We thank the reviewers for their thoughtful comments. Modifications to the manuscript are indented and in blue (below).

Reviewer #2 Comments

Introduction

Page 4429, Lines 5-6. Cite the USEPA's Cross State Air Pollution Rule, http://www.epa.gov/crossstaterule/

The following text has been added:

> Recognizing that long range transport affects local compliance of federally mandated standards, the EPA enacted the Cross State Air Pollution Rule (CSAPR) http://www.epa.gov/crossstaterule which reduces the emissions of ozone precursors from power plants. Phase 1 of the CSAPR emissions budgets is scheduled for implementation in 2015.

Page 4429, Lines 15-20. This could be due to the fact that NOx does not always control ozone. It depends which regime the region is in. For example, ozone changes in urban areas are typically VOC driven, while those in rural are NOx driven (e.g. Tsimpidi et al., 2008; Choi et al., 2012).

> As we state in the paper "The results of this study may not be applicable to regions where production of ozone is VOC dominant, which occurs primarily in rural regions such as the so-called isoprene volcano of the Ozarks (Carlton and Baker, 2011) or regions of intense hydrocarbon processing such as Houston, Texas (Li et al., 2007)."

Page 4430, Lines 20-24. Any specific reason why the Eastern United States? It would be nice if the authors could add in a few references to justify this.

> The model domain for this study is the Eastern United States (i.e. most of the states eastward of the Mississippi river), a region that has been the focus of intense SIP modeling efforts by mid-Atlantic states and for which detailed emissions inventories and meteorological fields are readily available.

Methodology

Page 4430, Line 25. Where is the reference web-link for NASA's Aura satellite?

> This following link has been added.
>
> http://aura.gsfc.nasa.gov/.

Page 4430, Line 27. What is LT?

> The following has been added.
>
> ~13:40 local time (LT).

Page 4431, Lines 6-7. A few lines could explain this better to a layman reader.

OMI tropospheric column NO2 is calculated by subtracting the stratospheric signal from the observations of total column NO2. The method of determining the stratospheric component varies between the GSFC and DOMINO product and is explained in Buscela et al., (2013) and Boersma et al., (2007), respectively. GSFC assumes that total column NO_2 over regions with little expected tropospheric influence represents the stratospheric column. This field of stratospheric column NO_2 is interpolated over nearby regions of high surface pollution and removed from the total column NO_2 retrieval to determine tropospheric column NO_2. For the DOMINO product, data assimilation of OMI slant columns with the TM4 model determines the stratospheric subtraction.

Page 4431, Lines 23-24. What does this mean- that there are some assumptions going into the calculations in case of missing data?

OMI retrievals depend upon an initial, a priori, assumption of the shape of the NO_2 profile. This quality flag assures us the data we are using data that are not unduly influenced by the choice of a priori NO_2 profile.

Page 4432, Lines 20-22. References for these models?

The following references have been added to the text

United States Environmental Protection Agency: EPA's National Inventory Model (NMIM), A Consolidated Emissions Modeling System for MOBILE6 and NONROAD, Office of Transportation and Air Quality, EPA420-B-09-015, 2005.

United States Environmental Protection Agency: Technical Guidance on the Use of MOVES2010 for Emission Inventory Preparation in State Implementation Plans and Transportation Conformity, EPA-420-B-10-023, 2010.

Analysis and Results

Page 4436, Line 5. I suggest replace "bias" with "low predicted values". Technically, "low bias" indicates good agreement with in-situ measurements, which is definitely not the case here.

We agree and have made the change to: low predicted values

Page 4437, Lines 25-28. NEI was available for 1999 and 2002. Which NEI did Yu et al. use?The authors need to be clearly specific here. Did Yu et al. use one of the above mentioned versions projected to 2006? If yes, did they see the same CO/NOy ratio of ~2?

Please see next comment

Page 4438, Lines 1-3. Was CMAQ higher or in-situ measured higher? The previous lines indicate modeled higher, and here they indicate in-situ higher. The authors need to be consistent and state the facts clearly. Otherwise this is muddying the scientific discussion.

> As stated in Yu et al., 2012, the authors used 2001 NEI emissions for point and area scaled to 2006. Yu et al., state that these emissions are the same as used in Otte et al., 2005 who also specifically state that 2001 NEI emissions were used. We have checked the NEI website and found criteria pollutant emissions for 2001:
>
> http://www.epa.gov/ttn/chief/net/critsummary.html
>
> and emissions used for a 2001 modeling platform
>
> http://www.epa.gov/ttn/chief/emch/index.html#2001
>
> We assume these are the emissions used by Yu et al. and Otte et al.
>
> The following text has been added:
>
> This conclusion is in agreement with a study by Yu et al. (2012) who compared CMAQ simulations, using the CB4.2 chemical mechanism, to aircraft data acquired during the TexAQS/GoMACCS campaign. National Emissions Inventory (NEI) point and area sources for year 2001 were projected to 2006 and mobile emissions were generated from the EPA MOBILE6 model. Yu et al. report modeled CO ~10% greater than measured. However, the ratio of observed CO/NOy=26.9 (determined using values from Table 4, Yu et al., 2012) is roughly a factor of 2 higher than the CMAQ calculated ratio of CO/NOy=13.1.

Page 4443, Lines 13-17. The authors should mention that their measurement comparison was similar to Anderson et al.

> Implementation of a factor of 2 reduction in NO_x emissions from mobile sources, based on Anderson et al. (2014) and analysis of ground-based observations for summer 2007, decreases NO_2 in urban regions that have a high density of vehicular traffic, which improves the CMAQ representation of the ratio of urban to rural NO_2.

Conclusions

Page 4443, Line 20. Isn't this due to lower radiation? The authors should indicate that here.

> The reduction in isoprene, which leads to a decrease in RO_2, is caused by the diminished sensitivity of isoprene emissions to PAR in the newer version of MEGAN.

Reviewer #3 comments

General comments:

1. Authors insisted that CMAQ calculations tend to overestimate NO2 columns over urban areas but underestimate over rural regions of the eastern US. Although authors used the OMI NO2 columns and AKs, they never discussed the errors and uncertainty of the OMI NO2 columns and AKs. Both the OMI products are not perfectly "true values", but possibly contain significant errors. Authors almost disregarded these errors and uncertainties in the manuscript. The errors and uncertainties in the tropospheric NO2 retrieval from the OMI sensor vary with analysis regions (urban vs. rural areas) and seasons. The comparison analysis between CMAQ-estimated and OMI-retrieved NO2 columns over the urban and rural areas could be greatly influenced by these errors and uncertainties (e.g., Boersma et al., 2011; Lamsal et al., 2014; Han et al., 2015). For example, Lamsal et al. (2014) reported that the OMI retrievals tend to be lower in urban regions and higher in remote areas, compared with several in-situ measurements.

To address the issues of uncertainty in the OMI columns and averaging kernels/scattering weights we use the uncertainty estimates provided in the OMI data files and include error bars with the satellite data on the scatter plot throughout the manuscript. We have also added the reduced chi squared metric (χ^2) to quantify how well the model agrees, within the given uncertainties, with the OMI retrievals of tropospheric column NO_2. Two tables have been added to the text that summarize the various calculations which compare model to observations

The following text has been added:

Comparison with model output is facilitated through the use of averaging kernels (DOMINO) or scattering weights (GSFC). No uncertainties are provided explicitly for the averaging kernels or scattering weights. Instead, the DOMINO retrieval team provides uncertainties ("VCDTropErrorUsingAVKernel") that account for errors in both the NO_2 column and the averaging kernel. The precision in 15 the GSFC NO_2 product is provided in the variable "ColumnAmountNO2TropStd". We use these uncertainties as the defacto way of comparing the two different retrievals of column NO_2 to model output of this quantity.

Table 1 summarizes the numerical comparisons between the DOMINO satellite retrievals and all model simulations presented in this study. Table 2 shows similar comparisons but for the GSFC retrieval. In a recent study, Lamsal et al. (2014) compared OMI NO2 to in situ and surface observations and reported OMI retrievals may be lower than observations in urban regions and higher in rural regions, on the order of 20 %. This is opposite of our results, however, the OMI/observation biases are not enough to explain the model/OMI disagreement presented here.

2. There are numerous issues that can increase or decrease the model-estimated NO2 columns (e.g., Han et al., 2015; Stavrakou et al., 2013). This reviewer wonders why authors chose only three factors of re-activation of organic nitrates and accuracy of the mobile and biogenic emissions in their manuscript. Obviously, there are more issues: (1) reaction rate constant of

NO2+OH+M has uncertainty; (2) NO+HO2 reaction is now on hot debate; (3) OH re-activation around the forest areas (like southeastern part of the US region) has been an issue; (4) reaction probability of N2O5 has uncertainty; and (5) daytime HONO chemistry is another one to include. All these issues can affect NOx lifetimes and therefore NOx levels. (1) and (2) affect the rates of HNO3 formation and therefore NOx loss rates. (4) would not be very important in "summer" (July and August), but authors should mention what values (or method) was used for their CMAQ simulations, because this is very important NOx loss pathway (particularly during winter).

We have added a section on model uncertainty as well as created supplemental material to address some of the points regarding updates to kinetics. We have performed two new model simulations to address (1) and (4). In brief, the decrease in the rate of reaction of OH+NO2+M, as recommend by Mollner et al., 2010 has little impact on our results. The same is true if the formation of HNO_3 if the heterogeneous reaction of N_2O_5 with liquid water is turned off (i.e. accommodation coefficient is set to zero in the model) in agreement with Yergorova et al., 2011 and Stavrakou et al., 2013.

The formation pathway of HNO_3 from NO+HO2 (point 2) is not included in the CB05 chemical mechanism. While this reaction may decrease model column NO_2, it will have the largest affect in the tropics (Cariolle et al., 2008, Søvde et al., 2011). Within the model domain, we could expect decreases in NO_2 but this will not solve the urban/rural discrepancy as outlined in the manuscript.

The following text has been added to the manuscript.

There are other possible sources of error within the model framework. Updates to the kinetics based on recent studies may affect the loss of NO_2. Mollner et al. (2010) report the reaction rate of OH+NO2+M is slower than what has been recommended by prior work (Atksinson et al. 2006, Sander et al., 2006). The uptake of N_2O_5 in aerosols is likely overestimated in models (Han et al., 2015, Stavrakou et al., 2013, Vinken et al., 2014, Vegorova et al., 2011). We have performed two model simulations that consider the slower reaction rate of OH+NO2+M ($CMAQ_{OH+NO2}$) and assume the heterogeneous removal of N_2O_5 is zero ($CMAQ_{N2O5}$). Both of these scenarios also include all of the changes made to the model framework in $CMAQ_{TOT}$. Results are presented in the supplemental material. Overall, both of these changes to the model show very little difference for column NO_2 compared to that found in $CMAQ_{TOT}$ simulation. This is in agreement with prior studies (Han et al., 2015, Stavrakou et al., 2013, Vinken et al., 2014, Vegorova et al., 2011).

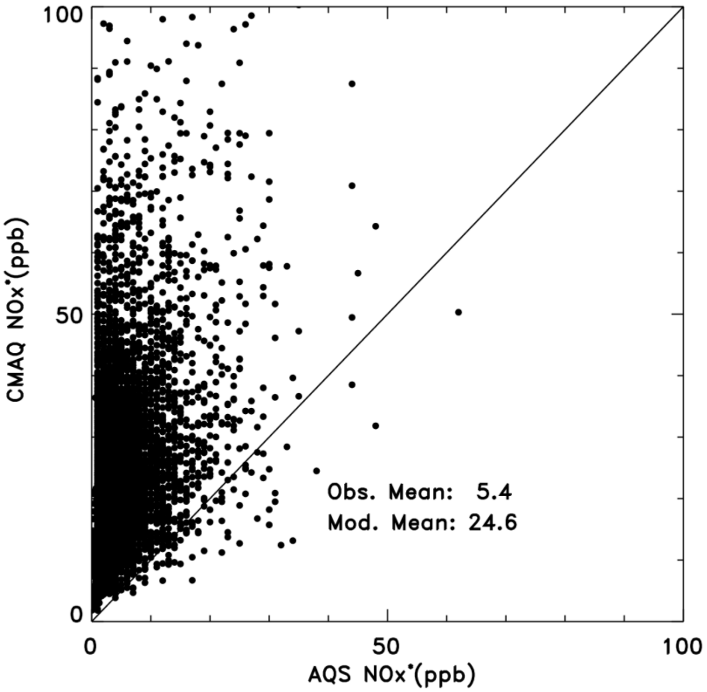
The production of HNO_3 from the reaction of NO+HO_2 (Butkovslaya et al., 2007) would lead to a decrease in NO_2. This channel of the NO+HO_2 reaction is not included in the CB05 chemical mechanism. Inclusion of this NO_x loss mechanism will have the largest impact in the tropics (Cariolle et al., 2008, Stavrakou et al., 2013). While changing the CB05 chemical mechanism may lead to better agreement between model output and satellite retrievals over the urban regions described in this study, it would exacerbate the model/measurement discrepancy in rural areas.

Futurework will investigate the importance of soil emissions of HONO, which are not included in the current versions of MEGAN and the chemical kinetics of other species that are important precursors to surface ozone. Prior studies indicate that soil emissions may account for 7% of column NO_2 during the summer ozone season (Choi et al., 2008) and that HONO could be an important morning source of OH in an urban, VOC rich environment (Ren et al., 2013).

3. In connection with 1, the CMAQ simulations over- and under-estimated NO2 columns over the urban and rural regions, respectively, throughout all the cases (Figs. 2–8). This reviewer wonders that the same results can also be found in the comparison between two NO2 concentrations from the CMAQ simulations and ground based in-situ AQS measurements.

This is a difficult comparison to draw conclusions from. As we state in the text, we think the AQS sites do not measure “true” NO_2 (see P4438, L7-21). It is more reasonable to compare the in-situ observations to the quantity $NO_x^*=NO_y - HNO_3$ from CMAQ. The figure below shows a scatter plot of baseline CMAQ NO_x^* vs AQS NO_x^* for the time of the OMI overpass for all surface monitoring sites within the model domain. The model is ~5 times greater than the observations. We know that the emission of NO_x from mobile sources in the model is too high by at least a factor of 2 (Anderson et al., 2014) so this results is not too surprising.

The comparison is further complicated by the paucity of ground based NO_2 monitors in the model domain and the lack of overlap with regions where CMAQ tropospheric column is 25% greater than the OMI data.



Minor comments

1. p.4430 L2-5, Again, this is a hasty statement. How about errors and uncertainty of NO_x columns and AKs over urban and rural areas?

> The sentence on p4430 L2-5, is in reference to the prior sentence which discusses results reported in Castellanos et al., 2011 who compared CMAQ output to surface observations.

2. p.4432 L12, CMAQ model does not include stratospheric chemistry. Therefore, vertical domain up to “20 km” is meaningless.

> CMAQ does not include stratospheric processes so the upper layers of the model atmosphere should not be used for research purposes. The analysis presented here is limited to altitudes below the tropopause.

3. p 4439, L 23-25, In the MDL(MGN) simulation (in Fig. 7), authors reported the increase in the CMAQ-estimated NO_2 column across the model domain. However, the directly-opposed result was described in Conclusions (p. 4443, L 17-20). Thus, the latter should be properly corrected as shown in Fig. 7.

> We regret this typographical error and sincerely appreciate the reviewer catching this mistake. The text has been corrected.

4. Since the ozone episodes are frequently taking place in summer, the consideration of summer months (July and August) is understandable. However, this reviewer thinks that the conclusion should be more generalized with other season analysis.

> We do not feel it is appropriate to make statements regarding other seasons unless we perform model simulations for these time periods. The study by Anderson et al., 2014, which is very important to this work, is based on data taken during summer months and it would not be suitable to apply the 50% reduction in mobile NO_x emissions for a winter time period unless we can first verify this finding. There were aircraft flights in winter 2015 in the Maryland/D.C. region and analysis of these data will be the subject of future work.

Supplement to Ozone and NO_x chemistry in the eastern US: evaluation of CMAQ/CB05 with satellite (OMI) data

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Section 5 mentions two additional model simulations performed in support of the manuscript which we describe in further detail here. Mollner et al. (2010) reported an update to the kinetics that govern the reaction rate of

$$OH + NO_2 + M \rightarrow HNO_3 + M \qquad (R1)$$

Figure S1 shows a comparison of the rate of this reaction based on the recommendations of IUPAC (Atkinson et al., 2006), JPL (Sander et al., 2006), and Mollner et al., (2010). The newer study gives a slower rate constant compared to the prior recommends. We have modified the CB05 chemical mechanism to use the results from Mollner et al. (2010). This change is in addition to the modification of alkyl nitrate (NTR) chemistry, a 50% reduction in emissions of NO_x from mobile sources, and an update to biogenic emissions, as described in the manuscript. This scenario is called $CMAQ_{OH+NO2}$ and was performed for a 20 day period spanning the end of July 2007 to the beginning of August 2007. To facilitate a comparison with the results from the $CMAQ_{TOT}$ simulation, we regenerate the scatter plots presented in Figure 3 of the manuscript for this time period. In Figure S2 we show the results from model runs $CMAQ_{TOT}$ and $CMAQ_{OH+NO2}$ for both the DOMINO and GSFC retrievals. Overall, this change has little effect on the model output with, perhaps, a slight improvement in the comparison of modeled and observed column NO_2 for rural regions.

The accommodation coefficient of N_2O_5 (called γ_{N2O5}) is most likely overestimated within CB05 (Vinken et al., 2014, Yegorova et al., 2011) and therefore NO_2 may be improperly suppressed. In CMAQ, the calculation of gamma is based on Davis et al. (2008). We have performed a simulation, $CMAQ_{N2O5}$, with γ_{N2O5} equal to zero and include all of the changes made to the model in the $CMAQ_{TOT}$ scenario. Results from $CMAQ_{N2O5}$ are presented in Fig S2. With this NO_x loss mechanism turned off, we would expect modeled column NO_2 to increase. Even though column NO_2 does rise, this scenario shows very little overall difference compared to $CMAQ_{TOT.}$ This is in agreement with prior studies (Han et al., 2015, Stavrakou et al., 2013).

References:

Atkinson, R., Blauch, D. L., Cox, R. A., Crowley, J., Hampson Jr., R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume I – gas phase reactions of Ox, HOx, NOx and SOx species, Atmos. Chem. Phys., 4, 1461–1738, 2004, Updated at http://www.iupac-kinetic.ch.cam.ac.uk, 2006.

Davis, J. M., Bhave, P. V., and Foley, K. M.: Parameterization of N2O5 reaction probabilities on the surface of particles containing ammonium, sulfate, and nitrate, Atmos. Chem. Phys., 8, 5295– 5311, 2008, http://www.atmos-chem-phys.net/8/5295/2008/.

Han, K. M., Lee, S., Chang, L. S., and Song, C. H.: A comparison study between CMAQ simulated and OMI-retrieved NO2 5 columns over East Asia for evaluation of NOx emission fluxes of INTEX–B, CAPSS, and REAS inventories, Atmos. Chem. Phys., 15, 1913–1938, doi:10.5194/acp-15-1913-2015, 2015.

Mollner, A. K., Valluvadasan, S., Feng, L., Sprague, M. K., Okumura, M., Milligan, D. B., Bloss, W. J., Sander, S. P., Martien, P. T., Harley, R. A., McCoy, A.'B., and Carter, W. P. L.: Rate of Gas Phase Association of Hydroxyl Radical and Nitrogen Dioxide, Science, 330, 646–649, doi:10.1126/science.1193030, 2010.

Stavrakou, T., Müller, J.-F., Boersma, K. F., van der A, R. J., Kurokawa, J., Ohara, T., and Zhang, Q.: Key chemical NOx sink uncertainties and how they influence top-down emissions of nitrogen oxides, Atmos. Chem. Phys., 13, 9057–9082, doi:10.5194/acp-13-9057-2013, 2013.

Vinken, G. C. M., Boersma, K. F., van Donkelaar, A., and Zhang, L.: Constraints on ship NO_x emissions in Europe using GEOS–Chem and OMI satellite NO2 observations, Atmos. Chem. Phys., 14, 1353–1369, doi:10.5194/acp-14-1353-2014, 2014.

Yegorova, E. A., Allen, D. J., Loughner, C. P., Pickering, K. E., and Dickerson, R. R.: Characterization of an eastern US severe air pollution episode using WRF/Chem, J. Geophys. Res., 116, D17306, doi:10.1029/2010JD015054, 2011.

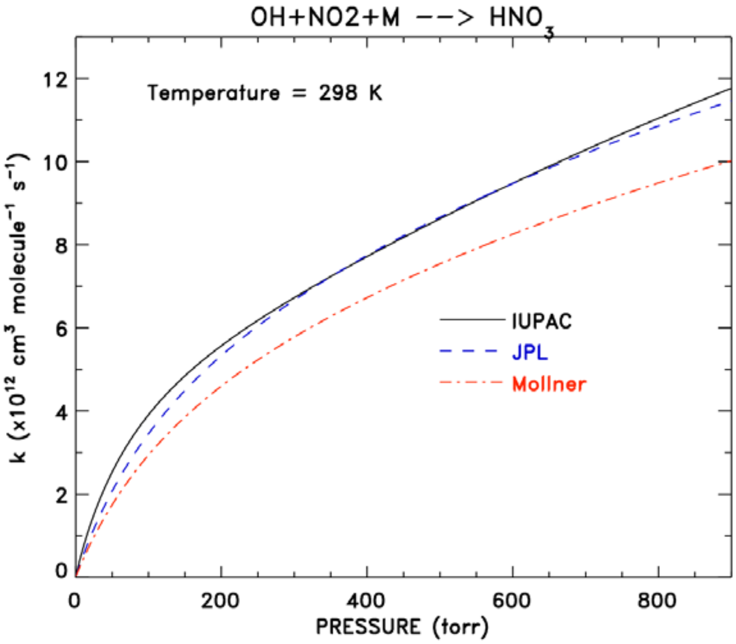

Fig S1. Reaction rate of OH+NO_2+M at 298K based on the recommendations from IUPAC (black), JPL (blue, dashed) and Mollner et al. 2010 (red, dashed dot).

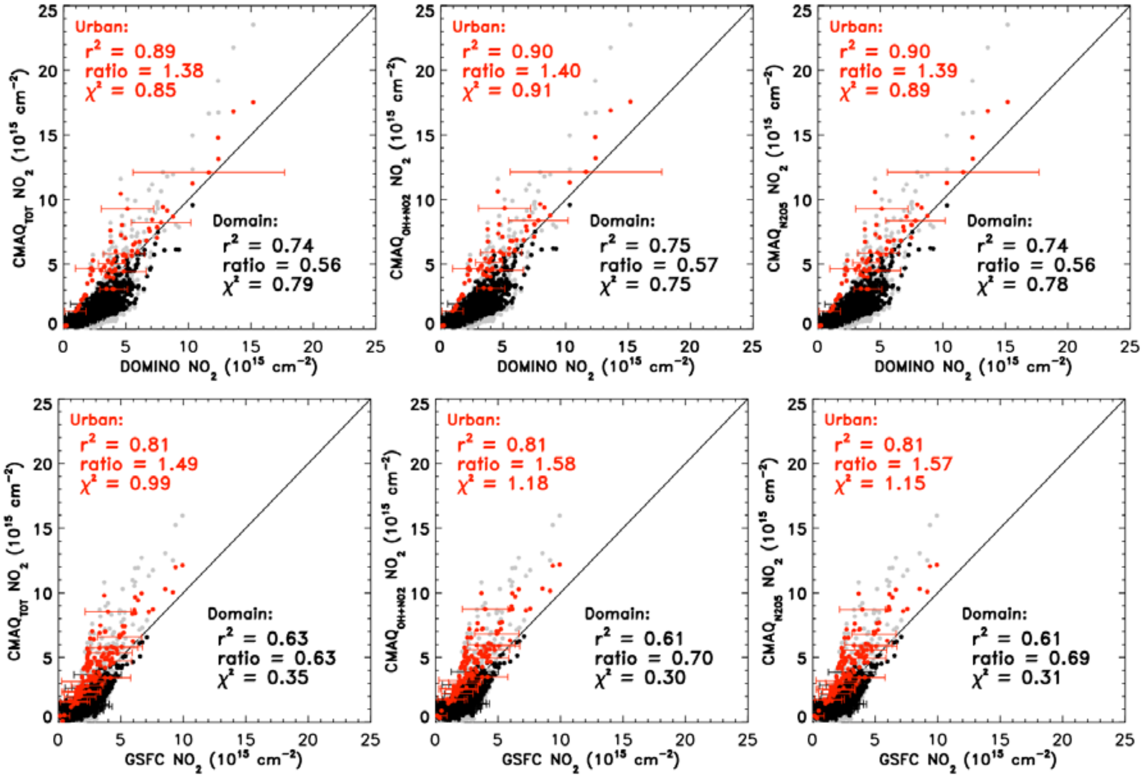

Fig S2. Scatter plots of model output to both the DOMINO (top panels) and GSFC (bottom panels) retrievals of tropospheric column NO_2. Results span late July/early August 2007. Gray points represent the results shown in Fig. 2 of the manuscript. Red points represent areas where the model is at least 25% greater than observations. Results from model scenario $CMAQ_{TOT}$ (left panels) for this time period are shown for comparison with results presented in the manuscript. $CMAQ_{OH+NO2}$ (center panels) includes the modifications made to $CMAQ_{TOT}$ as well as a change in the reaction rate of $OH+NO_2$. $CMAQ_{N2O5}$ (right panels) has the heterogeneous loss of N_2O_5 turned off and includes the modifications made to $CMAQ_{TOT}$.