Author's comments in reply to the anonymous referee for "Decadal changes in global surface NOx emissions from multi-constituent satellite data assimilation " by K. Miyazaki et al.

We want to thank the referee for the helpful comments. We have revised the manuscript according to the comments, and hope that the revised version is now suitable for publication. Below are the referee comments in italics with our replies in normal font.

Reply to Referee #1

The paper analyses the changes in NOx polluting emissions, by assimilating different constituents from different satellite instruments in the chemistry-transport model. The manuscript is clear and it has nice logic flow. Because there are several works dealing with emission estimation using satellite-based observations, I would recommend stressing the added value of this approach (for example already in the abstract and in the trend calculation in Sect. 5.4), i.e. the assimilation of non-NO2 observations as compared to previous work where only NO2 is assimilated in the system. I recommend publication after addressing the following specific and technical comments.

The impact of non-NO2 measurements is discussed more carefully in the revised manuscript. Table 5 has been added to discuss the impact of non-NO2 measurements on the a posteriori emissions. Linear trend estimations from the NO2-only assimilation have been included in Table 4. The following discussions have been added to Section 5.1:

"Table 5 compares the estimated emissions between the multiple-species data assimilation and a NO2-only data assimilation. The estimated emissions differ in many regions if non-NO2 data assimilation is considered because the ratio of predicted NOx emission and NO2 column has been adjusted by non-NO2 observations. The assimilation of non-NO2 measurements leads to changes of up to about 70 % in the regional monthly-mean emissions. The estimated ten-year total regional emissions for South America and Australia are about 10 % lower in the multiple-species assimilation than in the NO2-only assimilation. The RMSE between the two estimates for the monthly total regional emissions is 15.5 % for central Africa, 16.5 % for Australia, and about 5-8 % for major polluted regions during the ten-year period. The estimated monthly mean emissions are mostly smaller in the multiple-species assimilation than in the NO2-only assimilation, especially over the tropical and southern subtropical regions such as South America, central Africa, and Australia, suggesting that NO2-only data assimilation tends to overcorrect the emissions from the a priori. The monthly total global emissions decrease by up to 6 TgN (in boreal summer) if non-NO2 data assimilation is considered. The ten-year linear trend is also different over most industrial areas (Table 4). For instance, the positive trend for India is 34.3 %/decade in the NO2-only assimilation, which is larger than the 29.2 %/decade in the multiple-species assimilation. For the United States, the negative trend is larger in the multiple-species assimilation (-29.4 %/decade) than in the NO2-only assimilation (-23.9 %/decade). These results confirm that the assimilation of measurements for species other than NO2 provides additional constraints on the NOx emissions over both anthropogenic and biomass burning regions."

P9 L17 The larger pixel size for GOME-2 and SCIAMACHY could indeed produce a dilution effect (lower NO2 level for larger pixel) compare to the smaller OMI pixel and thus, in principle, partially reduce the difference due to the different overpass time. Could you comment about that in the text?

The concentration of individual observations over polluted regions can vary between sensors, corresponding to the pixel size. However, because we employed the super observation approach and averaged multiple observations within a large super observation grid (i.e., about 2.8 degrees) before data assimilation, the influence of different pixel size should have a small impact on the data assimilation result, assuming the super observation grid is well covered by observation pixels. To clarify this point, the sentence has been rewritten as:

"Therefore, the differences in overpass time and also in pixel size could be the principle cause of the differences between the three different satellite retrievals, although the use of super observations for all the sensors reduces the influence of different pixel sizes."

Figure 2: It is quite difficult to distinguish the differences in these maps. It could be useful to show the differences compared to the observations in the second and third row, instead of the absolute tropospheric NO2 columns. It should help in highlighting the differences.

Figure 2 has been revised to show the differences.

P11 L19 Are there any known/expected differences in the ways of reporting, that you could mention here between the a priori and the EDGAR-HTAP emission databases?
P11 L29-30 Again, is there an expected reason to explain the similarity between EDGAR_HTAP and a posteriori emissions, relative to the a priori?

To our best knowledge, no comprehensive comparison has been made between these inventories.

P18 L18 You might want to refer here to this work about in plume chemistry effect: Vinken, G. C. M., Boersma, K. F., Jacob, D. J., and Meijer, E. W.: Accounting for non- linear chemistry of ship plumes in *the GEOS-Chem global chemistry transport model, Atmos. Chem. Phys., 11, 11707-11722, doi:10.5194/acp-11-11707-2011, 2011.*

Added.

P18 L32-33 It is unclear for me what do you mean for "overcorrect". Do you mean that NO2-only gives too high emission values? According Table 3, the NO2-only data assimilation almost always (except South America) gives smaller values than the full assimilation. Could you clarify?

We have extended the sensitivity calculation using NO2-measurements only. The results confirm that the estimated regional emissions are mostly higher in the NO2-only assimilation than in the multiple-species assimilation. To clarify this, the sentence has been rewritten as follows:
"The estimated monthly mean emissions are mostly smaller in the multiple-species assimilation than in the NO2-only assimilation, especially over the tropical and southern subtropical regions such as South America, central Africa, and Australia, suggesting that NO2-only data assimilation tends to overcorrect the emissions."

Table 4 and section 5.4: Do these emission trends change when NO2-only assimilation is taken into account? I would include in Table 4 also the trends with NO2-only assimilation if the differences are sizeable.

The linear trends from the NO2-only assimilation have been included in Table 4 and discussed in the revised manuscript.

How your results reported in Table 4 and Fig.8 compare with those reported as NO2 tropospheric columns (OMI Standard Product not DOMINO as in you study) by Krotkov et al. (2016) in their Fig. 8?

The following sentence has been added:
"These year-to-year variations in the observed NO2 concentrations have previously been reported by Duncan et al. (2016) and Krotkov et al. (2016)."

It could be interesting also to compare your results in China and US to the results by Liu et al. (2016) in Table S2 of their supplement. Those results are not based on data assimilation but are based on satellite data only. Liu, F., Beirle, S., Zhang, Q., Dörner, S., He, K., and Wagner, T.: NOx lifetimes and emissions of cities and power plants in polluted background estimated by satellite observations, Atmos. Chem.

Phys., 16, 5283-5298, doi:10.5194/acp-16-5283-2016, 2016.

Thank you for the information. However, Liu et al (2016) estimated emissions sources at a 40 km × 40 km scale for point source areas (power plants and cities), which is about seven time higher resolution than that of our estimates. As the estimated emissions may be sensitive to the resolution, direct comparison with their results is difficult.

Technical corrections
P1 L6 biased -> biases

Corrected.

P2 L23 add reference Krotkov et al. 2016 here too

Added.

P2 L22 Kalam -> Kalman
P6 L32 GOME-II -> GOME-2

Corrected.

P7 L18-19 This needs reference

Added.

P7 L25 You might want to mention that those resolutions are valid in nadir direction only, but get bigger on the side of the swath and actually since 2008-2009 OMI row-anomaly doesn't allow complete daily global coverage.

The following sentence has been added:
"Since December 2009, approximately half of the pixels have been compromised by the so-called row anomaly, which reduced the daily coverage of the instrument."

Table 2 Australis -> Australia (and in the other tables too)
P14 L20 Los Angels -> Los Angeles

P20 L30 There are two dots at the end of the sentence

Corrected.

Table 4: Caption: OM ->OMI

Corrected.

Table 4 Is there a reason you put Table 4 before 5 and 6 but then you refer to Table 4 only in section 5.4, after mentioning 5 and 6? Please, clarify.

Table 4 is referred before Table 5 and 6 in the revised paper,

Author's comments in reply to the anonymous referee for "Decadal changes in global surface NOx emissions from multi-constituent satellite data assimilation " by K. Miyazaki et al.

We want to thank the referee for the helpful comments. We have revised the manuscript according to the comments, and hope that the revised version is now suitable for publication. Below are the referee comments in italics with our replies in normal font.

Reply to Referee #2

1. I certainly appreciate the effort made by the authors to incorporate more data. There is logic to it: more data should be better than just one dataset. It is argued (maybe a bit too emphatically) that non-NO2 datasets improve the NOx emission estimation because they should lead to better estimation of the NOx lifetime in the model. In general, that might be true, but I wouldn't be so sure that it is automatically the case. I find that adding more data from different species might contribute to obscure the interpretation of the results, because the additional data come with their own limitations and uncertainties (including biases) which are not all well characterized. I am not fully convinced that authors understand perfectly the role of the different datasets in the assimilation. I wonder in particular to what extent the NOx emission updates are driven by the non-NO2 datasets. For example, ozone is apparently biased low in the model. Increasing NOx emissions is naturally found to improve ozone. But ozone could be biased low due to other reasons (transport, deposition, NMVOC chemistry and emissions). So, is ozone improved for the good reasons? Who knows? Many other CTMs overestimate surface ozone. I encourage the authors to moderate their claims regarding the advantages of additional data.
That being said, I concur that assimilating non-NO2 dataset should contribute to improve (somewhat) the NOx lifetime in the model, which is a good thing. But I would expect the authors to provide a more quantitative and systematic analysis of how the non-NO2 datasets influence the assimilation results. I also encourage the authors to be more cautious in their discussion, to reflect the possible limitations and complications associated with the use of additional, non-NO2 measurements.

We appreciate the author's constructive comments. First, the possible limitations associated with the use of non-NO2 measurements are more clearly discussed in the revised manuscript. The following sentences have been added to Section 5.3:
"Although the assimilation of multiple-species data influences the representation of the entire chemical system (Miyazaki et al., 2012b, 2015), the influence of model and observation errors remains a concern. In the multiple-species data assimilation, model performance is critical for the correct propagation of observational information between chemical species and to improve the emission estimation, whereas

biases in any of the measurement data sets (including non-NO2 measurements) may seriously degrade the emission estimation (Miyazaki et al., 2013). Improvements in the model, data assimilation scheme, and retrieved observations are essential to reduce the uncertainty on the emission estimates from the multiple-species data assimilation."

Secondly, the impact of non-NO2 measurements is more clearly discussed in the revised manuscript. Table 5 has been added to demonstrate the impact of non-NO2 measurements on the a posteriori emissions. Linear trend estimations from the NO2-only assimilation have been added to Table 4. The relevant discussions in Section 5.1 have been rewritten as follows:

"Table 5 compares the estimated emissions between the multiple-species data assimilation and a NO2-only data assimilation. The estimated emissions differ in many regions if non-NO2 data assimilation is considered because the ratio of predicted NOx emission and NO2 column has been adjusted by non-NO2 observations. The assimilation of non-NO2 measurements leads to changes of up to about 70 % in the regional monthly-mean emissions. The estimated ten-year total regional emissions for South America and Australia are about 10 % lower in the multiple-species assimilation than in the NO2-only assimilation. The RMSE between the two estimates for the monthly total regional emissions is 15.5 % for central Africa, 16.5 % for Australia, and about 5-8 % for major polluted regions during the ten-year period. The estimated monthly mean emissions are mostly smaller in the multiple-species assimilation than in the NO2-only assimilation, especially over the tropical and southern subtropical regions such as South America, central Africa, and Australia, suggesting that NO2-only data assimilation tends to overcorrect the emissions from the a priori. The monthly total global emissions decrease by up to 6 TgN (in boreal summer) if non-NO2 data assimilation is considered. The ten-year linear trend is also different over most industrial areas (Table 4). For instance, the positive trend for India is 34.3 %/decade in the NO2-only assimilation, which is larger than the 29.2 %/decade in the multiple-species assimilation. For the United States, the negative trend is larger in the multiple-species assimilation (-29.4 %/decade) than in the NO2-only assimilation (-23.9 %/decade). These results confirm that the assimilation of measurements for species other than NO2 provides additional constraints on the NOx emissions over both anthropogenic and biomass burning regions."

Thirdly, as suggested by the reviewer, the model ozone low bias could be introduced by errors other than those for NOx emissions. To discuss this, the following sentences have been added to Section 5.1:

"Note that the emissions of O3 precursors other than NOx, such as VOCs, and various model processes in atmospheric transport and chemistry influences the model performance. The optimization of additional precursors emissions and the improvement of the forecast model could be important for improving O3 simulations, as discussed in our previous studies (Miyazaki et al., 2012b; 2015)."

2. Regarding the use of 3 different NO2 sensors, it is obvious (and I think the authors know) that the diurnal cycle alone cannot explain entirely the difference between NO2 columns from e.g. GOME-2 and OMI. And even if it would, it is also obvious that the diurnal cycle of NOx emissions is only one among many different processes affecting the diurnal cycle of NO2 columns. This article presents a smart but crude procedure to improve the match with the 3 sensors simultaneously in spite of their inconsistencies: additional control parameters are introduced which allow modifying the diurnal cycle of emissions at every model pixel. Unfortunately, the result is not much credible as it would imply much stronger rush hour emission peaks even in regions where mobile emissions (cars) are not the main NOx source category. Power plans, industries, etc. do not have peak activity around 8 AM. The most negative values of the Etc parameter (Fig. 13) are found in Inner Mongolia, which has only few cars but does have power plants. Even though the diurnal cycle adjustment serves its purpose, it is clearly artificial. The authors should provide a better explanation of why they choose this procedure. Maybe it is the only one which works since we don't really understand the reasons for the inconsistency between morning and afternoon sensors. More discussion is warranted.

I agree that the diurnal emission variation does not solely explain the simulated tropospheric NO2 column differences between the OMI and GOME-2 (or SCIAMACHY) overpass time. Because of model errors and differences between the satellite instruments, the obtained diurnal cycle adjustment can be artificial for some cases, as mentioned by the reviewer. The following sentences have been added to note this point more clearly:

In Section 3.2.1:

"Multiple satellite NO2 retrievals obtained at different overpass times have the potential to constrain diurnal emission variability (e.g., Lin et al., 2010), although differences between the different NO2 retrievals and errors in model processes could introduce artificial corrections (see also Section 5.2). Note that the retrievals from different instruments used are all based on the same retrieval method (DOMINO v2, TM4NO2A v2) and largely consistent ancillary data, which limits the discrepancies between the data sets to large degree (Boersma et al., 2008) (see Section 2.3.1). We also acknowledge that differences between the surface reflectivity and cloud data used may lead to some structural uncertainty between the morning and afternoon sensors, although numerous validation studies pointed out that the three NO2 column retrievals agree well with independent reference data (e.g., Irie et al., 2011; Ma et al., 2013)."

In Section 5.2:

"Thus, the model errors could artificially affect the diurnal emission variability."

Over Mongolia, the soil-type emission diurnal variability function was applied to the a priori emissions

with a maximum in the afternoon. Thus, the negative values of Etc may imply too much afternoon emission because of the applied a priori diurnal variability. To more precisely describe the applied diurnal emission variability function, the model description in Section 2.1 has been rewritten as follows:
"We applied anthropogenic-type diurnal variations for total emissions with maxima in morning and in evening with a factor of about 1.5 (black dotted line in Fig. 1, for which the daily mean hourly emission value is 1) in Europe, eastern China, South Korea, Japan, India, and North America; biomass burning-type variations with a rapid increase in morning and maximal emissions in the mid-day with a maximum factor of about 4 in North and central Africa, southeast Asia, and northern and central South America; and soil-type diurnal variations with maximal emissions in afternoon with a factor of about 1.2 in Australia, Sahara, western China, and Mongolia."

The relevant discussions in Section 5.2 have been rewritten as follows:
"The optimized Etc for biomass-burning and soil emission dominant regions are mostly slightly negative, which may suggest that the applied diurnal emission variability with an afternoon maximum (see Section 2.1) was misleading for some regions. In contrast, they are positive for most of the ocean. These results suggest the need to not only correct diurnal NO2 variations, but also account for the differences in the sampling and bias between OMI and other instruments as well as the influences of model errors."

3. Although the paper is already quite long, I would expect at least some comparisons with independent NO2 measurements. The reader has no clue regarding how the model performs for vertical profiles of NO2. Also, given the focus of the paper on the diurnal cycle, comparisons with ground-based remote sensing data could be useful. Therefore, although this article is clearly interesting and the methodology appears generally sound, I recommend that the authors try to address those main comments, as well as the other comments listed below, before it can be published in ACP.

Comparisons with independent airborne and ground-based lidar measurements have been added. The data used are described in Section 2.4, and the validation results of the vertical profile are shown in Fig. 4 and discussed in Section 3.4 of the revised manuscript. We will not discuss detailed diurnal variations of the simulated NO2 profiles, since this requires careful discussions and is beyond the scope of this paper.

Page 5, 1st full paragraph: I find odd to apply a unique diurnal cycle to all emissions in a given region, e.g. the anthropogenic-type cycle over Europe, eastern China, Japan, North America. This is strange. Why not make a weighted average based on the fractional a priori contribution of anthropogenic, biomass burning and soil emissions? The diurnal cycle in New York doesn't have to be the same as in Wyoming.

Considering the large uncertainty in the individual inventory, we decided to use the simple diurnal emission variability scheme based on the dominant emission category, as in other global model studies (e.g., Boersma et al., 2008; 2011). Nevertheless, we confirmed that this simple scheme leads to significant improvements on the model performance (Miyazaki et al., 2012a).

Page 5, 2nd paragraph: What is the vertical LNOx profile parameterization?

The following sentence has been added:
“The vertical profiles of the LNOx sources are determined on the basis of the C-shaped profile given by Pickering et al. (1998).”

Page 8, 1st full paragraph: Apparently the retrievals of Boersma et al. (2011, 2004) are used. But then the section goes on mentioning reduced errors based on Maasakkers (2013) even though the retrieval of Maasakkers is not used. This is difficult to understand.

The paragraph has been rewritten for easier understanding.

Page 10, lines 9-10: The assimilation effectively corrected the NO2 columns at the different overpass times. The complete diurnal cycle of NO2 concentration is an entirely different story. The model performance could be checked by comparisons with ground-based remote sensing data.

I agree with this comment. The sentence has been replaced by:
“Considering the short lifetime and rapid diurnal variation of biomass burning activity at low latitudes, these improvements suggest that the assimilation of multiple-species and multiple NO2 measurements effectively corrected the temporal changes in the tropospheric NO2 column between the different overpass times.”
Comparisons with ground-based measurements have been added. Please see my reply above.

Page 10, line 13: Here and elsewhere, the observation errors for highly polluted cases are considered very large. But the relative errors there are often of the order of 25-35% which is generally less than at more remote locations. Of course during the winter, things are different due to large zenith angles, clouds, and snow.

We here discuss the absolute errors, which are larger over polluted areas than over remote areas.

Page 10, line 17: Some explanation on why the model lifetime of NOx would be too short would be useful.

The sentence has been rewritten as:
"The remaining errors may also result from model errors such as too short lifetime of NOx through the NO2+OH and NO+HO2 reactions and the reactive uptake of NO2 and N2O5 by aerosols (e.g., Lin et al., 2012b; Stavrakou et al. 2013)."

Page 12, on trends: The total number of observations changes during the 10-year period. Also the different satellites provided data during different periods. Some comments on possible consequences for trend estimation are needed.

The relevant sentence in Section 5.3 has been rewritten as follows:
"Discontinuities in the assimilated measurements (e.g., lack of most TES retrievals after 2010, OMI row anomaly since January 2009, and the limited data coverage of SCIAMACHY (before February 2012) and GOME-2 (after January 2007)) may also affect long-term emission estimates."

Page 12, lines 15-17: The emission factors are indeed uncertain, but so are also the biomass burnt estimates.

The sentence has been rewritten as:
"... large uncertainties in emission factors and biomass burnt estimates used in the inventories."

Page 12, lines 17-18: Note that the year-to-year variations over South America are very large.

To clarify the meaning and in response to a suggestion from another referee, the sentence has been rewritten as:
"The weak year-to-year variations in the a priori emissions are partly attributable to the use of climatology after 2011"

Page 12, lines 30-34: the increases aren't highest just over cities and lowest over remote areas. The entire N-E China and the Guangzhou area show large increases. The Chengdu/Chongqing area (with emission decreases) is certainly not "remote". Over N-E China, given the model resolution, it is not possible to distinguish urban from rural areas. Furthermore, Inner Mongolia shows large increases.

Thank you for this point. The sentence has been rewritten as:
"At the grid scale, the estimated emissions are higher than the a priori emissions over northern and eastern China, such as Beijing (+58 % at the nearest grid point), Tianjin (+97 %), Nanjing (+30 %), and around Guangzhou (+78 %), whereas they are lower around Chengdu and Chongqing (Fig. 10)."

Page 14, 1st full paragraph: The results regarding the trends in Europe are difficult to understand. Could you compare with previous studies for Europe, e.g. Curier et al. (Remote Sens. Environ. 2014, doi:10.1016/j.rse.2014.03.032)?

The following sentence has been added:
"Strong negative emission trends over these regions were similarly found by Curier et al. (2014) for 2005--2010."

From Figure 3, the OMI observations indicate a positive NO2 trend, whereas GOME-2 shows the opposite trend. Such difference cannot be due the diurnal cycle of NO2. Apparently those instruments have drifts which can be interpreted as emission trends. Please comment on this.

Firstly, as the estimated emission does not follow a simple linear trend, the comparison of linear trends between the three sensors estimated for different time periods is difficult. Secondly, the positive trend in OMI is partly attributed to very high concentrations in November 2011. We confirmed that the weather for November 2011 was unusual in Europe. For instance, in the Netherlands, it was the driest month in 100 years of measurements, with ten times less rainfall than the climatological mean. Strong high-pressure systems prevented rain from washing out the NO2 pollution. GOME-2 and SCIAMACHY do not reveal such high concentrations in November 2011, although the reason for this is unclear (the different sampling rates between the sensors could partly explain this). This difference can partly explain the different trend between the sensors. Thirdly, we point out that the trends (or year-to-year variations) found from the three sensors are mostly consistent, except for Europe. Further efforts are required to investigate the observed NO2 trends from the three sensors. However, this is beyond the scope of this paper.

Page 14, line 23 "The summertime peak enhancement is obvious over remote regions": Could you substantiate that claim?

The sentence has been rewritten as:

“The summertime peak enhancement is obvious over remote regions such as high-temperature agricultural land over the South Atlantic, the East South Central, and the Southwestern United States,...”

Page 15, line 10: Couldn’t this be verified with e.g. MODIS fire counts or other biomass burning proxies?

The cited paper (Venkataraman et al., 2006) confirmed the fact using MODIS fire counts.

Page 15, line 27: Although temperature has some effect, the shorter NOx life times at tropical latitudes such as India are primarily due to higher photolysis rates and specific humidity.

The sentence has been rewritten as:
“In contrast, tropospheric NO2 columns over India are much lower compared to those in northern midlatitude polluted areas, as a result of the high values of temperature, photolysis rates, and specific humidity, leading to shorter NO2 lifetimes throughout the year (Beirle at al., 2011).”

Page 16, line 3: Why would high resolution analysis be required? This shouldn’t be so complicated. For example, biomass burning has a distinct seasonality which can be probed at coarse resolution.

This sentence describes point sources (i.e., power plants) over Southern Africa. For such cases, high-resolution analysis is required to distinguish between different emissions sources, whereas coarse resolution models are known to underestimate NO2 concentration (Valin et al., 2011). To clarify these points, the sentence has been rewritten as:
“The various emission sources may have experienced different variations, and high resolution emission analysis is required to understand the detailed spatial variation in these emissions and to obtain unbiased emission estimates (Valin et al., 2011).”

Page 16, end of section 4.2.6. The high temporal correlation between N. Africa and Central Africa is interesting. Would this be related to biomass burning or to soil emissions (or both)? Examination of MODIS fire counts could help, also possibly temperature data. Is this correlation also found in the NO2-only assimilation?

A similar correlation is found in the NO2-only assimilation. This is indeed interesting. However, detailed analysis of the causal mechanisms for individual cases is beyond the scope of this study.

Page 19, first paragraph: Basically, the improved ozone is due to the general increase in NOx emissions over all regions, whereas the a priori model seems to have a negative bias in surface ozone. In the study of Travis et al. (ACPD, 2016, doi:10.5194/acp-2016-110), NOx emissions over the U.S. are found to be largely overestimated in comparisons with aircraft data.

We understand some models have a positive ozone bias, and these models may have NO2 biases that also differ from our results. The description in this paper is of the MIROC simulation results, and we do not attempt to generalize the implication of this to other models.

Page 19, last full paragraph: Could you also provide the global tropospheric chemical lifetime of methane (or methyl chloroform) in the model?

The methane lifetime was not calculated in the simulation.

Page 20, first sentence: "The inverse lifetime is expected to be proportional to the ratio of NOx to NO2". It's the other way around. Increase the NOx to NO2 ratio should increase the fraction of NO (which does not react with OH) and therefore decrease the sink of NOx, i.e. the inverse lifetime. The main effect of a NOx emission increase is (most often) increased OH levels and therefore shorter NOx lifetime. The point which is made in this paragraph is unclear.

To clarify the meaning, the paragraph has been rewritten as follows:

"To elucidate the changes in the NOx chemical lifetime, Table 6 compares the lower tropospheric OH concentration and the ratio of the regional mean surface NOx emissions and lower tropospheric NO2 concentrations (averaged from the surface to 790 hPa) between the multiple-species data assimilation and the model simulation (NOx-emi/NO2) in the boreal summer. It was confirmed that both the concentration assimilation (mainly TES O3 and MOPITT CO measurements) and the changes in surface NOx emissions lead to an increase in the OH concentration in the lower troposphere. Meanwhile, the increased ratio of NOx to NO2 (i.e. increased fraction of NO) in the multiple-species assimilation compared to the model simulation indicates that the HO2+NO reaction, which is the source of OH, is enhanced in the multiple-species assimilation. These results suggest that NOx chemical lifetime is decreased because of increased OH concentrations (through the NO2+OH reaction, which acts as the main sink of NOx) in the multiple-species data assimilation over most industrial and biomass burning areas, and demonstrate the utility of the multiple-species assimilation to constrain the tropospheric chemistry (i.e. chemical regime) controlling NOx variations and to improve surface NOx emission inversions."

Page 20, lines 20-25: The large adjustments are first said to suggest a change in diurnal evolution of the emissions. Then they are said to suggest other possible causes related to the model or the retrievals. Correct, but then the first suggestion is not necessary. Values of Etc as negative as -0.6 or -0.8 are found at some locations, which are impossibly large. Large Etc should be found only in areas where traffic is the dominant source. This does not appear to be the case (Fig. 13).

I understand that some results are difficult to understand based on a change in the diurnal evolution of the emissions, but both possibilities remain valid. We cannot ignore either of them, without any evidence. Therefore, we believe that the current statement is reasonable. Please also see our reply above.

Page 22, line 4: Is the given observed NO2 concentration trend for OMI or for all sensors? The trend appears very different between GOME-2 and OMI.

Yes, the statement is based on the OMI observations, which is described in the revised manuscript. As shown by the black straight line in Fig. 3, the trend is different between the sensors. To explain this, the following sentence has been added. Please also see my reply above.
"Note that the linear trend in the observed concentration is different between the instruments over Europe (c.f., Fig. 3)."

Page 22, line 6: Why would NO2 have become more long-lived? Does OH show a negative trend in this region? If so, what are the causes for this trend? Note that the fraction of NO2 to NOx is determined mostly by ozone and the photolysis rate of NO2. A shift in NO2:NOx emission ratio does not matter much except directly over emission areas (titration effect). The paragraph seems to imply that the NO2:NOx emission ratio in the model has changed over the 10-year period. Is this true?

This paragraph describes how the NO2 concentration/NOx emission ratio has changed over the ten-year period over Europe. OH trends and the causal mechanisms are not discussed in the manuscript, since there could be many factors affecting them, as suggested by the reviewer. Therefore, as described in the manuscript, further efforts will be required to explain these mechanisms (in a separate study).

Technical corrections

Page 1: "Forkert" should be "Folkert"

Corrected.

p. 1 l. 6: “biased" should be “biases"

Corrected.

p.1 l. 8: “the development” : do you mean the evolution?

Yes, replaced.

p. 2 l. 2: “traffic rush hours, economic activity. . .” those are not “source categories”. Sentence is confusing, please rephrase.

The sentence has been replaced by:

“Examples include traffic rush hours, economic activity, biomass-burning activity, wintertime-heating of buildings, and rain-induced emission pulses of NOx”.

p. 2 l. 25: Kalam should be Kalman

Corrected.

p. 2 l. 33: insert a hyphen between “multi” and “constituent” same line: replace advancement by advance or progress

Corrected.

p. 3, l. 21-22: The sentence “The OH magnitude and gradient is the primary chemical pathway for propagating observational information...” does not make much sense. Rephrase or delete.

The sentence has been rewritten as follow:

“The changes in OH are the important chemical pathway for propagating observational information between various species and for modulating the chemical lifetimes among these species.”

p. 3 l. 31: Replace maybe “an EnKF technique” by “a variant of the EnKF technique”

Replaced.

p. 4 l. 25: Explain "background spread"

The sentence has been replaced by
"...of background error covariance in the stratosphere, as estimated from ensemble model simulations,.."

p. 4 l. 30: Isn't Yienger and Levy (1995) the correct reference for GEIA NOx? Please check.

Corrected.

p. 6 lines 12, 16, 22: I think "Ets" should be "Etc"

Corrected.

p. 6 l. 31: GOME-2 (not GOME-II)

Corrected.

p. 10 l. 24: Here and at other instances, replace "c.f." by more standard phrasing (e.g. "see")

Corrected.

p. 11 l. 12: the sentence seems to imply that the chemical lifetime of NOx might be underestimated, which is not what you mean here. Rephrase.

The words "(and/or chemical lifetime of NOx)" have been removed.

p. 11 l. 20: I suppose you mean GFED 3 here, not EDGAR 4.2 (see section 2.1)

Corrected.

p. 12 l. 9: "southern parts of the Eurasian continent" : don't you simply mean China? The seasonal variation over Southeast Asia does not show a summer maximum, so it does not fit into the point made in this sentence.

Corrected.

p. 12 l. 18 "assumptions applied for the a priori emissions" I think you could be more specific (use of climatology after 2011)

Corrected.

p. 12 l. 27: "The EDGAR v4 emissions are too low": that statement is too blunt for several reasons. Replace "EDGAR v4" by "our a priori inventory" (since EDGAR for 2008 is used after 2008, and since soil emissions are not from EDGAR). Furthermore, add something like "Our assimilation indicates that. . .".

Replaced by "Out a priori inventory is..."

p. 12 l. 28: "too low by a factor of 0.6": awkward. Should be too low by a factor of 1/0.6 (i.e. about 1.7)

Replaced by "by about 40 %".

p.12 l. 29: emissions are maximum in June, not July.

Replaced.

p. 13 l. 34: "in the reported mobile emissions": why specifically in this source category?

The sentence has been removed.

p. 14 l. 1: replace "reveal" by "show"

Replaced.

p. 14 l. 2: replace "by" by "after"

Replaced.

p. 14, l. 18: "around Atlanta (...) and Denver": this seems to indicate that increments are found mostly over cities, which is not true. Consider replacing by "Southeast US and most of Western US"

Replaced by “the Southeast United States (e.g., +23 % near Atlanta) and most of the Western United States (e.g., +26 % near Denver),”

p. 14 l. 19: delete “over” after “around”

Removed.

p. 14 l. 20: Los Angeles

Corrected.

p. 15 l. 9: I think the word “boreal” is superfluous here (and at many other instances in the text)

Removed.

p. 15 l. 20-21: “particularly strong increase around Delhi” but the changes over Delhi are lower than the regional average!

Delhi has been removed from this statement.

p. 16 l. 5: Replace “by data assimilation” by “due to data assimilation”

Replaced

p. 16 l. 33: replace “reflection” by “reflecting” same line: replace “when” by “whereas”

Replaced.

p. 19 l. 17: LNOx (instead of LNO)

Corrected.

p. 19 l. 34: here and elsewhere in the manuscript, insert hyphen between “multiple” and “species”

Corrected.

p. 20 l. 17: Replace "rom the three. . ." by "constrained by the three. . ."

Replaced.

p. 21 l. 8: "using either model after data assimilation" : awkward, the model is used for data assimilation

Replaced by "either model and data assimilation".

p. 32: Table 2 and elsewhere: Replace "Australis" by "Australia"

Corrected.

p. 41 Figure 6: it is impossible to distinguish black and dark blue on the "South America" plot. Consider using other colors.

Changed.

p. 44, Figure 9: the title of the middle panels should be "A posteriori – A priori". Same for the title of the right panels, the minus sign is missing.

Corrected.

Decadal changes in global surface NOx emissions from multi-constituent satellite data assimilation

\begin{abstract}

Global surface emissions of nitrogen oxides (\chem{NO_x}) over a ten-year period (2005--2014) are estimated from an assimilation of multiple satellite datasets: tropospheric \chem{NO_2} columns from OMI, GOME-2, and SCIAMACHY; \chem{O_3} profiles from TES; CO profiles from MOPITT; and \chem{O_3} and \chem{HNO_3} profiles from MLS using an ensemble Kalman filter technique. Chemical concentrations of various species and emission sources of several precursors are simultaneously optimized. This is expected to improve the emission inversion because the emission estimates are influenced by ~~biased~~ biases in the modelled tropospheric chemistry, which can be partly corrected by also optimizing the concentrations. We present detailed distributions of the estimated emission distributions for all major regions, the diurnal and seasonal variability, and the ~~development~~ evolution of these emissions over the ten-year period. The estimated regional total emissions show a strong positive trend over India (+29 \%/decade), China (+26 \%/decade), and the Middle East (+20 \%/decade), and a negative trend over the United States (-38 \%/decade), Southern Africa (-8.2 \%/decade), and western Europe (-8.8 \%/decade). The negative trends in the United States and western Europe are larger during 2005--2010 relative to 2011--2014, whereas the trend in China becomes negative after 2011. The data assimilation also suggests a large uncertainty in anthropogenic and fire-related emission factors and an important underestimation of soil \chem{NO_x} sources in the emission inventories. Despite the large trends observed for individual regions, the global total emission is almost constant between 2005 (47.9 \unit{Tg\,N\,yr^{-1}}) and 2014 (47.5 \unit{Tg\,N\,yr^{-1}}).

\end{abstract}

\introduction

Nitrogen oxides (\chem{NO_x}=\chem{NO}+\chem{NO_2}) play an important role in air quality, tropospheric chemistry, and climate. Tropospheric \chem{NO_x} concentrations are highly variable in both space and time, reflecting its short chemical lifetime in the atmosphere and the heterogeneous distribution of its sources and sinks. Emission sources are important in determining the amount and distribution of \chem{NO_x}. Natural \chem{NO_x} sources include biogenic emissions from bacteria in soils, biomass burning, and lightning. Anthropogenic \chem{NO_x} sources include fossil fuel and biofuel combustion, emissions from vehicle transport, and industrial emissions. Bottom-up inventories from different sources and regions contain large uncertainties, which result from inaccurate emission factors and activity rates for each source category.~~,~~ Examples include ~~including~~ traffic rush hours, economic activity, biomass-burning activity, wintertime-heating of buildings, and rain-induced emission pulses of \chem{NO_x} (e.g., Velders et al., 2001; Jaegl\'{e} et al., 2005; Wang et al., 2007; Xiao et al., 2010; Streets et al., 2013; Castellanos et al., 2014; Reuter et al., 2014; Vinken et al., 2014; Oikawa et al., 2015). As a result, bottom-up inventories generally do poorly at representing the spatial and temporal variability at multiple scales (i.e., diurnal, daily, seasonal, and interannual). Large uncertainties in biomass burning emissions mainly reflect a relative lack of observations for characterizing the large spatial and temporal variations of burning conditions (Castellanos et al., 2014). The wide range in soil \chem{NO_x} emission estimates in previous studies reflect incomplete knowledge of the emission factors and processes driving these emissions (Oikawa et al., 2015). Recent studies (e.g., Steinkamp and Lawrence, 2011, Hudman et al., 2012, Vinken et al., 2014) suggest that soil \chem{NO_x} emissions are likely around 10 \unit{Tg\,N\,yr^{-1}}, a considerable increase relative to earlier studies that assumed about 5 \unit{Tg\,N\,yr^{-1}} soil \chem{NO_x} emissions (Yienger and Levy, 1995). Large uncertainties are also in lightning \chem{NO_x} (\chem{LNO_x}) source estimates. Schumann and Huntrieser (2007) provided a best estimate of 5$\pm$3 \unit{Tg\,N\,yr^{-1}} for the annual global \chem{LNO_x} source. More recently, Murray et al. (2012), Stavrakou et al. (2013), and Miyazaki et al. (2014) estimated at 6$\pm$0.5, 3.3--5.9, and 6.3$\pm$1.4 \unit{Tg\,N\,yr^{-1}}, respectively.

Tropospheric \chem{NO_2} columns retrieved from satellite measurements, including the Global Ozone Monitoring Experiment (GOME), Scanning Imaging Absorption Spectrometer for Atmospheric Cartography (SCIAMACHY), GOME-~~II~~2, and the Ozone Monitoring Instrument (OMI), have been used to infer \chem{NO_x} emissions using top-down approaches (e.g., Martin et al., 2003; Richter, 2004; Jaegl\'{e} et al., 2005; van der A et al., 2006; Zhang et al., 2007; Boersma et al., 2008a; Stavrakou et al., 2008; van der A et al., 2008; Kurokawa et al., 2009; Zhao and Wang, 2009; Lamsal et al., 2010; Lin et al., 2010; Miyazaki et al., 2012a; Gu et al., 2013; Mijling et al., 2013; Vinken et al., 2014; Ding et al., 2015; Lu et al., 2015). Long-term tropospheric \chem{NO_2} column records have allowed us to investigate changes in the atmospheric environment over the past decade as a result of economic growth and emission controls over major polluted regions (Castellanos and Boersma, 2012; Hilboll et al., 2013; Cui et al., 2015; Lelieveld et al., 2015; Wang et al., 2015; Duncan et al., 2016; Krotkov et al. 2016).

Advanced data assimilation techniques such as four-dimensional variational assimilation (4D-VAR) (M\"{u}ller and Stavrakou, 2005; Kurokawa et al., 2009; Chai et al., 2009) and ensemble ~~Kalam~~ Kalman filter (EnKF) (Miyazaki et al., 2012a, 2012b, 2014, 2015) have been employed to take full advantage of the chemical transport model (CTM) and satellite retrievals in top-down emission estimates. These advanced techniques consider flow-dependent forecast error covariance and take errors from both the model and retrievals into account. These advantages are considered essential for improving long-term global emission estimates, as dominant atmospheric processes, the emission--concentration relationships, and observational sampling and errors must be incorporated into the analysis. These advanced methodologies can readily assimilate multiple~~-~~ species. The additional observations of \chem{O_3} and \chem{CO} constrain surface \chem{NO_x} emissions through their indirect impact on \chem{NO_2} concentrations through tropospheric chemistry. These species directly influence \chem{OH} concentrations, which control the \chem{NO_x} variability and lifetime, and indirectly the accuracy of the emission estimates. Chemically consistent, multi~~--~~constituent assimilation is an advance~~ment~~ over conventional approaches, which assume \chem{NO_2} observations are uniquely controlled by \chem{NO_x} emissions.

Various sources of error in current chemical transport models (CTMs) impact the simulated \chem{NO_x} lifetime and the accuracy of \chem{NO_x} emission inversions (Lin et al., 2012a; Miyazaki et al., 2012a; Stavrakou et al., 2013). Stavrakou et al. (2013) showed the strong effect of chemical \chem{NO_x} loss uncertainties on top-down \chem{NO_x} source inversions. \chem{OH} is the main radical responsible for the removal of atmospheric pollution and for determining the lifetime of many chemicals including \chem{NO_x} (Levy, 1971; Logan et al., 1981; Thompson, 1992), but its concentrations in CTMs are considered to have large uncertainties (Naik et al., 2013; Miyazaki et al., 2015; Patra et al., 2015). Meanwhile, representations of \chem{LNO_x} sources are essential for realistic representations of tropospheric \chem{NO_2} columns, but current parameterizations contain large uncertainties (Martin et al., 2007; Schumann and Huntrieser, 2007; Miyazaki et al., 2014). Errors in representing these natural sources of \chem{NO_2} can directly propagate into surface \chem{NO_x} emissions estimates.

Increasing attention has been paid to combining observations of ~~multiple ~~multiple-species to improve the analysis of tropospheric chemistry, including for \chem{NO_x} emission estimates. Measurements of species other than \chem{NO_2} (e.g., \chem{O_3} and \chem{HNO_3}) could improve the representation of \chem{NO_x} in models through their chemical interactions with \chem{NO_x} (e.g., Hamer et al., 2015). Advanced data assimilation techniques such as 4D-VAR and EnKF propagate observational information from a limited number of observed species to a wide range of chemical components. Miyazaki et al. (2012b, 2014, 2015) and Miyazaki and Eskes (2013) demonstrated that the assimilation of ~~multiple ~~multiple-species observations, taking their complex chemical interactions into account using an EnKF technique, can provide comprehensive constraints on both concentration and emissions, and this approach has the potential to improve emission inversions by accounting for confounding factors in the relationship between \chem{NO_x} emissions and \chem{NO_2} concentrations. Because of the simultaneous assimilation of multiple-species data with optimisation of both the concentrations and emission fields, the global distribution of \chem{OH} was modified considerably, decreasing the \chem{OH} gradient between NH and SH (Miyazaki et al., 2015). The –changes in ~~The ~~\chem{OH} ~~magnitude and gradient is~~are the ~~primary ~~important chemical pathway for propagating observational information between various species and for modulating the chemical lifetimes among these species.

In this study, we estimate global surface \chem{NO_x} emissions between 2005 and 2014 using the assimilation of ~~multiple-~~multiple-species data from OMI \chem{NO_2}, GOME-2 \chem{NO_2}, SCIAMACHY \chem{NO_2}, Tropospheric Emission Spectrometer (TES) \chem{O_3}, Measurement of Pollution in the Troposphere (MOPITT) \chem{CO}, and Microwave Limb Sounder (MLS) \chem{O_3} and \chem{HNO_3} retrievals using an EnKF technique. We attempted to optimize the diurnal variations in surface \chem{NO_x} emissions, while updating daily, seasonal, and interannual emission variations, based on a combination of three \chem{NO_2} retrievals obtained at different overpass times. The assimilation of multiple chemical data sets with different vertical sensitivity profiles provides comprehensive constraints on the global \chem{NO_x} emissions while improving the representations of the entire chemical system affecting tropospheric \chem{NO_2} column variations, including \chem{LNO_x} sources. Based on the EnKF estimations, this study presents detailed distributions of the surface \chem{NO_x} emissions for all major regions, the diurnal and seasonal variability, and the development over the ten-year period.

\section{Methodology}

The data assimilation system is constructed based on the global CTM MIROC-Chem (Watanabe et al. 2011) and on a variance of the~~n~~ EnKF technique. The basic framework is similar to the system used to produce tropospheric chemistry reanalysis data (http://www.jamstec.go.jp{\slash}res{\slash}ress{\slash}kmiyazaki{\slash}reanalysis{\slash}) in our previous study (Miyazaki et al., 2015); however, some updates to the data assimilation framework have been made and the calculation has been extended to cover the ten years from 2005 to 2014, as described below.

\subsection{MIROC-Chem model and a priori emissions}

The original forecast model used in our previous study (CHASER ; Sudo et al. 2002) is replaced by the newer MIROC-Chem model (Watanabe et al., 2011). MIROC-Chem represents the chemistry part of the MIROC-ESM Earth system model. It considers detailed photochemistry in the troposphere and stratosphere by simulating tracer transport, wet and dry deposition, and emissions, and calculates the concentrations of 92 chemical species and 262 chemical reactions (58 photolytic, 183 kinetic, and 21 heterogeneous reactions). Its tropospheric chemistry was developed based on the CHASER model, with many updates to chemical reactions and emissions, considering the fundamental chemical cycle of Ox-\chem{\chem{NO_x}}-HOx-\chem{CH_4}-CO along with oxidation of NMVOCs (ethane, ethane, propane, propene, butane, acetone, methanol, isoprene, and terpenes) to properly represent ozone chemistry in the troposphere. Its stratospheric chemistry was developed based on the CCSR/NIES stratospheric chemistry model (Akiyoshi et al., 2004), which calculates chlorine and bromine containing compounds, CFCs, HFCs, OCS, \chem{N_2O}, and the formation of PSCs and associated heterogeneous reactions on their surfaces.

MIROC-Chem has a T42 horizontal resolution (approximately 2.8$^\circ\times$2.8°) and uses the hybrid terrain-following pressure vertical coordinate system with 32 vertical levels from the surface to 4.4 hPa. It is coupled to the atmospheric general circulation model MIROC-AGCM version 4 (Watanabe et al., 2011). The radiative transfer scheme considers absorption within 37 bands, scattering by gases, aerosols, and clouds, and the effect of surface albedo. Detailed radiation calculations are used for photolysis calculation. The MIROC-AGCM fields were nudged toward the 6-hourly ERA-Interim (Dee et al., 2011) at every model time step to reproduce past meteorological fields and to simulate short-term (i.e., less than 6 hours) meteorological variability and sub-grid scale transport effects.

The forecast model update from CHASER to MIROC-Chem improved the simulated profiles of various tropospheric species (not shown). The inclusion of stratospheric chemistry in MIROC-Chem allowed us to provide reasonable estimates of a priori profiles and their ensemble spread in the stratosphere. Since TES \chem{O_3} and MOPITT CO retrievals in the troposphere, together with MLS retrievals, have sensitivity to the lower stratospheric concentration to some degree, the improved representation of background error covariance in the stratosphere, as estimated from ensemble model simulations, ~~spread in the stratosphere~~

meant that satellite retrievals are more effectively assimilated into the updated system throughout the troposphere and stratosphere through the use of observation operator (c.f., Sec. 2.3).

The a priori values for surface emissions of \chem{NO_x} and \chem{CO} were obtained from bottom-up emission inventories. Annual total anthropogenic \chem{NO_x} and \chem{CO} emissions were obtained from the Emission Database for Global Atmospheric Research (EDGAR) version 4.2 (EC JRC/PBL, 2012) for 2005--2008. Emissions from biomass burning were based on the monthly Global Fire Emissions Database (GFED) version 3.1 (van der Werf et al., 2010) for 2005--2011. Emissions from soils were based on monthly mean Global Emissions Inventory Activity (GEIA) (Yienger and Levy, 1995)~~(Graedel et al., 1993)~~. To cover data limitations during 2005--2014, EDGAR emissions for 2008 were used in the calculations for 2009--2014, and GFED emissions averaged over 2005--2011 were used in the 2012--2014 calculation. The global total a priori \chem{NO_x} emissions averaged over the 2005-2014 period from anthropogenic sources, biomass burning, and soils are 28.7, 4.3, and 5.4 \unit{Tg\,N\,yr^{-1}}, respectively. The total aircraft \chem{\chem{NO_x}} emission is 0.55 \unit{Tg\,N\,yr^{-1}}, which is obtained from the EDGAR inventory.

Following the settings of Lotos-Euros (Schaap et al., 2008) and Boersma et al. (2008b), we applied anthropogenic-type diurnal variations for total emissions with maxima in morning and in evening with a factor of about 1.5 (black dotted line in Fig. 1, for which the daily mean hourly emission value is 1) in Europe, eastern China, South Korea, Japan, India, and North America; biomass burning-type variations with a rapid increase in morning and maximal emissions in the mid-day with a maximum factor of about 4 in North and central Africa, southeast Asia, and northern and central South America; and soil-type diurnal variations with maximal emissions in afternoon with a factor of about 1.2 in Australia, Sahara, ~~and~~ western China, and Mongolia.

\chem{LNO_x} sources in MIROC-Chem were calculated in conjunction with the convection scheme of MIROC-AGCM. The global distribution of the flash rate was parameterised for convective clouds based on the relationship between lightning activity and cloud top height

(Price and Rind, 1992). The vertical profiles of the \chem{LNO_x} sources are determined on the basis of the C-shaped profile given by Pickering et al. (1998). The mean yearly global flash rate obtained for 2005--2014 was 42.4 \unit{flashes\,s^{-1}}, which is close to climatological estimates of 46 \unit{flashes\,s^{-1}} derived from Lightning Imaging Sensor (LIS) and Optical Transient Detector (OTD) measurements (Cecil et al., 2014). The \chem{LNO_x} sources were optimized in the data assimilation runs, following the method of Miyazaki et al. (2014).

\subsection{Emission estimates from EnKF data assimilation}

Data assimilation is based on an ensemble square root filter (SRF) EnKF approach (i.e., a local ensemble transform Kalman filter; LETKF; Hunt et al., 2007). As in other EnKF approaches, the background error covariance is estimated from ensemble model forecasts based on the assumption that background ensemble perturbations sample the forecast errors. Using the covariance matrices of observation error and background error, the data assimilation determines the relative weights given to the observation and the background, and then transforms a background ensemble into an analysis ensemble. Unlike standard EnKF analyses, the LETKF analysis is performed locally in space and time, which reduces sampling errors caused by limited ensemble size. Furthermore, the analysis is performed independently for different grid points, which reduces the computational cost through parallel computations. More details on the data assimilation technique are given in Miyazaki e al. (2015).

The emission estimation is based on a state augmentation technique, which was employed in our previous studies (Miyazaki et al., 2012a; 2012b; 2013; 2014; 2015). In this approach, the background error correlations, estimated from the ensemble model simulations at each analysis step, determine the relationship between the concentrations and emissions of related species for each grid point. This approach allows us to reflect temporal and geographical variations in transport and chemical reactions in the emission estimates. The state vector in this study is optimized following Miyazaki et al. (2015), which includes several emission sources (surface emissions of \chem{NO_x} and \chem{CO}, and \chem{LNO_x} sources) as well as the concentrations of 35 chemical species. In order to improve the filter performance, the covariance among non- or weakly related variables in the state vector is set to zero, as in Miyazaki et al (2012b) and Miyazaki et al (2015). The emissions in the state vector are represented by scaling factors for each surface grid cell for the total \chem{NO_x} and \chem{CO} emissions, and for each production rate profile of the \chem{LNO_x} sources. For surface \chem{NO_x} emissions, only the combined total emission is optimized in data assimilation. This is to reduce the degree of freedom in the analysis and to avoid the difficulty associated with estimating spatiotemporal variations in background errors for each category source separately.

In the MIROC-Chem simulations, an emission diurnal variability function (Et ($t=1,...,24$)) was applied following the approach of Miyazaki et al. (2012a). Its application generally improved the model simulation performance; however, because Et was constructed based on simple assumptions, and because it does not change with season and location within an area of the same dominant category, its application can cause large uncertainties in simulated \chem{NO_2} variations. Multiple satellite \chem{NO_2} retrievals obtained at different overpass times have a potential to constrain diurnal emission variability (e.g., Lin et al., 2010~~).~~), although differences between the different \chem{NO_2} retrievals and errors in model processes could introduce artificial corrections (see also Section 5.2). Note that the retrievals from different instruments used are all based on the same retrieval method (DOMINO v2, TM4NO2A v2) and largely consistent ancillary data, which limits the discrepancies between the data sets to large degree (Boersma et al., 2008) (see Section 2.3.1). We also acknowledge that differences between the surface reflectivity and cloud data used may lead to some structural uncertainty between the morning and afternoon sensors, although numerous validation studies pointed out that the three \chem{NO_2} column retrievals agree well with independent reference data (e.g., Irie et al., 2011; Ma et al., 2013).

We attempt to optimize Et using data assimilation of OMI, SCIAMACHY, and GOME-2 retrievals, with local equator overpass time of 13:45, 10:00 and 9:30, in order to improve the representation of diurnal emission variability. In our approach, a correction factor for emission diurnal variability (Etc) and an emission scaling factor (Es) for surface \chem{NO_x} emissions are simultaneously optimized in the analysis step using multiple

\chem{NO_2} retrievals, by adding them to the state vector together with other variables such as predicted concentrations. The background error correlation between Es and $~~Ets~~Etc$ is not considered; the two emission parameters are independently optimized using measurements from instruments with different overpass times. As in Miyazaki et al. (2012a), we apply covariance inflation to the emission factors to prevent covariance underestimation caused by the application of a persistent forecast model, by inflating the spread to a minimum predefined value (i.e., 30 \% of the initial standard deviation) at each analysis step for both Es and $~~Ets~~Etc$. The initial error is set to 40 \% for both Es and Etc. For concentrations, multiplication factors (5 \%) are applied to prevent an underestimation of background error covariance. The emission factors are analyzed and updated at every analysis step (i.e., two hours). Because of the lack of any applicable model, a persistent forecast model is used for the emission factors. When there is no observational information available in the analysis step, previously analyzed emission factors are used in the next forecast step.

Figure 1 depicts a schematic diagram of the emission correction scheme for anthropogenic emissions. First, we obtain optimal values of Es and $~~Ets~~Etc$ from the data assimilation analysis. Second, Es is applied to scale up/down daily total emissions while maintaining the a priori diurnal variability shape (black solid line). Third, optimized Etc is applied to modify the diurnal variability shape (red line). Considering the overpass time of the satellite retrievals and the typical daytime lifetime of \chem{NO_x} (i.e. 2--3 hours), a square-wave with amplitude of Etc and a wavelength of six hours was applied. This assumes that GOME-2 and SCIAMACHY measurements constrain emissions in the 07:30--10:30 window, and OMI measurements constrain the 10:30-13:30 window. Consequently, an analysis of the emission diurnal variability function is obtained as $Et^{a} = Et^{b}\times Es - Etc$ for 07:30--10:30, and $Et^{a}= Et^{b}\times Es + –Etc$ for 10:30--13:30), where a and b represent the analysis and background states, respectively. Etc is set to zero (i.e., $Et^{a}=Et^{b}\times Es$) from 13:30 to 07:30. The optimized emission factors are used as initial conditions in the next forecast step of ensemble model simulations.

\subsection{Measurements used in the assimilation}

Trace gas concentrations were obtained from OMI, SCIAMACHY, and GOME-~~II~~2 satellite measurements of \chem{NO_2}, from TES of \chem{O_3}, from MOPITT measurements of \chem{CO}, and from MLS of \chem{O_3} and \chem{HNO_3}. The retrieved concentration and observation error information were obtained for each retrieval, where the observation error included contributions from smoothing errors, model parameter errors, forward model errors, geophysical noise, and instrument errors. These combined errors, together with a representativeness error for super observations (Miyazaki et al., 2012a), were considered in the observation error matrix ($\mathbf{R}$) for data assimilation.

For the assimilation of the satellite retrievals, observation operators (H) were developed, consisting of the spatial interpolation operator (S), a priori profile in the satellite retrievals ($\vec{x}_{\text{apriori}} $), and an averaging kernel ($\mathbf{A}$). This operator mapped the model fields ($\vec{x}_{i}^{\mathrm{b}}$) into retrieval space ($\vec{y}_i^{\mathrm{b}}$), as follows:

\begin{align}

&

\vec{y}_i^{\mathrm{b}}= H(

\vec{x}_{i}^{\mathrm{b}}

) = \vec{x}_{\text{apriori}} + \vec{A} (S(\vec{x}_i^{\mathrm{b}})-\vec{x}_{\text{apriori}}),

\end{align}

where i indicates the ensemble member. The use of the averaging kernel A removes the dependence of the analysis or of the relative model retrieval comparison ($\vec{y}_i^{\mathrm{b}}-\vec{y}^{\mathrm{o}}$)/$\vec{y}_i^{\mathrm{b}}$ on the retrieval a priori profile (Eskes and Boersma, 2003; Jones et al., 2003).

We employed the super-observation approach to produce representative data with a horizontal resolution of MIROC-Chem (T42) for OMI, SCIAMACHY, GOME-2, and MOPITT observations. Super observations were generated by averaging all data located within a super observation grid cell, following the approach of Miyazaki et al. (2012a). Super observation measurement error was estimated by considering an error correlation of 15 \% among the data, although there is no evidence for this value. Representativeness error was introduced when the super-observation grid was not fully covered by observation pixels. The super-observation approach generally provided more representative data with reduced random error and resulted in more stable analysis increments than did the individual observations (Miyazaki et al., 2012a). Another popular approach in data assimilation is to apply data thinning. However, individual observations are much more noisy than super observations, and the representativity error is large. Note that, in our previous studies (Miyazaki et al., 2012a, 2012b, 2013, 2014, 2015), the super observation was produced with a resolution of \$2.5^\circ \times 2.5^\circ \$, which was similar but not equivalent to the model grid size (T42). In this study, the super observation was set to be equivalent to the model grid size (T42), which generally led to larger adjustments in the estimated emissions over industrial areas, and resulted in better data assimilation performance for most cases (e.g., reduced OmF).

\subsubsection{Tropospheric \chem{NO_2} columns from OMI, SCIAMACHY, and GOME-2}

The tropospheric \chem{NO_2} column retrievals used are from the version-2 DOMINO data product for OMI (Boersma et al., 2011) and version 2.3 TM4NO2A data products for SCIAMACHY and GOME-2 (Boersma et al., 2004) obtained through the TEMIS website (www.temis.nl). The ground pixel size of the OMI retrievals is 13--24 km with daily global coverage. Since December 2009, approximately half of the pixels have been compromised by the so-called row anomaly, which reduced the daily coverage of the instrument. GOME-2 retrievals have 80 km \$\times\$ 40 km ground pixel size with a global coverage within 1.5 days. SCIAMACHY retrievals have 60 km \$\times\$ 30 km ground pixel size with a global coverage once every 6 days. OMI measurements were assimilated throughout the analysis period during 2005--2014. In contrast, because of the data limitations, SCIAMACHY retrievals were assimilated before February 2012, and the GOME-2 measurements were assimilated after January 2007. Low-quality data were excluded before assimilation following the recommendations of the products' specification document (Boersma et al., 2011). We employed clear-sky data for surface \chem{NO_x} emission estimations and both clear-sky data and cloud-scene data for \chem{LNO_x} estimations, following the method of Miyazaki et al. (2014). The analysis increments in the assimilation of the \chem{NO_2} retrievals were limited to adjusting only the surface emissions of \chem{NO_x}, \chem{LNO_x} sources, and concentrations of \chem{NO_y} species using the estimated inter-species error correlations.

Boersma et al. (2011) summarized the general error characteristics of tropospheric \chem{NO_2} retrievals. More recently, Maasakkers (2013) presented the possibility of ~~several improvements for~~improving the tropospheric \chem{NO_2} column retrievals algorithm; for example, in the a priori profiles, the effective surface pressure calculation, and in the cloud retrieval. Maasakkers (2013) presented an improved error parameterization for the tropospheric \chem{NO_2} column, which reduced errors in high tropospheric columns by up to 41 \% and in the mean global error by 13 \%. Following this result, we modified the version-2 DOMINO and version 2.3 TM4NO2A data products (Boersma et al., 2004; 2011) and used in data assimilation; we reduced retrieval errors of individual \chem{NO_2} retrievals by 30 \% over polluted areas (for columns > 1.1×10^{15}\,\unit{molec\,cm^{-2}}) before producing super observation for all the \chem{NO_2} retrievals. The assimilation of \chem{NO_2} retrievals with reduced error increased the effective use of observational information (i.e., larger emission adjustments) and improved the chi-square statistics (not shown). The obtained super observation error is typically about 20--50 \%, 30--60 \%, and 25--50 \% of the \chem{NO_2} columns over polluted areas for OMI, SCIAMACHY, and GOME-2 retrievals, respectively (Fig. S1). The differences between the instruments mainly reflect the differences in coverage and pixel size.

\subsubsection{TES \chem{O_3}}

The Tropospheric Emission Spectrometer (TES) is a Fourier Transform Spectrometer (FTS) that measures spectrally-resolved outgoing longwave radiation of the Earth's surface and atmosphere. The TES \chem{O_3} data used are version 6 level 2 nadir data obtained from the global survey mode (Herman and Kulawik, 2013). This data set consists of 16 daily orbits with a spatial resolution of 5--8 km along the orbit track, with an equator crossing time of 13:40 and 02:29 local mean solar time. Retrievals of atmospheric parameters and their error characterization are based upon optimal estimation (Worden et al., 2004; Bowman et al., 2006; Kulawik et al., 2006) which provide the diagnostics (a priori, averaging kernels, and error covariances) needed to construct the observation operator. The standard quality flags were used to exclude low-quality data. The data assimilation of the TES \chem{O_3} retrievals was performed based on the logarithm of the mixing ratio following the retrieval product specification (Bowman et al., 2006).

\subsubsection{MLS \chem{O_3} and \chem{HNO_3}}

The MLS data used are the version 4.2 \chem{O_3} and \chem{HNO_3} level 2 products (Livesey et al., 2011). We excluded low quality data, following the recommendations of Livesey et al. (2011). We used data for pressures of less than 215 hPa for \chem{O_3} and 150 hPa for \chem{HNO_3}. The accuracy and precision of the measurement error, described in Livesey et al. (2011), were included as the diagonal element of the observation error covariance matrix.

\subsubsection{MOPITT CO}

The MOPITT CO data used are version 6 level 2 TIR products (Deeter et al., 2013). The MOPITT instrument is mainly sensitive to free-tropospheric CO, especially in the middle troposphere, with degrees of freedom for signals (DOFs) typically much larger than 0.5. Owing to data quality problems, we excluded data poleward of 65° and night-time data. Data at 700 hPa were used for constraining surface CO emissions.

\subsection{Measurements used in the validation}

We use vertical \chem{NO_2} profiles observed from in-situ and aircraft measurements to validate the simulated \chem{NO_2} distributions. The model simulation and assimilation fields were interpolated to the time and location of each measurement, and then compared with the measurements.

\subsubsection{DANDELIONS}

Vertical \chem{NO_2} profiles were measured using the Netherlands National Institute for Public Health and the Environment (RIVM) NO2 lidar during the Dutch Aerosol and Nitrogen Dioxide Experiments for Validation of OMI and SCIAMACHY (DANDELIONS) campaign (Volten et al., 2009). The lidar data have a spatial representation of 2 km in the viewing direction and approximately 12 km in the direction of the wind, which is much finer than the model resolution (approximately 2.8°). To avoid a possibly large error of representativeness in the validation, particularly under the different boundary layer condition, the profiles obtained in the morning (before 12:00 p.m.) were used.

\subsubsection{INTEX-B}

During the Intercontinental Chemical Transport Experiment Phase B (INTEX-B) campaign, vertical NO2 profiles were obtained using the UC Berkeley Laser-Induced Fluorescence (TD-LIF) instrument on a DC-8 over the Gulf of Mexico (Singh et al., 2009). We removed data over Mexico City and Houston from the comparison to avoid a serious representativeness error. The comparisons were made for two flights during the campaign, conducted on March 6 and March 9 in 2006. The spatial variability of the \chem{NO_2} concentration during the two flights was generally smaller than that obtained from other flights, since the two flights corrected air mostly over the oceans. In the comparison, the data were binned on a pressure grid, with an interval of 30 hPa.

\subsubsection{ARCTAS}

The Arctic Research of the Composition of the Troposphere from Aircraft and Satellites (ARCTAS) campaign (Jacob et al., 2010) was conducted over Alaska (between 60--90°N) in April 2008 (ARCTAS-A) and over western Canada (between 50--70°N) in June--July 2008 (ARCTAS-B). Since the data assimilation impact is limited at polar region, the profile data obtained during ARCTAS-B were used in the comparison.

\section{Simulated and retrieved tropospheric \chem{NO_2} columns}

Tropospheric \chem{NO_2} columns obtained from data assimilation and model simulation (without any assimilation) are compared with satellite observations. For these comparisons, concentrations were interpolated for the retrieval pixels to the overpass time of the satellite, while applying the averaging kernel of each retrieval, and both the retrieved and simulated concentrations were mapped on the horizontal grid of the super observation (i.e., T42).

\subsection{Global distribution}

Figure 2 compares global distributions of annual mean tropospheric \chem{NO_2} columns obtained from the three satellite retrievals (OMI for 2005-2014, SCIAMACHY for 2005--2011, and GOME-2 for 2007--2014), the MIROC-chem simulation, and the data assimilation. The three satellite measurements commonly reveal high tropospheric \chem{NO_2} concentrations over large industrial regions: eastern China, Europe, and the United States. High concentrations are also found over the Southern and Central Africa, India, Middle East, Japan, South Korea, and Southeast Asia. Tropospheric \chem{NO_2} concentrations are generally lower in OMI retrievals compared to GOME-2 and SCIAMACHY retrievals over polluted areas, reflecting the diurnal cycle of emissions and chemistry, with faster chemical loss of \chem{NO_2} at noon compared to early morning (e.g. Boersma et al., 2009). All of the retrievals are produced using the same retrieval approach (Boersma et al., 2011). Therefore, the differences in overpass time and also in pixel size could be the principle cause of the differences between the three different satellite retrievals, although ~~.~~the use of super observations for all the sensors reduces the influence of different pixel sizes.

The MIROC model reproduces the general features of observed tropospheric \chem{NO_2}, with a global spatial correlation of 0.86--0.94 for the annual mean concentration during the ten-year period between 2005--2014 (Fig. 2 and Table 1). However, the simulated regional mean tropospheric \chem{NO_2} columns are generally too low over most industrial areas and major biomass-burning areas and too high over remote areas. In the global mean, the model is negatively biased relative to the three retrievals (i.e., -0.04$-$-0.18$\times 10^{15}$\,\unit{molec\,cm^{-2}} compared with the three retrievals). Data assimilation improves agreements with the satellite retrievals for most industrial and biomass-burning areas mainly because of the optimized surface \chem{NO_x} emissions, with great reductions in the ten-year global mean negative bias (i.e., -0.02--+0.03$\times 10^{15}$\,\unit{molec\,cm^{-2}}) (Table 1). Improvements can also be found in the improved spatial correlation (from 0.86--0.94 to 0.95--0.98) and the reduced global root mean square error (RMSE: reduced by about 40, 30, and 50 \% compared with OMI, SCIAMACHY, and GOME-2, respectively). The annual mean analysis--observation differences show similar spatial distributions between SCIAMACHY and GOME-2 (r=0.93) and differed somewhat between OMI and other sensors (r=0.55--0.60).

\subsection{Regional distribution}

The regional mean tropospheric \chem{NO_2} columns are compared in Table 2. The data assimilation reduced the ten-year mean negative bias of the model by 40--62 \% over China and 48--50 \% over the United States compared to the three retrieval. The data assimilation also reduced the almost constant negative bias over Australia by 20--76 \%, over India by 57--60 \%, and over Southern Africa by 35--64 \%. The error reduction over China and southern Africa is generally smaller for the SCIAMACHY and GOME-2 retrievals compared with the OMI retrievals.

Improvements are also found over biomass burning areas. The ten-year mean negative model bias over Southeast Asia is reduced by 57--77 \%, which is mainly attributed to the positive adjustments in the biomass burning season (i.e., in boreal winter-spring). The persistent negative biases throughout the year over central and North Africa are also reduced, with a ten-year mean reduction of 66-80 \% and 78--86 \%, respectively. These improvements over the tropical regions are mostly commonly found in comparisons with the three retrievals. Considering the short lifetime and rapid diurnal variation of biomass burning activity at low latitudes, these improvements suggest that the assimilation of ~~multiple~~ multiple-species and multiple \chem{NO_2} measurements effectively corrected the ~~diurnal~~ temporal ~~variations~~ changes in the tropospheric \chem{NO_2} ~~concentration~~column between the different overpass times.

Despite the general improvement by data assimilation, disagreements remain between the simulated and observed \chem{NO_2} concentrations over polluted regions, such as Europe, Southern Africa, and China. The inadequacies of the improvements can be partly attributed to the small number of observations and large observation errors for highly polluted cases. The quality and abundance of the retrievals varies largely with season and area (Fig. S1), reflecting observation conditions (e.g., clouds, aerosols, and surface albedo), which have great impacts on the magnitude of data assimilation improvement. For instance, over Europe in winter, the number of observations is relatively small, and the observation error is relatively large. The remaining errors may also result from model errors such as too short lifetime of \chem{NO_x} through the \chem{NO_2}+\chem{OH} and \chem{NO}+\chem{HO_2} reactions and the reactive uptake of \chem{NO_2} and \chem{N_2O_5} by aerosols (e.g., Lin et al., 2012b; Stavrakou et al. 2013). This will further be discussed in Section 5.3.

\subsection{Seasonal and interannual variation}

The underestimation in the simulated concentrations is most obvious in winter over most of the industrial regions, such as China, Europe, the United States, and Southern Africa. Data assimilation greatly reduced the wintertime low bias by 50-70 \% over China, by about 50--90 \% over the United States, and by 50--70 \% over Southern Africa, as summarized in Table 2. Over Europe, the model's negative bias is reduced by about 10--80 \% in summer, but the negative bias compared with the OMI retrievals mostly remains in winter (c.f., Section 5.3).

Despite the persistent wintertime bias over Europe, the improved temporal correlation (from 0.64--0.89 in the model simulation to 0.90--0.95 in the data assimilation) confirms improved seasonality and year-to-year variation. Over India, the \chem{NO_2} columns in the model simulation do not reveal clear seasonal variation, whereas a significant seasonal variation is introduced by data assimilation, reflecting the observed high concentration in boreal winter-spring. The temporal correlation is largely improved over India (from -0.47--0.06 in the model simulation to 0.76--0.95 in the data assimilation).

The observed concentrations reveal large year-to-year variations over the industrial regions, which are generally underestimated in the model simulation (Fig. ~~3~~3). Over China, the difference between the model simulation and the observations becomes significant after 2010, suggesting a larger underestimation in the a priori inventories in that time period, relative to the period before 2010. The observed concentrations reveal positive trends over China, with an exceptional decrease in 2009, followed by a rapid increase in 2010, and a decrease in 2014, as found by Cui et al. (2015), Duncan et al. (2016), and Krotkov et al. (2016). The data assimilation better captures the observed variations, as indicated by the better agreement in the linear trend (+40 \%/decade in the OMI observation, +13 \%/decade in the model simulation, and +28 \%/decade in the data assimilation) and by the improved temporal correlation (from 0.85--0.94 to 0.95--0.99). Over the United States, the data assimilation removes most of the model's negative bias in 2005--2007 and reproduces the observed downward trend for the ten-year periods. These improved agreements suggest that the a posteriori emissions from data assimilation capture the actual anthropogenic emission variability.

The seasonal and year-to-year variations over Southeast Asia, and North and Central Africa are associated with changes in the biomass burning activity. Data assimilation improves the temporal variability, as confirmed by the improved temporal correlations (by 0.10--0.14 over North Africa, by 0.03--0.04 over Central Africa, and by 0.15--0.21 over Southeast Asia). Over Southeast Asia, the negative bias in the biomass burning season is largely removed by data assimilation. The systematic adjustments for North and Central Africa throughout the year suggests that the a priori emissions reasonably represent the seasonality of biomass burning activity, but emission factors~~ (and/or chemical lifetime of \chem{NO_x})~~ might be underestimated in the a priori setting, as discussed in Section 4.

\subsection{Vertical profiles}

Figure 4 compares the vertical profiles with the aircraft observations during the ARCTAS and INTEX-B campaigns and with the ground-based lidar observations obtained during the DANDELIONS campaign. For all the profiles, the observed \chem{NO_2} concentrations are high in the boundary layer and decrease with height above the boundary layer, and are higher in the morning than in the afternoon in the lower troposphere. Both the model simulation and data assimilation reproduced these observed general features.

For the ARCTAS profile, the data assimilation has a small effect on the lower and middle tropospheric \chem{NO_2} profiles, because of the large observational error of the \chem{NO_2} measurements at high latitudes. In contrast, the data assimilation mostly removed the model negative bias in the upper troposphere and lower stratosphere, mainly because of the MLS \chem{O_3} and \chem{HNO_3} data assimilation and through the use of the inter-species correlation. This improvement cannot be achieved using the \chem{NO_2} measurements only. During the INTEX-B and DANDELIONS campaigns, large variations in individual measurements along the flights were observed. Therefore we evaluate the variability, as well as the mean profiles, using scatter plots (Fig. 4). For the INTEX-B profiles, the data assimilation improves the agreement (i.e., the correlation and slope) with the observations in the lower and middle troposphere, except within the boundary layer (i.e., below 900 hPa). For the March 9 flight, the correlation (from 0.324 to 0.455) and the slope (from 0.26 to 0.53) increased in the lower troposphere (900--750 hPa) by data assimilation. The improvements are commonly found for the March 11 flight and for higher levels (750--600 hPa). The assimilation does not obviously change the model profile in the upper troposphere (600--300 hPa); the remaining negative bias could be attributed to errors in the model, such as in the chemical loss, \chem{NO_y} species partitioning, and atmospheric transport. For the DANDELIONS profiles, the data assimilation improves the agreement in the lower troposphere (e.g., the correlation and slope are increased from 0.14 to 0.46 and from

0.11 to 0.90, respectively, for 150--500 m), except near the surface (i.e., below 150 m). The improvement is generally more obvious in the morning than in the afternoon for these comparisons (not shown).

Note that, in all cases, the data assimilation increases positive biases in the surface concentrations. Because of the coarse model resolution (approximately 2.8°), the model has difficulty in representing the measurement locations. The near-surface concentration will be sensitive to the model resolution owing to fine-scale emission distribution and transport, as well as non-linear chemical processes, as discussed in Valin et al (2011) and Miyazaki et al (2012a). The positive bias in the data assimilation may also suggest errors in the assimilated measurements.

\section{Estimated surface \chem{NO_x} emissions}

The a posteriori emissions were compared against the a priori emissions for the 2005--2014 period and against an independent emission inventory from EDGAR-HTAP v2 (Janssens-Maenhout et al., 2015) for the years 2008 and 2010. EDGAR-HTAP v2 was produced using nationally reported emissions combined with regional scientific inventories from the European Monitoring and Evaluation Programme (EMEP), Environmental Protection Agency (EPA), Greenhouse Gas-Air Pollution Interactions and Synergies (GAINS), and Regional Emission Inventory in Asia (REAS). For the comparison against EDGAR-HTAP v2, emissions from biomass burning and soils were obtained based on ~~EDGAR~~ GFED version ~~4.2~~3.1 and GEIA inventories; they were used in the a priori emissions.

\subsection{Top-down vs. a priori global surface \chem{NO_x} emissions}

The global distributions of the estimated emission sources are depicted in Fig. ~~4~~5. As summarized in Table 3, the ten-year mean global total surface \chem{NO_x} emissions after data assimilation is 48.4 \unit{Tg\,N\,yr^{-1}}, which is about 26 \% higher than the a priori emissions (38.4 \unit{Tg\,N\,yr^{-1}}). The positive analysis increment in global total emissions is attributable to an approximate +21 \% increment in the Northern Hemisphere (NH, 20--90°N), a +35 \% increment in the tropics (20°S-20°N), and a 42 \% increment in the Southern Hemisphere (SH, 20--90°S). Strong positive increments are found over China (+39 \%), the United States (+10 \%), India (+22 \%), and Southern Africa (+50 \%). There are also positive increments in emissions over the biomass burning areas of Central Africa (+53 \%) and Southeast Asia (+39 \%). The a posteriori regional total emissions are clearly closer to the EDGAR-HTAP v2 emissions than the a priori emissions over China, the United States, and India. Since the same biomass burning and soil emission inventories are used in producing the total a priori and EDGAR-HTAP v2 emission data sets in this study, the emissions are similar between the two data sets over biomass burning and remote areas.

Fig. ~~5~~ 6 depicts the global distribution of the linear trend during the ten-year period. The trend is negative over most of the United States, Europe, some parts of eastern China, South Korea, Japan, central and Southern Africa, Northern South America, with strong negative trends over the eastern United States, some parts of Europe (e.g., Northwest Europe, Po valley, and northern Spain), and Japan. Strong positive trends are found over China, India, Middle East, around Sao Paulo in Brazil, and around Jakarta in Indonesia.

Data assimilation reveals significant temporal variations (Fig. ~~6~~7), including seasonal (Fig. ~~7~~8) and interannual (Fig. ~~8~~9) variations, in the emissions over major polluted regions. In northern mid-latitudes, the emissions are strongly enhanced in summer, and the timing of the summertime peak from data assimilation is earlier by 1--2 months over North America, Europe, and ~~southern parts of the Eurasian continent~~China (Fig. ~~7~~8), as similarly found in our previous study (Miyazaki and Eskes, 2013). Applying the ratio of different emission categories within the a priori emissions for each grid point to the estimated emissions after data assimilation (only the total emission is optimized in our estimates), global total \chem{NO_x} emissions from soils are 7.9 \unit{Tg\,N\,yr^{-1}} for the a posteriori emissions in contrast to 5.4 \unit{Tg\,N\,yr^{-1}} yr^{-1} for the a priori emissions. In line with recent studies by Hudman et al. (2012) and Vinken et al. (2014), our results suggest that the a priori emissions underestimate those by soils and misrepresent the seasonality.

Over biomass-burning areas, the time of the peak emissions does not change for most cases, suggesting that the a priori emissions describe the seasonality reasonably, but the systematic adjustment indicates large uncertainties in emission factors and biomass burnt estimates used in the inventories. The weak year-to-year variations in the a priori emissions are partly attributable to the use of climatology after 2011 ~~assumptions applied for the a priori emissions~~ (c.f., Sec. 2.1).

Despite the large year-to-year variations over many regions (c.f., Figs. ~~5~~ 6 and ~~6~~7), the global total emission is almost constant between 2005 (47.9 \unit{Tg\,N\,yr^{-1}}) and 2014 (47.5 \unit{Tg\,N\,yr^{-1}}), with a maximum in 2012 (50.9 \unit{Tg\,N\,yr^{-1}}) and a minimum in 2008 (46.7 \unit{Tg\,N\,yr^{-1}}). Over the ten-year period, the large emission increases over China, India, and the Middle East mostly compensate for the large emission decreases over the United State, western Europe, and Japan.

\subsection{Top-down vs. a priori regional surface \chem{NO_x} emissions and their trends}

\subsubsection{East Asia}

Data assimilation adjusts the total annual emissions from 4.47 to 6.21 \unit{Tg\,N\,yr^{-1}} over China for the 2005--2014 period (Table 3), whereas the a posteriori emissions show good agreement with the EDGAR-HTAP v2 emissions (6.19 \unit{Tg\,N\,yr^{-1}} in the a posteriori emissions and 6.25 \unit{Tg\,N\,yr^{-1}} in the EDGAR-HTAP v2 for 2008 and 2010). Our~~The~~ a priori inventory is~~EDGAR v4 emissions are~~ too low over China, by ~~a factor of 0.6~~about 40 \%. The seasonal variation is largely corrected by data assimilation (Fig. ~~7~~8), exhibiting maximum emissions in January and ~~July~~June.

At the grid scale, the estimated emissions are higher than the a priori emissions over northern and eastern China, ~~around large cities in East Asia,~~ such as Beijing (+58 \% at the nearest grid point), Tianjin (+97 \%), Nanjing (+30 \%), and around Guangzhou (+78 \%), whereas they are lower around Chengdu and Chongqing ~~in most remote areas~~ (Fig. ~~9~~10). ~~As a result,~~

~~differences between large cities and rural areas generally become larger for the a posteriori emissions than the a priori emissions over China.~~ In terms of the regional mean, the EDGAR-HTAP v2 is closer to the a posteriori emissions for China. However, there are disagreements at grid-scale around large cities, such as Shanghai (the a posteriori minus EDGAR-HTAP v2 is -25 \%), Guangzhou (+46 \%), and Chongqing (-19 \%), and also in South Korea around Seoul (+37 \%) and in Japan around Tokyo (+13 \%).

Our estimate of 12.5 TgN for July 2007 over East Asia (80-150°E, 10--50°N) is slightly larger than that of 11.0 TgN estimated using OMI observations (Zhao and Wang, 2009). The 6.6 TgN (8.0 TgN) estimated for July 2008 (January 2009) over east China (103.75--123.75°E, 19--45°N) from OMI and GOME-2 observations by Lin and McElroy (2010) is slightly smaller than (larger than) our estimates of 7.4 TgN (7.4 TgN). We emphasize that the estimated emissions are strongly constrained by the assimilation of non-\chem{NO_2} measurements in our estimates. The estimated emissions for July 2008 over east China for the above-mentioned case from a \chem{NO_2}-only assimilation (8.2 TgN) is 11 \% larger than the estimate using ~~multiple~~ multiple-species (7.4 TgN). The importance of ~~multiple~~ multiple-species assimilation is further discussed in Sect. 5.1.

The estimated emission for China does not follow a simple linear increase, but rather increasing from 2005 to 2011 with a slightly negative trend afterwards, as shown by Fig ~~8~~ 9 and Fig. 11~~1~~. The ten-year linear trend slope is estimated at +26 \%/decade (Table 4). The difference in the estimated emission trend between the two time periods (2005--2010 and 2011--2014) are most commonly found across the country, which can be attributed to the competing influences of economic growth and emission controls (Cui et al., 2015). The temporal strong decrease in the estimated emissions in 2008 summer (Fig. ~~6~~7) could be associated with the Beijing Olympic games, as suggested by Mijling et al. (2009), Witte et al. (2009), and Worden et al. (2012). The trend for 2005--2010 over China is estimated at +3.0 \%/year in our estimate, which is slightly smaller than the +4.0 \%/year estimate using OMI measurements by Gu et al. (2013). The increase from 2008 to 2010 for China is larger in the a posteriori emissions (+0.73 \unit{Tg\,N\,yr^{-1}}) than in EDGAR-HTAP v2 (+0.49 \unit{Tg\,N\,yr^{-1}}).

As shown by Fig. ~~10~~12, strong positive trends are found over large cities such as Wuhan (+42 \%/decade), Nanjing (+35 \%/decade), Tianjin (+35 \%/decade), Chengdu (+56 \%/decade), and over eastern China. A larger relative positive trend occurs over western China, especially over northwestern China (around 88--110°E, 37--48°N) where the rate of increase reaches +50--+110 \%/decade at grid scale. Despite the general large positive trend for the ten-year period, the three largest cities in China show a net reduction or a small increase during 2005--2014; Beijing (-0.6 \%/decade), Shanghai (-6.2 \%/decade), and Guangzhou (+4.5 \%/decade), as commonly found in the observed \chem{NO_2} concentrations (Wang et al., 2015). In East Asia, the estimated emissions also show strong negative trends over major cities in Japan and South Korea; Tokyo (-48 \%/decade), Osaka (-38 \%/decade), and Seoul (-11 \%/decade).

\subsubsection{Europe}

The total emissions for Europe are about 5 \% higher in the a posteriori than in the a priori emissions (Table 3), which is attributed to positive increments over some parts of western Europe, such as Belgium (+67 \%), western Germany (+23 \%), northern Italy (+62 \%), and Istanbul (+40.3 \%) (Fig. ~~9~~10). The a posteriori emissions for Europe are higher than the EDGAR-HTAP v2 inventory by 17 \% for 2008 and 2010, and the differences are large at the grid scale around London (+27 \%), Belgium (+87 \%), western Germany (+84 \%), Paris (+27 \%), Madrid (+55 \%), northern Italy (+90 \%), and Istanbul (+56 \%). ~~The lower emissions in the inventories could indicate an underestimate in the reported mobile emissions sources, but could also be attributed to other factors (c.f., Section 5.3).~~ Both the a priori and EDGAR-HTAP v2 emission inventories ~~reveal~~ show maximum emissions in summer (i.e., July), whereas the timing of peak emission becomes earlier by 1 month ~~by~~ after data assimilation (Fig. ~~7~~8). The estimated seasonal amplitude is larger over Eastern Europe than over Western Europe by about 40 \%, which suggests the possibility of more active summertime emissions from soil in Eastern Europe, as consistently revealed by Vinken et al. (2014).

The estimated emissions for Europe show a slightly negative trend during 2005--2014, with a sharp decrease from 2009 to 2010 (Fig. ~~8~~9). The estimated linear decrease for the ten-year period is small (-0.1 \%/decade) for Europe (10°W--30°E, 35--60°N), but is much larger (-8.8 \%/decade) over Western Europe (10°W--17°E, 36--54°N~~). ~~), as summarized in Table 4. At the grid scale (Fig. ~~10~~12), strong negative trends occur over large cities in Western Europe; Paris (-10 \%/decade), northwestern France (-57 \%/decade), London (-11 \%/decade), Belgium (-24 \%/decade), Athens (-22 \%/decade), and over a region with many power plants in northern Spain (-45 \%/decade) and Po valley (-52 \%/decade). These variations are considered to be the result of the global economic recession and emission controls, as pointed out by Castellanos and Boersma (2012). The negative trends are stronger during 2005--2010 than during 2011-2014 over some parts of western and southern Europe such as over northern Spain, northern Italy, and western Germany (Fig. ~~11~~12). Strong negative emission trends over these regions were similarly found by Curier et al. (2014) for 2005--2010. Zhou et al. (2012) revealed that \chem{NO_x} emissions from Spanish Power plants have been strongly reduced for the 2004-2009 period because of emission abatement strategies, which is consistent with our estimates.

\subsubsection{North America}

The ten-year mean a posteriori emissions are higher than both the a priori (5.73 \unit{Tg\,N\,yr^{-1}} v.s 5.23 \unit{Tg\,N\,yr^{-1}} for 2005--2014) and EDGAR-HTAP v2 (5.26 \unit{Tg\,N\,yr^{-1}} v.s 4.84 \unit{Tg\,N\,yr^{-1}} for 2008 and 2010) emissions over the United States (Table 3). Positive increments are found over most remote areas and around the Southeast United States (e.g., +23 \% near Atlanta) and most of the Western United States (e.g., +26 \% near Denver)~~Atlanta (+23 \%) and Denver (+26 \%)~~, whereas negative increments are found around ~~over ~~large cities such as New York (-28 \%), Toronto (-17 \%), Montreal (-19\%), Houston (-19 \%), and Los Angeles (-5 \%) (Fig. ~~9~~10). Despite the small adjustment for the ten-year mean regional total emissions, the data assimilation analysis increments for the regional total emission are strongly positive during 2005-2008, producing a long-term negative trend (Fig. ~~6~~7). The timing of maximum emissions becomes earlier by 2 months (from July to May) due to data assimilation (Fig. ~~7~~8). The summertime peak enhancement is obvious over remote regions such as high temperature agricultural land over the South Atlantic, the East South Central, and the Southwestern United States, which suggests that the a priori emissions underestimates emissions from soil, as suggested by Oikawa et al. (2015) for the western Unites States. The estimated emissions are larger than the EDGAR-HTAP v2 emissions around large cities such as New York (+24 \%), Chicago (+12 \%), Denver (+35 \%), Houston (+17 \%), San Francisco (+74 \%), and Los Angeles (+68 \%) but are smaller over remote areas in the eastern and central United States for 2008 and 2010 (Fig. ~~9~~10). The 0.73 \unit{Tg\,N} estimated over the United States (130--70°W, 25--50°N) from ICARTT observations between 1 July and 15 August in 2004 (Hudman et al., 2007) is close to our estimates of 0.82 TgN for 1 July to 15 August in 2005. The 0.465 TgN estimated over the eastern United States (102--64°W, 22--50°N) from the OMI observations for March 2006 (Boersma et al., 2008a) is slightly smaller than our estimate of 0.502 TgN.

The a posteriori regional emissions for the United States show a strong negative trend during 2005--2014 (-29.4\%/decade) (Table 4). The estimated trend for 2005--2012 (-32 \%) in this study is close to that reported by Tong et al. (2015) using OMI measurements (-35 \%). The ten-year linear trend is strongly negative over large cities such as New York (-48 \%/decade), Boston (-42 \%/decade), Chicago (-52 \%/decade), Atlanta (-47 \%/decade), Dallas (-19 \%/decade), Houston (-25 \%/decade), Denver (-16 \%/decade), and Los Angeles (-46 \%/decade) (Fig. ~~10~~11). Lu et al. (2015) estimated that total OMI-derived \chem{NO_x} emissions over selected urban areas decreased by 49 \% from 2005 to 2014, reflecting the success of \chem{NO_x} control programs for both mobile sources and power plants, with greater reductions before 2010 than after 2010. These variations are similarly found in our estimates (Fig. ~~11~~12). Both the a posteriori and EDGAR-HTAP v2 emissions consistently reveal a decrease in the regional emissions for the United States from 2008 to 2010 (-0.34 and -0.51 \unit{Tg\,N\,yr^{-1}}, respectively).

\subsubsection{India}

The ten-year total emissions from India are 22 \% higher in the a posteriori emissions than in the a priori emissions (Table 3). The positive adjustment for the country's total emissions is large in ~~boreal ~~spring, resulting in a Mar--June/July--September ratio of about 1.55$\pm$0.1 (Fig. ~~7~~8), which could be associated with the seasonality in open biomass burning (Venkataraman et al., 2006). The seasonal variation is mostly absent in the a priori and EDGAR-HTAP v2 inventories. The positive increment is large around large cities such as Lucknow (+110 \%), Patna (+25 \%), Mumbai (+50 \%), Hyderabad (+16 \%), and Madras (+21 \%) (Fig. ~~9~~10). In contrast, the country's total emissions are about 10 \% smaller in the a posteriori emissions than in the EDGAR-HTAP v2, with large negative biases (i.e., the a posteriori is smaller) around Delhi (-49 \%) and southern India (-20$-$-70 \%) and large positive biases over Lucknow (+68 \%), Gwalior (+45 \%), Raipur (+41 \%), Mumbai (+12 \%), and Hyderabad (+14 \%) at grid scale (Fig. ~~9~~10). These results suggest both EDGARv4 and EDGAR-HTAP v2 inventories largely underestimate emissions over some parts of India such as around Lucknow, Raipur, Mumbai, and also in Thailand around Bangkok (+26 \% compared with the a priori emissions and +118 \% compared with the EDGAR-HTAP v2 emissions) and Chiang Mai (+54 \% and +66 \%, respectively).

The a posteriori emissions for India increased continuously over the ten-year period, with a linear trend of +29 \%/decade (Fig. ~~8~~9). The positive trend is large across the country, with particularly strong increases around ~~Delhi (+25 \%/decade), ~~Lucknow (+29 \%/decade), Kolkata (+47 \%/decade), Raipur (+67 \%/decade), and Madras (+40 \%/decade) (Fig. ~~10~~12). The positive emissions trend could be associated with increased thermal power plants in India, as pointed out by Lu and Streets (2013). In 2014, the regional total emissions for India (i.e., 3.46 \unit{Tg\,N\,yr^{-1}}) are comparable to (about 83 \% of) the European-total emissions (i.e., 4.15 \unit{Tg\,N\,yr^{-1}}) and about 67 \% of the United States-total emission (i.e., 5.17 \unit{Tg\,N\,yr^{-1}}). In contrast, tropospheric \chem{NO_2} columns over India are much lower compared to those in northern midlatitude polluted areas, as a result of the high values of temperature, photolysis rates, and ~~s~~specific humidity, leading to shorter \chem{NO_2} lifetimes throughout the year (Beirle at al., 2011).

\subsubsection{Southern Africa}

A large adjustment in \chem{NO_x} emissions is apparent in the Highveld region of Southern Africa with a factor of about 1.5 (table 3). The positive adjustment is relatively large in the austral summer (Fig. ~~7~~8). The emissions from Southern Africa show a slight negative trend (-8 \%/decade), with a temporary increase in 2006--2007, followed by a rapid decrease in 2009, and almost constant emissions afterwards (Fig. ~~8~~9). The difference in emissions between 2008 and 2010 is small in EDGAR-HTAP v2 (+0.01 \unit{Tg\,N\,yr^{-1}}), whereas the a posteriori emissions show a negative trend (-0.09 \unit{Tg\,N\,yr^{-1}} (2010-2008)) (Table 3). The ten-year linear trend reaches about -40 \%/decade at grid scale over highly polluted areas. Duncan et al. (2016) highlighted a complex mixture of different emissions sources over Southern Africa. The various emission sources may have experienced different variations, and high resolution emission analysis is required to understand the detailed spatial variation in these emissions and to obtain unbiased emission estimates (Valin et al., 2011).

\subsubsection{North and central Africa}

Over North Africa, the ten-year mean emission increased by 40 \% ~~by~~ due to data assimilation from 2.07 to 2.90 \unit{Tg\,N\,yr^{-1}} (Table 3). The positive increment is large from boreal winter to summer, producing the second maximum in July that is absent in the a priori emission (Fig. ~~7~~8). The enhanced emissions for July and August are found throughout the 2005--2014 period and can mainly be attributed to emissions from the Sahel and Nigeria. This large positive increment may indicate an underestimation of soil \chem{NO_x} emissions in the a priori inventory. The short summer dry season in Nigeria may also lead to enhanced biomass burning emissions. The data assimilation largely corrects the spatial distribution during the peak season in January, with larger positive adjustments over the western (by about +60--+120 \% at grid scale around 5W$^\circ$--15W$^\circ$) rather than the eastern parts of North Africa (Fig. ~~4~~5). The data assimilation also introduced a distinct year-to-year variation, reflecting the observed concentration variations associated with changes in biomass burning activity. The estimated emissions are high in 2005, 2006, 2008, and 2009, and low in 2010 (Fig. ~~6~~7), which could be associated with drought events related to atmospheric variations such as ENSO (Janicot et al., 1996).

Over central Africa, the ten-year mean a posteriori emissions are larger than the a priori emissions by about 53 \% (2.57 \unit{Tg\,N\,yr^{-1}} v.s 1.68 \unit{Tg\,N\,yr^{-1}}) (Table 3). Large positive increments are found in the Congo region, with about +50--+150 \% increases for the ten-year mean emissions at the grid scale (Fig. ~~4~~5). The relative adjustment for the regional total emissions during the biomass burning season is +30--+40 \% over central Africa and about +40 \% over North Africa. These numbers may indicate a possible underestimation of the magnitude of fire-related emission factors in GFED v3. Although variation in the seasonal emissions is different between North Africa and Central Africa (almost in opposite phase, reflecting the transition of the Intertropical Convergence Zone (ITCZ)), the year-to-year variation revealed by data assimilation is similar between the two regions. The temporal correlation of the annual total emission between North Africa and central Africa for the 2005-2011 period (when the GFED emissions are available) is estimated at 0.90 for the a posteriori emissions, and 0.01 for the a priori emissions. This result may suggest that year-to-year emission variations over the two regions are controlled in the same manner by long-lasting atmospheric variations (e.g., ENSO), for which the a priori emissions have large uncertainties.

\subsubsection{Southeast Asia}

Over Southeast Asia, the data assimilation increases the annual mean emission by 45 \% from 0.47 to 0.68 \unit{Tg\,N\,yr^{-1}} (Table 3), with a large increase in boreal winter and spring (Fig. ~~7~~8). The regional emission increment is positive over peninsular Malaysia (+20--+40 \% for the ten-year mean emission), Borneo Island (+60--+100 \%), and central and northern Thailand (+50--+80 \%) (Fig.~~ 9~~ 10). Because of the large adjustment in boreal winter and spring, the peak-to-peak seasonal variation for southeast Asia is enhanced by 20 \% by data assimilation (Fig. ~~7~~8). The a priori inventories reveal enhanced emissions in 2005, 2007, and 2010, ~~reflection ~~reflecting year-to-year changes in biomass burning emissions, ~~when ~~whereas data assimilation further increased them by up to 30 \% (Fig. 7~~6~~). The relative adjustment in other years (i.e. years with weaker biomass-burning activity) is even higher during the boreal winter and spring (with a factor of more than 2), which can largely be attributed to large positive increments over central and northern Thailand. The Southeast Asia emissions can be characterized as a combination of various sources. Using the ratio between different emission categories in the a priori emission inventories at each grid point, the regional total emissions from anthropogenic sources, biomass burning, and soils are estimated at 0.51, 0.11, and 0.06 \unit{Tg\,N\,yr^{-1}}, respectively, which is 47, 32, and 58 \% higher than the a priori emissions.

\subsubsection{South America}

Over South America, the ten-year mean regional total emissions are comparable between the a priori and a posteriori emissions, whereas the spatial distribution is largely corrected, with large positive increments over eastern Brazil (+50--+110 \% at grid scale) and Peru (+90--+140 \%) and negative increments over the central Amazon (up to -30 \%) (Fig. ~~4~~5). The seasonal variation of the regional total emission for South America is largely corrected by data assimilation (Fig. ~~7~~8). A large decrease (by -30 \%) occurs in the biomass burning season in August-September in all of the years, which might be the result of an overestimation of emissions by forest (i.e., deforestation) fires in dry conditions in the emissions inventory, as similarly investigated by Castellanos et al. (2014) using GFED v3. This is in contrast to the increased emissions over central Africa in the biomass burning season (c.f., Section 4.2.6). In contrast to the negative increments in the biomass-burning season, the emissions in the biomass burning off-season are increased by 30--60 \% by data assimilation. Consequently, data assimilation decreased the seasonal amplitudes by 40 \%. The year-to-year variations are similar between the a priori and a posteriori emissions (Fig. ~~6~~7). As an exception, a large decrease in 2010 (with a 50 \% decrease from 6.9 \unit{Tg\,N} to 3.5 \unit{Tg\,N} in August by data assimilation) suggests large uncertainty in fire-related emission factors in the major fire year (Bloom et al., 2015).

\subsubsection{Other remote regions}

The data assimilation may capture signals related to soil emissions, for which the inventories may have large uncertainties. For instance, the regional mean emissions over Australia are higher by about 40 \%, with a large increase in boreal spring-early summer. The emissions are also higher over the central Eurasian continent, including eastern Europe and western China, and over the Sahel (Fig. ~~4~~5), as was similarly found by Vinken et al. (2014). The global total \chem{NO_x} emissions by soils for the ten-year period are estimated at 7.9 \unit{Tg\,N\,yr^{-1}} yr^{-1}, in contrast to 5.4 \unit{Tg\,N\,yr^{-1}} yr^{-1} for the a priori emissions. The results indicate large underestimates in the soil emission inventories over these regions. For instance, the nonlinear relationships between soil \chem{NO_x} emissions and time since fertilization, soil temperature, and soil moisture, are not properly considered in current inventories, as pointed out by Oikawa et al. (2015) for agricultural regions. Note that our estimate of 7.9 \unit{Tg\,N\,yr^{-1}} is smaller than other recent estimates (8.9 \unit{Tg\,N\,yr^{-1}} in Jaegl\'{e} et al. (2005), 8.6 \unit{Tg\,N\,yr^{-1}} in Steinkamp and Lawrence (2011), 10.7 \unit{Tg\,N\,yr^{-1}} in Hudman et al. (2012), and 12.9 ± 3.9 \unit{Tg\,N\,yr^{-1}} in Vinken et al. (2014)), which could partly be attributed to the assumed emission ratio between different categories for each model grid point, which is based on the a priori inventories and was not modified by the data assimilation in this study.

Among major industrialized areas, the Middle East has experienced a rapid increase in \chem{NO_2} levels (Lelieveld et al., 2015). Our estimates reveal a linear trend of +20 \%/decade in \chem{NO_x} emissions and a 45 \% positive adjustment from the a priori emissions for the Middle East (32--65°E, 12--40°N) during the ten-year period. Strong positive trends are found over major cities, such as Kuwait (+47 \%/decade), Cairo (+29 \%/decade), and Tehran (+37 \%/decade). In contrast, the trend in the estimated emission over Dubai is negative (-6 \%/decade). The rate of increase becomes larger after 2010 for many areas (Fig. ~~11~~11), as found in observed \chem{NO_2} levels (Lelieveld et al., 2015). Lelieveld et al. (2015) suggested that a combination of air quality control and political factors has drastically altered the emission landscape of \chem{NO_x} in the Middle East.

Over the oceans, the data assimilation decreases the ten-year mean global total emissions from ships. In contrast, at the regional scale, data assimilation increments are positive over the oceans around Europe (Fig. ~~10~~12), and a positive trend during 2005--2010 is introduced by data assimilation (Fig. ~~11~~11, note that the estimated positive trend is more pronounced during 2005--2008, as commonly found by Boersma et al. (2015)). The overall negative increment as well as the positive increment around Europe may indicate an overestimate and an underestimation around Europe of ship emissions in the a priori inventories and errors in modelled chemical processes in the exhaust plumes (Vinken et al., 2011), which occur at fine scales relative to the model grid. The overall negative increment can also be influenced by possible negative bias in \chem{NO_2} retrievals. Boersma et al. (2008a) showed negative bias over the ocean in \chem{NO_2} retrievals in version-1 DOMINO \chem{NO_2} retrievals, and the negative bias could not be fully removed in the version-2 DOMINO \chem{NO_2} retrievals (Boersma et al., 2011a).

\section{Discussion}

\subsection{Importance of assimilating multiple trace gases}

The differences between our \chem{NO_x} emissions estimates and previous studies, as discussed in Section 4, may be attributed to differences in the assimilated data, forecast model, and data assimilation approach. In particular, the use of non-\chem{NO_2} measurements is expected to improve emission estimates in our approach, as these affect the \chem{NO_x} chemistry and reduce model errors unrelated to surface emissions. Table ~~3~~ 5 compares the estimated emissions between the ~~multiple~~ multiple-species data assimilation and a \chem{NO_2}-only data assimilation~~ for 2008 and 2010~~. The estimated emissions differ in many regions if non-\chem{NO_2} data assimilation is considered because the ratio of predicted \chem{NO_x} emission and \chem{NO_2} column has been adjusted by non-\chem{NO_2} observations. T~~For instance, the estimated annual total regional emissions for central Africa for 2008 and 2010 is 8 \% lower in the \chem{NO_2}-only assimilation than in the multiple species assimilation. The assimilation of non-\chem{NO_2} measurements also influences the seasonal variability,~~ he assimilation of non-\chem{NO_2} measurements leads to changes of up to about 70 \% in the regional monthly-mean emissions. The estimated ten-year total regional emissions for South America and Australia are about 10 \% lower in the multiple-species assimilation than in the \chem{NO_2}-only assimilation. The RMSE between the two estimates for the monthly total regional emissions is 15.5 \% for central Africa, 16.5 \% for Australia, and about 5--8 \% for major polluted regions during the ten-year period. ~~which leads to changes of~~ The estimated monthly mean emissions are mostly smaller in the multiple-species assimilation than in the \chem{NO_2}-only assimilation, especially over the tropical and southern subtropical regions such as South America, central Africa, and Australia, suggesting that \chem{NO_2}-only data assimilation tends to overcorrect the emissions from the a priori. The monthly total global emissions decrease by up to 6 TgN (in boreal summer) if non-\chem{NO_2} data assimilation is considered. ~~-13 to +30 \% in the regional monthly-mean emissions (not shown).~~ The ten-year linear ~~year-to-year variability~~trend is also ~~largely~~ different over most industrial areas (Table ~~3~~4). For instance, the positive trend for India is 34.3 \%/decade in the \chem{NO_2}-only assimilation, which is ~~difference from 2008 to 2010 for the United States is -0.34 \unit{Tg\,N\,yr^{-1}} in the multiple species assimilation, which is much smaller~~larger than the -29.2 \%/decade in the multiple-species assimilation. ~~than -1.00 \unit{Tg\,N\,yr^{-1}} in the \chem{NO_2}-only assimilation and is closer to -0.51 \unit{Tg\,N\,yr^{-1}} in EDGAR-HTAP v2.~~ For the United States, the negative trend is larger in the multiple-species assimilation (-29.4 \%/decade) than in the \chem{NO_2}-only assimilation (-23.9 \%/decade). These results confirm that the assimilation of measurements for species other than \chem{NO_2} provides additional constraints on the \chem{NO_x} emissions over both anthropogenic and biomass burning regions~~, and further suggests that \chem{NO_2}-only data assimilation tends to overcorrect the emissions in some regions~~.

The improved representation of \chem{NO_x} emissions is confirmed by the better agreement of simulated \chem{O_3} concentrations with independent ozonesonde observations using \chem{NO_x} emissions from ~~multiple~~ multiple-species assimilation than those using \chem{NO_x} emissions from \chem{NO_2}-only data assimilation, which was also demonstrated by Miyazaki and Eskes (2013). After 2010, TES \chem{O_3} retrievals were not assimilated because of the lack of standard observations. Even so, the optimized surface \chem{NO_x} emissions from the ~~multiple~~ multiple-species assimilation improved agreements with TES \chem{O_3} ver. 6 special observations during 2011--2014 for most locations (Table S1). These results indicate that ~~multiple~~ multiple-species measurements provide important information for improving surface \chem{NO_x} source estimations and improve the chemical consistency including the relation between concentrations and the estimated emissions. Note that the emissions of \chem{O_3} precursors other than \chem{NO_x}, such as \chem{VOCs}, and various model processes in atmospheric transport and chemistry influences the model performance. The optimization of additional precursors emissions and the improvement of the forecast model could be important for improving \chem{O_3} simulations, as discussed in our previous studies (Miyazaki et al., 2012b; 2015).

\chem{LNO_x} sources are important for a realistic representation of tropospheric \chem{NO_2} columns, which are optimized from data assimilation in our framework. Using the ~~multiple~~ multiple-species data assimilation, the ten-year mean global \chem{LNO_x} source amount was estimated at 5.8 \unit{Tg\,N\,yr^{-1}}, in contrast to 5.3 \unit{Tg\,N\,yr^{-1}} estimated from the model simulation and 6.3$\pm$1.4 \unit{Tg\,N\,yr^{-1}} in our previous data assimilation estimate (Miyazaki et al., 2014). The data assimilation increments for \chem{LNO_x} sources are large in the upper troposphere in the NH and the TR, in which non-\chem{NO_2} measurements with different vertical sensitivities provided important constraints. Through its influence on simulated tropospheric \chem{NO_2} columns, for instance, the inclusion of the \chem{LNO_x} source optimisation altered the surface \chem{NO_x} emission estimates over eastern China by up to 12\% in summer. Moreover, surface CO emissions increased by 10 \% in the NH by the assimilation of MOPITT CO measurements in our system. Both optimised \chem{LNO_x} sources and CO emissions reveal enhanced seasonal and interannual variations over many regions after data assimilation, providing important constraints on long-term estimates of surface \chem{NO_x} emissions, through their influence on OH and thus the \chem{NO_x} chemical lifetime.

Figure ~~12~~ 13 shows changes in OH concentrations (Δ\chem{OH}) in the lower troposphere in the boreal summer (averaged over June--August) due to data assimilation. The ~~multiple~~ multiple-species assimilation changes the global OH distribution, increasing OH over most land areas. As summarised in Table ~~5~~6, the regional impact is large (greater than +20 \%) in tropical regions such as over the Middle East, Southeast Asia, and Central and North Africa, and over industrial areas (greater than +10 \%) such as over China, the United States, and India. These changes in OH concentrations can be partly introduced by changes in \chem{NO_x} emissions, but were largely influenced by the assimilation of non-\chem{NO_2} measurements, which was confirmed using observing system experiments (OSEs). In contrast to the increased surface CO emissions in the NH, the ten-year mean regional total CO emissions are reduced by 12\% in the tropics, leading to an increase of OH concentrations in the tropics. The assimilation of TES \chem{O_3} retrievals also significantly changes OH concentrations, which results in a significant increase in OH concentration in the extratropics by up to 15 \% in the NH extratropics in summer, as demonstrated by Miyazaki et al. (2012b). Note that the ten-year mean NH/SH OH ratio is estimated at 1.19 in the data assimilation run, in contrast to 1.27 in the MIROC model simulation, which is closer to 0.97$\pm$0.12 estimated based with the help of methyl chloroform observations (a proxy for OH concentrations) by Patra et al. (2014).

To elucidate the changes in the \chem{NO_x} chemical lifetime, Table ~~5~~ 6 compares the lower tropospheric \chem{OH} concentration and the ratio of the regional mean surface \chem{NO_x} emissions and lower tropospheric \chem{NO_2} concentrations (averaged from the surface to 790 hPa) between the ~~multiple~~ multiple-species data assimilation and the ~~\chem{NO_2}-only assimilation runs~~model simulation (Δ\chem{NO_x}-emi/\chem{NO_2}) in the boreal summer. It was confirmed that both the concentration assimilation (mainly TES \chem{O_3} and MOPITT CO measurements) and the changes in surface \chem{NO_x} emissions lead to an increase in the \chem{OH} concentration in the lower troposphere. Meanwhile, t~~The inverse lifetime of \chem{NO_x} is expected to be proportional to the ratio of \chem{NO_x} to \chem{NO_2}. T~~he increased ratio of \chem{NO_x} to \chem{NO_2} (i.e. ~~decreased~~ increased fraction of \chem{NO~~_2~~}) in the ~~multiple~~ multiple-species assimilation compared to the ~~\chem{NO_2}-only assimilation~~ model simulation indicates that the \chem{HO_2}+\chem{NO} reaction, which is the source of \chem{OH}, is enhanced in the multiple-species assimilation. ~~\chem{NO_x} chemical lifetime is decreased because of the assimilation of non-\chem{NO_2} measurements over most industrial and biomass burning areas, which can be associated with the increased OH concentrations by the assimilation of non-\chem{NO_2} species.~~ These results suggest that \chem{NO_x} chemical lifetime is decreased because of increased \chem{OH} concentrations (through the \chem{NO_2}+\chem{OH} reaction, which acts as the main sink of \chem{NO_x}) in the multiple-species data assimilation over most industrial and biomass burning areas, and demonstrate the utility of the ~~multiple~~ multiple-species assimilation to constrain the tropospheric chemistry (i.e. chemical regime) controlling \chem{NO_x} variations and to improve surface \chem{NO_x} emission inversions.

\subsection{Impact of assimilating \chem{NO_2} observations from multiple instruments}

Unlike most previous studies that used \chem{NO_2} retrievals from a single sensor, we assimilated multiple \chem{NO_2} measurements to constrain surface \chem{NO_x} emissions. When assimilating OMI retrievals only, the larger discrepancies with respect to the SCIAMACHY and GOME-2 retrievals for some regions may be attributed to errors in the simulated diurnal \chem{NO_2} variations, since both emission factors and tropospheric concentrations of \chem{NO_x} are constrained only in the early afternoon in this case. When assimilating multiple \chem{NO_2} measurements, the application of the correction factor (Etc) for the emission diurnal variability function (Et) modified the shape of the diurnal emission variability (Fig. 1), which improved the agreement with multiple \chem{NO_2} retrievals in both the morning and afternoon for many cases. The global RMSE for monthly mean tropospheric \chem{NO_2} column is reduced by 8 \% compared to the OMI retrievals and by 13 \% compared to the SCIAMACHY in January 2005 by assimilating multiple \chem{NO_2} measurements with applying Etc, compared to the case with the OMI retrievals only. The estimated monthly regional emissions ~~from~~ constrained by the three retrievals deceased by 18 \% over Europe and by 9 \% over Australia in January 2005 compared to those from the OMI retrievals only.

As shown in Fig. ~~13~~ 14 and Table ~~6~~7, the estimated Etc is negative for most industrial regions such as Europe and North America, and over biomass burning areas, such as southeast Asia. The large adjustments (Etc=-0.3$-$-0.4, for which the daily mean hourly emission value is 1) for the industrialized areas suggest that a positive adjustment to the assumed diurnal emission variability is required between 7:30--10:30 (and then a negative adjustment for emissions between 10:30--13:30), probably due to larger underestimations of emissions (e.g., morning traffic rush). These results also suggest a larger negative bias in simulated tropospheric \chem{NO_2} column in the morning, associated with errors in the chemical lifetime and atmospheric transports (e.g., boundary layer development) and also associated with biases between the different \chem{NO_2} retrievals. Thus, the model errors could artificially affect the diurnal emission variability. The optimized Etc for biomass-burning and soil emission dominant regions are mostly slightly negative, which may suggest that the applied diurnal emission variability with an afternoon maximum (see Section 2.1) was misleading for some regions. ~~whereas~~ In contrast, they are positive for most of the ocean. These results suggest the need to not only correct diurnal \chem{NO_2} variations, but also account for the differences in the sampling and bias between OMI and other instruments as well as the influences of model errors. Future geostationary satellite missions such as Sentinel-4, GEMS, and TEMPO will be able to provide dramatically more systematic constraints on diurnal emission variability and observational information.

\subsection{Possible error sources}

Biases in satellite retrievals and modeling affect the magnitude of estimated emissions. Miyazaki et al. (2012a) demonstrated that possible biases (up to 40 \%) in the \chem{NO_2} retrieval alter regional \chem{NO_x} emissions by 5--45 \%. The emission estimates may also be sensitive to measurement biases for species other than \chem{NO_2}. For example, a bias correction for the positive bias in the TES \chem{O_3} profiles altered monthly \chem{NO_x} emissions by 1--11 \% at the regional scale (Miyazaki and Eskes, 2013). Discontinuities in the assimilated measurements (e.g., lack of most TES retrievals after 2010, ~~and~~ OMI row anomaly since January 2009, and the limited data coverage of SCIAMACHY (before February 2012) and GOME-2 (after January 2007)) may also affect long-term emission estimates.

Estimated emissions are sensitive to the choice of forecast model and its resolution. Our analysis using a different forecast model (CHASER versus MIROC-Chem) showed up to 20 \% difference in monthly \chem{NO_x} emissions at the regional scale. Meanwhile, negative biases remain in tropospheric \chem{NO_2} columns over industrial regions, such as China, Europe, the United States, and Southern Africa, using either model ~~after~~ and data assimilation. The inadequacies of the improvements in simulated tropospheric \chem{NO_2} columns could be related to model biases in the \chem{NO_x} chemical lifetime (e.g., Stavarakou et al., 2013) and may also be partly attributed to the small number of observations and large observation errors for highly polluted cases (Fig. S1). Over polluted areas, observation errors increase almost linearly with the retrieved concentrations for most cases, and large observation errors may lead to the insufficient improvements by data assimilation for highly polluted cases. The remaining error may indicate a possible bias in the estimated emissions.

For example, over Europe, the increased wintertime negative bias against OMI retrievals (in contrast to the reduced bias against SCIAMACHY retrievals) in 2009 and 2010 could also be associated with difficulties in correcting the diurnal emission variation. For that time period over northern Europe, the number of OMI observations used for data assimilation is greatly reduced and observation errors are significantly increased, whereas those of SCIAMACHY vary differently (Fig. S1). More observational data (e.g., from ground-based measurements) may be required to further constrain surface \chem{NO_x} emissions for cloudy and snow-covered conditions and for high latitudes. Meanwhile, the diurnal variability correction scheme may need to be refined to further improve the agreement with various overpass time measurements.

Meanwhile, coarse resolution models are known to have negative biases in \chem{NO_2} over large sources (Valin et al., 2011). The emissions estimated at the T42 resolution in this study could potentially be overestimated over polluted areas, whereas the contrast between rural and urban areas could be underestimated. A high-resolution forecast model is important to accurately simulate nonlinear effects in \chem{NO_2} loss rate, while also providing insights into individual emission sources, such as power plants (e.g., de Foy et al., 2015).

Although the assimilation of multiple-species data influences the representation of the entire chemical system (Miyazaki et al., 2012b, 2015), the influence of model and observation errors remains a concern. In the multiple-species data assimilation, model performance is critical for the correct propagation of observational information between chemical species and to improve the emission estimation, whereas biases in any of the measurement data sets (including non-\chem{NO_2} measurements) may seriously degrade the emission estimation (Miyazaki et al., 2013). Improvements in the model, data assimilation scheme, and retrieved observations are essential to reduce the uncertainty on the emission estimates from the multiple-species data assimilation.

\subsection{Trends in \chem{NO_2} concentrations and \chem{NO_x} emissions}

We emphasize that the observed concentration variations do not necessarily correlate linearly with surface emissions, as similarly investigated by other inversion studies (e.g., Lamsal et al., 2011; Castellanos et al., 2012; Turner et al., 2012; Vinken et al., 2014). As summarised in Table 4, linear trends are significantly different between the observed concentrations and estimated emissions. The positive trend is larger in the observed \chem{NO_2} concentration (+39.6 \%/decade) than in the emission estimates (+26.0 \%/decade) for China, whereas the negative trend is larger in the emission estimates (-29.4 \%/decade) than in the observed \chem{NO_2} concentration (-6.3 \%/decade) for the United States. The relation between observed \chem{NO_2} concentration and estimated \chem{NO_x} emissions varies seasonally, as similarly expressed by Zhang et al. (2007), and the differences can be much larger at the grid scale. The results indicate that an accurate estimation of the long-term emission trends requires an emission-concentration relationship that explicitly accounts for tropospheric chemistry and non-\chem{NO_2} concentrations afforded by advanced data assimilation techniques (~~c.f.,~~see Section 5.1). These year-to-year variations in the observed \chem{NO_2} concentrations have previously been reported by Duncan et al. (2016) and Krotkov et al. (2016).

These results also suggest that the tropospheric chemical regime may have changed over the ten-year period. For instance, over Europe, the linear trend is positive for the observed \chem{NO_2} concentration (+13.6 \%/decade for all of Europe and +7.5 \%/decade for western Europe in OMI) and is negative for the emission estimates (-0.1 \%/decade and -8.8 \%/decade, respectively). This suggests that \chem{NO_2} may have become longer-lived or has become a larger fraction of \chem{NO_x} over Europe over the past decade. One possible explanation is that a shift in \chem{NO_2}:\chem{NO_x} emission ratios related to the increasing share of European diesel cars could have occurred~~.~~. Further efforts are required to explain the long-term variations of the tropospheric chemical regime and its causal mechanisms. Note that the linear trend in the observed concentration is different between the instruments over Europe (c.f., Fig. 3).

\conclusions

Global surface nitrogen oxides (\chem{NO_x}) emissions are estimated for the ten-year period between 2005--2014 from the assimilation of multiple satellite datasets: tropospheric \chem{NO_2} columns from OMI, GOME-2, and SCIAMACHY; \chem{O_3} profiles from TES; \chem{CO} profiles from MOPITT; and \chem{O_3} and \chem{HNO_3} profiles from MLS. The daily emission inversion is performed based on the ensemble Kalman filter data assimilation, which simultaneously optimises chemical concentrations of various species and emission sources of several precursors. Within the simultaneous emission and concentration optimisation framework, the analysis increment directly produced via chemical concentrations plays an important role in reducing model--observation mismatches arising from model errors unrelated to emissions, which can be expected to improve emission inversion. The assimilation of measurements for species other than \chem{NO_2} provides additional constraints on the \chem{NO_x} emissions over both anthropogenic and biomass burning regions, leading to changes in the regional monthly-mean emissions of -13 to +30 \%. The impact of non-\chem{NO_2} measurements varied largely with season, year, and region. In addition to daily emission factors, the diurnal emission variability function was optimised using multiple \chem{NO_2} retrievals, obtained in the morning (SCIAMACHY and GOME-2) and afternoon (OMI). The emission correction largely improved the agreement with observed tropospheric \chem{NO_2} columns, at both the seasonal and interannual time scales.

The ten-year mean global total surface \chem{NO_x} emissions after data assimilation is 48.4 \unit{Tg\,N\,yr^{-1}}, which is 26 \% higher than a priori emissions based on bottom-up inventories. The optimised ten-year mean emissions are higher over most industrialised areas. The data assimilation corrected the timing and strength of emissions from biomass burning, such as over central Africa (the ten-year mean regional emission is 1.68 \unit{Tg\,N\,yr^{-1}} in the a priori emissions and 2.57 \unit{Tg\,N\,yr^{-1}} in the a posteriori emissions), North

Africa (2.07 \unit{Tg\,N\,yr^{-1}} v.s 2.90 \unit{Tg\,N\,yr^{-1}}), Southeast Asia (0.47 \unit{Tg\,N\,yr^{-1}} v.s 0.68 \unit{Tg\,N\,yr^{-1}}), and South America (1.00 \unit{Tg\,N\,yr^{-1}} v.s 1.04 \unit{Tg\,N\,yr^{-1}}), suggesting a large uncertainty in fire-related emission factors in the emission inventories. At northern mid-latitudes and over Australia, the emissions are largely enhanced during summer, suggesting an important underestimation of soil sources in the a priori inventory. Using the emission ratio between different categories in the a priori emission inventories, the global total soil \chem{NO_x} emission for the 2005--2014 period is estimated at 7.9 \unit{Tg\,N\,yr^{-1}} yr^{-1}, which is much higher than the a priori estimate of 5.4 \unit{Tg\,N\,yr^{-1}} yr^{-1}. This soil \chem{NO_x} emission estimate may nevertheless be conservative, because the ratio between the source categories is kept fixed in our approach.

The estimated regional total emissions show strong positive trends over India (+29 \%/decade), China (+26 \%/decade), and the Middle East (+20 \%/decade), and negative trends over the United States (-29.4 \%/decade), Southern Africa (-8.2 \%/decade), and western Europe (-8.8 \%/decade). At the grid scale, strong positive trends are found over large cities in China (e.g., Wuhan (+42 \%/decade), Chengdu (+56 \%/decade), northwestern China (+50--+110 \%/decade)), India (e.g., Kolkata (+47 \%/decade), Raipur (+67 \%/decade), Madras (+40 \%/decade)), the Middle East (e.g., Kuwait (+47 \%/decade), Tehran (+37 \%/decade)), and Brazil (Sao Paulo (+40 \%/decade)), whereas large negative trends are found in Europe (e.g., northern Spain (-45 \%/decade), Po Valley (-52 \%/decade)), the United States (e.g., New York (-48 \%/decade), Boston (-42 \%/decade), Chicago (-52 \%/decade), Atlanta (-47 \%/decade), Los Angeles (-46 \%/decade)), and Japan (e.g., Tokyo (-48 \%/decade), Osaka (-38 \%/decade)). The yearly mean emissions for China reveal a large positive trend from 2005 to 2011, subsequently decreasing through 2014. For the United States and some parts of Europe, the negative trends are larger during 2005--2010 than 2011--2014. These changes are more variable as a result of the global economic recession and emission controls. Despite the large year-to-year variations over many regions, the global total emission is almost constant between 2005 (47.9 TgN) and 2014 (47.5 TgN).

The estimated emissions have great potential to contribute to better understanding of precursor variability influences on observed air quality (e.g., tropospheric \chem{O_3}) variations and associated climate impacts. The obtained emission data is also crucial to evaluate bottom-up inventories. The consistent data set comprising emissions and concentrations of various species, which were obtained from our simultaneous data assimilation framework, provides comprehensive information on atmospheric environmental variations, associated with both human and natural activity. Meanwhile, our results suggested that more observational constraints would be required to improve the global emission estimates. Observational information from future satellite missions such as TROPOMI and sensors on board geostationary satellites (Sentinel-4, GEMS, and TEMPO) in conjunction with exploitation of existing sounders, e.g., IASI and CrIS, can be expected to add constraints on more detailed spatiotemporal variability in surface \chem{NO_x} emissions and its impact on air quality (Bowman, 2013).

\begin{acknowledgements}

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Table 1: Comparisons of tropospheric \chem{NO_2} columns between data assimilation and satellite retrievals: OMI for the period 2005--2014, SCIAMACHY for the period 2005--2011, and GOME-2 for the period 2007--2014. Shown are the global spatial correlation (S-Corr), the mean bias (BIAS: the data assimilation minus the satellite retrievals) and the root-mean-square error (RMSE) in 10^{15}\,\unit{molec\,cm^{-2}}. The model simulation results (without data assimilation) are also shown in brackets.

Table 2: The monthly mean bias and temporal correlation of regional mean tropospheric \chem{NO_2} columns: the data assimilation minus the satellite retrievals from OMI for the period 2005--2014, SCIAMACHY for the period 2005--2011, and GOME-2 for the period

2007--2014 in 10^{15}\,\unit{molec\,cm^{-2}}. The results of the model simulation (without data assimilation) are also shown in brackets.

Table 3: The regional ten-year mean \chem{NO_x} emissions (in \unit{Tg\,N\,yr^{-1}}) obtained from the a priori emissions, a posteriori emissions, and the relative difference between these two emissions (in \%) for the period 2005-2014 (left columns). The results are also shown for EDGAR-HTAP v2 emissions (as a reference) averaged over the years 2008 and 2010, the a posteriori emissions (the same results as in the left columns, but averaged over the years 2008 and 2010), and the relative difference between these two estimates (in \%) (central columns), and for their difference from 2008 to 2010 (right columns). ~~The a posteriori emissions from assimilation of \chem{NO_2} measurements only for 2008 and 2010 are shown in brackets.~~ The results are also shown for the Northern Hemisphere (NH, 20--90°N), the tropics (TR, 20°S--20°N), the Southern Hemisphere (SH, 90--20°S), and the globe (GL, 90°S--90°N).

Table ~~4~~4: Linear trend (in \% per decade) of the regional a posteriori \chem{NO_x} emissions from the multiple-species assimilation (left column) and \chem{NO_2}-only assimilation (central column), and of the regional mean tropospheric \chem{NO_2} columns from OMI (right column) for the period 2005-2014.

Table 5: Difference between the a posteriori emissions from the multiple-species assimilation and \chem{NO_2}-only assimilation. Relative difference for the regional ten-year mean emissions (left column), RMSE for the monthly regional emissions (central column), and range of relative difference for the monthly regional emissions (right column) are shown.

Table ~~5~~6: Regional and ten-year mean difference in lower tropospheric OH concentration averaged below 790 hPa (Δ \chem{OH}) and the ratio of surface \chem{NO_x} emission and lower tropospheric \chem{NO_2} concentration averaged below 790 hPa

(Δ\chem{NO_x}-emi/\chem{NO_2}) between the data assimilation run and the model simulation in the boreal summer (averaged over June--August) over the 2005--2014 period.

Table ~~6~~7: Regional and ten-year mean correction factor for the emission diurnal variability (Etc) for 2005--2014.

Figure 1: Schematic diagram of the correction scheme for the emission diurnal variation for a case with $Etc=-0.3$. The black dotted time represents the a priori emission diurnal variability function (Et) for anthropogenic emissions. The black solid line represents the a posteriori emission variation after applying the daily emission scaling factor ($Et \times Es$). The blue line represents the correction factor for the emission diurnal variability (Etc). The red line represents the a posteriori emission variation after applying the daily emission scaling factor and the correction factor for the emission diurnal variability ($Et \times Es - Etc$ for 07:30--10:30, and $Et \times Es + Etc$ for 10:30--13:30).

Figure 2: Global distributions of the tropospheric \chem{NO_2} columns (in 10^{15}\,\unit{molec\,cm^{-2}}). The results are shown for OMI (left columns, sampling time $\approx$13:00 hrs) for 2005--2014, SCIAMACHY (middle columns, 10:00 hrs) for 2005--2011, and GOME-2 (right columns, 09:30 hrs) for 2007--2014. Upper rows show the tropospheric \chem{NO_2} columns obtained from the satellite retrievals (OBS); centre shows the difference between ~~rows from~~ the model simulation and the satellite retrievals (Model-OBS); and lower rows ~~from~~ show the difference between the data assimilation and the satellite retrievals (Assim-OBS).

Figure ~~3~~3: Time series of regional monthly mean tropospheric \chem{NO_2} columns (in 10^{15}\,\unit{molec\,cm^{-2}}) averaged over China (110--123°E, 30--40°N), Europe (10°W--30°E, 35--60°N), the United States (70--125°W, 28--50°N), South America (50--70°W, 20°S--Equator), North Africa (20°W--40°E, Equator--20°N), Central Africa (10--40°E, Equator--20°S), Southern Africa (25--34°E, 22--31°S), Southeast Asia (96--105°E, 10--20°N), Australia (113--155°E, 11--

44°S), and India (68--89°E, 8--33°N) obtained from the satellite retrievals (black), model simulation (blue), and the data assimilation (red). The model simulation and data assimilation results were obtained at the local overpass time of the retrievals with applying the averaging kernel.

Figure 4: (Left panel) Mean vertical \chem{NO_2} profiles obtained during the ARCTAS campaign in June--July 2009. The black represents the observation; the blue line represents the model simulation; the red line represents the data assimilation. The error bars represent the standard deviation. (Right six panels) Scatter plots of \chem{NO_2} concentrations for the data assimilation (top) and the model simulation (bottom) during the DANDELIONS campaign (in $\mu g m^{-3}$) in September 2006 (second left columns) and during the INTEX-B campaign (in \unit{pptv}) on March 9, 2006 (third left columns) and March 11, 2006 (right columns). The straight lines represent linear regression lines for each level. Each line represents a linear fit to the points of the same colour, and the colours represent the altitude (or pressure) level.

Figure 5~~4~~: Global distributions of surface \chem{NO_x} emissions (in $10^{-13}\unit{kg m^{-2} s^{-1}}$) averaged over 2005--2014. The a priori emissions (top), a posteriori emissions from the data assimilation run (middle), and analysis increment (bottom) are shown.

Figure 6~~5~~: Global distribution of linear trend of the a posteriori surface \chem{NO_x} emissions (in $10^{-13}\unit{kg m^{-2} s^{-1}}$ per decade) for the period 2005--2014. The red (blue) colour indicates positive (negative) trends.

Figure 7~~6~~: Time series of monthly total regional surface \chem{NO_x} emissions (in \unit{Tg\,N\,yr^{-1}}) obtained from the a priori emissions (black lines) and the a posteriori emissions (red lines) for the period 2005--2014. The results are also shown for EDGAR-HTAP v2 emissions (~~blue~~ green lines) for the years 2008 and 2010.

Figure 8~~7~~: Seasonal variations of the regional surface \chem{NO_x} emissions (in \unit{Tg\,N\,yr^{-1}}) obtained from the a priori emissions (black line) and the a posteriori emissions (red line) averaged over the period 2005--2014. The results are also shown for the a posteriori emissions for individual years during 2005--2014 (yellow lines).

Figure 9~~8~~: Time series of the difference (in \%) of the annual mean a posteriori surface \chem{NO_x} emissions relative to the 2005 emissions in the period 2005--2014 for India (yellow), China (blue), Europe (light blue), western Europe (light blue dashed line), Southern Africa (red), and the United States (green).

Figure 10~~9~~: The regional distribution of ten-year mean surface \chem{NO_x} emissions (in \$10^{-13}\unit{kg m^{-2} s^{-1}}\$) over East Asia (upper panels), Europe (upper middle panels), the United States (lower middle panels), and Southeast Asia (lower panels) obtained from the a posteriori emissions in the period 2005--2014 (left panels), and the difference between the a posteriori emissions and a priori emissions in the period 2005-2014 (centre panels), and between the a posteriori emissions and EDGAR-HTAP v2 emissions for the years 2008 and 2010 (right panels). The black square line represents the region used for the regional mean analysis.

Figure 11: Global distribution of linear trend of the a posteriori surface \chem{NO_x} emissions for the period 2005--2010 (left) and 2011--2014 (right). The red (blue) colour indicates positive (negative) trends.

Figure 12~~0~~: The regional distribution of the linear trend in surface \chem{NO_x} emissions (in \$10^{-13}\unit{kg m^{-2} s^{-1}}\$ per decade) during 2005--2014 over East Asia (upper left), Europe (upper right), the United States (bottom left), and Southeast Asia (bottom right), obtained from the a posteriori emissions. The black square line represents the region used for the regional mean analysis.

~~Figure 11: Global distribution of linear trend of the a posteriori surface \chem{NO_x} emissions for the period 2005--2010 (left) and 2011--2014 (right). The red (blue) colour indicates positive (negative) trends.~~

Figure 13~~2~~: Global distribution of the ten-year mean \chem{OH} concentration (in \$10^6\$ \unit{molecules cm^{-3}}) in the data assimilation run (top) and its difference between the data assimilation run and the model simulation (bottom) averaged over June, July, and August over the 2005--2014 period at 850 hPa.

Figure 14~~3~~: Global distribution of the annual mean correction factor for the emission diurnal variability (\$Etc\$) for the period 2005--2014.