We thank the reviewers for their thoughtful and detailed comments. Below we respond to the individual comments. In addition to the revisions discussed below, all figures (Figure 4, 5, 6, 7) and tables (Table 2), associated with sensitivity calculation, are recreated with the updated $NO_x$ and CO emission inventories. Its influence on the analysis is small.

**Reviewer #1**

*General comments*

**(1)** *As I mention below in one of the specific comments, the reader expects that the improved emission estimates that result from the information provided by the satellites (which are central to this study) would subsequently be used for the modelling in the sensitivity/attribution analysis performed later. This is also what the reader is left to believe in the abstract and in the conclusions (". . .we use satellite measurements. . .to quantify O3 precursor emissions for 2006 and their impact on free tropospheric O3. . ."; also first sentence of the Summary). However, on Page 19525, Lines 12-15, it is mentioned that this is not the case. This seems somewhat contradictory, given that the satellite information is apparently used to improve the emissions estimates. Could the authors perhaps include some discussion/evidence (in addition to the sentence on Lines 14-15 on that page) on how the main conclusions of the sensitivity analysis might have changed had the top-down emissions been used?*

Thanks for catching this issue. We have repeated our calculation by driving the model with the updated $NO_x$ and CO emission inventories. All figures, tables and discussions, associated with the sensitivity calculation, are replaced with the new results. The influence of these updates on the analysis is small.

**(2)** *Since the sensitivity/attribution analysis has been done for all seasons, it would have made more sense to evaluate the model for seasons outside of the summer as well. If that is too difficult at this stage, could you at least include some discussion on known model biases (e.g. based on previous studies) for non-summer seasons?*

Thanks for this suggestion! A new figure (Figure 4) was added to evaluate the model simulation. The bias in the CO simulation is significantly reduced. The improvement on the $O_3$ simulation is not significant suggesting that free-tropospheric ozone in the geos-chem model is not significantly sensitive changes in $NO_x$ and CO emissions.

*Specific Comments:*

**(1)** *Page 19516, Line 20: If not referring to statistical significance, please use the word "sizeable" or something equivalent.*

Thanks! It has been changed.

**(2)** *Page 19517, Line 2: Please change "there is" to "there was".*

Thanks! It has been changed.

**(3)** *Page 19517, Line 17: Why evaluate only then, if the model is going to be used for studying the whole year (see general comment above)?*

Thanks for your suggestion! All figures and tables have been updated.

**(4)** *Page 19518, Lines 15-16: Why only for CO?*

We use DOFS for CO as a metric for sensitivity of the data as 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. The description has been changed.

**(5)** *Section 2.1 (general): Worth mentioning here any known biases for TES ozone and CO in this version. That said, which version of the data is being used?*

Thanks! More description has been added.

**(6)** *Page 19519, Lines 6-7: Is this the same a priori as for TES? Please mention.*

Thanks! It has been changed.

**(7)** *Section 2.3 (general): Any known biases for this product? Please outline.*

Thanks! It has been changed.

**(8)** *Page 19521, Lines 4-5: Please explain why 2006 was selected? Perhaps due to data availability/quality?*

The major reason is that the data density of TES measurement is higher in 2006-2010. We focused on 2006 just because it is the first year of this five-year period. Explanation has been added.

**(9)** *Page 19523, Lines 5-6: Please rephrase to "We will also study the adjacent domain. . ."*

Thanks! It has been changed.

**(10)** *Page 19523, Line 8: Please rephrase to ". . ., using the GEOS-Chem model driven with a priori emission inventories."*

Thanks! It has been changed.

**(11)** *Page 19523, Lines 9-10: Is this 7ppb adjustment made for the comparison shown in Fig. 2? I presume no, but this needs to be clarified.*

We didn't remove the 7 ppb bias in the TES $O_3$ measurements. The reason is the World Ozone and Ultra-violet Radiation Data Centre (WOUDC) sites used in the validation (Verstraeten et al., 2013) are mainly located in Europe. The validation also shows larger bias in summer (8 ppb) and smaller bias in winter (5 ppb). It may not be an accurate evaluation for East Asia. Explanation has been added.

**(12)** *Page 19523, Line 11: Worth mentioning here that such negative biases for CO are common in present-day modelling (e.g. see Fig. 2 of Naik et al., 2013).*

More citations have been included.

**(13)** *Page 19523, Lines 19-21: Ozone and CO interannual variabilities and trends seem to be well correlated on Fig. 2. That is worth mentioning as well somewhere around here.*

We have added more description.

**(14)** *Figure 2 (general comment): The fact that with such CO biases ozone is still captured relatively ok (at least for July-August) implies that there may be biases in other aspects of the simulation that compensate for the CO influences. Please comment.*

According to new Figure 4, 10-20% change on CO emission can significantly reduce the bias on CO. The sensitivity of $O_3$ on CO is only about 20% of $O_3$ on $NO_x$ (Figure 5, 6), which means 20% change on CO emission can only result in 0.2 ppb change on $O_3$ concentration. Thus, it seems that the influence of CO bias on $O_3$ is very small.

**(15)** *Table 1: There are no red colors appearing. Also: Are the slopes/correlations calculated using daily mean values? Please mention.*

The model values are sampled at TES measurement time and location rather than daily mean values. Description has been added in the Caption.

**(16)** *Page 19524, Lines 13-16: Not clear from Table 1 that there are larger discrepancies over the ocean (outflow region). Looking at the mean values, slopes disagree more with TES in the outflow region but correlations look somewhat better there.*

Thanks for your comment! The discrepancies between TES/Model are larger for the outflow region in special months. However, as you indicated, it makes more sense to only compare the mean values because the data is sparse. The statement about the "larger discrepancies over the ocean" has been removed.

**(17)** *Page 19524, Lines 17-19: Suggested rephrasing: ". . .implies that the model captures oxidant-related processes well over East Asia and Northwest Pacific (or Asian outflow region)."*

Changed.

**(18-1)** *Page 19525, Line 6: Are the authors referring to the NOx emissions here? Not clear.*

**(18-2)** *Page 19525, Lines 7-9: The meaning of this sentence is somewhat non-transparent and does not follow from any previous discussion. Please expand and explain further.*

**(18-3)** *Page 19525, Lines 12-15: This could confuse a reader: the earlier text makes one think that the top-down estimates are made in order to get improved a posteriori emissions. Why would they then be ignored?*

We have repeated our calculation by using the updated inventories. This paragraph has been completely rewritten.

**(19)** *Page 19526, Lines 4-9: Are there any ideas on why the contribution from CO comes mainly from further north in China compared to the NOx contribution (see Fig. 4)?*

A very good question! Our speculation is North China Plain is more inclined to be VOC limited and therefore is not sensitive to $NO_x$ emission. On the other hand, it is sensitive to CO emission from this region. More discussion has been added.

**(20)** *Page 19528, Lines 2-3: Why are VOC sensitivities not shown on Table 2?*

It would be a good idea to have a sufficient estimation for VOCs. Unfortunately, the current model only allows us to calculate the sensitivity on biogenic isoprene. The values, based on biogenic isoprene, will be much smaller than the actual value based on total VOCs. For this reason, we believe it is not suitable to compare it with sensitivity on $NO_x$ directly.

**(21)** *Page 19528, Line 9: ROA has not been defined earlier.*

Changed.

**(22)** *Page 19529, Lines 18-19: The fact that Chinese NOx emissions have the largest contribution needs to be mentioned first. As it reads currently it may mislead the reader to believe that ROA emissions are more important than those from China.*

The discussion has been modified.

**(23)** *Page 19529, Lines 19-20: I agree that there will be some consequences for North America, but they have not been demonstrated here, so I suggest removing that part of*

*the sentence or writing something like "with potential implications for background O3 concentrations of North America".*

The discussion has been modified.

**Reviewer #2**

*General comments*

**(1)** *The opening sentence of the abstract sets the stage for a discussion of the rising Asian anthropogenic ozone precursors on tropospheric ozone, yet this is absent from much of the rest of the paper. From Figure 2, the year-to-year increases in ozone and CO in June and to some extent July over E China do not seem to be transported into the outflow region. Does this imply that even if Asian emissions are increasing, the impact is regional and not detectable downwind? Some discussion of the findings of this paper in the context of rising emission trends seems warranted. What are the reported changes in Chinese emission from 2006-2010 and to what extent are these incorporated into the model?*

In the period of Jun – Aug, East Asia is strongly affected by East Asian monsoon. The pollution was transported more northwardly rather than eastwardly, and consequently, the correlation between Eastern China and China outflow is low. However, according to our test, the effect is still detectable downwind.

Most recent studies believe the annual growth rate of Chinese $NO_x$ emission is 5-10%. In the GEOS-Chem model, the Eastern China (107.5-122.5E 20-44N) annual anthropogenic $NO_x$ emission is 16.5Tg (2006) and 20.7Tg (2010), with a 5% annual growth rate. These numbers have been added in the discussion.

**(2)** *It's not clear how much data is actually available from TES to construct the regional monthly means examined here. Table 1 should include the sample sizes. Is the model being sampled consistently with TES? Are any revisions to understanding based on earlier ozone-CO work needed based on the findings here?*

The model values are sampled at TES measurement time and location. Because TES data is sparse, the uncertainty in the monthly slope/correlation could be large. In a recent work, Voulgarakis et al. (2011) used multi-year seasonal mean value. Similar as Voulgarakis et al. (2011), we also calculated mean value, which is more reliable than the monthly mean.

The major objective of this work is the partition between natural and anthropogenic $O_3$ precursors. However, we need to ensure the chemical transport model can provide a good $O_3$ simulation. The analysis about $O_3$-CO slope/correlation and the top-down CO/$NO_x$

estimations are all designed to evaluate the model. The analysis about $O_3$-CO slope/correlation itself has no significant difference with previous works.

Voulgarakis, A., Telford, P. J., Aghedo, A. M., Braesicke, P., Faluvegi, G., Abraham, N. L., Bowman, K. W., Pyle, J. A., and Shindell, D. T.: Global multi-year O3–CO correlation patterns from models and TES satellite observations, Atmos. Chem. Phys., 11, 5819–5838, doi:10.5194/acp-11-5819-2011, 2011.

**(3)** *How do the findings for 2006 regarding model biases, and the emission updates needed to match the satellite data, compare with earlier studies using satellite and aircraft data from the NASA INTEX-B field campaign (April-May 2006)? In general, more context could be provided to state clearly the new contributions from this paper beyond prior work focused on this region.*

Kopacz et al. (2010) did a CO inversion using the same emission inventory as this work. Using the identical inversion approach as this work, we (Jiang et al. 2014) compared the inversion results and found the seasonal variation of the a posteriori combustion emissions of Jiang et al. (2014) is consistent with the results of Kopacz et al. (2010). A complete discussion about the emission inventories may not be suitable here as it is beyond the scope of this paper.

Kopacz, M., Jacob, D. J., Fisher, J. A., Logan, J. A., Zhang, L., Megretskaia, I. A., Yantosca, R. M., Singh, K., Henze, D. K., Burrows, J. P., Buchwitz, M., Khlystova, I., McMillan, W. W., Gille, J. C., Edwards, D. P., Eldering, A., Thouret, V. and Nedelec, P.: Global estimates of CO sources with high resolution by adjoint inversion of multiple satellite datasets (MOPITT, AIRS, SCIAMACHY, TES), Atmos. Chem. Phys.,10, 855-876, doi:10.5194/acp-10-855-2010, 2010.

Jiang, Z., Jones, D. B. A., Henze, D., Worden, H: Sensitivity of inferred regional CO source estimates to the vertical structure in CO as observed by MOPITT, Atmos. Chem. Phys. Discuss., 14, 22939-22984, doi:10.5194/acpd-14-22939-2014, 2014.

**(4)** *The seasonal variation in the ozone chemical regime discussed here could be compared with earlier work (e.g., Martin, R. V., A. M. Fiore, and A. Van Donkelaar (2004), Space-based diagnosis of surface ozone sensitivity to anthropogenic emissions, Geophys. Res. Lett., 31, L06120, doi:10.1029/2004GL019416) Has there been a change detected in the seasonality of the ozone chemistry due to changing emissions over the past decade(s)?*

Thanks for this interesting paper! Martin et al. (2004) showed that the chemical regime over northeast China near-surface levels is VOC limited in summer and NOx limited in winter. By checking the $O_3$ sensitivity in planetary boundary layer (PBL), this newer version of the GEOS-Chem model (relative to the model used in Martin *et al.* ) shows that the chemical regime over northeast China PBL is NOx limited in summer and VOC limited in winter, which is opposite with Martin et al. (2004). The reason for this difference is an interesting topic. However, discussion about the $O_3$ sensitivity in PBL in detail is beyond the scope of this paper as here we are focused on free-tropospheric ozone.

*Specific comments*

**(1)** *What year-to-year scaling is applied to the Chinese emissions from the INTEX-B 2006 base year inventory? Could the increases in the red line in June & July over E China be solely due to meteorological variability?*

The annual growth rate of Chinese anthropogenic $NO_x$ is 5% in the model. From Figure 2, the annual $O_3$ increase in June (E China) is about 3%, which seems larger than the expectation based on $NO_x$ increase. However, it is not a good idea to evaluate $O_3$ trend by using a single month. Because TES data is sparse, temporal and spatial representation errors could exist in the monthly mean. The influence of meteorological variability on the $O_3$ variation is an interesting question, which we hope to study in our next step.

**(2)** *The abstract comments on the seasonal variation of ozone; why not also the inter-annual variation? In the final sentence of the abstract, is this conclusion drawn from anthropogenic NOx contributions shown in Table 2 for the China outflow region? If so, it doesn't seem to hold for summer.*

Changed.

**(3)** *Is the 3-7 ppb noted here for Asian emission increases on western North American free tropospheric ozone referring to the 2003 to 2010 period? If so, what is the increase expected for the 2006-2010 period examined here, and is this consistent with Figure 2, and to what extent does it require chemical production to occur during trans-Pacific transport? Some discussion would need to be added to support the statement in the summary asserting that the emissions from ROA and E China influence background ozone over North America. Given the current analysis, that statement appears speculative and should be removed if evidence is not added to support it.*

The previous studies (Zhang et al. 2008 and Brown et al. 2011) focused on 2000-2006. As your indication, we didn't study the influence of East Asia $O_3$ pollution on US in this work, which will be the topic of our next step. The discussion in the summary part has been modified.

**(4)** *Why the summer focus here when spring is typically understood to be the season when Asian export peaks and has maximum impact on free tropospheric ozone and trans-Pacific transport (e.g., see www.htap.org reports from 2010 or 2007)?*

We focused on summer because we hope to observe the contribution of lightning $NO_x$ and the influence of East Asia monsoon on that. The contribution of East Asian lightning $NO_x$ is much smaller on other seasons.

**(5)** *Section 2.3. It seems appropriate to provide a short description of the data treatment.*

More description has been added.

**(6)** *If the Jiang et al. 2014ab are not yet available in ACPD, the relevant information for which they are being cited needs to be incorporated here.*

Jiang et al. 2014b has been published in ACPD and the reference list has been updated. We haven't submitted Jiang et al. 2014a yet, and thus the status has been changed to "in preparation." Fortunately, we published another paper using the same code recently. The citation has been added.

Mao, Y. H., Li, Q. B., Henze, D. K., Jiang, Z., Jones, D. B. A., Kopacz, M., He, C., Qi, L., Gao, M., Hao, W.-M., and Liou, K.-N.: Variational estimates of black carbon emissions in the western United States, Atmos. Chem. Phys. Discuss., 14, 21865-21916, doi:10.5194/acpd-14-21865-2014, 2014.

**(7)** *The assumption of a proportional relationship between emissions and $NO_2$ VCDs seems problematic for lightning NOx (and possibly biomass burning NOx), which would probably have longer lifetimes than NOx from the other sources.*

I agree with this point. Lin et al. 2012 has indicated that "any $NO_2$ molecule originating from lightning is 1.5 times as likely to be observed by OMI than a $NO_2$ molecule of anthropogenic origin". In this work, only the a posteriori anthropogenic NOx emission was used.

**(8)** *Section 4.1 Is the 7 ppb TES bias specific to the region/time period being studied here? Is this determined relative to ozone sondes?*

It is relative to ozone sondes. However, because the World Ozone and Ultra-violet Radiation Data Centre (WOUDC) sites used in the validation (Verstraeten et al., 2013) are mainly located in Europe, and consequently it may not be an accurate evaluation for East Asia. More discussion has been added.

**(9)** *How are the correlations in Table 1 calculated? Is the regional average first calculated for ozone and CO, and then the correlation is done for daily regional means? See also comment G3.*

The model values are sampled at TES measurement time and location rather than daily mean values. Description has been added in the Caption.

**(10)** *The conclusion of consistency between model and TES ozone-CO relationships (p19524) is subjective. It looks like in 5 out of 12 examples over E China, the model and TES suggest opposite signed changes from year to year. The abstract discusses seasonal variations, but the year-to-year changes seem more relevant given the motivation of rising emission trends.*

The consistency between model and TES CO is really not satisfying. We speculate a possible reason is: "the TES CO data are biased towards polluted air parcels because of its relatively low sensitivity whereas the model captures background values", which is normal in the comparison between model and measurements, particularly when the measurements are sparse. Fortunately, the consistency on $O_3$ is much better. The abstract has been changed.

(**11**) *In terms of the optimized emissions in Fig 1, how do we know this isn't correcting for the OH bias discussed in the text? Is there seasonal variation in anthropogenic emissions in the model?*

A very good question! The bias in OH has significant influence on the estimation of CO emission. In Jiang et al. 2014, we evaluated its effect in detail. We will try to improve our results with a full-chemistry inversion in next step. The seasonal variation in the anthropogenic emission is small in the a priori emission inventory, as shown in Jiang et al. 2014.

Jiang, Z., Jones, D. B. A., Henze, D., Worden, H: Sensitivity of inferred regional CO source estimates to the vertical structure in CO as observed by MOPITT, Atmos. Chem. Phys. Discuss., 14, 22939-22984, doi:10.5194/acpd-14-22939-2014, 2014.

**(12)** *Figure 4 suggests a similar spatial pattern for lightning and anthropogenic NOx so how is this a clean separation of anthropogenic vs. natural?*

In the adjoint model, both transport and chemistry components are run backwards. The $O_3$ in free troposphere will be transported to where it is produced and then be converted to $NO_2$. Because anthropogenic and lightning NOx has different altitude, they are able to be distinguished.

(**13**) *Please explain why the chemical scheme is sufficient to evaluate this partitioning on the evidence of a small relative bias (Section 4.1 p 19525). The language in the final paragraph of 4.1 is confusing.*

A very good question! It may not suitable to say the "the chemical scheme is sufficient" as there are still potential issues in it. The discussion has been rewritten.

**(14)** *P19526 statement referring to Mao et al. 2013. Please comment as to what current understanding suggests and whether the effects seen in Figures 4 and 5, showing ozone decreases associated with isoprene emissions, are consistent with this understanding.*

Mao et al. 2013 demonstrated the sensitivity of surface $O_3$ concentration over southeast United States on isoprene could change sign, from negative to positive, with two different isoprene scheme. It implies the sensitivity to biogenic isoprene is highly dependent on the isoprene chemistry scheme. More discussion has been added.

**(15)** *Where did we see the anthropogenic VOC contribution from China (P19529 L 24-25)?*

The current model only allows us to calculate the sensitivity of $O_3$ on anthropogenic CO and biogenic isoprene, as shown in Figure 5 and 6. The conclusion is obtained by assuming anthropogenic CO is a proxy of anthropogenic VOC and biogenic isoprene is a proxy of biogenic VOC. Thus, in Page 19526, we have: "It implies China is the major source of anthropogenic hydrocarbons and Southeast Asia is the major source of biogenic hydrocarbons". We have added more discussion about it.

*Technical comments*

**(1)** *Please provide a short description of what a major quality flag equals 1 means.*

We use only those data for which the "speciesretrievalqualityflag" is set to one in the data products. 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. Description has been added.

**(2)** *For the MOPITT a priori, are the MOZART-4 fields averaged over the same 10 degree x 60 degree grid as for TES?*

The MOPITT a priori doesn't have the 10º latitude x 60º longitude average. The description has been changed.

**(3)** *Section 2.2 please define what is meant by free troposphere; which retrieval levels are examined?*

Thanks! It has been changed.

**(4)** *Figures 4,5,6 should state the year for the adjoint calculations (2006)?*

Thanks! It has been changed.

**(5)** *Figure 2, is the model red line also smoothed with the TES AK?*

Yes, the model is smoothed with TES AK. The caption has been changed.

# 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 show that the modeled seasonal and interannual variation of $O_3$ based on these updated $O_3$ pre-cursor emissions is consistent with the observed $O_3$ variability and amount, after accounting for known biases in the TES $O_3$ data. Using the adjoint of GEOS-Chem we then partition the relative contributions of natural and anthropogenic sources to free troposphere $O_3$ in this region. We find that the influence of lightning $NO_x$ is important in summer. The contribution from anthropogenic $NO_x$ is dominant in other seasons. China is the major contributor of anthropogenic VOCs (Volatile Organic Compounds), whereas the influence of biogenic VOCs is mainly from Southeast Asia. Our result shows that the influence of India and Southeast Asia emissions on $O_3$ pollution export is sizeable, comparable with Chinese emisisons in winter and about 50% of Chinese emissions in spring and fall.


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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 (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.

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## 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 10° latitude x 60° 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 the 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.

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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 are 7 ppb bias from the TES measurements in free troposphere, and the magnitude is larger in summer and smaller in winter. We didn't remove the 7 ppb bias from the TES measurements because the WOUDC sites used in the validation are mainly located in Europe, and consequently it may not be an accurate evaluation for East Asia. TES CO measurement was evaluated by Luo et al. (2007) using the aircraft measurents from INTEX-B campaingn. They showed that TES CO profile has good agreement with the aircraft data.

**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 10° latitude x 60° longitude average. We reject MOPITT data with CO column amounts less than $5x10^{17}$ molec/cm$^2$ and if low clouds are observed. The

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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.

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### 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

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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 will observe the interannual variability of $O_3$ and CO and evaluate the model simulation with TES measurements in the period of 2006 to 2010, while the data density of TES measurements is higher. 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. The first term of the cost function represents the mismatch between the simulated and observed concentrations. The second term represents the departure of the estimate from the a priori.

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The cost function in Equation 3 is minimized by reducing the gradient, $\partial J/\partial x$, using the

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adjoint of GEOS-Chem model in a 4DVAR approach (Henze et al., 2007), which has been previously used for assimilation of CO and $O_3$ (Kopacz et al., 2010; Singh et al. 2011; Parrington et al., 2012; Jiang et al., 2014b). Similar as in Jiang et al. (2013, 2014b), we produce improved initial conditions by assimilating MOPITT version 6 data, using the sequential sub-optimal Kalman filter (Parrington et al. 2008), from 1 January 2006 to 1 January 2007. The optimized initial conditions are archived at the beginning of each month. Consequently, the initial conditions for the model simulation are independent from the inverse analyses.

### 3.2. Regression-based inversion for China $NO_x$ emissions

The 2006 Chinese $NO_x$ emissions are optimized with a regression-based multi-step method exploiting the distinctive seasonality of different sources (Lin 2012). Neglecting horizontal transport and assuming a linear relationship between the total VCD of $NO_2$ and VCDs from individual sources, the predicted VCD ($\Omega_p$) for a given grid can be expressed as the sum of individual emission sources, multiplied by certain scaling factors:

$$\Omega_p = k_a\Omega_a + k_l\Omega_l + k_s\Omega_s + k_b\Omega_b \quad (4)$$

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The subscripts "a", "l", "s", and "b" indicate anthropogenic, lightning, soil and biomass burning sources of $NO_x$, respectively. The updated emission estimates can be obtained by reducing the sum of $[(\Omega_r - \Omega_p)/\sigma]^2$ across the 12 months; here $\Omega_r$ is the retrieved VCD and $\sigma$ is the standard deviation. To better represent the resolution-dependent $NO_x$ chemistry (Valin et al. 2011), the inversion was conducted with the highest resolution of GEOS-Chem. The seasonality-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. We will also study the adjacent domain where outflow of Asian pollution dominates. 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 could be associated with the positive bias in OH, as indicated by Jiang et al. ( 2014b). The bias 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 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. It indicats that changes in the modeled emissions and their chemical production of ozone are well described with the changes in the bottom up emissions.

$O_3$-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 $O_3$

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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, which become stronger from continent to the ocean outflow domains. As in previous studies (Zhang et al. 2006; Voulgarakis et al. 2011; Kim et al. 2013), there are small difference between the simulation and observation.

The consistency between model and TES in the interannual varations, correlation coefficients and slopes implies that the model captures oxidant-related processes well over East Asia and Northwest Pacific (or Asian outflow region). The next step is an evaluation of the uncertainties in the emission inventories. 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 anthropogenic $NO_x$ emission in June 2006 is enhanced by 14%, from 1.86 Tg to 2.11 Tg. Similar adjustment is obtained for winter with smaller magnitude.

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In June 2006, the Chinese anthropogenic CO emission is increased from 17.09 Tg to 18.93 Tg, with a mean scaling factor of 1.11. The small uncertainty in the CO emission in summer is consistent with Jiang et al. (2014b).

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 dramatically 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-tropospheric ozone.

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**Deleted:** January 2006, with updated inventories of $NO_x$ and CO. Over the China outflow region, the updated simulation reduces the bias relative to TES by 30% for CO and 20% for $O_3$. Over eastern China, the bias relative to TES is reduced by 40% for CO. It is not surprising to see the updated inventories had only a modest impact for $O_3$ since the agreement between the a priori and the observation was already good (to within 10% in June and better than 1% in July and August). The significant reduction in the relative bias provides confidence that the chemical scheme is sufficient to evaluate the partitioning of the natural and anthropogenic emissions.

### 4.2. Dependency of $O_3$ on anthropogenic and natural $NO_x$, CO and VOCs

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

traditional approach by perturbing emissions.

Figure 5 shows the contributions of anthropogenic $NO_x$, lightning $NO_x$, anthropogenic CO and biogenic isoprene on free tropospheric (819 - 396 hPa) $O_3$ over eastern China. The value can be explained as the percentage change of regional mean $O_3$ due to a fractional change in emissions in a particular grid. For example, assuming unchanged chemical environment, one particular grid with contribution 0.02% implies mean free tropospheric $O_3$ over eastern China will be increased by 0.02%, if the $NO_x$ emission in this gird is increased by 100%. The result shows that anthropogenic $NO_x$ contributes significantly to the $O_3$ distribution in this region. Although the influence of lightning $NO_x$ is weaker, the larger geographical distribution of lightning $NO_x$ makes it an important source. The contribution of anthropogenic CO is mainly from China, whereas Southeast Asia is the major contributor of biogenic isoprene with a negative sensitivity. Assuming anthropogenic CO is a proxy of anthropogenic hydrocarbons and biogenic isoprene is a proxy of biogenic hydrocarbons, it implies China is the major source of anthropogenic hydrocarbons and Southeast Asia is the major source of biogenic hydrocarbons. As shown in Figure 1, North China Plain has strong $NO_x$ emission, but its effect on $O_3$ is not significant. On the other hand, Eastern China $O_3$ is sensitive to CO emission from North China Plain. The contribution of CO is marked consistent with the distribution of CO source. The obvious discrepancy between $NO_x$ and CO implies North China Plain is more inclined to VOC limited.

It should be reminded that the sensitivity 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 scheme. The contributions on the

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China Outflow region free troposphere $O_3$ 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 Korean 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, which will be discussed later. 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 unchanged chemical environment, it can be explained as the percentage change of regional mean $O_3$ due to 100% change in $NO_x$ emission with current $O_3$ production efficiency. For example, 100% increase of

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Chinese anthropogenic $NO_x$ emission 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 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 troposphere $O_3$ 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. Furthermore, $O_3$ distribution in initial conditions are not affected by the change of $NO_x$ emission. Because of the long $O_3$ lifetime in the free troposphere, $O_3$ from initial conditions have a substantial influence on the

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distribution of ozone. A 15-month continous perturbation simulation, started on 1 September 2005, will enhance the effect of Chinese anthropogenic $NO_x$ to 3.0% in winter and 10.5% in summer.

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. The large contribution of ROA is mainly due to the fact that free tropospheric (819 - 396 hPa) $O_3$ values are used in this analysis. According to our test, the boundary layer (surface – 819 hPa) $O_3$ is highly dependent on China local emission rather than long-range transport.

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). Our results show that the influence of ROA on $O_3$ pollution export is significant. In the China Outflow region, the influence of ROA is comparable with Chinese emisisons in winter and about 50% of Chinese emissions in other seasons. 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.

## 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

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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 was 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 quite well. 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 pronounced. 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 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 Aisa and consequently potential implication for background $O_3$ concentrations of North America. 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.

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## 6. Acknowledgments.

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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.

**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.

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