I don't see that the paper has been sufficiently re-written in terms of clearly framing the questions being addressed and articulating the new contributions. I still have some concerns regarding the communication and interpretation of the analysis, including regarding queries in my previous review, detailed below, along with a few other points in the text that would benefit from some clarification.

We thank the reviewers for their valuable comments. Below we respond to the individual comments.

(1) *L37-40 implies that the updates to the emissions are needed to capture the ozone distribution observed by TES, but it seems from the new Figure 4 that the free tropospheric ozone is not very sensitive to the emission changes. This needs to be clarified in the abstract and also in the conclusions (L460-464 seem a bit contradictory; first it's stated that ozone doesn't change much following the updated emissions, but then it's asserted that the good agreement reflects reliability of… updated inventories (I think the latter is meant for CO, but it's not clear as written)).*

The abstract and conclusion have been changed to highlight this result. In retrospect, we believe an interesting result of this paper is that the free-tropospheric ozone over Asia is not that sensitive to moderate changes in the surface emissions. A quantitative statement to that effect has been added in the abstract. As noted by the reviewer, the improved agreement in the ozone/CO comparisons is due to the improved agreement with CO and this language has been added to the paper.

(2) *L43 It seems misleading to report influence from anthropogenic VOC in the abstract when that has not been explicitly examined in the same way as the biogenic VOCs.*

We have removed the sentence discussing the role of VOC's because we do not have direct constraints on the amount and partitioning of the VOC's.

(3) *L45-47. Is this export to a particular region?*

The pollution from East Asia is primarily exported to the Northwest Pacific as discussed by Zhang et al., 2009 and many others. The abstract has been changed.

(4) *L59-60. The time period over which these numbers apply should be stated.*

The time period has been added.

(5) *L114 It would be best to quantify what is meant by "good agreement".*

Changed: we state that TES CO profiles are on between 0-10% lower than aircraft data.

(6) *L127. What is the resolution of the a priori from MOZART-4?*

The key number for examining the influence of the *a priori* on the results is how the *a priori* is gridded. As discussed in the paper, the *a priori* is gridded in 10 x 10 degree bins.

(7) *L252-253. Is it solely due to emissions or is it also that the meteorology is well represented?*

Thanks! The effect of meteorology is important. The discussion has been modified.

(8) *L276. Isn't some of the correlation driven by transport (as opposed to chemistry)?*

Transport of nearby CO emissions into the pollution plume can change the correlation, especially in the free-troposphere. We have added a Worden *et al.* (2013) reference.

(9) *I don't feel the authors adequately addressed my previous query (General comments #2) regarding the number of data points going into each correlation in Table 1. Their response suggests they are calculating monthly averages over the region, but I'm obviously misunderstanding since there would then be only 1 point for each table entry. Is it the correlation of the monthly average at each sampling location (and if so, does this mean that many points only include two values for a monthly mean?) Please add the number of data points for each entry in the table and provide a detailed explanation of the approach. This is crucial for understanding how good the constraints actually are on the O3/CO relationship in the model and thus the strength of the evaluation being done.*

The calculation of slope and correlation is based on individual measurements within a month rather than the monthly mean value. The right column of Table 1 is the mean value of 15 months. We have added these statements to the Table 1 description. However, because Table 1 is already quite large, we have provided the number of measurements used to compute the correlations in the supplemental (also discussed in the Table 1 description).

(10) *In response to previous General Comment #4, why is the ozone chemical regime being discussed at all if it's beyond scope of the paper?*

We are still puzzled by this question but hopefully our response addresses the concern. The Martin et al. (2004) paper discussed surface ozone, whereas this paper is focused on free-tropospheric ozone.

As our previous response, our results, based on the newer GEOS-Chem model, shows that free tropospheric O_3 over northeast China in summer has positive sensitivity to NOx, which is opposite with Martin et al. (2004), who showed surface O_3 decrease with increase of NO_x. We speculate it could be associated increased VOC levels discussed in the Martin et al. paper and because the sensitivity of the free-tropospheric ozone depends on ozone production in the surface (which could be VOC limited) and in the free-

troposphere (which is more NOx limited). We also add the following reference to support these arguments

Zhang, Q., Yuan, B., Shao, M., Wang, X., Lu, S., Lu, K., Wang, M., Chen, L., Chang, C.-C., and Liu, S. C.: Variations of ground-level O_3 and its precursors in Beijing in summertime between 2005 and 2011, Atmos. Chem. Phys., 14, 6089-6101, doi:10.5194/acp-14-6089-2014, 2014.

(11) *Response to Specific Comment #7, why assume a proportional relationship if it's already been established that the instrument is more sensitive to lightning NO2 (vs. surface anthropogenic)?*

For the NO_x emissions, we had separated the contributions of anthropogenic from natural sources, with differences in seasonality between anthropogenic and natural sources. Using several simulations, we modeled contributions to NO_2 columns of individual NO_x emission sources, and then applied the averaging kernels to match the satellite NO_2 columns. As such, we took into account differences in satellite sensitivity to different NO_x sources when separating the anthropogenic from natural sources.

(12) *Response to Specific Comment #11: please include in the text what was found by the Jiang et al. 2014 evaluation of the OH bias on the CO estimates.*

More discussion has been added to show that biases in OH strongly affect CO emissions estimates but not necessarily our conclusions as posterior CO concentrations remain approximately the same.

(13) *Response to Specific Comment #14. Here, I had hoped that the authors would present their findings in the context of the current understanding (OH recycling from isoprene oxidation in low-NOx conditions) and specifically whether the sign of the response they find in the model is consistent with this latest understanding.*

The isoprene scheme, reported by Mao et al. (2013), was released in January 2014. As this isoprene scheme is quite new, both our forward and adjoint models don't include it. In Mao et al. (2013), the surface O_3 concentration over southeast US was changed by about 2 ppb with the new scheme. The influence of the isoprene scheme on free tropospheric O_3 should therefore be much smaller. Considering the contribution of isoprene on free tropospheric O_3 is even smaller than CO, we believe the discrepancy in isoprene scheme will not have an important influence on our analysis and conclusions.

Constraints on Asian ozone using Aura TES, OMI and Terra MOPITT

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Abstract

Rapid industrialization in Asia in the last two decades has resulted in a significant increase in Asian ozone (O_3) pre-cursor emissions with likely a corresponding increase in the export of O_3 and its pre-cursors. However, the relationship between this increasing O_3, the chemical environment, O_3 production efficiency, and the partitioning between anthropogenic and natural precursors is unclear. In this work, we use satellite measurements of O_3, CO and NO_2 from TES (Tropospheric Emission Spectrometer), MOPITT (Measurement of Pollution In The Troposphere) and OMI (Ozone Monitoring Instrument) to quantify O_3 pre-cursor emissions for 2006 and their impact on free-tropospheric O_3 over North-East Asia, where pollution is typically exported globally due to strong westerlies. Using the GEOS-Chem global chemical transport model, we test the modeled seasonal and interannual variation of O_3 based on prior and updated O_3 pre-cursor emissions where the updated emissions of CO and NO_x are based on satellite measurements of CO and NO_2. We show that the observed TES O_3 variability and amount are consistent with the model for these updated emissions. However, there is little difference in the modeled ozone between the updated and prior emissions. For example, for the 2006 June time period, the prior and posterior NOx emissions were 14% different over China but the modeled ozone in the free-troposphere was only 2.5% different. Using the adjoint of GEOS-Chem we partition the relative contributions of natural and anthropogenic sources to free troposphere O_3 in this region. We find that the influence of lightning NO_x in the summer is comparable to the contribution from surface emissions but smaller for other seasons. China is the primary contributor of anthropogenic CO emissions and their export during the summer. While the posterior CO emissions improved the comparison between model and TES by 32%, on average, this change also had only a small effect on the free-tropospheric ozone. Our results show that the

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influence of India and Southeast Asia emissions on O_3 pollution export to the Northwest Pacific is sizeable, comparable with Chinese emisisons in winter, about 50% of Chinese emissions in spring and fall, and approximately 20% in the summer.

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1. Introduction

Unprecedented growth in transportation, coal-fired power plants and the industrial sector in China has resulted in a substantial increase in the emissions of O_3 precursors (Lin et al. 2014a). Recent studies (Lamsal et al. 2011; Lin 2012; Mijling et al. 2013) show 5-10% annual growth rate of NO_x emission in China. Wang et al. (2012) found there was 3% annual growth rate of O_3 in Beijing in the period of 2003-2010. East Asian O_3 can be transported to the surface of North America in about 2-3 weeks (Liu and Mauzerall 2005) by midlatitude westerly winds (Liang et al 2004, 2005), which likely results in an increase of background O_3 concentration in western North America by 3-7 ppbv during the period of 2000 - 2006 (Zhang et al. 2008; Brown et al. 2011).

Use of inverse (top-down) methods to better quantify the emission of NO_x (Lamsal et al. 2011; Lin and McElroy 2011; Lin 2012; Mijling et al. 2013), VOCs (Shim et al. 2005; Fu et al. 2007) and CO (Kopacz et al. 2010; Fortems-Cheiney et al. 2011; Gonzi et al. 2011) are needed to ensure consistency between bottom-up inventories and observations. However, large discrepancies can still exist between bottom-up and top-down based inventories (e.g., Kopacz et al., 2010, Lin et al. 2012b). In this work, we perform a multi-tracer assimilation with the GEOS-Chem model to evaluate the top-down estimates of O_3 precursors (NO_x and CO) in East Asia. We firstly optimized the CO and NO_x emission with MOPITT CO and OMI NO_2 retrievals respectively and then evaluate the a posteriori simulation of CO and O_3 by comparing the values

with measurements from TES in the period of Dec 2005 – Nov 2006. Using the adjoint of the GEOS-Chem model (Henze et al., 2007), we then quantify source contributions (NO_x, CO, VOC) to free tropospheric O_3 pollution over East China and the China outflow region in Dec 2005 – Nov 2006.

2. Observations and Model

2.1. TES CO and O_3

The TES instrument was launched on NASA's Aura spacecraft on 15 July 2004. The satellite is in a sun-synchronous polar orbit of 705 km and crosses the equator at 1:45 and 13:45 local time. With a footprint of 8km x 5km, TES measures radiances between 3.3-15.4μm with global coverage of 16 days (Beer et al. 2001) of observations. In the troposphere, TES O_3 profile retrievals have 1-2 degrees of freedom for signal (DOFS), and about 1 DOFS for CO. We use data from the "lite" product (http://tes.jpl.nasa.gov/data/) which reports volume mixing ratios (VMR) on 26 pressure levels for O_3 and 14 pressure levels for CO. Using an optimal estimation approach, the TES retrievals are conducted with respect to the logarithm of the VMR. The relationship between the retrieved profiles and the true atmospheric state can be expressed as:

$$\hat{\mathbf{z}}^{TES} = \mathbf{z}_a^{TES} + \mathbf{A}^{TES}(\mathbf{z} - \mathbf{z}_a^{TES}) + \mathbf{G}\varepsilon \quad (1)$$

where $\mathbf{z}$ is the true atmospheric state (expressed as log(VMR)), $\mathbf{z}_a^{TES}$ is the TES a priori O_3 or CO profile, $\mathbf{A}^{TES}$ is the TES averaging kernel matrix and $\mathbf{G}\varepsilon$ describes the retrieval error. The averaging kernel matrix represents the sensitivity of the retrieval to the actual trace gas in the atmosphere. The TES retrievals use a monthly mean profile of the trace gas from the MOZART-4 CTM (chemical transport model), averaged over a 10º latitude x 60º longitude, as the a priori information $\mathbf{z}_a^{TES}$. According to the recommended quality control criterion, we only

use CO and O_3 data with major quality flag equals 1. These data have passed all major quality flags used to assess the TES data related to chi-2 tests, biases in the radiance residuals, and residual non-linearity checks. The data with small DOFS (Degree of Freedom for Signal for CO is smaller than 0.8), are dropped as the limited sensitivity reduces the robustness of calculated O_3-CO correlations. We empirically find that the sensitivity of CO is the limiting factor in these comparisons, that is, if DOFS of CO is > 0.8 then the DOFS of O_3 is > 0.8. Recently, Verstraeten et al. (2013) evaluated TES O_3 measurement by using data from World Ozone and Ultra-violet Radiation Data Centre (WOUDC) sites and found that there is a ~7 ppb bias in the TES measurements in free troposphere, and the magnitude is slightly larger in summer and smaller in winter. TES CO measurements were evaluated by Luo et al. (2007) using the aircraft measurents from INTEX-B campaingn. They showed that TES CO VMR profiles are 0-10% lower than the aircraft measurements in the lower and middle troposphere.

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2.2. MOPITT CO

The MOPITT instrument was launched on NASA's Terra spacecraft on 18 December 1999. The satellite is in a sun-synchronous polar orbit of 705 km and crosses the equator at 10:30 local time. With a footprint of 22km x 22km, MOPITT (version 6) combines TIR (4.7μm) with the NIR (2.3μm) and has better sensitivity to lower tropospheric CO over land (Worden et al. 2010). MOPITT CO retrievals are reported on 10 pressure levels (surface, 900, 800, 700, 600, 500, 400, 300, 200 and 100 hPa). Similar to the TES product, relationship between the retrieved CO profiles and the true atmospheric state can be expressed as:

$$\hat{\mathbf{z}}^{MOP} = \mathbf{z}_a^{MOP} + \mathbf{A}^{MOP}(\mathbf{z} - \mathbf{z}_a^{MOP}) + \mathbf{G}\varepsilon \quad (2)$$

where $\mathbf{z}$ is the true atmospheric state (expressed as log(VMR)), $\mathbf{z}_a^{MOP}$ is the MOPITT a priori CO

profile, $\mathbf{A}^{MOP}$ is the MOPITT averaging kernel matrix and $\mathbf{G}\varepsilon$ describes the retrieval error. Same as TES, the a priori information of MOPITT retrievals is from monthly mean profile of the MOZART-4 CTM, without the 10º latitude x 60º longitude average. We reject MOPITT data with CO column amounts less than $5x10^{17}$ molec/cm^2 and if low clouds are observed. The nighttime data is excluded in the assimilation, due to the NIR radiances measure reflected solar radiation. The version 5 data have been evaluated recently against NOAA aircraft measurements (Deeter et al., 2013), which shows small bias in the low and middle troposphere, but 14% positive bias at 200 hPa retrieval level. The new version 6 data significantly reduces the bias in the upper troposphere but magnifies the positive bias at the surface level. In this work, we decide to use the new version 6 data, as we focus on the free troposphere (above 800 hPa), which is not affected by the positive bias in the retrieval at the surface level.

2.3. OMI NO_2

The OMI instrument was also launched on NASA's Aura spacecraft. The sensor has a spatial resolution of 13 km x 24 km (Levelt et al. 2006). OMI provides daily global coverage with measurements of both direct and atmosphere-backscattered sunlight in the ultraviolet-visible range from 270 to 500 nm; 405-465 nm is used to retrieve tropospheric NO_2 columns. In this study, the daily level-2 data from KNMI DOMINO-2 product (Boersma et al. 2011) are averaged to obtain monthly mean vertical column densities (VCDs) for subsequent emission inversion. The total error for the retrievaled VCDs is about 30% plus $0.7x10^{15}$ molec/cm$_2$, and the magnitude is larger in winter than in summer (Boersma et al. 2011, Lin and McElroy 2011). The pixels with cloud radiance fraction exceeding 50% are removed. In order to have a better analysis of the spatial distribution of VCDs within short distance, we only uses data from the 30 pixels around the swath center. The details for the data treatment are described in Lin (2012).

2.4. GEOS-Chem

The GEOS-Chem CTM (http://www.geos-chem.org) is driven by assimilated meteorological observation from the NASA Goddard Earth Observing System (GEOS-5) at the Global Modeling and data Assimilation Office. We use version v34 of the GEOS-Chem adjoint, which is based on v8-02-01 of GEOS-Chem, with relevant updates through v9-01-01. The standard GEOS-Chem chemistry mechanism includes 43 tracers, which can simulate detailed tropospheric O_3-NO_x-hydrocarbon chemistry, including the radiative and heterogeneous effects of aerosols. The GEOS-5 meteorological fields have 72 vertical levels and the lowest 31 levels are terrain following levels. In order to minimize the amount of memory required to run GEOS–Chem, the model is run with a reduced vertical resolution, in which the levels in the stratosphere are lumped together online.

The native horizontal resolution of GEOS-5 is 0.5º x 0.667º, but it is usually degraded to 4°x5° or 2°x2.5° in global scale simulations. A nested simulation can be achieved by running a 0.5º x 0.667º resolution model within a regional domain using the boundary condition provided from a global, coarse resolution mode (Wang et al. 2004; Chen et al. 2009). Recently, the adjoint of nested GEOS-Chem was developed by Jiang et al. (2014). In this work, following Jiang et al. (2014) and Mao et al. (2014), we run the model with 0.5º x 0.667º resolution over Asia. The boundary condition is generated with a global-scale 4°x5° resolution simulation.

The anthropogenic emission inventories are identical to those used in Jiang et al. (2013). The global anthropogenic emission inventory is EDGAR 3.2FT2000 (Olivier et al., 2001), updated by the following regional emission inventories: the INTEX-B Asia emissions inventory for 2006 (Zhang et al., 2009b), the Cooperative Program for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP) inventory for Europe in 2000

(Vestreng et al., 2002), the US Environmental Protection Agency National Emission Inventory (NEI) for 2005 in North America, the Criteria Air Contaminants (CAC) inventory for Canada, and the Big Bend Regional Aerosol and Visibility Observational (BRAVO) Study Emissions Inventory for Mexico (Kuhns et al., 2003). Biomass burning emissions are from the inter-annual GFED3 inventory with 3-hour resolution (van der Werf et al., 2010). The biogenic emissions are from MEGAN 2.0 (Millet et al. 2008). Figure 1 shows the anthropogenic emission of NO_x and CO in Asia in June 2006. There are strong pollutant emissions in the North China Plain. The urban emission centers can also be clearly identified. The annual anthropogenic NO_x emission over Eastern China is 16.5Tg (2006) and 20.7Tg (2010), with a 5% annual growth rate.

3. Inversion Approach

3.1. 4DVAR inversion for global CO emission

In this work, we evaluate the observed interannual variability of O_3 and CO and the GEOS-Chem model simulation for the period of 2006 to 2010, where the data density of TES measurements is higher relative to subsequent years. As the first year of this five-year period, the relative contributions of O_3 precursors to free troposphere O_3 in 2006 will be studied in detail. The 2006 global CO emissions are optimized with a 4DVAR method. The inverse method minimizes the cost function $J(\mathbf{x})$ to provide an optimal estimate of the CO sources,

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$$J(\mathbf{x}) = (\mathbf{F(x)} - \mathbf{y})^{\mathrm{T}} \mathbf{S}_{\Sigma}^{-1} (\mathbf{F(x)} - \mathbf{y}) + (\mathbf{x} - \mathbf{x}_a)^{\mathrm{T}} \mathbf{S}_a^{-1} (\mathbf{x} - \mathbf{x}_a) \quad (3)$$

where $\mathbf{x}$ is the state vector of emissions, $\mathbf{x}_a$ is the a priori estimate, $\mathbf{y}$ is a vector of observed concentrations, and $\mathbf{F(x)}$ is the forward model, which represents the transport of the CO emissions in the GEOS-Chem model and accounts for the vertical smoothing of the MOPITT retrieval. $\mathbf{S}_{\Sigma}$ and $\mathbf{S}_a$ are the observational and a priori error covariance matrices, respectively.

221 The first term of the cost function represents the mismatch between the simulated and observed
222 concentrations. The second term represents the departure of the estimate from the a priori.
223 The cost function in Equation 3 is minimized by reducing the gradient, $\partial J/\partial x$, using the
224 adjoint of GEOS-Chem model in a 4DVAR approach (Henze et al., 2007), which has been
225 previously used for assimilation of CO and O_3 (Kopacz et al., 2010; Singh et al. 2011; Parrington
226 et al., 2012; Jiang et al., 2014b). Similar as in Jiang et al. (2013, 2014b), we produce improved
227 initial conditions by assimilating MOPITT version 6 data, using the sequential sub-optimal
228 Kalman filter (Parrington et al. 2008), from 1 January 2006 to 1 January 2007. The optimized
229 initial conditions are archived at the beginning of each month. Consequently, the initial
230 conditions for the model simulation are independent from the inverse analyses.
231 **3.2. Regression-based inversion for China NO_x emissions**
232 The 2006 Chinese NO_x emissions are optimized with a regression-based multi-step
233 method exploiting the distinctive seasonality of different sources (Lin 2012). Neglecting
234 horizontal transport and assuming a linear relationship between the total VCD of NO_2 and VCDs
235 from individual sources, the predicted VCD (Ω_p) for a given grid can be expressed as the sum
236 of individual emission sources, multiplied by certain scaling factors:
237 $$\Omega_p = k_a\Omega_a + k_l\Omega_l + k_s\Omega_s + k_b\Omega_b \quad (4)$$
238 The subscripts "a", "l", "s", and "b" indicate anthropogenic, lightning, soil and biomass burning
239 sources of NO_x, respectively. The updated emission estimates can be obtained by reducing the
240 sum of $[(\Omega_r - \Omega_p)/\sigma]^2$ across the 12 months; here Ω_r is the retrieved VCD and σ is the
241 standard deviation. To better represent the resolution-dependent NO_x chemistry (Valin et al.
242 2011), the inversion was conducted with the highest resolution of GEOS-Chem. The seasonality-
243 based inversion method also reduced the influence of potential biases in OMI NO_2 data (Lin et al.

2014b), particularly in winter. The details for the inversion process were described in Lin (2012).

4. Results and Discussion

4.1. Evaluation of the model simulation and top-down estimates of O_3 precursors

In this work, we are interested in the domain of East China, as shown in Figure 1, because it is the largest pollutant emission contributor in East Asia and the adjacent domain where outflow of Asian pollution is significant. Figure 2 shows the monthly regional mean O_3 and CO concentration at free troposhere (681 - 383 hPa) for June, July and August for the period 2006-2010, using the GEOS-Chem model driven with a priori emission inventories. The modeled O_3 concentrations are generally within 10% of the TES data after accounting for the approximately 7 ppb bias in the TES O_3 measurements (e.g., H. Worden et al., 2007, Verstraeten et al., 2013). On the other hand, the modeled CO is biased low, which is consistent with previous studies (Shindell et al. 2006, Kopacz et al. 2010, Naik et al. 2013). This low bias could be associated with a positive bias in OH, as indicated by Jiang et al. (2014b). The bias in CO can be reduced by integrating the coarse-resolution global and fine-resolution nested simulations in a two-way coupled manner, such that results from the nested model can be used to improve the global model (within the nested domain) and ultimately affect its lateral boundary conditions (via the global transport of CO and other species) (Yan et al. 2014). Another possible reason for the CO bias is that the TES CO data are biased towards polluted air parcels because of its relatively low sensitivity whereas the model captures background values as discussed in Pechony et al. (2013). Although the model is biased low, the interannual variabilities and trends of O_3 and CO are well correlated between the model and TES, indicating that changes in the modeled emissions, chemical production of ozone, and meterology are well described (e.g., Zhang et al., 2006; Kim et al., 2013).

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O_3-CO correlations can be used to constrain O_3 sources and transport (e.g., Zhang et al., 2006). Positive correlations usually indicate that a region has experienced photochemical O_3 production, whereas negative correlations may result from O_3 chemical loss or influence of stratospheric air. For example, Zhang et al. (2006) demonstrated that TES data can be used to examine global distribution of O_3-CO correlations. Voulgarakis et al. (2011) found significant positive correlations in the northern Pacific during the summer of 2005-2008. Kim et al. (2013) used OMI O_3 and AIRS CO to show that the GEOS-Chem model is able to reproduce the observed O_3-CO correlations and slopes in western Pacific, but failed in some tropical regions due to model transport error associated with deep convection.

Table 1 shows the monthly regional mean O_3 and CO correlation and slope values for the free troposphere (825 - 383 hPa) for June, July and August 2006-2010; the model is driven by a priori emissions. The uncertainty in the O_3 and CO concentrations are due to random errors in the TES O_3 and CO observations and natural variability (Zhang et al., 2006). For this reason, we also show the mean value over the analysis time period. The correlation and slope values of TES and GEOS-Chem are generally consistent for both domains. The positive correlation coefficients imply influence of photochemical O_3 production, but also transport of nearby CO emissions into pollution plumes (e.g., Worden *et al.*, 2013). As in previous studies (Zhang et al. 2006; Voulgarakis et al. 2011; Kim et al. 2013), there are small differences between the simulation and observation. A possible reason for these discrepancies, particularly over the ocean, is the model transport error because transport of "clean" air from the Pacific can have substantially different chemical charateristics from Asian air.

The consistency between model and TES in the interannual varations, correlation coefficients and slopes implies that the spatio-temporal distribution of the CO emissions and

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oxidative chemical processes are consistent. As described in Section 3, the 2006 global CO emission are constrained with MOPITT data; the 2006 Chinese NO_x emission are constrained with OMI data. As shown in Figure 3, Chinese *posterior* anthropogenic NO_x emissions in June 2006 are increased by 14% over the *a priori* emissions, from 1.86 Tg to 2.11 Tg. Smaller adjustments are obtained for winter. In June 2006, the Chinese anthropogenic CO emissions are increased from 17.09 Tg to 18.93 Tg, with a mean scaling factor of 1.11. In December 2005, the Chinese *posterior* anthropogenic CO emission is increased over the *prior* from 14.95 Tg to 19.78 Tg. However, as indicated by Jiang et al. (2014b), a potential bias in OH fields could have a significant influence on the inferred CO emission estimates. By using the OH fields from a different GEOS-Chem version, they found that a posteriori CO emissions over East Asia in June - August 2004 are reduced by 28% for the different OH fields. This large potential error in the CO emissions do not strongly affect our conclusions because the modeled CO concentrations, based on the model OH distributions and CO emissions, are consistent with the MOPITT data.

The monthly regional mean O_3 and CO concentrations in the period of Dec 2005 -Nov 2006 are shown in Figure 4. In order to remove the influence of the initial conditions, the updated-simulation is obtained by running the model from 1 September 2005, with updated inventories of NO_x and CO. Both model and data shows increase of O_3 concentration from winter to spring, due to enhancement of photochemical production, and a substantial decrease in Jun – Aug, due to the effect of East Asian monsoon (Yang et al. 2014). The CO concentration peaks in March, which is consistent with Shindell et al. (2006). The boreal spring CO maximum is associated with the accumulation of CO emission in winter, while CO lifetime is longer (Ducan et al. 2007). The updated inventories significantly reduced the bias on the CO simulation. However, these changes in the NOx and CO emissions do not significantly change free-

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348 tropospheric ozone.

349 **4.2. Dependency of O_3 on anthropogenic and natural NO_x, CO and VOCs**

350 In this section, we will use the adjoint of the GEOS-Chem model (Henze et al., 2007) to
351 quantify source contributions (NO_x, CO, VOC) to free tropospheric O_3 pollution over East China
352 and the China Outflow region. The updated NO_x and CO emission inventories is intended to
353 improve the simulation. We are interested in these two domains as they have significant
354 influence on the long-range pollution transport (e.g., Zhang et al., 2009a). Similar to previous
355 studies (Zhang et al. 2009; Bowman et al. 2012; Lapina et al. 2014), the analysis is based on a
356 sensitivity calculation from an adjoint model. In this work, both transport and chemistry
357 components are run backwards and thus provide a more computationally efficient method for a
358 receptor-oriented problem than the traditional approach by perturbing emissions.

359 Figure 5 shows the contributions of anthropogenic NO_x, lightning NO_x, anthropogenic
360 CO and biogenic isoprene on free tropospheric (819 - 396 hPa) O_3 over eastern China. The value
361 can be explained as the percentage change of regional mean O_3 due to a fractional change in
362 emissions in a particular grid. For example, assuming an unchanged chemical environment, one
363 particular grid with contribution 0.02% implies mean free tropospheric O_3 over eastern China
364 will be increased by 0.02%, if the NO_x emission in this gird is increased by 100%. The result
365 shows that anthropogenic NO_x contributes significantly to the O_3 distribution in this region.
366 Although the influence of lightning NO_x is weaker, the larger geographical distribution of
367 lightning NO_x makes it an important source. The contribution of anthropogenic CO is mainly
368 from China, whereas Southeast Asia is the major contributor of biogenic isoprene with a
369 negative sensitivity. Assuming anthropogenic CO is a proxy of anthropogenic hydrocarbons and
370 biogenic isoprene is a proxy of biogenic hydrocarbons, these sensitivity calculations indicates

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that China is a major source of anthropogenic hydrocarbons while Southeast Asia is the major source of biogenic hydrocarbons. As shown in Figure 1, the North China Plain has strong NO_x emission, but its effect on O_3 is not significant. On the other hand, Eastern China free-tropospheric O_3 is more directly sensitive to CO emission from North China Plain. The contribution of CO to ozone production (3rd set of panels in Figure 5) is similar to the CO emission distribution. Discrepancies exist between the spatial distribution of the sensitivity of ozone to NO_x and CO. For example, the sensitivity of ozone to NO_x in the Bejing area is relatively small because there is too much NO_x, thus limiting ozone production. Martin et al. (2004) showed that an increase of NO_x emission over northeast China in summer will decrease surface O_3 concentration, which is opposite with the positive sensitivity in this work. This difference could be associated with the larger concentrations of VOC levels (e.g., Martin et al. 2006; Zhang et al. 2014) and because the sensitivities shown in Figure 5 depend on both surface ozone production and ozone production in the free-troposphere, which is more NOx limited.

It should be reminded that the sensitivity of ozone to biogenic isoprene is highly dependent on the isoprene chemistry scheme, as indicated by Mao et al. (2013). They demonstrated that the sensitivity of surface O_3 concentration over southeast United States on isoprene could change sign, from negative to positive, with two different isoprene schemes. However, as shown in Figure 5 the influence of the isoprene scheme on free tropospheric O_3 is small relative to that from NOx so that we do not expect that errors in the isoprene scheme to significantly alter our conclusions. These results are consistent with Mao et al. (2013) as they show that a change in sign in the sensitivity of ozone to isoprene only affected their surface ozone concentrations by 2 ppb or less and therefore an even smaller effect on free-tropospheric ozone concentrations.

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The contributions to the free tropospheric ozone in the the China Outflow region are shown in Figure 6. The O_3 distribution is more sensitive to the anthropogenic NO_x emission from the coast rather than from the inland continent. The sensitivity hotspots clearly show a northeastward movement as the season progresses, from Southeast China (June) to Korea and Japan (August), reflecting the influence of the East Asia monsoon.

To understand the seasonal variation of O_3 production efficiency, we calculated the global scale sensitivities of anthropogenic and lightning NO_x during December 2005 – November 2006 with 4°x5° resolution. The values of sensitivities, as shown in Figure 7, are significantly larger than those in Figure 5 and Figure 6, due to the change of grid size and smaller effect from initial condition. The sensitivity of O_3 to anthropogenic NO_x, has a marked seasonal variation, increasing from the Northern Hemisphere winter to the summer. Kondo et al. (2008) found the slope of East Asia O_3 formation to NO_x is proportional to HO_2 and thus increases from winter to spring. Increased solar radiation is another reason for the high O_3 production rate in the summer. Figure 7 also highlights the effect of anthropogenic NO_x from southwest China, showing a significant effect on free troposphere O_3 over eastern China, particularly in September-November. Similar to anthropogenic NO_x, the contribution of lightning NO_x is maximum in the Northern Hemisphere summer, partly associated with the East Asia monsoon. The sensitivities of O_3 over eastern China and the China Outflow region have similar distributions, although the China Outflow O_3 is more sensitive to coastal emissions.

Table 2 shows the regional total contributions of anthropogenic and lightning NO_x, calculated by summing the sensitivities shown in Figure 7. Assuming an unchanged chemical environment, it can be explained as the percentage change of regional mean O_3 due to 100% change in NO_x emission. For example, a 100% increase of Chinese anthropogenic NO_x emission

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in June-August 2006 will result in 10.2% increase of tropospheric mean O_3 over eastern China. Of course, the result of an actual 100% change of NO_x will be different to quantify because of non-linear chemistry. Furthermore, this sensitivity depends on the modeled transport and the robustness of the chemical production of ozone. For example, if the production of ozone is too "fast" then the sensitivity of free-tropospheric ozone to surface emissions is too small as too much ozone is produced in the boundary layer (where loss-mechanisms dominate) versus the free-troposphere. To evaluate the sensitivities further, we enhanced Chinese anthropogenic NO_x emission by 10% uniformly as a perturbation. Using the initial conditions provided from standard simulation, the 3-month perturbation simulations are started on 1 December 2005, 1 March 2006, 1 June 2006 and 1 September 2006, individually. The relative difference of regional mean O_3, between the perturbation and standard simulations, is then multiplied by 10. As shown in Table 2, the results of two methods are highly consistent, which demonstrates our sensitivity analysis works well. Similar as Wild et al. (2012), the consistency also confirms that 10% NO_x perturbation gives a linear O_3 responses over East Asia. Considering the high computation efficiency, adjoint sensitivity analysis is thus a good alternative to the traditional perturbation method.

As shown in Table 2, the effect of increased Chinese anthropogenic NO_x on free tropospheric O_3 is limited. Assuming an unchanged chemical environment, a 100% increase of Chinese anthropogenic NO_x, during a 3-month period, will only result in 2.4% increase of free tropospheric O_3 in the winter and 10.2% in the summer, associated with the chemical environment of China, which is is more inclined to be VOC limited. Because of the long O_3 lifetime in the free troposphere, O_3 from initial conditions have a substantial influence on the distribution of ozone. A 15-month continous perturbation simulation, started on 1 September

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2005, will enhance the effect of Chinese anthropogenic NO_x to 3.0% in winter and 10.5% in summer.

Because of the rapid growth of pollutant emission, transpacific transport of Asian pollutant to North America has attractted significant attention (Zhang et al. 2008, 2009; Walker et al. 2010; Bertram et al. 2013; Lin et al. 2008, 2014a). The major transport mechanisms includes northeastward export of Asian pollution to about 50°N, and then cross the Pacific in midlatitude westerly winds (Liang et al. 2004, 2005). Over eastern China, the effect of anthrogogenic NO_x emission from the Rest of Asia (ROA) on free tropospheric O_3 is about 50% of Chinese local emission in winter and spring, whereas Chinese local emission dominates in the summer and fall. Our results show that the influence of ROA on O_3 pollution export is significant because the influence of ROA is comparable with Chinese emisisons in winter and about 50% of Chinese emissions in other seasons for the outflow region. The contribution of lightning NO_x over China is generally small relative to anthropogenic emisisons except during the summer (Table 2). The effect of ROA lightning NO_x is similar as the Chinese contribution but slightly larger.

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5. Summary

We quantified Asian O_3 and the contributions of its precursors, during the period December 2005 – November 2006, using the GEOS-Chem model and O_3 precursor observations of NO_2 from OMI and CO from MOPITT. The 2006 global CO emissions are constrained with a 4DVAR method, using MOPITT CO (version 6) measurements. In June 2006, the inversion increases the China anthropogenic CO emission by 11%. The 2006 China NO_x emission is constrained with a regression-based multi-step approach, using OMI data. In June 2006, the anthropogenic NO_x emission in China is increased by 14%.

The model simulation is evaluated with TES O_3 and CO observations. The modeled concentrations are underestimated for both O_3 and CO, but reproduces the O_3(CO) interannual varation. As with previous studies (Zhang et al. 2006; Voulgarakis et al. 2011; Kim et al. 2013), the modeled O_3-CO correlation and slope are consistent with the data. The updated inventories significantly reduces the bias relative to TES CO measurements. But the improvement on the O_3 simulation is not large (~1-2%). The good agreement between model O_3 and CO and its correlations with observations from TES demonstrate the reliability of the model simulation, the chemical scheme and the updated CO inventories.

We quantified source contributions (NO_x, CO, VOC) to free tropospheric O_3 pollution over East China and the China Outflow region with a sensitivity calculation approach. Our results show anthropogenic emissions from China is the major contributor on free tropospheric O_3 over Eastern Asia and corresponding outflow region. The anthropogenic emissions from the Rest-of-Asia (ROA) has an important influence on free tropospheric O_3 over this region. The observed seasonal variation in O_3 is due to the seasonal change in the O_3 production efficiency, related with HO_2 and solar radiation. The contributions of lightning NO_x to free-tropospheric O_3 from China and ROA is small, except in June-August due to the effect of the East Asia monsoon. Finally, our result shows that China is the major contributor of anthropogenic VOCs, whereas the influence of biogenic VOCs is mainly from Southeast Asia.

6. Acknowledgments.

Part of this research was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under a contract with the National Aeronautics and Space Administration. This Research was supported by the NASA ROSES Aura Science Team NNH10ZDA001N-AURA. Daven K. Henze was funded by NASA ACMAP NNX13AK86G. Willem W. Verstraeten was

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532 funded by the Netherlands Organization for Scientific Research, NWO Vidi grant 864.09.001.

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Tables and Figures

Table 1. Monthly regional mean O_3 and CO correlation and slope for the free troposphere (825 - 383 hPa) for June, July and August 2006-2010 for both TES and model (in the parentheses). The model values are sampled at TES measurement time and location and smoothed with the TES averaging kernels. The calculation of slope and correlation is based on individual measurements within a month. The numbers of measurements used to compute the correlations are shown in the supplemental. The right column is the mean value of 15 months.

Table 2. Regional total contributions of anthropogenic and lightning NO_x on free tropospheric (819 - 396 hPa) O_3 over eastern China and the China Outflow region. The value can be explained as the percentage change of regional mean O_3 (Eastern China, China Outflow) due to 100% increase of NO_x in a particular region (China and ROA). The regions of China and ROA (Rest of Asia) are defined in Figure 3. The perturbation values (Pt) are the relative difference between standard and perturbation simulations.

Figure 1. Anthropogenic emission of (a) NO_x and (b) CO in June 2006 as used in GEOS-Chem. The unit is molec/cm^2/s. The black box defines the domains studied in this work. The "East

China" domain includes the grids of Chinese mainland within the black box. The "China Outflow region" are grids within the black box, excluding the Chinese mainland.

Figure 2. Monthly regional mean O_3 and CO concentration at free troposphere (681 - 383 hPa) in June, July and August 2006-2010. Red line is GEOS-Chem model simulation with a priori emission inventories and black line is TES measurements. The model results are smoothed wth the TES averaging kernels. The TES ozone data are biased high by 7 ppbv.

Figure 3. (a) Scaling factors of anthropogenic NO_x for June 2006. (b) Scaling factor of total CO emission (combustion + oxidation from biogenic VOCs) for June 2006.

Figure 4. Monthly regional mean O_3 and CO concentration at free troposphere (681 - 383 hPa) in the period of Dec 2005 – Nov 2006. Red line is GEOS-Chem model simulation with a priori emission inventories. Blue line is model simulation with updated NO_x and CO emission inventories. Black line is TES measurements. The model results are smoothed wth the TES averaging kernels. The positive bias in the TES O_3 data is larger in summer and smaller in winter.

Figure 5. Contributions of anthropogenic NO_x, lightning NO_x, anthropogenic CO, biogenic isoprene on free tropospheric (819 - 396 hPa) O_3 over eastern China derived from the adjoint of GEOS-Chem in June, July and August 2006. The contributions can be explained as the percentage change of regional mean ozone due to a fractional change in the emissions in a particular grid assuming unchanged chemical environment. The numbers are the total of absolute value of pre-cursor contributions for the whole domain shown in the figures.

Figure 6. Contributions of anthropogenic NOx, lightning NOx, anthropogenic CO, biogenic isoprene on free tropospheric (819 - 396 hPa) O_3 over China Outflow region derived from the adjoint of GEOS-Chem in June, July and August 2006.

Figure 7. Contributions of anthropogenic NO_x and lightning NO_x on free tropospheric (819 - 396 hPa) O_3 over eastern China and China outflow region in December 2005 – November 2006.