

MIT Open Access Articles

Contrasting Reactive Organic Carbon Observations in the Southeast United States (SOAS) and Southern California (CalNex)

The MIT Faculty has made this article openly available. **Please share** how this access benefits you. Your story matters.

Citation: Heald, Colette L, Gouw, Joost de, Goldstein, Allen H, Guenther, Alex B, Hayes, Patrick L et al. 2020. "Contrasting Reactive Organic Carbon Observations in the Southeast United States (SOAS) and Southern California (CalNex)." *Environmental Science and Technology*, 54 (23).

As Published: 10.1021/ACS.EST.0C05027

Publisher: American Chemical Society (ACS)

Persistent URL: <https://hdl.handle.net/1721.1/138426>

Version: Author's final manuscript: final author's manuscript post peer review, without publisher's formatting or copy editing

Terms of use: Creative Commons Attribution-Noncommercial-Share Alike



1 Contrasting Reactive Organic Carbon Observations
2 in the Southeast United States (SOAS) and Southern
3 California (CalNex)

4 Colette L. Heald^{1,*}, Joost de Gouw^{2,3}, Allen H. Goldstein^{4,5}, Alex B. Guenther⁶, Patrick L.
5 Hayes^{2,‡}, Weiwei Hu^{2,3,*}, Gabriel Isaacman-VanWertz^{4,†}, Jose L. Jimenez^{2,3}, Frank N. Keutsch⁷,
6 Abigail R. Koss^{3,8,§}, Pawel K. Misztal^{4,‡}, Bernhard Rappenglück⁹, James M. Roberts⁸, Philip S.
7 Stevens^{10,11}, Rebecca A. Washenfelder⁸, Carsten Warneke^{3,8}, Cora J. Young^{3,**}

8
9 ¹ Department of Civil and Environmental Engineering, MIT, Cambridge, MA

10 ² Department of Chemistry, University of Colorado, Boulder, CO

11 ³ Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder,
12 CO, USA

13 ⁴ Department of Environmental Science, Policy, and Management, University of California,
14 Berkeley, CA

15 ⁵ Department of Civil and Environmental Engineering, University of California, Berkeley, CA

16 ⁶ Department of Earth System Science, University of California, Irvine CA

17 ⁷ Department of Chemistry and Chemical Biology, Harvard University, Cambridge, MA

18 ⁸ Chemical Sciences Laboratory, National Oceanic and Atmospheric Administration, Boulder

19 ⁹ Department of Earth and Atmospheric Sciences, University of Houston, Houston, TX
20 CO

21 ¹⁰ O'Neill School of Public and Environmental Affairs, Indiana University, Bloomington, IN

22 ¹¹ Department of Chemistry, Indiana University, Bloomington, IN

23 * corresponding author (heald@mit.edu)

24

25 **Keywords:** atmosphere, reactive organic carbon, OH reactivity, SOA, ozone production

26

27 **Abstract**

28 Despite the central role of reactive organic carbon (ROC) in the formation of secondary species
29 that impact global air quality and climate, our assessment of ROC abundance and impacts is
30 challenged by the diversity of species that contribute to it. We re-visit measurements of ROC
31 species made during two field campaigns in the United States: the 2013 SOAS campaign in
32 forested Centreville, AL, and the 2010 CalNex campaign in urban Pasadena, CA. We find that
33 average measured ROC concentrations are about twice as high in Pasadena ($73.8 \mu\text{gCsm}^{-3}$) than
34 in Centreville ($36.5 \mu\text{gCsm}^{-3}$). However, the OH reactivity (OHR) measured at these sites is similar
35 (20.1 and 19.3 s^{-1}). The shortfall in OHR when summing up measured contributions is 31%, at
36 Pasadena and 14% at Centreville, suggesting that there may be a larger reservoir of unmeasured
37 ROC at the former site. Estimated O_3 production and SOA potential (defined as concentration x
38 yield) are both higher during CalNex than SOAS. This analysis suggests that the ROC in urban
39 California is less reactive, but due to higher concentrations of oxides of nitrogen and hydroxyl
40 radicals, is more efficient in terms of O_3 and SOA production, than in the forested southeastern
41 U.S.

42 1. Introduction

43 Reactive organic carbon (ROC, defined as the family of all atmosphere organics in any phase,
44 other than methane¹) compounds are emitted into the atmosphere from anthropogenic, pyrogenic,
45 and natural sources²⁻⁴, whereupon they are oxidized primarily by OH, O₃, and NO₃ to form a suite
46 of products, including particulate matter (PM), ozone, and CO₂⁵. At a global scale, models suggest
47 that ROC is the dominant source for the production of these secondary species^{1,6-7}. The first two
48 of these secondary products, PM and O₃, are the principal global air pollutants, associated with the
49 premature mortality of over 8 million people each year⁸. All three of these products impact
50 climate, the last two as greenhouse gases, and organic aerosols that, through scattering and cloud
51 formation, act to counter-balance some of the warming from greenhouse gases⁹.

52 Despite the central place of ROC in tropospheric chemistry, our understanding of its abundance,
53 lifecycle, and ultimate impacts remain highly uncertain. This is largely due to the complexity of
54 ROC, which is estimated to consist of many thousands of compounds¹⁰, a small subset of which
55 are routinely measured and modeled in the atmosphere. Previous attempts to develop approaches
56 to measure total carbon mass in the gas phase¹¹⁻¹³ have lacked the precision necessary to constrain
57 a global budget. The alternative is to try to build a picture of the total mass of carbon by summing
58 up speciated measurements from more routine instrumentation. Such an approach demonstrated
59 that average observed ROC concentrations over North America spanned two orders of magnitude
60 from 4 to 456 μgCm^{-3} ¹⁴. This approach fails to identify whether carbon closure is achieved, but
61 can provide insight into the abundance of key species of ROC and their fate. Over the last two
62 decades, instrumentation has been developed to routinely detect a wider range of compounds⁵.
63 The most comprehensive effort to date to sum measurements that span the range of volatility (and
64 thus are thought to achieve mass closure), suggested that compounds that are not typically

65 measured during field campaigns contributed $\sim 1/3$ of the mass of ROC in a forested environment
66 in Colorado ¹⁵.

67 The atmospheric burden of ROC is dominated by long-lived species such as alkanes and acetone,
68 whereas reactivity is dominated by short-lived species such as isoprene ¹. Together, these
69 complementary metrics capture both those species highest in abundance and those most important
70 for chemical processing. Techniques to measure total OH reactivity (OHR, the inverse of the OH
71 lifetime) were developed over a decade ago, and are now routinely deployed in field campaigns
72 (see Yang et al. ¹⁶ for a review). OHR is typically dominated by ROC, other than in some urban
73 or remote environments where the bulk of OHR may come from inorganics or long-lived species
74 (e.g. CH₄, CO), respectively ¹⁷⁻¹⁹. When deployed alongside speciated measurements, OHR
75 measurements can be used to estimate the “missing OHR” not accounted for by routine
76 instrumentation. This missing OHR has been estimated at 30-50% in urban environments, and
77 higher (more than half missing in some cases) in forests ¹⁶. This missing OHR may represent
78 unmeasured emitted species or oxidation products.

79 While the measurements of OHR provide a powerful framework to assess chemical processing in
80 the atmosphere, it is crucial to acknowledge that the term “missing reactivity” has been applied
81 somewhat fluidly. The “missing reactivity” can be the shortfall between the contribution from
82 measured species and the total OHR measurement (as described above and used in this study), or
83 it can be the difference between modeled OHR and the total OHR measurement. The former having
84 the virtue of a direct constraint, the latter accounting for known unmeasured compounds. When
85 “missing reactivity” is assessed based solely on measurements, it reflects the suite of
86 instrumentation deployed under varying operating conditions in any given campaign (which may,
87 for example, dictate detection limits and the number of species reported). This suite can be more

88 or less comprehensive, and is certainly not consistent across campaigns, challenging our ability to
89 compare “missing reactivity” estimates. The summed reactivity also relies on assumed rate
90 constants, which may differ across studies. Furthermore, the measurement of total OHR is itself
91 operationally defined. For example, some semi-volatile or intermediate volatility compounds
92 (S/IVOC) may not be sampled through an inlet, or chemical reactions may rapidly reform OH,
93 resulting in the measured OH loss being lower than the OHR calculations that do not consider this
94 recycling. These definitional and operational factors may influence the interpretation of OHR
95 results.

96 Field observations provide a snapshot of the local atmospheric environment and can be used to
97 probe specific sources and atmospheric processes. While field campaigns are often constructed
98 with specific scientific questions in mind, the observational capital may be relevant to additional
99 future lines of inquiry. In this study, we revisit measurements made during two field campaigns
100 over the United States: the Southern Aerosol and Oxidant Study (SOAS) of 2013 and the California
101 Research at the Nexus of Air Quality and Climate (CalNex) campaign of 2010. While numerous
102 studies have explored the processes controlling atmospheric composition for each of these two
103 campaigns, this study applies a new lens to contrast the abundance and role of ROC in these two
104 very different environments.

105

106 **2. Materials and Methods**

107 The CalNex campaign was based in Southern California, a region which has undergone a major
108 air quality clean-up since the 1970s but remains under the influence of over 10 million people who
109 live in Los Angeles County ²⁰. Southern California represents a modern urban environment,
110 characterized by reductions in vehicle emissions over recent decades ²¹, with increasingly

111 important emissions from other source categories including volatile consumer products (VCPs)²².
112 Here we investigate measurements made at the Pasadena, California ground site from May 15-
113 June 16, 2010, from towers located 10m above an empty parking lot (note that the AMS had a
114 separate inlet sampling above a trailer at a height of ~6m). See Table 1 for details and Ryerson et
115 al.²⁰ for more information. In particular, we include here an expanded set of ROC measurements
116 made by gas chromatography mass spectrometry (GC-MS) based on new peak identification
117 methods²²⁻²³. A 2D-TAG was deployed during the last 4 days of the campaign, but given the lack
118 of overlap with other measurements, that data is not included here²⁴⁻²⁵. Meteorological conditions
119 varied during the CalNex campaign with both sunny, clear days and cool, overcast days²⁰.

120 SOAS was a part of the larger Southeast Atmospheric Study (SAS) of 2013²⁶. The Southeast
121 United States (SEUS) represents a mix of biogenic and anthropogenic sources, with urban centers
122 embedded in large swaths of forests. Air quality regulations have led to declines in anthropogenic
123 emissions of NO_x, SO_x, and organic aerosol in the region for more than a decade preceding SOAS
124²⁷⁻²⁸. Here we explore the measurements made at the ground site in Centreville, Alabama, from
125 June 1 to July 15, 2013. The majority of the gas phase measurements analyzed here were made
126 from a tower located 16.5 m above the ground in a clearing near the edge of a forest and well above
127 the forest canopy (Table 2). The aerosol measurements and the gas phase measurements operated
128 by the SEARCH network (see Table 2) were made nearby at ground-level near the center of the
129 clearing. This rural site is located within the Talladega National Forest, a dense mixed forest of
130 pine and broadleaf trees. The summer of 2013 was consistently cooler and rainier than average
131 conditions²⁶.

132 In this study, we revisit the online measurements of ROC, OH reactivity and related trace species
133 measured at Centreville and Pasadena. For both campaigns, all observations are first averaged to

134 an hourly time base and individual ROC species concentrations are converted into units of μgCm^{-3}
135 ³ at standard temperature and pressure (STP, 298 K, 1 atm). Given that not all instrumentation
136 operated continuously over the entirety of the campaigns, in particular for SOAS (see Table 2), we
137 only present diurnal averages or 24-hour averages for each campaign. We further note that while
138 much of the same key instrumentation was deployed at both sites, this suite and its operation are
139 not identical, and not all species are observed at concentrations above detection limits at both sites,
140 thus the list of ROC species measured/reported for the SOAS and CalNex campaigns differ.

141

142 **3. Results**

143 *3.1: Reactive Organic Carbon Mass Concentrations*

144 Figure 1 shows the average ROC mass concentrations measured for the CalNex and SOAS
145 campaigns, highlighting the contributions from different chemical families. Table S1 provides
146 average concentrations for each individual species.

147 Average ROC concentrations during SOAS total $36.5 \mu\text{gCsm}^{-3}$, with sizeable contributions from
148 primary biogenic species, in particular isoprene ($8.6 \mu\text{gCsm}^{-3}$) and monoterpenes ($4.8 \mu\text{gCsm}^{-3}$).
149 The top 10 species (isoprene, methanol, acetone, organic aerosol, ethanol, α -pinene, MVK, ethane,
150 other monoterpenes, and β -pinene) contribute 70% of the mean ROC mass concentrations
151 observed during SOAS. In contrast, CalNex ROC (average $73.8 \mu\text{gCsm}^{-3}$) is dominated by
152 anthropogenic species, including alkanes ($24.9 \mu\text{gCsm}^{-3}$) and ethanol ($9.0 \mu\text{gCsm}^{-3}$), the latter of
153 which has been highlighted as a product of VCP emissions as well as from mobile sources in the
154 Los Angeles region^{22,29}. The top 10 species measured during CalNex (ethanol, acetone, ethane,
155 propane, i-pentane, methanol, organic aerosol, propanol, propionic acid, and n-butane) make up

156 58% of the mean ROC. Overall, measured ROC is twice as abundant in the atmosphere during
157 CalNex compared to SOAS, consistent with expectations of higher ROC in a “polluted
158 environment”. When compared to a previous compilation of ROC concentrations over North
159 America¹⁴, the ROC reported at CalNex is second only to Mexico City, and exceeds ROC reported
160 in Pittsburgh in 2002. Similarly, ROC levels during SOAS are higher than all non-urban sites
161 reported in Heald et al.¹⁴, as well as the Manitou Forest site where Hunter et al.¹⁵ report average
162 ROC concentrations of 26.7 μgCm^{-3} . Despite the substantial differences in ROC abundance and
163 speciation during CalNex and SOAS, we find that organic aerosol contributes ~5% of ROC in both
164 environments.

165 Figure 2a demonstrates that ROC concentrations peak in the early afternoon for both SOAS and
166 CalNex. This maximum is driven by isoprene for SOAS (this daytime peak is dampened by the
167 night-time peak in monoterpenes), and OA, acetone, and propane for CalNex. There are modest
168 differences between weekday and weekend ROC, with slightly higher values (<10%) on weekends
169 in both Pasadena and Centreville. The slightly higher weekend concentrations of biogenics such
170 as isoprene during SOAS may be the result of lower NO_x and lower OH over the weekend
171 extending the lifetime of these primary species.

172 We note that our analysis includes only the identified and calibrated S/IVOC (semi-volatile to
173 intermediate volatility, with saturation vapor pressures $C^*=1-10^5 \mu\text{g m}^{-3}$) species measured by SV-
174 TAG during SOAS³⁰; these compounds contribute 0.25 μgCsm^{-3} . A preliminary calibration of all
175 the additional SV-TAG measured compounds with the formulas C₁₅H₂₄ and C₁₅H₂₂³¹, which
176 should provide an upper-bound on sesquiterpene concentrations, indicates that sesquiterpenes
177 contribute less than 100 ngCm^{-3} throughout the SOAS campaign. It is not clear how much
178 additional mass may be contributed by unmeasured/unidentified S/IVOC species. We also note

179 that a nitrate CIMS was deployed during SOAS which detected an additional 87 compounds which
180 make a negligible contribution to ROC mass concentrations ($0.03 \mu\text{gCsm}^{-3}$) and are not included
181 in further analysis. No online speciated S/IVOC measurements are available during CalNex.
182 Unspeciated gas-phase SVOC concentrations ($C^*=1 \mu\text{g m}^{-3}$) estimated by Ma et al.³² average 2.77
183 $\mu\text{g m}^{-3}$ (assuming an OM:OC=1.3, equivalent to $\sim 2.1 \mu\text{gC m}^{-3}$), or less than 3% of the measured
184 ROC. Zhao et al.³³ report 3-hour integrated IVOC measurements (both speciated and unspeciated,
185 equivalent to C₁₂-C₂₂ n-alkanes) made offline from Tenax glass tubes during CalNex, with a
186 campaign average concentration of primary IVOC of $6.3 \mu\text{gm}^{-3}$ (assuming an OM:OC of 1.1 for a
187 C₁₅ n-alkane this gives $\sim 5.7 \mu\text{gCsm}^{-3}$). This represents an additional 8% in ROC mass
188 concentrations. Measurement and quantification challenges for these samples are discussed in
189 Zhao et al.³³.

190

191 *3.2: OH Reactivity*

192 We translate the observed mass concentrations during CalNex and SOAS into calculated OH
193 reactivity (cOHR), which is defined here as $\Sigma(k_{\text{OH}+\text{X}_i} [\text{X}_i])$, the sum of OH reactivity contributed
194 by each species (X_i). We note that this includes not only ROC species, but also other key gas phase
195 species that react with OH (CO, O₃, NO, NO₂, SO₂, OH, HO₂). We use here reaction rate constants
196 ($k_{\text{OH}+\text{X}_i}$) at 298K, taken from JPL kinetics compilation³⁴, the IUPAC evaluated kinetic data³⁵ the
197 GEOS-Chem chemical mechanism v12.7.0 (www.geos-chem.org), or from EPI Suite³⁶ (see
198 Tables S1 and S2). As in Hunter et al.¹⁵, we make no effort to adjust reaction rates for ambient
199 temperatures during SOAS and CalNex; this is reasonable for SOAS where average temperatures
200 are similar to 298K, but likely leads to a slight overestimate of cOHR at night during CalNex when
201 temperatures drop to $\sim 288\text{K}$. Aerosols are not expected to contribute significantly to OHR. For

202 example, following equation 3.38 of Seinfeld and Pandis ³⁷, we calculate that under moderately
203 polluted conditions ($50 \mu\text{gm}^{-3}$, assuming a mean diameter of 200nm) the upper-limit first order
204 rate coefficient for OH loss to particles (given an average molecular velocity of OH of 609 ms^{-1}
205 and assuming an upper limit for the uptake coefficient of 1) is 0.23 s^{-1} , equivalent to $\sim 1\%$ of the
206 measured OHR during CalNex and SOAS (see below). It is therefore reasonable to neglect the
207 aerosol contribution to OHR during these campaigns.

208 Figure 3 shows the average cOHR for CalNex and SOAS. The total cOHR for SOAS is 16.6 s^{-1} ,
209 with a large contribution of 9.4 s^{-1} from a single species, isoprene, and a further 0.7 s^{-1} from its
210 immediate oxidation products MVK and methacrolein. Monoterpenes contribute an additional 2.9
211 s^{-1} . Over 85% of cOHR at the SOAS site is from ROC species, largely biogenics. By contrast, the
212 average cOHR during CalNex (13.9 s^{-1}) is dominated by NO_x (4.7 s^{-1}), with ROC species
213 contributing 51% of the reactivity. Despite the urban nature of this site, isoprene remains the single
214 largest ROC contributor to reactivity during CalNex (0.9 s^{-1}), though the amount is an order of
215 magnitude lower than for SOAS. Washenfelder et al. ³⁸ noted that oak and eucalyptus trees upwind
216 of Pasadena likely represent a local biogenic source during CalNex. The second most important
217 individual ROC contributor to reactivity during CalNex is acetaldehyde, a product of ethanol and
218 alkene oxidation, concentrations of which have increased in ambient air, including over California,
219 in recent decades due to ethanol fuel additives and VCP emissions ^{22, 29}. In general, we find that
220 many of the measured ROC species that contribute to mass concentrations during CalNex (Figure
221 1) do not substantially impact calculated reactivity (Figure 3), suggesting that OH loss in southern
222 California is not primarily driven by anthropogenic (or biogenic) ROC emissions. The reactivity
223 per mass concentration of ROC is more than 4 times higher for SOAS than for CalNex (0.10 for

224 CalNex vs 0.42 for SOAS). However, we note that despite all of these differences, the total cOHR
225 estimated for CalNex and SOAS are quite similar.

226 Figure 2b shows that the diurnal cycle for cOHR is even more muted during CalNex than ROC
227 concentrations shown in Figure 2a, given that cOHR from highly-reactive alkenes peaks at night
228 ³⁹, compensating for the daytime peak driven by isoprene and acetaldehyde. The large contribution
229 of isoprene to reactivity during SOAS enhances the diurnal cycle observed in ROC concentrations
230 at that site (Figures 2a and 2b). Weekday and weekend differences in cOHR are negligible (not
231 shown).

232 During both SOAS and CalNex measurements of total OHR were deployed using laser-induced
233 fluorescence techniques and both datasets were corrected for chemical interferences ⁴⁰⁻⁴¹. Thus,
234 these measurements and the cOHR compiled here provide a critical opportunity to contrast the
235 “missing OH reactivity” at two very different sites in the United States. However, as discussed in
236 Section 1, operational differences in measured OHR may remain. Measured OHR is similar at
237 Pasadena and Centreville, with average values of 20.1 and 19.3 s⁻¹, respectively. Figure 3 shows
238 that 31 and 14% of the measured reactivity is not accounted for by the cOHR (6.3 s⁻¹ for for CalNex
239 and 2.6 s⁻¹ for SOAS). The “missing reactivity” for SOAS is well within the uncertainty of the
240 OHR measurement and rate constants used to estimate cOHR, and may indicate that all the
241 reactivity is accounted for at this site. Kaiser et al. ⁴² suggest that in their analysis missing OHR
242 during SOAS may be attributed to unmeasured primary emissions (e.g. sesquiterpenes). Some
243 studies⁴³⁻⁴⁴ (though not all⁴⁵) have shown that sesquiterpene concentrations peak at night this may
244 offer an explanation for Figure 2b which shows a nighttime peak in missing OHR, with little
245 missing OHR in daytime. However, while sesquiterpene measurements made by SV-TAG during
246 SOAS (see Section 3.2) show a pronounced nighttime peak, concentrations were substantially

247 lower than monoterpene concentrations, consistent with previous studies that suggest that
248 sesquiterpene concentrations are relatively low outside of the forest canopy⁴⁴, and thus unlikely
249 to fully explain the missing OHR at night. In Pasadena, however, there may be a larger reservoir
250 of unmeasured ROC species (or inorganics). As shown in McDonald et al.²², the ROC
251 measurements during CalNex (including the expanded suite of species measured by GC-MS, see
252 Table 1) capture much of the reactivity from VCP sources, however they also suggest that
253 unmeasured ROC species from VCP sources could contribute additional OHR (see Table S8 of
254 that study). An analysis of comprehensive ROC measurements at Manitou Forest in Colorado
255 during 2011 suggested that previously unmeasured S/IVOCs compounds, contributed ~25% of the
256 OHR at that site. S/IVOC compounds may also make an important contribution to OHR in
257 Southern California and in the SEUS. However, the subset of SVOCs measured by SV-TAG
258 during SOAS contribute only 3% (0.56 s^{-1}) of the cOHR. Applying OH reaction rates to the average
259 primary IVOCs concentrations measured offline during CalNex (see Tables S5 and S7 of³³), yields
260 an additional 0.33 s^{-1} of cOHR, suggesting that these IVOC contribute only ~5% of the missing
261 OHR during CalNex. The missing OHR during CalNex appears to be consistent throughout the
262 day (Figure 2b), and therefore is not suggestive of a clear local primary emission signature.

263

264 **3.3: Ozone Production**

265 We can use the estimated cOHR to explore ozone formation associated with ROC during CalNex
266 and SOAS. Ozone formation is initiated by the reaction of peroxy radicals with NO, as described
267 by Jacob⁴⁶ and applied in Sinha et al.⁴⁷:

$$268 \quad P_{\text{O}_3} = 2k[\text{RO}_2][\text{NO}] \quad (1)$$

269 with the resulting NO₂ photolyzing to produce ozone. If we assume the rapid cycling of radicals
270 in a polluted atmosphere:

$$271 \quad k_{\text{OH}+\text{ROC}}[\text{ROC}][\text{OH}] = k[\text{RO}_2][\text{NO}] \quad (2)$$

272 therefore,

$$273 \quad P_{\text{O}_3} = 2\text{OHR}_{\text{ROC}}[\text{OH}] \quad (3)$$

274 Figure 2c shows the estimated diurnal pattern in P_{O₃} based on equation 3 for both CalNex and
275 SOAS. As described in Section 3.2, CalNex is characterized by much lower ROC reactivity (7.1
276 s⁻¹) than SOAS (15.5 s⁻¹), however OH concentrations during CalNex are about a factor of four
277 higher than during SOAS, with mid-day peaks of 4x10⁶ molec cm⁻³ and 1x10⁶ molec cm⁻³,
278 respectively. Thus the resulting ozone production rate is about 50% higher during CalNex, with
279 peak early afternoon values of ~9 ppb hr⁻¹, compared to ~6 ppb hr⁻¹ for SOAS. We note that there
280 is little weekday-weekend difference in measured OH during CalNex in contrast with estimated
281 OH concentrations based on simple-steady state models⁴⁸; constraining these estimates to
282 measured OHR yields better agreement with measured OH⁴¹.

283 Figure 2d shows the mid-day increase in ozone concentrations observed during CalNex and SOAS.
284 CalNex is characterized by ~40 ppb increase over 7 hours, with a more modest increase of ~15
285 ppb over the same time interval for SOAS. These daytime increases likely reflect local production
286 integrated over the immediate upwind region, as well as the mixing down of the residual layer
287 from the previous day. The diurnal profile of typical ozone deposition velocities for urban and
288 forested land classes⁴⁹ produce a small sink of 0.3-0.6 ppb hr⁻¹ peaking mid-day; this is negligible
289 compared to the daytime ozone production rates calculated at Pasadena and Centreville. The
290 observed ozone increase in Southern California is roughly consistent with the ozone production

291 rate calculated using equation 3, however this relationship appears to substantially overestimate
292 the observed daytime increase in ozone in the SEUS. This is true even when the calculated ozone
293 production rate is tempered by the estimated ozone dry deposition flux over forested land.

294 The lower ozone formation during SOAS is the result of NO_x limitations at this forested site. This
295 can be illustrated by a metric ($\vartheta = \text{OHR}_{\text{NO}_x} / \text{OHR}_{\text{ROC}}$) suggested by Kirchner et al.⁵⁰ to assess ozone
296 production regimes. The observations at CalNex produce an average ϑ of 0.52 which is well above
297 the 0.2 boundary to indicate VOC-limitation. Average early afternoon ϑ is lower on weekends due
298 to lower NO, but stays above 0.35 consistent with VOC-limitation, whereas using an alternate
299 metric Griffith et al.⁴¹ suggest that observations during afternoons on weekends are NO_x-limited
300 during CalNex. We note that if we assume that all of the missing OHR comes from unmeasured
301 ROC species, the re-calculated ϑ briefly dips below the 0.2 boundary on weekend afternoons
302 suggesting a transition from VOC to NO_x limited. Conversely, the average ϑ at SOAS exhibits a
303 strong diurnal cycle where ϑ drops below the NO_x limitation boundary (0.01) from 9am-4pm on
304 average (on both weekday and weekends), and increases over night (campaign average ϑ of 0.012).
305 Thus, despite very high reactivity from ROC in the SEUS, the lower daytime OH and NO_x depress
306 the ozone production potential of these organics during SOAS.

307 We note that the OHR from IVOC during CalNex discussed in Section 3.2 could contribute an
308 additional ~5% to the ozone production rate calculated using equation 3; well within the
309 uncertainty associated with estimating the ozone production rate from its observed daytime
310 increase in Figure 2c. However, if the remaining missing OHR during CalNex were attributed to
311 ROC, the resulting calculated ozone production would substantially exceed the observed rise in
312 ozone concentrations. This suggests that either (1) some of the missing OHR may be the result of
313 non-ROC species, or (2) conditions during CalNex may not be uniformly NO_x-saturated (as

314 assumed in equation 3), reducing ozone production efficiency, or (3) that there are larger,
315 unaccounted for, sinks of ozone during CalNex. Deployment of instrumentation at an upwind site,
316 as well as an O₃ reactivity instrument ⁵¹, alongside the suite of instrumentation deployed in
317 Pasadena during CalNex, could provide further insight into the role of ROC in controlling ozone
318 concentrations in the LA basin.

319

320 **3.4: SOA Formation Potential**

321 ROC oxidation leads to the formation of secondary organic aerosol (SOA), a substantial and
322 sometimes dominant contributor to fine particulate matter ⁵². The vast potential number of
323 precursors which produce SOA at varying timescales, coupled with gaps in our understanding of
324 this chemistry, combined with the addition of primary organic aerosol, complicate any assessment
325 of regional SOA formation. Here we explore the instantaneous SOA formation potential of ROC
326 at Centreville and Pasadena.

327 To estimate the SOA formation potential (the potential amount of SOA formed from the measured
328 precursors), we multiply mass concentrations of ROC with carbon yields (Y_C) based on the
329 approach of Hunter et al. ¹⁵. A subset of yields for more well-studied SOA precursors (aromatics,
330 isoprene, monoterpenes) are taken from Hunter et al. ¹⁵ based on chamber studies. The remaining
331 yields are estimated based on the vapour pressure of each species taken from EPI Suite ³⁶,
332 converted to the saturation vapor pressure (C*), and then to yield using the functional form of
333 Donahue et al. ⁵³ (as given in caption of Table S1). The resulting yields vary from <1% to 19% (see
334 Table S1). We employ this approach as it allows us to systematically estimate the SOA yields for
335 all considered species, however, we note that the uncertainty on these estimated yields is high;
336 Hunter et al. ¹⁵ suggest a factor of three. While a detailed review of all estimated yields is beyond

337 the scope of this study, we note that the systematic application of the relationship between vapor
338 pressure and carbon yield⁵³ leads to large estimated yields for alcohols ($Y_C=3-5\%$); however, there
339 is no laboratory evidence to date to suggest that the oxidation of alcohols yields appreciable SOA,
340 in fact some previous CalNex studies assume that the SOA yield from alcohols is zero^{22,54}. Thus,
341 in what follows, we assume zero SOA potential for alcohols (SOA potentials for these species as
342 calculated using the approach of Donahue et al.⁵³ are given in brackets in Table S1). In addition,
343 we note that the SOA potential metric as used here only captures SOA formed in the gas-phase.

344 Figure 4 summarizes the SOA formation potential at Pasadena and Centreville. CalNex SOA
345 formation potential is $1.46 \mu\text{gCsm}^{-3}$, with large contribution from aromatics ($0.45 \mu\text{gCsm}^{-3}$, $Y_C=2-$
346 11%); propionic acid, toluene, and m-p xylenes have the highest SOA potential. Applying the SOA
347 yields from Zhao et al.³³ (see their Tables S5 and S7) to the reported average mass concentrations
348 and assuming an OM:OC of 2 for the SOA formed would give an additional $0.80 \mu\text{gCsm}^{-3}$ from
349 IVOC. This is equivalent to more than half of the SOA formation potential of all the online
350 measured species, consistent with the major role that IVOCs play in SOA formation in southern
351 California, as suggested by Hayes et al.⁵⁴.

352 The SOA formation potential at SOAS ($0.90 \mu\text{gCsm}^{-3}$) is a little more than half of that during
353 CalNex. More than half of this is from isoprene and monoterpenes (0.15 and $0.36 \mu\text{gCsm}^{-3}$). The
354 dominance of monoterpene SOA is consistent with the analysis of observed SOA concentrations
355 in the SEUS by Zhang et al.⁵⁵. This is considerably less than the SOA formation potential of 1.4
356 μgCsm^{-3} reported for a ponderosa forest site¹⁵, however approximately half of the SOA formation
357 potential assessed at that site was estimated to come from previously unmeasured S/IVOCs, some
358 of which are not measured during SOAS. Sesquiterpenes, with their high SOA yields⁵⁶, could also
359 contribute to SOA in this region, however, as noted in Section 3.2, concentrations of these species

360 are small during SOAS and even assuming 100% yield would contribute less than $0.1 \mu\text{gCsm}^{-3}$ to
361 the SOA potential. Using an apportionment analysis of FIGAERO-CIMS, Lee et al.⁵⁷ also rule out
362 any substantial contribution of sesquiterpene SOA to OA measured during SOAS.

363 SOA formation potential cannot be directly compared to the observed OA concentrations which
364 reflect contributions from up-wind (both primary and secondary), as well as multi-phase
365 chemistry. However, for context, we note that observed OA concentrations from CalNex (3.37
366 μgCsm^{-3}) and SOAS ($1.84 \mu\text{gCsm}^{-3}$) are both more than double the instantaneous SOA formation
367 potential estimated at these sites. Furthermore, oxidation flow reactor (OFR) measurements during
368 CalNex report an average of $10.5 \mu\text{gsm}^{-3}$ ($\sim 5.25 \mu\text{gCsm}^{-3}$)⁵⁸, $\sim 1.9 \mu\text{gCsm}^{-3}$ above ambient loading.
369 Our estimated SOA potential (including IVOCs) of $2.3 \mu\text{gCsm}^{-3}$, is similar, but the OFR constraint
370 may suggest that our yields for SOA potential are overestimated. Similar analysis of the SOAS
371 OFR measurements suggest an enhancement over ambient of $1.2 \mu\text{gCsm}^{-3}$, $\sim 30\%$ higher than our
372 estimated SOA potential. Thus the application of estimated yields based primarily on vapor
373 pressures (with the exception of aromatics and primary biogenics, for which we follow Hunter et
374 al.¹⁵) may overestimate SOA potential in an urban environment and underestimate SOA potential
375 in a biogenic environment. Further exploration of how estimated SOA potential compares with
376 OFR measurements at various sites, particularly with better constrained contributions from
377 S/IVOCs, may provide constraints on assumed SOA yields.

378

379 **4. Discussion**

380 Reactive organic carbon (ROC) is a key fuel for atmospheric chemical transformations and the
381 production of secondary pollutants. In this study we contrast the mass concentrations, OH

382 reactivity, and SOA formation potential of ROC in two very different environments in the United
383 States: Southern California and the SEUS. This comparison allows us to explore how these simple
384 metrics can be used to characterize and contrast the local atmospheric environment. We find that
385 the average ROC mass concentration during CalNex is twice that observed during SOAS, with the
386 former dominated by anthropogenic species, and the later characterized by biogenics. Despite
387 these considerable differences, we find that the OHR is similar at the two sites; however, only
388 about half of the cOHR observed during CalNex comes from organics. Thus, the ROC measured
389 in Southern California is, on average, about a factor of 4 less reactive with OH than that in the
390 SEUS. This could translate to much higher ozone production in the SEUS, however NO_x-
391 limitation and lower OH concentrations depress ozone production rates compared to Southern
392 California. In addition, the lower OH in the SEUS extends the isoprene lifetime, increasing the
393 observed reactivity⁵⁹. Finally, the SOA formation potential for all the ROC species measured in
394 CalNex is almost twice that estimated for SOAS, largely driven by aromatics. Thus we conclude
395 that the ROC species in Southern California are more abundant, less reactive, and (due to the
396 presence of elevated NO_x and OH) more efficiently produce ozone and SOA than the ROC species
397 present in the SEUS.

398 This analysis is based on a bottom-up characterization of ROC, by adding up the contributions of
399 measured individual species. Given the absence of any top-down total carbon measurement, we
400 cannot assess the degree of mass closure obtained with this suite of measurements. However, the
401 total OHR measurements from these campaigns suggest that the bottom-up tally of cOHR is short
402 by 14% (SOAS) and 31% (CalNex). This missing OHR likely represents some combination of
403 missing primary species (e.g. sesquiterpenes and oxygenated VCP emissions) and unmeasured
404 secondary products. We highlight throughout the potential role of intermediate volatility species,

405 using as an example the offline measurements made during CalNex³³. While these species likely
406 make a modest contribution to mass concentrations, OHR, and ozone formation, they may well
407 contribute more than a quarter of the SOA formation potential in that region. This illustrates the
408 importance of characterizing the role of IVOC species in PM formation, particularly in urban
409 environments. For SOAS, the missing reactivity is limited to the nighttime and is much more
410 modest, perhaps within the uncertainty of the measurements. This raises the interesting question
411 of how measurement and reaction rate uncertainties may dictate the limit of how OHR
412 measurements can be used to constrain ROC.

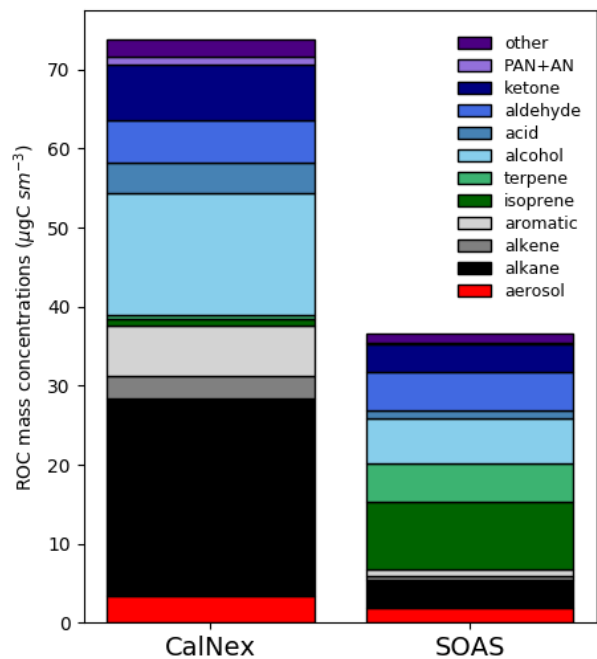
413 Of the 112 different organic species measured during CalNex and SOAS, many are not routinely
414 reported in field campaigns or simulated in models, however the importance of these constituents
415 varies with location. For example, the chemical mechanism used in the GEOS-Chem global model
416 represents the majority of the species reported during SOAS, and could represent (individually or
417 lumped) 87-95% of the mass, OHR, and SOA formation potential reported here. This same
418 chemical mechanism could represent 85% of the mass concentrations measured during CalNex,
419 but only 80% of the SOA formation potential and 76% of the OHR. Thus, the more diverse suite
420 of anthropogenic compounds emitted in urban environments may be challenging to represent in
421 current models. The number of species routinely detected by new instrumentation deployed in the
422 field continues to grow (e.g.⁶⁰), and as future campaigns likely report a greater fraction of the ROC
423 in the atmosphere, it may become more challenging for simplified models to represent this
424 diversity and the resulting chemistry.

425 The results presented here represent a snapshot in time: 2010 in Southern California, and 2013 in
426 the SEUS. Anthropogenic emissions of many key pollutants and precursors continue to decline in
427 the United States, driven by the Clean Air Act. Thus the emissions of ROC, as well as the chemical

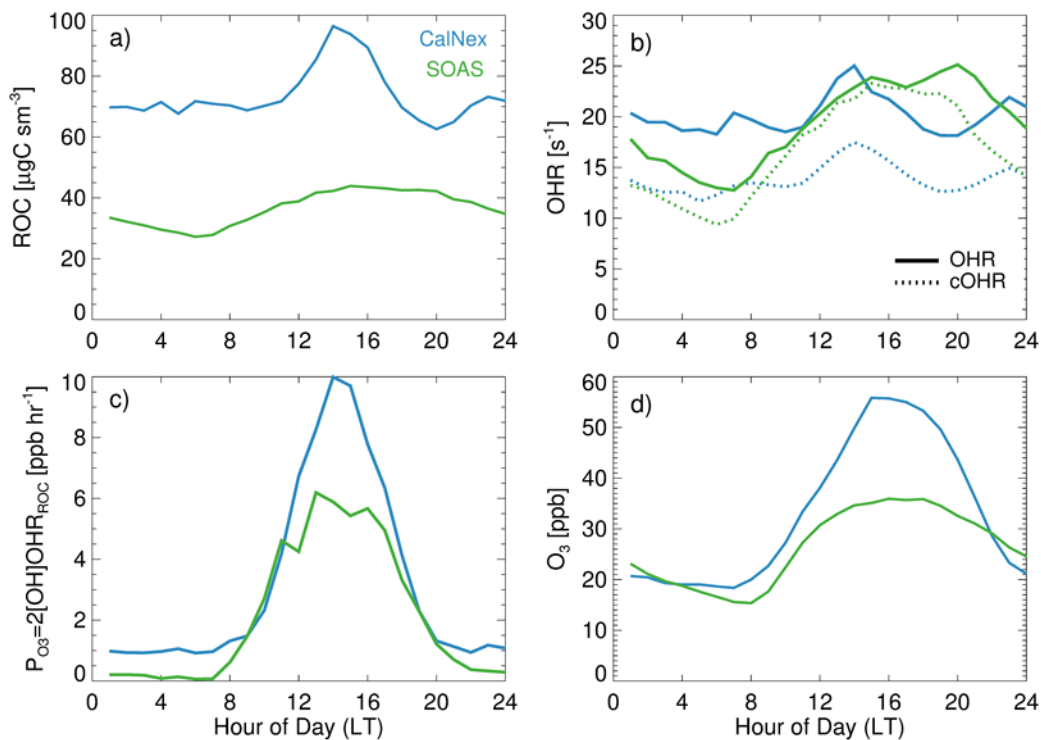
428 environment into which these species are emitted, are dynamic. In particular, NO_x concentrations
429 in Southern California have decreased considerably since the CalNex campaign. The NO₂
430 measurements reported at Pasadena (EPA AQS site 06-037-2005) fell by 30% from 2010 to 2019.
431 This alone would imply a decrease in OHR of 7% (1.4 s⁻¹) from 2010. Warneke et al.²¹ show that
432 anthropogenic hydrocarbon concentrations in Los Angeles declined at a rate of 7.5%/yr⁻¹ from 1960
433 to 2010; it is unclear if that trend has continued over the last decade. Though the ratio of NO_x
434 reactivity to ROC reactivity shown here suggests that Pasadena was, on average, in the VOC-
435 limited regime during CalNex, Griffith et al.⁴¹ suggest that the region was on the cusp of the
436 transition between NO_x-limited and VOC-limited at that time. If indeed NO_x reductions have
437 outpaced decreases in ROC reactivity, Pasadena could have moved into an NO_x-limited ozone
438 production regime in recent years. Laughner and Cohen⁶¹ suggest that this is the case for the
439 greater Los Angeles region based on trends in satellite-derived NO_x lifetimes. Furthermore, the
440 precipitous decline in OHR in the region suggests that OHR in Southern California is currently
441 substantially lower than OHR in the SEUS, a conclusion which emphasizes the importance of
442 biogenic emissions in driving atmospheric reactivity. This is also illustrative of the potential for
443 the modern urban environment in the United States and elsewhere, to move towards the air quality
444 trajectory of cleaner remote regions.

445 As shown here, comprehensive ROC measurements alongside ancillary gas-phase measurements
446 and top-down constraints such as OHR can be used to better understand the atmospheric chemical
447 environment and how precursors translate to pollutants of interest. The routine deployment of such
448 measurements is critically needed to accurately characterize the effectiveness of air pollution
449 policies over time.

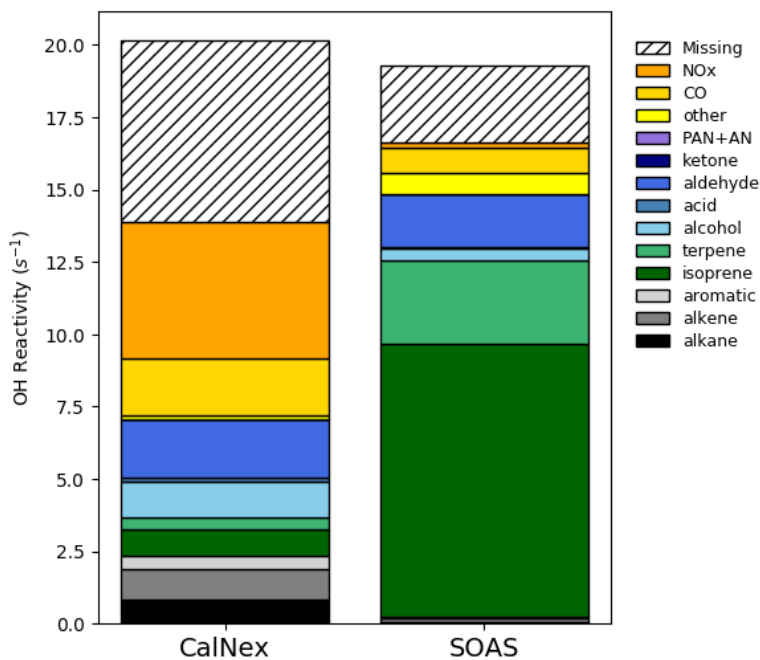
450 FIGURES
 451



452
 453 **Figure 1.** Average ROC mass concentrations for CalNex and SOAS field campaigns at standard
 454 temperature and pressure (STP).
 455

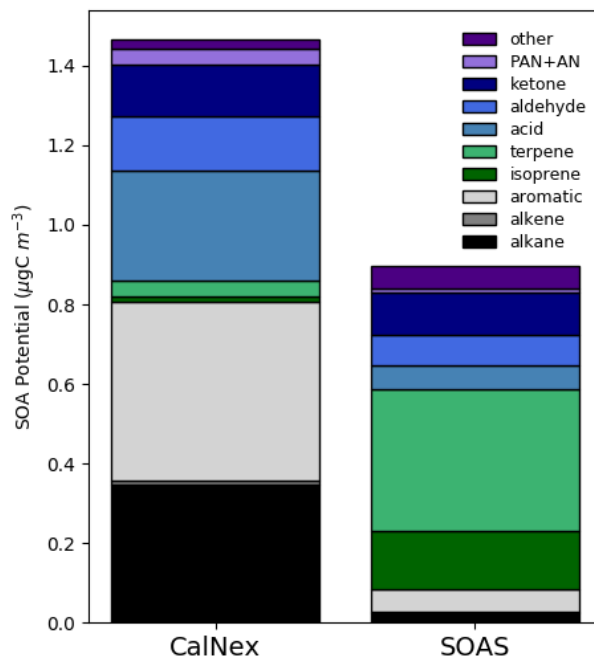


456
 457 **Figure 2.** Mean diurnal cycle for CalNex (blue) and SOAS (green) campaigns of a) observed ROC mass
 458 concentrations at STP, b) observed OH reactivity and calculated OHR (cOHR, dotted lines)), c) estimated
 459 ozone production rate, and d) observed O₃ mixing ratios.



461

462 **Figure 3.** Average calculated OH reactivity for CalNex and SOAS field campaigns. The missing
 463 reactivity is defined as the difference between the measured total OH reactivity and the summed
 464 calculated OH reactivity. The uncertainty on individual OHR measurements is given as 30% and 20% for
 465 CalNex and SOAS respectively (see Tables 1 and 2). The calculated standard error (defined as θ/\sqrt{N}) on
 466 campaign average OHR is 0.32 s^{-1} and 0.28 s^{-1} respectively (too small to be shown on the plot).



467

468 **Figure 4.** Average estimated SOA potential for CalNex and SOAS field campaigns.

470 TABLES

471

472 Table 1. Description of measurements used to explore reactive organic carbon during CalNex

Measurement	Instrument	Operational Dates During CalNex	Uncertainty	Reference	PI
OA	High Resolution Time of Flight Aerosol mass spectrometer (HR-ToF-AMS)	May 15-June 16, 2010	38%	Hayes et al., ²⁴	Jimenez
HCHO	Hantzsch reaction	May 15-June 16, 2010	10%	Rappenglück et al., ⁶²	Rappenglück
CHOCHO	Broadband Cavity Enhanced Absorption Spectrometer (IBBCEAS/CRDS)	May 15-June 16, 2010	40 pptv + 15%	Washenfelder et al., ³⁸	Washenfelder, Young
PAN, PPN	Gas Chromatograph with Electron Capture Detector (GC-ECD)	May 15-June 16, 2010	15%+0.005ppb 20%+0.005ppb	Roberts et al., ⁶³	Roberts
HNCO, HCOOH, acrylic acid, propionic acid, methacrylic acid, pyruvic acid	Negative Ion Proton Transfer Chemical Ionization Mass Spectrometer (NI-PT-CIMS)	May 15-June 16, 2010	15-35%	Veres et al., ⁶⁴	Veres and Roberts
Ethane, propane, i-butane, n-butane, i-pentane, n-pentane, hexane, nonane, undecane, ethene, propene, acetylene, 2-methyl-propene, 1-butene, cis2-butene, trans2-butene, 1,3-butadiene, benzene, toluene, o-xylene, m+p-xylene, 1-ethyl-benzene, styrene, ipropyl-benzene, npropyl-benzene, 1ethyl-3,4methyl-benzene, 1ethyl-2methy-benzene, 135TMB, 124TMB, 123TMB, 13dichlorobenzene, isoprene, alpha-pinene, beta-pinene, limonene, acetaldehyde, propanal, butanal, benzaldehyde, acetone, MVK, methacrolein, 2-butanone, methanol, ethanol, iso-propanol, bromoform, DMS, acetonitrile, 2,3-butadione,	Gas Chromatography Mass Spectrometer (GC-MS-TACOH)	May 15-June 16, 2010	15-25% for hydrocarbons, 20-35% for oxygenates	Kuster et al., ⁶⁵	Gilman
2methyl-pentane, 3methyl-pentane, n-heptane, 2methyl-hexane, 3methyl-hexane, i-octane, n-octane, methyl-acetate, 1,3-methyl-butene, trichlorofluoromethane,	Extended analysis of GC-MS	May 15-June 16, 2010		McDonald et al., ²²	Gilman

trichloroethene, chloroform, dichloromethane, cyclohexane, cis1,3dimethyl-cyclohexane, methyl-cyclohexane, trans1,2dimethyl-cyclohexane, trans1,3dimethyl-cyclohexane, methyl-cyclopentane, methyl-formate, 3-furaldehyde, n-hexanal, nitromethane, 2methyl-propanal, 2-propenal, vinyl-acetylene, ethyl-nitrate					
total monoterpenes	Proton Transfer Reaction Ion Trap Mass Spectrometer (PIT-MS)	May 15-June 16, 2010	15-25%	Warneke et al., ⁶⁶	Warneke, de Gouw, Graus
OH, HO ₂ , OHR	Fluorescent Assay by Gas Expansion	May 15-June 16, 2010	38% (OH, HO ₂), 30% (OHR)	Griffith et al., ⁴¹ ; Hansen et al. ⁶⁷	Stevens
O ₃ , SO ₂ , NO, NO ₂	Thermo Scientific (49c, 48i-TLE, 42i-TL)	May 16-June 16, 2010	4%, 4%, 4%, 6%	Lefer et al., ⁶⁸ Luke et al. ⁶⁹ Pollack et al. ⁷⁰ Drummond et al. ⁷¹	Lefer
CO	VUV resonance fluorescence AeroLaser AL5002	May 15-June 16, 2010	4%	Gerbig et al., ⁷²	Holloway

473
474
475
476

Table 2. Description of measurements used to explore reactive organic carbon during SOAS

Measurement	Instrument	Operational Dates During SOAS	Uncertainty Accuracy	Reference	PI
Organic aerosol	High Resolution Time of Flight Aerosol mass spectrometer (HR-ToF-AMS)	June 6-July 15, 2013	38%	Hu et al., ⁷³	Jimenez
HCHO	Fiber-Laser Induced Fluorescence (FiLIF-II)	June 1-July 15, 2013	15%	DiGangi et al., ⁷⁴ ; Hottle et al. ⁷⁵	Keutsch
CHOCHO	Madison Laser Induced Phosphorescence (Mad-LIP)	June 1-July 15, 2013	9%	Huisman et al., ⁷⁶	Keutsch
Formic acid, HCN, HAC (hydroxyacetone), PAA (peroxyacetic acid), C ₅ H ₈ O ₃ (HPALD), C ₅ H ₁₀ O ₃ (IEPOX+ISOPOOH), ethanol nitrate, propanone nitrate, isoprene nitrate	Caltech Chemical Ionization Time of Flight Mass Spectrometer (CIT-ToF-CIMS)	June 1-July 3, 2013	100 ppt +30-50% [X]	Nguyen et al. ⁷⁷	Wennberg

PNs (peroxynitrates)	Thermal Dissociation – Laser Induced Fluorescence (TD-LIF)	June 1-July 15, 2013	15%	Romer et al., ⁷⁸	Cohen
Ethane, ethene, propane, propene, ethyne, i-butane, n-butane, i-pentane, n-pentane, n-hexane, n-decane, benzene, toluene, 1ethyl-benzene, m-xylene+p-xylene, o-xylene, 1ethyl-3and4methylbenzene, 135TMB, 124TMB, isoprene, alpha-pinene, beta-pinene, limonene, camphene, myrcene,p-cymene, acetaldehyde, methanol, ethanol, propanal, butanal, benzaldehyde, acetone, MVK, methacrolein, MEK, DMS, acetonitrile, butadiene-23, 1ethyl-nitrate, ipropyl-nitrate	Gas Chromatography Mass Spectrometer (GC-MS TACOH)	June 1- July 15, 2013	20%	Gilman et al., ⁷⁹	Goldstein & de Gouw
total monoterpenes	Proton Transfer Mass Spectrometer (PTR-MS)	June 16- July 5, 2013	20%	Graus et al., ⁸⁰	Goldstein, Guenther
3-hydroxyglutaric acid, pinic acid, pinonic acid, 2-methylthreitol, 2-methylerythritol, 3methyl-2,3,4-trihydroxy-butene, cis2methyl-1,3,4, trihydroxy-butene, 2-methylglyceric acid, levoglucosan	Semi-Volatile Thermal desorption Aerosol Gas chromatograph (SV-TAG)	June 4-July 15, 2013	20%	Isaacman Van Wertz et al., ³⁰	Goldstein,
OH, HO ₂ , OHR	Ground Based Tropospheric Hydrogen Oxides Sensor (GTHOS)	June 1- July 15, 2013	2% 20%	Feiner et al., ⁴⁰ ; Faloona et al., ⁸¹	Brune
	<i>Other measurements (operated by SEARCH network)</i>				
O ₃	Thermo Scientific UV absorption (49i)	June 1- July 15, 2013	6.1%		Edgerton
CO	Thermo Scientific, IR absorption with gas filter correlation (GFC) (48i)	June 1- July 15, 2013	7.4%		Edgerton
SO ₂	Thermo Scientific, pulsed UV fluorescence (43i)	June 1- July 15, 2013	6.1%		Edgerton
NO, NO ₂	Thermo Scientific, Chemiluminescence (42i)	June 1- July 15, 2013	5.5%, 15%		Edgerton

477
478
479

480 **ASSOCIATED CONTENT**

481 **Supporting Information:** Table S1 with reaction rates, SOA yields and ROC mass
482 concentrations, cOHR, and SOA potential for each species measured during SOAS and CalNex.

483

484 **AUTHOR INFORMATION**

485 **Corresponding Author**

486 * Colette L. Heald (heald@mit.edu)

487

488 **Present Addresses**

489 † now at: Department of Civil and Environmental Engineering, Virginia Tech, Blacksburg, VA

490 ‡ now at Department of Chemistry, Université de Montréal, Québec, Canada

491 * now at State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry,
492 Chinese Academy of Sciences, Guangzhou China

493 § now at Tofwerk USA, Boulder, CO

494 † now at: Department of Civil, Architectural and Environmental Engineering, University of Texas
495 at Austin, Austin, TX

496 ** now at: Department of Chemistry, York University, Toronto, Ontario, Canada

497

498 **Author Contributions**

499 CLH designed the study and undertook the analysis. JDG, GIVW, AHG, ABG, PLH, WH, JLJ,
500 FNK, ARK. PKM, BR, JMR, PSS, RAW, CW, CJY provided measurements used in the analysis.

501 CLH wrote the paper with input from the co-authors. All authors have given approval to the final
502 version of the manuscript.

503

504 **Funding Sources**

505 This study was supported by the National Science Foundation (AGS 1936642).

506

507 **ACKNOWLEDGEMENT**

508 We thank the following for measurements used in this work: SOAS: Ron Cohen, Paul Wennberg,
509 John Crouse, Jason St. Clair, Tran Nguyen, Bill Brune, and Dave Worton, as well as from the
510 SEARCH network; CalNex: Barry Lefer, Patrick Veres, and John Holloway during CalNex. We
511 thank Jesse Kroll for useful conversations.

512 **REFERENCES**

- 513 1. Safieddine, S. A.; Heald, C. L.; Henderson, B. H., The global nonmethane reactive organic
514 carbon budget: A modeling perspective. *Geophys. Res. Lett.* **2017**, *44* (8), 3897-3906.
- 515 2. Guenther, A. B.; Jiang, X.; Heald, C. L.; Sakulyanontvittaya, T.; Duhl, T.; Emmons, L. K.; Wang,
516 X., The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN 2.1): an extended
517 and updated framework for modeling biogenic emissions. *Geosci. Model Dev.* **2012**, *5*, 1471-1492.
- 518 3. Akagi, S. K.; Yokelson, R. J.; Wiedinmyer, C.; Alvarado, M. J.; Reid, J. S.; Karl, T.; Crouse, J.
519 D.; Wennberg, P. O., Emission factors for open and domestic biomass burning for use in atmospheric
520 models. *Atmospheric Chemistry and Physics* **2011**, *11* (9), 4039-4072.
- 521 4. Schultz, M. G. *REanalysis of the TROpospheric chemical composition over the past 40 years*
522 Max Planck Institute for Meteorology: Julich/Hamburg, Germany, 2007.
- 523 5. Heald, C. L.; Kroll, J. H., The fuel of atmospheric chemistry: Toward a complete description of
524 reactive organic carbon. *Science Advances* **2020**, *6* (6), eaay8967.
- 525 6. Heald, C. L.; Ridley, D. A.; Kroll, J. H.; Barrett, S. R. H.; Cady-Pereira, K. E.; Alvarado, M. J.;
526 Holmes, C. D., Contrasting the direct radiative effect and direct radiative forcing of aerosols. *Atmos.*
527 *Chem. Phys.* **2014**, *14* (11), 5513-5527.
- 528 7. Butler, T.; Lupascu, A.; Coates, J.; Zhu, S., TOAST 1.0: Tropospheric Ozone Attribution of
529 Sources with Tagging for CESM 1.2.2. *Geosci. Model Dev.* **2018**, *11* (7), 2825-2840.
- 530 8. Burnett, R.; Chen, H.; Szyszkowicz, M.; Fann, N.; Hubbell, B.; Pope, C. A.; Apte, J. S.; Brauer,
531 M.; Cohen, A.; Weichenthal, S.; Coggins, J.; Di, Q.; Brunekreef, B.; Frostad, J.; Lim, S. S.; Kan, H. D.;
532 Walker, K. D.; Thurston, G. D.; Hayes, R. B.; Lim, C. C.; Turner, M. C.; Jerrett, M.; Krewski, D.;
533 Gapstur, S. M.; Diver, W. R.; Ostro, B.; Goldberg, D.; Crouse, D. L.; Martin, R. V.; Peters, P.; Pinault,
534 L.; Tjepkema, M.; Donkelaar, A.; Villeneuve, P. J.; Miller, A. B.; Yin, P.; Zhou, M. G.; Wang, L. J.;
535 Janssen, N. A. H.; Marra, M.; Atkinson, R. W.; Tsang, H.; Thach, Q.; Cannon, J. B.; Allen, R. T.; Hart, J.
536 E.; Laden, F.; Cesaroni, G.; Forastiere, F.; Weinmayr, G.; Jaensch, A.; Nagel, G.; Concin, H.; Spadaro, J.
537 V., Global estimates of mortality associated with long-term exposure to outdoor fine particulate matter.
538 *Proc. Natl. Acad. Sci. U. S. A.* **2018**, *115* (38), 9592-9597.
- 539 9. IPCC *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the*
540 *Fifth Assessment Report of the Intergovernmental Panel on Climate Change* Cambridge, UK, 2013; p
541 1535.
- 542 10. Goldstein, A. H.; Galbally, I. E., Known and unexplored organic constituents in the earth's
543 atmosphere. *Environ. Sci. Technol.* **2007**, *41* (5), 1514-1521.
- 544 11. Roberts, J. M.; Bertman, S. B.; Jobson, T.; Niki, H.; Tanner, R., Measurement of total
545 nonmethane organic carbon (C-y): Development and application at Chebogue Point, Nova Scotia, during
546 the 1993 North Atlantic Regional Experiment campaign. *J. Geophys. Res.-Atmos.* **1998**, *103* (D11),
547 13581-13592.
- 548 12. Maris, C.; Chung, M. Y.; Lueb, R.; Krischke, U.; Meller, R.; Fox, M. J.; Paulson, S. E.,
549 Development of instrumentation for simultaneous analysis of total non-methane organic carbon and
550 volatile organic compounds in ambient air. *Atmos. Environ.* **2003**, *37*, S149-S158.

- 551 13. Yang, M. X.; Fleming, Z. L., Estimation of atmospheric total organic carbon (TOC) - paving the
552 path towards carbon budget closure. *Atmospheric Chemistry and Physics* **2019**, *19* (1), 459-471.
- 553 14. Heald, C. L.; Goldstein, A. H.; Allan, J. D.; Aiken, A. C.; Apel, E.; Atlas, E. L.; Baker, A. K.;
554 Bates, T. S.; Beyersdorf, A. J.; Blake, D. R.; Campos, T.; Coe, H.; Crounse, J. D.; DeCarlo, P. F.; de
555 Gouw, J. A.; Dunlea, E. J.; Flocke, F. M.; Fried, A.; Goldan, P.; Griffin, R. J.; Herndon, S. C.; Holloway,
556 J. S.; Holzinger, R.; Jimenez, J. L.; Junkermann, W.; Kuster, W. C.; Lewis, A. C.; Meinardi, S.; Millet, D.
557 B.; Onasch, T.; Polidori, A.; Quinn, P. K.; Riemer, D. D.; Roberts, J. M.; Salcedo, D.; Sive, B.; Swanson,
558 A. L.; Talbot, R.; Warneke, C.; Weber, R. J.; Weibring, P.; Wennberg, P. O.; Worsnop, D. R.; Wittig, A.
559 E.; Zhang, R.; Zheng, J.; Zheng, W., Total observed organic carbon (TOOC) in the atmosphere: a
560 synthesis of North American observations. *Atmos. Chem. Phys.* **2008**, *8* (7), 2007-2025.
- 561 15. Hunter, J. F.; Day, D. A.; Palm, B. B.; Yatavelli, R. L. N.; Chan, A. H.; Kaser, L.; Cappellin, L.;
562 Hayes, P. L.; Cross, E. S.; Carrasquillo, A. J.; Campuzano-Jost, P.; Stark, H.; Zhao, Y. L.; Hohaus, T.;
563 Smith, J. N.; Hansel, A.; Karl, T.; Goldstein, A. H.; Guenther, A.; Worsnop, D. R.; Thornton, J. A.;
564 Heald, C. L.; Jimenez, J. L.; Kroll, J. H., Comprehensive characterization of atmospheric organic carbon
565 at a forested site. *Nat. Geosci.* **2017**, *10* (10), 748+.
- 566 16. Yang, Y. D.; Shao, M.; Wang, X. M.; Nolscher, A. C.; Kessel, S.; Guenther, A.; Williams, J.,
567 Towards a quantitative understanding of total OH reactivity: A review. *Atmos. Environ.* **2016**, *134*, 147-
568 161.
- 569 17. Mao, J.; Ren, X.; Brune, W. H.; Olson, J. R.; Crawford, J. H.; Fried, A.; Huey, L. G.; Cohen, R.
570 C.; Heikes, B.; Singh, H. B.; Blake, D. R.; Sachse, G. W.; Diskin, G. S.; Hall, S. R.; Shetter, R. E.,
571 Airborne measurement of OH reactivity during INTEX-B. *Atmospheric Chemistry and Physics* **2009**, *9*
572 (1), 163-173.
- 573 18. Dolgorouky, C.; Gros, V.; Sarda-Estevé, R.; Sinha, V.; Williams, J.; Marchand, N.; Sauvage, S.;
574 Poulain, L.; Sciare, J.; Bonsang, B., Total OH reactivity measurements in Paris during the 2010
575 MEGAPOLI winter campaign. *Atmospheric Chemistry and Physics* **2012**, *12* (20), 9593-9612.
- 576 19. Travis, K. R.; Heald, C. L.; Allen, H. M.; Apel, E. C.; Arnold, S. R.; Blake, D. R.; Brune, W. H.;
577 Chen, X.; Commane, R.; Crounse, J. D.; Daube, B. C.; Diskin, G. S.; Elkins, J. W.; Evans, M. J.; Hall, S.
578 R.; Hints, E. J.; Hornbrook, R. S.; Kasibhatla, P. S.; Kim, M. J.; Luo, G.; McKain, K.; Millet, D. B.;
579 Moore, F. L.; Peischl, J.; Ryerson, T. B.; Sherwen, T.; Thames, A. B.; Ullmann, K.; Wang, X.;
580 Wennberg, P. O.; Wolfe, G. M.; Yu, F., Constraining remote oxidation capacity with ATom observations.
581 *Atmos. Chem. Phys.* **2020**, *20* (13), 7753-7781.
- 582 20. Ryerson, T. B.; Andrews, A. E.; Angevine, W. M.; Bates, T. S.; Brock, C. A.; Cairns, B.; Cohen,
583 R. C.; Cooper, O. R.; de Gouw, J. A.; Fehsenfeld, F. C.; Ferrare, R. A.; Fischer, M. L.; Flagan, R. C.;
584 Goldstein, A. H.; Hair, J. W.; Hardesty, R. M.; Hostetler, C. A.; Jimenez, J. L.; Langford, A. O.;
585 McCauley, E.; McKeen, S. A.; Molina, L. T.; Nenes, A.; Oltmans, S. J.; Parrish, D. D.; Pederson, J. R.;
586 Pierce, R. B.; Prather, K.; Quinn, P. K.; Seinfeld, J. H.; Senff, C. J.; Sorooshian, A.; Stutz, J.; Surratt, J.
587 D.; Trainer, M.; Volkamer, R.; Williams, E. J.; Wofsy, S. C., The 2010 California Research at the Nexus
588 of Air Quality and Climate Change (CalNex) field study. *Journal of Geophysical Research-Atmospheres*
589 **2013**, *118* (11), 5830-5866.
- 590 21. Warneke, C.; de Gouw, J. A.; Holloway, J. S.; Peischl, J.; Ryerson, T. B.; Atlas, E.; Blake, D.;
591 Trainer, M.; Parrish, D. D., Multiyear trends in volatile organic compounds in Los Angeles, California:
592 Five decades of decreasing emissions. *J. Geophys. Res.-Atmos.* **2012**, *117*, 10.

- 593 22. McDonald, B. C.; de Gouw, J. A.; Gilman, J. B.; Jathar, S. H.; Akherati, A.; Cappa, C. D.;
594 Jimenez, J. L.; Lee-Taylor, J.; Hayes, P. L.; McKeen, S. A.; Cui, Y. Y.; Kim, S. W.; Gentner, D. R.;
595 Isaacman-VanWertz, G.; Goldstein, A. H.; Harley, R. A.; Frost, G. J.; Roberts, J. M.; Ryerson, T. B.;
596 Trainer, M., Volatile chemical products emerging as largest petrochemical source of urban organic
597 emissions. *Science* **2018**, *359* (6377), 760-764.
- 598 23. Isaacman-VanWertz, G.; Sueper, D. T.; Aikin, K. C.; Lerner, B. M.; Gilman, J. B.; de Gouw, J.
599 A.; Worsnop, D. R.; Goldstein, A. H., Automated single-ion peak fitting as an efficient approach for
600 analyzing complex chromatographic data. *J. Chromatogr. A* **2017**, *1529*, 81-92.
- 601 24. Hayes, P. L.; Ortega, A. M.; Cubison, M. J.; Froyd, K. D.; Zhao, Y.; Cliff, S. S.; Hu, W. W.;
602 Toohey, D. W.; Flynn, J. H.; Lefer, B. L.; Grossberg, N.; Alvarez, S.; Rappenglück, B.; Taylor, J. W.;
603 Allan, J. D.; Holloway, J. S.; Gilman, J. B.; Kuster, W. C.; De Gouw, J. A.; Massoli, P.; Zhang, X.; Liu,
604 J.; Weber, R. J.; Corrigan, A. L.; Russell, L. M.; Isaacman, G.; Worton, D. R.; Kreisberg, N. M.;
605 Goldstein, A. H.; Thalman, R.; Waxman, E. M.; Volkamer, R.; Lin, Y. H.; Surratt, J. D.; Kleindienst, T.
606 E.; Offenberg, J. H.; Dusanter, S.; Griffith, S.; Stevens, P. S.; Brioude, J.; Angevine, W. M.; Jimenez, J.
607 L., Organic aerosol composition and sources in Pasadena, California, during the 2010 CalNex campaign.
608 *J. Geophys. Res.-Atmos.* **2013**, *118* (16), 9233-9257.
- 609 25. Worton, D. R.; Kreisberg, N. M.; Isaacman, G.; Teng, A. P.; McNeish, C.; Gorecki, T.; Hering, S.
610 V.; Goldstein, A. H., Thermal Desorption Comprehensive Two-Dimensional Gas Chromatography: An
611 Improved Instrument for In-Situ Speciated Measurements of Organic Aerosols. *Aerosol Sci. Technol.*
612 **2012**, *46* (4), 380-393.
- 613 26. Carlton, A. G.; de Gouw, J.; Jimenez, J. L.; Ambrose, J. L.; Attwood, A. R.; Brown, S.; Baker, K.
614 R.; Brock, C.; Cohen, R. C.; Edgerton, S.; Farkas, C. M.; Farmer, D.; Goldstein, A. H.; Gratz, L.;
615 Guenther, A.; Hunt, S.; Jaegle, L.; Jaffe, D. A.; Mak, J.; McClure, C.; Nenes, A.; Nguyen, T. K.; Pierce, J.
616 R.; de Sa, S.; Selin, N. E.; Shah, V.; Shaw, S.; Shepson, P. B.; Song, S. J.; Stutz, J.; Surratt, J. D.; Turpin,
617 B. J.; Warneke, C.; Washenfelder, R. A.; Wennberg, P. O.; Zhou, X. L., Synthesis of the Southeast
618 Atmosphere Studies: Investigating Fundamental Atmospheric Chemistry Questions. *Bull. Amer.*
619 *Meteorol. Soc.* **2018**, *99* (3), 547-567.
- 620 27. Blanchard, C. L.; Hidy, G. M.; Tanenbaum, S.; Edgerton, E. S.; Hartsell, B. E., The Southeastern
621 Aerosol Research and Characterization (SEARCH) study: Temporal trends in gas and PM concentrations
622 and composition, 1999-2010. *J. Air Waste Manage. Assoc.* **2013**, *63* (3), 247-259.
- 623 28. Ridley, D. A.; Heald, C. L.; Ridley, K. J.; Kroll, J. H., Causes and consequences of decreasing
624 atmospheric organic aerosol in the United States. *Proc Natl Acad Sci USA* **2018**, *115* (2), 290-295.
- 625 29. de Gouw, J. A.; Gilman, J. B.; Borbon, A.; Warneke, C.; Kuster, W. C.; Goldan, P. D.; Holloway,
626 J. S.; Peischl, J.; Ryerson, T. B.; Parrish, D. D.; Gentner, D. R.; Goldstein, A. H.; Harley, R. A.,
627 Increasing atmospheric burden of ethanol in the United States. *Geophys. Res. Lett.* **2012**, *39*, 6.
- 628 30. Isaacman-VanWertz, G.; Yee, L. D.; Kreisberg, N. M.; Wernis, R.; Moss, J. A.; Hering, S. V.; de
629 Sa, S. S.; Martin, S. T.; Alexander, M. L.; Palm, B. B.; Hu, W. W.; Campuzano-Jost, P.; Day, D. A.;
630 Jimenez, J. L.; Riva, M.; Surratt, J. D.; Viegas, J.; Manzi, A.; Edgerton, E.; Baumann, K.; Souza, R.;
631 Artaxo, P.; Goldstein, A. H., Ambient Gas-Particle Partitioning of Tracers for Biogenic Oxidation.
632 *Environ. Sci. Technol.* **2016**, *50* (18), 9952-9962.

- 633 31. Isaacman-VanWertz, G.; Lu, X.; Weiner, E.; Smiley, E.; Widdowson, M., Characterization of
634 Hydrocarbon Groups in Complex Mixtures Using Gas Chromatography with Unit-Mass Resolution
635 Electron Ionization Mass Spectrometry. *Analytical Chemistry* **2020**, *92* (18), 12481-12488.
- 636 32. Ma, P. K.; Zhao, Y. L.; Robinson, A. L.; Worton, D. R.; Goldstein, A. H.; Ortega, A. M.;
637 Jimenez, J. L.; Zotter, P.; Prevot, A. S. H.; Szidat, S.; Hayes, P. L., Evaluating the impact of new
638 observational constraints on P-S/IVOC emissions, multi-generation oxidation, and chamber wall losses on
639 SOA modeling for Los Angeles, CA. *Atmospheric Chemistry and Physics* **2017**, *17* (15), 9237-9259.
- 640 33. Zhao, Y. L.; Hennigan, C. J.; May, A. A.; Tkacik, D. S.; de Gouw, J. A.; Gilman, J. B.; Kuster,
641 W. C.; Borbon, A.; Robinson, A. L., Intermediate-Volatility Organic Compounds: A Large Source of
642 Secondary Organic Aerosol. *Environ. Sci. Technol.* **2014**, *48* (23), 13743-13750.
- 643 34. Burkholder, J. B.; Sander, S. P.; Abbatt, J. P.; Barker, J. R.; Huie, R. E.; Kolb, C. E.; Kurylo, M.
644 J.; Orkin, V. L.; Wilmouth, D. M.; Wine, P. H. *Chemical Kinetics and Photochemical Data for Use in*
645 *Atmospheric Studies, Evaluation No. 18*; Jet Propulsion Laboratory: 2015.
- 646 35. Atkinson, R.; Baulch, D. L.; Cox, R. A.; Crowley, J. N.; Hampson, R. F.; Hynes, R. G.; Jenkin,
647 M. E.; Rossi, M. J.; Troe, J., Evaluated kinetic and photochemical data for atmospheric chemistry:
648 Volume II - gas phase reactions of organic species. *Atmospheric Chemistry and Physics* **2006**, *6*, 3625-
649 4055.
- 650 36. EPA, U., Estimation Programs Interface Suite™ for Microsoft® Windows, v 4.11. Agency, U. S.
651 E. P., Ed. Washington, DC, USA, 2012.
- 652 37. Seinfeld, J. H.; Pandis, S. N., *Atmospheric Chemistry and Physics: From Air Pollution to Climate*
653 *Change, 3rd edition*. John Wiley & Sons: 2016; p 1152.
- 654 38. Washenfelder, R. A.; Young, C. J.; Brown, S. S.; Angevine, W. M.; Atlas, E. L.; Blake, D. R.;
655 Bon, D. M.; Cubison, M. J.; de Gouw, J. A.; Dusanter, S.; Flynn, J.; Gilman, J. B.; Graus, M.; Griffith, S.;
656 Grossberg, N.; Hayes, P. L.; Jimenez, J. L.; Kuster, W. C.; Lefer, B. L.; Pollack, I. B.; Ryerson, T. B.;
657 Stark, H.; Stevens, P. S.; Trainer, M. K., The glyoxal budget and its contribution to organic aerosol for
658 Los Angeles, California, during CalNex 2010. *J. Geophys. Res.-Atmos.* **2011**, *116*, 17.
- 659 39. de Gouw, J. A.; Gilman, J. B.; Kim, S. W.; Lerner, B. M.; Isaacman-VanWertz, G.; McDonald,
660 B. C.; Warneke, C.; Kuster, W. C.; Lefer, B. L.; Griffith, S. M.; Dusanter, S.; Stevens, P. S.; Stutz, J.,
661 Chemistry of Volatile Organic Compounds in the Los Angeles basin: Nighttime Removal of Alkenes and
662 Determination of Emission Ratios. *J. Geophys. Res.-Atmos.* **2017**, *122* (21), 11843-11861.
- 663 40. Feiner, P. A.; Brune, W. H.; Miller, D. O.; Zhang, L.; Cohen, R. C.; Romer, P. S.; Goldstein, A.
664 H.; Keutsch, F. N.; Skog, K. M.; Wennberg, P. O.; Nguyen, T. B.; Teng, A. P.; DeGouw, J.; Koss, A.;
665 Wild, R. J.; Brown, S. S.; Guenther, A.; Edgerton, E.; Baumann, K.; Fry, J. L., Testing Atmospheric
666 Oxidation in an Alabama Forest. *J. Atmos. Sci.* **2016**, *73* (12), 4699-4710.
- 667 41. Griffith, S. M.; Hansen, R. F.; Dusanter, S.; Michoud, V.; Gilman, J. B.; Kuster, W. C.; Veres, P.
668 R.; Graus, M.; de Gouw, J. A.; Roberts, J.; Young, C.; Washenfelder, R.; Brown, S. S.; Thalman, R.;
669 Waxman, E.; Volkamer, R.; Tsai, C.; Stutz, J.; Flynn, J. H.; Grossberg, N.; Lefer, B.; Alvarez, S. L.;
670 Rappenglück, B.; Mielke, L. H.; Osthoff, H. D.; Stevens, P. S., Measurements of hydroxyl and
671 hydroperoxy radicals during CalNex-LA: Model comparisons and radical budgets. *J. Geophys. Res.-*
672 *Atmos.* **2016**, *121* (8), 4211-4232.

- 673 42. Kaiser, J.; Skog, K. M.; Baumann, K.; Bertman, S. B.; Brown, S. B.; Brune, W. H.; Crouse, J.
674 D.; de Gouw, J. A.; Edgerton, E. S.; Feiner, P. A.; Goldstein, A. H.; Koss, A.; Misztal, P. K.; Nguyen, T.
675 B.; Olson, K. F.; St Clair, J. M.; Teng, A. P.; Toma, S.; Wennberg, P. O.; Wild, R. J.; Zhang, L.; Keutsch,
676 F. N., Speciation of OH reactivity above the canopy of an isoprene-dominated forest. *Atmospheric*
677 *Chemistry and Physics* **2016**, *16* (14), 9349-9359.
- 678 43. Hellen, H.; Praplan, A. P.; Tykka, T.; Ylivinkka, I.; Vakkari, V.; Back, J.; Petaja, T.; Kulmala,
679 M.; Hakola, H., Long-term measurements of volatile organic compounds highlight the importance of
680 sesquiterpenes for the atmospheric chemistry of a boreal forest. *Atmospheric Chemistry and Physics*
681 **2018**, *18* (19), 13839-13863.
- 682 44. Yee, L. D.; Isaacman-VanWertz, G.; Wernis, R. A.; Meng, M.; Rivera, V.; Kreisberg, N. M.;
683 Hering, S. V.; Bering, M. S.; Glasius, M.; Upshur, M. A.; Be, A. G.; Thomson, R. J.; Geiger, F. M.;
684 Offenberg, J. H.; Lewandowski, M.; Kourtchev, I.; Kalberer, M.; de Sa, S.; Martin, S. T.; Alexander, M.
685 L.; Palm, B. B.; Hu, W. W.; Campuzano-Jost, P.; Day, D. A.; Jimenez, J. L.; Liu, Y. J.; McKinney, K. A.;
686 Artaxo, P.; Viegas, J.; Manzi, A.; Oliveira, M. B.; de Souza, R.; Machado, L. A. T.; Longo, K.; Goldstein,
687 A. H., Observations of sesquiterpenes and their oxidation products in central Amazonia during the wet
688 and dry seasons. *Atmospheric Chemistry and Physics* **2018**, *18* (14), 10433-10457.
- 689 45. Bouvier-Brown, N. C.; Goldstein, A. H.; Gilman, J. B.; Kuster, W. C.; de Gouw, J. A., In-situ
690 ambient quantification of monoterpenes, sesquiterpenes, and related oxygenated compounds during
691 BEARPEX 2007: implications for gas- and particle-phase chemistry. *Atmospheric Chemistry and Physics*
692 **2009**, *9* (15), 5505-5518.
- 693 46. Jacob, D. J., *Introduction to Atmospheric Chemistry*. Princeton University Press: Princeton, NJ,
694 1999.
- 695 47. Sinha, V.; Williams, J.; Diesch, J. M.; Drewnick, F.; Martinez, M.; Harder, H.; Regelin, E.;
696 Kubistin, D.; Bozem, H.; Hosaynali-Beygi, Z.; Fischer, H.; Andres-Hernandez, M. D.; Kartal, D.; Adame,
697 J. A.; Lelieveld, J., Constraints on instantaneous ozone production rates and regimes during DOMINO
698 derived using in-situ OH reactivity measurements. *Atmospheric Chemistry and Physics* **2012**, *12* (15),
699 7269-7283.
- 700 48. Bahreini, R.; Middlebrook, A. M.; de Gouw, J. A.; Warneke, C.; Trainer, M.; Brock, C. A.; Stark,
701 H.; Brown, S. S.; Dube, W. P.; Gilman, J. B.; Hall, K.; Holloway, J. S.; Kuster, W. C.; Perring, A. E.;
702 Prevot, A. S. H.; Schwarz, J. P.; Spackman, J. R.; Szidat, S.; Wagner, N. L.; Weber, R. J.; Zotter, P.;
703 Parrish, D. D., Gasoline emissions dominate over diesel in formation of secondary organic aerosol mass.
704 *Geophys. Res. Lett.* **2012**, *39*, 6.
- 705 49. Silva, S. J.; Heald, C. L., Investigating Dry Deposition of Ozone to Vegetation. *J. Geophys. Res.-*
706 *Atmos.* **2018**, *123* (1), 559-573.
- 707 50. Kirchner, F.; Jeanneret, F.; Clappier, A.; Kruger, B.; van den Bergh, H.; Calpini, B., Total VOC
708 reactivity in the planetary boundary layer 2. A new indicator for determining the sensitivity of the ozone
709 production to VOC and NO_x. *J. Geophys. Res.-Atmos.* **2001**, *106* (D3), 3095-3110.
- 710 51. Matsumoto, J., Measuring Biogenic Volatile Organic Compounds (BVOCs) from Vegetation in
711 Terms of Ozone Reactivity. *Aerosol Air Qual. Res.* **2014**, *14* (1), 197-206.
- 712 52. Jimenez, J. L.; Canagaratna, M. R.; Donahue, N. M.; Prevot, A. S. H.; Zhang, Q.; Kroll, J. H.;
713 DeCarlo, P. F.; Allan, J. D.; Coe, H.; Ng, N. L.; Aiken, A. C.; Docherty, K. S.; Ulbrich, I. M.; Grieshop,

- 714 A. P.; Robinson, A. L.; Duplissy, J.; Smith, J. D.; Wilson, K. R.; Lanz, V. A.; Hueglin, C.; Sun, Y. L.;
715 Tian, J.; Laaksonen, A.; Raatikainen, T.; Rautiainen, J.; Vaattovaara, P.; Ehn, M.; Kulmala, M.;
716 Tomlinson, J. M.; Collins, D. R.; Cubison, M. J.; Dunlea, E. J.; Huffman, J. A.; Onasch, T. B.; Alfarra,
717 M. R.; Williams, P. I.; Bower, K.; Kondo, Y.; Schneider, J.; Drewnick, F.; Borrmann, S.; Weimer, S.;
718 Demerjian, K.; Salcedo, D.; Cottrell, L.; Griffin, R.; Takami, A.; Miyoshi, T.; Hatakeyama, S.; Shimojo,
719 A.; Sun, J. Y.; Zhang, Y. M.; Dzepina, K.; Kimmel, J. R.; Sueper, D.; Jayne, J. T.; Herndon, S. C.;
720 Trimborn, A. M.; Williams, L. R.; Wood, E. C.; Middlebrook, A. M.; Kolb, C. E.; Baltensperger, U.;
721 Worsnop, D. R., Evolution of Organic Aerosols in the Atmosphere. *Science* **2009**, *326* (5959), 1525-
722 1529.
- 723 53. Donahue, N. M.; Robinson, A. L.; Pandis, S. N., Atmospheric organic particulate matter: From
724 smoke to secondary organic aerosol. *Atmos. Environ.* **2009**, *43* (1), 94-106.
- 725 54. Hayes, P. L.; Carlton, A. G.; Baker, K. R.; Ahmadov, R.; Washenfelder, R. A.; Alvarez, S.;
726 Rappenglück, B.; Gilman, J. B.; Kuster, W. C.; de Gouw, J. A.; Zotter, P.; Prevot, A. S. H.; Szidat, S.;
727 Kleindienst, T. E.; Offenberg, J. H.; Ma, P. K.; Jimenez, J. L., Modeling the formation and aging of
728 secondary organic aerosols in Los Angeles during CalNex 2010. *Atmospheric Chemistry and Physics*
729 **2015**, *15* (10), 5773-5801.
- 730 55. Zhang, H. F.; Yee, L. D.; Lee, B. H.; Curtis, M. P.; Worton, D. R.; Isaacman-VanWertz, G.;
731 Offenberg, J. H.; Lewandowski, M.; Kleindienst, T. E.; Beaver, M. R.; Holder, A. L.; Lonneman, W. A.;
732 Docherty, K. S.; Jaoui, M.; Pye, H. O. T.; Hu, W. W.; Day, D. A.; Campuzano-Jost, P.; Jimenez, J. L.;
733 Guo, H. Y.; Weber, R. J.; de Gouw, J.; Koss, A. R.; Edgerton, E. S.; Brune, W.; Mohr, C.; Lopez-
734 Hilfiker, F. D.; Lutz, A.; Kreisberg, N. M.; Spielman, S. R.; Hering, S. V.; Wilson, K. R.; Thornton, J. A.;
735 Goldstein, A. H., Monoterpenes are the largest source of summertime organic aerosol in the southeastern
736 United States. *Proc. Natl. Acad. Sci. U. S. A.* **2018**, *115* (9), 2038-2043.
- 737 56. Lee, A.; Goldstein, A. H.; Kroll, J. H.; Ng, N. L.; Varutbangkul, V.; Flagan, R. C.; Seinfeld, J. H.,
738 Gas-phase products and secondary aerosol yields from the photooxidation of 16 different terpenes. *J.*
739 *Geophys. Res.-Atmos.* **2006**, *111* (D17), doi:10.1029/2006JD007050.
- 740 57. Lee, B. H.; D'Ambro, E. L.; Lopez-Hilfiker, F. D.; Schobesberger, S.; Mohr, C.; Zawadowicz, M.
741 A.; Liu, J.; Shilling, J. E.; Hu, W.; Palm, B. B.; Jimenez, J. L.; Hao, L.; Virtanen, A.; Zhang, H.;
742 Goldstein, A. H.; Pye, H. O. T.; Thornton, J. A., Resolving Ambient Organic Aerosol Formation and
743 Aging Pathways with Simultaneous Molecular Composition and Volatility Observations. *ACS Earth and*
744 *Space Chemistry* **2020**, *4* (3), 391-402.
- 745 58. Ortega, A. M.; Hayes, P. L.; Peng, Z.; Palm, B. B.; Hu, W. W.; Day, D. A.; Li, R.; Cubison, M.
746 J.; Brune, W. H.; Graus, M.; Warneke, C.; Gilman, J. B.; Kuster, W. C.; de Gouw, J.; Gutierrez-Montes,
747 C.; Jimenez, J. L., Real-time measurements of secondary organic aerosol formation and aging from
748 ambient air in an oxidation flow reactor in the Los Angeles area. *Atmospheric Chemistry and Physics*
749 **2016**, *16* (11), 7411-7433.
- 750 59. de Gouw, J. A.; Parrish, D. D.; Brown, S. S.; Edwards, P.; Gilman, J. B.; Graus, M.; Hanisco, T.
751 F.; Kaiser, J.; Keutsch, F. N.; Kim, S. W.; Lerner, B. M.; Neuman, J. A.; Nowak, J. B.; Pollack, I. B.;
752 Roberts, J. M.; Ryerson, T. B.; Veres, P. R.; Warneke, C.; Wolfe, G. M., Hydrocarbon Removal in Power
753 Plant Plumes Shows Nitrogen Oxide Dependence of Hydroxyl Radicals. *Geophys. Res. Lett.* **2019**, *46*
754 (13), 7752-7760.
- 755 60. Millet, D. B.; Alwe, H. D.; Chen, X.; Deventer, M. J.; Griffis, T. J.; Holzinger, R.; Bertman, S.
756 B.; Rickly, P. S.; Stevens, P. S.; Leonardis, T.; Locoge, N.; Dusanter, S.; Tyndall, G. S.; Alvarez, S. L.;

757 Erickson, M. H.; Flynn, J. H., Bidirectional Ecosystem-Atmosphere Fluxes of Volatile Organic
758 Compounds Across the Mass Spectrum: How Many Matter? *Acs Earth and Space Chemistry* **2018**, *2* (8),
759 764-777.

760 61. Laughner, J. L.; Cohen, R. C., Direct observation of changing NO_x lifetime in North American
761 cities. *Science* **2019**, *366* (6466), 723-+.

762 62. Rappenglück, B.; Dasgupta, P. K.; Leuchner, M.; Li, Q.; Luke, W., Formaldehyde and its relation
763 to CO, PAN, and SO₂ in the Houston-Galveston airshed. *Atmospheric Chemistry and Physics* **2010**, *10*
764 (5), 2413-2424.

765 63. Roberts, J. M.; Marchewka, M.; Bertman, S. B.; Sommariva, R.; Warneke, C.; de Gouw, J.;
766 Kuster, W.; Goldan, P.; Williams, E.; Lerner, B. M.; Murphy, P.; Fehsenfeld, F. C., Measurements of
767 PANs during the New England air quality study 2002. *J. Geophys. Res.-Atmos.* **2007**, *112* (D20), 14.

768 64. Veres, P. R.; Roberts, J. M.; Cochran, A. K.; Gilman, J. B.; Kuster, W. C.; Holloway, J. S.;
769 Graus, M.; Flynn, J.; Lefer, B.; Warneke, C.; de Gouw, J., Evidence of rapid production of organic acids
770 in an urban air mass. *Geophys. Res. Lett.* **2011**, *38*, 5.

771 65. Kuster, W. C.; Jobson, B. T.; Karl, T.; Riemer, D.; Apel, E.; Goldan, P. D.; Fehsenfeld, F. C.,
772 Intercomparison of volatile organic carbon measurement techniques and data at la porte during the
773 TexAQS2000 Air Quality Study. *Environ. Sci. Technol.* **2004**, *38* (1), 221-228.

774 66. Warneke, C.; Kato, S.; De Gouw, J. A.; Goldan, P. D.; Kuster, W. C.; Shao, M.; Lovejoy, E. R.;
775 Fall, R.; Fehsenfeld, F. C., Online volatile organic compound measurements using a newly developed
776 proton-transfer ion-trap mass spectrometry instrument during New England Air Quality Study -
777 Intercontinental Transport and Chemical Transformation 2004: Performance, intercomparison, and
778 compound identification. *Environ. Sci. Technol.* **2005**, *39* (14), 5390-5397.

779 67. Hansen, R. F.; Griffith, S. M.; Dusanter, S.; Rickly, P. S.; Stevens, P. S.; Bertman, S. B.; Carroll,
780 M. A.; Erickson, M. H.; Flynn, J. H.; Grossberg, N.; Jobson, B. T.; Lefer, B. L.; Wallace, H. W.,
781 Measurements of total hydroxyl radical reactivity during CABINEX 2009-Part 1: field measurements.
782 *Atmospheric Chemistry and Physics* **2014**, *14* (6), 2923-2937.

783 68. Lefer, B.; Rappenglück, B.; Flynn, J.; Haman, C., Photochemical and meteorological
784 relationships during the Texas-II Radical and Aerosol Measurement Project (TRAMP). *Atmos. Environ.*
785 **2010**, *44* (33), 4005-4013.

786 69. Luke, W. T.; Kok, G. L.; Schillawski, R. D.; Zimmerman, P. R.; Greenberg, J. P.; Kadavanich,
787 M., TRACE GAS MEASUREMENTS IN THE KUWAIT OIL FIRE SMOKE PLUME. *Journal of*
788 *Geophysical Research-Atmospheres* **1992**, *97* (D13), 14499-14506.

789 70. Pollack, I. B.; Lerner, B. M.; Ryerson, T. B., Evaluation of ultraviolet light-emitting diodes for
790 detection of atmospheric NO₂ by photolysis - chemiluminescence. *Journal of Atmospheric Chemistry*
791 **2010**, *65* (2-3), 111-125.

792 71. Drummond, J. W.; Volz, A.; Ehhalt, D. H., AN OPTIMIZED CHEMI-LUMINESCENCE
793 DETECTOR FOR TROPOSPHERIC NO MEASUREMENTS. *Journal of Atmospheric Chemistry* **1985**,
794 *2* (3), 287-306.

- 795 72. Gerbig, C.; Schmitgen, S.; Kley, D.; Volz-Thomas, A.; Dewey, K.; Haaks, D., An improved fast-
796 response vacuum-UV resonance fluorescence CO instrument. *J. Geophys. Res.-Atmos.* **1999**, *104* (D1),
797 1699-1704.
- 798 73. Hu, W. W.; Palm, B. B.; Day, D. A.; Campuzano-Jost, P.; Krechmer, J. E.; Peng, Z.; de Sa, S. S.;
799 Martin, S. T.; Alexander, M. L.; Baumann, K.; Hacker, L.; Kiendler-Scharr, A.; Koss, A. R.; de Gouw, J.
800 A.; Goldstein, A. H.; Seco, R.; Sjostedt, S. J.; Park, J. H.; Guenther, A. B.; Kim, S.; Canonaco, F.; Prevot,
801 A. S. H.; Brune, W. H.; Jimenez, J. L., Volatility and lifetime against OH heterogeneous reaction of
802 ambient isoprene-epoxydiols-derived secondary organic aerosol (IEPOX-SOA). *Atmospheric Chemistry
803 and Physics* **2016**, *16* (18), 11563-11580.
- 804 74. DiGangi, J. P.; Boyle, E. S.; Karl, T.; Harley, P.; Turnipseed, A.; Kim, S.; Cantrell, C.; Maudlin,
805 R. L.; Zheng, W.; Flocke, F.; Hall, S. R.; Ullmann, K.; Nakashima, Y.; Paul, J. B.; Wolfe, G. M.; Desai,
806 A. R.; Kajii, Y.; Guenther, A.; Keutsch, F. N., First direct measurements of formaldehyde flux via eddy
807 covariance: implications for missing in-canopy formaldehyde sources. *Atmospheric Chemistry and
808 Physics* **2011**, *11* (20), 10565-10578.
- 809 75. Hottle, J. R.; Huisman, A. J.; Digangi, J. P.; Kammrath, A.; Galloway, M. M.; Coens, K. L.;
810 Keutsch, F. N., A Laser Induced Fluorescence-Based Instrument for In-Situ Measurements of
811 Atmospheric Formaldehyde. *Environ. Sci. Technol.* **2009**, *43* (3), 790-795.
- 812 76. Huisman, A. J.; Hottle, J. R.; Coens, K. L.; DiGangi, J. P.; Galloway, M. M.; Kammrath, A.;
813 Keutsch, F. N., Laser-induced phosphorescence for the in situ detection of glyoxal at part per trillion
814 mixing ratios. *Analytical Chemistry* **2008**, *80* (15), 5884-5891.
- 815 77. Nguyen, T. B.; Crounse, J. D.; Teng, A. P.; St. Clair, J. M.; Paulot, F.; Wolfe, G. M.; Wennberg,
816 P. O., Rapid deposition of oxidized biogenic compounds to a temperate forest. *Proceedings of the
817 National Academy of Sciences* **2015**, *112* (5), E392-E401.
- 818 78. Romer, P. S.; Duffey, K. C.; Wooldridge, P. J.; Allen, H. M.; Ayres, B. R.; Brown, S. S.; Brune,
819 W. H.; Crounse, J. D.; de Gouw, J.; Draper, D. C.; Feiner, P. A.; Fry, J. L.; Goldstein, A. H.; Koss, A.;
820 Misztal, P. K.; Nguyen, T. B.; Olson, K.; Teng, A. P.; Wennberg, P. O.; Wild, R. J.; Zhang, L.; Cohen, R.
821 C., The lifetime of nitrogen oxides in an isoprene-dominated forest. *Atmospheric Chemistry and Physics*
822 **2016**, *16* (12), 7623-7637.
- 823 79. Gilman, J. B.; Burkhardt, J. F.; Lerner, B. M.; Williams, E. J.; Kuster, W. C.; Goldan, P. D.;
824 Murphy, P. C.; Warneke, C.; Fowler, C.; Montzka, S. A.; Miller, B. R.; Miller, L.; Oltmans, S. J.;
825 Ryerson, T. B.; Cooper, O. R.; Stohl, A.; de Gouw, J. A., Ozone variability and halogen oxidation within
826 the Arctic and sub-Arctic springtime boundary layer. *Atmospheric Chemistry and Physics* **2010**, *10* (21),
827 10223-10236.
- 828 80. Graus, M.; Muller, M.; Hansel, A., High Resolution PTR-TOF: Quantification and Formula
829 Confirmation of VOC in Real Time. *J. Am. Soc. Mass Spectrom.* **2010**, *21* (6), 1037-1044.
- 830 81. Faloon, I. C.; Tan, D.; Leshner, R. L.; Hazen, N. L.; Frame, C. L.; Simpas, J. B.; Harder, H.;
831 Martinez, M.; Di Carlo, P.; Ren, X. R.; Brune, W. H., A laser-induced fluorescence instrument for
832 detecting tropospheric OH and HO₂: Characteristics and calibration. *J. Atmos. Chem.* **2004**, *47* (2), 139-
833 167.
- 834
- 835