

Reviewer Number 1

It is obvious that most chemical transformations occurring in the troposphere are induced by photochemically produced radicals. This paper demonstrates that OH radicals are formed by photolysis of secondary organic aerosol (SOA) material formed by terpene ozonolysis. This is an interesting contribution and points toward the potential importance of the photochemistry of hydroperoxide produced during the ozonolysis process as source of OH radicals in the particles. Similar processes have been discussed for cloud and fog conditions. However, due to the potentially higher mass loadings of such functionalized products, such pathways maybe have an increased importance in SOA. The experiments have been performed according to the best available standards. Basically, SOA particles were collected on filters, dissolved in water containing a radical trap (benzoic acid), and then exposed to ultraviolet light in a photochemical reactor. The OH formation rates, which are similar for both α -pinene and limonene SOA, were measured from the formation rate of p-hydroxybenzoic acid as measured using offline HPLC analysis.

Did the authors vary the ozone concentration in the chamber, or more exactly the ozone/terpene ratio, which could impact on the ROOH/ROOR ration, in order to check whether that could alter the OH production rates in SOA?

Response: We did not systematically vary the ozone-to-terpene ratio in the chamber, but this would be an interesting experiment to try in future experiments.

Figure 2 presents the photon flux inside the reactor and the SOA absorption cross section. However, I'm wondering how informative this is. In fact, wouldn't the hydroperoxide absorption be blue shifted (compared to SOA) and therefore with a quite reduced overlap with the photon flux?

Response: This is a useful point, which we now elaborate upon in the paper. We agree that the tail in the SOA absorption spectrum to long wavelengths may not arise from peroxides. However, much of the overlap between the light intensity and the cross-section is at lower wavelengths (e.g. from 300 to roughly 340 nm) where contribution from peroxides is possible. Given that carbonyls may contribute to this absorption to an unknown degree, we now add a caveat to the paper that the product yield calculation explicitly assumes that hydroperoxides represent the major adsorbing functional group but that others may also be important (section 4.2, paragraph 3).

Figure 3 presents a nicely linear behavior of the PHBA concentration as a function of time (or OH production rate), up to one hour. But what happens at longer times? In fact, a back-of-the-envelope calculation (250 μ M of SOA, 1% yield of hydroperoxide, 10⁻⁴ s⁻¹ J values) would led to ca. 10-20% of the OH precursors being consumed, so that I would expected a levelling-off of the OH production rate. Has this been observed? If this production rate is sustained over longer times, could it be that other processes are involved such as

1 photochemistry of carbonyls (as recently discussed for pyruvic acid, SOA formation, etc.)? This would may also
2 explain a red shifted absorption spectrum. In the same vein, could a chain reaction be initiated where 1,4
3 isomerization steps are taking place in the condensed phase (similarly to those occurring during
4 the formation of ELVOVs), leading to steady-state ROOH concentrations. Maybe the authors could comment on
5 that?

6

7 *Response: This is an excellent point. We did not extend the measurements beyond 1 hour observation time.*
8 *However, the reviewer is entirely correct that even for one hour and for the inferred initial first-order formation*
9 *rate of OH, we should have observed levelling off of the OH production rate if the primary photolysis of the*
10 *peroxides was the only OH production route. As we described in detail in the original version of the paper (see*
11 *Section 4.2), we cannot assess how much of the OH formation is primary and how much from secondary*
12 *processes (such as carbonyl photolysis). We now stress that the linearity of the OH production rate over the*
13 *one hour time scale may indeed be evidence for some component of the OH formation being secondary*
14 *(section 4.2, paragraph 7). We also add the possibility that 1,4-isomerizations leading to ELVOC-like*
15 *compounds may be leading to hydroperoxide formation.*

16

17 Finally, the author concluded that these processes may be important for cloud chemistry by comparing the in-
18 cloud H₂O₂ and SOA concentrations. However, the mass fluxes from the gas phase to the cloud droplets are
19 then also quite important and potentially dominating the overall OH production flux. Maybe the authors could
20 comment on that too?

21

22 *Response: Yes, the reviewer is correct that OH mass transfer from the gas phase may be important too,*
23 *increasingly so for smaller cloud droplets. The importance of this process is now mentioned in the manuscript*
24 *(section 4.2, last paragraph).*

25

26 I like very much that study and would recommend its publication with minor comments.

27

28 *Response: We would like to thank the reviewer for their useful comments.*

29

30 Minor comments

31 Page 4119: line 23, isn't a word missing in this sentence?

32

33 *Response: We think the sentence is ok as written.*

34

35 Page 4122: the indications of the "MFC" number could be somehow confusing to the reader and could be
36 removed.

1

2 *Response: We would prefer to leave the MFC number labelling, to help orient the reader to the different MFCs*
3 *used in the experiment, i.e. as indicated in the upper half of Figure 1.*

4

5

6 Reviewer 2

7

8 General

9 This is a very interesting contribution by the group of Jon Abbatt which identifies OH formation from SOA,
10 apparently for the first time. The photolytic OH production appears logical as SOA contains organic
11 hydroperoxides and particle containing SOA as well contain H₂O₂. It is deduced that rather ROOH than H₂O₂
12 causes the OH production. An absolute quantum yield of OH production is provided. A very interesting and
13 substantial contribution which clearly merits publication in ACP.

14

15 *Response: We thank the reviewer for their comments.*

16

17 Details

18 Page 7, line 15ff: It would be great if the authors could explain why they decided for the chosen technique for
19 peroxide determination as literature describes different methods, cf. page 4, lines 18/19.

20

21 *Response: The iodide method for peroxide detection (e.g. as used by Docherty et al. (2005)) measures both*
22 *ROOR and ROOH species, as well as H₂O₂. And so, it was not viewed as being as useful because much of the*
23 *response would be due to ROOR, especially at the high mixing ratios used in the chamber to generate SOA.*
24 *On the other hand, as described in the paper, the HRP-DCF assay responds to only H₂O₂ and to some*
25 *unknown degree to ROOH species also. This is a relatively easy assay to run and provides an overall measure*
26 *of hydroperoxide formation (albeit with uncertainties related to ROOH response). Another approach would*
27 *have been to use chromatographic separation and derivitization to try to identify some specific small ROOH*
28 *species, but the analytical methods for detection of high molecular weight species, as would have formed in this*
29 *case, have not been developed. In general, the standard analytical methods for peroxide detection are poor*
30 *and this is a serious limitation for firm conclusions that can be made in this field. This point is now made in the*
31 *paper (section 4.1, paragraph 1).*

32

33 Page 8, line 2.4.: Apparently, BA as a OH scavenger together with the detection of PHBA seems to be a good
34 choice when this product can only be formed when OH reacts with OH. Are there any additional pathways
35 which can lead to the formation of PHBA ? What can happen if a one-electron oxidation of the aromatic forms a
36 radical cation which then reacts with water ? Can alternative pathways for the formation of PHBA be excluded?
37 Maybe this can be discussed to some extent.

38

1 *Response: We are only aware of the formation route of PHBA via addition of OH to aromatic ring. A one-*
2 *electron oxidation of BA seems unlikely to occur given the electron-withdrawing properties of the carboxylic acid*
3 *group. In addition, this would require a very strong oxidizing agent in solution, different from OH, which seems*
4 *unlikely. We did control experiments with only light and BA, but no SOA, and we do not see any PBHA*
5 *formation.*

6

7 Page 10, line 21ff: Doesn't this discussion call for an alternative technique of peroxide determination with a
8 method which does not show such a strong sensitivity for H₂O₂ compared to ROOH ?

9

10 *Response: Absolutely, as mentioned above, this study would have been greatly strengthened by a*
11 *characterization of the different ROOH species present.*

12

13 Page 14, line 13ff: The deduction of an absolute quantum yield is great and very helpful for future modelling.

14

15 *Response: Thanks. Note that we have described the important assumptions that go into arriving at this value,*
16 *of which modelers should be aware.*

17

1 Formation of Hydroxyl Radicals from Photolysis of

2 Secondary Organic Aerosol Material

3
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8 9 Abstract

10 This paper demonstrates that OH radicals are formed by photolysis of secondary organic aerosol
11 (SOA) material formed by terpene ozonolysis. The SOA ~~aerosol~~ is collected on filters, dissolved
12 in water containing a radical trap (benzoic acid), and then exposed to ultraviolet light in a
13 photochemical reactor. The OH formation rates, which are similar for both α -pinene and
14 limonene SOA, are measured from the formation rate of p-hydroxybenzoic acid as measured
15 using offline HPLC analysis. To evaluate whether the OH is formed by photolysis of H_2O_2 or
16 organic hydroperoxides (ROOH), the peroxide content of the SOA was measured using the
17 horseradish peroxidase-dichlorofluorescein (HRP-DCF) assay, which was calibrated using H_2O_2 .
18 The OH formation rates from SOA are five times faster than from the photolysis of H_2O_2
19 solutions whose concentrations correspond to the peroxide content of the SOA solutions
20 assuming that the HRP-DCF signal arises from H_2O_2 alone. The higher rates of OH formation
21 from SOA are likely due to ROOH photolysis, but we cannot rule out a contribution from
22 secondary processes as well. —This result is substantiated by photolysis experiments conducted
23 with t-butyl hydroperoxide and cumene hydroperoxide which produce over three times more OH
24 than photolysis of equivalent concentrations of H_2O_2 . Relative to the peroxide level in the SOA
25 and assuming that the peroxides drive most of the ultraviolet absorption, the quantum yield for
26 OH generation from α -pinene SOA is 0.8 ± 0.4 . T—This is the first demonstration of an efficient
27 photolytic source of OH in SOA, one that may affect both cloudwater and aerosol chemistry.

1 **1 Introduction**

2 Given the importance of secondary organic aerosol (SOA) to both climate and air quality,
3 considerable attention has been given to studying the formation pathways and composition of
4 SOA, both in the lab and the field (Hallquist et al., 2009). However, less attention has been paid
5 to its reactive properties and how the chemical nature of the particles may change as they transit
6 through the atmosphere (Jimenez et al., 2009). If the particles become more hygroscopic, then
7 they will be wet scavenged more easily. Similarly, their resultant health effects may transform if
8 reactive functional groups are either produced or lost during processing.

9 One direction has been to address the multi-phase oxidation processes in which SOA participates,
10 primarily via oxidation by gas-phase OH radicals (George and Abbatt, 2010). The conclusions
11 from these studies are that heterogeneous exposure to OH leads to a more oxidized and
12 hygroscopic aerosol, with small amounts of mass loss occurring through fragmentation reactions
13 occurring on a timescale of a few days of equivalent OH exposure in the atmosphere.

14 A second, less explored direction for SOA processing studies has been with respect to
15 photochemical aging in the presence of ultraviolet light. In initial studies, many by Nizkorodov
16 and co-workers, it has been shown that oxidative aging can also occur, leading to the formation
17 of small molecules in the gas phase (e.g. HCHO, HCOOH, CO), rapid loss of condensed phase
18 carbonyls, and some degree of mass loss (Walser et al., 2007; Mang et al., 2008; Bateman et al.,
19 2011; Henry and Donahue, 2012; Epstein et al., 2014; Wong et al., 2014). The rates of this
20 chemistry are dependent on environmental conditions, such as relative humidity (Wong et al.,
21 2014). It is not clear from these experiments whether the aging occurs through only primary
22 photochemical reactions or whether secondary processes also occur, initiated by radical
23 production in a primary photochemical step. These photochemical aging experiments may be
24 especially important for the change in optical properties of organic aerosol, especially for
25 photobleaching of brown carbon species that absorb in the visible and near UV range (Sareen et
26 al., 2013; Lee et al., 2014; Zhong and Jang, 2014; Zhao et al., 2015).

27 To further our understanding of this photochemical aging mechanism, it is necessary to evaluate
28 the potential for oxidant production within tropospheric particles. Although it is known that gas-
29 phase OH radicals collide with particles giving rise to oxidation, probably at the surface of the
30 particle, the intrinsic sources of OH within a particle have not been well quantified. There are a

1 number of routes that OH could form (Herrmann et al., 2010). The presence of soluble iron, for
2 example, could lead to OH production through the Fenton reaction. Photochemical processes
3 have been suggested as well, primarily through analogy to chemistry occurring in cloudwater,
4 such as the production of OH through the photolysis of efficient photochemical sources such as
5 dissolved nitrate, nitrite and hydrogen peroxide.

6 In this paper we measure the formation rate of OH radicals that occurs when SOA constituents
7 are photolyzed, most likely through the photodissociation of organohydroperoxides (ROOH).
8 The presence of ROOH in SOA, especially ozonolysis SOA formed from terpenes, is likely (Ehn
9 et al., 2014). They may form via Criegee biradicals, generated when ozone reacts with a carbon-
10 carbon double bond, and also through H-abstractions that are part of chain oxidation mechanisms
11 (Crouse et al., 2013; Ehn et al., 2014). Indeed, it is likely that the molecular structures of
12 extremely low volatility organic compounds (ELVOCs) formed in the ozonolysis of α -pinene
13 consist of numerous hydroperoxide functional groups mounted on the background of ring-
14 opened, functionalized α -pinene starting material. Secondary chemistry may also occur in
15 aerosol subsequent to initial photolytic formation of radicals, producing additional photoactive
16 ROOH species.

17 A number of past studies have quantitatively investigated the association of different peroxide
18 species with SOA (Li et al., 2002; Docherty et al., 2005; Chen and Hopke, 2009a, b, 2010; Wang
19 et al., 2011; Bateman et al., 2011; Mertes et al., 2012; Mutzel et al., 2013). In a study conducted
20 by Li et al., the concentrations of H_2O_2 and ROOH formed during the ozonolysis of limonene
21 were measured in both the gas and particle phases simultaneously. It was estimated that roughly 1
22 ppb of peroxide was generated from the reaction at limonene and ozone levels relevant to indoor
23 conditions (Li et al., 2002). A study by Docherty et al. measured the yields of total organic
24 peroxides in SOA formed through the ozonolysis of α - and β -pinene, Δ -3-carene, and sabinene,
25 reporting high yields of 47-85 % of the SOA mass (Docherty et al., 2005). Chen and Hopke
26 measured peroxides associated with particles formed using α -pinene, limonene, and linalool VOC
27 precursors and measured their stability under different conditions (Chen and Hopke, 2009a, b,
28 2010), followed by the work of Wang et al. who also investigated peroxide formation and
29 stability associated with SOA formed through the oxidation of α - and β -pinene and toluene
30 precursors (Wang et al., 2011). Mertes et al. generated α -pinene SOA, measuring peroxide yields
31 of 12-34 % of the SOA mass (Mertes et al., 2012). A study by Bateman et al. measured the yields

1 of peroxides from limonene SOA, reporting a value of 2% in terms of the moles of SOA
2 collected (Bateman et al., 2011). The stability of the peroxides under photolytic conditions was
3 also evaluated, finding that there was no significant change in peroxide levels following 14 hours
4 of photolysis, probably because of the formation of smaller peroxides during photoprocessing.

5 The importance of a photochemical OH source in SOA is that the OH radical may lead to
6 oxidation processes within aerosol particles and cloudwater. In aerosol particles in particular,
7 with small aqueous volumes, the partitioning properties of volatile species such as H₂O₂ indicate
8 that little is expected to reside in the particles. As well, it is possible that other OH sources, such
9 as nitrate ions, are not fully mixed with the SOA, especially if the particle has phase separated
10 into inorganic-rich and organic-rich components. However, OH generated from SOA will be
11 well mixed on a molecular scale with other SOA materials, so able to drive oxidative processes.
12 A recent laboratory study has illustrated how OH generation within particles can lead to rapid
13 oxidation of organic constituents (Daumit et al., 2014).

14 We describe experiments where we photolyze SOA material generated in an environmental
15 chamber after it is collected and then dissolved in water. We use an aqueous radical trap, benzoic
16 acid (Klein et al., 1975; Anastasio and McGregor, 2001), to measure the OH production rate. To
17 relate OH generation rates to the composition of the SOA, we apply a standard assay (HRP-DCF)
18 to measure the peroxide content of the aerosol components (Keston and Brandt, 1965).
19 Assuming that the peroxide signal arising from the HRP-DCF assay is due to the presence of
20 H₂O₂, we compare the OH production rates from dissolved SOA to the rate from solutions with
21 corresponding concentrations of H₂O₂. We find that the OH production rates from SOA are
22 substantially higher than from the pure H₂O₂ solutions, implying that species other than hydrogen
23 peroxide – likely organohydroperoxides – are photolyzing into OH. To our knowledge, this is
24 the first quantitative evaluation of the potential for SOA material to photolyze to form OH. As
25 part of the study, we also perform detailed stability tests of the peroxides within SOA, as
26 measured with the HRP-DCF assay, both in solution and on filter, to better establish their
27 environmental relevance.

28

1 **2 Methods**

2 **2.1 SOA Collection using an Environmental Chamber**

3 An environmental chamber was used to collect SOA samples, both to evaluate peroxide yields
4 and for the photolysis experiments (see Figure 1a). The chamber is a 1 m³ Teflon bag supported
5 by a Teflon-coated frame. The bag is externally surrounded by metal panels, preventing exposure
6 to outside light. The chamber was operated in continuous mode with all flows controlled by
7 mass flow controllers. Ozone was generated by flowing purified air over a 185 nm mercury pen-
8 ray lamp, with a flow rate of 6 slpm (MFC 5, see Figure 1a). A dilution flow of air of 7 slpm
9 (MFC 4) is mixed with the ozone flow prior to being introduced into the chamber. Limonene was
10 introduced to the chamber using a 10 sccm flow of nitrogen through a headspace bubbler chilled
11 at 5 °C (MFC 1). α -pinene was introduced to the chamber through a 12 sccm flow from a custom
12 cylinder with a certified mixing ratio (320 ppm \pm 20 % α -pinene in nitrogen, Air Liquide). The
13 VOC flows were carried with a dilution flow of air of 500 sccm (MFC 2), meeting an additional
14 dilution flow of 2.2 slpm (MFC 3) before entering the chamber through a stainless steel port. The
15 total flow rate through the chamber was held at 15 slpm using a diaphragm pump (MFC 6).
16 Aerosol samples were collected on supported PTFE filters (Zefluor, Pall Life Sciences, 47 mm
17 diameter, 2.0 μ m pore size) for 2 hours, collecting an average of 185 μ g and 900 μ g of α -pinene
18 and limonene SOA, respectively.

19 The ozone levels within the chamber were periodically measured using an ozone analyzer
20 (Thermo Environmental Instruments Inc, Model 49C). Approximately 320 ppb of ozone was
21 introduced to the chamber, while excesses of 85 ppb and 140 ppb of ozone were measured at the
22 exit of the chamber during α -pinene and limonene experiments respectively. The mixing ratio of
23 limonene in the chamber was measured prior to oxidation to be 250 ppbv by a proton-transfer
24 reaction mass spectrometer (PTR-MS, Ionicon Analytik GmbH), whereas that for α -pinene was
25 also 250 ppbv as determined from flow rates from the certified cylinder. The mass loadings of
26 SOA within the chamber while collection was proceeding were roughly 100 μ g/m³ for α -pinene
27 experiments, and 500 μ g/m³ for limonene experiments, as inferred from the mass of aerosol
28 collected on the filter, the flow rate, and the collection time.

29

1 **2.2 SOA Storage and Extraction**

2 Following collection, SOA samples were either extracted immediately or else stored for stability
3 studies. To extract, filter samples were placed in a foil-covered Teflon bottle with 15 mL
4 deionized water (18 mΩ, Millipore) and placed on a shake table for 15 minutes at 420 rpm.
5 Following extraction, an aliquot of each sample was immediately prepared for analysis using the
6 HRP-DCF assay or used for photochemistry experiments.

7 To evaluate in-solution stability, extracted solutions were covered with parafilm and foil, and
8 stored in the dark at room temperature. Those for on-filter stability testing were weighed and
9 immediately placed in a sealed plastic filter holder (Analyslide Petri Dish, Pall Life Sciences).
10 For the stability studies, samples were placed either in a dark cupboard at room temperature or in
11 a sealed plastic bag and stored in a dark freezer at -20 °C. Frozen samples were brought to room
12 temperature before being removed from the filter holder to prevent the condensation of
13 contaminants onto the filter surface.

14

15 **2.3 Horseradish Peroxidase-Dichlorofluorescein Assay**

16 A stock solution of 2',7'-dichlorofluorescein diacetate (1 mM DCFHDA, C₂₄H₁₄C₁₂O₇, Sigma-
17 Aldrich) was prepared in methanol and stored at -20 °C. The DCFHDA was converted to the
18 hydrolyzed 2',7'-dichlorofluorescein (DCFH) form by adding 1.0 mL DCFHDA to 4.0 mL
19 sodium hydroxide (0.01 M, NaOH) and allowing the hydrolysis to proceed for 30 minutes at
20 room temperature. The fluorescing solution, referred to as HRP-DCF, was prepared by mixing
21 4.0 mL of DCFH with 7.0 mg of peroxidase from horseradish (HRP, Type I, Sigma-Aldrich),
22 brought to a final volume of 100 mL with pH 7.2 phosphate buffer (7.35 mM KH₂PO₄, 17.6 mM
23 Na₂HPO₄). The HRP-DCF solution was kept in amber bottles on ice until needed.

24 Hydrogen peroxide standards were freshly prepared for the calibration of each assay. A stock
25 solution (1 mM H₂O₂, made with H₂O₂ 30% wt ACS reagent, Sigma Aldrich) was prepared in
26 deionized water, used for standard dilutions ranging from 2 to 20 μM H₂O₂. Calibration standards
27 were stored in amber bottles on ice until needed. The limit of detection of the HRP-DCF assay is
28 0.1 μM H₂O₂.

1 Calibration curves were also prepared using commercial sources of t-butyl hydroperoxide
2 (Luperox TBH70X, 70% wt. in H₂O, Sigma Aldrich), cumene hydroperoxide (technical grade,
3 80%, Sigma Aldrich), and di-t-butyl peroxide (Luperox DI, 98%, Sigma Aldrich). The signal
4 responses were 97, 94, and 96 % lower, respectively, than for hydrogen peroxide. Commercially
5 available organic peroxides are those that are relatively stable. And so we conclude that the
6 HRP-DCF response will be either due to dissolved H₂O₂ or to peroxides more unstable than those
7 commercially available.

8 Assay samples were prepared by adding 250 μL of the sample with 2.25 mL HRP-DCF in
9 Teflon-capped amber vials. Samples were briefly mixed before reacting at room temperature in
10 the dark for 30 minutes. The reaction was quenched by putting vials on ice for 30 seconds, before
11 measuring the sample fluorescence. A spectrometer/fluorometer (SpectroVis Plus, Vernier) was
12 operated in fluorescence mode with a 500 nm excitation light source, measuring sample spectra at
13 523.9 nm. Data were collected using Logger Pro software (Version 3.8.2, Vernier).

14

15 **2.4 Measurement of OH Production Rates**

16 Photolysis of 50 mL volumes of SOA solutions was conducted in a photochemical reactor in
17 which a 100 mL glass vessel was situated in the center of an array of UV-B fluorescent lamps
18 (see Figure 1b). The spectrum of the lamps was measured with a spectral radiometer (StellaNet
19 Inc.) and the magnitude of the flux (see Figure 2) was calibrated by measuring the
20 photoisomerization rate of 2-nitrobenzaldehyde (for details, see Zhao et al., 2015).

21 SOA solutions were prepared by mixing equal volumes of aqueous solutions of SOA and benzoic
22 acid (BA), a known OH radical trap, resulting in final SOA and BA concentrations of 250 μM
23 and 1.0 mM, respectively, where the SOA material is assumed to have an average effective
24 molecular weight of 200 g/mole (Bateman et al., 2011). The solutions were photolyzed for one
25 hour with 2.5 mL samples taken at 30 and 60 minutes for subsequent analysis. OH production
26 rates are measured by the formation of parahydroxybenzoic acid (PHBA), measured using HPLC,
27 where all sample solutions were acidified immediately prior to injection with 2 drops of 1.0 mM
28 H₂SO₄. A 40 μM glass injection syringe was rinsed five times with deionized water and five
29 times with sample solution. Sample solutions were analyzed using a 150 mm C-18 column with
30 fixed wavelength detector at $\lambda = 256$ nm and detector range = 0.01. A 15-minute, 4-step gradient

1 elution method was employed using mobile phase composed of acetonitrile and trifluoroacetic
2 acid in deionized water.

3 PHBA forms in solution from OH reacting with benzoic acid, with a yield of 20% (Klein et al.,
4 1975; Anastasio and McGregor, 2001). Based on experiments conducted with 0.25, 0.50 and 1.0
5 mM benzoic acid, it was determined that 1.0 mM solutions trap all the OH generated. In
6 particular, more OH was trapped in SOA photolysis experiments conducted with 0.50 mM BA
7 solutions than with 0.25 mM solutions but the amount trapped in 0.50 and 1.0 mM runs was the
8 same within experimental error. Overall, the detection limit for OH production rate within the
9 SOA solutions was on the order of 1×10^{-10} M/s, as determined largely by background amounts of
10 PHBA present in the solutions without illumination.

11 Photolysis experiments were also performed with 12.5 μ M solutions of commercial organic
12 hydroperoxides, namely t-butyl hydroperoxide and cumene hydroperoxide, and hydrogen
13 peroxide.

14

15 **3 Results and Discussion**

16 **3.1 SOA Peroxide Yields and Thermal Stability**

17 A series of experiments was conducted with the HRP-DCF assay both to determine how best to
18 handle SOA samples to preserve their peroxide content and also to gain some information on the
19 nature of the peroxides present in the SOA, especially when dissolved in water. In particular,
20 HRP-DCF peroxide yields (see Table 1) from fresh SOA samples were measured immediately
21 following collection and the 15 minute aqueous extraction period. The yields have been reported
22 in three ways: 1) % mole, moles of peroxides/moles of SOA $\times 100\%$, where the molecular weight
23 of SOA is assumed to be 200 g/mole (Bateman et al., 2011); 2) % mass, mass of peroxides/mass
24 of SOA collected $\times 100\%$, where the molecular weight of peroxides is assumed to be 34 g/mole;
25 and 3) normalized yield, moles of peroxides/mass of SOA collected, where the peroxides are
26 assumed to be H_2O_2 .

27 Peroxide yields were also measured using SOA generated in a flow tube (see Supplementary
28 Information, Figure S1) with mass loadings at least 10 times higher than those generated in the
29 chamber. These results demonstrate that mass loading does not have a large effect on peroxide

1 yields in SOA, at least over the range of conditions explored. For example, the fresh yields from
2 chamber SOA were 3.1 ± 0.5 % mole for α -pinene and 5.1 ± 0.1 % mole for limonene, very
3 similar to those from SOA collected using the flow tube: 4.2 ± 0.6 % mole and 3.8 ± 0.7 % mole,
4 respectively. Uncertainties quoted reflect variability from between 3 and 7 replicates, whereas
5 we estimate absolute uncertainties are on the order of $\pm 20\%$.

6 The HRP-DCF peroxide yields from α -pinene and limonene SOA only comprise a few percent of
7 the total moles of SOA material. These values are comparable to the results reported by Chen and
8 Hopke, who also used the HRP-DCF assay to measure peroxides from SOA formed through α -
9 pinene and limonene ozonolysis (Chen and Hopke, 2009a, 2010). The studies by both Docherty
10 et al. and Mertes et al. used the iodide technique to quantify their peroxide species (Docherty et
11 al., 2005; Mertes et al., 2012). This technique is sensitive to organic peroxides (i.e. ROOH and
12 ROOR), and therefore the yields reported by these studies are considered to be the total peroxide
13 content of the SOA. The study by Bateman et al. also used the iodide method to quantify
14 peroxides, using H_2O_2 to calibrate the fluorescence response (Bateman et al., 2011). The other
15 studies using the iodide method calibrated the assay using benzoyl peroxide, an organic peroxide
16 that may have a different sensitivity to the assay than hydrogen peroxide. Finally, the study by
17 Wang et al. reported yields that were somewhat lower than the α -pinene yields in this study
18 (Wang et al., 2011). This study also used HRP as their catalyst, however they used a HPLC
19 technique to speciate the peroxides, and para-hydroxyphenyl-acetic acid was used in the place of
20 dichlorofluorescein.

21 As noted in the Methods section, the sensitivity of the HRP-DCF assay heavily favours H_2O_2
22 although a weak sensitivity to commercial organic hydroperoxides exists. A control experiment
23 was conducted in which a very high gas-phase concentration of H_2O_2 (created by bubbling 250
24 sccm N_2 through 30% H_2O_2 solution) was passed through a Teflon filter for an hour. Upon
25 extraction in water and HRP-DCF analysis, it was found that no measurable amount of H_2O_2 had
26 adhered to the filter. This indicates that the peroxides measured in this work were not in the form
27 of H_2O_2 when present in the aerosol particles, as expected from the high volatility of H_2O_2 .
28 Rather, the signal is most likely due to ROOH in the particle. These molecules may have a direct
29 response in the HRP-DCF assay, higher than the stable commercial organic hydroperoxides.
30 And, it is possible that some of the signal arises from H_2O_2 when SOA material is put into
31 solution. For example, a general class of compounds, the α -hydroxyhydroperoxides, exist in

1 equilibrium in water with hydrogen peroxide and organics containing carbonyl functional groups,
2 especially aldehydes (Zhao et al., 2013). These species can be formed through the hydrolysis
3 reaction of Criegee intermediates. Similar conclusions have been made previously (Wang et al.,
4 2011).

5 Support for the formation of some H_2O_2 in solution comes from a set of stability experiments
6 conducted both in solution and on the filter, using SOA generated in the flow tube. As shown in
7 the Supplementary [InformationMaterial](#) (see Figure S2), the stability in aqueous solutions of α -
8 pinene and limonene SOA had very similar trends following extraction. Within the first 48 hours
9 after extraction, the amount of peroxide in solution increased by approximately 50% of its
10 original yield. After 48 hours, the peroxide slowly decayed. A control experiment was performed
11 in which the Teflon filter was removed from the aqueous solution following the initial 15 minute
12 extraction period. In this sample, the same increase in peroxide yields was observed within the
13 first 48 hours following extraction. If the peroxides in the particle begin as organic
14 hydroperoxides, the increase in yield may be due to a gradual decomposition reaction to form
15 H_2O_2 within the first 48 hours. Although the total peroxide content in the extract may not be
16 changing, a larger fraction would be present in the H_2O_2 form. Since the HRP-DCF assay is very
17 sensitive to H_2O_2 , this could account for the increase in yields. We note that the increase in signal
18 in aqueous solutions is similar to that reported by Wang et al. where an increase in H_2O_2 content
19 was observed within the initial 20 hours following extraction, followed by a period of stability
20 until approximately 80 hours after extraction (Wang et al., 2011).

21 A suite of experiments was also conducted to examine the thermal stability of the peroxide
22 yields, as shown in Figure S2 as a function of filter age before extraction. At room temperature, a
23 loss of peroxide was observed with increasing filter age for both α -pinene and limonene SOA.
24 Unlike the stability at room temperature, the peroxide yields were stable when the filters were
25 stored in the freezer at $-20\text{ }^\circ\text{C}$ for up to 7 days. The loss observed at room temperature is likely
26 due to volatilization of small species, or perhaps the decomposition of species such as the α -
27 hydroxyhydroperoxides present on the filter into H_2O_2 (as discussed above), followed by
28 volatilization. At low temperature, the volatilization and reaction rates of the organic peroxides
29 are expected to be much slower than at room temperature, thus stabilizing the signal. This is in
30 accord with previous work (Chen and Hopke, 2010; Wang et al., 2011).

31

1 **3.2 OH Generation Rates from Photolysis**

2 The rates of PHBA formation from the 250 μM α -pinene and limonene SOA solutions are shown
3 in Figure 3. For each set of data, a small background signal of PHBA measured with no light
4 exposure at zero time has been subtracted from the data. The backgrounds are no larger than
5 20% of the signal at full time exposure. As well, four sets of control experiments were conducted
6 for one hour each – SOA mixed with benzoic acid in the dark, SOA on its own with light, SOA
7 on its own in the dark, benzoic acid on its own in light – to confirm that the PHBA signal
8 measured arises from SOA photolysis to form OH. In each control experiment, the change of
9 signal over an hour was negligible, no more than 10% of the PHBA signal with SOA, benzoic
10 acid and light present simultaneously. Additional control experiments were conducted to confirm
11 that BA and PHBA were photolytically stable for our conditions.

12 It is seen in Figure 3 that PHBA forms in a linear manner with time when SOA is photolyzed for
13 an hour in the presence of benzoic acid, arising from the formation of OH in solution. Both types
14 of SOA form OH with roughly the same efficiency. In the same figure are also included the
15 results for photolysis experiments conducted with 12.5 μM solutions of the two commercial
16 organic hydroperoxides and H_2O_2 . Note that the concentrations of the latter solutions are 5% of
17 the concentration of the SOA solution, i.e. roughly matching the measured peroxide yields from
18 the SOA with the HRP-DCF assay (see Table 1). Interestingly, the OH yields from the hydrogen
19 peroxide solutions are a factor of five times smaller than those from SOA, whereas those from the
20 organic hydroperoxides are more comparable, within a factor of two. This indicates that the
21 signal from the HRP-DRF assay for the SOA solutions does not arise solely from H_2O_2
22 photolysis. Instead, there must be other species in solution, likely ROOH molecules, that form
23 OH upon UV illumination.

24

25 **4 Conclusions and Environmental Implications**

26 **4.1 SOA Peroxides**

27 Although total peroxide yields have been reported previously there is considerable uncertainty in
28 their interpretation as described above, dependent in part on the methods of analysis (see Table
29 1). The assays that have been used are non-specific, with the iodide approach sensitive to both

1 ROOH and ROOR species and the HRP-DCF method sensitive to H_2O_2 and probably some
2 ROOH species. As described above, the peroxide stability studies indicate that the HRP-DCF
3 peroxide signal is stable when filters are stored frozen, likely because there is no decomposition
4 and subsequent loss of volatile species that are HRF-DCF active. As well, the solution studies
5 show that a more active species, likely H_2O_2 , is slowly formed in solution within the first 24
6 hours, perhaps from the decomposition of soluble species such as α -hydroxyhydroperoxides.
7 These molecules are known to decompose to form hydrogen peroxide and organics with carbonyl
8 functional groups (Wang et al., 2011; Zhao et al., 2013). [We note in general that methods for the](#)
9 [accurate speciation and quantification of complex ROOH species are poorly developed, and limit](#)
10 [some of the conclusions that can be made in this work and in the field in general.](#)

11 The peroxides present in the particles have potential to influence photochemical pathways, as will
12 be discussed below, but also to affect human health. SOA can be either inhaled directly or it can
13 deposit on indoor surfaces where it can become part of the semi-volatile organic matter that is
14 known to be ubiquitously present (Liu et al., 2003). For the airborne particles, peroxides
15 associated with the SOA, as one component of the general class of molecules referred to as
16 Reactive Oxygen Species (ROS), have the potential to cause oxidative stress upon inhalation.
17 Based on our work, it is expected that the peroxides exist as organic hydroperoxides in the
18 particles – and not as H_2O_2 – thus allowing them to be carried deep into the respiratory system.
19 Being volatile and soluble, it is unlikely that gas phase H_2O_2 can pass long distances into the
20 respiratory pathways. Once the particles deposit and dissolve in the lung fluid, the organic
21 hydroperoxides may decompose to form H_2O_2 , a potent ROS constituent.

22
23

24 **4.2 Photochemical Generation of OH**

25 The primary result from this work is that photolysis of SOA material generates OH in solution,
26 likely from ROOH species. In particular, the quantum yield for gas-phase t-butyl hydroperoxide
27 is unity (Baasandorj et al., 2010). As well, the effective quantum yield for OH formation from
28 H_2O_2 in solution is also close to unity (Herrmann et al., 2010; Goldstein et al., 2007).

29 For this work, to calculate the overall quantum yield of OH from α -pinene SOA peroxides we
30 first calculate the first-order rate constant (k_{OH}) describing OH formation:

1 $[\text{OH}]_t = [\text{Peroxide}]_o (1 - \exp(-k_{\text{OH}}t))$ (1)

2 where $[\text{OH}]_t$ refers to the time dependent concentration of OH and $[\text{Peroxide}]_o$ represents the
3 maximum concentration of OH that will form from peroxide photolysis at infinite time, assuming
4 that one OH radical can form from one peroxide molecule. To make this calculation, we convert
5 the PHBA formation rates in Figure 3 (i.e. the slopes of the lines-of-best-fit) into OH formation
6 rates assuming a yield of 20% of PHBA from reaction of OH with benzoic acid (Klein et al.,
7 1975; Anastasio and McGregor, 2001). The results are given in Table 2. Using Eq. (1), the rate
8 constant for OH production from α -pinene SOA photolysis is thus calculated to be $(1.4 \pm$
9 $0.4) \times 10^{-4} \text{ s}^{-1}$, where the uncertainty arises from estimated absolute uncertainties in the measured
10 OH production rate and the peroxide concentration of the α -pinene SOA solution.

11 We then express this photolysis rate constant, k_{OH} , in terms of the wavelength (λ) dependent light
12 intensity in the reactor ($I(\lambda)$), the SOA absorption cross section ($\sigma(\lambda)$) and the quantum yield
13 ($\phi(\lambda)$):

14 $k_{\text{OH}} = \int I(\lambda)\sigma(\lambda)\phi(\lambda) d(\lambda)$ (2)

15 where we have previously published the molecular absorption cross section for α -pinene SOA
16 generated in the same environmental chamber (Wong et al., 2014). Note that by doing so we are
17 referencing the quantum yield to the total concentration of peroxides in solution (i.e. assuming
18 that the OH is arising from the peroxides) and we are assuming that the absorption cross section
19 measured for SOA is determined by these peroxides in the pertinent wavelength range. [While the absorption in the long-wavelength tail is likely due to other species, peroxides are likely to contribute to some degree to the short wavelength absorption. We do not know the degree to which other functional groups, such as carbonyls, also contribute.](#)

23 By integrating this expression and equating it to the experimental k_{OH} value (i.e. $(1.4 \pm 0.4) \times 10^{-4}$
24 s^{-1}), we calculate the peroxide quantum yield for aqueous α -pinene SOA to be 0.8 ± 0.4 . This
25 value represents an average effective quantum yield, assumed to be wavelength independent, for
26 all routes to OH formation in solution. Its large value close to unity provides support that SOA
27 peroxides are indeed the source of the OH measured. Using the same approach and literature
28 values for the absorption cross section (Finlayson-Pitts and Pitts, 2000), we calculate the
29 quantum yield for OH production from H_2O_2 in our experiments to be 1.1 ± 0.4 , in agreement

1 within experimental uncertainties with values in the literature (Goldstein et al., 2007; Herrmann
2 et al., 2010).

3 We cannot determine from these data alone whether the OH is formed only in a primary step, as
4 from the photolysis of a ROOH functional group that is part of the original SOA material, or
5 whether secondary chemistry also contributes. For example, subsequent chemistry might involve:



11
12 The HO_2 that is needed in Reaction (6) can be formed by photolysis of aldehydes that are part of
13 the SOA material or from those generated in Reaction (4):



16 and potentially from the oxidation of benzoic acid. The HO_2 can then go on to form H_2O_2 (Hullar
17 and Anastasio, 2011):



19 which may generate OH upon photolysis.

20 [An indication that secondary chemistry may be occurring is that we would have expected the](#)
21 [primary OH production rate to start to level off at one hour reaction time due to the consumption](#)
22 [of hydroperoxide species for the measured initial rate constant of \$1.4 \times 10^{-4} \text{ s}^{-1}\$, if primary](#)
23 [photolysis is the only production route of OH. The fact that the production rate remains linear](#)
24 [with time may indicate a secondary source of OH. Catalytic formation of ELVOC-like](#)
25 [compounds during the OH oxidation may represent a sustained source of hydroperoxides, in](#)
26 [addition to the mechanisms outlined above.](#)

27 There are different approaches to assess the potential impact that SOA materials may have on
28 condensed phase OH production rates in the atmosphere. To start, it is important to distinguish

1 between cloudwater and aerosol environments. For the very high liquid water volumes present in
2 cloudwater, highly soluble species that are also OH sources are present in reasonably high
3 amounts. For example, H₂O₂ is present through Henry's Law solubility at the 10 to 100 μM level
4 for ambient gas phase mixing ratios of 0.1 to 1 ppbv (Sakugawa et al., 1990). The corresponding
5 concentration of SOA materials is not straightforward to estimate. Cloudwater [dissolved organic](#)
6 [carbon \(DOC\)](#) amounts range from a few mgC/L up to many tens of mgC/L in polluted
7 environments (Herckes et al., 2013). Taking 10 mgC/L as a representative value, an OM/OC
8 ratio of 2, and assuming a molecular weight of 100 g/mole for dissolved species (i.e. a
9 combination of low molecular soluble species and higher molecular weight humic-acid-like
10 molecules), this corresponds to a concentration of ~~dissolved organic carbon (DOC)~~ species on the
11 order of 200 μM. Only 10 to 50% of DOC species have been identified at the molecular level as
12 small, soluble molecules (Herckes et al., 2013), making it possible that dissolved organics from
13 SOA and other sources constitute the remaining fraction, i.e. roughly on the order of 100 μM.
14 Thus, the SOA concentrations in cloudwater may be comparable to those of H₂O₂, or even
15 higher. In terms of OH-generating efficiency, Table 2 illustrates that SOA, on a per molar basis,
16 is about 5 times less efficient than H₂O₂. However, the lower efficiency of OH production from
17 SOA as compared to H₂O₂ may be offset by higher dissolved concentrations, making the SOA an
18 important OH source in cloudwater. Confirmation of this hypothesis requires better speciation of
19 organic materials in cloudwater that arise from SOA.

20 Following this line-of-thought forward to aerosol particles, the concentrations of dissolved
21 species such as H₂O₂ will not be significantly higher than in cloudwater. However, the
22 concentrations of SOA materials will be very much larger, approaching molar values, which will
23 make the SOA much more important as a photolytic OH source.

24 From another perspective, we can compare our OH photolytic formation rates to the formation
25 rates of OH in cloud and aerosol that have been calculated, based on known concentrations of
26 constituents, known photochemistry and taking into account mass transfer from the gas phase
27 (Arakaki et al., 2013). Formation rates vary widely from values of 10⁻¹⁰ M/s in rainwater, to 10⁻⁹
28 M/s in cloud and fog, to 10⁻⁷ to 10⁻⁶ M/s in marine aerosol particles. By comparison, we observed
29 OH production rates of 10⁻⁹ M/s for our 250 μM SOA solutions. Given that 250 μM is not an
30 inappropriate DOC concentration for cloudwater conditions, especially if highly polluted
31 (Herckes et al., 2013), this shows that the source has the potential to compete with more

1 conventional OH sources, such as H₂O₂. The formation rate would be very much higher under
2 aerosol water conditions, given the high concentrations of SOA in such particles. [We note that](#)
3 [mass transfer of OH from the gas phase is also important for the overall OH flux, and can](#)
4 [compete with these condensed-phase formation pathways.](#)

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38

1 **Figures and Tables**

2 **Table 1.** Peroxide yields from fresh SOA samples (this study) and from literature reports (see
 3 text for explanation).

| α-Pinene | Detection method | Yield (% mole) | Yield (% mass) | Normalized (mole/μg) |
|-----------------------------------|-------------------------|-----------------------|-----------------------|--|
| This study – Chamber | HRP-DCF | 3.1 ± 0.5 | 0.5 ± 0.1 | $(1.6 \pm 0.3) \times 10^{-10}$ |
| Docherty <i>et al.</i> , 2005 | Iodide | -- | 47 ± 12 | -- |
| Chen and Hopke, 2009 | HRP-DCF | -- | -- | $(1.8 \pm 0.8) \times 10^{-10}$ |
| Wang <i>et al.</i> , 2011 | HRP-PHOPAA ^a | -- | -- | $(2.7 \pm 1.1) \times 10^{-11}$ |
| Mertes <i>et al.</i> , 2012 | Iodide | -- | 34 ± 4 | -- |

| Limonene | Detection method | Yield (% mole) | Yield (% mass) | Normalized (mole/μg) |
|------------------------------|-------------------------|-----------------------|-----------------------|--|
| This study - Chamber | HRP-DCF | 5.1 ± 0.1 | 0.45 ± 0.01 | $(1.42 \pm 0.03) \times 10^{-10}$ |
| Chen and Hopke, 2010 | HRP-DCF | -- | -- | $(1.6 \pm 0.1) \times 10^{-10}$ |
| Bateman <i>et al.</i> , 2011 | Iodide | 2 | -- | $\sim 1 \times 10^{-10}$ |

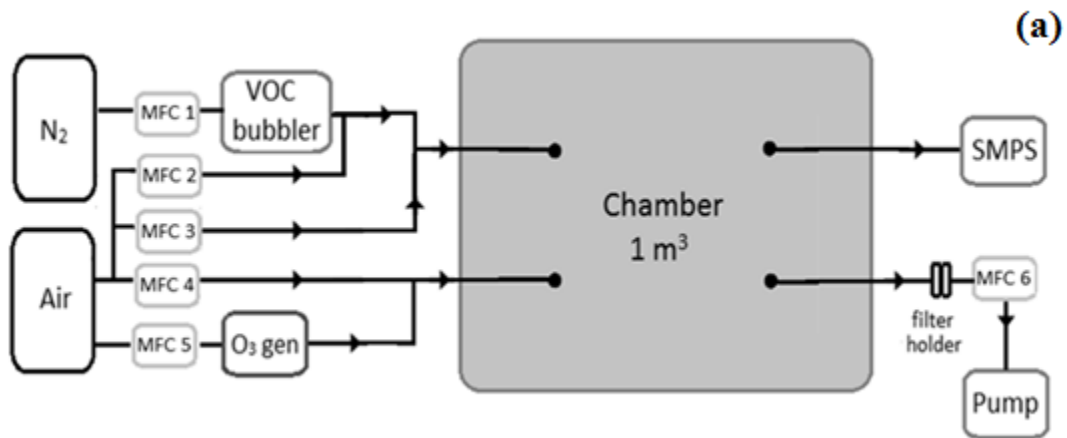
4 ^a - PHOPAA is para-hydroxyphenyl-acetic acid

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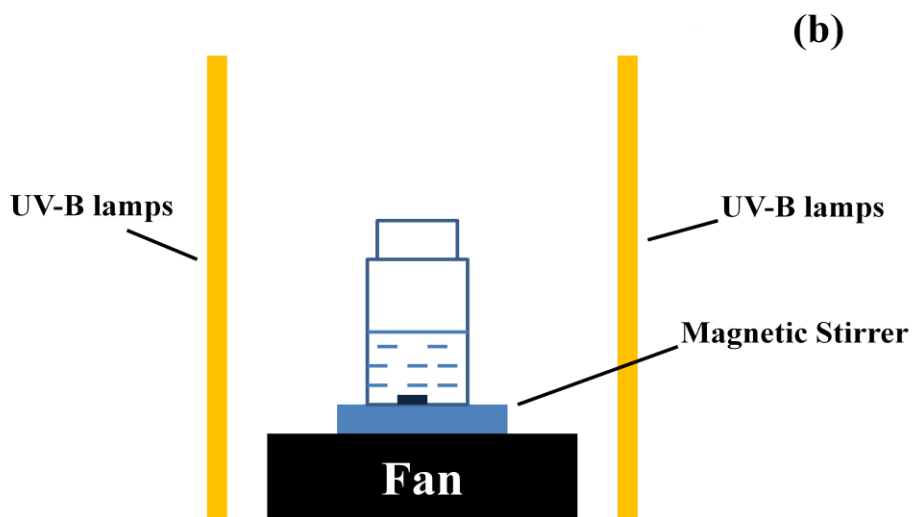
1 **Table 2.** OH radical production rates from photolysis of 250 μM solutions of SOA and 12.5 μM
2 solutions of commercial peroxides, as calculated from the data in Figure 3 using literature values
3 for the yield of PHBA from the OH oxidation of benzoic acid (see text for details).

| Sample | OH Production Rate ($\times 10^{-10}$ M/s) |
|-----------------------|--|
| α -pinene SOA | 11.0 ± 0.5 |
| limonene SOA | 9.0 ± 1.5 |
| hydrogen peroxide | 2.0 ± 0.5 |
| t-butyl hydroperoxide | 6.5 ± 1.5 |
| cumene hydroperoxide | 6.5 ± 0.5 |

4



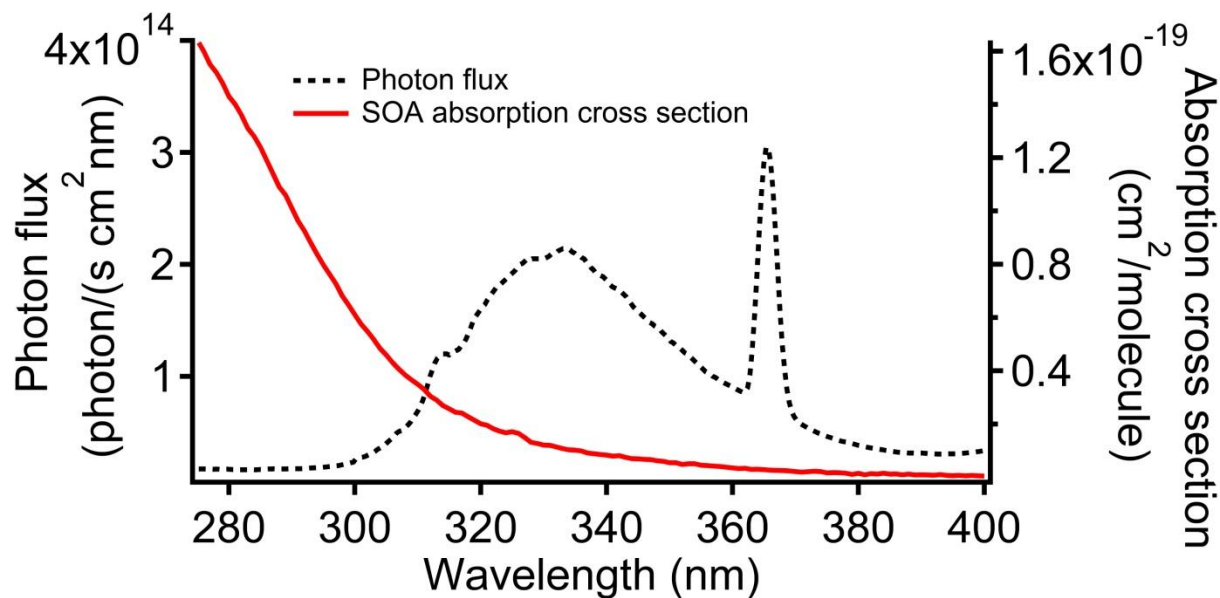
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4 **Figure 1.** Schematic diagrams of the environmental chamber (a) and the photoreactor (b).

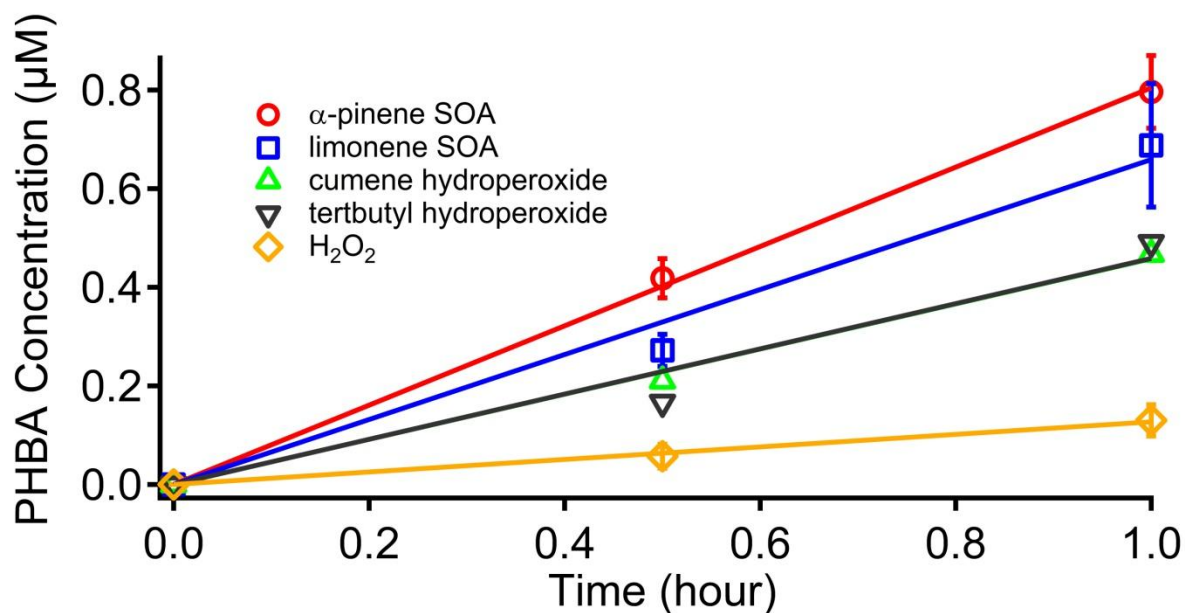


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2 **Figure 2.** Photon flux (dashed line) inside the glass vessel in the photoreactor and SOA
 3 absorption cross section from (Wong et al., 2014) (solid line).

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8 **Figure 3.** Concentrations of p-hydroxybenzoic acid (PHBA) formed by photolysis experiments
 9 for: 250 µM solutions of SOA and 12.5 µM solutions of commercial hydroperoxides. Fits are
 10 lines of best fit, forced through the origin.