

1 **Influence of aerosol acidity on the formation of secondary organic aerosol from biogenic**
2 **precursor hydrocarbons.**

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11
12 **Abstract.** Secondary organic carbon (SOC) concentrations in steady-state aerosol were measured in a series of α -
13 pinene/NO_x and one series of β -caryophyllene/NO_x irradiation experiments. The acidity of the inorganic seed
14 aerosol was varied while the hydrocarbon and NO_x concentrations were held constant in each series of experiments.
15 Measurements were made for acidity levels and SOC concentrations much closer to ambient levels than had been
16 previously achieved for α -pinene, while there are no previous measurements for SOC increases due to acidity for β -
17 caryophyllene. The observed enhancement in SOC concentration linearly increases with the measured hydrogen ion
18 concentration in air for each system. For the conditions of these studies, SOC increased by 0.04% per nmol H⁺ m⁻³
19 for α -pinene under two conditions where the organic carbon concentration differed by a factor of five. For α -pinene,
20 this level of response to acidic aerosol was a factor of eight lower than was reported by Surratt *et al.* for similar
21 series of experiments for SOC from the photooxidation of isoprene/NO_x mixtures. By contrast, SOC from β -
22 caryophyllene showed an increase of 0.22% per nmol H⁺ m⁻³, roughly two thirds of the response in the isoprene
23 system. Mass fractions for SOC particle-phase tracers for α -pinene decreased slightly with increasing aerosol
24 acidity, although remaining within previously stated uncertainties. Below 200 nmol H⁺ m⁻³, the mass fraction of β -
25 caryophyllenic acid, the only identified tracer for β -caryophyllene SOC, was constant, although β -caryophyllenic
26 acid showed a substantial decrease for acidities greater than 400 nmol H⁺ m⁻³.

1 **Introduction.**

2 Secondary organic aerosol (SOA) formation and dynamics may be important factors for the role of aerosols in
3 adverse health effects, visibility and climate change (1 – 4). Formation of SOA occurs when a parent volatile
4 organic compound is oxidized to create products that form in a condensed phase (5). The suite of major precursor
5 compounds is not fully known, though several precursor compounds are currently thought to contribute to ambient
6 SOA (6).

7
8 Recent work has shown that particle formation from isoprene (2-methyl-1,3-butadiene) as well as from other
9 biogenic hydrocarbons such as α -pinene (2,6,6-Trimethyl-bicyclo[3.1.1]hept-2-ene), and β -caryophyllene (4,11,11-
10 trimethyl-8-methylene-bicyclo[7.2.0]undec-4-ene) can contribute significantly to ambient SOA (6, 7) in areas where
11 biogenic emissions are strong. In addition, laboratory experiments have determined that aerosol acidity may also
12 play a role in increasing SOA formation yields from biogenic hydrocarbons (8 – 13). However, these studies have
13 been conducted without a measure of the aerosol acidity, and most of them typically compared a single level of
14 aerosol acidity to a base case level. As such, a more quantitative understanding of the role of particle-phase acidity
15 on SOA formation under most ambient conditions remains unavailable.

16
17 Surratt et al. (14) recently conducted a laboratory investigation of the role of acidity on isoprene SOA using
18 controlled levels of hydrogen ion air concentrations, $[H^+]_{air}$. Measured organic carbon mass concentrations were
19 found to correlate linearly with $[H^+]_{air}$ for acidic levels representative of atmospheric conditions. Moreover,
20 concentrations of the major isoprene SOA products, 2-methylthreitol and 2-methylerythritol, were also found to
21 increase with increased aerosol sulfate acidity. These results suggested that particle-phase reactions could contribute
22 to the increased isoprene aerosol yields and compound concentrations. At the present time, there have been no
23 further studies of the effect of acidic aerosol on SOA tracer compounds from other biogenic hydrocarbons.

24
25 However, that work left a number of issues for further study, summarized as follows: 1) while isoprene is the major
26 biogenic emitted into the atmosphere, other biogenics, such as monoterpenes and sesquiterpenes, can contribute
27 substantially to ambient SOA. These compounds, while having lower emission rates, typically have far higher
28 aerosol yields than isoprene. The effect of sulfate acidity on monoterpene yields have only been measured in a few

1 studies. For example, Kleindienst et al. (13) found that the SOA products from an irradiated α -pinene/ NO_x mixture
2 increased in a nonlinear fashion to about 40% at extremely high acidic sulfate levels, far higher than those
3 representative of atmospheric acidity. There are no data available for acidity effects on any sesquiterpenes. Thus,
4 fundamental data on increases in SOA yields from monoterpenes and sesquiterpenes at representative atmospheric
5 acidity levels are needed. 2) Most measurements of the effect of acidity on SOC yields have been made at organic
6 carbon concentrations one-to-two orders of magnitude higher than that found in the atmosphere. Measurements by
7 Surratt et al. (14) were made only at a single organic mass levels and the effect of aerosol mass was not tested. 3)
8 For a single H^+ air concentration increasing the relative humidity will decrease the H^+ concentration in the aerosol
9 solution. At the present time, experiments have been conducted at only a single relative humidity of 30%. Thus, the
10 effect of changing relative humidity on the SOA yields from biogenic systems needs to be determined. The present
11 paper considers the first two of these issues, as well as the influence of sulfate acidity on levels of the organic tracer
12 compounds previously measured for biogenic SOA.

13

14 In this study, secondary organic carbon (SOC) is formed from laboratory irradiations of representative C_{10} and C_{15}
15 biogenic hydrocarbons (monoterpene and sesquiterpene, respectively). Mixtures of α -pinene/ NO_x or β -
16 caryophyllene/ NO_x were irradiated in a smog chamber in the presence of seed aerosol of varying acidity. The
17 chamber was operated in a dynamic mode under conditions which permitted the SOA chemistry to remain constant
18 while the seed aerosol acidity could be changed systematically. In addition, α -pinene measurements were conducted
19 at two organic carbon mass concentrations (thus, two different organic-to-inorganic aerosol mass ratios) by varying
20 the amount of SOA generated.

21

22 **Experimental Methods.**

23 Secondary organic aerosol was generated in a 14.5 m^3 fixed-volume, Teflon-coated reaction chamber. The chamber
24 used a combination of UV-fluorescent bulbs that provided radiation from 300-400 nm with a distribution similar to
25 that of solar radiation to the extent that can be achieved with UV bulbs (13). The reaction chamber was operated as a
26 continuous stirred tank reactor having a residence time of 6 h, to produce a constant, steady-state aerosol distribution
27 which could be repeatedly sampled at different seed aerosol acidities.

28

1 To generate the biogenic reactants, two different approaches were used due mainly to the different volatilities of the
2 liquids. For α -pinene, air was bubbled through the thermostatted undiluted liquid (> 99.5% purity) and then mixed
3 with other reactants in a 4 L heated inlet manifold prior to introduction into the chamber. By contrast, β -
4 caryophyllene (> 99.5% purity) was continuously injected into a separate 250 mL heated glass manifold using a KD
5 Scientific Model KDS100 syringe pump with a 2.5mL Hamilton Gastight syringe (Hamilton Co, Reno, NV) and
6 swept into the chamber with air at a flow of 1 L min⁻¹. The NO was added from a high pressure cylinders through a
7 flow controller and was diluted with N₂ before entry into the inlet manifold. Acidified ammonium sulfate seed
8 aerosol was added to the chamber by nebulizing dilute aqueous ammonium sulfate-sulfuric acid solutions. The seed
9 aerosol stream then passed through a ⁸⁵Kr neutralizer (TSI, Model 3077, Shoreville, MN) and equilibrated to a
10 computer-controlled relative humidity of 30% in the chamber. To change the acidity of the seed aerosol, the ratio of
11 the two liquids was changed to produce a constant aerosol sulfate concentration (ca. 30 $\mu\text{g m}^{-3}$) across the range of
12 acidities used. After changing the seed aerosol solution, the photochemical mixture in the chamber was allowed to
13 reach steady-state, typically by waiting more than 4 residence times, prior to the beginning of the subsequent sample
14 collection.

15
16 Concentrations of α -pinene and β -caryophyllene in the inlet manifold and chamber were measured using a gas
17 chromatograph with flame ionization detection (Hewlett-Packard, Model 5890 GC). The NO and total NO_y were
18 measured with a ThermoElectron (Model 8840, Thermo Environmental, Inc., Franklin, MA) oxides of nitrogen
19 chemiluminescence analyzer. Temperature and relative humidity were measured with an Omega Digital Thermo-
20 Hydrometer (Model RH411, Omega Engineering, Inc., Stamford, CT). The average temperature was 24 °C.

21
22 Aerosol samples were collected on 47 mm Teflo membrane filters (Pall Corporation, Ann Arbor, MI) for
23 determination of the aerosol hydrogen ion concentration per unit volume of air ($[\text{H}^+]_{\text{air}}$), expressed as nmol H⁺ m⁻³.
24 Aerosol produced in the chamber was collected at a rate of 8 L min⁻¹ over a period of 4 h. Filters were extracted by
25 sonication for 30 min using 10 mL of distilled, deionized water in a 50 mL polypropylene vial. Once the extract
26 cooled to room temperature, the pH of each extract was measured with a Mettler-Toledo MP220 pH meter using an
27 InLab 413 pH electrode. The hydrogen ion concentrations in air ($[\text{H}^+]_{\text{air}}$) were calculated by dividing the measured
28 aqueous concentration of hydrogen ion by the volume of air collected, as described by Surratt et al. (14).

1
2 Measurements of particulate organic carbon were performed with an on-line thermal optical transmittance carbon
3 analyzer using a parallel plate, carbon strip denuder (Sunset Laboratories, Tigard, OR; 15) prior to aerosol collection
4 on the quartz filter within the instrument. Other details of operation for the carbon analyzer on the photochemical
5 reaction chamber are described elsewhere (16). The duty cycle for this measurement was 0.75 h (i.e., 0.5 h sampling
6 and 0.25 h analysis times, respectively). All particulate carbon concentrations measured during the interval of
7 aerosol filter collections were averaged for comparison with the integrated measurements of aerosol acidity.

8
9 For analysis of SOC tracer compounds, chamber effluent was collected at a rate of 16.7 L min⁻¹ for 24 hours on
10 Teflon impregnated glass fiber filters preceded by carbon strip denuder. Each filter was ultrasonically extracted
11 with 1:1 dichloromethane/methanol mixture after the addition of 20 µg of *cis*-ketopinic acid (KPA) as an internal
12 standard. The resultant extracts were dried and derivatized with *bis*(trimethyl silyl)trifluoroaccedimide (BSTFA)
13 containing 1% trimethylchlorosilane according to the method of Jaoui et al. (17). After derivatization, all extracts
14 were analyzed by a ThermoQuest (Austin, TX) GC coupled to an ion-trap MS operated in the positive chemical
15 ionization (CI) mode using the procedure of Jaoui et al. (18). Due to a lack of authentic standards, concentrations
16 were calculated assuming a response factor of unity relative to KPA. Compounds used as tracers, as well as the basis
17 for their identifications and properties, are described by Kleindienst et al. (6). Statistical analyses of measured
18 concentrations were performed using SAS v.8.0 (SAS Institute, Cary, NC).

19

20 **Results.**

21 **Influence of acidity on SOC concentrations.** Initial conditions and measured concentrations of secondary organic
22 carbon and [H⁺]_{air} of the aerosol produced are listed in **Table 1**. Measured [H⁺]_{air} ranged from 153 to 1010 nmol H⁺
23 m⁻³ and 68 to 1230 nmol H⁺ m⁻³ for the first and second series of α-pinene experiments, respectively. Likewise,
24 measured [H⁺]_{air} ranged from 112 to 1150 nmol H⁺ m⁻³ for the series of β-caryophyllene experiments. In each series
25 of experiments, higher SOC levels were observed at higher levels of acidic sulfate aerosol. For comparison, field
26 measurements of aerosol acidity as [H⁺]_{air} have been reported as high as 400 nmol H⁺ m⁻³ (19).

27

1 For the initial series of α -pinene irradiations (1.6 ppmC/100 ppbV NO), measured SOC concentrations ranged from
2 40.5 to 55.3 $\mu\text{g C m}^{-3}$. In general, higher SOC concentrations were detected with increased levels of acidic sulfate
3 aerosol from the measured $[\text{H}^+]_{\text{air}}$. The SOC produced from α -pinene increased by factor of 1.37 over the
4 experimental range of seed aerosol conditions as seen in the upper curve of **Figure 1**. The correlation between SOC
5 and $[\text{H}^+]_{\text{air}}$ is linear with an R^2 value of 0.817. Statistical parameters are given in **Table 2** with a more detailed set
6 including error estimates being given in the Supporting Information **Table S1**. Under the conditions of this first
7 series, a one nmol m^{-3} increase in $[\text{H}^+]_{\text{air}}$ led to a 0.015 $\mu\text{g C m}^{-3}$ increase in SOC. However, normalizing the
8 measured SOC concentrations to the SOC concentration from the neutral seed aerosol acidity gives a useful means
9 for comparing the effect of acidity with that from other reactive conditions or even other hydrocarbons. Thus, for
10 the α -pinene system in this series, the normalized SOC and $[\text{H}^+]_{\text{air}}$ shows a linear correlation with a slope of
11 0.00039. Thus, a one nmol m^{-3} increase in $[\text{H}^+]_{\text{air}}$ leads to a 0.039% increase in SOC for this system.

12
13 A similar analysis was performed for the second α -pinene experiment (α -pinene: 0.69 ppmC; NO: 120 ppbV) where
14 the irradiation produced a substantially reduced SOC concentration compared to the first series. In the absence of
15 acidic sulfate as seen in **Table 1**, the SOC produced in this system was reduced by a factor of five (8.0 $\mu\text{g C m}^{-3}$).
16 Under these conditions, the SOC increased by factor of 1.45 over the range of acidities employed. Again, as seen by
17 the lower curve in **Figure 1**, the increase in SOC is linear with respect to $[\text{H}^+]_{\text{air}}$ with an R^2 value of 0.874. The SOC
18 concentrations can be normalized to the neutral ammonium sulfate seed condition to show an increase of 0.044% per
19 $\text{nmol H}^+ \text{m}^{-3}$. On a normalized basis, both of these sets of α -pinene experiments show very similar increases in SOC
20 (0.039% and 0.044%) as seen in the lower curve in **Figure 2**. Thus, the fractional increase in SOC produced in these
21 α -pinene/NO_x systems appears to be independent of the SOC concentration over the range of acidities tested.
22 Moreover, it is seen that the relative increase in SOC from the α -pinene/NO_x system is considerably lower than the
23 SOC increase from a similar isoprene/NO_x irradiation (0.04% vs. 0.32%; 14).

24
25 For β -caryophyllene, measured SOC concentrations ranged from 9.97 to 34.0 $\mu\text{g C m}^{-3}$. As with the α -pinene
26 system, higher SOC concentrations were measured in the presence of increased acidic sulfate aerosol, with the
27 highest acidity tested leading to an increase in SOC of a factor of 3.4. Following the normalization procedure, the

1 measured SOC from the β -caryophyllene system showed a linear correlation ($R^2 = 0.977$) between the normalized
2 SOC and $[H^+]_{air}$, as seen in **Figure 2**. The slope of this relationship, 0.221% per $nmol H^+ m^{-3}$, is slightly smaller than
3 the 0.32% increase per unit $nmol H^+ m^{-3}$ determined for the isoprene SOC. However, if the value at the highest
4 aerosol acidity ($1147 nmol H^+ m^{-3}$) is removed from this correlation, the resulting slope equals 0.00305. At the most
5 atmospherically relevant aerosol acidities this represents a 0.30% increase in SOC per unit increase in $nmol H^+ m^{-3}$,
6 which is nearly identical to the behavior of isoprene that was reported by Surratt et al.

7
8 **Influence of acidity on measured tracer concentrations.** Kleindienst et al. (6) identified a series of nine
9 compounds, most of which were substituted dicarboxylic acids, that could serve as tracer compounds for SOC
10 generated from the photooxidation of α -pinene. The effect of acidic aerosol on the tracer concentrations (or more
11 precisely on the sum of the concentrations) was determined in these experiments. In the first series of α -pinene
12 experiments (α -pinene: 1.6 ppmC), the sum of the tracer concentrations for α -pinene SOC (Σ_9 -[tracers]) showed a
13 slight decrease with increasing aerosol acidity as found in **Table 1**. For a unit increase in $[H^+]_{air}$, the measured
14 concentration of α -pinene SOC tracers ($\mu g (\Sigma_9$ -[tracers]) m^{-3}) decreased linearly by $0.00383 \mu g m^{-3}$ per $nmol H^+ m^{-3}$.
15 The intercept of this relationship suggests the expected sum of the concentrations of the nine compounds formed in
16 the presence of fully neutralized seed aerosol is $11.7 \mu g \Sigma_9$ -[tracers] m^{-3} . The relationship indicates that the sum of
17 nine tracers should decrease by $1.5 \mu g m^{-3}$ while the aerosol acidity increased from neutral to $400 nmol H^+ m^{-3}$. The
18 two features taken together indicate that the acidity of the seed aerosol does not substantially influence the formation
19 of these tracer compounds.

20
21 The metric used by Kleindienst et al. (6) for associating the tracer concentrations to SOC formation was the mass
22 fraction (mf) obtained by dividing the sum of the measured tracer concentrations (Σ_9 -[tracers]) by the measured SOC
23 concentration for an individual experiment. For α -pinene SOC in the first series of experiments, the mass fraction of
24 the nine α -pinene tracer compounds ($\mu g \Sigma_9$ -[tracers] $\mu g C^{-1}$) showed a negative correlation with the observed $[H^+]_{air}$.
25 The calculation shows that the mass fraction of the α -pinene tracers decreased from 0.299 to 0.239 as $[H^+]_{air}$
26 increased from 0 to $400 nmol H^+ m^{-3}$. However, these values are well within the average mass fraction measured by

1 Kleindienst et al. (6) of 0.231 ± 0.111 (range of 0.081 to 0.370) for an set of α -pinene and NO_x experiments in the
2 presence of neutral seed aerosol.

3
4 The measured concentrations of the tracer compounds in the second series of α -pinene experiments (α -pinene: 0.69
5 ppmC) are consistent with the above results. The sum of the nine tracer concentrations was again only slightly
6 influenced by the changes in acidity. The slope of this relationship was not significantly different from zero at the
7 90% confidence interval (c.i.), as can be seen in **Table 1**. While the absolute tracer concentrations increased very
8 slightly with sulfate acidity, the mass fraction decreased slightly, although this decrease was also not significant at
9 the 90% c.i.. Furthermore, the minor variation in the mass fraction of the nine α -pinene tracers for an increase in
10 aerosol acidity from neutral to $400 \text{ nmol H}^+ \text{ m}^{-3}$ falls entirely within the range (0.11 to 0.51 ($\mu\text{g } \Sigma_9\text{-[tracers]} \mu\text{g C}^{-1}$)
11 reported by Kleindienst et al., (6). While lower concentrations of SOC introduce larger uncertainties, especially with
12 regard to measurement of the tracer concentrations and resulting mass fractions, the overall agreement between the
13 two experiments is excellent considering the five-fold decreased SOC concentration under neutral seed conditions.
14 From the two series of experiments taken together, acidic sulfate aerosol is expected to have little effect on the
15 calculated contribution of α -pinene SOC to ambient SOC using the mass fraction approach.

16
17 For the series of β -caryophyllene/ NO irradiations, the concentration of β -caryophyllenic acid was used as the tracer
18 species. This compound was previously identified in laboratory and field samples by Jaoui et al. (20, 21), and
19 recently used as a tracer compound for β -caryophyllene SOC (6, 7, 22). Concentrations of β -caryophyllenic acid in
20 these experiments are shown in **Table 1** (as Σ tracers for β -caryophyllene). The tracer did not show any statistically
21 significant relationship with increasing aerosol acidity at the 90% c.i.. Moreover, the concentration of the tracer
22 compound decreased by nearly a factor of 10 across the series of experiments. The mass fraction, seen in **Figure 3**,
23 was also determined and was not significantly correlated with the observed $[\text{H}^+]_{\text{air}}$ at the 90% c.i.. However, the
24 observed lower concentrations of β -caryophyllenic acid with increasing seed aerosol acidity, along with the smaller
25 mass fractions at higher acidity suggests either formation of β -caryophyllenic acid is limited at higher aerosol
26 acidities or that particle phase destruction of β -caryophyllenic acid may be enhanced at higher $[\text{H}^+]_{\text{air}}$. Additionally,

1 the neutral seed case in this β -caryophyllene experiment produced a factor of three lower mass fraction of β -
2 caryophyllenic acid than was reported by Kleindienst et al. (6).

3
4 For the isoprene system which was previously studied by Surratt et al. (14), the concentrations of the three tracer
5 compounds, 2-methylglyceric acid and the 2-methyltetrols (2-methylthreitol and 2-methylerythritol), can be
6 evaluated in a similar manner. The mass fraction of these three compounds has been used to estimate the
7 contribution of isoprene to ambient SOC (6, 7, 22). For the conditions in these experiments, the sum of these three
8 tracers increased linearly with sulfate aerosol acidity as noted by Surratt et al. (14). The intercept at zero $[H^+]_{air}$
9 represents the sum of the concentrations of the three tracer compounds ($0.184 \mu\text{g } \Sigma_3\text{-[isoprene tracers] m}^{-3}$) that is
10 expected if the seed aerosol were fully neutralized, though this value is not statistically significantly different from
11 zero and due largely to the uncertainties in the tracer measurements at the different acidities. The mass fraction of
12 the isoprene tracers is found to correlate positively with the observed $[H^+]_{air}$. The slope of the relationship (0.000222
13 $\pm 0.000071 \mu\text{g } \Sigma_3\text{-[isoprene tracers] } \mu\text{g C}^{-1}$) indicates that the mass fraction of the isoprene tracers increase is
14 expected to rise over the range of acidities examined. Despite this increase of mass fraction with acidity, the value
15 predicted for $[H^+]_{air}$ at $400 \text{ nmol H}^+ \text{ m}^{-3}$ ($0.142 \mu\text{g } \Sigma_3\text{-[isoprene tracers] } \mu\text{g C}^{-1}$) falls within the range (0.108 to 0.201
16 $\mu\text{g } \Sigma_3\text{-[isoprene tracers] } \mu\text{g OC}^{-1}$; average = $0.147 \mu\text{g } \Sigma_3\text{-[isoprene tracers] } \mu\text{g C}^{-1}$) reported by Kleindienst et al. (6).

17 18 **Discussion.**

19 Changes in the inorganic seed aerosol in the present study had no significant direct effect on the gas-phase chemistry
20 in these series of experiments (**Table S1** in supporting information), although in the case of β -caryophyllene an
21 increase in acetone was observed. As such, the increase in the SOC concentration is likely to arise only from acid-
22 enhanced particle phase reactions. Other confirmatory techniques, such as MALDI-MS and LC-MS, which have
23 provided chemical evidence for oligomer or organosulfate formation have previously helped substantiate acid-
24 enhanced SOC formation from isoprene (23,24,14), were not part of this study. As noted by Surratt et al. (25),
25 difficulty remains in isolating the reactions which dominate the observed acid effect despite the observed
26 enhancements of these biogenic SOC products, even when additional analytical techniques are used. Thus, we
27 currently must rely on macroscopic techniques such as increases in SOC or SOA.

1 The observed enhancement in the SOC for α -pinene upon increasing acidity of the inorganic seed aerosol is
2 consistent with the findings of Kleindienst et al (13) where aerosol acidity was generated from the photooxidation of
3 SO_2 . Kleindienst et al. (2006), while measuring the inorganic sulfate, did not measure aerosol acidity, so a
4 comparison can be made only by estimating aerosol acidity for those experiments. By assuming all measured sulfate
5 was sulfuric acid, hydrogen ion concentrations in air likely ranged from nearly neutral in the absence of SO_2 , up to
6 approximately $1000 \text{ nmol H}^+ \text{ m}^{-3}$ for the experiments in which SO_2 was added to the α -pinene + NO_x
7 photooxidations. While the dependence appears to be nonlinear, the results at a single acidity estimated at 400 nmol
8 $\text{H}^+ \text{ m}^{-3}$ gave a 33% increase in α -pinene SOC or a 0.0825% increase per unit $\text{nmol H}^+ \text{ m}^{-3}$. Thus, the effect of
9 aerosol acidity on SOC as estimated from Kleindienst et al. (2006) was roughly twice that measured in the present
10 study. However, considering potential differences between the use of SO_2 to generate acidity *in situ* instead of the
11 use of acidic seed aerosol, as well as the oversimplification in the assumptions in calculating aerosol acidity from
12 sulfate concentrations, these results are quite consistent. Moreover, in the α -pinene system, SOC concentrations
13 from Kleindienst et al. (13) were a factor of 2 – 20 higher than those in the present study.

14
15 The results of this study suggest that factors influencing aerosol acidity and neutralization may play a role in
16 influencing SOC formation for α -pinene and β -caryophyllene as it does for isoprene. The extent and significance of
17 these processes is currently unknown and would need to be explored through application of an air quality model.
18 However, further examination may be necessary for satisfactory integration of the results of these investigations in
19 air quality models. For the conditions of these experiments, an increase in seed aerosol acidity from neutral to 200
20 $\text{nmol H}^+ \text{ m}^{-3}$ could increase the α -pinene SOC by 8%. The corresponding increase for β -caryophyllene SOC would
21 be 44%, which is smaller than that suggested for isoprene by the laboratory investigation of Surratt et al. (14) from
22 which one might estimate an increase of 64% for the same increase in aerosol acidity.

23
24 These results show that while SOC concentrations increase when seed aerosols are more acidic, the applicability of
25 the tracer technique of Kleindienst et al. (6) for α -pinene and β -caryophyllene is not greatly affected by these
26 findings for modest changes in acidity. While there are small changes in the tracer concentrations and mass
27 fractions, these changes are not statistically significant. For α -pinene, the tracers levels do not increase at higher
28 acidity, unlike isoprene, which suggests that the increase in α -pinene SOC may occur through reaction pathways

1 that may not involve the tracer compounds, although the increase in SOC is very modest. For acidity levels below
2 $200 \text{ nmol H}^+ \text{ m}^{-3}$, β -caryophyllenic acid increases by about 50% which is fairly consistent with the SOA increase
3 over the same acidity range. This leaves the mass fraction constant over the range of weak acidities, as seen in
4 **Figure 3**. However, as seen in **Table 1** between 400 and 1150 $\text{nmol H}^+ \text{ m}^{-3}$, the β -caryophyllenic acid concentration
5 decreases by approximately a factor of ten which decreases the mass fraction by an even greater amount again as
6 seen in **Figure 3**. Thus, at higher acidities, β -caryophyllenic acid is probably a poor tracer for β -caryophyllene given
7 the large changes in the mass fraction above 400 $\text{nmol H}^+ \text{ m}^{-3}$.

8
9 The observed small changes in the α -pinene tracers with increased acidity together with the large change in β -
10 caryophyllenic acid can be rationalized by considering the compound structures for each type of tracer. For α -
11 pinene, most of the tracer compounds contributing substantially to the SOC mass fraction are substituted
12 dicarboxylic acids which are already heavily oxidized compounds and are unlikely to react further at the acidities
13 used. By contrast, β -caryophyllenic acid ($\text{C}_{14}\text{H}_{11}\text{O}_4$; 20, 21) contains an unsaturated ring, that according to the
14 observations of this study, may react at higher levels of acidity to produce a product undetected by the analytical
15 methods used here. As such, this makes this compound a less than an ideal tracer, especially under strongly acidic
16 conditions.

17
18 In addition, the changes in tracer concentrations are small relative to the uncertainties in the tracer technique, which
19 suffers from considerable uncertainty due to the simplification of replacing the complex set of chemical reactions
20 generating SOC with a laboratory-derived, single-valued mass fraction. The mass fractions, calculated using the sum
21 of tracer compounds rather than tracer profiles (commonly employed in apportionment studies of primary organic
22 aerosols) were determined from single hydrocarbon/NO irradiations under a limited set of conditions. Due to the
23 complexity of tropospheric, radical-driven chemical mechanisms, the wide assortment of inorganic and organic
24 compounds introduced into the troposphere at varying emission rates, and the broad range of possible
25 meteorological conditions, there is necessarily considerable error associated with using a single-valued mass fraction
26 for each precursor. Much of this uncertainty is already reflected in the significant standard deviations reported by
27 Kleindienst et al. (6) for the mass fractions of α -pinene (48%), β -caryophyllene (22%), and isoprene (25%). Clearly,

1 additional research is required to better understand the chemical stability of the tracers and whether additional
2 atmospheric sources are present.

3
4 While this study provides valuable information on two biogenic systems shown to form significant SOC in ambient
5 locations in the Southeast and Midwest U.S. (6, 7), two sets of conditions were studied for α -pinene, and a single set
6 for β -caryophyllene. In particular, as noted earlier, a broader range of relative humidities will be necessary to more
7 completely understand the applicability of these results to SOC formation in the atmosphere. Further experiments
8 examining the influence of aerosol acidity on SOC formation at a range of atmospherically relevant relative
9 humidities have been initiated in our laboratory.

10
11 Recent field studies have indicated that any increases in ambient SOC due to ambient acidity are probably very
12 subtle. Peltier et al. (26) examining SOA downwind of power plant plumes over the metropolitan Atlanta, GA, area
13 found no increase in water soluble organic compounds even in the presence of moderately acidic aerosol. Similarly,
14 Zhang et al. (27) in an examination of increases of SOA species in the Pittsburgh area under acidic conditions found
15 at most a 25% increase in ambient SOA that could be attributed to acid catalyzed effects. Since emissions of
16 biogenic compounds or the fraction of biogenic SOA were not specified in the study, it is difficult to directly
17 reconcile these results to ambient measurements. However, as suggested in this study where acidic levels much
18 closer to atmospheric levels are used (and as noted previously), any effects on ambient SOC due to atmospheric
19 acidity are likely to be at most 25 – 50% and not factors of two or more.

20
21 The empirical relationships between SOC mass and aerosol acidity derived from this study may prove useful for
22 regional and global scale atmospheric models within the limitations described above. Including the impact of acidity
23 on SOC formation from isoprene in an air quality model has recently been shown to decrease the gap for SOC
24 between model predictions and observations (28). These results suggest that inclusion of the influence of seed
25 aerosol acidity on SOC formation from other biogenic sources, especially from β -caryophyllene which exhibits a
26 relative increase much closer to that of isoprene, and in areas where ambient aerosol has been shown to be acidic,
27 could decrease the gap between model predictions and observations.

28

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25 Houyoux, M. Improved Treatment of Secondary Organic Aerosol in CMAQ. *Environ. Sci. Technol.* **2009**, in
26 Preparation.

- 1 **Table 1.** Experimental conditions and measured secondary
- 2 organic carbon concentrations for laboratory biogenic
- 3 hydrocarbon/NO_x photooxidation experiments.

Hydrocarbons	Reactants			Products	
	[HC]	[NO _x]	[H ⁺] _{air}	[SOC]	Σ-Trace _s
	ppmC	ppbV	nmol m ⁻³	μg m ⁻³	μg m ⁻³
α-pinene	1.6	100	153	40.5	10.8
	"	"	157	42.7	11.2
	"	"	313	39.1	11.3
	"	"	699	45.6	7.3
	"	"	1010	55.3	8.7
α-pinene	0.69	120	68	7.99	1.60
	"	"	363	7.41	1.71
	"	"	850	9.99	1.63
	"	"	1230	11.6	1.76
β-caryophyllene	0.58	200	112	9.97	0.0595
	"	"	204	14.7	0.0923
	"	"	467	21.3	0.0343
	"	"	1150	34.0	0.00561

Table 2. Parameters of Linear Correlations vs. $[H^+]_{air}$ ($nmol\ H\ m^{-3}$).

System		[SOC] $\mu g\ C\ m^{-3}$	Normalized SOC [SOC] _i / [SOC] _{neutral}	[Σ -Tracers] $\mu g\ C\ m^{-3}$	Mass Fraction [Σ -Tracers] / [SOC] $\mu g\ \mu g^{-1}\ C^{-1}$
α-pinene (1.6 ppmC)	Slope:	0.01546	0.0003953	-0.00380	-0.0001521
	Intercept:	37.431	0.9575	11.633	0.2981
α-pinene (0.69 ppmC)	Slope:	0.00348	0.0004369	<i>0.0000929</i>	<i>-0.0000572</i>
	Intercept:	7.0614	0.8833	1.6167	0.2224
β-caryophyllene (0.58 ppmC)	Slope:	0.02197	0.00220	<i>-0.0000676</i>	<i>-0.0000059</i>
	Intercept:	9.3733	0.9395	0.08068	0.00635
Isoprene* (6.75 ppmC)	Slope:	0.03905	0.00320	0.00925	0.0002216
	Intercept:	10.632	0.8716	<i>0.1837</i>	<i>0.05322</i>

Values in italics are not significant at the 90% confidence interval. More complete statistical parameters of these correlations are listed in **Table S2** of the Supporting Information. *original data from Surratt et al., (2007).

Figure 1. Relationships between SOC ($\mu\text{g C m}^{-3}$) and measured seed aerosol acidity ($[\text{H}^+]_{\text{air}} \text{ nmol m}^{-3}$) in the photooxidation of α -pinene (1.6 ppmC \bullet ; 0.69 ppmC \circ).

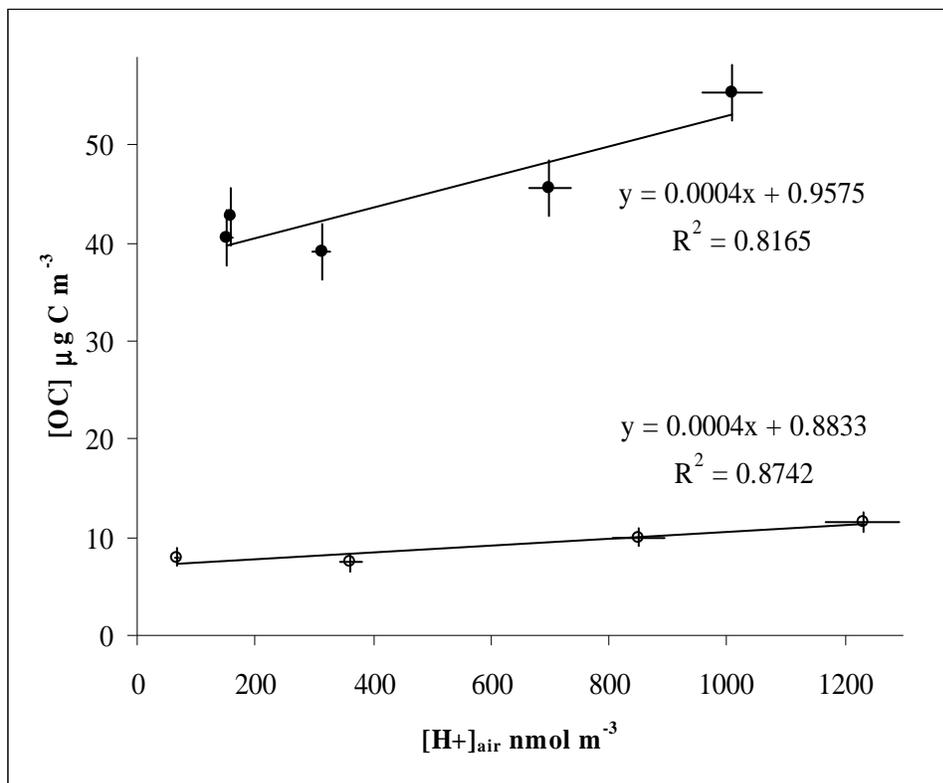


Figure 2. Relationships between the ratio of the SOC concentration at elevated acidity relative to the neutral seed case (no units) and measured seed aerosol acidity ($[H^+]_{air}$ nmol m⁻³) in the photooxidation of α -pinene (1.6 ppmC ●; 0.69 ppmC ○), β -caryophyllene (▲) and isoprene (□). Isoprene data from Surratt et al. (2007).

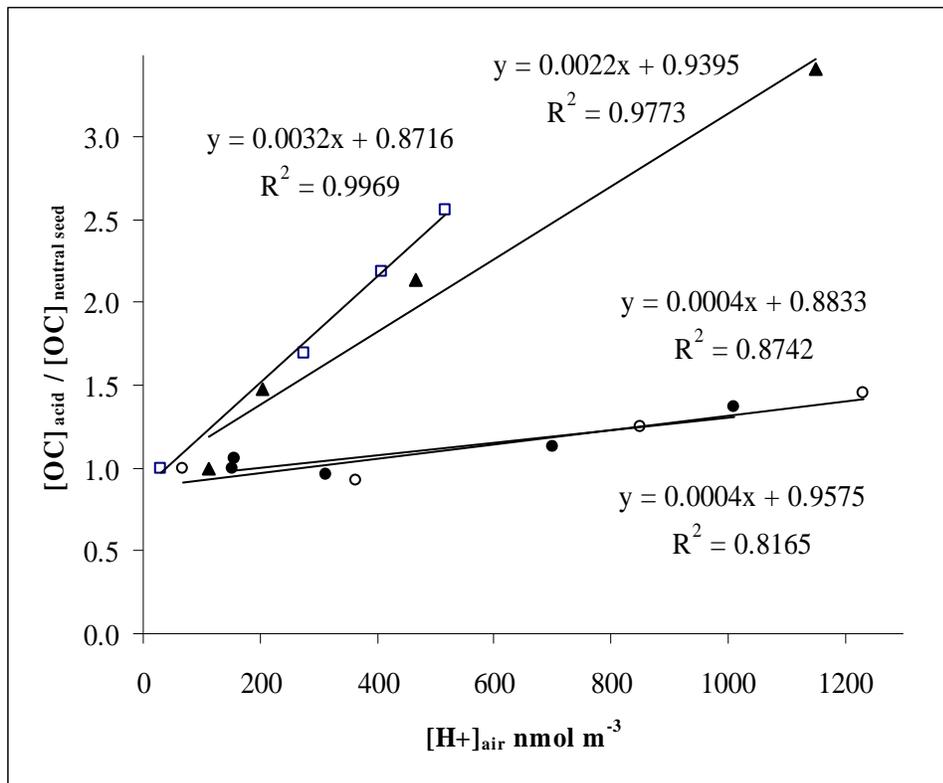
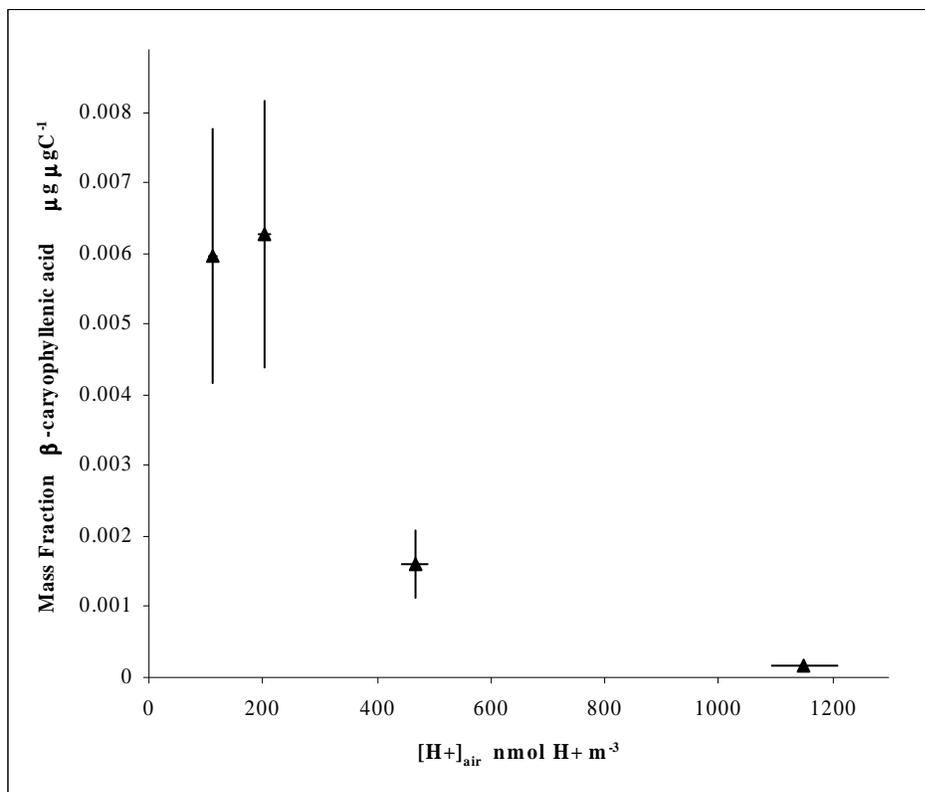


Figure 3. Relationship between the mass fractions of β -caryophyllenic acid ($\mu\text{g } \mu\text{gC}^{-3}$) and measured seed aerosol acidity ($[\text{H}^+]_{\text{air}} \text{ nmol m}^{-3}$) in the photooxidation of β -caryophyllene (\blacktriangle).



Supporting Information: Influence of aerosol acidity on the formation of secondary organic aerosol from biogenic precursor hydrocarbons.

by John H. Offenberg, Michael Lewandowski, Edward O. Edney, Tadeusz E. Kleindienst, Mohammed Jaoui

Table S1. Steady-state concentrations of gas-phase compounds.

	Seed Acidity	Δ Hydrocarbon	Ozone	NO	NO _x -NO	HCHO	CH ₃ CHO	Acetone	Glyoxal	Methylglyoxal	Pinonaldehyde
	nmol H+ m ⁻³	ppm C	ppbV	ppbV	ppbV	ppbV	ppbV	ppbV	ppbV	ppbV	ppbV
α-pinene	153	1.5	39	6	66	26	2	22	3	4	14
1.6 ppmC	157	1.6	74	2	58	40	2	35	5	6	21
	313	1.6	73	0	63	29	1	42	3	4	14
	699	1.6	49	1	59	42	3	43	5	4	23
	1010	1.6	73	1	62	40	3	34	5	5	23
α-pinene	68	0.55	1	199	3	14
0.69 ppmC	363	0.57	1	197	4	12	.	.	4	4	.
	850	0.56	1	178	3	31	.	.	7	7	.
	1230	0.56	1	150	12	19
β-caryophyllene	112	0.58	25	60	51	8	.	.	.	1	.
0.58 ppmC	204	0.58	24	61	51	9	.	.	.	4	.
	467	0.58	29	63	54	7	.	.	.	7	.
	1150	0.58	24	65	53	21

Table S2. Parameters of Linear Correlations vs. $[\text{H}^+]_{\text{air}}$ (nmol H m^{-3}).

System		[SOC]	Normalized SOC	$[\Sigma\text{-Tracers}]$	Mass Fraction
			$[\text{SOC}]_i / [\text{SOC}]_{\text{neutral}}$		$[\Sigma\text{-Tracers}] / [\text{SOC}]$
		$\mu\text{g C m}^{-3}$		$\mu\text{g C m}^{-3}$	$\mu\text{g } \mu\text{g}^{-1} \text{C}^{-1}$
α-pinene 1.6 ppmC	Slope:	0.01546 ± 0.004215	0.0003953 ± 0.0001082	-0.00380 ± 0.00162	-0.0001521 ± 0.0000410
	Intercept:	37.431 ± 2.442	0.9575 ± 0.0622	11.633 ± 0.931	0.2981 ± 0.0236
	R ² :	0.8155	0.8165	0.6479	0.8211
	<i>p</i> :	0.0357	0.0354	0.0998	0.0340
α-pinene 0.69 ppmC	Slope:	0.00348 ± 0.000933	0.0004369 ± 0.0001172	<i>0.0000929 ± 0.0000762</i>	<i>-0.0000572 ± 0.0000285</i>
	Intercept:	7.0614 ± 0.7183	0.8833 ± 0.0903	1.6167 ± 0.0586	0.2224 ± 0.0220
	R ² :	0.8746	0.8742	0.4266	0.6679
	<i>p</i> :	0.0648	0.0650	0.3368	0.1827
β-caryophyllene 0.58 ppmC	Slope:	0.02197 ± 0.00236	0.00220 ± 0.00024	<i>-0.0000676 ± 0.0000283</i>	<i>-0.0000059 ± 0.0000021</i>
	Intercept:	9.3733 ± 1.4917	0.9395 ± 0.1498	0.08068 ± 0.01786	0.00635 ± 0.00131
	R ² :	0.9774	0.9773	0.7408	0.8015
	<i>p</i> :	0.0114	0.0114	0.1393	0.1047
Isoprene*	Slope:	0.03905 ± 0.00156	0.00320 ± 0.0001271	0.00925 ± 0.00243	0.0002216 ± 0.0000717
	Intercept:	10.632 ± 0.5561	0.8716 ± 0.04535	<i>0.1837 ± 0.8659</i>	<i>0.05322 ± 0.02559</i>
	R ² :	0.9968	0.9969	0.8729	0.8269
	<i>p</i> :	0.0016	0.0016	0.0624	0.0906

Values in Italics are not significant at the 90% c.i. *original data from Surratt et al., (2007).

Table S3. Identification of SOA tracer compounds associated with precursor hydrocarbons.

Precursor	Associated Tracer Compound
α -pinene	3-acetyl pentanedioic acid
α -pinene	3-acetyl hexanedioic acid
α -pinene	3-methyl-1,2,3-butanetricarboxylic acid
α -pinene	3-Hydroxyglutaric acid
α -pinene	2-Hydroxy-4,4-dimethylglutaric acid
α -pinene	3-(2-Hydroxy-ethyl)-2,2-dimethyl-cyclobutane-carboxylic acid
α -pinene	Pinic acid
α -pinene	Pinonic acid
β -caryophyllene	β -caryophyllenic acid

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