⁿᵈ-order (k) (M⁻¹ s⁻¹)</th>
<th>(k'_{\text{ORG}}) (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sugars</td>
<td>0.28</td>
<td>(10^4)</td>
<td>(10^4)</td>
<td>2800</td>
</tr>
<tr>
<td>Phenols</td>
<td>0.14</td>
<td>(10^6 - 10^7)</td>
<td>(10^7)</td>
<td>(1.4 \times 10^6)</td>
</tr>
<tr>
<td>Organic Nitrogen</td>
<td>0.14</td>
<td>(10^3 - 10^7)</td>
<td>(10^7)</td>
<td>(1.4 \times 10^6)</td>
</tr>
</tbody>
</table>

The resulting estimate for the steady-state concentration of \(^1\)O₂* in drops and particles is:

\[
[\text{O}_2^*] = P_{\text{O}_2^*}/(k'_{\text{H}_2\text{O}} + k'_{\text{LD}} + k'_{\text{ORG}}) \quad \text{(S12)}
\]

where the numerator, i.e., the rate of \(^1\)O₂* photoformation increases with increasing solute concentration according to the linear regression of our PME3D values (with the y-intercept fixed.
at zero): \( P_{1O2^*} = 5.0 \times 10^{-4} \text{ M s}^{-1}/(\mu\text{g-PM/\mu g-water}) \). This gives rates of singlet oxygen formation that range from \( 1.5 \times 10^{-8} \text{ M s}^{-1} \) in dilute drops to \( 5.0 \times 10^{-4} \text{ M s}^{-1} \) for our standard particle condition. The denominator of Eq. S12 is \( 2.2 \times 10^{5} \text{ s}^{-1} \) in dilute drops and remains at this value until the particle concentration reaches \( 10^{-3} \mu\text{g-PM/\mu g-water} \), at which point it increases because of the increasingly concentrated organic sinks. At the particle condition of \( 1 \mu\text{g-PM/\mu g-H}_2\text{O} \), the denominator is \( 3.1 \times 10^{6} \text{ s}^{-1} \) and organic sinks account for 92% of \( {^{1}O_2*} \) loss. Calculated values of \([^{1}O_2*]\) range from \( 6.7 \times 10^{-14} \text{ M} \) in dilute drops to \( 1.6 \times 10^{-10} \text{ M} \) for the particle liquid water condition.

For triplet excited states we fit our experimental data to a hyperbolic fit:

\[
\left[^3C^*\right] = \frac{a[m_{PM}/m_{H2O}]}{1+b[m_{PM}/m_{H2O}]} \quad (\text{S13})
\]

where \( m_{PM}/m_{H2O} \) is the PM mass/water mass ratio, the numerator represents the formation of triplets and the denominator represents the sinks. We fit our experimental data to this equation in Excel in two ways: (1) a best fit, where the hyperbolic equation parameters were tuned to minimize the regression error, and (2) a high estimate fit, where the parameters were tuned so that the regression line passed near the top of the error bar for the most concentrated sample extract (PME3D0.5). The parameters for these two fits are: (1) \( a = 3.08 \times 10^{-10} \text{ M} \) and \( b = 1.31 \times 10^3 \), and (2) \( a = 2.26 \times 10^{-10} \text{ M} \) and \( b = 17.0 \). We did not include the data point for PME3D10 when determining the regression fits (but do show it in the plots) because of the larger uncertainty in its triplet concentration, a result of the significant \(^{1}OH \) perturbation by MBO in this most dilute sample. Our interpretation of the curvature in these regression fits (Figure 5) is that as the solutions get more concentrated, organics become the major triplet sink, causing \([^3C^*]\) to plateau at higher PM mass/water mass ratios; we estimate the size of this organic sink in the next section. Thus, these fits should account for the organic sinks that will be important under particle conditions.

To a first approximation, we expect that mass transport will have no significant impact on the concentrations of triplets. Since most of the BrC precursors for \(^3C^*\) are likely in the particle phase (rather than the gas phase) we expect that gas-phase concentrations of triplets are relatively small and that the gas phase is not a significant source of triplets to the particles. We also expect that evaporation of triplets is minor since their lifetimes are relatively short (1 \( \mu \text{s} \) based just on
O₂ as a sink) and their gas-particle partitioning (like that of their BrC precursors) is strongly tilted toward the particle phase. Thus we assume that the particle concentration of triplets is relatively unaffected by mass transport. As for potential organic sinks of \(^3\)C*, the curvature shown in Figures 4 and 5 is likely due to organics becoming major sinks in the more concentrated PM extracts; this is accounted for in our hyperbolic fit. However, it is also possible that the curvature is noise and that the \(^3\)C* concentration in particles is much higher than extrapolated using the hyperbolic fit in Figure 5; we explore both of these scenarios in the main text.

S5. Estimating triplet characteristics in particle extract PME3

We can use our measurements of triplet steady-state concentrations in the PME3 dilution series to derive the first-order rate constant for triplet formation and the overall rate constant for triplet reaction and quenching by DOC. The rate of triplet formation \((P_{3C*})\) from the photoexcitation of chromophores ‘C’ in the extracts can be expressed as:

\[
P_{3C*} = j_{\text{abs}} \times \Phi_{\text{ISC}} \times [C]
\]

\((S1.4)\)

where \(j_{\text{abs}}\) is the rate constant for light absorption \((s^{-1})\) by C and \(\Phi_{\text{ISC}}\) is the intersystem crossing quantum yield, i.e., the fraction of the first excited single state, \(S_1\), that forms the lowest triplet excited state, \(T_1\). Assuming the chromophore concentration is a fraction \(f\) (mole-chromophore mole-C⁻¹) of the DOC concentration (mole-C L⁻¹), the rate of triplet formation can be expressed as:

\[
P_{3C*} = j_{\text{abs}} \times \Phi_{\text{ISC}} \times f \times [\text{DOC}]
\]

\((S1.5)\)

The rate constant for loss of the triplet \((k'_{3C*}; s^{-1})\) in an extract is the sum of all its loss pathways:

\[
k'_{3C*} = k_{3C*+O2} [O_2] + k_{\text{rxn}} [\text{DOC}] + k_Q [\text{DOC}]
\]

\((S1.6)\)

where \(k_{3C*+O2}\) is the bimolecular rate constant for O₂ quenching (we use the average value for the three model triplets with measurements, \(2.8 (± 0.4) \times 10^9 M^{-1}s^{-1}\); Table S11); \([O_2]\) is the
dissolved oxygen concentration (284 μM at 20 °C) (USGS, 2018); \( k_{rxn} (M^{-1}s^{-1}) \) is the rate constant for reaction of triplet with dissolved organics; and \( k_Q (M^{-1}s^{-1}) \) is the rate constant for the non-reactive quenching of triplet by DOC (Smith et al., 2014).

Assuming steady state, the triplet concentration is the ratio of its rate of photoproduction and its rate constant for loss:

\[
[3C^*] = \frac{P3C^*}{k'3C^*} = \frac{j_{abs} \times \Phi_{ISC} \times f \times [DOC]}{k_{3C^++O2}[O2] + (k_{rxn} + k_Q)[DOC]} \quad (S17)
\]

This can be re-written as

\[
[3C^*] = \frac{\left(\frac{j_{abs} \times \Phi_{ISC} \times f}{k_{3C^++O2}[O2]}\right) [DOC]}{1 + \left(\frac{k_{rxn} + k_Q}{k_{3C^++O2}[O2]}\right) [DOC]} \quad (S18)
\]

We then fit our triplet steady-state concentration measurements in the PME3D extracts to the following two-parameter equation:

\[
[3C^*] = \frac{c[DOC]}{1 + d [DOC]} \quad (S19)
\]

The regression fit is shown in Fig. S13; the parameters for the fit obtained using Excel are \( c = 2.9 \times 10^{-11} \) and \( d = 117 \ M^{-1} \); we did not include the data point for PME3D10 in determining the regression fit because of the larger uncertainty in its triplet concentration, a result of the significant probe perturbation in this most dilute sample. Using the regression parameters, we calculate that the rate constant for triplet formation, i.e., \( j_{abs} \times \Phi_{ISC} \times f \), is \( 2.3 (\pm 0.3) \times 10^{-5} \ s^{-1} \) and the sum of the reaction and quenching rate constants for the triplets by DOC, i.e.,\( k_{rxn} + k_Q \), is \( 9.3 (\pm 1.3) \times 10^7 \ L \ mol^{-1} \ s^{-1} \).
Figure S13. Change in triplet steady-state concentration with dissolved organic carbon concentration in the PME3D extracts. Error bars represent ± 1 standard error in measured triplet concentrations (Table S13). The regression line is a fit of Equation S19 to the experimental data in Excel, yielding parameter estimates of $c = 2.90 \times 10^{-11}$ and $d = 117$ M$^{-1}$. The PME3D10 point was not included in the regression fit (although is shown on the plot) because of issues with too-high probe concentrations in the $^\bullet$OH determination. The DOC value for sample PME3D0.5 (which had very limited volume) is estimated based on results for the other four dilutions and given in Table S2.
S6. References


California Air Resources Board, iADAM database: Air Quality Data Statistics: https://www.arb.ca.gov/adam, access: June 6, 2018.


