1   **Formation of late-generation atmospheric compounds inhibited by rapid deposition**

2   Chenyang Bi[1,†,#], Gabriel Isaacman-VanWertz[1,†,*]

3   [1] Department of Civil and Environmental Engineering, Virginia Tech, Blacksburg, Virginia, 24060,

4   USA

5   [†] Equally contributing authors

6   [#] Now at Aerodyne Research Inc., Billerica, Massachusetts, 01821, USA

7   *Correspondence to*: Gabriel Isaacman-VanWertz (ivw@vt.edu)

8   **Abstract**

9   Reactive organic carbon species are important fuel for atmospheric chemical reactions, including

10   the formation of secondary organic aerosol. However, in parallel to atmospheric oxidation

11   processes, deposition can remove compounds from the atmosphere and impact downstream

12   environments. To understand the impact of deposition on atmospheric oxidation, we present a

13   framework for predicting and visualizing the fate of a molecule based on the physicochemical

14   properties of compounds (Henry's law constant, vapor pressure, and reaction rate constants),

15   which are used to estimate timescales for oxidation and deposition. By implementing our

16   deposition rates in chemical models, we show that deposition substantially suppresses

17   atmospheric reactivity and aerosol formation by removing early-generation products and

18   preventing the formation of large fractions (up to 90%) of downstream, late-generation

19   compounds. Deposition is frequently missing in the laboratory experiments and detailed

20   chemical modeling, which likely biases our understanding of atmospheric composition.

21

Oxidation in the atmosphere of reactive organic carbon (ROC) produces secondary organic aerosol (SOA), fuels the formation of a majority of tropospheric ozone (O_3), and contributes to secondary carbon dioxide (CO_2). These products may have major impacts on the ecosystem, human health, and climate.[1,2] ROC species emitted directly from a variety of sources[3-8] go on to oxidize through complex chains of photochemical reactions. As a result, oxidation on a timescale of several hours to days[9] produces hundreds of thousands of chemical products[10,11] that may be in the gas or particle phase. The oxidation reactions forming these products, which might be either fragmented small molecules or functionalized less volatile species, occur in parallel with their deposition to the Earth's surfaces. Dry deposition is driven by turbulence and concentration gradients at the surface while wet deposition is driven by scavenging by precipitation. Both deposition processes are governed by the tendency of a molecule to partition to an aqueous phase (e.g., precipitation or leaf surfaces), quantified as its Henry's law constant, H. As a result, deposition rates can be predicted as a function of Henry's law constants for a given set of precipitation and leaf area conditions.[12] H is also correlated closely with vapor pressure for atmospheric oxidation products.[13,14]

Deposition of condensable gases has been demonstrated in regional modeling studies to reduce surface concentrations of organic gases and particulate matter substantially.[13,15] However, because chemical mechanisms within regional transport models have to reduce complexity by lumping chemical species together by source or process,[16-18] the impact of deposition in the model simulations may not necessarily reflect real world losses or their impacts on subsequent oxidation chemistry. There is a critical need for computationally light and convenient approaches to assess the influence of deposition on atmospheric chemistry, particularly reactive carbon budgets, SOA formation, and oxidant reactivity. Deposition of early-generation oxidation

45 products may reduce the production of late-generation species, but no good current framework

46 exists to understand this process in a chemically explicit or fundamental way. Although many

47 methods have been proposed to classify molecules by their molecular formula and/or

48 physicochemical properties[19,20,21,22,23], they do not evaluate the impact of deposition on the

49 oxidation chemistry. In this work, a framework capturing the competition between oxidation and

50 deposition provides insight into the atmospheric fate of a molecule. By implementing this

51 competition into both a chemically explicit and a lumped volatility-basis 0-dimensional box

52 model, we find that deposition effectively competes with oxidation, removing ROC species that

53 would otherwise go on to form late-generational products, with major impacts on reactivity and

54 SOA formation.

55 **Predicting the fate of atmospheric compounds**

56 With basic assumptions regarding the state of the atmosphere (e.g., boundary layer height,

57 probability of rain, oxidant concentrations) and surface properties (e.g., leaf area index), the

58 timescales for both oxidation and deposition of a compound depend primarily on its volatility,

59 tendency to partition to aqueous phases (essentially "solubility"), and oxidation rate constants.[9,12]

60 These physicochemical parameters can all be estimated from molecular structure, or, with higher

61 uncertainty, from molecular formula.[14] Furthermore, due to the correlation between vapor

62 pressure and Henry's law constant for atmospheric oxidation products,[13,14] the fate of a molecule

63 can be visualized in a relatively simple two-dimensional space (Figure 1). The bounds of the

64 axes in Figure 1 roughly encompass the region found in the atmosphere, and compounds in only

65 a relatively narrow range of properties have a competitive fate between oxidation by OH radicals

66 and deposition (calculated as f_{fate} using Eqn S17). Only OH oxidation is included here, but other

67 gas-phase oxidation processes yield similar conclusions. Highly soluble species are mostly in the

68   particle phase and will be deposited as airborne particles (i.e., the green region in Figure 1) or go

69   on to react through in-particle chemistry, which is not considered here (discussed below).

70   Soluble but high volatility compounds will likely undergo gas deposition (i.e., blue region) while

71   less soluble and highly reactive species get oxidized (i.e., purple region). Oxidation is only

72   strongly competitive with deposition for compounds that are either highly insoluble, or have k_{OH}

73   greater than ~3×10^{-11} cm^3 molec^{-1} s^{-1}, faster than the typical reaction rate for oxidation

74   products.[14] The correlation between vapor pressure and Henry's law constant is an

75   oversimplification, but it is useful for visualizing complex atmospheric mixtures. For

76   quantitative evaluation, each property can be treated separately and for other analyses in this

77   work is estimated individually for each molecule.

78   A more direct approach to determine the fate of an individual molecule is to compare the

79   timescales of the two competing loss processes, oxidation and deposition (Figure 2). This

80   approach does not require the same assumption of correlated Henry's law and vapor pressure.

81   Instead, each property is estimated from molecular structure using established structure-activity

82   relationships[24,25];in most cases uncertainties in these relationships will not impact the region of

83   Figure 1 in which a compound lies. Using parameters representative of the southeastern U.S. and

84   confirmed by observations there,[26] we find that dry deposition is much faster (~6 hours for

85   highly soluble gases) than wet deposition (over 100 hours).[12] We examine the competition

86   between predicted fates for thousands of atmospherically relevant compounds, using a published

87   list[27] of ~38000 model-predicted oxidation products of toluene, α-pinene, and n-decane.[11]

88   Relatively few compounds, those in the upper-left (magenta markers), are expected to be lost

89   primarily by oxidation (less than 1% of compounds accounting for 18% of total mass), while a

90   large fraction (lower-right, blue markers, roughly one-third of total mass) is likely to be

91 deposited prior to oxidation. Roughly half of the total mass has a quarter or more of the molecule

92 lost by each pathway (region between the 3:1 or 1:3 lines). These compounds potentially require

93 more detailed analysis given that their fates are less clear. Conditions of the southeastern U.S. are

94 used to estimate deposition, but less-forested conditions where deposition is expected to occur

95 more slowly exhibit similar trends (Extended Data Figure 1). In addition, transport away from

96 the surface and to the free troposphere increases deposition lifetimes for longer-lived gases

97 (leading to an empty region in the lower right), but does not have a strong impact on more

98 reactive compounds. This approach can be applied to quickly identify key compounds from a

99 large pool of oxidation products to reduce the efforts of data analysis. For example, the wide use

100 of field deployable, online mass spectrometers generates extraordinarily large datasets containing

101 the time series of hundreds to thousands of chemical formulas. The approach can be applied to

102 narrow down the range of compounds that may be more or less important for aerosol formation

103 or downstream impacts, or may be used to reduce the need for including the oxidation of certain

104 compounds in chemical models.

105 **Impact of Deposition on Downstream Chemistry**

106 It is clear from Figures 1 and 2 that deposition is a significant loss pathway for compounds

107 across a large region of the physicochemical space observed in the atmosphere, and for many of

108 the oxidation products formed by common precursors. To investigate this impact quantitatively,

109 deposition is implemented into a 0-dimensional box model (chemically-explicit Framework for

110 0-D Atmospheric Modeling (F0AM) v3.1[28]) simulating the atmospheric oxidation of single

111 precursors and a complex mixture. These deposition processes are occurring in ambient

112 atmospheres, but are generally not considered by box models of the atmosphere, nor are they

113 captured by oxidation experiments in laboratory chambers. Here, we demonstrate that

114   depositional loss has significant impacts on the mixture of products, and particularly that

115   removal of gaseous early-generation species may sharply reduce the formation of late-generation

116   species and organic aerosol.

117   Deposition greatly reduces aerosol formation and OH reactivity (the availability of reactive

118   carbon to fuel oxidation reactions) in both single-precursor and complex-mixture oxidation

119   systems (i.e., precursors in the southeastern United States summarized in Table S1) (Figure 3)..

120   For α-pinene oxidation by OH, deposition reduced maximum SOA mass yield from 34% to 20%

121   and peak OH reactivity from 0.28 to 0.18 $s^{-1.}$ After 2 days of simulated oxidation, deposition has

122   removed nearly all remaining OH reactivity, with only long-lived volatile gases remaining in the

123   system. Similar strong impacts were observed for the simulated southeastern U.S., with

124   maximum aerosol concentration reduced by a factor of three from 0.6 to 0.2 $\mu g\ m^{-3}$, peak OH

125   reactivity reduced from 3.9 to 3.6 s^{-1}, and two-thirds of OH reactivity removed after several days.

126   These conditions are illustrative and are based on parameters for the southeastern U.S.; real-

127   world atmospheric conditions vary substantially, but significant deposition of OH reactivity is

128   observed consistently for a wide range of oxidation systems (Figures S1 and S2). Large removals

129   of aerosol formation are also observed for these other oxidation systems, but the chemically

130   explicit model does not include many low-volatility species and may underestimate aerosol

131   formation.[29-31] Significantly reduced aerosol formation due to deposition is also observed when

132   using a box model (SimpleSOM) in which the complex mixture is binned by volatility[32] (Figure

133   4). The conclusions of these box models are consistent with work in regional chemical models

134   that found dry deposition of semi-volatile oxidation products leads to a roughly 30 -50%

135   reduction in SOA concentration for the continental U.S.[33] We find not only that there is a general

136   reduction in SOA, but also that SOA formation nearly stops after the first few hours of oxidation.

137   Nearly all SOA formation in these simulations occurs through condensation of low-volatility

138   early-generation products, while other products that might go on to oxidize and form additional

139   SOA are mostly removed instead by deposition. This is in contrast to many chamber studies that

140   observe continued growth of SOA after depletion of the precursor.[34] Impacts are stronger in

141   modeled OH systems (Extended Data Figure 2) compared to modeled O_3 systems (Extended

142   Data Figure 3) because there is little downstream chemistry in ozonolysis following the

143   oxidation of the precursor double bond(s).

Impact of Deposition on Late-forming Species

145   The loss of early-generation oxidation products may substantially impact the formation of

146   downstream products yielding indirect depositional loss (i.e., loss of production). This is

147   suggested in the reduced formation of OA after several hours (Figrues 3 and 4), but can be

148   examined directly by categorizing each product by its generation (Figure 5). Due to the cascade

149   of oxidation reactions, the loss of early-generation compounds results in substantial losses of

150   late-generation compounds (e.g., 50% at 2 lifetimes and 98% at 48 hours for α-pinene OH

151   oxiation, Figures 6a and S3a, respectively) in both the gas and particle. A snapshot of the fraction

152   of particle-phase mass lost due to deposition at 9 hours of oxidation (approximately 2 lifetimes

153   of α-pinene) shows that the median removal is 26%, 43%, and 54% for first- through third- and

154   later-generation compounds, respectively (Figure 6b). The losses of second- and third-generation

155   species, many of which are simply never formed rather than directly deposited, contribute

156   roughly half of the overall reduction in SOA due to deposition, and change the chemical

157   composition of the particles (Extended Data Figure 4).

158   The impact of deposition captured here, though large, may actually be more modest in the α-

159   pinene + OH system than other systems, because a large fraction of SOA is known to be formed

160   through first-generation autoxidation products. In any system for which late-generation SOA

161   formation may be significant, the impact of deposition can be significantly stronger since more

162   than 90% of 3rd and later-generation species were removed by deposition by the end of the

163   simulation (Extended Data Figure 5). Even in complex mixture of precursors and oxidants (i.e.,

164   southeastern U.S. model conditions), there are strong downstream effects, with two-thirds of the

165   SOA never formed (Figure 3b).

166   **Atmospheric Implications and Limitations**

167   This work suggests new strategies to reduce the complexity of atmospheric oxidation reactions

168   and impacts interpretions of laboratory experiments and models. By using physicochemical

169   parameters to predict the timescales for critical atmospheric fates, molecules can be grouped by

170   their probable impacts in the atmosphere. A large subset of oxidation products are likely to be

171   deposited without ever having the chance to oxidize, so their oxidation can likely be ignored in

172   simplified models. Furthermore, a major fraction of late-generation oxidation products are likely

173   to be never formed. It is possible that including the first few generations of oxidation products is

174   enough to reach carbon closure in environments with moderately fast deposition.

175   The goal of this work is to create a simplified approach for understanding a complex atmosphere.

176   Consequently, some processes are not well captured and could be significant for certain

177   compounds. To evaluate the sensitivity of these conclusions to some of the processes that impact

178   aerosol formation, we also examined both the influence of transport to the free troposphere and

179   the influence of partitioning of soluble gases to an aqueous particle phase using simplified

180   implementations in the chemical box model. The impacts of deposition were not sensitive to

181   transport to the free troposphere across a broad range of mixing timescales (Supplementary

182   Figure 4). Though gas-water partitioning substantially increased the magnitude of aerosol

183   formation, the impact of deposition was not strongly affected (Supplementary Figure 5), likely

184   because deposition affects a wide range of compounds that are not sensitive to uptake to the

185   aqueous aerosol (Supplementary Figure 3). Other processes such as condensed-phase

186   reactions,[35-37] heterogeneous reactions[38], and reactive uptake[39] were not considered in this

187   framework though they may be important generally or for specific molecules. However, the

188   general conclusions regarding the high impact of deposition are found to apply across the range

189   of precursors, model approaches, and model complexity examined here. It should be noted that

190   the calculation of deposition timescales here is based on conditions in the forested southeast

191   United States where deposition occurs rapidly. In real-world conditions, atmospheric gases and

192   particles may travel a long distance while they react with oxidants and get deposited to surfaces,

193   so representative deposition timescales may need to be averaged over the range of transport.

194   While regions with slower deposition will decrease the impact of deposition (Extended Data

195   Figure 1), our sensitivity analysis shows that slower deposition (i.e., decreasing the LAI from 4.7

196   to 0.47) still strongly suppresses concentrations after multiple lifetimes of oxidation.

197   Furthermore, a large fraction of emissions occurs in regions of high leaf area, so many early-

198   generation oxidation products will be subject to rapid deposition. However, a global analysis of

199   competition between oxidation and deposition would significantly improve understanding of the

200   global impacts of deposition.

201   The strong impact of deposition observed here raises interesting questions for our general

202   understanding of atmospheric chemistry and our interpretation of laboratory experiments. Prior

203   work has demonstrated both first-generation and later-generation aerosol formation in

204   chambers[34,40-42], but this work suggests that a substantial fraction of later-generation components

205   may not actually be formed under ambient conditions. Recent work has sought to reconcile

206 laboratory data with ambient conditions by accounting for losses of particle-forming gases to

207 chamber wall surfaces.[43,44] In fact, deposition has a weaker influence than wall loss on early-

208 generation SOA and a stronger effect on late-generation products (Extended Data Figure 6).

209 After simulated multi-hour oxidation experiments, aerosol mass loadings in the chamber

210 experiments are higher than would be expected in an ambient environment exposed to

211 deposition. Any corrections for wall loss would further overestimate late-generation SOA, while

212 improving estimates of early-forming mass. Further investigating the similarities between

213 laboratory and real-world deposition is necessary to better understand and resolve these issues.

214 Thes findings in this work may also provide new sights in improving regional-scale models.

215 Since all regional-scale models rely on condensed chemical mechanisms in which chemicals in

216 many cascades of reactions are binned into some representative species, they may not capture the

217 impact of upstream species on downstream ones which is critical for the impact of deposition.

218 This work highlights the importance of considering Henry's law constants when assigning

219 properties or surrogate compounds to chemical bins, which may not currently be one of the

220 criteria considered.

221

Acknowledgements

227 the National Science Foundation Atmospheric and Geospace Sciences CAREER program (AGS-

228 2046367, supporting G.I-VW.).

229

230 **Author Contributions**

231 C.B. and G.I.V.W. contributed equally to this work. C.B. performed data analysis and led model

232 implementations and interpration. G.I.V.W. conceived of the study, contributed to data analysis,

233 and conducted modeling. Both authors contributed significantly to writing and editing.

234

235 **Competing interests**

236 The authors declare no competing interests.

237

238 **Figure Captions**

239 **Figure 1.** Prediction of the fate of a molecule based on its Henry's law constant and OH reaction

240 rate constant. Molecules in the purple, blue, and green regions are primarily removed via

241 oxidation, gas deposition, and particle deposition, respectively. Dashed lines with a grey scale

242 indicate the boundary of the fraction of compounds removed by a specific pathway. The figure

243 assumes deposition conditions in the forested southeast United States and $[OH] = 1\times10^6$

244 molecules cm^{-3}.

245

246 **Figure 2.** Modeled oxidation and deposition timescales of atmospheric oxidation products. The

247 timescales are predicted by explicit chemical modeling of oxidation of toluene, α-pinene, and *n*-

11

248   decane assuming deposition conditions in the forested southeast United States and $[OH] = 1 \times 10^6$

249   molecules cm^{-3}. Each marker represents one oxidation product and is sized by its relative

250   concentration in the model. Dashed lines are the boundaries where compounds have a ratio of

251   timescales at 3:1 or 1:3. A timescale of 2.5 days is assumed for transport from the planetary

252   boundary layer to the free troposphere, which matches some global aircraft observations but may

253   be slower than expected in summertime continental conditions such as those explored here;

254   conclusions are not sensitive to the selection of this parameter (Supplementary Figure 4).

255

256   **Figure 3.** Impact of deposition on modeled organic aerosol formation and OH reactivity in a

257   chemically-explicit model. F0AM model cases of (a) α-pinene (introduced with an initial level of

258   1 ppb) + OH (held at 1×10^6 molecules cm^{-3}) oxidation reactions and (b) mixture of precursors

259   and oxidants in the southeastern U.S. Model with deposition is dashed lines (orange: OH

260   reactivity; blue: total OA) and without deposition is solid lines. Deposition parameters were

261   constrained by measurements in the forested southeast United States. Precursors are excluded in

262   the calculation of OH reactivity. Diurnal cycle of daylight is included in southeastern U.S.

263   model.

264

265   **Figure 4.** Impact of deposition on the modeled organic aerosol formation in a volatility-binned

266   box model. The SimpleSOM[32] model simulates the oxidation of 1 ppb α-pinene (by OH=1×10^6

267   molecules cm^{-3}) under the low NO_x condition as a function of (a) model time and (b) percent of

268   precursor consumed. Deposition parameters were constrained by measurements in the forested

269   southeast United States.

270

271   **Figure 5.** Concentrations of gas- and particle-phase oxidation products categorized by their

272   oxidation generation under model conditions with and without considering deposition. The

273   model is the same as that in Figure 3a and simulates the case of (a) and (c) without the

274   implementation of deposition and (b) and (d) with deposition implemented. Deposition

275   parameters were constrained by measurements in the forested southeast United States.

276

277   **Figure 6.** Removal of compounds due to deposition as a function of oxidation generation.

278   Fractional loss is shown for (a) gas-phase species and (b) particle-phase species via deposition.

279   Dots represent chemical species simulated in F0AM at 9 hours (i.e., 2 lifetimes) for the α-pinene

280   + OH oxidation reactions. The width of the violin at a given level is proportional to the

281   aggregated relative abundance of chemicals near that level.

282

283   **References**

284   1.   Burnett RT, Pope CA, Ezzati M, Olives C, Lim SS, Mehta S*, et al.* An integrated risk

285   function for estimating the global burden of disease attributable to ambient fine

286   particulate matter exposure. *Environmental Health Perspectives* 2014, **122**(4)**:** 397-403.

287

288   2.   Heald CL, Kroll JH. The fuel of atmospheric chemistry Toward a complete description of

289   reactive organic carbon. *Science Advances* 2020, **6**(6).

290

291   3.   Jin L, Permar W, Selimovic V, Ketcherside D, Yokelson RJ, Hornbrook RS*, et al.*

292   Constraining emissions of volatile organic compounds from western US wildfires with

293   WE-CAN and FIREX-AQ airborne observations. *Atmospheric Chemistry and Physics*

294   2023, **23**(10)**:** 5969-5991.

295

296   4.   Guenther AB, Jiang X, Heald CL, Sakulyanontvittaya T, Duhl T, Emmons LK, Wang X.

297   The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1):

298   an extended and updated framework for modeling biogenic emissions. *Geoscientific*

299   *Model Development* 2012, **5**(6)**:** 1471-1492.

300

301   5.   Murphy BN, Sonntag D, Seltzer KM, Pye HOT, Allen C, Murray E*, et al.* Reactive

302   Organic Carbon Air Emissions from Mobile Sources in the United States. *EGUsphere*

303   2023, **2023:** 1-24.

304

305   6.   Mattila JM, Arata C, Abeleira A, Zhou Y, Wang C, Katz EF*, et al.* Contrasting Chemical

306   Complexity and the Reactive Organic Carbon Budget of Indoor and Outdoor Air. *Environ*

307   *Sci Technol* 2022, **56**(1)**:** 109-118.

308

309   7.   McDonald BC, De Gouw JA, Gilman JB, Jathar SH, Akherati A, Cappa CD*, et al.*

310   Volatile chemical products emerging as largest petrochemical source of urban organic

311   emissions. *Science* 2018, **359**(6377)**:** 760-764.

312

313   8.   Seltzer KM, Pennington E, Rao V, Murphy BN, Strum M, Isaacs KK, Pye HOT. Reactive

314   organic carbon emissions from volatile chemical products. *Atmospheric Chemistry and*

315   *Physics* 2021, **21**(6)**:** 5079-5100.

316

317   9.   Isaacman-Vanwertz G, Massoli P, O'Brien R, Lim C, Franklin JP, Moss JA*, et al.*

318   Chemical evolution of atmospheric organic carbon over multiple generations of

319   oxidation. *Nature Chemistry* 2018, **10**(4)**:** 462-468.

320

321   10.   Goldstein AH, Galbally IE. Known and unexplored organic constituents in the earth's

322   atmosphere. *Environmental Science and Technology* 2007, **41**(5)**:** 1514-1521.

323

324   11.   Aumont B, Szopa S, Madronich S. Modelling the evolution of organic carbon during its

325   gas-phase tropospheric oxidation: development of an explicit model based on a self

326   generating approach. *Atmos Chem Phys* 2005, **5**(9)**:** 2497-2517.

327

328   12.   Bi C, Isaacman-VanWertz G. Estimated timescales for wet deposition of organic

329   compounds as a function of Henry's law constants. *Environmental Science: Atmospheres*

330   2022, **2**(6)**:** 1526-1533.

331

332   13.   Hodzic A, Aumont B, Knote C, Lee-Taylor J, Madronich S, Tyndall G. Volatility

333   dependence of Henry's law constants of condensable organics: Application to estimate

334   depositional loss of secondary organic aerosols. *Geophysical Research Letters* 2014,

335   **41**(13)**:** 4795-4804.

336

337   14.   Isaacman-VanWertz G, Aumont B. Impact of organic molecular structure on the

338   estimation of atmospherically relevant physicochemical parameters. *Atmospheric*

339   *Chemistry and Physics* 2021, **21**(8)**:** 6541-6563.

340

341   15.   Safieddine SA, Heald CL, Henderson BH. The global nonmethane reactive organic

342   carbon budget: A modeling perspective. *Geophysical Research Letters* 2017, **44**(8)**:** 3897-

343   3906.

344

345   16.   Pye HOT, Place BK, Murphy BN, Seltzer KM, D'Ambro EL, Allen C*, et al.* Linking gas,

346   particulate, and toxic endpoints to air emissions in the Community Regional Atmospheric

347   Chemistry Multiphase Mechanism (CRACMM). *Atmos Chem Phys* 2023, **23**(9)**:** 5043-

348   5099.

349

350   17.   Carter WPL. Development of the SAPRC-07 chemical mechanism. *Atmospheric*

351   *Environment* 2010, **44**(40)**:** 5324-5335.

352

353   18.   Sarwar G, Godowitch J, Henderson BH, Fahey K, Pouliot G, Hutzell WT*, et al.* A

354   comparison of atmospheric composition using the Carbon Bond and Regional

Atmospheric Chemistry Mechanisms. *Atmospheric Chemistry and Physics* 2013, **13**(19)**:** 9695-9712.

19.   Donahue NM, Epstein SA, Pandis SN, Robinson AL. A two-dimensional volatility basis set: 1. organic-aerosol mixing thermodynamics. *Atmospheric Chemistry and Physics* 2011, **11**(7)**:** 3303-3318.

20.   Kroll JH, Donahue NM, Jimenez JL, Kessler SH, Canagaratna MR, Wilson KR*, et al.* Carbon oxidation state as a metric for describing the chemistry of atmospheric organic aerosol. *Nat Chem* 2011, **3**(2)**:** 133-139.

21.   Heald CL, Kroll JH, Jimenez JL, Docherty KS, DeCarlo PF, Aiken AC*, et al.* A simplified description of the evolution of organic aerosol composition in the atmosphere. *Geophysical Research Letters* 2010, **37**(8).

22.   Cappa CD, Wilson KR. Multi-generation gas-phase oxidation, equilibrium partitioning, and the formation and evolution of secondary organic aerosol. *Atmospheric Chemistry and Physics* 2012, **12**(20)**:** 9505-9528.

23.   Pankow JF, Barsanti KC. The carbon number-polarity grid: A means to manage the complexity of the mix of organic compounds when modeling atmospheric organic particulate matter. *Atmospheric Environment* 2009, **43**(17)**:** 2829-2835.

377

24.   EPA U. Estimation Programs Interface Suite™ for Microsoft® Windows, v 4.11. *United*

      States Environmental Protection Agency, Washington, DC, USA 2012.

380

25.   Compernolle S, Ceulemans K, Müller JF. EVAPORATION: a new vapour pressure

      estimation methodfor organic molecules including non-additivity and intramolecular

      interactions. *Atmos Chem Phys* 2011, **11**(18)**:** 9431-9450.

384

26.   Nguyen TB, Crounse JD, Teng AP, St Clair JM, Paulot F, Wolfe GM, Wennberg PO.

      Rapid deposition of oxidized biogenic compounds to a temperate forest. *Proc Natl Acad*

      Sci U S A 2015, **112**(5)**:** E392-401.

388

27.   Isaacman-VanWertz G, Aumont B. SMILES and physicochemical parameters - pinene,

      decane, toluene oxidation products. V2 ed: Mendeley Data; 2021.

391

28.   Wolfe GM, Marvin MR, Roberts SJ, Travis KR, Liao J. The Framework for 0-D

      Atmospheric Modeling (F0AM) v3.1. *Geoscientific Model Development* 2016, **9**(9)**:**

      3309-3319.

395

29.   Pye HOT, D'Ambro EL, Lee BH, Schobesberger S, Takeuchi M, Zhao Y*, et al.*

      Anthropogenic enhancements to production of highly oxygenated molecules from

      autoxidation. *Proc Natl Acad Sci U S A* 2019, **116**(14)**:** 6641-6646.

399

30. Li J, Mao J, Min KE, Washenfelder RA, Brown SS, Kaiser J, *et al.* Observational constraints on glyoxal production from isoprene oxidation and its contribution to organic aerosol over the Southeast United States. *J Geophys Res Atmos* 2016, **121**(16)**:** 9849-9861.

404

31. Zhu Y, Tilgner A, Hoffmann EH, Herrmann H, Kawamura K, Yang L, *et al.* Multiphase MCM–CAPRAM modeling of the formation and processing of secondary aerosol constituents observed during the Mt. Tai summer campaign in 2014. *Atmospheric Chemistry and Physics* 2020, **20**(11)**:** 6725-6747.

409

32. Jathar SH, Cappa CD, He Y, Pierce JR, Chuang W, Bilsback KR, *et al.* A computationally efficient model to represent the chemistry, thermodynamics, and microphysics of secondary organic aerosols (simpleSOM): model development and application to α-pinene SOA. *Environmental Science: Atmospheres* 2021, **1**(6)**:** 372-394.

414

33. Knote C, Hodzic A, Jimenez JL. The effect of dry and wet deposition of condensable vapors on secondary organic aerosols concentrations over the continental US. *Atmospheric Chemistry and Physics* 2015, **15**(1)**:** 1-18.

418

34. Ng NL, Kroll JH, Keywood MD, Bahreini R, Varutbangkul V, Flagan RC, *et al.* Contribution of First- versus Second-Generation Products to Secondary Organic Aerosols

421 Formed in the Oxidation of Biogenic Hydrocarbons. *Environmental Science &*

422 *Technology* 2006, **40**(7)**:** 2283-2297.

423

424 35. Witkowski B, Al-Sharafi M, Blaziak K, Gierczak T. Aging of alpha-Pinene Secondary

425 Organic Aerosol by Hydroxyl Radicals in the Aqueous Phase: Kinetics and Products.

426 *Environ Sci Technol* 2023, **57**(15)**:** 6040-6051.

427

428 36. Marais EA, Jacob DJ, Jimenez JL, Campuzano-Jost P, Day DA, Hu W*, et al.* Aqueous-

429 phase mechanism for secondary organic aerosol formation from isoprene: application to

430 the Southeast United States and co-benefit of SO(2) emission controls. *Atmos Chem Phys*

431 2016, **16**(3)**:** 1603-1618.

432

433 37. Knote C, Hodzic A, Jimenez JL, Volkamer R, Orlando JJ, Baidar S*, et al.* Simulation of

434 semi-explicit mechanisms of SOA formation from glyoxal in aerosol in a 3-D model.

435 *Atmospheric Chemistry and Physics* 2014, **14**(12)**:** 6213-6239.

436

437 38. Shen X, Zhao Y, Chen Z, Huang D. Heterogeneous reactions of volatile organic

438 compounds in the atmosphere. *Atmospheric Environment* 2013, **68:** 297-314.

439

440 39. Lin YH, Zhang Z, Docherty KS, Zhang H, Budisulistiorini SH, Rubitschun CL*, et al.*

441 Isoprene epoxydiols as precursors to secondary organic aerosol formation: acid-catalyzed

442   reactive uptake studies with authentic compounds. *Environ Sci Technol* 2012, **46**(1)**:** 250-

443   258.

444

445   40.   Kroll JH, Ng NL, Murphy SM, Flagan RC, Seinfeld JH. Secondary Organic Aerosol

446   Formation from Isoprene Photooxidation. *Environmental Science & Technology* 2006,

447   **40**(6)**:** 1869-1877.

448

449   41.   Kroll JH, Seinfeld JH. Chemistry of secondary organic aerosol: Formation and evolution

450   of low-volatility organics in the atmosphere. *Atmospheric Environment* 2008, **42**(16)**:**

451   3593-3624.

452

453   42.   Ng NL, Kroll JH, Chan AWH, Chhabra PS, Flagan RC, Seinfeld JH. Secondary organic

454   aerosol formation from *m*-xylene, toluene, and benzene. *Atmos Chem Phys* 2007,

455   **7**(14)**:** 3909-3922.

456

457   43.   Wang N, Jorga SD, Pierce JR, Donahue NM, Pandis SN. Particle wall-loss correction

458   methods in smog chamber experiments. *Atmospheric Measurement Techniques* 2018,

459   **11**(12)**:** 6577-6588.

460

461   44.   Zhang X, Cappa CD, Jathar SH, McVay RC, Ensberg JJ, Kleeman MJ, Seinfeld JH.

462   Influence of vapor wall loss in laboratory chambers on yields of secondary organic

463   aerosol. *Proc Natl Acad Sci U S A* 2014, **111**(16)**:** 5802-5807.

464

Methods

466 **Deposition of gases.** Dry deposition timescales were estimated as a function of Henry's law

467 constants and molecular weight based on the resistance-in-series model of deposition velocities

468 at the surface.[45] Since dry deposition timescales may vary significantly depending on multiple

469 factors such as location, atmospheric conditions, and characteristics of the surfaces, we apply

470 parameters used by Nguyen et al.[26] for the southeastern U.S.; this environment represents

471 relatively rapid dry deposition due to high coverage of vegetation, but for the same reason is a

472 hotspot of ROC emissions and has observationally constrained dry deposition timescales.

473 Deposition velocities for each compound are converted to first-order timescales for dry

474 deposition by assuming a deposition height of 750 m, representative of the approximate middle

475 of the continental planetary boundary layer. Uncertainty in dry deposition timescales is driven by

476 variability in leaf area index, for which a sensitivity analysis is performed in Extended Data

477 Figure 5.

478 Wet deposition timescales were estimated as a function of Henry's law constants as previously

479 reported by Bi and Isaacman-VanWertz[12] This study found that precipitation characteristics are

480 sufficiently similar across different globally distributed sites that the precipitation frequency and

481 duration, rather than its intensity or droplet size distribution, govern the overall wet deposition

482 timescales. One-minute rain data at the Mobile, AL International Airport was used to estimate a

483 timescale of wet deposition of 104 hours for the most soluble gases (uncertainty ~30%) in the

484 southeastern U.S. Timescales for gases with $H < 10^5$ M atm^{-1} were estimated using the empirical

485 relationship reported in that work.

486 Henry's law constants and molecular weight of oxidation products of ROC species including

487 isoprene, terpenes, aromatics, and oxygenates (detailed list in Table S1) were obtained by the

488 HenryWIN bond contribution method (HWINb) using the Simplified Molecular Input Line Entry

489 System (SMILES) as inputs to the Estimation Programs Interface (EPI) Suite software (version

490 4.1) developed US Environmental Protection Agency.[46]

491 Additional details of the estimation approach for both wet and dry deposition timescales are

492 described by Supplementary Equations 1 through 10 and discussions thereof.

493 Compounds for which deposition were modeled include those used in the 0-dimensional model

494 (described below), and those predicted to be formed in the atmospheric oxidation of α-pinene,

495 toluene, and n-decane using the Generator for Explicit Chemistry and Kinetics of Organics in the

496 Atmosphere (GECKO-A).[11] These compounds are obtained from a published dataset[27] of 38,000

497 gas- and particle-phase oxidation products of these three precursors under oxidation conditions

498 approximately representative of average continental conditions.[14]

499 **Deposition of particles.** A constant deposition velocity was assigned to airborne particles,

500 yielding a particle-phase deposition timescale of 7 days. Gas-particle partitioning for each

501 compound was estimated by an equilibrium absorptive partitioning model based on saturation

502 concentration of gases (calculated from vapor pressure) and airborne particle-phase organic mass

503 concentration (calculated directly in the box model, and assumed to 5 ug m^{-3} for calculated

504 general lifetimes). Vapor pressure is estimated using EVAPORATION[25]. For visualization only,

505 the close linear correlation between Henry's law constants and vapor pressure atmospheric

506 oxidation products[13, 14] is used to collapse the vapor pressure and Henry's law constant axes into

507 a single axis

508   **Oxidation of gases.** Oxidation timescales were estimated using reaction rate constants with

509   oxidants. Since almost all closed-shell species react with OH radicals, we use the OH reaction

510   rate constant, k_{OH}, and an average OH concentration in the atmosphere $\overline{[OH]} = 1 \times 10^6$ molecules

511   cm^{-3} as the indicators for the oxidation timescale of ROC species in this study. Particle-phase

512   reactions with OH are treated as negligible as they remain poorly constrained. This may

513   underestimate oxidation rates as some compounds have competitive O_3 oxidation rates; however,

514   most of the species examined here do not contain non-aromatic double bounds subject to O_3

515   reaction. Similarly, most species can undergo NO_3 reaction, which is not considered here as rates

516   are still poorly constrained and structure-activity relationships are uncertain. The reaction rate

517   constant for each molecule, k_{OH}, was obtained based on SMILES using the AOPWIN module of

518   the EPI Suite[46], which is primarily an implementation of the Kwok and Atkinson [47] structure-

519   activity relationship. The details of the estimation of oxidation timescales are described by

520   Supplementary Equations 18 and 19 and discussion thereof.

521   **0-dimensional chemical box models.** To examine the role of deposition in the atmosphere,

522   deposition was implemented into two 0-dimensional box models as a first-order loss process,

523   including a chemically explicit model and a volatility-binned model.

524   The chemically-explicit Framework for 0-D Atmospheric Modeling (F0AM) v3.1[28] was used,

525   including the Washington Aerosol Module (WAM) extension[48] for gas-particle partitioning. The

526   oxidation chemistry of all precursors followed the Master Chemical Mechanism (MCM) v3.1.1,

527   with additional pathways for the formation of highly oxygenated peroxyl radicals and coproducts

528   added for α-pinene oxidation, developed by Pye, D'Ambro [29] Molecules were classified by their

529   generation, defined as the least number of reactions of OH, O_3, or photolysis reactions needed to

530   produce this compound. Deposition of all gas-phase species was added as a first-order constant

531 proceeding at a rate inverse to the deposition lifetime while particle deposition was not included.

532 All compounds except the precursors were allowed to deposit in the simulations. Compounds

533 with saturation vapor concentrations less than 100 μg m^{-3} were configured to dynamically

534 partition between the gas and aerosol phases using vapor pressures determined by

535 EVAPORATION;[25, 49] sensitivity to this threshold was explored, particularly in investigating the

536 impacts of gas-water partitioning, and conclusions of this work were not found to be sensitive to

537 the value selected. Both single-precursor and simulated southeastern U.S. atmospheres were

538 modeled. For the single precursor-oxidant simulation, oxidants are held at constant levels (i.e.,

539 O$_3$ at 60 ppb and/or OH at 1×10^6 molecules cm^{-3}) and an initial aliquot of the precursor was

540 added (1 ppb of α-pinene). Oxidation of a mixture of precursors that roughly represents the

541 southeastern U.S. was performed using the sample model scenario provided with the F0AM

542 model based on concentrations measured in the 2013 Southern Oxidant and Aerosol Study

543 (SOAS).[50] Oxidants were held at their observed values within each hour and changed hourly

544 based on the measurements in a typical diurnal cycle while precursors, including alkanes,

545 aromatics, oxygenates, and monoterpenes were introduced as a mixture at the beginning of the

546 simulation and allowed to decay photochemically. For each oxidation product, two nonreactive

547 tracers including one for cumulative depositional loss and the other for cumulative production

548 were added to the chemical mechanisms to track the mass balance of formed species throughout

549 the simulation. OH reactivity is quantified as the sum of the concentrations of each compound

550 times its OH reaction rates; precursors are excluded from the calculation for purposes of all

551 figures.

552 A computationally-efficient version of the volatility-binned statistical oxidation model

553 (SimpleSOM)[32], originally developed by Cappa and Wilson [22] was modified by adding

554   deposition of gases into the box model and was used to validate the strong effects of deposition

555   on oxidation observed in F0AM. SimpleSOM simulates multigenerational gas-phase chemistry,

556   phase-state-influenced kinetic gas/particle partitioning, heterogeneous chemistry, oligomerization

557   reactions, and vapor losses to the walls of chambers. Baseline model parameters for α-pinene

558   oxidation were used that reproduce observed chamber measurements in low-NO_x photooxidation

559   chamber experiments.[51] Baseline conditions include a vapor wall loss correction based on

560   measured parameters. The model was modified by implementing deposition as a first-order

561   removal process within the chemistry module that does not yield any product (i.e., removes,

562   rather than transforms, mass). The Henry's law constant of each volatility bin was obtained by

563   assuming the previously-demonstrated linear relationship based on the vapor pressure; though

564   this introduces uncertainty due to differences in the slope of this relationship for different

565   precursors, there is no other mechanism for this estimation as each volatility bin has no

566   associated structure, and the relationship used is an average for products of multiple precursors

567   to keep the implementation as general as possible.[14] Deposition rates were determined as a

568   function of Henry's law constants for each volatility bin using the empirical relationship shown

569   in Supplementary Figure 1. In the baseline conditions, precursor and oxidation concentrations

570   were reduced from chamber concentrations to make the results more representative of real-world

571   conditions (i.e., α-pinene at 1 ppb and OH at 1×10^6 molecules cm^{-3}).

572

573   **Data availability**

574   Lifetimes for compounds shown in Figure 2 are provided as Source Data, and are estimated

575   alongside their physicochemical properties for these compounds and an additional ~140,000

576   compounds in a publicly available dataset (DOI: 10.17632/3rgvkf7c9n).[27] Compounds used in

577 chemically explicity modeling are freely available through the Master Chemical Mechanism

578 (https://mcm.york.ac.uk/MCM/) and referenced publicly available works. Deposition lifetimes

579 for all compounds used in the chemically explicit box model are provided as Supplementary

580 Dataset 1. These data and the referenced publicly available models are used generate Figures 3,

581 5, and 6, as well as Extended Data Figures 2-4. All information to generate Figures 1 and 4 are

582 described in the Methods and Supplementary Information. Source Data are provided for

583 Extended Data Figures 1 and 6.

584

585 **Code availability**

586 Models used in this work are publicly available as cited. The F0AM model was used as provided,

587 with additional reactions added as described in the manuscript and Supplementary Information.

588 The SimpleSOM model was modified slightly to include deposition as described in the

589 manuscript; the modified code has been provided to the authors of the model for inclusion in

590 their next publicly available release.

591

592 **Methods References**

593 45.   Weseley ML. Parameterization of Surface Resistances to Gaseous Dry Deposition in

594   Regional-Scale Numerical Models. *Atmospheric Environment* 1989, **23**(6)**:** 1293-1304.

595

596 46.   EPA U. Estimation Programs Interface Suite for Microsoft Windows v4.1. United States

597   Environmental Protection Agency, Washington, DC,USA; 2015.

598

47. Kwok ESC, Atkinson R. Estimation of hydroxyl radical reaction rate constants for gas-phase organic compounds using a structure-reactivity relationship: An update. *Atmospheric Environment* 1995, **29**(14)**:** 1685-1695.

48. D'Ambro EL, Møller KH, Lopez-Hilfiker FD, Schobesberger S, Liu J, Shilling JE*, et al.* Isomerization of Second-Generation Isoprene Peroxy Radicals: Epoxide Formation and Implications for Secondary Organic Aerosol Yields. *Environmental Science & Technology* 2017, **51**(9)**:** 4978-4987.

49. Topping D, Barley M, Bane MK, Higham N, Aumont B, Dingle N, McFiggans G. UManSysProp v1.0: an online and open-source facility for molecular property prediction and atmospheric aerosol calculations. *Geoscientific Model Development* 2016, **9:** 899-914.

50. Heald CL, Gouw J, Goldstein AH, Guenther AB, Hayes PL, Hu W*, et al.* Contrasting Reactive Organic Carbon Observations in the Southeast United States (SOAS) and Southern California (CalNex). *Environ Sci Technol* 2020, **54**(23)**:** 14923-14935.

51. Chhabra PS, Lambe AT, Canagaratna MR, Stark H, Jayne JT, Onasch TB, Davidovits P. Application of high-resolution time-of-flight chemical ionization mass spectrometry

619 measurements to estimate volatility distributions of α -pinene and naphthalene oxidation

620 products. 2015**:** 1-18.

621

(a)

Without deposition

With deposition

(b)

Without deposition

With deposition

(a) Total Organic Aerosol (µg/m³) vs Model Time (hr): Without deposition; With deposition. (b) Total Organic Aerosol (µg/m³) vs Precursor consumed (%): Without deposition; With deposition.

(a)

Normalized Δconcentration due to deposition

0.0   0.2   0.4   0.6

southeastern U.S.

Deposition timescale (hr) assuming LAI = 4.7

10⁴

10³

10²

10¹

10¹   10²   10³   10⁴

Oxidation timescale (hr)

(b)

Normalized Δconcentration due to deposition

0.0   0.1   0.2   0.3

southeastern U.S.

Deposition timescale (hr) assuming LAI = 0.47

10⁴

10³

10²

10¹

10¹   10²   10³   10⁴

Oxidation timescale (hr)

a) Isoprene-O$_3$

b) Benzene-O$_3$

c) Toluene-O$_3$

d) Limonene-O$_3$

a) Without deposition

Others

C10H18O7B29
C10H14O10PDbL2306
C10H18O6
C10H18O7B20
C10H18O7B19

b) With deposition

Others

C10H17O8B22
C10H18O7B29
C10H18O6
C10H18O7B20
C10H18O7B19