Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "Key chemical NO$_x$ sink uncertainties and how they influence top-down emissions of nitrogen oxides" *by* T. Stavrakou et al.

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We would like to thank the reviewer for his/her very careful reading and for the many comments which helped us to greatly improve our manuscript. In the following, we address the concerns raised. Reviewer's comments are *italicized*.

The paper by Stavrakou et al. evaluates uncertainties in several chemical parameters affecting the simulation of NO$_2$ in linking satellite NO$_2$ data to NOx emissions. The paper further compares the modeled NO$_2$ and retrieved NOx emissions with aircraft data, satellite NO$_2$ data and bottom-up emission inventories. The analysis, however,

has various issues that prevent its publication in the current form.

Model uncertainties have been evaluated by Lin et al. (2012) in a comprehensive manner for China. Lin et al. examined (almost) all chemical and meteorological parameters/processes that are important to NO$_2$ simulations at a fine resolution (0.5 degree$\times$0.667 degree) using GEOS-Chem, including chemical parameters analyzed by the current paper and those not evaluated by the current paper. The current paper extends the analysis for a global simulation (IMAGE), but only evaluating a subset of chemical parameters by Lin et al. and only on a relatively coarse resolution (2$\times$2.5 degree). Therefore, the current paper should state clearly how it builds upon Lin et al. throughout the text (abstract, introduction, Sect. 2, results, conclusion).

We cannot agree that our paper "builds upon Lin et al.", as the reviewer puts it. Our study was initiated independently of Lin et al. and has a clearly very different scope due to its global scale and to our exploration of consequences for top-down NOx emissions. As clearly stated in our manuscript, we limit our analysis to clearly identified uncertainties on chemical NOx sinks. It is well beyond the scope of this study (or of *any* study) to explore the consequences of every possible process affecting NO$_2$ simulations. With all due respect, although Lin et al. did examine the relevance of a large number of model parameters, (i) there are many more processes which could deserve attention (e.g. HONO chemistry, dry deposition, chemical mechanisms of many poorly represented NMVOCs, to name a few), and (ii) the range of values considered for each examined parameter was often quite arbitrary. Furthermore, the process which contributes most to the overall uncertainty in our study – the HNO$_3$-forming channel in HO$_2$+NO – was not taken seriously in Lin et al., since only constant HNO$_3$ yields (1 and 5%) were tested, ignoring completely the strong T-, p- and H$_2$O-dependence of this parameter measured by Butkovskaya and co-workers, and since this process was not retained in their evaluation of the overall uncertainty of NO$_2$ columns (it is not even mentioned in the abstract and conclusions).

Regarding the role of the model resolution pointed out by the referee, we added the following sentence in the first paragraph of Section 3.2:

"As a drawback of the global model domain, its relatively coarse resolution should be acknowledged as a possible source of error in NO_2 abundances and sensitivities, given the non-linear character of tropospheric chemistry."

More specifically,

1. *The paper focuses on OH+NO_2 reaction rate, NO+$HO_2 \rightarrow HNO_3$, N_2O_5 uptake on aerosols and OH regeneration from isoprene chemistry. However, other chemical processes are important too, including the HO_2 uptake on aerosols, anthropogenic aromatics, organic (isoprene) nitrates, PAN formation and thermal-decomposition, and emissions of CO and VOC affecting OH. The importance of these processes has been found for various months and regions by Lin et al. For example, HO_2 uptake is critical for all seasons, anthropogenic aromatics is important for winter, isoprene nitrates are important for summer in vegetated areas. The paper should better justify the choice of not including these additional chemical uncertainties and their potential consequences.*

   • HO_2 uptake on aerosols: we agree that its effect was possibly underestimated in our model calculations, because (i) we considered only the uptake on sulfate/nitrate/ammonium aerosol, which represents only a fraction of the total fine mode aerosols over continents, and (ii) we did not consider the possibility of a very efficient uptake (γ_{HO_2} close to unity) leading to the formation of H_2O (instead of H_2O_2) as recently proposed in the modelling study of Mao et al. (2013). Therefore, a completely new set of simulations has been conducted using an updated version of the IMAGESv2 model which now includes revised organic aerosol sources. We added the following text in Section 2.5:

   "Furthermore, the presence of iron favors pathways leading ultimately to H_2O (i.e.

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$Y_{H_2O_2} = 0$) instead of H_2O_2 (Mao et al., 2013), thereby increasing the overall HOx depleting effect of aerosols. Under molar concentrations of copper and iron typically found in fine aerosols in the United States and in other (moderately) polluted areas, Mao et al. (2013) estimated using a detailed aerosol model that the reactive uptake coefficient of HO_2 should be close to unity, with H_2O as main reaction product. This result was found to be consistent with HOx measurements in field studies in various environments. Its impact on the global tropospheric composition was calculated using a global CTM and found to be substantial (Mao et al., 2013), although the adopted assumptions ($\gamma_{HO_2} = 1$ and $Y_{H_2O_2} = 0$ on all aerosol types) clearly represent an exaggeration, since the HO_2 uptake cannot be expected to be efficient on dry aerosols, and since laboratory determinations of γ_{HO_2} indicate values significantly lower than unity even for Cu-doped aerosols. Nevertheless, this efficient uptake scenario is also adopted in our baseline simulation (MINLOSS), except that only fine mode aqueous aerosols (i.e. hydrophilic carbonaceous and sulfate/ammonium/nitrate aerosols) are allowed to promote HO_2 uptake. Neglecting the effect of coarse mode aerosols should not lead to large errors, since sulfate and organic aerosols largely dominate the aerosol loading and therefore the aerosol surface area over most continental areas, especially over NOx source regions (Jimenez et al., 2009). (...) We test the sensitivity of the model with respect to uncertainties in HO_2 aerosol uptake by carrying out a simulation where γ_{HO_2} is set to a lower value (0.2), and $Y_{H_2O_2}$ is set equal to 0.5 (HO2L run of Table 1)."

Needless to say, these new settings lead to a much stronger impact of HO_2 uptake on NO_2 simulations, in particular over East and South Asia. This process becomes even the largest source of uncertainty over China, since e.g. the a posteriori anthropogenic NOx source over China is decreased from 6 TgN/year in MAXLOSS to only 3.8 TgN/year in the MINLOSS case, due to the substantially lower OH levels in that scenario.

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• aromatics: Lin et al. (2012) increased the emissions of propene by 300% in their CTM in order to represent the effects of aromatics based on top-down constraints derived by Liu et al. (2010, 2011). The latter studies suggested an underestimation of aromatic compounds emissions by a large factor (4–10) in current inventories. However, this conclusion is contradicted by recent campaign measurements (e.g. Yuan et al., 2013) indicating a surprisingly good agreement of measured VOC/CO ratios with values derived from the emission inventory of Zhang et al. (2009), in particular for aromatic compounds. The measured aromatic/CO ratios were also found to be quite similar to values measured in the N-E United States. Note that the main argument of Liu et al. (2011) in favor of high aromatic compounds emissions was the strong underestimation of glyoxal columns over China in comparison with satellite data. However, there might be other causes for the underestimation, including possible biases in satellite columns as well as other glyoxal sources, besides the oxidation of aromatic compounds.

• organic (isoprene) nitrates: their possible importance is shortly discussed in our manuscript. Their current treatment in IMAGESv2 is too crude for a reasonably realistic uncertainty estimate. Their treatment in the version of GEOS-Chem used by Lin et al. is even more simplistic: HNO_3 is formed in lieu of an explicit organic nitrate in the reaction of isoprene peroxy radicals with NO (acmg.seas.harvard.edu/geos/wiki_docs/chemistry/chemistry_updates_v5.pdf – the "Paulot scheme" option was presumably not used, given the 10% nitrate yield mentioned by Lin et al.), leading to a strong overestimation of the associated NOx sink, as discussed by Paulot et al. (2012). The uncertainty estimate based on GEOS-Chem simulations using either the nominal (10%) or a very low nitrate yield (2.4%) is therefore very likely largely overestimated, especially since the 2.4% yield lies well below the range determined from model comparisons with field measurements (Perring et al., 2009).

• PAN formation and thermal decomposition: those processes are acknowledged

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to be important, but they are no net sink of NOx, except locally. The sensitivity simulation by Lin et al. assuming a decreased equilibrium constant lead to only small changes (a few percents) in NO_2 abundances.

• emissions of CO and VOC: those emissions have uncertainties which are however difficult to assess. Simple tests such as conducted by Lin et al. (a 50% uniform increase in emissions) would not be justified at the global scale of our study. A thorough evaluation of the emission uncertainties (based on network and satellite data) is beyond the scope of the present study.

2. *The role of aerosols is important because aerosols affect both radiation and uptake of HO_2 and N_2O_5. There are no analyses of model aerosol performance for the reader to judge the validity of the model sensitivity to N_2O_5 and HO_2 uptake rate.*

We agree with the reviewer that the role of aerosols was underestimated in the ACPD version of the manuscript. Their treatment is now described in the Supplement of the article, which also provides comparisons with a large number of ground-based and aircraft measurements of the main fine mode aerosol components over continents (organic and sulfate aerosols). In addition, the following text was added in the main body of the article (Section 3.2):

"Inorganic (i.e. sulfate/ammonium/nitrate/water) aerosols are calculated using EQSAM (Metzger et al., 2002). The calculation of organic aerosols (OA) and black carbon (BC) follows Stavrakou et al. (2012). Since, however, the model using unadjusted anthropogenic POA emissions (Bond et al., 2004) and SOA parameterization (Ceulemans, 2011) largely underestimates organic carbon (OC) measurements over polluted areas, an additional OA source is included, of magnitude equal to three times the POA source over the United States, and five times the POA source in other regions. Moreover, the parameterized SOA production due to monoterpene oxidation in low-NOx conditions is reduced by a factor of 5 in order to provide a better match with observations in biogenically-influenced

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regions. Although crude, this adjustment strongly reduces the biases with the measurements, as detailed in the Supplement. Previous model-based analyses (Spracklen et al. 2011; Heald et al., 2011) have pointed to the existence of a large OA source over anthropogenically-influenced regions, of the order of 100 Tg year^{-1}. The precise nature of the additional source is currently unclear, although SOA very likely makes up for a large fraction of it (Yuan et al., 2013). The additional source included in IMAGESv2 amounts to 68 Tg(OA) per year, whereas the global SOA source amounts to 53 Tg year^{-1}, primarily due to biogenic emissions. More details on the treatment of inorganic and carbonaceous aerosols in IMAGESv2 is provided in the Supplement."

3. *Much larger HO_2 uptake rate on aerosols than previously thought is recently established, due to the findings of significant transition metal ions in aerosols catalyzing the uptake. HO_2 uptake on aerosols is found to be extremely important for OH, ozone and NO_2 (Mao et al., 2012, ACP; Lin et al., 2012). The current paper appears to suggest the opposite without clear explanation and comparison. Is it because of low aerosol loadings or other model issues? It is very hard to believe the HO_2 uptake is not important. Macintyre and Evans (2011) parameterization does not include the effect of transition metal ions. However, they did show significant effects on HOx and ozone when the HO_2 uptake rate reduces from 0.2 to 0, and they further recognized the potential importance of transition metal catalysis in the conclusion.*

See points 1 and 2 above. The uptake by hydrophilic carbonaceous aerosols was ignored in the ACPD version of the article. The assumption by Mao et al. (2012) and Lin et al. (2012) that HO_2 uptake proceeds efficiently on dry aerosols is not well-justified since an aqueous phase is needed for the reactions considered by Mao et al. to occur. Over Northern China and parts of Southern China, dry and cold conditions caused inorganic aerosols (dominated by ammonium sulfate and ammonium nitrate) to be predominantly solid in the model, which explains the

very low effect of HO_2 and N_2O_5 uptake calculated in this region in the ACPD version. The determination of the physical state of inorganic aerosol is described in the Supplement:

"Composition- and temperature-dependent deliquescence relative humidities (DRH) are calculated according to ISORROPIA (Nenes et al., 1998). Below the DRH, and above the crystallisation relative humidity (CRH) (Carrico et al., 2003b), the aerosol state depends on its history through the hysteresis effect (Tang et al., 1995); here the aerosol is assumed to be solid only if relative humidity remained below the DRH during the last 24 hours. The aerosol physical state is highly relevant to heterogeneous chemistry: heterogeneous uptake on solid particles is very slow in the case of N_2O_5 (Davis et al., 2008) and HO_2 (Taketani et al., 2008)."

4. *Model meteorology is also important. For example, Lin et al. found errors in PBL mixing, cloud optical depth, and water vapor to be very important for their GEOS-Chem simulation. How about IMAGE? Although the current paper tries to focus on chemical uncertainties, errors in IMAGE met fields may have important effects on the model performance and NOx emission inversion, and may affect to some extent the sensitivity of model NO_2 to chemical uncertainties (e.g., relative humidity affects aerosol scattering). This is critical since the current paper appears to suggest an upper/lower bound of model NO_2 and NOx emission inversion in comparison with aircraft/satellite/emission inventories. The potential effect of met field errors should be discussed more clearly.*

Again, this paper addresses chemical uncertainties. Moreover, the effects of meteorological parameters calculated by Lin et al. (typically 10–20% or less) cannot be qualified as "very important", especially in comparison with the effects of uncertainties on chemical sinks calculated in our study. The influence of meteorological uncertainties on the calculated sensitivity of model NO_2 to chemical uncertainties is a second order effect and is certainly not "critical". Besides, the

magnitude of meteorological uncertainties is very difficult to assess, and the parameter values tested by Lin et al. were often arbitrary. Finally, the upper and lower bounds of NOx emissions given in this paper provide a measure of the uncertainty associated to the sink processes investigated in our analysis. Any reader can readily understand that the overall uncertainty is even larger.

5. *How about the effect of model resolution affecting the nonlinear chemistry?*

   This limitation of the model has been acknowledged (see above).

6. *Sensitivity to model chemistry/meteorology uncertainties may be model dependent. For example, if the model only produces small amounts of aerosols, the effect of HO_2/N_2O_5 uptake rate would be less important. The importance of isoprene nitrate depends on the assumed yield and recycling ratio. The met field errors may be highly model and region dependent.*

   As mentioned above, the calculation of aerosols was updated for this revision, and detailed comparisons with observations are provided in the Supplement. The possible errors associated to isoprene nitrate formation are acknowledged in the manuscript. As is true for every model study (except intercomparisons), we can't afford the luxury of running many models. We expect readers to be aware that model results are (somewhat) model dependent. We note that the referee claimed that "model uncertainties have been evaluated by Lin et al. (2012) in a comprehensive manner", despite the fact that only one specific model was used in that study.

7. *There are many over-statements without justifications throughout the paper. For example, "four key parameters believed to be of primary importance" and "largely overlooked in previous inversion exercises" in the abstract. These statements are against the fact that Lin et al. have done lots of work in this regard and that they found many other parameters to be model important as well.*

   We changed "four key parameters" into "five key parameters" to include HO_2 uptake. Why would it be an over-statement that those chemical uncertainties were overlooked in previous inversion studies? This is the reality. Not only Lin et al. was not an inversion study, but also, their evaluated uncertainties were considerably lower (typically $< 20\%$) than in our study (up to a factor of 2 or even more). As pointed out in the manuscript,

   "Note that other model uncertainties could affect the modelled NOx columns, e.g. in meteorological parameters, in the emissions of other compounds (e.g. NMVOCs) or in chemical parameters other than those considered in this study (Lin et al., 2012a). The comparison of our MINLOSS and MAXLOSS simulations should, nevertheless, provide a measure of the uncertainties associated to the major chemical NOx pathways. The analysis of Lin et al. (2012a) suggests that the uncertainties due to other factors are generally much lower than the overall uncertainty considered in this study. "

8. *Section 2 provides a useful analysis of the parameters being investigated. However, it should be made more explicit how the choice of these parameters is built upon Lin et al.*

   The choice of parameters is not built upon Lin et al. It is based on our evaluation of the relative importance of the the different NOx sinks, and on a number of recent experimental studies pointing to new processes and revised rate constants. In addition, for each parameter, the range of values we considered differs substantially from the values tested by Lin et al., in particular for the most critical processes (HO_2+NO and, in the revised version of the manuscript, HO_2 uptake).

9. *The current paper should state clearly how it proceeds beyond Lin et al. throughout the text (abstract, introduction, Sect. 2, results, conclusion).*

   The study of Lin et al. is mentioned in the Introduction, and comparisons with their results can be found at many instances in the discussion.

Model simulations and inversion procedures are not clearly defined in the current paper. More specifically,

1. *What is the PBL scheme? What is the convection scheme? How about aerosol simulations? How about aromatics? How about the vertical distribution of lightning emissions in comparison with recent development by Ott et al. (2010)? The vertical distribution is very important since the averaging kernel depends on height. The authors should describe/analyze these model aspects.*

   The simulation of aerosols and the degradation mechanism of NMVOCs are now described in the Supplement. We believe that an extensive description of every aspect of the model would not be justified in the context of this study. Regarding the model transport, we now state in the text:

   "Meteorological fields are obtained from ERA-Interim analyses of the European Center of Medium-Range Weather Forecasts (ECMWF) for the year of the simulation (2007). Convection follows the parameterization of Costen et al. (1988). Turbulent mixing in the planetary boundary layer (PBL) is parameterized as vertical diffusion based on ERA-Interim boundary layer heights. Details about the model, including its evaluation against radionuclide data (^{222}Rn and ^{85}Kr), airborne and satellite measurements, and other CTMs can be found in previously published work (e.g., Müller and Brasseur, 1995; Müller and Stavrakou, 2005; van Noije et al., 2006; Stavrakou et al., 2008; Stavrakou et al., 2012)."

   Regarding NMVOC anthropogenic emissions, the following sentence has been added:

   "Anthropogenic emissions of NMVOCs (ethane, propane, ethene, propene, acetylene, methanol, benzene, toluene, xylenes, formic and acetic acids, and the sum of other NMVOCs) are provided by the RETRO inventory for year 2000 (Schultz et al., 2007) overwritten by REASv1 over Asia."

   Uncertainties in the vertical distribution of lightning emissions are beyond the scope of our study since our focus is on chemical sink uncertainties. Of course many other factors, including the horizontal and vertical distribution of all emission categories (not just lightning) might contribute to the overall NO_2 column uncertainty.

2. *The time step of 4 hours raises questions about the model performance, particularly when the lifetime of NOx in midday is shorter than 4 hours and that the radiation (and photochemistry) changes rapidly during a 4-hour period. The authors should justify the choice of the particular time step.*

   The following sentence was added:

   "Note that the chemical solver uses an adaptable internal timestep, which is often much shorter than the external timestep of 4 hours."

   Furthermore, as already stated in the article, diurnal variations are calculated from model runs using a 20-minutes time step.

3. *The use of OMI data is not clearly described. How was the row anomaly treated? What do you mean by "cloud free"? Did you match OMI data with model for each day before obtaining the monthly mean? How to deal with gridding of averaging kernels to model gridcells? What is "super-observation"? Same issues for comparison with SCIAMACHY data.*

   We now state in the text:

   "Cloudy pixels (i.e. with cloud fraction > 0.2) and pixels affected by the so-called row anomaly (i.e. track positions 53-54, since June 2007) were excluded." (Section 3.1)

   "The monthly averages are calculated from daily values accounting for the number of measurements and averaging kernel for each day (also binned onto the

model resolution) and for the sampling times of observation at each location."
(Section 3.2)

"The errors associated to the monthly DOMINO v2 averages are estimated from
the reported retrieval errors, following a super-observation approach as in Eskes
et al. (2003). The super-observations are the measurement averages at the
model resolution." (Section 3.2)

4. *Furthermore, quantitative uncertainty values in emission sources are given in
Sect. 3 without justification. These values are also inconsistent with Stavrakou
et al. (2008) without further explanations of the change. The error values are
very important because they determine whether the "optimized" emissions are
closer to top-down emissions or to a priori emissions, with further consequences
in comparison with other emission inventories.*

We agree that the a priori errors in emission parameters are important, however
the values given in Sect. 3 are actually only slightly higher than the corresponding
values in Stavrakou et al. (2008) (factors of 1.5 and 2 for anthropogenic emissions
in OECD and non-OECD countries, respectively, and factors of 1.8, 2 and 1.8
for soil, biomass burning and lightning emissions, respectively). The reviewer's
confusion is understandable and we apologize for it: the error values given in
Stavrakou et al. (2008) are the errors (Δf_i) on the actual emission parameters
(f_i, with i the parameter index) which are proportional to the logarithm of the
optimized emission fluxes ($E_i^{opt} = E_i^0 \times \exp(f_i)$), whereas the values given above
are error factors given by $\exp(\Delta f_i)$. For a more detailed overview of the inversion
method, we refer to Stavrakou and Müller (2006).

5. *The importance of individual chemical uncertainties may be different before and
after the averaging kernel is applied, because these uncertainties may affect the
vertical distribution of NO_2.*

The following text was added in the first paragraph of Section 4:

"Note that for simplicity, the results given in this section concern the daily aver-
aged sink rate of the tropospheric column calculated without averaging kernels;
in some cases, however, the sensitivity of the sink rate in the hours preceding
the satellite overpass time and weighted by the altitude-dependent instrument
sensitivity might differ markedly from the sensitivity shown here. This is most ev-
ident in the case of the sink due to N_2O_5 uptake by aerosols, which is primarily a
nighttime process. "

*Section 4 and Figs. 2,3. The analysis of the effects of chemical uncertainties is
unclear/incorrect.*

We strongly disagree that our analysis was incorrect. In some cases, clarifications
were needed. See our responses below.

*For example, how does increased $OH+NO_2$ reaction rate (from Henderson et al. to
Mollner et al. and to JPL) result in little change/reduction in NO_2 loss rate in most
regions?*

The text was modified as follows: "The use of the JPL recommendation for its rate con-
stant (JPL run) leads to increased NOx loss rate by about 10–15% in most areas, and
by up to 20% over the remote Southern Ocean (Table 1, Figs. 2–3). This appears con-
sistent with the 15–20% difference in the rate constants in the boundary layer (Fig. 1),
given that this reaction represents ca. 60% of the total NOx sink."

*How does additional $NO+HO_2 \rightarrow HNO_3$ result in little change/reduction of NO_2 loss rate
in East U.S., EU and E. China?*

The text was modified as follows: "Over polluted regions, the relative impact of this
loss process is found to be lower, due to the predominance of other sinks ($OH+NO_2$ in

summer and N_2O_5+H_2O in winter) in those regions." The contribution of each process to the sink rate is shown on Fig. 5.

How does increased N_2O_5 uptake rate (from Brown et al. to DAVIS) lead to reduction in NO_2 loss rate in several continental and oceanic regions and little change/reduction in North China in January?

The following text was added: "Note that the increased NOx sink e.g. over Europe leads to decreased NOx levels over neighboring areas (e.g. Northern Africa) and therefore to decreased OH levels, explaining the decreased NOx sink rate in those areas. Over Northern China, the very low effect of N_2O_5 uptake is explained by dry and cold conditions causing inorganic aerosols (dominated by ammonium sulfate and ammonium nitrate) to be predominantly solid in the model in this region. The heterogeneous uptake is believed to be very slow on dry particles (Davis et al., 2008). A comparatively stronger sensitivity to N_2O_5 uptake was calculated by Lin et al. (2012a), with NO_2 column changes exceeding 10% when decreasing the uptake coefficient by a factor of 10. This is explained by the fact that the reduction was applied by Lin et al. to all aerosol types, i.e. not just to inorganic aerosols as in the DAVIS simulation. Furthermore, the parameterization of Evans and Jacob (2005) used in the reference run by Lin et al. (2012a) does not account for the suppression of $\gamma_{N_2O_5}$ on dry particles."

How does the OH regeneration from isoprene chemistry not have effects on NO_2 loss rate in vegetated EU and S. China?

The recycling mechanism in MIM2+ increases OH only in low-NOx areas. The text has been adapted, e.g. "The increased OH concentrations over low-NOx forested areas (...)"

How does HO_2 uptake on aerosols (gamma = 0.2) not have large impacts on NO_2 even in those areas with high aerosol loadings?

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See above. The text has been changed to "Finally, the model using a less efficient HOx loss ($\gamma_{HO_2} = 0.2$ and $Y_{H_2O_2}$=0.5) due to HO_2 uptake by aerosols (HO2L simulation) exhibits a strong sensitivity in regions with high aerosol concentrations, in particular over East and South Asia as well as over biomass burning areas such as Africa in the winter hemisphere and Central Canada during summer (Fig. 2-3(f)). In fact, HO_2 uptake appears to be the largest source of uncertainty over much of Europe and the Northeastern U.S. in July, as well as over China in both seasons, where the NOx sink rate is increased by up to 30% (up to 50% in January) when HO_2 uptake is assumed to be less efficient. Those changes are primarirly due to the strong impact of the reaction on OH levels, as shown by the 11% decrease in mass-weighted tropospheric OH concentration in the HO2L run, very similar to the 12% change in tropospheric OH reported by Mao et al. (2013) between simulations either ignoring HO_2 uptake or adopting the same efficient uptake scenario ($\gamma_{HO_2} = 1$ and $Y_{H_2O_2}$=0) as in MINLOSS. Annually averaged OH and HO_2 concentrations are increased by factors of up to 2 and 3, respectively, over both China and India; those changes over China are lower than in the modelling study of Mao et al. (2013), as expected since HO_2 was allowed to react on all aerosol types in the latter study, irrespective of the aerosol state. In contrast, the calculated changes over India are much lower in Mao et al. (2013), presumably due to lower organic aerosol loadings in GEOS-Chem compared with IMAGESv2. The NO_2 column changes calculated in IMAGESv2 over China are larger in January (20-35%) compared to July (between 10% in Southern China and almost 20% in Northern China), in qualitative agreement with Lin et al. (2012a) where the impact of a reduction of $\gamma_{N_2O_5}$ from 0.2 to 0.05 was estimated. "

In any case, the section should be expanded with more analyses over the polluted areas, and the results from all these chemical sensitivity tests should be compared with Lin et al. and differences should be explained. Also, the color scheme in Figs2-3 is confusing. It is much better to use warm colors for positive values and cool colors for negative values, and to separate negative from positive values.

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This section has been expanded with more discussion and comparison with Lin et al. We disagree regarding the use of warm and cool colors; most figures show fields which are almost uniformly positive. Furthermore, the visual distinction of shades of the same color is much more difficult than the distinction of shades/colors ranging from deep blue to dark brown through green, yellow, orange and red.

The lifetime analyzed in most of the text and in Fig. 4 and Table 1 is somehow misleading. It represents the average lifetime of NOx throughout the day rather than the "local" lifetime for early afternoon which is more relevant to linking OMI NO_2 with NOx emissions. In addition, the impacts of chemical uncertainties on the average lifetime (sink rate) shown in Fig. 4 and Table 1 are not the same as the impacts on the local lifetime (sink rate) relevant to early afternoon NO_2. For example, the effect of N_2O_5 uptake is much less important for early afternoon NO_2 than NO_2 at night. Also, in Fig. 4, the lifetime are longer than 6 hours, as opposed to the lifetime shown in Fig. 13 (i.e., less than 6 hours). The definition of lifetime should be made clear throughout the text, i.e., daily average lifetime or daytime lifetime or local lifetime (most relevant to OMI NO_2). The discussion of lifetime is quite confusing currently.

The comparison of model lifetimes with the results of Beirle et al. (Fig. 13) has been removed (see below) and therefore the lifetime definition is now unique throughout the paper. Daily averaged lifetimes might not be the most relevant to OMI NO_2 data, but this limitation is acknowledged when necessary (e.g. in the case of N_2O_5 sink on aerosols).

The current paper compares model NO_2, model lifetime and retrieved NOx emissions with other datasets. While these comparisons are interesting to some extent, they are complicated by the model/retrieval issues raised above. More comments specific to individual comparisons are as below:

1. *The good comparison of model NO_2 (driven by "optimized" NOx emissions) with*

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OMI data appears to suggest that the emission retrieval simply finds NOx emissions that best fit OMI data in the first place. This is a result of much larger biases assumed for a priori emissions than the biases assumed for the model-retrieval system – in this case, the "optimized" NOx emissions simply reflect the "top-down" emissions. It is not surprising that using such emissions, model can reproduce satellite data, especially at the coarse resolution.

We agree with the reviewer: the comparison shows that the inversion can successfully reproduce the OMI data, and this is why we think important to show this figure.

2. *The comparison with SCIAMACHY does not tell much about the model performance nor about emission inversion. This is because satellite data are always subject to errors and thus do not represent the true state of atmosphere. In addition, SCIAMACHY is further subject to data coverage such that the data representativeness is an issue.*

We disagree. SCIAMACHY is a different instrument, with a different overpass time and it is therefore of interest to use such data for evaluation. Of course SCIAMACHY has errors, much like OMI has errors. We don't see why e.g. the model overprediction with respect to SCIAMACHY over tropical ecosystems such as South-East Asia would not be worth mentioning.

3. *The comparison with bottom-up inventories is not a good constraint of model/inversion either. It is well known that bottom-up inventories contain large uncertainties, which is the primary reason of the efforts to developing top-down emission constraint.*

Again, we disagree. Of course inventories have errors, but the errors in most recent, very detailed inventories such as MEIC and REASv2 are expected to be lower than in older inventories such as REASv1. The poor agreement between

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MINLOSS and the recent inventories is no definitive proof, but it is a valid indication that the NOx sinks are underestimated over China in the MINLOSS scenario.

4. *The comparison with aircraft data is potentially useful for model constraint. However, inadequate information is provided to justify the comparison. For example, is the mean or median of aircraft measurements used? This makes a huge difference. In addition, these aircraft measurements do not sample 0-500m above the ground. This causes a lot of problems interpreting the model-aircraft comparison for NO_2 which is concentrated near the ground. Furthermore, the comparison should focus on the lowest 2-3 km at higher vertical resolution. The current 1-km resolution may skew the comparison especially considering the coarse model vertical resolution. Only on a high vertical resolution can the model PBL mixing be evaluated properly.*

The mean of aircraft measurements is shown, as now indicated in the legend. It is simply not true that INTEX-A or INTEX-B measurements did not sample the layer 0-500 m above the ground. Altitudes as low as ca. 100 m were frequently sampled in INTEX-A and INTEX-B. In any case this is no big issue since the model averages take the real measurement altitudes into account, as now also indicated in the legend. We disagree that the comparison should be restricted to the lowest 2-3 km. When so many measurements are available at higher altitudes, why not use them and show the comparison? The 1-km resolution in the plot does not skew the comparison, since the real measurement altitudes are taken into account when deriving the averages shown in the comparison. The model vertical resolution is not coarse: there are 40 levels between the surface and the lower stratosphere, with a large fraction (about 14) in the lowest 2 km above the surface.

5. *The comparison of lifetime with Beirle et al. (2011) should be interpreted with caution. Beirle et al. shows the local (early afternoon) lifetime corresponding to*

the OMI NO_2 data, on the local spatial scale. The model lifetime is however for the 2×3 degree resolution. Such differences should be made explicit and discussed, especially in light of Valin et al. (2012) showing the dependence of NOx lifetime on resolution.

We agree that the comparison could be deceptive due to representativity issues, and decided to remove that subsection.

Table 2. The total source is not equal to sink. The authors explain the difference (1.9-5.4 Tg) as the effect of HNO_3+OH. This may not be true given the low oxidation rate. Please double check. In any case, this imbalance should be clarified in a more visible place.

The Table now provides both the total direct source and the total source including NOx formation due to HNO_3 photolysis and reaction with OH. Note that the calculation of "other sinks" in the Table was erroneous in the ACPD version. The corrected imbalance between direct sources and sinks is larger (>5 TgN/year) and is explained by HNO_3 oxidation and photolysis. The text was adapted as follows:

"Note that the direct NOx sources are not exactly balanced by the sinks due to the conversion of HNO_3 back to NOx totaling >5 TgN/year in the troposphere. The calculated global photochemical lifetime of tropospheric HNO_3 ranges between 23 and 27 days, depending on the simulation. About 55% of the photochemical sink is due to photolysis, the rest being due to reaction with OH. "

Page 2893, L20. The explanation for the weak sensitivity of top-down emissions to NOx sink rates is unclear. I suspect these results are related to the strange results in Sect. 4 and Fig. 2-3 (see above point).

The results in Sect. 4 are not "strange"; they make perfect sense, as explained above. We provide the following, more detailed explanation regarding the role of chemical

feedbacks in tropical regions (Section 5, 4th paragraph):

"In most tropospheric conditions, a NOx emission increase leads to an increase in OH (through the HO_2+NO $\rightarrow$ OH+NO_2 reaction) and therefore in the NOx sink rate. In the context of inverse modelling, this implies that larger emission increments are required in order to match the observations, to compensate for this negative chemical feedback, compared to an emission inversion neglecting feedbacks. Since the NOx emission increments are larger in MAXLOSS compared to MINLOSS, the NOx lifetime decreases (relative to the a priori) are also larger in MAXLOSS compared to MINLOSS, which amplifies the differences between the emission increments in MAXLOSS and MINLOSS."

Over very polluted areas such as Northestern China, characterized by lower radiation and very high NOx levels, this chemical feedback does not operate, because OH levels do not increase much with increasing NOx. In fact, at sufficiently high NOx concentrations, further NOx increases lead to OH levels decreases, due to the lower HO_2/OH ratio and to the growing importance of the OH+NO_2 reaction as a sink for HOx.

However, because of the strong HO_2 sink on aerosols now adopted in the MINLOSS scenario, the difference between MINLOSS and MAXLOSS has become important (factor 1.6). The discussion has been adapted accordingly.

More specific comments:

1. *P7885. Last paragraph. Descriptions of natural emissions could be placed in a separate paragraph.*

   Done as suggested.

2. *P7886, L1. Discussion on aerosols is out of place. Should place it somewhere else. Analyses of aerosol simulations should be largely extended.*

   Done as suggested.

3. *P7889, L5, MOLLNER has weaker T dependence than Henderson et al. In several places, the test on HO_2 uptake is forgotten to mention.*

   Wrong: the temperature dependence of OH+NO_2 is T^{-3} in Mollner et al. and $T^{-1.8}$ in Henderson et al. (see Sect. 2.1).

4. *Fig. 10. Quantitative errors in SCIAMACHY are not described here nor in the text.*

   This has been corrected.

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