Review 1

Response: We appreciate the positive comments from the Anonymous Referee #1. We further clarified the manuscript following the reviewer's suggestions. Reviews are in red, while responses are in black.

General Comments:

This paper presents an online version of the GEOS-chem chemistry module with an aim of simulating tropospheric chemistry at very high horizontal resolution for a global model (appox. 12.5km). More importantly the authors have developed a consistency between the GEOS-chem CTM and the online ESM which enables the ESM to keep up with the state of the art science. The main aim is to serve observing simulation experiments for satellite monitoring systems but also has the added advantage of being able to simulate high-resolution impacts of climate change on air quality. The high resolution of the output will also be of interest to the health and vegetation impacts communities. The paper is very well written and easy to follow and will be of great interest to the wider atmospheric science community. Therefore I recommend publication in GMD after the following relatively minor comments are addressed.

Specific Comments:

Page 5, Line 9: You mention that the model has 72 vertical levels here up to a height of 0.01hPa. Would you be able to clarify what the spacing of the lower vertical model levels are, specifically in the boundary layer region? This will be important if one of the intended uses of the model is for air quality simulations as can have important implications for the rise of emissions plumes, mixing of emissions throughout the BL and ultimately concentrations of key secondary species such as ozone. Further to this the spacing of vertical layers near to the surface can also impact which height emissions are injected at which could have implications for ozone destruction pathways (E.g. NOx titration) and thus concentrations. This could be one of the potential reasons why the model is failing to capture the surface concentrations in Europe (although it is doing a reasonably good job at present). I think the discussion of model performance could benefit further from some extra discussion in relation to this matter. Page 5, Line 25: Please provide a brief summary of the VOCs included. From an air quality perspective it would be interesting to know the most reactive VOCs from an ozone formation potential. Higher reactive VOCs (E.g. Butanes and aromatics) are important for looking at air quality issues over highly polluted regions such as northern China where models with more basic chemistry schemes struggle to reproduce high levels of O3.

Response: The vertical model levels can be found at the GEOS-Chem Wiki page (http://wiki.seas.harvard.edu/geos-chem/index.php/GEOS-Chem_vertical_grids#72-layer_vertical_grid). Specifically, 14 layers are below 2 km altitude, with spacing spanning from 64 m to 128 m and the lowest layer from the surface to 58 m above ground. There are 15 layers between 2 km and 10 km; the rest 43 layers between 10 and the top of atmosphere (80 km). Developing higher vertical resolution with more layers in the boundary layer and near tropopause is ongoing work at the NASA GMAO; thus, when ready it will benefit both GEOS and GEOS-Chem models.

Anthropogenic emissions are distributed vertically according to the corresponding emission inventories when information is available. We agree with the reviewer that reasons for model ozone bias could be related to vertical distribution for emission and lowest model layer height, thus it was mentioned in the manuscript that 'Part of the systematic bias is due to the subgrid vertical gradient between the lowest model level and the measurement altitude (60 m above ground vs. 10 m, Travis et al., 2017).'

Same as GEOS-Chem, the G5NR-chem includes the following non-methane VOCs with direct emissions: isoprene, $\geq C_4$ alkanes, $\geq C_4$ ketones, propane, acetone, $\geq C_3$ alkenes, ethane, ethene, acetaldehyde, formaldehyde, and this is summarized by Hu et al 2017 and cited in the manuscript. Aromatic chemistry is not included in this version of the models, but is being under development for the future GEOS-Chem version (Yan et al., 2018). This will be passed on to the future GEOS-5 simulation when available. We added this into the discussion on the model ozone bias.

Page 5, Line 26: Which aerosol microphysics scheme is being used?

Response: The regular GEOS-Chem aerosol scheme TOMAS is used here. We note that in the G5NR-chem configuration, GEOS-Chem is run 'passively', i.e. the aerosols and trace gases do not influence the meteorology. We clarified it in the revised manuscript.

Page 5, Line 27: Is Fast-JX fully coupled to cloud and aerosol species, to simulate feedbacks? This could have implications on chemical processes. This is especially important given that the focus of evaluation is ozone.

Response: See above. GEOS-Chem tracers are not impacting the meteorology. The primary purpose of the simulation was to evaluate newly developed GEOS-5 ESM with GEOS-Chem chemical model at very high resolution, without the additional complication of chemistry-climate feedbacks that are not included in a CTM. We clarified it in the revised manuscript.

Technical corrections:

Page 3, Line 22: Double period at the end of the sentence please remove. **Response**: Thanks for pointing this. We corrected it in the revised manuscript.

Page 4: Lines 32-33: Which boundary layer scheme is being used here? Please provide some detail.

Response: We use the GEOS-5 boundary layer scheme, which uses a combination of Lock et al. (2000) and Louis and Geleyn (1982).

Page 7, Lines 23 and 24: The observed/literature values for O3 are shown in the text and Table 1 but the values for CO and OH are only shown in Table 1. Please be consistent and either refer to all observed values in the text or remove the mention to the O3 values in the text and refer to Table 1. **Response:** Done.

References:

Lock, A. P., Brown, A. R., Bush, M. R., Martin, G. M., and Smith, R. N. B.: A New Boundary Layer Mixing Scheme. Part I: Scheme Description and Single-Column Model Tests, Monthly Weather Review, 128, 3187–3199, https://doi.org/10.1175/1520-0493(2000)128<3187:ANBLMS>2.0.CO;2, 2000 Louis, J.-F., Tiedtke, M., and Geleyn, J.-F.: A short history of the PBL parameterization at ECMWF, in: Workshop on Planetary Boundary Layer parameterization, 25-27 November 1981, pp. 59–79, ECMWF, ECMWF, Shinfield Park, Reading, 1982

Yan, Y., Cabrera-Perez, D., Lin, J., Pozzer, A., Hu, L., Millet, D. B., Porter, W. C., and Lelieveld, J.: Global tropospheric effects of aromatic chemistry with the SAPRC-11 mechanism implemented in GEOS-Chem, Geosci. Model Dev. Discuss., https://doi.org/10.5194/gmd-2018-196, in review, 2018.

Review 2

Review of GMDD 2018-111

This paper presents and extraordinary and highly valuable piece of work. It is well written and succinct, most unusual given the scope of work involved. It is publishable as is, but given the unique nature of developing a 12.5-km gridded chemistry run, the authors should add just a bit more of information to address some of the obvious questions.

Response: We appreciate the reviewer #2's positive feedback. We further clarified the manuscript following the reviewer's comments.

(1) Comment on the lack of improvement in vertical resolution (L72) while jumping up the horizontal. For example, ECMWF now uses L91 or L137 with high-res models.

Response: See the response to the review 1. Increasing vertical resolution is an ongoing work for improving the NASA GEOS ESM.

(2) You talk of a 300 s heartbeat step across the physics and dynamics, but what is the exchange time with the chemistry and how fast is the chemistry updated for tracer transport? There is some confusion in Sect 3.1 about the chemistry time step.

Response: Correct. Chemistry is done every 300s, and the chemical tracer fields are exchanged with all other components at the heartbeat. We clarified it in the revisions.

(3) As one gets to 10 km, there are a number of issues that arise in our standard treatment of the continuity equations. Presumably the large-scale transport adjust u,v,w such that the hybrid coordinate system is maintained when it passes to the chemistry? This creates a problem when doing convection and scavenging of tracers in the chemistry package because convective mass fluxes are balanced by u,v flows – especially when one gets to 10 km scales. If the chemistry package does convective upward fluxes and then balances with downward flow to balance the coordinate system, then there is a false downward transport in the column, and the results will have increasing errors as the resolution gets smaller. This really should be discussed, explained what is actually done (this is not here), and then assess possible errors from the formulation. To be correct one has to have the large-scale and convective w's done together, since convection involves neighboring columns. For example, some CTMs allow the u,v step to leave the air mass in each layer that may not be according to the hybrid coords and then the convection in the single column corrects it back to the std levels. If you did this typical operator split, then say so. If not, note it.

Response: The GEOS-Chem chemical module is fully embedded in GEOS-5 ESM, sharing the same cube-sphere and vertical coordinates at all times. We further added a discussion on the impact of resolution on convection in the revised manuscript: "Radon-222 tracer simulation tests

within GEOS-5 show that the GEOS-Chem convection scheme closely reproduces the GEOS-5 convective transport (Yu et al., 2018). As convection becomes increasingly resolved at higher model resolutions, the GEOS-5 sub-grid convection parameterization (Moorthi and Suarez, 1992) is invoked less frequently. As a consequence, an increasing fraction of the washout in GEOS-Chem becomes characterized as large-scale, as opposed to convective. No attempts were made to offset the possible increase in washout efficiency that may arise from this."

(4) The approach taken here for assessing the surface ozone (air quality) simulation is very disappointing and this is the only area that needs a substantial redo. First, they build a 12 km model and then go back to the old-fashioned way of correcting for bad simulations of air quality that may be needed in 2 deg models (i.e., only compare with 4 pm values). Further, with G5NRchem there should be no need to compare only with "background sites" – the polluted regions should be included in the comparisons. (There are reasons to remove of the "traffic sites" in the EU data, but eliminating all urban data gives you the wrong comparison. The idea that you compare with only afternoon ozone dates back to models that could not really do realistic surface ozone- this model should be able to compare with the true AQ data and for all hours. You have all the simulated data (since this is save for an OSSE) and so it is straightforward and essential that a more serious and more accurate comparison with surface ozone be done. There are numerous better publications, including multi-model evaluations, please start with one of those. For example, you could be using the Schnell gridded surface ozone and doing the comparisons as in the Schnell 2015 ACP paper Figure 1 – It would be good to see how the seasonal and diurnal cycles differ between the 2 chemistry models. Figures A3 and A5 are very interesting – presumably this includes all 24-hr data?

Response: We appreciate the reviewer's perspectives. However, even at ~12.5km it is unrealistic to expect that sites with large local influence (e.g. roadside, city center, or heavily trafficked sites) would be captured. As many sites classified by European and USA data providers as without large local influence were therefore included. Thus as stated in the manuscript (Page 7 lines 18-22), "urban background" and "rural background" sites were used for Europe and "suburban" and "rural" for USA locations. It is worth stating that analysis here was limited by the supporting data for observations (ie. descriptions of site locations), which is hoped will be ameliorated in future with the availability of datasets with enhanced supporting data (such as the Tropospheric Ozone Assessment Report (TOAR) dataset - Schultz et al 2017).

As the review notes, gridded datasets exist for comparisons with models. However, these are at coarser resolution (up to 1x1 degree resolution; Sofen et al 2016, Schnell et al 2015) than the "Nature run" presented here. The preference was therefore to compare to point observations, rather than degrading the resolution of the "Nature run" for comparison against existing datasets.

As stated in the manuscript, models tend to have troubles to simulate diurnal cycles of ozone particularly at night, and we don't expect the "Nature run" would solve all model issues. Indeed, even regional air quality models at higher resolution cannot reproduce the diurnal cycle (e.g., Herwehe et al., 2011; Solazzo et al., 2012).

(5) The concept of tropospheric burden depends a lot on the resolution of the tropopause structures. It would be very useful to discuss (show may be too much here) how the G5NR-Chem model reproduces the folds around (above and below) the jet where the STE takes place.

Is the tropospheric mass the same in both chem models at 0.1 and 2.0 degrees? STE flux is a very important model diagnostic, and since you are running Linoz in both models it is trivial to evaluate from the flux needed (presumably archived) to reset the O3strat in the boundary layer. Such a simple monthly, hemispheric value would help greatly in understanding differences between the two models.

Response: Without the individual tendency terms (transport, washout, chemistry) it is difficult to evaluate the STE. The diagnostic O3strat as the reviewer suggested was not available when the Nature run was carried out, thus we are not able the access the STE flux directly. We try to minimize the impact of the tropopause by using the ozonopause in the burden calculations as the boundary between the troposphere and stratosphere. We also note that Knowland et al (2017) have demonstrated that the GEOS has skills in reproducing stratospheric intrusions. The main focus on the evaluation of tropospheric ozone (particularly through comparisons with ozonesonde data in the upper troposphere) does not suggest any significant discrepancy in STE. Indeed, the G5NR-Chem does a better job of simulating the upper tropospheric ozone than the GEOS-Chem CTM.

(6) Another problem with increased resolution is the need to connect neighboring columns for the radiation and photolysis. In terms of radiation, the direct sunlight in one column often passes through and is scattered or absorbed by a neighboring columns. The overhead ozone column is often not the effective ozone column. The effect of neighboring (unknown) columns is very important for clouds. I doubt that the model is able to considers this effect, but it should be noted as this may be a case where increasing resolution may actually be worse. Related to this, it is also important to described how the Fast-J code treats clouds and aerosols. This later is an easy fix. **Response**: Thank you for pointing out these. We use the overhead column and don't consider the neighboring columns. For Fast-JX we use the approximate randomized cloud overlap method. The reviewer is correct that the high-res model may be worse here than the 2x25 degree CTM model, especially at high Solar Zenith Angles.

(7) The authors have not really shown off the capability of a 12-km global chemistry model. Particularly disappointing the comparisons with data from sondes or surface sites where the resolution of the G5NR is dumbed-down to compare with the GEOSchem reference run at 222 km [I think this is what saw]. It is important to see what the 222 km result from G5NR looks like when comparing with GEOSchem, but then to see the better structures and better match when using 12-km results.

Response: As an important model development as the implementation of a new chemical module into GEOS ESM, examining the consistency between the GEOS-Chem chemical module within the GEOS ESM and the off-line GEOS-Chem CTM is a critical step. Differences between the G5NR-chem and the CTM cannot be solely attributed to the different resolution, but should also be due to differences in transport, meteorological data, etc. The impact of high resolution on atmospheric chemistry and air quality would be better addressed with the GEOS-5 ESM run at the different resolution, which will be investigated in the future.

Minor: p.6 l.22: 'a : : : OSSEs : : :' singular or plural? p.9 l29: what is code availability for G5NR-chem?

Response: Done. G5NR-chem is the model output simulated by the GEOS-5 ESM with the GEOS-Chem, thus GEOS-5 code availability is reported while G5NR-chem data availability is reported.

References:

Herwehe, J. A., Otte, T. L., Mathur, R., & Rao, S. T. (2011). Diagnostic analysis of ozone concentrations simulated by two regional-scale air quality models. Atmospheric Environment, 45(33), 5957–5969. <u>https://doi.org/10.1016/j.atmosenv.2011.08.011</u>

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Schultz, M. G. and 96 co-authors (2017), Tropospheric Ozone Assessment Report: Database and metrics data of global surface ozone observations, Elem Sci. Anth, 5, DOI: http://doi.org/10.1525/elementa.244

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Solazzo, E., Bianconi, R., Vautard, R., Appel, K. W., Moran, M. D., Hogrefe, C., ... Galmarini, S. (2012). Model evaluation and ensemble modelling of surface-level ozone in Europe and North America in the context of AQMEII. Atmospheric Environment, 53, 60–74. https://doi.org/10.1016/j.atmosenv.2012.01.003

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A list of all relevant changes made in the manuscript

- New additions to the manuscript following reviewers' comments are highlighted in yellow in the make-up file.
- Deleted text: Page 7 line 21: '320-370 Tg' was deleted according to the Reviewer 1's comment.

Global simulation of tropospheric chemistry at 12.5 km resolution: performance and evaluation of the GEOS-Chem chemical module (v10-1) within the NASA GEOS Earth System Model (GEOS-5 ESM)

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Abstract. We present a full-year on-line global simulation of tropospheric chemistry (158 coupled species) at cubed-sphere c720 ($\sim 12.5 \times 12.5 \text{ km}^2$) resolution in the NASA GEOS Earth System Model, Version 5 (GEOS-5 ESM) with GEOS-Chem as a chemical module (G5NR-chem). The GEOS-Chem module within GEOS uses the exact same code as the off-line GEOS-Chem chemical transport model (CTM) developed by a large atmospheric chemistry research community. In this way, continual

- 5 updates to the GEOS-Chem CTM by that community can be seamlessly passed on to the GEOS chemical module, which remains state-of-the-science and referenceable to the latest version of GEOS-Chem. The 1-year G5NR-chem simulation was conducted to serve as Nature Run for observing system simulation experiments (OSSEs) in support of the future geostationary satellite constellation for tropospheric chemistry. It required 31 walltime days on 4707 compute cores with only 24% of the time spent on the GEOS-Chem chemical module. Results from the GEOS-5 Nature Run with GEOS-Chem chemistry were shown to
- 10 be consistent to the off-line GEOS-Chem CTM and were further compared to global and regional observations. The simulation shows no significant global bias for tropospheric ozone relative to the Ozone Monitoring Instrument (OMI) satellite, and is highly correlated with observations spatially and seasonally. It successfully captures the ozone vertical distributions measured by ozonesondes over different regions of the world, as well as observations for ozone and its precursors from the Aug-Sep 2013 SEAC⁴RS aircraft campaign over the Southeast US. It systematically overestimates surface ozone concentrations by 10 ppbv
- 15 at sites in the US and Europe, a problem currently being addressed by the GEOS-Chem CTM community and from which the GEOS ESM will benefit through the seamless update of the on-line code.

1 Introduction

Integration of atmospheric chemistry into Earth Science Models (ESMs) has been identified as a next frontier for ESM development (National Research Council, 2012) and is as a priority science area for atmospheric chemistry research (National Academies of Sciences, Engineering, and Medicine, 2016). Atmospheric chemistry drives climate forcing and feedbacks, is

- 5 an essential component of global biogeochemical cycling, and is key to air quality applications. A growing ensemble of atmospheric chemistry observations from space needs to be integrated into ESM-based data assimilation systems. Models of atmospheric chemistry are rapidly evolving, and an atmospheric chemistry module within an ESM must be able to readily update to the state-of-the-science. We have developed such a capability by integrating the GEOS-Chem chemical transport model (CTM) as a comprehensive and seamlessly updatable atmospheric chemistry module in the NASA Goddard Earth Ob-
- 10 serving System (GEOS) ESM (Long et al., 2015). Here we present the first application and evaluation of this GEOS-Chem capability within GEOS Version 5 (GEOS-5) for a full-year global simulation of tropospheric ozone chemistry at cubed-sphere $c720 (\sim 12.5 \times 12.5 \text{ km}^2)$ resolution. This simulation is now serving as Nature Run (pseudo-atmosphere) for observing system simulation experiments (OSSEs) in support of the near-future geostationary satellite constellation for tropospheric chemistry (Zoogman et al., 2017).
- 15 GEOS-Chem (http://geos-chem.org) is an open-source global 3-D Eulerian model of atmospheric chemistry driven by GEOS-5 assimilated meteorological data. It includes state-of-science capabilities for tropospheric and stratospheric gas-aerosol chemistry (Eastham et al., 2014; Hu et al., 2017), with additional capabilities for aerosol microphysics (Trivitayanurak et al., 2008; Yu and Luo, 2009). It is used by over a hundred active research groups in 25 countries around the world for a wide range of atmospheric chemistry applications, providing a continual stream of innovation (Hu et al., 2017). Strong version control and
- 20 benchmarking maintain the integrity and referenceability of the model. The code is freely available through an open license (http://acmg.seas.harvard.edu/geos/geos_licensing.html).

GEOS-Chem as used by the atmospheric chemistry community operates in an "off-line" CTM mode, without explicit simulation of meteorology. Meteorological data are input to the model to simulate chemical transport and other processes. The off-line approach makes the model simple to use, and facilitates community development of the core chemical module that describes

25 local chemical sources and sinks from emissions, reactions, thermodynamics, and deposition. Implementing the GEOS-Chem chemical module into ESMs offers a state-of-the-science and referenceable representation of atmospheric chemistry, but it is essential that the module be able to automatically incorporate new updates as the off-line model evolves. Otherwise it would become quickly dated and unsupported.

From a GEOS-Chem atmospheric chemistry user perspective, there are a number of reasons why an on-line simulation capability is of interest. Users working on both climate and atmospheric chemistry modeling can use the same module for both, improving the consistency of their approach. Some atmospheric chemistry problems involving fast coupling between chemistry and dynamics, such as aerosol-cloud interactions, require on-line coupling. As the resolution of ESMs increases, use of archived meteorological data becomes more difficult and incurs increased error (Yu et al., 2018), so on-line simulation can become more attractive. Finally, on-line simulations can take advantage of vast computational resources available at climate modeling centers to achieve very high resolution as illustrated in this paper. Such high-resolution model outputs are particularly important for air quality and human health applications (Cohen et al., 2017) and for OSSEs to support the design of satellite missions (Claeyman et al., 2011; Fishman et al., 2012; Yumimoto, 2013; Zoogman et al., 2014; Barré et al., 2016). A future *modus operandi* for the GEOS-Chem community might involve development in the off-line model at coarse resolution, and on line simulations when high resolution is required.

5 on-line simulations when high resolution is required.

We have developed the capability to efficiently integrate the GEOS-Chem chemical module into ESMs in a way that enables seamless updating to the latest standard version of GEOS-Chem. This involved transformation of GEOS-Chem into a grid-independent and Earth System Modeling Framework (ESMF)-compliant model (Long et al., 2015). The exact same code is now used in stand-alone off-line mode (CTM) by the GEOS-Chem community and as an on-line chemical module within

- 10 GEOS-5 (Figure 1). Using the exact same code for both applications ensures that the chemical module in the ESM keeps current with the latest well-documented standard version of GEOS-Chem. An important component is the Harvard-NASA EMission COmponent (HEMCO; Keller et al., 2014), which allows GEOS-Chem users to build customized layers of emission inventories on any grid and with no editing of the GEOS-Chem source code. HEMCO is now the standard emission module in GEOS-Chem and is used in GEOS-5 as an independent module for applications when full chemistry is not needed.
- Here we apply the GEOS-Chem chemical module within GEOS-5 in a very-high-resolution (VHR) simulation of global tropospheric ozone chemistry. The simulation is conducted for one full year (2013-2014) at c720 cubed-sphere resolution (\sim 12.5 × 12.5 km²) with 158 coupled chemical species. To the best of our knowledge, such a resolution in a state-of-the-science global simulation of tropospheric chemistry is unprecedented. Resolution not only increases the quality of local information, e.g., for air quality, but it also provides better representation of chemical non-linearities. We compare the model outputs with
- 20 coarse off-line GEOS-Chem CTM results and with independent observations for tropospheric ozone and precursors as a test of fidelity and increased power. We refer to this VHR simulation as GEOS-5 Nature Run with GEOS-Chem chemistry, or G5NR-chem.

2 GEOS-Chem as an atmospheric chemistry module in the GEOS ESM

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An Eulerian (fixed frame of reference) CTM such as GEOS-Chem solves the system of coupled continuity equations for an ensemble of m species with number density vector $\mathbf{n} = (n_1, \dots, n_m)^T$,

$$\frac{\partial n_i}{\partial t} = -\nabla \cdot (n_i \mathbf{U}) + (P_i - L_i)(\mathbf{n}) + E_i - D_i \qquad i \in [1, m]$$
(1)

where **U** is the wind vector including subgrid components to be parameterized as turbulent diffusion or convection. $(P_i - L_i)(\mathbf{n})$, E_i , and D_i are the local chemical production and loss, emission, and deposition rates respectively of species *i*. Coupling across species is through the chemical term $(P_i - L_i)$. In GEOS-Chem, as in all 3-D CTMs, Eq. 1 is solved by operator splitting to separate the transport and local components over finite time steps. The local operator,

$$\frac{dn_i}{dt} = (P_i - L_i)(\mathbf{n}) + E_i - D_i \qquad i \in [1, m]$$

$$\tag{2}$$

includes no transport terms (no spatial coupling) and thus reduces to a system of coupled ordinary differential equations (ODEs). It is commonly called the chemical operator even though emission and deposition terms are included. The transport operator,

$$\frac{\partial n_i}{\partial t} = -\nabla \cdot (n_i \mathbf{U}) \qquad i \in [1, m] \tag{3}$$

5 does not involve coupling between chemical species.

Use of GEOS-Chem as chemical module in an ESM requires only the code that updates concentrations over a given time step for local production and loss as given by Eq. 2 (Figure 1). The CTM has its own transport modules to solve Eq. 3 using archived meteorological inputs (off-line), but these are not needed in the ESM where transport is computed as part of atmospheric dynamics (on-line).

- 10 The ESM chemical module is tasked with updating chemical concentrations by integration of Eq. 2 on the ESM grid and timestep. Exchange of information between the chemical module and other ESM modules can be done by various couplers such as ESMF (Hill et al., 2004). Our guiding principle is that the CTM and the ESM chemical module share the exact same code. This required restructuring GEOS-Chem to a grid-independent form, and making the code compliant with the ESMF Modeling Analysis and Prediction Layer (MAPL) coupler used by GEOS (Long et al., 2015). 1-D vertical columns are the
- 15 smallest efficient unit of computation for the chemical module because several operations are vertically coupled including radiative transfer, vertically distributed emissions, wet scavenging, and particle settling. In the now grid-independent GEOS-Chem code, horizontal grid points are selected at runtime through the ESMF interface. The chemical and emission modules proceed to solve Eq. 2 on 1-D columns for the specified horizontal gridpoints (Figure 1). We managed to carry out this major software transformation in GEOS-Chem in a way that was completely transparent to CTM users (Long et al., 2015). The exact
- 20 same ESMF-compliant, grid-independent GEOS-Chem code is now used both in the stand-alone CTM and within GEOS. This enables seamless integration of future new GEOS-Chem scientific developments into the GEOS chemical module, which thus always remains current and referenced to the latest standard version of GEOS-Chem.

An important step in transforming GEOS-Chem to a grid-independent structure was to reconfigure the emission module. The emission module consists of multiple layers of databases and algorithms describing emissions for different species and regions,

- 25 with scaling factors defining diurnal/weekly/seasonal/secular trends or dependences on environmental variables. The databases are on different grids and time stamps, and may add to or supersede each other as controlled by the user. The HEMCO module allows users to choose any combination of emission inventories in NetCDF format, on any grid and with any scaling factors, and apply them to any model grid specified at runtime (Keller et al., 2014). HEMCO provides a complete functional separation of emissions from transport, deposition, and chemistry in GEOS-Chem. The purpose of this separation is that the ESM may need
- 30 emissions independently from atmospheric chemistry, for example to simulate species such as CO_2 and methane. HEMCO is thus configured as a stand-alone component in the ESM, accessed separately through the ESMF interface (Figure 1).

Some care is needed in when interfacing the GEOS-Chem chemical module with fast vertical transport processes in GEOS-5 involving boundary layer mixing (Lock et al., 2000; Louis et al., 1982) and deep convection with wet scavenging. Here we apply boundary layer mixing at every time step in GEOS-5 with emissions and dry deposition updates from GEOS-Chem, but

before applying chemistry. This avoids anomalies in the lowest model layer when the timescale for boundary layer mixing is shorter than the timestep for emissions. Deep convective transport of chemical species including scavenging in the updrafts is performed by the GEOS-Chem convection scheme driven by instantaneous diagnostic variables from the GEOS-5 convection component (Molod et al., 2015). This takes advantage of the gas and aerosol scavenging capability of the GEOS-Chem scheme

5 (Liu et al., 2001; Amos et al., 2012). Radon-222 tracer simulation tests within GEOS-5 show that the GEOS-Chem convection scheme closely reproduces the GEOS-5 convective transport (Yu et al., 2018). As convection becomes increasingly resolved at higher model resolution, the GEOS-5 sub-grid convection parameterization (Moorthi and Suarez, 1992) is invoked less frequently. As a consequence, an increasing fraction of the washout in GEOS-Chem becomes characterized as large-scale, as opposed to convective. No attempts were made to offset the possible increase in washout efficiency that may arise from this.

10 3 GEOS-5 Nature Run with GEOS-Chem chemistry

We perform a year-long (July 1 2013 to July 1 2014) GEOS-5 simulation with GEOS-Chem at cubed-sphere c720 (~12.5 \times 12.5 km²) horizontal resolution and 72 vertical levels extending up to 0.01 hPa. For initialization, we use 12 months at c48 resolution (~200 \times 200 km²) followed by 6 months at c720 resolution. Figure 2 shows a snapshot of the simulated 500 hPa ozone field, illustrating the fine detail enabled by the very high resolution.

15 3.1 General description

The GEOS-5 Nature Run with GEOS-Chem chemistry is performed with the Heracles version of GEOS-5 (tag 'M2R12K-3_0_GCC'). The finite-volume dynamics is run in a non-hydrostatic mode with a heartbeat time of 300 seconds applied to the physics, chemical and dynamics components. The simulation is forced by downscaled meteorological data from the lower resolution MERRA-2 reanalysis (Molod et al., 2015; Gelaro et al., 2017). The downscaling is performed by using the replay

- 20 capability in GEOS, which adds a forcing term to the model equations, constraining them to a specific trajectory to simulate the 2013-2014 meteorological year (Orbe et al., 2017). Downscaling applications filter the replay increments so that only the larger scales of the flow are constrained, allowing scales finer than the analysis to evolve freely. In this simulation, a wave number of 60 was chosen as the cutoff. The simulation is performed in two segments, the first with GEOS-Chem turned off ('regular replay'). The analysis increment produced during the first run segment is saved and reused in the subsequent run with
- 25 GEOS-Chem turned on ('exact increment'). This two segment process is computationally more efficient as it avoids rewinding and checkpointing the model with full chemistry during the regular replay stage.

The chemical module is GEOS-Chem version v10-01 in tropospheric-only mode. It is run 'passisvely' in G5NR-chem thus aerosols and trace gases do not influence the meteorology. It includes detailed HO_x -NO_x-VOC-ozone-BrO_x-aerosol tropospheric chemistry with 158 species and 412 reactions, following JPL and IUPAC recommendations for chemical kinetics

30 (Sander et al., 2011) and updates for BrOx and isoprene chemistry (Parrella et al., 2012; Mao et al., 2013). The aerosol microphysics is simulated using the TwO-Moment Aerosol Sectional (TOMAS) package (Trivitayanurak et al., 2008). The Fast-JX scheme with approximate randomized cloud overlap method is used to calculate photolysis frequencies (Bian and Prather, 2002) as implemented by (Mao et al., 2010). Linearized stratospheric chemistry is used (McLinden et al., 2000; Murray et al., 2012). The dry deposition calculation is based on a resistance-in-series model (Wesely, 1989) as implemented by Wang et al. (1998). Wet scavenging of aerosols and gases is as described by Liu et al. (2001) and Amos et al. (2012).

- Emissions are calculated through HEMCO v1.1.008 (Keller et al., 2014). They are the default 2013-2014 emissions for
 GEOS-Chem (see Table 1 in Hu et al., 2017), with a few modifications. Open fire emissions are from the Quick Fire Emissions Dataset (QFED) version 2.4-r6 (Darmenov and Da Silva, 2015). US NO_x emissions follow Travis et al. (2016). Parameterizations for lightning NO_x (Murray et al., 2012) and mineral dust aerosol emissions (Zender et al., 2003) have large dependencies on grid resolution, and are scaled globally following general GEOS-Chem practice to annual totals of 6.5 TgN for lightning and 840 TgC for dust. No adjustments are made to emission of biogenic VOCs (MEGANv2.1; Guenther et al., 2012; Hu et al.,
- 10 2015b) and sea salt aerosol (Jaeglé et al., 2011), both of which agree with GEOS-Chem emissions within 15%. GEOS-Chem uses in-plume chemistry of ship emissions (PARANOx) to account for the excessive dilution of ship exhaust plumes at coarse model resolution (Vinken et al., 2011); this was disabled in the VHR simulation given that the Nature Run resolution is fine enough to resolve the non-linear chemistry associated with ship plume emissions. A summary of the various emission sources used for the simulation is given in Table A2.

15 3.2 Computational environment and cost

The computations were carried out on the Discover supercomputing cluster of the NASA Center for Climate Simulation (https: //www.nccs.nasa.gov/services/discover). One day of simulation took approximately 2 walltime hours, using 4705 compute cores with 45% spent on dynamics and physics, 24% on chemistry, and 31% on input/output (I/O) (Table A1). The large I/O wall time is due to bottlenecks in the MAPL software version used for the simulation, with excessive reading and remapping of the hourly high-resolution emission fields. This issue has been addressed in newer versions of MAPL. As first shown by

20 of the hourly high-resolution emission fields. This issue has been addressed in newer versions of MAPL. As first shown by Long et al. (2015), the chemical module has excellent scalability even when running with thousands of cores. The percentage of the walltime spent on chemistry in the G5NR-chem (24%) is much lower than in coarse resolution simulations that are typically done with only a small number of cores (Eastham et al., 2018). The computational cost of chemistry relative to dynamics/transport decreases as grid resolution increases, thus it is no longer the computing bottleneck in ESM simulations.

25 4 Model evaluation

4.1 Observational datasets and off-line CTM

The GEOS-5 Nature Run with GEOS-Chem chemistry simulation is intended to support geostationary constellation OSSEs focused on tropospheric ozone and related satellite measurements (Zoogman et al., 2017), and ozone is therefore our evaluation focus. We use 2013-2014 observations that were previously compared to the GEOS-Chem CTM including (1) global

30 ozonesondes and OMI (Ozone Monitoring Instrument) satellite data (Hu et al., 2017), (2) aircraft data for ozone and precursors from the NASA SEAC⁴RS campaign over the Southeast US (Travis et al., 2016), and (3) surface ozone monitoring data over Europe and the US (Yan et al., 2016; Grange, 2017). An important goal of the evaluation here is to examine consistency between the GEOS-Chem chemical module within the GEOS ESM c720 environment and the off-line GEOS-Chem CTM. Although the GEOS-Chem simulation is at coarser resolution and off-line transport may incur errors (Yu et al., 2018), it is extensively diagnosed by the GEOS-Chem user community including recently by Hu et al. (2017) for global tropospheric

- 5 ozone. Two GEOS-Chem CTM v10-01 simulations are used for comparison to the G5NR-chem: a global simulation with $2^{\circ} \times 2.5^{\circ}$ resolution, and a nested simulation for North America with $0.25^{\circ} \times 0.3125^{\circ}$ resolution. Both are driven by GEOS-5 Forward-Processing (GEOS-5.7.2 and later versions) assimilated meteorological data. Some differences with the G5NR-chem are to be expected because of differences in the transport modules, resolution, distribution of natural sources computed on-line such as lightning NO_x, and meteorological data from different versions of the GEOS system (MERRA-2 vs GEOS-FP). All
- 10 comparisons to observations use model output sampled at the location and time of observations.

Observational datasets are described in the above references. Briefly, global ozonesonde observations are extracted from the WOUDC (World Ozone and Ultraviolet Data Center, http://www.woudc.org) and the NOAA ESRL-GMD (Earth System Research Laboratory – Global Monitoring Division, ftp://ftp.cmdl.noaa.gov/ozwv/Ozonesonde/). Ozonesonde stations are grouped into coherent regions for model evaluation (Tilmes et al., 2012). OMI middle tropospheric ozone data at 700–400 hPa

- 15 are from the Smithsonian Astrophysical Observatory (SAO TROPOZ) retrieval (Liu et al., 2010; Huang et al., 2017) and are regridded to $2^{\circ} \times 2.5^{\circ}$ resolution to reduce retrieval noise. The NASA SEAC⁴RS data set for Southeast US described by Toon et al. (2016) are filtered following Travis et al. (2016) to remove open fire plumes (CH₃CN > 200 pptv), stratospheric air (O₃/CO > 1.25 mol mol⁻¹), and urban plumes (NO₂ > 4 ppbv). Hourly surface observations for ozone are taken from the European Environment Agency database (complied by Grange (2017)) and the US Environmental Protection Agency Air Quality
- 20 System (http://aqsdr1.epa.gov/aqsweb/aqstmp/airdata/download_files.html#Raw). Only "background" sites are considered in the analysis: For the USA this includes sites defined by the EPA as "suburban" and "rural"; For Europe this included sites categorized as "urban background", "background", and "rural" (see Figure A2).

4.2 Global burdens

Standard global metrics for evaluation of tropospheric chemistry models include the global burdens of tropospheric ozone, CO,

- and OH (Table 1). The global annual average ozone burden in the G5NR-chem amounts to 348 Tg, consistent with the GEOS-Chem CTM and with the Tropospheric Ozone Assessment Report (Hu et al., 2017; Young et al., 2018). The global burden of tropospheric CO of 294 Tg is consistent with the GEOS-Chem CTM and on the low end of the observationally-based estimate of Gaubert et al. (2016). The global mean OH concentration is lower than in the GEOS-Chem CTM and more consistent with observational constraints (Prinn et al., 2005; Prather et al., 2012). The differences appear to be mainly driven by differences in
- 30 the meteorological data.

4.3 Free tropospheric evaluation: OMI, ozonesonde, SEAC⁴RS

Figure 3 compares the GEOS-5 Nature Run with GEOS-Chem chemistry to OMI mid-tropospheric ozone. GEOS-Chem CTM results from Hu et al. (2017) are also shown. OMI data have been reprocessed with a single fixed a priori profile (so that

variability is solely due to observations), corrected for their global mean bias relative to ozonesondes, and filtered for high latitudes because of large biases (Hu et al., 2017). Model outputs are sampled along the OMI tracks and smoothed with the OMI averaging kernels. The G5NR-chem captures well-known major features of the ozone distribution, such as ozone enhancements at northern mid-latitudes during MAM and JJA, and downwind of South America and Africa during SON. It

5 shows no significant global bias relative to OMI and relative to the off-line GEOS-Chem CTM. The global mean seasonal biases are less than 2.7 ± 3.2 ppbv. Spatial correlations for the four seasons on the $2^{\circ} \times 2.5^{\circ}$ grid scale are high and show no significant latitudinal bias (R=0.81-0.93; Figure 4).

Figure 5 further evaluates the simulated vertical distribution of ozone in comparison to ozonesonde data. There are differences between the G5NR-chem and the GEOS-Chem CTM that could be due to a number of factors including differences in

- 10 tropopause altitude and the distribution of lightning. For example, although the annual total lightning NO_x emission in G5NR-chem is scaled to that in GEOS-Chem CTM, the lightning location is not constrained by satellite lightning flash data as the CTM does. Annual mean ozone biases in the G5NR-chem are generally less than 6 ppbv in the lower troposphere. There are some larger biases in the upper troposphere including differences with the GEOS-Chem CTM that could be due to the spatial distribution of lightning. Overall the G5NR-chem tends to improve the simulation of ozone vertical profiles compared to the
- 15 GEOS-Chem CTM, most dramatically at high southern latitudes.

Figure 6 compares the model to mean vertical profiles of ozone and precursors measured over the Southeast US during the SEAC⁴RS aircraft campaign. Here the GEOS-Chem CTM results are from a nested $0.25^{\circ} \times 0.3125^{\circ}$ simulation by Travis et al. (2016). The lower ozone in the northern mid-latitudes upper troposphere in the G5NR-chem appears to be due to a weaker lightning NO_x source. The G5NR-chem overestimates ozone in the lower troposphere by 10 ppbv, while such bias is reduced

20 in the GEOS-Chem CTM, even through both show almost identical NO_x levels. The lower HCHO over the Southeast US is due to weaker isoprene emission because of lower temperatures. Both models underestimate CO in the free troposphere but the bias is more apparent in the CTM, likely due to differences in fire emissions, global OH fields, or transport error in off-line simulations (Yu et al., 2018).

4.4 Evaluation with surface observations over US and Europe

- Figure 7 shows monthly median surface ozone concentrations grouped by regions in the US and Europe. Here hourly data between noon and 16:00 local time are used to remove the known issue that models typically underestimate the ozone nighttime depletion at surface sites (e.g., Millet et al., 2015). The G5NR-chem systematically overestimates surface ozone in almost all months by about 10 ppbv in all regions; while the GEOS-Chem CTM has no or small bias in winter and spring, but shows similar overestimates as in the G5NR-chem during summer and fall. In general the GEOS-5 Nature Run with GEOS-Chem
- 30 chemistry better captures the observed seasonality. Expanding the analysis to all hourly data does not affect the systematic bias in the G5NR-chem significantly, but tends to increases the summer/fall bias in the CTM (Figure A5). Part of the systematic bias is due to the subgrid vertical gradient between the lowest model level and the measurement altitude (60 m above ground vs 10 m, Travis et al., 2017). Recent model developments such as improved halogen chemistry, aromatic chemistry, and ozone dry deposition are expected to reduce the surface high bias (Schmidt et al., 2016; Sherwen et al., 2016a, b, 2017; Silva and Heald,

2018; Yan et al., 2018). These updates are being incorporated into the GEOS-Chem version currently under development and will be passed on to the GEOS-5 simulation as they become available.

5 Conclusions

We presented a 1-year global simulation of tropospheric chemistry within the NASA GEOS ESM, version 5 (GEOS-5) at
cubed-sphere c720 (~12.5 × 12.5 km²) resolution. This demonstrated the success of implementing the GEOS-Chem chemical module within an ESM for on-line simulations with detailed chemistry. The GEOS-Chem chemical module on-line within GEOS and off-line as the GEOS-Chem CTM uses exactly the same code. In this way, the continual stream of chemical updates from the large GEOS-Chem CTM community can be seamlessly incorporated as updates to the on-line model, which always remains state-of-the-science and referenceable to the latest version of the GEOS-Chem. This 1-year simulation addressed an
immediate need to generate the Nature Run for OSSEs in support of the geostationary satellite constellation for tropospheric chemistry. More broadly, implementation of the GEOS-Chem capability opens up a new capability for GEOS to address aerosol-chemistry-climate interactions, to assimilate satellite data of atmospheric composition, and to develop global air quality

forecasts. The 1-year GEOS-5 simulation at c720 resolution required 31 days walltime on 4705 cores. 45% of the wall time was

- 15 spent on model dynamics and physics, 31% on input/output, and 24% on chemistry. Chemistry has near-perfect scalability in massively parallel architectures because it operates on individual grid columns, thus it is no longer a computing bottleneck in ESM simulations. Transporting the large number of species involved in atmospheric chemistry simulations may be a greater challenge.
- We evaluated the GEOS-5 Nature Run with GEOS-Chem chemistry for consistency with the off-line GEOS-Chem CTM at coarser resolution (2° × 2.5° global and 0.25° × 0.3125° nested over North America) as well as an ensemble of global observations for tropospheric ozone and aircraft observations of ozone precursors over the Southeast US. The model shows no significant global bias relative to OMI mid-tropospheric ozone data and the off-line GEOS-Chem CTM. Evaluations with ozonesondes show reduced model biases for high-latitude ozone. The GEOS-5 Nature Run with GEOS-Chem chemistry systematically overestimates surface ozone concentrations by 10 ppbv all year round in the US and Europe, but is able to capture the observed seasonality; while the off-line GEOS-Chem CTM reproduces observed surface ozone levels in winter and spring.
- but has similar biases in summer and fall in all regions. Resolving this surface bias is presently a focus of attention in the GEOS-Chem CTM community and future model updates to address that bias can then be readily implemented into GEOS-5.

Data availability. All model outputs are available for download at https://portal.nccs.nasa.gov/datashare/G5NR-Chem/Heracles/12.5km/ DATA or can be accessed through the OpenDAP framework at the portal https://opendap.nccs.nasa.gov/dods/OSSE/G5NR-Chem/Heracles/

30 12.5km.

Code availability. GEOS-Chem CTM is available at http://geos-chem.org/. GEOS-5 is available https://geos5.org/wiki/index.php?title=GEOS-5_public_AGCM_Documentation_and_Access.

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Figure 1. Schematic of GEOS-Chem chemical module used either off-line as a Chemical Transport Model (CTM) or on-line in an Earth System Model (ESM), with interfaces managed through the Earth System Modeling Framework (ESMF). The module is grid-independent with individual computations done on atmospheric columns at user-selected gridpoints. It computes local changes in concentrations with time (dn/dt) as a result of emissions (*E*), chemical production (*P*), chemical loss (*L*), and deposition (*D*). Emissions are handled through HEMCO to provide ESM users the option of only integrating emissions.



Figure 2. 500 hPa ozone distribution on August 1, 2013 at 0Z simulated by GEOS-5 with the GEOS-Chem chemical module at cubed-sphere c720 (\sim 12.5 × 12.5 km²) resolution.



Figure 3. Middle tropospheric ozone distribution at 700-400 hPa from GEOS-5 Nature Run with GEOS-Chem chemistry (left column), OMI satellite observations (middle column), and the off-line GEOS-Chem CTM (right column) for four seasons covering July 2013 - June 2014. The data are on a $2^{\circ} \times 2.5^{\circ}$ grid. All data are smoothed by the OMI averaging kernels, using a single fixed a priori profile so that variability is solely driven by observations. The OMI observations have been further corrected for a global mean positive bias of 3.6 ppbv (Hu et al., 2017). Both models are sampled along the OMI tracks. Numbers in the left and right columns are the mean model bias \pm standard deviation. Gray shading indicates regions where OMI data are unreliable and not used (poleward of 45° in winter-spring and poleward of 60° year-round; see Hu et al. (2017)).



Figure 4. Comparison of GEOS-5 Nature Run with GEOS-Chem chemistry to OMI 700-400 hPa ozone measurements for four seasons in July 2013 - June 2014, colored by the latitude of the observations. Each point represents the seasonal mean for a $2^{\circ} \times 2.5^{\circ}$ grid cell. Black dashed lines show the best fit (reduced major axis regression) with regression parameters given inset. Numbers on the bottom right are the global mean model bias ± standard deviation. The 1:1 line is shown in red.



Figure 5. Annual mean ozonesonde profiles in July 2013 - June 2014 for representative global regions (Tilmes et al., 2012). Results from the GEOS-5 Nature Run with GEOS-Chem chemistry (red) are compared to observations (black) and to the GEOS-Chem CTM (blue; $2^{\circ} \times 2.5^{\circ}$ version in Hu et al. (2017)). The models are sampled at the ozonesonde launch times and locations.



Figure 6. Mean vertical profiles of trace gas concentrations over the Southeast US during the NASA SEAC⁴RS aircraft campaign (Aug-Sep 2013, Toon et al. (2016)). Results from the GEOS-5 Nature Run with GEOS-Chem chemistry are compared to observations for ozone and NO_x, CO, peroxyacetyl nitrate (PAN), and formaldehyde (HCHO), and to the GEOS-Chem CTM (nested $0.25^{\circ} \times 0.3125^{\circ}$ version in Travis et al. (2016)). Model results are sampled along the flight tracks at the time of flights.



Figure 7. Monthly median afternoon (12-16 local time) ozone concentrations (ppbv) for 2013/2014 at surface sites in the US and Europe, with interquartile range shaded. Surface monitoring sites are grouped according to Figure A2. Also shown are the GEOS-5 Nature Run with GEOS-Chem chemistry (red) and the off-line GEOS-Chem CTM (blue). Hourly model outputs are sampled for the locations and time of observations at the surface (lowest) level.

Table 1. Global tropospheric burdens.

	GEOS-5 Nature Run with GEOS-Chem chemistry	GEOS-Chem CTM a	Literature range
O ₃ burden [Tg]	348 ^b	347 ^b	320-370 ^c
CO burden [Tg]	294	285	290-370 ^d
mean OH $[1 \times 10^5 \mathrm{molecule}\mathrm{cm}^{-3}]^{e}$	10.2	12.5	9.5-12.7 ^f

^a Hu et al. (2017).

^c Interquartile range of 50 models summarized in Young et al. (2018); limited observational estimates fall within that range.

^d Gaubert et al. (2016).

 e Global mean airmass-weighted OH concentration.

^f From 16 model results summarized in Naik et al. (2013)

^b Calculated with a chemical tropopause as the 150 ppbv ozone isopleth.



Figure A1. Same as Figure 5 but for Western US, Equatorial American, and Atlantic/Equatorial Africa.

Appendix A



Northeastern US



Pacific US



Benelux



Northeastern Europe



Southeastern Europe









Figure A2. Surface monitoring sites in the US and Europe grouped by subregions as analyzed in the text. Background image ©Natural Earth (public domain license)



Figure A3. Probability distribution of afternoon (12-16 local time) ozone concentrations (ppbv) for 2013/2014 at surface sites in the US and Europe.



Figure A4. Monthly median ozone concentrations (ppbv; all 24-h data) for 2013/2014 at surface sites in the US and Europe, with interquartile range shaded. Surface monitoring sites are grouped according to Figure A2. Also shown are the GEOS-5 Nature Run with GEOS-Chem chemistry (red) and the off-line GEOS-Chem CTM (blue). Hourly model outputs are sampled for the locations and time of observations at the surface (lowest) level.



Figure A5. Probability distribution of ozone concentrations (ppbv; all 24-h) data) for 2013/2014 at surface sites in the US and Europe.

Table A1. Computing resources for the GEOS-5 Nature Run with GEOS-Chem chemistry ^a

	Wall time breakdown	Wall time	Compute cores	Disk storage
Transport	45%	31 days	4705 cores ^b	180 Tb c
Chemistry	24%			
Input	25%			
Output	6%			

^a The simulation is from July 1 2013 - July 1 2014 in GEOS ESM with GEOS-Chem as a chemical module at $12.5 \times 12.5 \text{ km}^2$. The computation was carried out at NASA Discover supercomputing cluster.

^b The simulation uses 337 14-core 2.6 GHz Intel Xeon Haswell compute nodes with 128 GB of memory per node, and an Infiniband FDR interconnect using the Intel compiler suite (v. 15.0.0.090) and MPT v. 2.11.

 c 158 species are simulated and transported by the GEOS ESM; among them 29 species are saved out as hourly outputs. Data is available at

https://portal.nccs.nasa.gov/datashare/G5NR-Chem/Heracles/12.5km/DATA/

Species			Anthropogenic a			Aircraft	Ship	Volcanoes ^b	Biomass burning	Biogenic	Soil & agriculture c	Lightning d	Oceanic/Sea spray ^e	Dust ^f	Annual emission (Tg/y or TgC/y) g
	EDGAR HTAP v2 ^h	RETRO ⁴	Xiao et al. (2008)	NEI 2011 ³	MIX k	AEIC ¹	HTAP h		QFED "	MEGAN n					
ON	×			x		×	x		×		×	x			117
CO	х			х		x	x		x	х					958
SO_2	х			х		х	х	х	х						129
SO_4	х			х		х									2.93
Organic carbon	х			х		x	x		x	х					72.1
Black carbon	х			х		x	x		x						10.3
NH ₃	х			х							х				60.5
$\geq C_4$ alkanes		x		х	x	x									32.1
Acetone		х		х	х	х				х			х		77.6
MEK		x		х	x										4.09
CH ₃ CHO		х		х	x	x				х					20.9
C_3H_6		х		х	х	х				х					31.3
C_3H_8		x		х	x	x									6.33
CH_2O		х		х	х	x									4.58
Isoprene										х					345
C_2H_6			х			x									15.3
CHB ₁₃													х		0.429
CH_2Br_2													х		0.0621
Br_2													х		0.63
Sea salt A $(0.1 - 0.5 \mu g)$													х		65.9
Sea salt C $(0.5-4.0\mu{\rm g})$													х		3990
DMS													х		35.2
Dustl $(0.1 - 1.0 \mu g)$														x	103
Dust2 $(1.0 - 1.8 \mu g)$														x	212
Dust3 $(1.8 - 3.0 \mu g)$														х	271
Dust4 $(3.0 - 6.0 \mu g)$														x	254
^a Excluding aircraf	t and ships, whic	h are liste	ed separately.												

Table A2. Emissions in the GEOS-5 Nature Run with GEOS-Chem chemistry

 b http://aerocom.met.no/download/emissions/AEROCOM_HC/volc/.

^c Hudman et al. (2012).

 d Murray et al. (2012).

 $^e\,$ Jaeglé et al. (2011) and Fischer et al. (2012).

f Zender et al. (2003).

 g TgC/y for $\geq C_4$ alkanes, Acetone, MEK, CH₃CHO, C₃H₆, C₃H₈, Isoprene, and C₂H₆. Tg/y for the rest species.

^h http://edgar.jrc.ec.europa.eu/htap_v2/index.php?SECURE=123

ⁱ RETRO monthly global inventory for 2000 (Schultz et al., 2007) implemented as described by Hu et al. (2015a).

^j US EPA National Emission Inventory 2008 http://www.epa.gov/ttn/chief/net/2008report.pdf and scaled to 2013 https://www3.epa.gov/airtrends/.

 $^k\,$ Asian anthropogenic emissions (Li et al., 2014).

l Stettler et al. (2011).

 n MEGANv2.1 (Guenther et al., 2012) implemented in GEOS-Chem as described by Hu et al. (2015b). m Quick Fire Emissions Dataset (QFED) version 2.4-r6 (Darmenov and Da Silva, 2015).

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