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1 **Impact of aromatics and monoterpenes on simulated tropospheric ozone** 2 **and total OH reactivity**

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6

7 **Abstract**

8 The accurate representation of volatile organic compounds (VOCs) in models is an important
9 step towards the goal of understanding and predicting many changes in atmospheric constituents
10 relevant to climate change and human health. While isoprene is the most abundant non-methane
11 VOC, many other compounds play a large role in governing pollutant formation and the overall
12 oxidative capacity of the atmosphere. We quantify the impacts of aromatics and monoterpenes,
13 two classes of VOC not included in the standard gas-phase chemistry of the chemical transport
14 model GEOS-Chem, on atmospheric composition. We find that including these compounds
15 increases mean total summer OH reactivity by an average of 11% over the United States,
16 Europe, and Asia. This increased reactivity results in higher simulated levels of O₃, raising
17 maximum daily 8-hour average O₃ in the summer by up to 14 ppb at some NO_x-saturated
18 locations.

19 **1 Introduction**

20 Volatile organic compounds (VOCs) play a critical role within the Earth's troposphere, affecting
21 the global climate, controlling the formation of common pollutants, and influencing the lifetimes
22 of other key atmospheric compounds. VOCs are emitted from both natural and anthropogenic
23 sources, including combustion and industrial production processes (Piccot et al., 1992), as well
24 as natural emissions from trees and other plant life (Guenther et al., 2012). The accurate
25 representation of these compounds within atmospheric models is a key goal of the atmospheric
26 chemistry community, largely because they are direct precursors of ozone (O₃) and fine
27 particular matter (PM_{2.5}), known pollutants which can also influence the global climate (Jenkin
28 and Clemitshaw, 2000). VOCs also have major impacts on other key atmospheric species,
29 including the hydroxyl radical (OH), one of the key contributors to the oxidation capacity of the
30 atmosphere.

31 Tropospheric O₃ is an EPA criteria pollutant responsible for an estimated 200,000 premature
32 mortalities worldwide each year (Lim et al., 2013). Ozone concentrations are typically highest on
33 hot, stagnant days in the presence of abundant nitrogen oxides (NO_x) and VOCs. While there has
34 been some success in reducing the magnitude of extreme summertime O₃ events across the
35 United States and Europe, especially in urban areas (Guerreiro et al., 2014; Simon et al., 2015),
36 difficulties in predicting and reducing global tropospheric O₃ levels remain (Cooper et al., 2014).
37 Among the causes of these difficulties are uncertainties surrounding the emissions, chemistry,
38 and removal of VOCs and other O₃ precursors, especially due to the non-linearity of the
39 relationship between precursor concentrations and O₃ production. Understanding spatial and
40 temporal variability in atmospheric oxidative capacity, O₃ formation rates, and other
41 consequences of VOCs will require that gap to be closed, both in ambient observations of the

42 atmosphere and within the models used to represent it. Many studies have reported a gap
43 between summed observed OH reactivity and observations based on OH lifetimes, a discrepancy
44 which could be explained by the presence of unidentifiable VOCs and/or their oxidation products
45 (Yang et al., 2016). Meanwhile, although the current generation of chemical transport models
46 typically includes a variety of species representing the most common and influential VOCs, this
47 is a small fraction of the 3,000-4,000 currently identifiable species, which is, in turn, only a small
48 fraction of the total compounds (estimated to be on the order of 10^4 - 10^5) present in the
49 atmosphere (Goldstein and Galbally, 2007).

50 GEOS-Chem, a model often used for the study of pollutants and tropospheric composition,
51 simulates the emission and oxidation of many of the most important atmospheric non-methane
52 VOC (NMVOC) classes, including natural compounds such as isoprene, monoterpenes, and
53 sesquiterpenes, as well as anthropogenically emitted compounds such as the aromatics benzene,
54 toluene, and xylene. However, while all of these species contribute to modeled $PM_{2.5}$ through the
55 formation of secondary organic aerosol (SOA, Pye et al., 2010), only isoprene, the most
56 abundant of the VOCs, is included in the standard gas-phase chemical mechanism. This
57 represents a gap in modeled OH reactivity, with potential consequences on the accuracy of
58 predicted O_3 formation, OH lifetimes, and other related species.

59 **2 Methodology**

60 To explore the impact of aromatics and monoterpenes on tropospheric chemistry, we use the
61 chemical transport model GEOS-Chem (www.geos-chem.org) v9-02, modified to include
62 additional VOC species within the gas-phase chemical mechanism. We performed two years of
63 global simulations (2010 and 2011) using a $2^\circ \times 2.5^\circ$ horizontal resolution and 47 vertical levels.
64 We also use these global simulations to produce boundary conditions for higher resolution (0.5°
65 $\times 0.6^\circ$) nested regional simulations over North America, Europe, and Asia. With high O_3 events
66 primarily a summertime phenomenon, we focus on the months of June, July, and August in our
67 figures and analyses.

68 To better represent the chemical impacts of monoterpenes and aromatics, the GEOS-Chem gas-
69 phase chemical mechanism was modified using mechanisms from (Knote et al., 2014)) for
70 aromatics and (Fisher et al., 2016)) for monoterpenes as part of a larger effort to track total
71 reactive carbon with GEOS-Chem (Safieddine et al., 2017). To this end, we bring several
72 aromatic and monoterpene species (previously included only as contributors to SOA formation)
73 online with respect to OH reactivity and O_3 formation, tracking several generations of oxidation
74 products. These additions build upon the existing isoprene oxidation scheme (Paulot et al.,
75 2009b, 2009a), providing a fuller representation of VOC chemistry and ozone formation. All
76 added species are shown on the left-hand side of Table 1, and include the aromatics benzene,
77 toluene, and xylene, along with two lumped monoterpene tracers representing α -pinene, β -
78 pinene, sabinene, Δ -3-carene, limonene, myrcene, and ocimene. These two sets of modifications
79 were made separately in individual simulations (AROM and TERP), as well as combined
80 together in merged simulations (FULL) including all 42 additional compounds (32 associated
81 with aromatics and 10 with monoterpenes). In addition to these three cases, we evaluate a
82 simplified mechanism (SIMPLE) that delivers much of the total increased OH reactivity of the
83 FULL set, with only 14 additional species, and therefore less computational overhead. These two
84 additional mechanisms represent increases of 45% and 15%, respectively, over the original 93
85 species in the base GEOS-Chem mechanism. The tracers added to the SIMPLE cases, along with

86 their literature sources, are listed on the right-hand side of Table 1. We compare these modified
87 cases to base simulations (BASE) which lack the additional chemistry of the test cases, but are
88 otherwise identical.

89 **Table 1:** Species added to FULL and SIMPLE GEOS-Chem simulations, with sources indicated
 90 by color.

FULL		SIMPLE	
Name	Description	Name	Description
BENZ	Benzene	BENZ	Benzene
TOLU	Toluene	TOLU	Toluene
XYLE	Xylene	XYLE	Xylene
BENP	Benzene peroxy radical	BENP	Benzene peroxy radical
TOLP	Toluene peroxy radical	TOLP	Toluene peroxy radical
XYLP	Xylene peroxy radical	XYLP	Xylene peroxy radical
CSL	Cresol	CSL	Cresol
PHEN	Phenol	PHEN	Phenol
BEPOMUC	Unsaturated epoxide-dialdehyde	EPX	Epoxide from BENZ
PHENO2	Bicyclic peroxy radical from OH addition to phenol	DCB	Unsaturated dicarbonyl
PHENO	Bicyclic oxy radical from OH addition to phenol	TCO3	Unsaturated acyl peroxy radical
PHENOOH	Bicyclic hydroperoxide from OH addition to phenol	MONX	Total monoterpenes
C6H5O2	C6H5O2	TERPO2	Terpene peroxy radicals
C6H5OOH	C6H5OOH	TERPOOH	Terpene hydroperoxide
BENZOOH	Bicyclic hydroperoxide from OH addition to benzene		
BIGALD1	Unsaturated dialdehyde		<i>from Knote et al., 2014 (also in AROM case)</i>
BIGALD2	Unsaturated dicarbonyl		<i>from Fischer et al., 2016 (also in TERP case)</i>
BIGALD3	Unsaturated dialdehyde		<i>from (Goliff et al., 2013)13</i>
BIGALD4	Unsaturated dicarbonyls from xylene oxidation		<i>from (Stockwell et al., 1990)90</i>
MALO2	Acyl radical from "BIGALD1" photolysis		<i>from (Emmons et al., 2010)10</i>
PBZNIT	Peroxybenzoyl nitrate		
TEPOMUC	Unsaturated epoxide-dialdehyde		
BZOO	Peroxy radical formed following OH abstraction from toluene		
BZOOH	C6H5CH2OOH		
BZALD	Benzaldehyde		
ACBZO2	Acylperoxy radical obtained from benzaldehyde		
DICARBO2	Acylperoxy radical obtained from photolysis of unsaturated dicarbonyls		
MDIALO2	Acylperoxy radical obtained from photolysis of unsaturated dicarbonyls		
XYLOL	Isomers of C6H3(CH3)2(OH)		
XYLOLOOH	Bicyclic hydroperoxide from OH addition to xylenols		
XYLENO2	Bicyclic peroxy radicals from OH addition to xylenes		
XYLENOOH	Bicyclic hydroperoxides from OH addition to xylenes		
API	α -pinene, β -pinene, sabinene, and Δ -3-carene		
APIO2	Peroxy radical formed from API		
LIM	Limonene, myrcene, and ocimene		
LIMO2	Peroxy radical formed from LIM		
PIP	Peroxides from API & LIM		
OLND	monoterpene-derived NO3-alkene adduct that primarily decomposes		
OLNN	monoterpene-derived NO3-alkene adduct that primarily retains the NO3 functional group		
MONITS	saturated first-generation monoterpene organic nitrate		
MONITU	unsaturated first-generation monoterpene organic nitrate		
HONIT	second generation monoterpene organic nitrate		

91 We use standard inventories for most emissions, including EDGARv3 for CO, NO_x, and SO_x,
92 along with RETRO for VOCs other than ethane, including benzene, toluene, and xylene – the
93 aromatics examined in this work (Olivier and Berdowski, 2001; Pulles et al., 2007). We take
94 ethane emissions from (Xiao et al., 2008)). Where available, high resolution regional alternatives
95 are used in place of global inventories, including the EPA’s NEI2005 inventory over the United
96 States, the CAC inventory over Canada, BRAVO for emissions over Mexico (Kuhns et al.,
97 2005), EMEP emissions over Europe (Auvray and Bey, 2005), and the Streets 2006 inventory for
98 Asia (Zhang et al., 2009). In following with recent literature results suggesting that NEI NO_x
99 emissions are too high by a factor of 2, we reduce anthropogenic NO_x emissions over the United
100 States following the recommendations of Travis et al., (2016), after first scaling up the NEI2005
101 emissions to match NEI2011 totals for the years 2010 and 2011. Global emissions from biomass
102 burning are taken from the GFED3 inventory, while biogenic emissions (including those of the
103 additional monoterpene species) are calculated online using MEGAN v2.02 (Mu et al., 2011;
104 Guenther et al., 2006).

105 For comparison to observations in the United States, we use hourly station O₃ data taken from
106 the EPA’s AQS network (US Environmental Protection Agency, n.d.) to calculate daily
107 maximum 8-hour averages.

108 3 Results

109 3.1 Increases in summer surface OH reactivity

110 The inclusion of aromatics and monoterpenes increases the simulated total summertime surface
111 OH reactivity, with rural increases largely resulting from new monoterpene reactivity, and urban
112 centers showing aromatic-driven changes. In the United States (Figure 1), regional reactivity
113 peaks in the southeast, coincident with extremely high rates of biogenic emissions. Highest
114 relative changes in OH reactivity occur over regions where both anthropogenic and natural
115 emissions are present. For example, OH reactivity increases by 20-30% over much of the
116 southeast, which sees overall reactivity increases of over 2 s⁻¹.

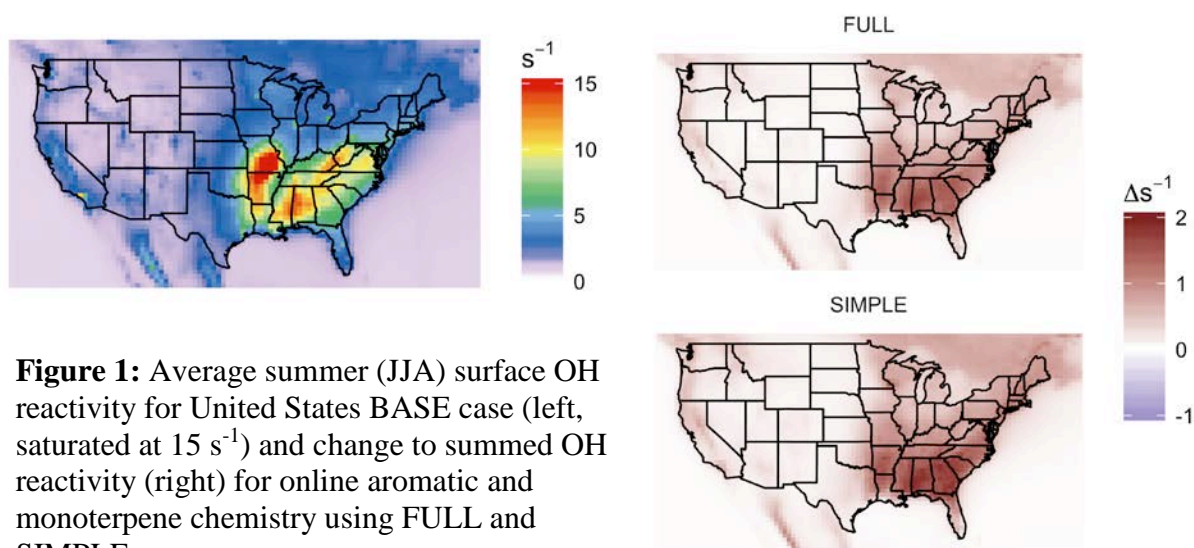


Figure 1: Average summer (JJA) surface OH reactivity for United States BASE case (left, saturated at 15 s⁻¹) and change to summed OH reactivity (right) for online aromatic and monoterpene chemistry using FULL and SIMPLE cases.

117 BASE OH reactivity for Europe (Figure 2) is lower, overall, than that of the United States, with
118 only a few scattered maxima primarily associated with anthropogenic emissions near high
119 population areas. We also note elevated BASE OH reactivity over Russia in 2010 as a result of
120 widespread wildfires over the region that summer. This region in particular shows low or even
121 negative changes in total OH reactivity due to drops in the extremely high levels of NO_x with
122 additional VOC chemistry. Increases in reactivity from aromatics and monoterpenes are more
123 homogeneous in Western Europe than in the United States, with increases between 0.2 s^{-1} and
124 0.5 s^{-1} throughout most of the region, representing relative increases of 4-20%.
125

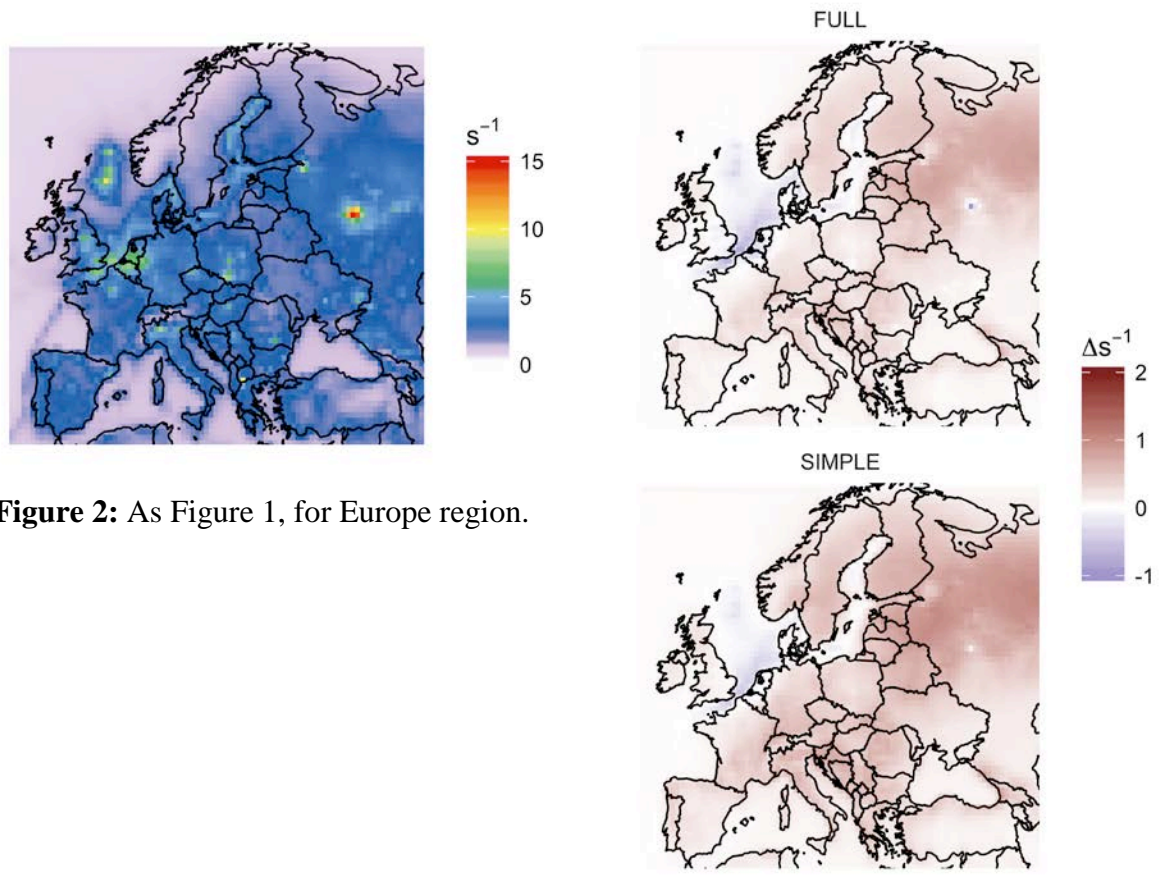


Figure 2: As Figure 1, for Europe region.

126 BASE case OH reactivity in China and Southeast Asia (Figure 3) is heavily concentrated in the
127 south and east, roughly following population density, with biogenic peaks to the south in
128 Myanmar and Vietnam. Reactivity increases in China due to the addition of monoterpene and
129 aromatic chemistry are most pronounced in the southeast, where changes average 0.4 s^{-1} , or 7%
130 of BASE values. Negative changes in reactivity along the east coast from Beijing to Shanghai in
131 the FULL case are again the result of decreases in the exceptionally high NO_x concentrations due
132 to the additional chemical sinks provided by this mechanism.

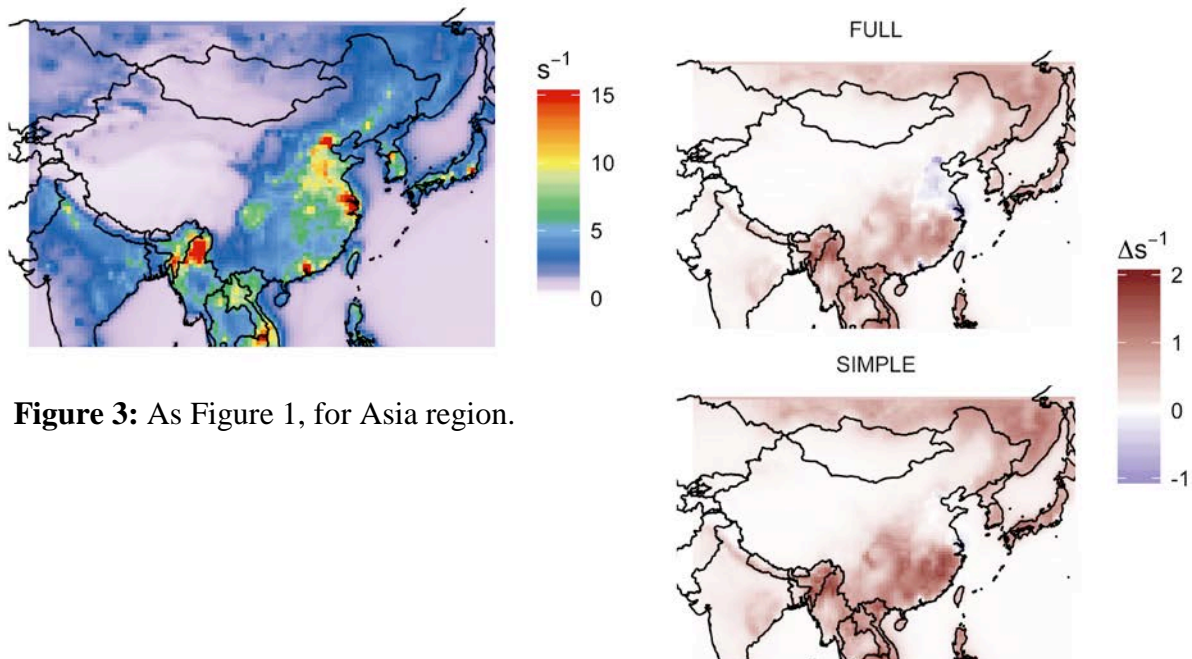


Figure 3: As Figure 1, for Asia region.

134 Overall, increases in OH reactivity are similar between the FULL and SIMPLE cases, though
 135 magnitudes of changes are slightly higher in the SIMPLE cases (0.1 s^{-1} higher on average across
 136 all regions). This increased magnitude in the SIMPLE case is driven by two primary differences:
 137 differences in monoterpene oxidation products, and differences in NO_x sink efficiency. While the
 138 FULL case includes explicit bins for monoterpene oxidation products, the simplified SIMPLE
 139 case employs methyl vinyl ketone (MVK) and methacrolein (MACR). Differences in the
 140 reactivity and fate of the species in these two pathways end up leading to a net reactivity increase
 141 for the SIMPLE case in most regions. Furthermore, reaction pathways present in the FULL case
 142 tend to lead to greater removal of NO_x , for example via reaction with the phenol oxidation
 143 product PHENO, which does not exist in the SIMPLE case. In areas with extremely high NO_x
 144 levels, particularly in the Europe and Asia regions, this decrease in NO_x appears as a net decrease
 145 in total OH reactivity. While the FULL case adds reactive species and sinks that the SIMPLE
 146 case does not (Figure 4), in most locations this is balanced by increases in other species. For
 147 example, while the FULL simulation contains two monoterpene species (API and LIM) and the
 148 SIMPLE case uses only one (MONX) representing the binned sum of both FULL case species,
 149 total reactivity differences from the addition of these groups remains relatively balanced overall.
 150 On average, changes in these monoterpenes proved most relevant to changes in summed OH
 151 reactivity, as aromatic emissions are in general more localized. The additional aromatic and
 152 monoterpene species in both the FULL and SIMPLE cases, along with their products, contribute

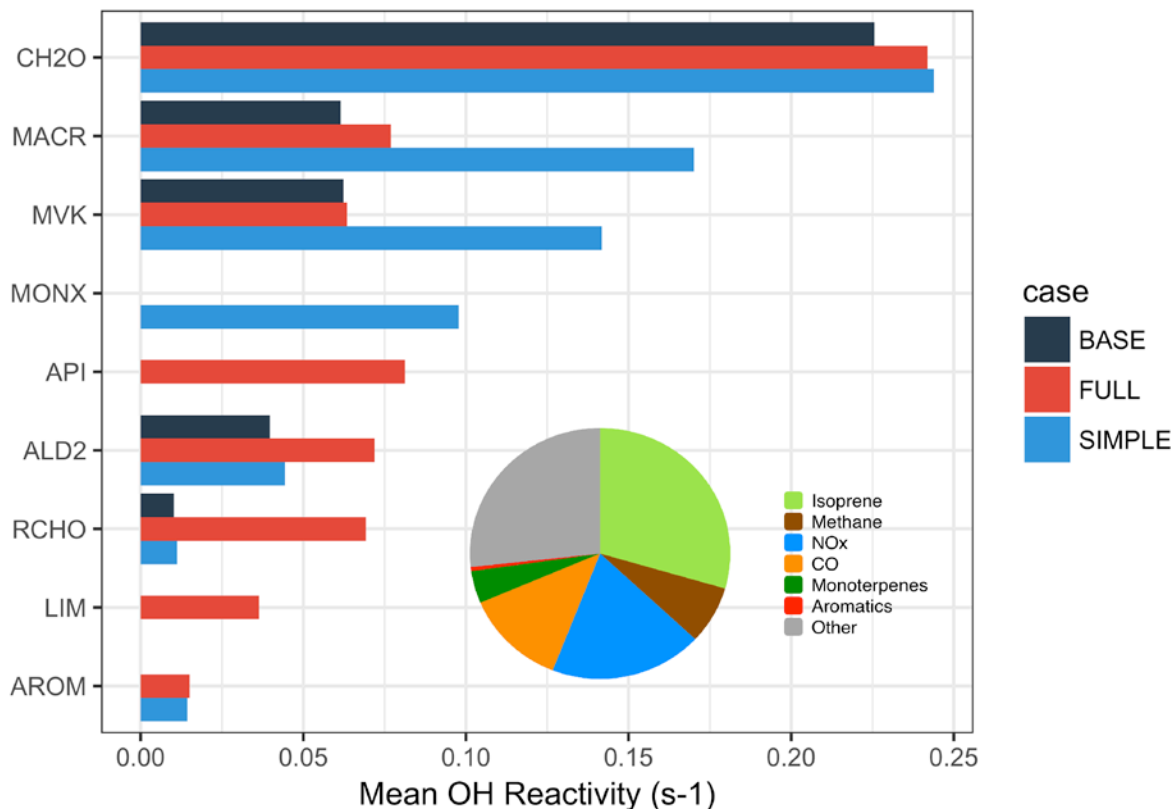


Figure 4: Mean contribution of select species to total average surface summertime OH reactivity. Pie chart shows relative contributions to global terrestrial OH reactivity for FULL case, while bars highlight the OH reactivity of key species impacted by the addition of monoterpene and aromatic chemistry.

153 an additional 7-12% to the total summed surface OHR in each of the three regions, or 18-35% of
154 the OH reactivity from VOCs.

155 The increases in total OH reactivity bring model results closer to observed totals, though large
156 gaps do remain. In general, modeled summed OH reactivity is much lower than observations,
157 mirroring the gap between observed and calculated reactivity in campaigns worldwide. For
158 example, observed OH reactivities at forested sites in northern Michigan and Finland both
159 showed mean measured OH reactivities of around 11-12 s⁻¹, while the calculated reactivities
160 from the summation of known species contributions could explain only 30-50% of this,
161 depending on the time of day (Hansen et al., 2014; Nölscher et al., 2012). Summed simulated
162 summer reactivities for the grid cells containing these locations in the BASE case are each
163 around 2.5 s⁻¹, and additional reactivity provided by the FULL case adds only 0.5 s⁻¹ to that
164 value. Comparison to summer observations at urban sites in Houston and London show similar
165 model underpredictions and relative changes (Mao et al., 2010; Whalley et al., 2016). Together,
166 these results suggest that the inclusion of known aromatic and monoterpene chemistry is
167 insufficient to significantly close the gap between observed and modeled OH reactivities.

168 While the additional OH reactivity provided by including aromatics and monoterpenes in the
169 model does not close the gap between modeled and observed OH reactivities, it represents one
170 step towards a better representation of observed behaviors. Additional improvements may be
171 found through higher resolution simulations, as well as ongoing improvements to emission
172 inventories and multi-generational oxidative chemistry. Previous studies have indicated that
173 highly reactive hydrocarbons and secondary oxidation products missing from current inventories
174 and mechanisms may be responsible for the large gaps in both calculated and modeled reactivity
175 totals (Yang et al., 2016).

176 3.2 *Increases in tropospheric O₃*

177 In most locations, the increased OH reactivity produced by the inclusion of aromatics and
178 monoterpenes leads to increases in surface O₃ levels as well, especially in regions rich in NO_x.
179 These changes are significant; for example they are comparable to or larger than the impact of
180 climate change on surface ozone concentrations (Tai et al., 2013). In the United States (Figure
181 5), increases in daily maximum 8-hour average summertime O₃ exceed 10 ppb over southern
182 California with the addition of aromatics alone. For context, a change of 14 ppb O₃ (the
183 maximum simulated increase due to the additional VOCs) is equivalent to 19% of the current 70
184 ppb EPA daily maximum 8-hr standard in the United States. Outside of southern California,
185 increases of 0.5 ppb are apparent throughout most of the country in the FULL case (1.5 ppb in
186 SIMPLE case), with the exception of the southeast, where VOC-insensitive O₃ production is
187 consistent with high pre-existing VOC concentrations. Peak O₃ increases are largely driven by
188 the additional aromatic chemistry, though mean changes are strongly influenced by the
189 additional monoterpene reactivity, due to greater area of impact. In Europe (Figure 6), changes in
190 O₃ are more uniform, showing few spatial features, and peaks at 5 ppb. In Asia, increases of
191 around 4 ppb occur over eastern China and neighboring regions, where high existing NO_x
192 concentrations enhance the impact of additional aromatic reactivity on O₃ levels (Figure 7).
193 Relatively small O₃ changes are observed in Burma and Thailand, where large increases in OH
194 reactivity from monoterpenes do little to change an already VOC-saturated regime.

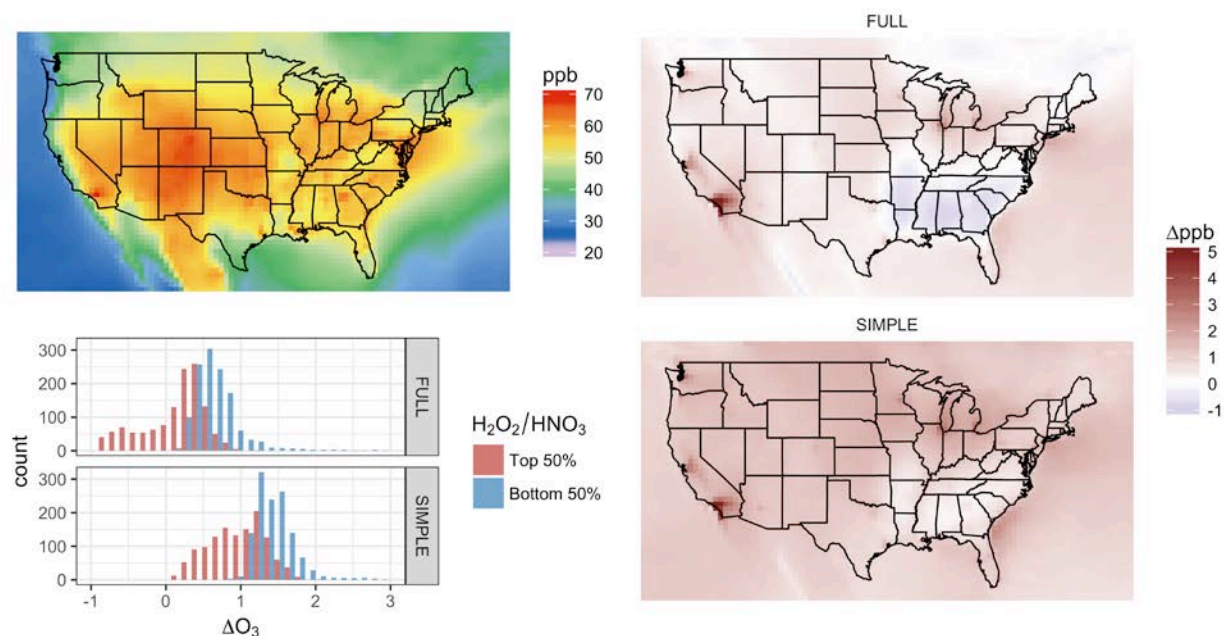


Figure 5: Mean peak 8-hour average O₃ in the United States summer (upper left), changes with additional VOC chemistry in FULL and SIMPLE cases (right), and the distribution of terrestrial O₃ changes for the FULL case (compared to BASE) segregated by mean simulated H₂O₂/HNO₃ ratio as a proxy representation of NO_x/VOC sensitivity (lower left). Histogram x-axis is trimmed for visibility. Full range of values extends from -1 ppb to 14 ppb (FULL) and 0 to 11 ppb (SIMPLE).

195 In all cases, changes in O₃ are heavily dependent on ambient NO_x/VOC ratios, as indicated by
 196 lower-left panels of Figures 5-7. Here, the distribution of changes in O₃ are shown, divided into
 197 two categories based on the ratio of hydrogen peroxide (H₂O₂) vs. nitric acid (HNO₃). This ratio
 198 is a simple metric for estimating NO_x/VOC sensitivity, assuming that nitric acid is the main NO_x
 199 sink (Milford et al., 1994; Sillman et al., 1997). In each region, terrestrial grid cells in the bottom
 200 50% of this ratio (indicating more VOC sensitivity) showed much more pronounced positive
 201 increases in O₃, while more VOC-saturated regions showed reduced O₃ increases, or even
 202 reductions associated with the addition of monoterpene and aromatic chemistry. This highlights
 203 how the response of ozone to additional VOC sources is strongly dependent on chemical
 204 environment. The SIMPLE implementation also shows stronger positive changes in O₃ in all
 205 three regions, averaging around 1 ppb higher values than found in the FULL case.

206 Comparison to O₃ observations through the EPA's AQS network of stations in the United States
 207 show mixed results. The BASE case simulation overpredicts O₃ at most sites (total mean bias of
 208 8.2 ± 6.5 ppb). California's San Joaquin Valley region stands as one notable exception, where
 209 modeled O₃ actually underpredicts average summer observations for these years by up to 18 ppb.
 210 As would be expected, the additional O₃ generated by aromatic and monoterpene chemistry in
 211 most areas increases an already positive bias; the FULL case shows a total mean bias of 9 ppb,
 212 ± 7 ppb. Exceptions to this can be found in California, where the previously noted O₃
 213 underprediction is improved by an average of 1.6 ppb in the FULL case, as well as in the
 214 Southeast, where reductions in O₃ resulting from additional VOC reactivity in an already

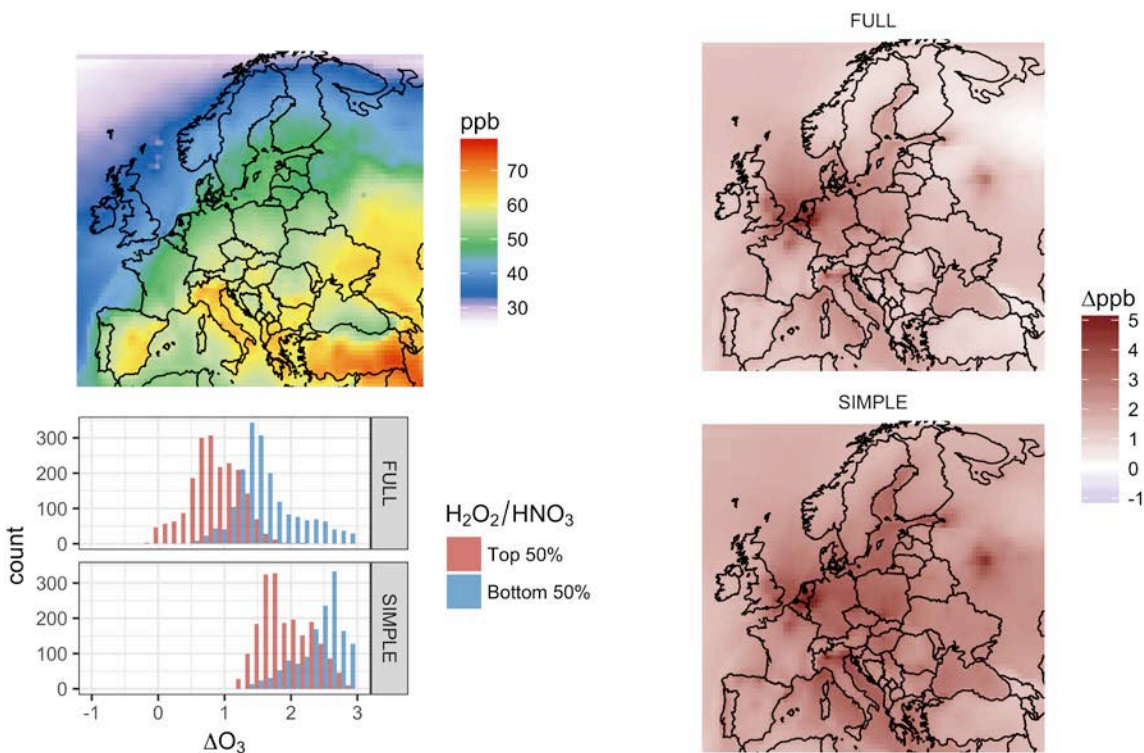


Figure 6: As Figure 5, for Europe. Histogram x-axis is trimmed for visibility. Full range of values extends from 0 ppb to 5 ppb (FULL) and 1 ppb to 4 ppb (SIMPLE).

215 saturated region slightly improve agreement with observations. In Europe, BASE case
 216 comparison with observations from the EEA's AirBase inventory shows a similar overprediction
 217 of surface summertime O₃ of 9.5 ± 6.9 ppb. The additional VOC chemistry of the FULL case
 218 enhances this bias by an average of 2.0 ± 0.8 ppb.

219 Comparison of aromatic levels themselves to AQS observations (not shown) shows a modest
 220 overprediction in urban areas and a comparable underprediction in rural areas (overall bias of -
 221 0.03 ppb, RMSE of 0.45 ppb), differences which may stem from uncertainties in aromatic
 222 emissions inventories. Unfortunately, no such record of systematic observations exist for
 223 monoterpenes at this time, making a direct comparison of these modeled species impossible.

224 4 Conclusions

225 By integrating aromatics and monoterpenes into the GEOS-Chem gas-phase chemistry
 226 mechanism, we quantify the potential impacts of these species on total OH reactivity and O₃
 227 production, finding important contributions to each. Although an already positive O₃ bias is
 228 exacerbated by the additional effective VOC burden, we find slightly improved agreement with
 229 observed OH reactivity totals, a metric that in general has shown a significant negative bias in
 230 model results. Furthermore, many uncertainties surround each step of O₃ formation, including
 231 precursor emissions, oxidative chemistry, transport, and removal. While the additional reactivity
 232 provided by bringing these species online pushes overpredicted O₃ even higher in these
 233 simulations, other ongoing and proposed changes (such as the addition of halogen chemistry,
 234 (Sherwen et al., 2016)) may reduce O₃ values, making the additional production from aromatics

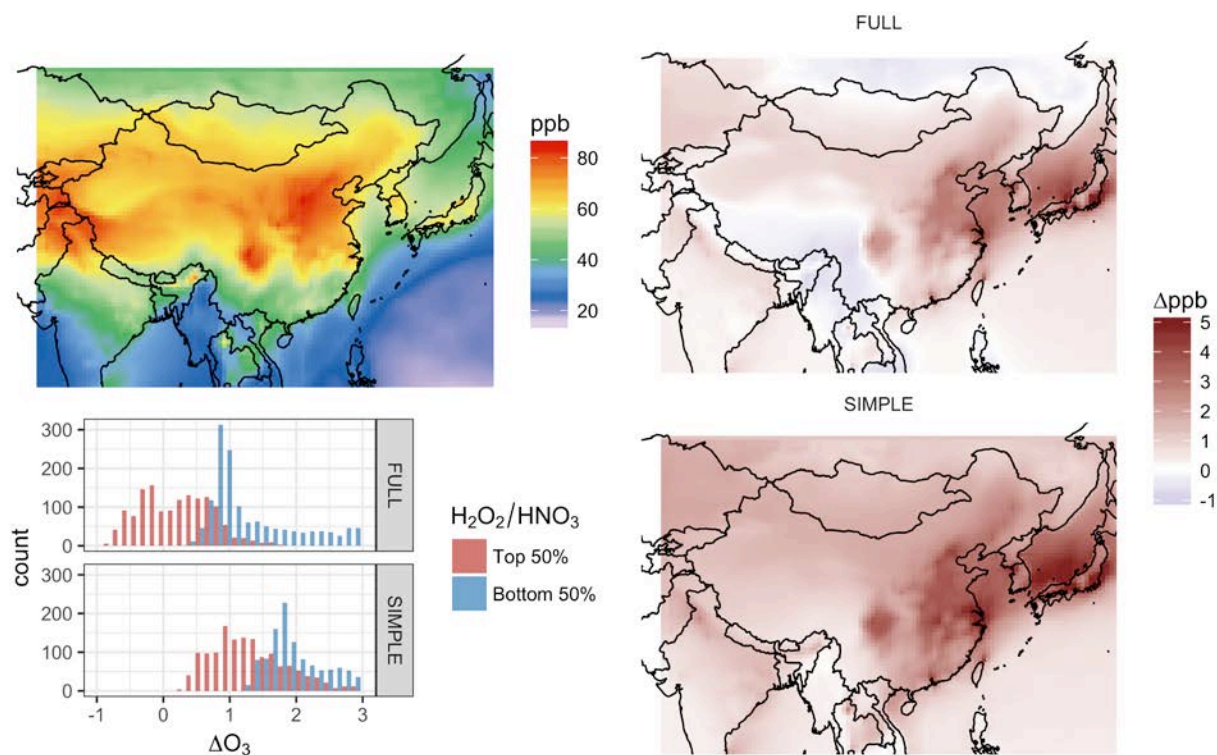


Figure 7: As Figure 5, for Asia. Histogram x-axis is trimmed for visibility. Full range of values extends from -1 ppb to 4 ppb (FULL) and 0 ppb to 6 ppb (SIMPLE).

235 and monoterpenes more beneficial to model skill. For these reasons, we propose that the
 236 inclusion of aromatic and monoterpene chemistry is important for the effective representation
 237 and prediction of ozone pollution, despite substantial uncertainties regarding product distribution
 238 and rates of multigenerational chemistry. While the inclusion of additional advected species
 239 increases computational demands, we show that this can be mitigated through a simplified
 240 representation of this chemistry, representing the increased OH reactivity with less
 241 computational cost. To further optimize these improvements, future laboratory experiments
 242 targeting the relevant chemical kinetics will be necessary, along with ongoing efforts to develop
 243 a robust, efficient, and accurate chemical mechanism for the representation of these products and
 244 their reactions in large-scale models.

245

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