Evaluating the impact of chemical complexity and horizontal resolution on tropospheric ozone with a global variable resolution chemistry model

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Key Points: 32

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33	•	A new configuration of the Community Atmosphere Model with full chemistry sup-
34		porting horizontal mesh refinement is developed
35	•	This configuration is the beginning of the Multi-Scale Infrastructure for Chem-
36		istry and Aerosols (MUSICA)
37	•	Updating chemistry and horizontal resolution improves simulated ozone and ozone
38		precursors compared to aircraft observations

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39 Abstract

A new configuration of the Community Earth System Model (CESM)/Community At-40 mosphere Model with full chemistry (CAM-chem) supporting the capability of horizon-41 tal mesh refinement through the use of the spectral element (SE) dynamical core is de-42 veloped and called CESM/CAM-chem-SE. Horizontal mesh refinement in CESM/CAM-43 chem-SE is unique and novel in that pollutants such as ozone are accurately represented 44 at human exposure relevant scales while also directly including global feedbacks. CESM/CAM-45 chem-SE with mesh refinement down to ~ 14 km over the contiguous US is the begin-46 ning of the Multi-Scale Infrastructure for Chemistry and Aerosols (MUSICAv0). Here 47 CESM/CAM-chem-SE is evaluated and used to better understand how horizontal res-48 olution and chemical complexity impact ozone and ozone precursors as compared to mea-49 surements from five aircraft campaigns, which occurred in 2013. This field campaign anal-50 ysis demonstrates the importance of using finer horizontal resolution to accurately sim-51 ulate ozone precursors such as nitrogen oxides and carbon monoxide. In general, the im-52 pact of using more complex chemistry on ozone and other oxidation products is more 53 pronounced when using finer horizontal resolution where a larger number of chemical regimes 54 are resolved. Large model biases for ozone near the surface remain in the Southeast US 55 as compared to the aircraft observations even with updated chemistry and finer horizon-56 tal resolution. Results from this work suggest a need for adding the capability for replac-57 ing sections of the global emission inventories with regional inventories, increasing the 58 vertical resolution in the planetary boundary layer, and reducing model biases in me-59 teorological variables such as temperature and clouds. 60

⁶¹ Plain Language Summary

A new configuration of the Community Earth System Model (CESM)/Community 62 Atmosphere Model with full chemistry (CAM-chem) supporting the capability of hor-63 izontal mesh refinement is developed. This configuration is the beginning of MUSICA 64 (Multi-Scale Infrastructure for Chemistry and Aerosols), which will create a unified in-65 frastructure to model atmospheric chemistry and aerosols across scales in the Earth sys-66 tem. The capability in CESM/CAM-chem to use grids with horizontal mesh refinement 67 is a novel advancement because the regional and global model components are seamlessly 68 connected such that there is consistency in the physical and chemical processes between 69 the components, which increases accuracy in prediction and efficiency in model devel-70 opment. This work evaluates this new model configuration against measurements from 71 five aircraft campaigns, which occurred during 2013. By evaluating model results against 72 observations not only for ozone, but also ozone precursors, photolysis rate constants, tem-73 perature, planetary boundary layer height, etc., model skill at representing processes im-74 portant for ozone formation and loss is inferred. Updates to horizontal resolution and 75 chemistry improve simulated ozone and ozone precursors as compared to observations, 76 but biases remain. The physical and chemical processes that are missing or erroneous 77 in the model are highlighted to help prioritize future work. 78

79 **1 Introduction**

Because ozone is a short-lived climate forcer, negatively impacts human health, dam-80 ages ecosystems, and is fundamental to atmospheric chemistry through its role in pho-81 tooxidation processes (Monks et al., 2015), accurately predicting ozone in 3D models for 82 the right reasons is important (Young et al., 2018). Generally, models have reasonable 83 skill at simulating large-scale spatial and seasonal features of tropospheric ozone, but bi-84 ases exist (Young et al., 2018). For example, surface ozone is generally over-predicted 85 in models, especially in the northern hemisphere (Young et al., 2018). When compar-86 ing a wide variety of global models, more variability exists in the processes that deter-87 mine the ozone distribution (e.g., chemical production and loss, deposition, and troposphere-88

stratosphere exchange) than in the total tropospheric ozone burden (Young et al., 2018) suggesting a need for more evaluation and improvement of model physical and chemical processes. In order to correctly simulate ozone, many processes including meteorology, biogenic and anthropogenic emissions, deposition, and chemistry need to be accurately represented.

In many cases, global model simulations are not performed at horizontal and ver-94 tical resolutions fine enough to accurately represent the nonlinear processes responsible 95 for ozone formation and loss. To fill this gap, regional models with the capability of per-96 forming simulations at finer horizontal resolution are used. These regional models require 97 the use of lateral and upper boundary conditions (BCs), which are often either fixed or 98 derived from a global model. Past studies (Herron-Thorpe et al., 2012; Huang et al., 2017; 99 Im et al., 2018; Tang et al., 2007, 2009) have identified that the selection of BCs impacts 100 simulated ozone especially in regions near the boundaries of the regional model domain. 101 Model performance is often enhanced by using BCs derived from a global model instead 102 of fixed BCs to better capture the temporal variability of ozone and ozone precursors 103 entering the regional model domain; however, general biases present in global models are 104 transferred into regional models through BCs (Herron-Thorpe et al., 2012; Tang et al., 105 2007, 2009). Because of this connection, in order to improve model skill at simulating 106 ozone in a regional model, model performance needs to be improved in both regional and 107 global models. Since the chemical and physical processes are often different between global 108 and regional models, separately improving both models is time consuming and inefficient. 109 Additionally, differences in the physical and chemical processes between the regional and 110 global models can cause inconsistencies in the regional model results (Neal et al., 2017). 111

112 This, along with recent reports summarizing the status and future direction of climate and Earth system modeling (Bellucci et al., 2015; NRC, 2012; Pfister et al., 2020), 113 demonstrates the importance of efforts to unify regional and global models in order to 114 seamlessly model across scales. To contribute to this unification effort, this work along 115 with a parallel paper by Lacey et al. (in prep) will bring a global atmospheric chemistry 116 model, the Community Earth System Model/Community Atmosphere Model with full 117 chemistry (CESM/CAM-chem) to regional scales. The capability of horizontal mesh re-118 finement is already supported in CESM/CAM through the use of the spectral element 119 (SE) dynamical core (Baer et al., 2006; Fournier et al., 2004; Lauritzen et al., 2018; Zarzy-120 cki, Levy, et al., 2014; Zarzycki, Jablonowski, & Taylor, 2014). This work expands on 121 this past work to add full gas and aerosol chemistry into CESM/CAM-SE to create CESM/CAM-122 chem-SE. The capability in CESM/CAM-chem-SE to use grids with horizontal mesh re-123 finement is a novel advancement. The regional and global model components are seam-124 lessly connected such that direct feedbacks occur, which is ideal for accurately simulat-125 ing air quality from global to regional scales. The capability of mesh refinement within 126 a single model ensures consistency in the physical and chemical processes in the regional 127 and global components. This framework also increases efficiency in model development 128 such that an update to a model component can be easily incorporated into the entire 129 system. The development of CESM/CAM-chem-SE is the beginning of a community-130 wide effort called MUSICA, The Multi-Scale Infrastructure for Chemistry and Aerosols. 131 which will create a unified infrastructure to model atmospheric chemistry and aerosols 132 across local to regional to global scales in the Earth system (Pfister et al., 2020). The 133 capability of regional refinement down to ~ 14 km over the contiguous US (CONUS) is 134 called MUSICAv0 (https://www2.acom.ucar.edu/sections/musica-v0). 135

Better understanding the connections between air quality and climate (Monks et al., 2015) will be an important future use of CESM/CAM-chem-SE. Climate mitigation strategies through reductions in air pollutant precursors co-emitted with greenhouse gases have the potential to greatly reduce air pollution, which will improve human health and potentially offset the economic costs associated with climate mitigation (Chang et al., 2017; Thompson et al., 2014). Many past studies have either used coarse horizontal resolution in a global model (e.g., Garcia-Menendez et al., 2015; Y. Lee et al., 2016; Stohl
et al., 2015) or relied on connecting results from inconsistent regional and global models (e.g., Colette et al., 2013; Kumar et al., 2018; Pfister et al., 2014) in order to answer
how various climate mitigation strategies will impact air quality. CESM/CAM-chemSE, which is a climate model and has fine enough horizontal resolution to simulate human health exposure to air pollutants, will provide a novel and more consistent tool to
better study the connections between air quality and climate in the future.

Several past studies have demonstrated the importance of using finer horizontal res-149 olution for simulating ozone production. Coarser horizontal resolution causes unrealis-150 tic dilution of transported pollution plumes of volatile organic compounds (VOCs) and 151 nitrogen oxides (NO_x) as well as smoothing local topography, which artificially impacts 152 the transport of air pollutants (Monks et al., 2015). This dilution of NO_x in particular 153 can cause ozone production to be inaccurately simulated due to nonlinearities in the pro-154 cess (Cohan et al., 2006). Several studies have demonstrated that using ~ 12 km hori-155 zontal resolution is generally sufficient to represent ozone formation and loss processes 156 (Cohan et al., 2006), NO_2 (Valin et al., 2011; Yamaji et al., 2014), and mortality from 157 population-weighted MDA8 (maximum daily 8-hour average) ozone (Thompson & Selin, 158 2012) at the regional scale. Other studies have emphasized the need for even finer hor-159 izontal resolution for modeling local events such as shipping (D. D. Davis et al., 2001; 160 Vinken et al., 2011), power plants (Valin et al., 2011), urban/industrial regions (Colette 161 et al., 2014; Gan et al., 2016; Liang & Jacobson, 2000; Yamaji et al., 2014) especially 162 at night (Zakoura & Pandis, 2018), and complex terrain/coastal regions (Gan et al., 2016). 163 Here CESM/CAM-chem-SE is used to explore the importance of finer horizontal reso-164 lution on accurately simulating ozone and ozone precursors at the regional scale. Sim-165 ulations are performed at a typical global horizontal resolution of ~ 111 km ($\sim 1^{\circ}$) and 166 also with mesh refinement down to $\sim 14 \text{ km} (\sim 1/8^{\circ})$ over the contiguous US (CONUS). 167

CESM/CAM-chem also has the capability to use different chemical mechanisms 168 of varying chemical complexity. The default MOZART-TS1 chemical mechanism has full 169 tropospheric and stratospheric chemistry (Emmons et al., 2020) and includes a volatil-170 ity basis set (VBS) scheme for secondary organic aerosol (SOA) formation (Tilmes et al., 171 2019). More complex and updated gas-phase chemistry for isoprene and terpenes (bio-172 genic VOCs) was recently added into MOZART-TS1 to create the MOZART-TS2 chem-173 ical mechanism (Schwantes et al., 2020). In CESM/CAM-chem, using MOZART-TS2 174 compared to MOZART-TS1 reduces the model overprediction of MDA8 surface ozone 175 as compared to the US EPA CASTNET monitoring data particularly over the South-176 east US (Schwantes et al., 2020) where emissions of biogenic VOCs are most important. 177 However, a large MDA8 surface ozone bias remains, which is potentially due to the coarse 178 horizontal resolution of $0.9^{\circ} \ge 1.25^{\circ}$ used by Schwantes et al. (2020). This work expands 179 on this previous work to explore whether more complex chemistry has a greater impact 180 on simulated ozone at finer horizontal resolutions, or in other words whether more com-181 plex chemistry is needed to achieve the full benefit of using finer horizontal resolution. 182

In this work, CESM/CAM-chem-SE or MUSICAv0 is described in section 2.1. Model 183 simulations varying horizontal resolution and chemical complexity are performed (sec-184 tion 2.2) to demonstrate the capabilities of CESM/CAM-chem-SE and better understand 185 186 the impact of horizontal resolution and chemical complexity on ozone and ozone precursors (section 3.1). The model results are compared to observations collected during five 187 aircraft campaigns across the US in 2013 described in section 2.3. By comparing the model 188 results to ozone, ozone precursors, meteorological variables, and VOC oxidation prod-189 ucts measured in these aircraft campaigns, model skill at representing ozone and the phys-190 ical and chemical processes that determine the ozone distribution is evaluated (section 191 3.2). By more accurately simulating ozone and the physical and chemical processes re-192 sponsible for ozone formation and loss, this work increases the accuracy and confidence 193 in the model's predictive capability, which is important for forecasting, source apportion-194

¹⁹⁵ ment, and other model applications. This work focuses on evaluating CESM/CAM-chem-

¹⁹⁶ SE against aircraft campaigns and a parallel effort by Lacey et al. (in prep) compares

 $_{197}$ CESM/CAM-chem-SE results against surface observations of ozone and PM_{2.5}. Finally,

the physical and chemical processes that are missing or erroneous in the model are high-

lighted (section 4) to help prioritize future work (section 5).

200 2 Methods

The model configuration is described in section 2.1, the simulations performed are summarized in section 2.2, and the five aircraft campaigns used to evaluate the model are described in section 2.3.

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2.1 Model Description

Numerous past studies (Baer et al., 2006; Dennis et al., 2012; Fournier et al., 2004; 205 Lauritzen et al., 2018; Zarzycki, Levy, et al., 2014; Zarzycki, Jablonowski, & Taylor, 2014) 206 have incrementally developed a configuration of CESM/CAM that uses the SE dynam-207 ical core to support both uniform horizontal resolution grids and grids with the capa-208 bility of mesh refinement (i.e., local increases in horizontal resolution). CAM-SE with 209 mesh refinement has led to improved representation of tropical cyclones (Zarzycki, Jablonowski, 210 & Taylor, 2014), orographic precipitation (Rhoades et al., 2016), and better understand-211 ing of how finer horizontal resolution impacts climate simulations (Zarzycki, Levy, et al., 212 2014). This work expands on these past studies to add full gas and aerosol chemistry into 213 CESM/CAM-SE to create CESM/CAM-chem-SE or MUSICAv0. CESM2.2 beta code 214 is used in this work and the model advancements have been released for community use 215 in CESM2.2 (https://wiki.ucar.edu/display/MUSICA/MUSICA+Home). 216

Two SE grids described previously by Lauritzen et al. (2018) are used: the uniform 217 ne30 grid and the ne0conus30x8 grid with mesh refinement over CONUS. In ne30, the 218 grid cells are nominally $\sim 111 \text{ km} (\sim 1^{\circ})$ across, so hereafter this is referred to as ~ 111 219 km horizontal resolution. In ne0conus30x8, the grid cells are nominally ~ 14 km ($\sim 1/8^{\circ}$) 220 across over CONUS and ~ 111 km across over the rest of the globe, so hereafter this is 221 referred to as ~ 14 km horizontal resolution. In all figures, the value is plotted based on 222 the center latitude longitude of each grid cell and not the native area. The ~ 111 km and 223 ~ 14 km horizontal resolution simulations use a physical/chemical time step of 30 min 224 and 3.75 min, respectively. Using the ne0conus30x8 grid increases the simulation cost 225 by approximately a factor of 29 compared to the ne30 grid due to the increased num-226 ber of grid cells and the decreased physical/chemical time step needed to satisfy the Courant-227 Friedrichs-Lewy criterion. 228

A major step in developing CESM/CAM-chem-SE with mesh refinement is imple-229 menting input and emission datasets appropriate for finer grid sizes. Biogenic emissions 230 are calculated online using the Model of Emissions of Gases and Aerosols from Nature 231 (MEGAN) v2.1 (Guenther et al., 2012) in the community land model (CLM) as further 232 described in Lamarque et al. (2012). The CLM model uses the same horizontal grid res-233 olution as CAM-chem. The plant functional type (PFT) and leaf area index (LAI) in-234 put files to CLM are regridded to the two grids described above. The list of biogenic VOCs is extended to include all VOCs available in MEGAN for both chemical mechanisms as 236 done in Schwantes et al. (2020). Because the biogenic emissions are calculated online in 237 the CLM model, differences in meteorological variables such as temperature between the 238 simulations will directly impact the emission rates of the biogenic VOCs. 239

The remaining emissions are generated offline. Daily fire emissions are from the Fire INventory from NCAR (FINN) v1.5 (Wiedinmyer et al., 2011), which are provided as point sources and are conservatively mapped to the SE grids using a new tool available for download here: https://wiki.ucar.edu/display/MUSICA/Grid+FINN. Anthropogenic

emissions from the CAMS version 3.1 global inventory with a native horizontal resolu-244 tion of $0.1^{\circ} \ge 0.1^{\circ}$ (Granier et al., 2018) are regridded conservatively to the SE grids. When 245 these fire and anthropogenic emission inventories are regridded, emissions from fine scale 246 features are better resolved and less artificially diluted when using the ne0conus30x8 grid 247 with ~ 14 km horizontal resolution over CONUS compared with using the ne30 grid with 248 \sim 111 km horizontal resolution uniformly. Ocean and soil emissions are from the POET 249 inventory (Granier et al., 2005). Aircraft emissions are from the Community Emissions 250 Data System (CEDS) (Hoesly et al., 2018). Volcanic emissions are from the GEIA in-251 ventory (Andres & Kasgnoc, 1998) and based on the Volcanic Emissions for Earth Sys-252 tem Models dataset, version 3.11 (Neely III & Schmidt, 2016). Tools for regridding emis-253 sion inventories to SE uniform and mesh refinement grids are available for download here: 254 https://wiki.ucar.edu/display/MUSICA/Regridding+emissions. 255

Temperature and horizontal winds are nudged to GEOS5 meteorology from the NASA 256 Global Modeling and Assimilation Office. The GEOS5 data are available at $0.67^{\circ} \ge 0.5^{\circ}$ 257 horizontal resolution every 6 hours for 2010-2012 and at $0.31^{\circ} \ge 0.25^{\circ}$ every 3 hours for 258 2013. The GEOS5 meteorological fields (56 vertical levels) are interpolated vertically and 259 horizontally to each CAM grid mesh (32 vertical levels) and a correction for differences 260 in the topography between GEOS5 and CAM is applied. A new specified dynamics scheme, 261 which is fully described in the CAM6 user guide (NCAR, 2017), is used in this work. The 262 new scheme is more flexible, contains more features, and works with the SE dynamical core compared to past specified dynamics schemes used in CAM-chem (Emmons et al... 264 2020; Lamarque et al., 2012; Schwantes et al., 2020). Nudging occurred at each time step 265 using the next target nudging force option and the weak time scale option. 266

267 Separate approaches are used to generate the initial conditions for CLM and CAMchem. To generate CLM initial conditions for the ne0conus30x8 grid, a CAM simulation 268 is performed using the ne0conus30x8 grid for 3 years (January 2010-December 2012) with 269 specified dynamics using a relaxation time of 50 h. The CAM simulation uses a highly 270 reduced chemical mechanism compared to that in CAM-chem, which reduces the cost 271 of the long simulation needed to spin-up the land model. To generate CAM-chem ini-272 tial conditions for the ne0conus30x8 grid, for each chemical mechanism a CAM-chem sim-273 ulation is performed with the ne30 grid for two years, the ne30 file is regridded to the 274 ne0conus30x8 grid, and an additional one month spin-up is performed using CAM-chem 275 with the ne0conus30x8 grid. 276

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2.2 Description of Simulations

Four main model simulations (Table 1, #1-4) are performed for the entire year of 278 2013 to evaluate the new configuration of CESM/CAM-chem-SE and better understand 279 the impact of chemical complexity and horizontal resolution on ozone and ozone precur-280 sors. Two horizontal resolutions are tested: a global uniform resolution of ~ 111 km and 281 \sim 111 km horizontal resolution globally and mesh refinement over CONUS down to \sim 14 km. Two chemical mechanisms of varying complexity are also evaluated: MOZART-TS1 283 and MOZART-TS2.1. MOZART-TS1, or TS1 hereafter, is the default chemical mech-284 anism used within CESM2/CAM-chem (Emmons et al., 2020) and includes full tropo-285 spheric and stratospheric chemistry. The VBS SOA scheme in TS1 (Tilmes et al., 2019) 286 uses SOA yields from the low- NO_x pathway for all SOA formation under the assump-287 tion that SOA forms dominantly from the low-NO_x pathway over most of the Earth. MOZART-288 TS2.1, or TS2.1 hereafter, includes more complex isoprene and terpene gas-phase chem-280 istry as developed by Schwantes et al. (2020) (MOZART-TS2) and a more complex VBS 290 SOA scheme developed by Hodzic et al. (2016) and implemented into CESM/CAM-chem 201 by Jo et al. (2021). The SOA scheme in TS2.1 includes SOA yields from both the low-292 and high-NO_x pathways for anthropogenic and biogenic VOCs. Because SOA yields un-293 der low- NO_x conditions are generally higher than under high- NO_x conditions, the im-294 pact of switching from TS1 to TS2.1 is to reduce SOA formation particularly in regions 295

#	$Mechanism^a$	Grid Name ^b	US Res. $(\mathrm{km})^c$	SD Time $(h)^d$	Time Period^e
Che	Chemistry and Horizontal Resolution Evaluation				
1	TS1	ne30	~111	50	Jan - Dec
2	TS1	ne0conus30x8	~ 14	50	Jan - Dec
3	TS2.1	ne30	~ 111	50	Jan - Dec
4	TS2.1	ne0conus30x8	~ 14	50	Jan - Dec
Specified Dynamics Sensitivity Tests					
5	TS2.1	ne30	~111	6	Aug - Sept
6	TS2.1	ne30	~111	12	Aug - Sept
7	TS2.1	ne30	~111	no \mathbf{CONUS}^f	Aug - Sept
8	TS2.1	ne0conus30x8	~ 14	6	Aug - Sept
9	TS2.1	ne0conus30x8	~ 14	12	Aug - Sept
10	TS2.1	ne0conus30x8	~ 14	no \mathbf{CONUS}^f	Aug - Sept

Table 1. List of Simulations

^{*a*} TS1 is the MOZART-TS1 mechanism (Emmons et al., 2020) and TS2.1 is the MOZART-TS2.1 mechanism (Hodzic et al., 2016; Jo et al., 2021; Schwantes et al., 2020) ^{*b*} ne30 = \sim 111 km globally uniform resolution and ne0conus30x8 = \sim 111 km global resolution with mesh refinement down to \sim 14 km over CONUS

 c Average horizontal resolution over CONUS for the selected grid

 d Specified dynamics (SD) relaxation time

 e Months simulated in year 2013

 f No nudging over CONUS, but a 50-h relaxation time everywhere else.

with high NO_x concentrations. New species and reactions added to TS2 to create TS2.1 296 are listed in Tables S1 and S2 of the supplement. TS2.1 contains 46 more transported 297 species and 50 more non-transported species (i.e., radicals) compared to TS1. Using the 298 TS2.1 mechanism increases the simulation cost by around a factor of 1.6 in CESM2.2/CAM-299 chem-SE compared with the TS1 mechanism. Cost estimates will depend on many fac-300 tors including the computational system used and the amount of output saved, for the 301 latest cost estimates of different configurations, refer to https://wiki.ucar.edu/display/ 302 MUSICA/MUSICA+version+0. 303

These four chemistry and horizontal resolution evaluation tests are nudged lightly 304 with a 50-h relaxation time throughout the entire model domain (i.e., globally and for 305 all vertical levels) to GEOS5 meteorological data. To evaluate the impact of different spec-306 ified dynamics options on the results, six sensitivity tests (Table 1, #5-10) are performed 307 for August - September 2013. For each of the two horizontal resolutions using TS2.1 chem-308 istry, three different specified dynamics options are tested: 6-h relaxation time over the 309 entire domain, 12-h relaxation time over the entire domain, and no nudging over CONUS, 310 but a 50-h relaxation time everywhere else. 311

2.3 Description of Observations

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The flight tracks for the five aircraft campaigns conducted in 2013 used to evaluate CESM/CAM-chem-SE are shown in Figure S1. Two aircraft campaigns focused more on urban regions: DISCOVER-AQ-TX (Deriving Information on Surface conditions from Column and Vertically Resolved Observations Relevant to Air Quality) over Houston, Texas, in September and DISCOVER-AQ-CA over California in January-February (Crawford & Pickering, 2014). The other three aircraft campaigns focused mostly on the Southeast US and include the SENEX (Southeast Nexus) campaign in June-July (Warneke

et al., 2016); the NOMADSS (Nitrogen, Oxidants, Mercury and Aerosol Distributions, 320 Sources, and Sinks) campaign in June-July (Carlton et al., 2018); and the SEAC⁴RS (Stud-321 ies of Emissions, Atmospheric Composition, Clouds, and Climate Coupling by Regional 322 Surveys) campaign in August-September (Toon et al., 2016). Tables S3 and S4 describe 323 the observations used throughout this work including the instrumentation, uncertain-324 ties, and contributors. As shown with the blue boxes in Figure S1, the analysis is restricted 325 to include only data from the Southeast US $[94.5 - 75^{\circ} \text{ W}, 29.5 - 40^{\circ} \text{ N}]$ for three of these 326 aircraft campaigns: SENEX, NOMADSS, and SEAC⁴RS, only data from Los Angeles 327 and Central Valley region of California [122.2 - 117.5° W, 34.5 - 39.5° N] for DISCOVER-328 AQ-CA, and only data from Houston, Texas, [97 - 94.5° W, 28.5 - 31.5° N] for DISCOVER-329 AQ-TX. The 1-minute merges for SEAC⁴RS Revision 7, SENEX Revision D, NOMADSS 330 Revision 5, DISCOVER-AQ-CA Revision 4, and DISCOVER-AQ-TX Revision 3 are used. 331

The model output is saved along the aircraft flight tracks corresponding to the ob-332 servational times at runtime such that any improvement due to the reduction in the chem-333 ical timestep when using finer horizontal resolution is included in the analysis. Vertical 334 interpolation is applied. In the horizontal direction, the two grid cells closest in distance 335 to the observational point based on the grid cell center are averaged with a weight based 336 on the inverse distance. This two grid cell horizontal interpolation produced nearly iden-337 tical overall results to simply selecting the grid cell whose center is closest in distance 338 to each observational point (Figure S10). To facilitate further evaluation of this exten-339 sive dataset, model output of the closest nine grid cells to each observational point for 340 all five aircraft campaigns discussed are available publicly online (see the Model Data 341 Availability description in the Acknowledgments) 342

343 **3 Results**

The impact of using more complex chemistry (TS1 and TS2.1) and finer horizon-344 tal resolution (~ 111 km and ~ 14 km) on ozone and ozone precursors is evaluated at the 345 surface averaged over August 2013 (section 3.1). Because the emissions and input datasets 346 to CESM/CAM-SE have been regridded (section 2.1), biogenic, fire, and anthropogenic 347 emissions using the ~ 14 km horizontal resolution are less artificially diluted compared 348 to that using the ~ 111 km horizontal resolution. These differences in emissions between 349 the horizontal resolutions combined with differences in meteorology and chemistry cause 350 large differences in ozone and ozone precursors at the surface especially when simulat-351 ing fine scale features such as urban and fire plumes. Additionally, using more complex 352 gas and SOA chemistry causes more pronounced differences in simulated surface con-353 centrations of ozone, organic aerosol, formaldehyde, and isoprene oxidation products when 354 using finer horizontal resolution where chemical regimes are better resolved. Compar-355 isons with five aircraft campaigns during 2013 (section 3.2) demonstrate that finer hor-356 izontal resolution reduces model biases compared to the aircraft observations in ozone 357 precursors such as NO_x and CO, but has less of an impact on model biases in ozone it-358 self. 359

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3.1 Differences at the Surface

Differences due to changes in horizontal resolution and chemistry averaged over Au-361 gust 2013 at the first model level, hereafter referred to as surface, are shown for MDA8 362 ozone, organic aerosol, and formaldehyde (Figures 1 - 3). Similar figures for NO_x , car-363 bon monoxide (CO), hydrogen oxide radicals (HO_x), isoprene and isoprene oxidation prod-364 ucts including isoprene hydroxy hydroperoxide, isoprene hydroxy nitrate, methacrolein, 365 and methyl vinyl ketone are presented in the supplement (Figures S2 - S9). When the 366 grids are different, the coarser resolution results are interpolated to the finer resolution 367 grid prior to subtraction. 368



Figure 1. August 2013 average MDA8 surface ozone differences between different horizontal resolutions with chemistry fixed (a & b) and different chemical mechanisms with horizontal resolution fixed (c & d).

In Figure 1a & b, the differences in MDA8 ozone between the horizontal resolu-369 tions are largest in and downwind of urban regions where NO_x emissions are less arti-370 ficially diluted at ~ 14 km compared to ~ 111 km horizontal resolution (Figure S2a & b). 371 The concentrated patches of high organic aerosol throughout the Northwest US in Fig-372 ure 2a & b display the location of large wildfires during August 2013. These wildfires 373 are clearly better represented using the ~ 14 km resolution than at the ~ 111 km reso-374 lution for organic aerosol, but also to some degree for ozone (Figure 1a & b) and formalde-375 hyde (Figure 3a & b). Differences in the area-weighted averages at the surface over the 376 same regions defined in the field campaign analysis (Figure S1) are listed in Table S5. 377 On average, differences between the ~ 111 km and ~ 14 km resolutions for MDA8 ozone 378 and many other compounds are modest. 379

Generally, MDA8 surface ozone decreases across the Eastern US when using TS2.1 380 compared with TS1 at ~ 111 km horizontal resolution (Figure 1d). However, at ~ 14 km 381 horizontal resolution, using TS2.1 versus TS1 reduces MDA8 ozone to an even greater 382 degree up to ~ 15 ppbv (Figure 1c). This suggests that using more complex chemistry may be more important at finer horizontal resolutions where a greater range of chem-384 ical regimes are resolved. In a complementary study by Lacey et al. (in prep), the up-385 dates to both horizontal resolution and chemistry independently reduce biases in sim-386 ulated MDA8 surface ozone compared to surface monitoring networks throughout the 387 summer, but a bias remains. In the Southeast US, on average MDA8 ozone is reduced 388 more with updates to chemistry (-2.9 ppbv at \sim 111 km and -3.2 ppbv at \sim 14 km) than 389 updates to horizontal resolution (0.9 ppbv with TS1 and 0.6 ppbv with TS2.1) as shown 390 in Table S5. These results demonstrate that updating and adding more complexity in 391 model processes such as chemistry can have a large impact on regional ozone. 392

Likely the differences in simulated ozone between TS2.1 and TS1 especially at finer horizontal resolution are caused by TS2.1 including a more complex representation of organic nitrate formation and fate than TS1 (Schwantes et al., 2020). Additionally TS2.1



Figure 2. August 2013 average surface organic aerosol differences between different horizontal resolutions with chemistry fixed (a & b) and different chemical mechanisms with horizontal resolution fixed (c & d).

does not fix the second-generation peroxy radical (RO_2) fate to that of the first-generation 396 (Schwantes et al., 2020). For example, organic nitrates which form from the $RO_2 + NO$ 397 pathway in the first-generation step react with the hydroxyl radical, OH, in TS2.1 to form 398 peroxy radicals that isomerize or react with NO or HO₂. Most reduced chemical mech-399 anisms like TS1 assume that the first-generation organic nitrates react with OH to con-400 tinue to form products from the $RO_2 + NO$ channel in the second-generation step, con-401 trary to observations from field campaigns, which have detected products from mixed 402 peroxy radical fates such as isoprene dihydroxy hydroperoxy nitrates (B. H. Lee et al., 403 2016; Xiong et al., 2016). 404

The TS2.1 mechanism also includes updates to the SOA VBS scheme to include 405 SOA formation from both low- and high- NO_x pathways (section 2.2). The ultimate im-406 pact of using TS2.1 compared to TS1 is to decrease SOA in regions with higher NO_x con-407 centrations. The effect is enhanced at ~ 14 km horizontal resolution where NO_x emis-408 sions are less artificially diluted (Figure 2c & d) than at ~ 111 km horizontal resolution. 409 However, even at the ~ 111 km horizontal resolution, the organic aerosol is reduced by 410 up to 4.1 $\mu g m^{-3}$ and on average by 1.9 $\mu g m^{-3}$ (Table S5) across the Southeast US. Thus, 411 the more complex SOA scheme is important even at the coarse resolution used in global 412 models. At the finer horizontal resolution, the decrease in organic aerosol (Figure 2c) 413 reduces the loss of gas-phase NO_x reservoir compounds including NO₂, N₂O₅, and or-414 ganic nitrates to aerosols, which ultimately increases the NO_x concentrations in cities 415 (Figure S2c). Due to the non-linearity in ozone production and the high NO_x concen-416 trations in these cities, surface ozone declines, which is particularly apparent in the Los 417 Angeles region in Figure 1c. This heterogeneous chemistry is not included in all reduced 418 mechanisms used in 3D models. CESM2 does not include the feedback of aerosols on pho-419 tolysis rates (Lamarque et al., 2012), so this is not contributing to the differences in ozone 420 in Figure 1. 421



Figure 3. August 2013 average surface formaldehyde (CH₂O) differences between different horizontal resolutions with chemistry fixed (a & b) and different chemical mechanisms with horizontal resolution fixed (c & d).

Formaldehyde, representative of the impact of using more complex chemistry and 422 finer horizontal resolution on secondary oxidation products, is shown in Figure 3. Formalde-423 hyde plays an important role for inferring ozone sensitivity (e.g., Schroeder et al., 2017) 424 and is used to estimate isoprene emissions from satellite measurements (Kaiser et al., 425 2018). Here, formaldehyde is enhanced when using finer horizontal resolution (Figure 426 3a & b). This may be partially due to improved representation of the spatial segrega-427 tion of NO_x and isoprene emissions at ~14 km resolution (Kaiser et al., 2018) because 428 formaldehyde production from isoprene is NO_x sensitive (i.e., higher NO_x concentrations 429 produce more formaldehyde). However, because Yu et al. (2016) found that formalde-430 hyde generally decreases with finer horizontal resolution in the Southeast US when iso-431 prene emissions are kept constant, the increase in formaldehyde at finer horizontal res-432 olution in Figure 3a & b is likely due mostly to the increase in isoprene at ~ 14 km res-433 olution (Figure S5 and Table S5). At the ~ 14 km resolution, using TS2.1 produces more 434 pronounced differences compared to TS1 for formaldehyde, CO, HO_x , and isoprene ox-435 idation products than at the ~ 111 km resolution (panels c & d in Figures 3, S3, S4, and 436 S6 - S9), suggesting that using more complex chemistry is more important at finer hor-437 izontal resolutions. 438

To better understand whether the increase in isoprene (Figure S5 and Table S5) 439 when using ~ 14 km compared to ~ 111 km horizontal resolution is caused by changes 440 in oxidants or emissions, the area-weighted isoprene emissions averaged over August 2013 441 for the Southeast US are compared. As expected, isoprene emissions do not change with 442 changes to chemistry at both resolutions (i.e., factor of 1.01 from TS1 to TS2.1). Con-443 versely, using ~ 14 km compared to ~ 111 km horizontal resolution, increases the isoprene 444 emissions by a factor of 1.6 for both chemical mechanisms. In comparison, the area-weighted 445 average surface isoprene concentration increases by a factor of 2.3 when using ~ 14 km 446 compared to ~ 111 km horizontal resolution for both chemical mechanisms. Because the 447 changes in the surface isoprene concentration are higher than the changes in isoprene emis-448

sions, both direct and indirect effects are likely contributing to the differences in isoprene 449 concentrations between the different horizontal resolutions. Higher isoprene emissions 450 are increasing the isoprene concentrations directly, but also indirectly by increasing OH 451 consumption regionally, which leads to less isoprene oxidation, and higher isoprene con-452 centrations. Additionally, improved spatial segregation of isoprene and NO_x at ~14 km 453 resolution may also change regional oxidant concentrations. For example, Yu et al. (2016) 454 found isoprene concentrations increase at finer horizontal resolution even when isoprene 455 emissions are kept constant. 456

457 **3.2**

3.2 Comparison with Observations

A wide variety of observations from the five field campaigns described in section 458 2.3 are compared with the model results. Ozone is a complicated pollutant to accurately 459 simulate in models. By evaluating model results against observations not only for ozone, 460 but also ozone precursors (i.e., NO_x and VOCs), NO_x reservoir compounds, VOC ox-461 idation products, organic aerosol, photolysis rate constants, and temperature, model skill 462 at representing processes important for ozone formation and loss is inferred. For all field 463 campaigns, data influenced by fire plumes (i.e., acetonitrile greater than 0.2 ppbv) are removed from the analysis. We note that if the acetonitrile measurements are intermit-465 tent, this method may not completely filter out all fire plumes. For each field campaign, 466 data representative of a single region are selected for analysis as summarized by the blue 467 boxes in Figure S1. For SEAC⁴RS, SENEX, and NOMADSS data in the Southeast US region only are included. For DISCOVER-AQ-TX, data in the region around Houston, 469 Texas, only are included and for DISCOVER-AQ-CA, data in the Central Valley and 470 Los Angeles region of California only are included. For field campaigns where limit of 471 detection flags are provided in the merge (SEAC⁴RS and DISCOVER-AQ), data flagged 472 as lower limit of detection are set to 0 and data flagged as upper limit of detection are 473 removed from the analysis. For field campaigns where limit of detection flags are not pro-474 vided in the merge (SENEX and NOMADSS), we verified that this did not impact the 475 measurements used in this work. For all field campaigns, data flagged as missing are re-476 moved from the analysis. In Figures 4 - 8, the median vertical profiles for the observa-477 tions (black markers) are compared with that for the model simulations (colored lines). 478 The 25th and 75th percentile for the observations (black horizontal line) are compared 479 with the 25th and 75th percentile for the most complex model simulation, TS2.1 chem-480 istry and ~ 14 km horizontal resolution (purple shading). 481

482

3.2.1 Ozone and Ozone Precursors

For all three campaigns in the Southeast US, more complex chemistry and finer horizontal resolution reduce ozone biases near the surface, but the impact is modest and an ozone bias remains (Figure 4). In two of the campaigns, SENEX and SEAC⁴RS, using more complex chemistry reduces the ozone bias near the surface more than increasing the horizontal resolution. For both SENEX and SEAC⁴RS, the 25th percentile model results are above the median in the observations below 1 km in altitude demonstrating that a large bias in ozone remains.



Figure 4. Median vertical profile plots of the five aircraft campaigns for observations (black markers) and the model simulations (colored lines). The black horizontal lines and the purple shading show the 25^{th} and 75^{th} percentiles for the observations and the TS2.1, 14 km model simulation, respectively. Abbreviations are ozone (O₃), stratospheric ozone tracer (O₃ Strat), nitrogen oxide (NO), and nitrogen dioxide (NO₂).

490 491

As diagnosed by the stratospheric ozone tracer $(O_3 \text{ Strat})$ in CAM-chem, only a small amount of ozone near the surface in the Southeast US is transported down from the stratosphere (Figure 4). The stratospheric ozone tracer concentration near the sur-492 face is consistent between the ~ 111 km and ~ 14 km resolutions verifying that at least 493 in the Southeast US the finer horizontal resolution is not leading to an unexpected en-494 hancement of stratospheric ozone near the surface during the summer. The vertical pro-495 file of various compounds for the $SEAC^4RS$ campaign is extended to 12 km in altitude 496 in Figures S11 and S12. Ozone and the stratospheric ozone tracer are enhanced in the 497 upper troposphere (UT) in the simulations performed at ~ 14 km compared to that us-498 ing ~ 111 km (Figure S11) suggesting that finer horizontal resolution impacts troposphere-499

stratosphere exchange and also possibly UT chemistry, which is influenced by convective outflow and lightning- NO_x (Cuchiara et al., 2020).

Although the increased horizontal resolution only moderately impacts ozone itself 502 in the Southeast US, larger changes are observed for ozone precursors such as NO, NO₂ 503 (Figure 4), carbon monoxide (CO), formaldehyde (CH_2O), isoprene, and monoterpenes (Figure 5). The changes in these ozone precursors demonstrate that ozone formation pro-505 cesses are different at finer horizontal resolution. NO and NO_2 decrease at both hori-506 zontal resolutions when increasing the chemical complexity from TS1 to TS2.1 in the South-507 east US for all three aircraft campaign comparisons suggesting that NO_x biases within models are not only caused by emissions. Differences in chemistry such as NO_x recycling 509 and the formation and fate of NO_x reservoir compounds can also impact NO_x concen-510 trations. Even with improvements to horizontal resolution and chemical complexity, NO 511 and NO_2 are overpredicted compared to the observations in both the median and 25^{th} 512 and 75^{th} percentiles. This bias in NO_x likely contributes to the high bias in ozone in the 513 Southeast US. 514

In all three campaigns in the Southeast US, the median of isoprene and monoter-515 penes for all simulations is generally near to that of the observations, but the simula-516 tions using the ~ 14 km horizontal resolution sometimes overpredict near the surface. The 517 75th percentile of isoprene and monoterpenes is greatly overpredicted in the simulations 518 using ~ 14 km horizontal resolution compared to that of the observations (Figure 5). Be-519 cause the model bias in isoprene and monoterpenes increases when using finer horizon-520 tal resolution, this bias is further explored in section 4. The 75^{th} percentile of CH₂O in 521 the model is much higher than the observations likely caused by the high bias in the 75^{th} 522 percentile of isoprene. 523

The other two campaigns, DISCOVER-AQ-TX and DISCOVER-AQ-CA, focused more on urban regions with greater NO_x and less biogenic VOC emissions than that in the Southeast US (Figures 4 and 5). As expected, using more complex isoprene and terpene chemistry generally does not impact ozone or NO_x in California and Houston, TX, (Figure 4). Clear differences in the ozone vertical profile shape occur when switching from ~111 km to ~14 km resolution. Ozone is underestimated compared to the observations near the surface especially in Houston, TX.

⁵³¹ While finer horizontal resolution only moderately impacts ozone and ozone precur-⁵³² sors in the Southeast US, finer horizontal resolution more substantially impacts NO_x (Fig-⁵³³ ure 4), CO, and CH₂O (Figure 5) in Texas and California. In both DISCOVER-AQ-TX ⁵³⁴ and DISCOVER-AQ-CA, NO_x is over-predicted in the model compared to the obser-⁵³⁵ vations in the median and sometimes also the 75th percentile using ~14 km horizontal ⁵³⁶ resolution. In these high NO_x urban regions, over-predicting NO_x in the model is likely ⁵³⁷ leading to the underprediction of ozone.

In general, these results demonstrate that ozone precursors and as such the processes forming ozone are better simulated at ~14 km especially in urban regions even if there are not large differences in the magnitude of ozone itself. Now that we can move seamlessly between ~14 km and ~111 km horizontal resolutions in CESM, the model processes can be more extensively evaluated and improved, which will hopefully improve model skill at simulating ozone across all scales in the future.

3.2.2 Photolysis

544

Consistent with previous evaluations of CESM/CAM-chem against the SEAC⁴RS field campaign (Schwantes et al., 2020), simulated NO₂ photolysis in all three campaigns in the Southeast US and also in Texas (Figure 6) is overpredicted below 1 km and underpredicted between 2-4 km (Figure 6). Using finer horizontal resolution does not improve the model bias in NO₂ photolysis vertical shape. In California, NO₂ photolysis is



Figure 5. Identical to Figure 4, but median vertical profile plots for carbon monoxide (CO), formaldehyde (CH_2O), isoprene and monoterpenes.



Figure 6. Identical to Figure 4, but for photolysis of NO_2 (j NO_2) and when available photolysis of O_3 (j O_3).

underpredicted in CESM/CAM-chem at all altitudes below 4 km. The model bias in NO_2 550 photolysis may be partially caused by some field campaigns avoiding the sampling of clouds 551 on scales not well-resolved by the model (Hall et al., 2018). Additionally, the 2 grid-cell 552 horizontal interpolation applied here may not fully account for the impact of clouds in 553 neighboring model grid cells on the photolysis rate constant, but the ~ 14 km horizon-554 tal resolution is likely too coarse for this correction to systematically impact the results. 555 Future work using even finer horizontal resolutions in CESM/CAM-chem may need to 556 consider applying a correction. 557

As described by Schwantes et al. (2020), the model bias in the NO₂ photolysis ver-558 tical shape in the Southeast US is likely due to a model bias in clouds. Ryu et al. (2018) 559 using WRF-Chem demonstrated that incorporating satellite derived clouds improved the 560 NO₂ photolysis vertical profile and reduced simulated MDA8 surface ozone by 1-5 ppbv. 561 Given the results in Ryu et al. (2018) and that the model bias in the NO₂ photolysis ver-562 tical shape is not improved by using ~ 14 km horizontal resolution, evaluating and im-563 proving regional cloud biases in CESM/CAM-chem and better understanding the impact of cloud biases on ozone should be prioritized in the future. Additionally, CESM2 565 does not include the feedback of absorbing and scattering aerosols on reducing or enhanc-566 ing photolysis rates, which impacts oxidants such as HO_x and ozone (e.g., Dickerson et 567 al., 1997; Tie et al., 2005; Li et al., 2011). Adding this aerosol-photolysis feedback into CESM is a priority for future work. 569

3.2.3 Organic Aerosol

570

Accurately simulating aerosols is important for simulating ozone for the right reasons in models because aerosols impact photolysis rates (Dickerson et al., 1997) and heterogeneous reactions (Jacob, 2000). To evaluate, model skill at simulating organic aerosol with the updated SOA scheme incorporated into TS2.1 (section 2.2) the model results are compared to the measured organic aerosol from the aerosol mass spectrometer (AMS) during the SENEX and SEAC⁴RS campaigns. The AMS measures submicron organic



Figure 7. Identical to Figure 4, but for organic aerosol for the two field campaigns that measured organic aerosol by aerosol mass spectrometry.

aerosol with an upper limit 50% transmission efficiency at an aerodynamic diameter of 577 \sim 750 nm as measured during the Atmospheric Tomography Mission (Guo et al., 2021). 578 Consistent with past work (Hodzic et al., 2020; Jo et al., 2021; Tilmes et al., 2019), to 579 compare organic aerosol from CESM/CAM-chem with the organic aerosol measured by 580 the AMS, the Aitken and accumulation modes in CESM/CAM-chem are summed for 581 both primary organic aerosol (POA) and SOA. Aerosols are modeled in CESM2/CAM-582 chem with a four-mode version of the Modal Aerosol Module (MAM4) (Liu et al., 2016) 583 with updated size bins from Mills et al. (2016). The accumulation mode in CESM gen-58/ erally represents submicron aerosol (Hodzic et al., 2020; Liu et al., 2012; Tilmes et al., 585 2019) observable by the AMS. A more detailed evaluation of how well the MAM4 scheme 586 simulates the aerosol size distribution in CESM and accounting for possible differences 587 in the aerosol size distribution simulated in CESM and that measured by the AMS is 588 warranted for future work. 589

Consistent with the differences in surface organic aerosol shown in Figure 2, organic 590 aerosol clearly changes when updating chemistry and using finer horizontal resolution 591 along the SENEX and SEAC⁴RS flight tracks (Figure 7). For SEAC⁴RS, the most com-592 plex model configuration (TS2.1 and ~ 14 km) represents the organic aerosol observa-593 tions the best. When using the TS1 mechanism at ~ 14 km horizontal resolution, the or-594 ganic aerosol is biased high, but by applying the updated SOA mechanism in TS2.1 the 595 organic aerosol decreases in line with the observations (Figure 7). In SENEX, the up-596 dated TS2.1 chemistry generally underpredicts the organic aerosol compared to the ob-597 servations and performs worse than the TS1 chemistry. The SENEX campaign occurred earlier in the summer (June - July) and had lower concentrations of isoprene and monoter-599 penes at the 75th percentile (Figure 5) than SEAC⁴RS (August - September). Addition-600 ally, the SENEX campaign focused on urban and urban outflow regions and the $SEAC^4RS$ 601 campaign focused on a more regional perspective of the Southeast US. To better under-602 stand the differences in model biases between SENEX and SEAC⁴RS, the spatial biases 603 in organic aerosol are further explored in section 4. 604

3.2.4 Isoprene Oxidation Products

Isoprene oxidation products are well represented in CESM/CAM-chem when using the ~ 14 km horizontal resolution and updated TS2.1 chemistry. Because isoprene itself is overpredicted at the 75th percentile in the model (Figure 5), the first-generation oxidation products including isoprene hydroxy hydroperoxides (ISOPOOH) and also to a lesser extent isoprene hydroxy nitrates (ISOPN) are also overpredicted at the 75th per-



Figure 8. Identical to Figure 4, but for isoprene hydroxy hydroperoxide (ISOPOOH); $C_5O_3H_8$, which includes all isomers of HPALDs (isoprene hydroperoxy aldehydes), ICHE (isoprene carbonyl hydroxy epoxide), and likely other unknown products; isoprene hydroxy nitrate (ISOPN); propanone nitrate (NOA); methacrolein and methyl vinyl ketone hydroxy nitrates and other isomers of $C_4O_5H_7N$ (MACRN + MVKN); ethanal nitrate (NO₃CH₂CHO); total organic nitrates; and total peroxy acyl nitrates (PANs).

centile in the model (Figure 8). Likely once the isoprene overprediction is corrected, the model bias in first-generation isoprene oxidation products will also improve.

The observations of $C_5O_3H_8$ include all isomers of HPALD (isoprene hydroperoxy 613 aldehydes), ICHE (isoprene carbonyl hydroxy epoxides), and likely other unknown prod-614 ucts. These observations are compared with HPALD in TS1 and the sum of four HPALD 615 isomers and ICHE in TS2.1. Even with using the finer horizontal resolution and updated 616 TS2.1 chemistry, the model is underpredicting $C_5O_3H_8$ products (Figure 8). Given the 617 inability of CESM/CAM-chem to accurately capture C₅O₃H₈ products and the impor-618 tance of HPALD for HO_x recycling, more laboratory studies are needed to identify any 619 unknown $C_5O_3H_8$ products and better understand the formation and loss pathways of 620 HPALD and ICHE, which are still quite uncertain. 621

The total organic nitrates are also underpredicted in all model configurations and 622 the finer horizontal resolution only moderately impacts the bias (Figure 8). TS1 and TS2.1 623 mechanisms do not track organic nitrates produced from C_1 - C_3 alkane oxidation. As shown 624 by Fisher et al. (2016), this likely contributes to part of this underprediction because of 625 large oil and gas activities in the US and the long atmospheric lifetime of the C_1 - C_3 alkane 626 organic nitrates. Additionally, CESM/CAM-chem does not currently track particulate 627 organic nitrates. Adding this is an important priority for future work to better constrain 628 organic nitrate uptake to aerosol and evaluate the total organic nitrate and NO_v bud-629 get. Additionally, Kenagy et al. (2020) suggest that organic nitrate production from NO_3 -630 initiated VOC oxidation at night is comparable to that from OH-initiated VOC oxida-631 tion during the day in the Southeast US. Further evaluation of how well CESM/CAM-632

chem represents the boundary layer and chemistry at night may also be needed to fully understand this organic nitrate model bias.

4 Discussion

With the added capability of performing simulations with higher horizontal res-636 olution within CESM/CAM-chem, confidence that ozone formation and loss processes 637 are accurately represented in the model is increased and the remaining biases in the most 638 complex version of the model (i.e., TS2.1 chemistry at ~ 14 km resolution) can be inves-639 tigated to better understand which processes are missing or erroneous in the model that 640 prevent accurate simulation of ozone. Box and whisker plots for the bias (model - ob-641 servations) along the SEAC⁴RS flight tracks below 1 km in altitude are presented in Fig-642 ure 9 and the spatial distribution of biases along the $SEAC^4RS$ and SENEX flight tracks below 1 km altitude are shown for the most complex model simulation (TS2.1 chemistry 644 and ~ 14 km horizontal resolution) in Figure 10 and for all the model simulations in Fig-645 ures S16 - S23. 646

Ozone is overpredicted in all model simulations across much of the Southeast US 647 (Figure 10a & b) and the median bias is improved more by updating chemistry than hor-648 izontal resolution (Figure 9). Not all processes necessarily improve with finer horizon-649 tal resolution. As expected, biases in anthropogenic ozone precursors like CO and NO_x 650 clearly decrease, but other biases (e.g., isoprene and water vapor) increase as shown in 651 Figure 9. The impact of these competing processes may counteract each other leading 652 to only minor net changes in ozone when using finer horizontal resolution. As described 653 below, improvements to model processes including emissions (section 4.1), chemistry (sec-654 tion 4.2), and meteorology (section 4.3) are needed to reduce systematic biases in CESM/CAM-655 chem-SE across all scales. 656

4.1 Emissions

Reductions in biases of anthropogenic pollutants like NO, NO_2 , and CO are achieved 658 most by improvements to finer horizontal resolution. There is still a high bias in NO_2 659 in CESM/CAM-chem even for the most complex simulation (TS2.1 chemistry and ~ 14 660 km horizontal resolution). Generally, in the Southeast US NO_x is underpredicted in ur-661 ban regions (e.g., St. Louis and Indianapolis in SENEX) and elsewhere large variabil-662 ity exists in the NO_x bias favoring a general overprediction of NO_x (Figure 10c & d). Higher 663 resolution than ~ 14 km may be needed to accurately capture NO_x in urban and urban 664 outflow regions. Simulations at ~ 111 km horizontal resolution generally had higher bi-665 ases in NO_x than those at ~14 km, but interestingly in certain locations the NO_x bias 666 was higher at ~ 14 km (Figures S18 and S19). This mixture of improvement in simulated 667 NO_x is likely a contributing factor for why the median ozone vertical profile (Figure 4) 668 did not greatly differ between the coarse and fine horizontal resolutions. 669

The high bias in the median and $25^{\text{th}} \& 75^{\text{th}}$ percentiles for NO_x (Figure 4) com-670 bined with the spatial pattern of NO_x biases in Figure 10 suggest the need for additional 671 capabilities within the MUSICA framework to replace sections of global anthropogenic 672 emission inventories with regional inventories like the US EPA National Emissions In-673 ventory (NEI). The CAMS anthropogenic emissions used in this work are available at 674 fine horizontal resolution, but only on a monthly timescale. The NEI inventory, along 675 with having improved regional skill, would also add diurnal variation, weekend/weekday 676 effects, and vertical information to the anthropogenic emissions. These improvements 677 will likely reduce NO_x emissions and improve comparisons to observations shown in sec-678 tion 3.2. Possibly further adjustments to these regional inventories will also be needed 679 (e.g., NO_x reductions from mobile sources (McDonald, McKeen, et al., 2018; Travis et 680 al., 2016)). With the new mesh refinement capability in CESM/CAM-chem, evaluation 681



Figure 9. Box and whisker plots for bias (model - observations) along the SEAC⁴RS flight tracks below 1 km pressure altitude for TS1 at 111 km resolution (red), TS1 at 14 km resolution (gold), TS2.1 at 111 km resolution (light blue), and TS2.1 at 14 km resolution (purple). To highlight differences between the coarse and refined horizontal resolutions, the medians for each case are shown as a blue line for ~111 km resolution and a magenta line for ~14 km resolution. The boxes extend to the 25th (Q₁) and 75th (Q₃) percentiles, the whiskers extend to the extremes, and the outliers are displayed as black markers. Outliers are defined as less than Q₁ - 1.5*IQR or greater than Q₃ + 1.5*IQR where IQR is the interquartile range (Q₃ - Q₁).

of emission updates can easily be done across multiple scales, which will lead to more cohesive model improvements at the global and regional scale.



Figure 10. Biases (model (TS2.1, 14 km) - observations) for ozone (a & b), NO_x (c & d), isoprene (e & f), and organic aerosol (g & h) for SEAC⁴RS left and SENEX right flight tracks below 1 km pressure altitude. Markers indicate cities targeted during the SENEX campaign: Atlanta (circle), Birmingham (square), Nashville (upward triangle), St. Louis (downward triangle), and Indianapolis (diamond). Here only results from the best case model simulation with TS2.1 chemistry and 14 km horizontal resolution are shown.

Additionally, a global soil NO_x inventory at $0.5^{\circ} \times 0.5^{\circ}$ horizontal resolution is used in this work. Updating the resolution of soil NO_x emissions in CAM-chem may also improve comparisons of modeled NO_x and ozone against field campaign observations (Figure 4). This should include incorporating updates from recent regional modeling studies (Almaraz et al., 2018; Oikawa et al., 2015; Souri et al., 2016) that identify the importance of increasing soil NO_x emissions in biogenic inventories such as MEGAN and BEIS (Biogenic Emission Inventory System).

Isoprene and monoterpenes are unique in that model biases are lower using the ~ 111 km versus ~ 14 km horizontal resolution. There is a high temperature bias in CESM/CAM-

chem in all the simulations (Figure 9). MEGAN v2.1 used in CESM/CAM-chem appears 693 to be more sensitive to the high temperature bias at finer horizontal resolutions. As ex-694 plained previously, isoprene is higher in simulations at the ~ 14 km than those at ~ 111 695 km and this enhancement is especially important in Louisiana, Arkansas, and Missouri 696 (Figures S20 and S21). These same regions have fairly high values of isoprene in gen-697 eral and as expected are the regions where updating the biogenic chemistry (TS2.1) re-698 duced the ozone bias (Figures S16 and S17). Ozone is often overpredicted (Figure 10a 699 & b) where isoprene is also biased high (Figure 10e & f), but most often the highest bi-700 ases in ozone do not correspond to where isoprene is also biased high. Thus, improving 701 the biases in isoprene emissions, while important, may have a limited impact on the gen-702 eral ozone bias in the Southeast US in CESM/CAM-chem-SE. 703

The dust emissions used in CESM/CAM-chem-SE are based on a parameteriza-704 tion that uses a soil erodibility map that is at coarse $(2^{\circ} \ge 2^{\circ})$ horizontal resolution (Albani 705 et al., 2014). Development of dust emission schemes that do not require resolution de-706 pendent soil erodibility maps and include other scale aware parameterizations (e.g., ac-707 curately handling higher wind speeds that are resolved at finer horizontal resolution) are 708 underway in CAM and will be especially important for future CAM-chem simulations 709 with mesh refinement over regions of the Earth where dust emissions are more preva-710 lent than CONUS. Although not the focus of this analysis, further constraints and eval-711 uation of fire emissions, which vary widely between different emission inventories (e.g., 712 Al-Saadi et al., 2008; Pan et al., 2020; Pereira et al., 2016), fire plume injection height, 713 and transport of smoke are also needed to accurately simulate ozone production from 714 wildfires in CESM/CAM-chem-SE (Jaffe & Wigder, 2012). 715

Although this work has focused more on evaluating and discussing biases in emissions, deposition of ozone itself (Clifton et al., 2020) and VOC oxidation products (Nguyen et al., 2015) including ozone precursors and NO_x reservoir compounds are also important for accurately simulating ozone. Future work evaluating and improving deposition especially at a process level (e.g., Clifton et al., 2017; Kavassalis & Murphy, 2017) is also recommended.

722 4.2 Chemistry

In the ambient atmosphere gas and aerosol chemistry are intrinsically linked, but 723 gas and aerosol processes are often represented separately in 3D models. Better under-724 standing and incorporating gas and aerosol feedbacks into models will be crucial for ac-725 curately representing ozone and aerosols in the future. This includes adding the impact 726 of aerosols on photolysis rates into CESM. Additionally, more complex representation 727 of heterogenous chemistry is needed both for inorganic compounds (Jacob, 2000) as well 728 as VOC oxidation products. For example, the loss of tertiary organic nitrates to aerosol 729 and clouds and subsequent hydrolysis is an important NO_x loss pathway as demonstrated 730 by novel experimental work (Darer et al., 2011; Hu et al., 2011; Jacobs et al., 2014; Teng 731 et al., 2017) and recently applied to several 3D atmospheric chemistry models (Bates & 732 Jacob, 2019; Muller et al., 2019; Schwantes et al., 2020; Zare et al., 2018, 2019). In par-733 ticular, recent work by Vasquez et al. (2020) provides further constraints on the atmo-734 spheric fate of the different isoprene hydroxy nitrate (IHN) isomers. Loss of the dom-735 inant tertiary IHN by aerosol uptake and subsequent hydrolysis is on par with OH-oxidation 736 even in Pasadena, CA, with low relative humidity and high OH and even more impor-737 tant over forested regions with high relative humidity and low OH. These past exper-738 imental and modeling studies emphasize the importance of expanding the representa-739 tion of heterogenous chemistry in CESM/CAM-chem to better represent the loss path-740 ways of organic nitrates to aerosols and clouds in the future. 741

Using TS2.1 compared to TS1 chemistry reduces the positive model bias in organic aerosol during the SEAC⁴RS campaign, but causes a negative model bias during the SENEX

campaign (Figures 7, S22, and S23). In particular, organic aerosol is underpredicted dur-744 ing the SENEX campaign especially in urban and urban outflow regions (Figure 10h) 745 suggesting urban SOA is not well represented in CESM/CAM-chem. CESM/CAM-chem 746 is likely missing emerging urban SOA sources such as VOCs from volatile chemical prod-747 ucts (VCPs) or cooking (Klein et al., 2016; McDonald, de Gouw, et al., 2018; Nault et 748 al., 2021; Qin et al., 2021). Additionally, finer horizontal resolution than ~ 14 km may 749 be needed to resolve the urban and power plant plumes sampled during the SENEX cam-750 paign (Warneke et al., 2016). Improving the representation of SOA in urban and urban 751 outflow regions in CESM/CAM-chem including performing simulations at even finer hor-752 izontal resolution and updates to emissions and chemistry to include emerging emission 753 sources such as those from VCPs and cooking should be prioritized in future work. Ad-754 ditionally, MAM4 does not simulate inorganic particulate nitrate. Incorporation of in-755 organic particulate nitrate through MOSAIC (Model for Simulating Aerosol Interactions 756 and Chemistry) into CESM is currently under development. 757

In general, increasing chemical complexity increases the number of transported trac-758 ers, which then increases the simulation cost. How computational cost scales with adding 759 additional transported tracers depends on the transport scheme. For uniform grids in 760 CESM/CAM-chem-SE, users can optionally use the CSLAM (Conservative Semi-Lagrangian 761 Multitracer) scheme, which improves the efficiency and accuracy of tracer transport (Lauritzen 762 et al., 2017) compared to the default transport scheme. The uniform resolution config-763 uration using CSLAM passes the state to physical parameterizations on a more "equal-764 area" grid compared to the spectral-element quadrature grid. This alleviates spurious 765 noise near the element boundaries (Herrington, Lauritzen, Taylor, et al., 2019) and al-766 lows for running parameterizations on a lower or higher resolution grid compared to the dynamics (Herrington, Lauritzen, Reed, et al., 2019). Currently, the variable resolution 768 configurations do not support CSLAM and the separate physics grid, but there are no 769 theoretical constraints preventing this development. Further development of computa-770 tionally efficient transport schemes like CSLAM will be particularly useful for predict-771 ing air quality, which requires a large number of transported chemical tracers, within the 772 MUSICA framework. 773

4.3 Meteorology

As shown in Figure 9, large biases exist in CESM/CAM-chem-SE for key meteo-775 rological variables important for atmospheric chemistry including temperature, water va-776 por, clouds (as evaluated by photolysis rates), and the planetary boundary layer (PBL) 777 height (PBLH). As mentioned in section 4.1, the high temperature bias in CESM seems 778 to impact isoprene emissions more at finer horizontal resolution (Figure 9). Addition-779 ally, photolysis rates of NO_2 and O_3 are too high and the water (H₂O) vapor mixing ra-780 tio is too low (Figure 9). Combined this possibly suggests there are not enough low clouds 781 in the model, which would increase the water vapor, lower the photolysis rate constants, 782 and likely lower the temperature as well. 783

Given these biases, a series of sensitivity simulations (Table 1) are performed to 784 evaluate the impact of the specified dynamics nudging strength. Temperature and winds 785 are nudged to the GEOS5 meteorology (section 2.2). The finest horizontal resolution used 786 in this study (~ 14 km, $\sim 0.125^{\circ}$) is finer than that available in the GEOS5 meteorology 787 $(0.31^{\circ} \ge 0.25^{\circ})$. Thus, the base simulations to evaluate updates to chemistry and hor-788 izontal resolution are all performed using a light nudging with a relaxation time of 50 789 h, in order to achieve the full benefit of using finer horizontal resolution. Box and whisker 790 plots for the bias (model - observations) along the SEAC⁴RS flight tracks below 1 km 791 altitude at both ~ 111 km (blue median lines) and ~ 14 km (magenta median lines) hor-792 izontal resolutions are shown in Figure 11 for the following specified dynamics sensitiv-793 ity tests: 6-h relaxation time, 12-h relaxation time, 50-h relaxation time, and no nudg-794 ing over CONUS, but a 50-h relaxation time everywhere else. A 6-h relaxation time is 795

a strong nudging case where full nudging towards reanalysis occurs every 6 hours, but
distributed fractionally over each model time step. The stronger nudging to temperature and winds reduces the model bias in temperature for both horizontal resolutions,
but even with a 6-h relaxation time the model is still biased high for temperature. At
~14 km horizontal resolution, using the 6-h nudging has the lowest bias in isoprene and
ozone likely due to reductions in the temperature bias.



Figure 11. Identical to Figure 9, but for the specified dynamics sensitivity simulations listed in Table 1. The box and whiskers are colored by relaxation time: 6 h (red), 12 h (gold), 50 h (light blue), and 50 h globally, but no nudging within the CONUS region (purple). The medians are colored by the horizontal resolution: ~ 111 km (blue line) and ~ 14 km (magenta line).

Although the analysis against the SEAC⁴RS campaign results suggests that stronger 802 nudging improves ozone, clear regional differences exist when using 6-h versus 50-h re-803 laxation times as shown in Figure 12a at ~ 14 km and Figure S13a at ~ 111 km horizon-804 tal resolution. There are negligible differences between the 6-h and 50-h nudging sim-805 ulations for the stratospheric ozone tracer at the surface (Figures 12b and S13b) veri-806 fying that the differences in surface MDA8 ozone are not caused by changes in troposphere-807 stratosphere exchange. Isoprene concentrations (Figures 12d and S13d) and emissions 808 (Figures S14a and S15a) in the Southeast US are higher using the 50-h compared with 809 the 6-h relaxation time especially at ~ 14 km horizontal resolution. There are also clear 810 differences in clouds (Figures S14c and S15c) and thereby photolysis of NO_2 (Figures 811 12e and S13e). 812

Interestingly, the model bias in water vapor is worse at the finer horizontal reso-813 lution (Figure 9) and changes in water vapor due to nudging strength (Figures 12f and 814 S13f) are generally inversely correlated with changes in ozone. The impact of water va-815 por on ozone production and loss is complicated. Photolysis of O_3 leads to the produc-816 tion of $O(^{1}D)$ (R1). $O(^{1}D)$ either reacts with H_2O to destroy O_3 (R2) or with O_2 or N_2 817 to form $O(^{3}P)$ (R3), which generally reacts with O_{2} to reform O_{3} (R4). In remote re-818 gions, higher water vapor leads to a net reduction in tropospheric ozone due to the com-819 petition between reactions 2 and 3 (Jacob & Winner, 2009; Johnson et al., 1999). In re-820 gions with NO_x pollution, the impact is more complex. For example, OH generated from 821 reaction 2 can react with CO and VOCs in the presence of NO_x and sunlight to produce 822 O_3 or react with NO₂ to produce HNO₃ generally preventing O_3 production (Jacob & 823 Winner, 2009; Monks et al., 2015). The low model bias in water vapor using the ~ 14 824 km horizontal resolution shown in Figure 9 falsely reduces reaction 2 biasing the O_3 loss 825 term low. Falsely reducing reaction 2 also reduces OH generation, which in the South-826 east US where there is modest NO_x pollution biases the O_3 production term low too. 827 Due to this complexity, careful examination and reduction of biases in meteorology met-828 rics like temperature, water vapor, and photolysis rates are important for accurately sim-829 ulating ozone production and loss terms. 830

$$O_3 + hv \to O_2 + O(^1D) \tag{R1}$$

$$O(^{1}D) + H_{2}O \rightarrow OH + OH$$
 (R2)

$$O(^{1}D) + O_{2}/N_{2} \rightarrow O(^{3}P) + O_{2}/N_{2}$$
 (R3)

$$O(^{3}P) + O_{2} + M \rightarrow O_{3} + M$$
(R4)

The PBLH is over-predicted in all simulations (Figures 9 and 11). CESM/CAM-831 chem only has 32 vertical levels extending from the surface into the lower stratosphere 832 $(\sim 40 \text{ km})$. Increasing the vertical resolution would require re-tuning many of the pa-833 rameterizations in CESM/CAM-chem. Regional models typically have many more ver-834 tical levels especially in the PBL. Interestingly, as shown in Figure 11, using different spec-835 ified dynamics options does not impact the PBLH at the ~ 111 km resolution, but at the 836 \sim 14 km resolution the PBLH is best represented when no nudging occurs over the CONUS 837 region. Further investigation of how nudging temperature and winds impact the plan-838 etary boundary layer parameterizations in CESM/CAM-chem would also be beneficial. 839 The CESM community is moving toward adding additional vertical levels in the PBL 840 (Simpson et al., 2020), which will hopefully improve the simulated PBLH and the chem-841 ical and physical processes within the PBL. 842





Figure 12. Changes at the surface caused by using a 50-h minus a 6-h specified dynamics (SD) relaxation time with the TS2.1 chemical mechanism at ~ 14 km horizontal resolution for (a) MDA8 surface ozone, (b) MDA8 surface stratospheric ozone tracer, (c) temperature, (d) isoprene, (e) photolysis rate of NO_2 , (f) water mixing ratio, (g) organic aerosol, and (h) NO_x .

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The selection of nudging strength to temperature and winds strongly impacts other aspects of the model such as clouds, photolysis, water vapor, isoprene, and ozone. For example, in some regions differences in MDA8 ozone caused by selecting a 50-h versus 6-h relaxation time (Figure 12a) are similar in magnitude to using finer horizontal resolution or more complex chemistry (Figure 1). While nudging is needed to reduce dynamical variability, nudging can also lead to spurious results especially when the climatologies of the reanalysis meteorology and model are different (N. A. Davis et al., 2020). Development and evaluation of new nudging techniques that account for differences in 850 the climatologies between the model and reanalysis meteorology (e.g., nudging toward

climatological anomalies as done by N. A. Davis et al. (2020)) are needed. Future work 852 to improve ozone predictions in CESM/CAM-chem should prioritize reducing system-853 atic regional biases in temperature rather than relying on specified dynamics to correct 854 biases. In general, CESM/CAM-chem has been tuned at coarser resolution, so develop-855 ment of scale-independent parameterizations and tuning parameters are likely needed 856 to reduce biases in meteorological variables. Additionally, the ability to test parameter-857 izations developed for mesoscale processes within the MUSICA framework will also be 858 useful. 859

5 Future Model Development

This work along with a complementary study by Lacey et al. (in prep) brings a global atmospheric chemistry model, CESM/CAM-chem, to regional scales through mesh refinement using the SE dycore. Based on the evaluation described in section 3 and 4, several capabilities have been identified as important priorities for future work. Those with the highest priority are:

866	1. Add capability to replace the CAMS global anthropogenic emission inventory in
867	specific locations with regional inventories (e.g., US EPA NEI inventory) that have
868	improved local information and greater detail such as weekend/weekday effects,
869	diurnal variation, and vertical information.
870	2. Update the resolution of soil NO_x and dust emissions used in CAM-chem
871	3. Improve feedbacks between gas and aerosols in CESM/CAM-chem including in-
872	corporating the feedback of aerosols on photolysis rates and improving the rep-
873	resentation of heterogeneous chemistry including the loss of organic nitrates to aerosols
874	and clouds.
875	4. Further development of computationally efficient transport schemes like CSLAM,
876	which will limit the computational costs of using more complex chemical mech-
877	anisms.
878	5. Improve understanding and reduction of regional biases in meteorology in CAM-
879	chem, especially temperature, water vapor, clouds, and planetary boundary layer
880	height, which includes:
881	(a) Developing scale-independent parameterizations and tuning factors.
882	(b) Adding the capability to test parameterizations developed for mesoscale pro-
883	cesses within MUSICA.
884	(c) Increasing the vertical resolution within the PBL.
885	6. Incorporate a nonhydrostatic dynamical core into CESM, in order to achieve an
886	objective of MUSICA to model from global to local scales all within the same mod-
887	eling framework.

6 Conclusions

A new configuration of CESM/CAM-chem called CESM/CAM-chem-SE with the capability of horizontal mesh refinement has been developed and evaluated in this work along with a parallel paper by Lacey et al. (in prep). This new capability not only creates a model ideally suited to simulate air quality across scales including global feedbacks without the limitations of lateral boundary conditions, but also allows studies like this one to evaluate the importance of horizontal resolution and chemical complexity all within a single model framework.

Even with finer horizontal resolution and more complex chemistry, biases in ozone remain as compared to observations from five aircraft campaigns in 2013. The aircraft observations provide a wide variety of measurements of ozone precursors (VOCs, CO, and NO_x) and meteorological metrics (water vapor, temperature, photolysis rate con-

stants, PBLH), which enable a more careful examination of model processes. In partic-900 ular, this analysis suggests further work reducing biases in meteorology like temperature, 901 water vapor, clouds, and PBLH will be important for improving simulated ozone in CESM/CAM-902 chem-SE. Because inter-model comparisons typically have better agreement for the ozone 903 budget than for ozone production and loss terms (Young et al., 2018), continued eval-904 uation against field campaign data with comprehensive measurement payloads is impor-905 tant for understanding whether the model physical and chemical processes, which de-906 termine the ozone distribution, are accurately represented. 907

We recognize that several regional model capabilities still need to be incorporated into CESM as described in section 5 including updates to anthropogenic emissions, soil NO_x emissions, dust emissions, vertical resolution, and better coupling gas and aerosol chemistry. Additionally, various chemical and physical processes in CESM need to be updated to be scale-independent and/or scale-aware (Pfister et al., 2020). These activities will be a priority for future work.

This work demonstrates the importance of balancing the simulation costs of hor-914 izontal resolution, vertical resolution, and physical and chemical processes complexity. 915 Ozone precursors are all more impacted by horizontal resolution than ozone itself sug-916 gesting that ozone formation processes clearly change when using ~ 14 km compared to 917 \sim 111 km horizontal resolution. Future studies investigating fine scale features such as 918 urban and fire plumes will gain the most benefit from using the mesh refinement capa-919 bility added to CESM/CAM-chem in this work. Updating isoprene and terpene chem-920 istry reduces surface ozone in the Eastern US at varying horizontal resolutions and es-921 pecially at finer horizontal resolution where a greater range of NO_x and VOC chemical 922 regimes are resolved. 923

Because the impact of using more complex isoprene and terpene chemistry on ozone 924 and other compounds such as formaldehyde and isoprene oxidation products is more pro-925 nounced at finer horizontal resolution, more complex chemistry is needed to achieve the 926 full benefit of using finer horizontal resolution. This demonstrates the importance of bal-927 ancing increases in finer horizontal resolution with model physical and chemical process 928 complexity. Model process complexity often only increases simulation costs by fractional 929 amounts compared to increases in horizontal resolution, which increase simulation costs 930 by orders of magnitude. A CESM/CAM-chem-SE simulation using the grid with regional 931 refinement down to ~ 14 km over CONUS is a factor of ~ 29 more expensive than that 932 using the uniform ~ 111 km resolution and comparable in cost to a WRF-Chem simu-933 lation over CONUS after roughly accounting for differences in the chemical/physical timestep 934 and the number of grid cells and tracers used. For comparison, using TS2.1 chemistry 935 increases the cost by a factor of ~ 1.6 compared with using TS1 chemistry in CESM2.2/CAM-936 chem-SE. 937

This is only the beginning of the community effort called MUSICA to create a uni-938 fied infrastructure to model atmospheric chemistry across local to regional to global scales 939 in the Earth system (Pfister et al., 2020). Connecting the local scale will be an impor-940 tant goal for future work to simulate atmospheric chemistry in urban environments to 941 fire plumes to forest canopies. Although moving to finer and finer horizontal resolutions 942 to capture fine scale features is important, results from this work suggest improvements 943 to model physical and chemical processes and vertical resolution are equally important 944 for reducing model biases of ozone. Now that CESM has the capability of moving seam-945 lessly between regional and global scales, model processes can be more extensively eval-946 uated and improved, which will hopefully lead to future improvements in model perfor-947 mance at simulating ozone across all scales. 948

949 Open Research

Model Code Availability: CESM is an open-source community model available 950 from: http://www.cesm.ucar.edu/. The regional refined capability over CONUS devel-951 oped in this work was released as a component set in CESM2.2. The following webpage 952 describes how to download and use CESM2.2: (https://wiki.ucar.edu/display/MUSICA/ 953 MUSICA+Home). The TS2.1 and TS1.1 chemical mechanisms are also available in the lat-954 est release of CESM2.2. The TS2.1 mechanism includes the gas-phase updates to MOZART-955 TS2 (Schwantes et al., 2020) and SOA mechanism updates applied here. Considering the 956 importance of these SOA mechanism updates at all scales as demonstrated in this work, 957 similar updates were applied to the MOZART-TS1 (Emmons et al., 2020) chemical mech-958 anism to create TS1.1. The CESM namelist files used to perform the simulations listed 959 in Table 1 are provided here: https://github.com/rschwant/cesm_cam_chem_se_evaluation 960 _aircraft_schwantes 961

Model Data Availability: To facilitate further evaluation of this dataset, the unprocessed model flight track data including all vertical levels and the closest 9 grid cells to each observational point are provided online along with global monthly averaged data for August 2013. Please contact Rebecca Schwantes (Rebecca.Schwantes@noaa.gov) or Louisa Emmons (emmons@ucar.edu) with questions about this dataset. (Note this data will be uploaded to NCAR DASH (https://www2.cisl.ucar.edu/dash) repository after the review process, but before publication).

Observational Data Availability: The field campaign data used in this work 969 are available for download at the following websites: SEAC⁴RS Revision 7 (https:// 970 www-air.larc.nasa.gov/cgi-bin/ArcView/seac4rs?MERGE=1#60_SECOND.DC8_MRG/, 971 (NASA, 2018)), SENEX Revision D (https://esrl.noaa.gov/csd/groups/csd7/measurements/ 972 2013senex/P3/DataDownload/mergeFiles.html), NOMADSS Revision 5 (https:// 973 data.eol.ucar.edu/dataset/373.046 - Emmons (2016)), DISCOVER-AQ-CA Revi-974 sion 4 and DISCOVER-AQ-TX Revision 3 (https://www-air.larc.nasa.gov/missions/ 975 merges/, (NASA, 2014)). The NOMADSS data is provided by NCAR/EOL under the 976 sponsorship of the National Science Foundation (https://data.eol.ucar.edu/) and 977 part of the larger Southeast Atmosphere Study dataset (https://data.eol.ucar.edu/ 978 master_lists/generated/sas/). 979

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