

RESPONSE TO REVIEWERS

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Title: Sensitivity to grid resolution in the ability of a chemical transport model to simulate observed oxidant chemistry under high-isoprene conditions

Journal: Atmos. Chem. Phys. Discuss.

Reviewer comments are in red. Responses are in black, with changes to the text in italics.

Responses to Reviewer #1:

The manuscript by Yu et al. is a valuable contribution to a long-term discussion on the role of spatial resolution in determining the total error of an atmospheric chemistry transport model. In brief, the authors focus on the analysis of an aircraft campaign in the South-Eastern US, which is a region characterized by large biogenic isoprene emissions, and compare the observations with simulations carried out with the same model (GEOS-Chem) at three spatial resolution (increasing from c.a. 400 to c.a. 28 km). They found a little impact by increased resolution on simulated values of ozone and NO_x, especially in the free troposphere. They thus conclude that a coarse resolution model is adequate to resolve regional contributions to ozone export on a global perspective.

I found the manuscript concise, clear and well written, and I tend to agree with the main conclusions of the authors, based on the material showed here. I only have a few comments, which are more requests of clarification from an interested reader, that may further improve the interpretation of some of the results:

Specific comments

page 2, lines 19-29: in this paragraph the authors review previous similar studies on the horizontal resolution issue, but at the end of the manuscript it is not clear to the reader what is the advancement/difference/similarity (if any) with these studies. I recommend including a short paragraph in the conclusions on that.

We have updated the abstract, body of text, and conclusions to reflect these concerns.

In the abstract, the following text has been added:

The good agreement of simulated and observed concentration variances implies that smaller-scale non-linearities (urban and power plant plumes) are not important on the regional scale.

In the body of the text, on line 14 of page 6, we add the following:

Non-linear effects have been reported in previous model studies at the km-scale of urban areas (Kumar and Russell, 1996; Chock et al., 2002; Shrestha et al., 2009; Tie et al., 2010) or pollution plumes (Henderson et al., 2010; Valin et al., 2011), and these small-scale effects are not resolved here even at $0.25^\circ \times 0.3125^\circ$ resolution.

In the conclusions, we update the following paragraph (addition in italics):

Spatial correlations between model and observations improve as resolution increases from $4^\circ \times 5^\circ$ to $2^\circ \times 2.5^\circ$ but then decrease as resolution increases further to $0.25^\circ \times 0.3125^\circ$. This shows

that finer modes of variability are more difficult to capture in models of commensurate resolution, consistent with the results of previous studies such as Fiore et al. (2003) and Valari and Menut (2008).

And add the following sentence:

Previous model studies have pointed out significant chemical non-linearities at the scale of urban and industrial plumes, smaller than the $0.25^\circ \times 0.3125^\circ$ resolution used here. However, the ability of GEOS-Chem to simulate the variability of concentrations observed in SEAC4RS implies that such small-scale effects are not important on the regional scale.

page 5, lines 4-5: the varying ISOP-NO_x relationship in the model is one of the most intriguing results presented in the manuscript. However, its interpretation is left too much to speculations by the reader. Can this analysis be improved? For example, can the referred statement on "temperature and stagnation" be proved calculating correlatons with temperature and a stagnation index?

We now compute correlations with temperature and update line 5 on page 5 to read as follows: The $4^\circ \times 5^\circ$ simulation actually shows positive correlations, likely reflecting a common sensitivity to regional stagnation and resulting high temperatures. We find in the model that NO_x concentrations are strongly correlated with surface air temperature on the $4^\circ \times 5^\circ$ scale ($r = 0.66$) but not on the $0.25^\circ \times 0.3125^\circ$ scale ($r = 0.17$).

page 5, lines 13-15: The role of OH is recurring here and throughout the manuscript. Please consider to include some visualization of the changing OH or related species fields, this may help the reader in the interpretation of results.

We have updated Figure 2 to include panels colored by OH to show more clearly OH depletion under low-NO_x conditions.

page 6, lines 26-27: I do not completely agree with this statement, in particular for isoprene. Looking at Figure 4, all the model realizations look pretty similar to observations, however Taylor diagram in Figure 5 display a dramatic decrease of model skills with increasing resolution. It is not clear to the reader why it happens at this point, it comes as some sort of surprise, so it needs further analysis and discussion. Perhaps, here and for other purposes it would be beneficial to include some sort of more direct visualization of the model-to-obs comparisons (e.g. simple timeseries of data, or scatter plots), maybe in the supplement, in order to keep the main text concise

We amended the text to clarify that correlations are computed using observations averaged to model grid and timestep. We average observations to model grid and timestep as this is a fairer way to compare model output to observations when computing correlations, but it also means correlations will worsen at higher resolution because higher resolution features are inherently more difficult to capture.

Responses to Reviewer #2:

The authors explain and show concisely the main thesis of the manuscript which falls within the scope of the journal. References and discussion of previous work is sufficient. I recommend publication with minor revisions.

Main comments

Many aspects (mostly chemical) are left to other papers which are not all available in ACPD yet (e.g. Travis et al.). Therefore, I would like to see in the manuscript the relative differences for the simulated daytime ozone levels going from $2^\circ \times 2.5^\circ$ to $0.25^\circ \times 0.3125^\circ$ resolution. Such a figure for August at the surface and at 4 km would be sufficient and help make the point of the authors clearer.

Travis et al., (2016) and the other GEOS-Chem papers referenced are now either published or in ACPD. References have been updated in our manuscript.

The authors discuss the segregation of isoprene and NO_x emissions and of isoprene oxidation pathways. These statements need some abstraction by the reader and are obvious. They should be substantiated by calculations. The literature I am aware of discusses the intensity of chemical segregation between two species like isoprene and OH and not between two pathways or emissions. Please add mathematical definitions, calculations and a figure for different model resolutions.

Additional discussion of isoprene oxidation pathways can be found in Travis et al., (2016).

We have updated Figure 2 to include panels colored by OH to show more clearly OH depletion under low-NO_x conditions (see response to reviewer 1).

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Sensitivity to grid resolution in the ability of a chemical transport model to simulate observed oxidant chemistry under high-isoprene conditions

Karen Yu¹, Daniel J. Jacob^{1,2}, Jenny A. Fisher^{3,4}, Patrick S. Kim², Eloise A. Marais¹, Christopher C. Miller¹, Katherine R. Travis¹, Lei Zhu¹, Robert M. Yantosca¹, Melissa P. Sulprizio¹, Ron C. Cohen⁵, Jack E. Dibb⁶, Alan Fried⁷, Tomas Mikoviny⁸, Thomas B. Ryerson⁹, Paul O. Wennberg^{10,11}, and Armin Wisthaler^{8,12}

¹School of Engineering and Applied Sciences, Harvard University, Cambridge, MA, USA

²Department of Earth and Planetary Sciences, Harvard University, Cambridge, MA, USA

³Center for Atmospheric Chemistry, School of Chemistry, University of Wollongong, Wollongong, NSW, Australia

⁴School of Earth and Environmental Sciences, University of Wollongong, Wollongong, NSW, Australia

⁵Department of Chemistry, University of California, Berkeley, CA, USA

⁶Earth System Research Center, University of New Hampshire, Durham, NH, USA

⁷Institute for Arctic and Alpine Research, University of Colorado, Boulder, CO, USA

⁸Department of Chemistry, University of Oslo, Oslo, Norway

⁹Earth System Research Laboratory, National Oceanic and Atmospheric Administration, Boulder, CO, USA

¹⁰Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA, USA

¹¹Division of Engineering and Applied Sciences, California Institute of Technology, Pasadena, CA, USA

¹²Institute for Ion Physics and Applied Physics, University of Innsbruck, Innsbruck, Austria

Correspondence to: Karen Yu (kyu@seas.harvard.edu)

Abstract. Formation of ozone and organic aerosol in continental atmospheres depends on whether isoprene emitted by vegetation is oxidized by the high-NO_x pathway (where peroxy radicals react with NO) or by low-NO_x pathways (where peroxy radicals react by alternate channels, mostly with HO₂). We used mixed layer observations from the SEAC⁴RS aircraft campaign over the Southeast US to test the ability of the GEOS-Chem chemical transport model at different grid resolutions (0.25° × 0.3125°, 2° × 2.5°, 4° × 5°) to simulate this chemistry under high-isoprene, variable-NO_x conditions. Observations of isoprene and NO_x over the Southeast US show a negative correlation, reflecting ~~in-part~~ the spatial segregation of emissions; this negative correlation is captured in the model at 0.25° × 0.3125° resolution but not at coarser resolutions. As a result, less isoprene oxidation takes place by the high-NO_x pathway in the model at 0.25° × 0.3125° resolution (54%) than at coarser resolution (59%). The cumulative probability distribution functions (CDFs) of NO_x, isoprene, and ozone concentrations show little difference across model resolutions and good agreement with observations, while formaldehyde is overestimated at coarse resolution because excessive isoprene oxidation takes place by the high-NO_x pathway (~~which has with~~ high formaldehyde yield). The good agreement of simulated and observed concentration variances implies that smaller-scale non-linearities (urban and power plant plumes) are not important on the regional scale. Correlations of simulated vs. observed concentrations do not improve with grid resolution because finer modes of variability are intrinsically more difficult to capture. Higher model resolution leads to decreased conversion of NO_x to organic nitrates and increased conversion to nitric acid, with total reactive nitrogen

oxides (NO_y) changing little across model resolutions. ~~In Model concentrations in the lower free troposphere, model output is similarly are also~~ insensitive to grid resolution, ~~indicating that the effect on export of ozone and NO_x is small.~~ The overall low sensitivity of modeled concentrations to grid resolution implies that coarse resolution is adequate when modeling ~~regional~~ continental boundary layer chemistry for global applications.

5 1 Introduction

Global simulations of tropospheric chemistry present a major computational challenge. Chemical mechanisms typically include over one hundred coupled species, with lifetimes ranging from less than a second to more than a year, interacting with transport on all scales from concentrated emission plumes to the remote troposphere. This complexity has hindered the inclusion of detailed tropospheric chemistry in climate models (National Research Council, 2012) and ~~raises concern over~~ generated considerable discussion over the importance of spatial resolution. Global models typically have a horizontal resolution of ~ 100 km, which does not properly resolve chemical gradients and may lead to large errors from non-linear chemistry and coupling to transport. ~~Increasing~~ On the other hand, increasing resolution is computationally expensive and may require trade-offs in other aspects of the model. Here we apply a global chemical transport model (GEOS-Chem CTM) to simulate extensive boundary layer observations of ozone and related species over the Southeast US from the SEAC⁴RS aircraft campaign (Toon et al., 15 2016). We explore how varying grid resolution from $4^\circ \times 5^\circ$ ($\approx 400 \times 400 \text{ km}^2$) to $0.25^\circ \times 0.3125^\circ$ ($\approx 28 \times 28 \text{ km}^2$) affects model results and the ability to simulate observations.

Ozone (O_3) production is central to driving the complexity of chemical mechanisms. It is controlled by reaction chains involving hydrogen oxide radicals ($\text{HO}_x \equiv \text{OH} + \text{peroxy radicals}$), nitrogen oxide radicals ($\text{NO}_x \equiv \text{NO} + \text{NO}_2$), halogen radicals, volatile organic compounds (VOCs), and a large ensemble of reservoir and product species. NO and VOCs are emitted 20 by a wide range of sources, both natural and anthropogenic. NO_x typically has a lifetime of hours while VOCs have lifetimes ranging from minutes to years (Atkinson and Arey, 2003). Their interactions result in a diversity of chemical regimes.

A number of studies have examined the effect of model resolution on ozone production in urban regions (Sillman et al., 1990; Jang et al., 1995; Gillani and Pleim, 1996; Kumar and Russell, 1996; Chock et al., 2002; Esler et al., 2004). A typical result is that dilution from grid averaging causes positive bias in the ozone production efficiency (OPE) per unit NO_x emitted (Liu 25 et al., 1987). Liang and Jacobson (2000) showed that premature mixing of urban and background airmasses can lead to either overestimates or underestimates of OPE. Model simulations of ship plumes indicate particularly large ozone overestimates when mixing NO_x from the plumes into otherwise clean grid cells (Davis et al., 2001; Vinken et al., 2011). On a global scale, Wild and Prather (2006) found from an asymptotic error convergence method that grid averaging in a $2.8^\circ \times 2.8^\circ$ model caused a +4% bias in the global tropospheric ozone burden, with larger errors on regional scales. Ito et al. (2009) compared global 30 models of varying resolutions and concluded that artificial mixing of biogenic VOC emissions into coarse grid cells ~~yield drives~~ excessive conversion of NO_x to organic nitrate reservoirs, leading to release of NO_x downwind under higher-OPE conditions and thereby causing excessive ozone production.

The interaction between NO_2 and OH, the dominant NO_2 oxidant, can also lead to biases in model estimates of NO_x tropospheric columns for comparison to satellite observations. Valin et al. (2011) found that large point sources of NO_x ~~suppress-titrate~~ OH, producing long-lived NO_x plumes. Dilution of these plumes into coarse resolution grid cells shortens the NO_x lifetime, leading to underestimation of NO_2 columns ~~over large sources and overestimation over small sources~~.
 5 ~~Yamaji et al. (2014) similarly~~. Yamaji et al. (2014) found that coarse resolution CTMs tend to underestimate retrievals of NO_2 columns over industrial regions.

The SEAC⁴RS observations provide an opportunity to investigate the effect of chemical non-linearity in an environment with very high biogenic VOC emissions (mainly isoprene) and variable levels of NO_x (mostly from combustion). The interactions between these species ~~impact oxidant~~ define oxidant (ozone and OH) chemistry. Isoprene is oxidized by the OH radical
 10 on a time scale of an hour to produce isoprene peroxy radicals (ISOPO_2). These ISOPO_2 radicals may either react with NO to produce ozone (high- NO_x pathway) or react by other channels (low- NO_x pathways). Grid averaging may affect the ability to resolve the different pathways with implications for ozone, oxidant chemistry in general, and the formation of secondary organic aerosol ~~(Marais et al., 2016)~~. ~~We also use the SEAC⁴RS data to examine the effect of grid resolution on model~~ (SOA)
(Marais et al., 2016). ~~It may also affect the~~ ability to simulate variability in chemical concentrations, especially events at the
 15 high tails of the probability distributions ~~that may be of particular interest~~. Higher resolution enables better simulation of chemical gradients, with some benefit for capturing extreme values (Zhang et al., 2011). However, ~~Rastigejev et al. (2010) suggested that much of that advantage may be lost during long-range transport because of numerical diffusion in divergent flow. Higher~~
higher model resolution does not always improve the correlations with observed concentrations (Kiley et al., 2003; Mathur et al., 2005; Arunachalam et al., 2006; Valari and Menut, 2008) because finer modes of variability are harder to capture than
 20 coarser modes (Fiore et al., 2003).

2 Methods

The GEOS-Chem simulation for the SEAC⁴RS period (August-September 2013) uses GEOS-5 assimilated meteorological data produced by GMAO-the NASA Global Modeling and Assimilation Office (GMAO) at $0.25^\circ \times 0.3125^\circ$ horizontal resolution with 72 vertical layers ~~(lumped to 47 layers in GEOS-Chem)~~ and 3-h temporal resolution (1-h for surface quantities and
 25 mixing depths). Here we use that native resolution as reference for comparison to the $2^\circ \times 2.5^\circ$ and $4^\circ \times 5^\circ$ resolutions ~~that would be used in~~ routinely adopted by the GEOS-Chem user community (<http://geos-chem.org>) for global applications. ~~Other~~
Companion GEOS-Chem studies ~~of the SEAC⁴RS period apply the simulation apply the model~~ with $0.25^\circ \times 0.3125^\circ$ resolution to interpret SEAC⁴RS observations of organic nitrates (Fisher et al., 2016), ozone (Travis et al., 2016), aerosols (Kim et al., 2015), and formaldehyde (Zhu et al., 2016). Marais et al. (2016) uses $2^\circ \times 2.5^\circ$ resolution to simulate isoprene secondary
 30 organic aerosol in SEAC⁴RS. These references present relevant model descriptions and evaluation ~~evaluation~~.

The $0.25^\circ \times 0.3125^\circ$ simulation extends over a continental-scale North America window ($130^\circ - 60^\circ\text{W}$, $9.75^\circ - 60^\circ\text{N}$) ~~for two months (August-September 2013)~~. Initial and dynamic boundary conditions are from a global simulation with $4^\circ \times 5^\circ$ resolution ~~.GEOS-Chem uses operator splitting to separately solve the equations for transport and chemistry. serving as outer~~

[nest \(Chen et al., 2009\)](#). The chemical time-step is 10 minutes at $0.25^\circ \times 0.3125^\circ$ resolution, 30 minutes at $2^\circ \times 2.5^\circ$, and 60 minutes at $4^\circ \times 5^\circ$. The transport time-step is half the chemical time-step. ~~Boundary layer mixing depths is scaled down from the GEOS values by 40% to match observations from aircraft lidar during SEAC⁴RS (Zhu et al., 2016).~~

The SEAC⁴RS simulation is based on GEOS-Chem version 9-02 (http://wiki.seas.harvard.edu/geos-chem/index.php/GEOS-Chem_v9-02) including a detailed mechanism for HO_x-NO_x-VOC-O₃-bromine-aerosol tropospheric chemistry with 196 chemical species (Parrella et al., 2012; Mao et al., 2013). ~~A number of updates to isoprene chemistry were implemented~~ [Isoprene chemistry is updated](#) as described by [Fisher et al. \(2016\)](#), [Marais et al. \(2016\)](#), and [Travis et al. \(2016\)](#). US anthropogenic emissions are from the 2011 National Emissions Inventory (NEI), with national scaling for 2013 and 60% downward correction for NO_x as described in [Travis et al. \(2016\)](#). Biogenic emissions are from the Model of Emissions of Gases and Aerosols from Nature (MEGANv2.1) ([Guenther et al., 2012](#)) with 15% downward correction for isoprene [emission](#) ([Zhu et al., 2016](#)). Lightning NO_x emissions are constrained by satellite observations as described in [Murray et al. \(2012\)](#). Soil NO_x emissions, including fertilizer, are from [Hudman et al. \(2012\)](#) with [Jacob and Wofsy \(1990\)](#) canopy reduction factors.

Figure 1 shows the emissions of NO_x and isoprene over the Southeast US domain at $0.25^\circ \times 0.3125^\circ$ resolution. ~~In this domain, isoprene~~ [Isoprene](#) emission is mainly from forests and NO_x emission ~~largely follows population~~ [is mostly from mobile sources](#) and power plants ([Travis et al., 2016](#)). The resulting spatial segregation between isoprene and NO_x emissions has important implications for whether isoprene oxidation takes place by high-NO_x or low-NO_x pathways. We ensure that emission totals are the same at all model resolutions so that they are not a factor of differences in results. This required minor scaling of ~~natural~~ [biogenic](#) VOC emissions that depend on environmental variables.

Comparisons between model and aircraft observations use model output sampled along the DC-8 flight tracks (Figure 1), and observations from a 60-s merged data set. For computing aggregate statistics, such as probability distributions, we use observations directly from the 60-s data set. For computing correlations between model and observations ([Figure 5](#)), we average data over model grid cells along individual flight tracks. We focus on daytime continental data over the Southeast US domain ($94.5^\circ - 75^\circ\text{W}$, $29.5^\circ - 40^\circ\text{N}$, box in Figure 1) and within the mixed layer ~~defined along the flight track as determined~~ [from lidar measurements aboard the aircraft](#) ([Hair et al., 2008](#)). Typical mixed layer heights (10th and 90th percentiles) during the campaign ranged from 600 m to 2200 m, with a mean value of 1500 m. The aircraft occasionally targeted fire plumes and we remove those as diagnosed by measured acetonitrile concentrations exceeding 225 ppt. Our analysis domain also excludes the Houston plume, targeted on two SEAC⁴RS flights (Sep 16 and 18) and for which our model would not be expected to give a representative simulation ~~due to potentially large highly reactive petrochemical emissions. Unlike Travis et al. (2016), we do not remove urban plumes as diagnosed by NO₂ concentrations exceeding 8 ppb.~~

3 ~~Prevalence~~ [Segregation](#) of high-NO_x and low-NO_x isoprene oxidation pathways

Oxidant chemistry [and SOA formation](#) over the Southeast US in summer is largely determined by ~~the interactions between isoprene and NO_x. Isoprene oxidation by whether isoprene oxidation follows the high-NO_x pathway produces ozone and also organic nitrates that act as either sinks or reservoirs for NO~~ [or low-NO_x](#), while oxidation by the HO₂ pathway tends to scavenge

~~HO_x radicals. The different pathways also lead to formation of different types of secondary organic aerosol, with higher yields by the HO₂ pathway (Marais et al., 2016).~~ pathways (Marais et al., 2016; Travis et al., 2016). Travis et al. (2016) diagnosed the prevalence of different isoprene oxidation pathways in the GEOS-Chem ($0.25^\circ \times 0.3125^\circ$) simulation of the Southeast US during SEAC⁴RS on the basis of the ~~fraction-fate~~ of the first-generation ISOPO₂ radicals~~that react with NO~~. They found on average that 56% of ISOPO₂ radicals reacted ~~by the~~ with NO (high-NO_x pathway). The low-NO_x pathways mostly involved reaction of ISOPO₂ with HO₂ (25%), ~~producing isoprene hydroperoxides (ISOP₂OOH), and minor channels from~~ ISOPO₂ isomerization (15%), and reactions with other organic peroxy radicals (4%). The transition from high- to low-NO_x pathways occurred at a NO concentration of about 60 ppt, corresponding to a NO_x concentration of about 300 ppt.

The effect of the geographical segregation between NO_x and isoprene emissions is illustrated in Figure 2, which shows the relationship between NO_x and isoprene concentrations along the flight tracks. NO_x was measured by chemiluminescence (Ryerson et al., 2000) and isoprene by proton-transfer-reaction mass spectrometry (PTR-MS) (Hansel et al., 1999). The observations show a negative correlation that is captured in the simulation at $0.25^\circ \times 0.3125^\circ$ resolution but not at coarser resolutions. The $4^\circ \times 5^\circ$ simulation actually shows positive correlations, likely reflecting a common sensitivity to ~~regional temperature and stagnation~~ stagnation and resulting high temperatures. We find in the model that NO_x concentrations are strongly correlated with surface air temperature on the $4^\circ \times 5^\circ$ ($r = 0.66$) but not on the $0.25^\circ \times 0.3125^\circ$ scale ($r = 0.17$).

For the SEAC⁴RS data set sampled along the flight tracks, the $0.25^\circ \times 0.3125^\circ$ simulation finds that 42% of the ISOPO₂ radicals react with NO. That fraction increases to 44% for the $2^\circ \times 2.5^\circ$ simulation and 49% for the $4^\circ \times 5^\circ$ simulation. Over the whole Southeast US domain (box in Figure 1), the fraction of ISOPO₂ radicals reacting by the high-NO_x pathway is 54% at $0.25^\circ \times 0.3125^\circ$ resolution and 59% at the $2^\circ \times 2.5^\circ$ and $4^\circ \times 5^\circ$ resolutions. Our values differ slightly from Travis et al. (2016) because we did not exclude ocean grid cells in the domain in order to keep comparisons between different resolutions consistent.

~~There is more variability at the $0.25^\circ \times 0.3125^\circ$ resolution, with the~~ We see that the branching ratio between high-NO_x pathway dominating in 55% of grid cells averaged over August and September 2013 vs. 74% at both $2^\circ \times 2.5^\circ$ and $4^\circ \times 5^\circ$. Still, we find that the segregation between the different pathways is dampened relative to the segregation between low-NO_x pathways for isoprene oxidation is much less sensitive to model resolution than would be expected from the segregation of isoprene and NO_x and isoprene emissions. This is due to OH depletion under low-NO_x conditions prolonging the lifetime of isoprene and its oxidation products, allowing them to travel to higher-NO_x environments before being oxidized. The bottom panels of Figure 2 show the dependence of midday, mixed layer model OH concentrations at different resolutions on NO_x and isoprene concentrations along the SEAC⁴RS flight tracks. The depletion of OH under low-NO_x, high-isoprene conditions is apparent and is better represented at the finer resolution: the implication is that isoprene is more likely to be oxidized under higher NO_x conditions than at its point of emission. Although regional mean OH concentration (computed along flight tracks) varies with grid resolution, the change is not monotononic as shown inset in the figure.

The SEAC⁴RS aircraft payload included measurements of first-generation isoprene nitrates (ISOPN), a product of the high-NO_x pathway, and ISOP₂OOH, the principal product of the HO₂ pathway (Crounse et al., 2006). Figure 3 shows a cumulative probability distribution function (CDF) plot of the [ISOPN]/([ISOP₂OOH] + [ISOPN]) ratio in the Southeast US mixed layer,

providing a diagnostic of whether isoprene oxidation proceeds by the high- NO_x pathway (high ratio) or the low- NO_x pathways (low ratio). We see that the $0.25^\circ \times 0.3125^\circ$ simulation is ~~much~~ more consistent with observations than the $2^\circ \times 2.5^\circ$ and $4^\circ \times 5^\circ$ simulations. ~~Although the ratios are sensitive to ISOPN and ISOPPOOH lifetimes, and model error in those lifetimes would affect the ratio, the increased variance in the $0.25^\circ \times 0.3125^\circ$ model clearly demonstrates better partitioning between the different pathways, although the difference is mainly for the high tail of the distribution.~~

4 Chemical variability and bias

Figure 4 shows the simulated and observed CDFs of NO_x , isoprene, formaldehyde, and ozone concentrations sampled along the flight tracks in the Southeast US mixed layer. Formaldehyde was measured by the Compact Atmospheric Multispecies Spectrometer (CAMS) (Richter et al., 2015) and ozone by chemiluminescence (Ryerson et al., 2000). NO_x and isoprene are primary (directly emitted) and have mean lifetimes against chemical loss of a few hours and less than an hour, respectively. The NO_x distribution is approximately lognormal while isoprene is better described by a Weibull distribution. Formaldehyde and ozone are secondary (chemically produced) and their distributions are more normal. Most of the formaldehyde in SEAC⁴RS originated from isoprene oxidation (Zhu et al., 2016).

We find that, with the exception of formaldehyde, differences between the different model resolutions are mainly at the high tails of the distributions. In the case of NO_x , the highest resolution model better captures the high tail in the observations due to urban plumes. In the case of isoprene the highest resolution model over-predicts the high tail in the observations, which could reflect errors in the fine structure of MEGAN emissions or excessive local depletion of OH (the main isoprene sink) as a result of high isoprene. In the case of ozone, the highest resolution model only marginally improves the simulation of the high tail in the observations (industrial plumes downwind of Port Arthur, Texas), for which even $0.25^\circ \times 0.3125^\circ$ may not provide adequate resolution. In the case of formaldehyde, the highest resolution model actually produces weaker maxima that are more consistent with observations. Production of formaldehyde from isoprene oxidation has higher yield in the high- NO_x pathway than the low- NO_x pathways (Marais et al., 2012). High isoprene is associated with low NO_x in the observations (Figure 2) and therefore with a low formaldehyde yield but this is captured only at the highest model resolution. This result ~~would have~~ has important implications for the ~~generally-assumed-linear-relationship-used-use of formaldehyde-isoprene model relationships~~ to infer isoprene emissions from satellite measurements of formaldehyde columns (Palmer et al., 2003). Relationships derived from coarse-resolution models overestimate the yield of formaldehyde from isoprene emission.

~~These high-tails aside~~ Except for formaldehyde, the bulk of the distributions shows very little difference between model results at different resolutions, despite NO_x levels spanning 4 orders of magnitude. This suggests that the coarser resolutions are adequate for simulating regional averages ~~across the domain studied. An exception is formaldehyde, where the higher resolution better reproduces the observations above the median. As pointed out above, formaldehyde is particularly sensitive to the separation between the high- NO_x pathway and low- NO_x pathways. One important caveat is that although the Southeast US represents a variety of different chemical environments, we only explored non-linear effects down to the scale of~~ Non-linear effects have been reported in previous model studies at the km-scale of urban areas (Kumar and Russell, 1996; Chock et al., 2002; Shrestha

or pollution plumes (Henderson et al., 2010; Valin et al., 2011), and these small-scale effects are not resolved here even at $0.25^\circ \times 0.3125^\circ$ (≈ 28 km). Features below that scale have been shown to have strong gradients that can result in biases. Investigation of non-linear effects on the scale of a few kilometers has demonstrated strong resolution effects for highly urbanized regions (Shrestha et al., 2009; Tie et al., 2010), power plant or industrial plumes (Valin et al., 2011; Henderson et al., 2010), and ship plumes (Davis et al., 2001; Charlton-Perez et al., 2009; Vinken et al., 2011) resolution. Nevertheless, the general ability of the GEOS-Chem simulation to capture the variance in the SEAC⁴RS observations implies that these small-scale effects are not dominant of major importance at least for the Southeast US.

Figure 5 presents a Taylor Diagram of modeled NO_x, isoprene, formaldehyde, and ozone concentration statistics compared to observations averaged to the corresponding model grid and timestep. The Taylor Diagram is a concise graphical summary of how well two patterns match each other in terms of their correlation, root-mean-squared difference, and variances (Taylor, 2001). Comparison of variances for different resolutions is consistent with the previously discussed information from Figure 4. Correlations with observations improve when resolution is increased from $4^\circ \times 5^\circ$ to $2^\circ \times 2.5^\circ$, but then generally degrade at $0.25^\circ \times 0.3125^\circ$ (except for NO_x). This is because finer-scale features are more difficult to model (Kiley et al., 2003; Mathur et al., 2005; Arunachalam et al., 2006; Valari and Menut, 2008). A higher resolution model will be penalized for placing these features in the wrong place or time, while a coarse resolution model does not attempt to resolve them.

5 Implications for global influence models

From a global modeling perspective, the ability to simulate local extrema in a chemical source region is generally not critical and the focus instead is on simulation of regional means and export to the global atmosphere. From that standpoint, the general insensitivity of concentrations to model resolution over the bulk of the distributions suggests that coarse resolution is adequate for global modeling purposes. We confirm this result by examination of the regional budgets of total reactive nitrogen oxides (NO_y \equiv NO_x + oxidation products) and ozone over the Southeast US at different model resolutions.

Figure 6 shows mean simulated and observed daytime concentrations of NO_y species in the Southeast US mixed layer during SEAC⁴RS. Total NO_y in the model is within 10% of observations, at all resolutions, but there is somewhat more difference in the speciation of NO_x oxidation products. The $0.25^\circ \times 0.3125^\circ$ simulation has lower peroxyacetyl nitrate (PAN) than the coarser resolutions, in better agreement with observations, due to less artificial mixing of NO_x and isoprene emissions as previously pointed out by Ito et al. (2009). All model resolutions show similar low bias relative to observed total alkyl nitrates (Σ ANs). This low bias is discussed in Fisher et al. (2016). The model has larger nitric acid concentrations at higher resolution because it resolves better the positive correlation between NO_x and OH concentrations. Artificial mixing of NO_x with isoprene in the coarser-resolution models slows down oxidation by OH to nitric acid (since isoprene provides a sink for OH) and increases the production of organic nitrates. The $0.25^\circ \times 0.3125^\circ$ model has a 17% high bias relative to observed nitric acid from the SAGA instrument shown in Figure 6, and the bias would be larger relative to nitric acid measurements from the Caltech Chemical Ionization Mass Spectrometer also flown on the aircraft. (Figure 2). We find that the regional mean NO_x lifetime with respect to conversion to nitric acid is 0.66 days for the $4^\circ \times 5^\circ$ model, 0.62 days for the $2^\circ \times 2.5^\circ$ model, and 0.51 days for

the $0.25^\circ \times 0.3125^\circ$ model. Although ~~there is no significant change in the~~ simulated regional mean OH ~~concentrations across~~
~~different resolutions~~concentrations do not change monotonically with resolution, the higher resolution model captures better
the association of elevated OH with NO_x .

From a global model perspective, chemical venting from continental source regions such as the Southeast US is of paramount
5 importance. Figure 7 shows CDF plots for ozone and NO_x in the lower free troposphere (from mixed layer top to 4 km altitude).
Model results are insensitive to resolution, with differences even smaller than in the mixed layer. As in the mixed layer, all
model resolutions simulate the median of the distributions well, and differences across model resolution occur mainly at the
tails of the distributions. Overall, we find that grid resolution has little effect on the export of ozone and its precursors out of
the mixed layer.

10 6 Conclusions

Production of ozone and organic aerosol in continental atmospheres is highly sensitive to whether isoprene emitted by vegeta-
tion is oxidized by the high- NO_x pathway (where peroxy radicals react with NO) or by the low- NO_x pathways (where peroxy
radicals react mostly with HO_2). This distinction between pathways is becoming increasingly relevant in the US as anthro-
pogenic NO_x emissions decrease. In this work, we used SEAC⁴RS aircraft observations in the mixed layer over the Southeast
15 US to test the ability of the GEOS-Chem chemical transport model (CTM) at different horizontal resolutions ($0.25^\circ \times 0.3125^\circ$,
 $2^\circ \times 2.5^\circ$, $4^\circ \times 5^\circ$) to simulate the different pathways and the resulting variability in concentrations. $2^\circ \times 2.5^\circ$ and $4^\circ \times 5^\circ$
are the standard resolutions used in global GEOS-Chem simulations of tropospheric chemistry while the $0.25^\circ \times 0.3125^\circ$
continental-scale resolution is a new GEOS-Chem capability~~developed for interpretation of the SEAC⁴RS data~~.

Emissions of NO_x and isoprene ~~tend to be spatially segregated~~are spatially segregated (NO_x in urban centers, isoprene
20 in forests). SEAC⁴RS observations in the mixed layer show a negative correlation between isoprene and NO_x concentrations
that is captured in the model at $0.25^\circ \times 0.3125^\circ$ resolution but not at coarser resolution. ~~In the $0.25^\circ \times 0.3125^\circ$ resolution~~
~~model~~, 54% of isoprene oxidation in the Southeast US takes place by the high- NO_x pathway in the $0.25^\circ \times 0.3125^\circ$ resolution
model, as compared to 59% at the coarser resolutions. Observed ratios of isoprene nitrates (ISOPN) to isoprene hydroperoxides
(ISOPOOH) show segregation between high- and low- NO_x pathways that is ~~much~~ better captured at $0.25^\circ \times 0.3125^\circ$ than at
25 coarser resolutions. The segregation between high- and low- NO_x pathways is less than would be expected from the segregation
of NO_x and isoprene emissions because OH depletion in low- NO_x environments allows isoprene to travel to higher- NO_x
environments to become oxidized.

We examined the ability of the model at different resolutions to simulate the observed probability distributions of NO_x ,
isoprene, formaldehyde, and ozone concentrations across the Southeast US. Differences between model resolutions are mainly
30 at the high tails of the distributions. There is remarkably little difference for the bulk of the distributions. An exception is
formaldehyde, which is overestimated at coarser model resolution ~~as because~~ more isoprene is oxidized by the high- NO_x
pathway, ~~producing more formaldehyde~~. ~~Isoprene oxidation is more likely to proceed by the low- NO_x pathways where~~
~~isoprene emissions are high, and this has important implications for inferring isoprene emissions~~with a higher formaldehyde

yield. Inference of isoprene emissions from satellite observations of formaldehyde columns may be biased high if a coarse-resolution model is used for the formaldehyde-isoprene relationship.

Spatial correlations between model and observations improve as resolution increases from $4^\circ \times 5^\circ$ to $2^\circ \times 2.5^\circ$ but then decrease as resolution increases further to $0.25^\circ \times 0.3125^\circ$. This shows that finer modes of variability are more difficult to capture in models of commensurate resolution, consistent with the results of previous studies such as Fiore et al. (2003); Valari and Menut (2008).

Increasing model resolution leads to faster conversion of NO_x to nitric acid, because OH correlates positively with NO_x , while slowing down conversion to organic nitrates. However, the effect on the mean budget of reactive nitrogen oxides (NO_y) in the mixed layer is small. Furthermore, comparisons of NO_x and ozone concentrations in the lower free troposphere indicate no significant sensitivity to model resolution. ~~Although higher resolution models are necessary for certain purposes, such as examining the tails of distributions and for studying the relative importance of different chemical pathways, the~~ Previous model studies have pointed out significant chemical non-linearities at the scale of urban and industrial plumes, smaller than the $0.25^\circ \times 0.3125^\circ$ resolution used here. However, the ability of GEOS-Chem to simulate the variability of concentrations observed in SEAC⁴RS implies that such small-scale effects are not important on the regional scale.

The overall relative insensitivity of oxidant chemistry to model resolution in the challenging environment of the Southeast US suggests that mean statistics of regional boundary layer chemistry can be simulated adequately at coarse resolution (such as $2^\circ \times 2.5^\circ$) for global modeling purposes.

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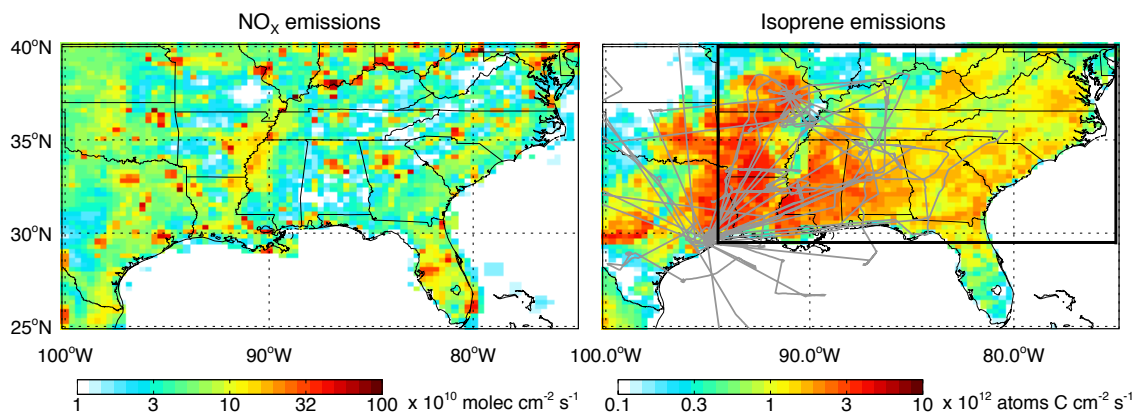


Figure 1. GEOS-Chem surface emissions of NO_x and isoprene in August 2013 at $0.25^\circ \times 0.3125^\circ$ resolution. See text for emission inventory references. NO_x emissions shown here include contributions from combustion and soils but not lightning. Grey lines on isoprene panel indicate flight tracks of the DC-8 during the SEAC⁴RS campaign. The black line delineates the Southeast US as used for regional budget analyses in the text.

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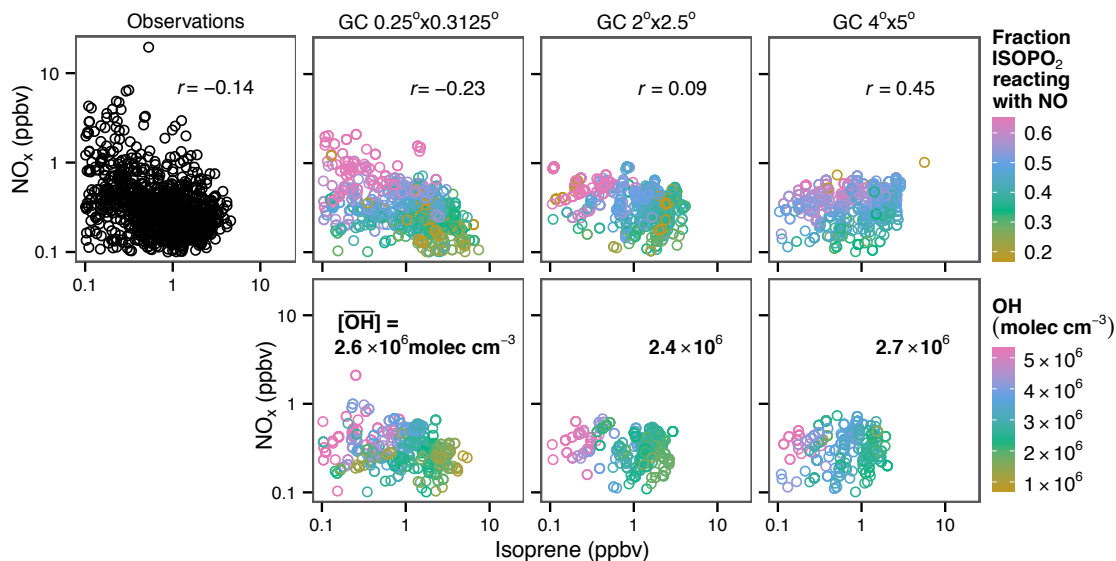


Figure 2. Relationship between NO_x and isoprene concentrations in the mixed layer in SEAC⁴RS. Observations (60-s average) are compared to the GEOS-Chem (GC) simulations at different resolutions sampled along the flight tracks over the Southeast US domain of Figure 1. Pearson's correlation coefficients (r) are inset. The [top](#) model panels are colored by the fraction of the first-generation isoprene peroxy radical (ISOPO_2) reacting with NO . [A](#) fraction less than 0.5 indicates that low- NO_x pathways dominate for isoprene oxidation. [The bottom model panels are colored by the OH concentration, restricted to midday points \(10:30-14:30 local time\). Regional mean values computed along the flight tracks \(primarily daytime\) are given inset.](#)

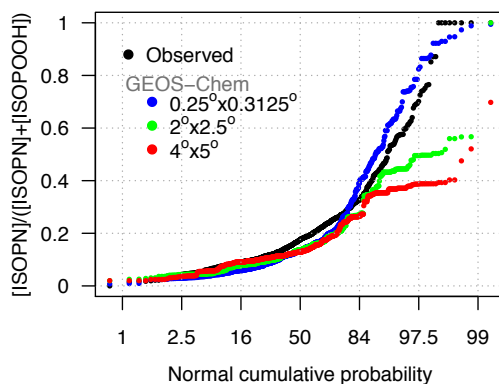


Figure 3. Cumulative probability distribution functions (CDFs) of the $\frac{[\text{ISOPN}]}{[\text{ISOPN}] + [\text{ISOPOOH}]}$ ratio measuring the relative importance of the high- NO_x pathway vs. low- NO_x pathways for isoprene oxidation. High values of the ratio indicate a dominant high- NO_x pathway. Mixed layer observations from the SEAC⁴RS aircraft over the Southeast US are compared to GEOS-Chem output along the flight tracks at different resolutions. The x -axis is a normal probability scale such that a normal distribution would plot on a straight line.

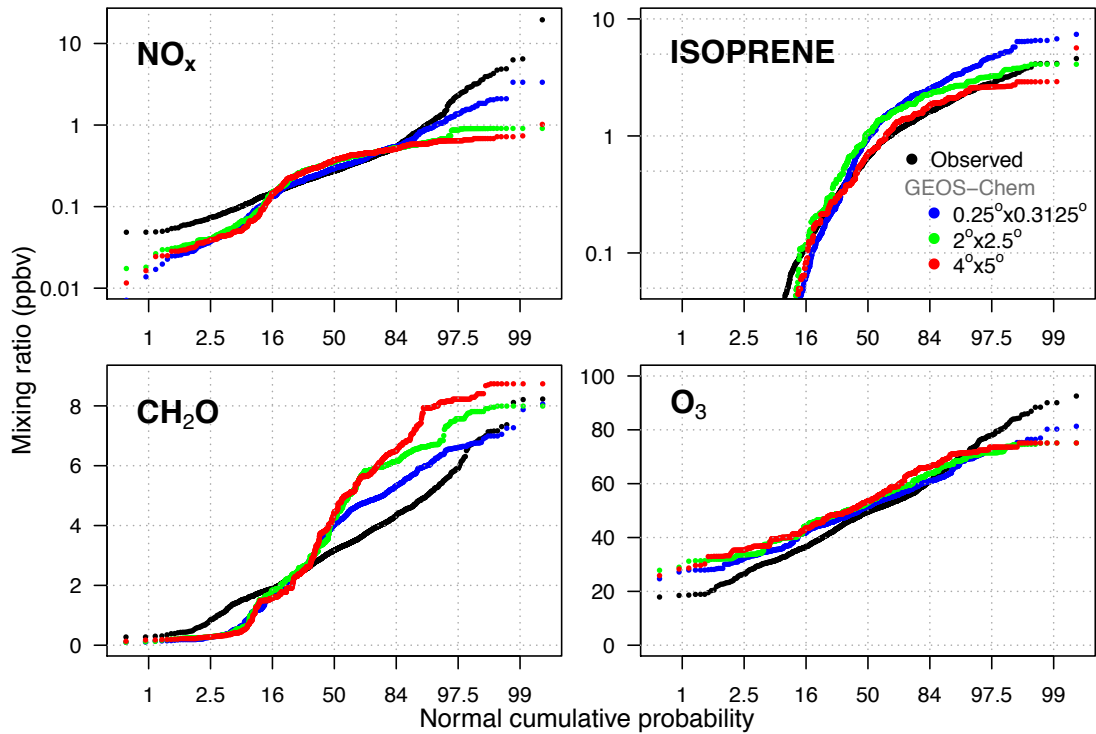


Figure 4. Cumulative probability distribution functions (CDFs) of NO_x , isoprene, formaldehyde (CH_2O), and ozone (O_3) concentrations in the Southeast US mixed layer during the SEAC⁴RS aircraft campaign. Observations are compared to GEOS-Chem model values at different resolutions ($0.25^\circ \times 0.3125^\circ$, $2^\circ \times 2.5^\circ$, $4^\circ \times 5^\circ$) sampled along the flight tracks over the Southeast US domain of Figure 1. The x -axis is a normal probability scale such that a normal distribution (formaldehyde, ozone) or lognormal distribution (NO_x , isoprene) would plot on a straight line.

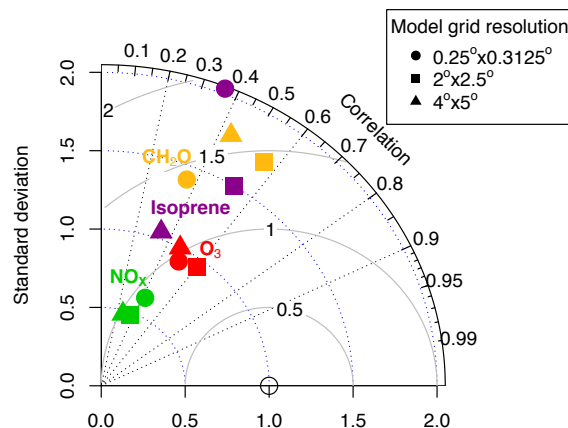


Figure 5. Taylor Diagram for NO_x , isoprene, formaldehyde, and ozone concentration statistics sampled in the Southeast US mixed layer along SEAC⁴RS flight tracks (Figures 1 and 4). GEOS-Chem model results at different grid resolutions are compared to observations at the corresponding resolutions. Standard deviation is plotted along the radial coordinate, while the angular coordinate denotes the Pearson's correlation coefficient between model and observations. Model standard deviation is normalized to the observations, so that a value above 1 indicates greater variance than observed. The open circle located at (1, 1) represents the observations. The grey arcs represent the root-mean-squared error between model and observations after the mean bias has been removed.

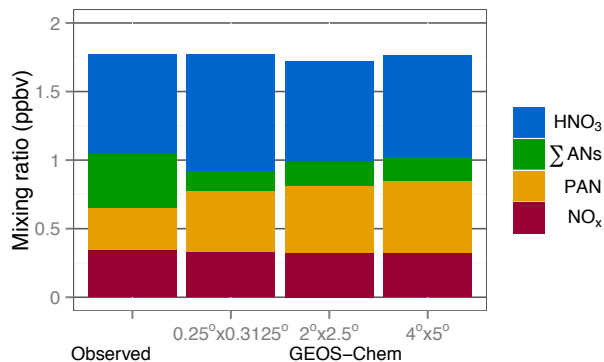


Figure 6. Mean concentrations of reactive nitrogen oxides (NO_y) species over the Southeast US during SEAC⁴RS. Aircraft observations in the mixed layer over the Southeast US domain of Figure 1 are compared to GEOS-Chem model values at different resolutions. ΣANs refers to the sum of alkyl and multifunctional nitrates and PAN to peroxyacetylnitrate. Observations are from T. Ryerson for NO_x , R. Cohen for ΣANs , G. Huey for PAN, and J. Dibb for nitric acid (HNO_3) (Toon et al., 2016).

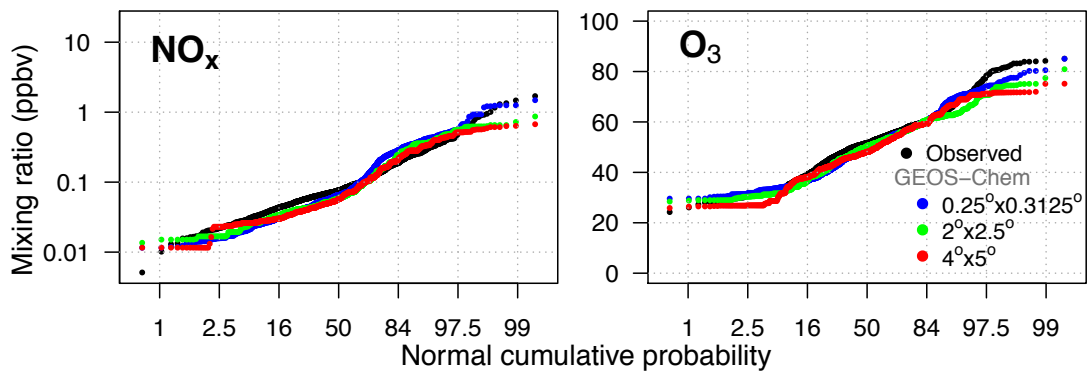


Figure 7. Cumulative probability distribution functions (CDFs) of NO_x and ozone (O_3) concentrations in the lower free troposphere over the Southeast US (from mixed layer top to 4 km altitude) during the SEAC⁴RS aircraft campaign. Observations are compared to GEOS-Chem model values at different resolutions sampled along the flight tracks over the Southeast US domain of Figure 1. The x -axis is a normal probability scale such that a normal distribution (ozone) or lognormal distribution (NO_x) would plot as a straight line.