Author response to the referee comments to the paper by Barten et al.: Evaluation of nitrogen oxides sources and sinks and ozone production in Colombia and surrounding areas

We would like to thank the two reviewers for their constructive feedback on the manuscript. Those reviews indicate that both reviewers support publication of this paper on an Colombian AQ assessment but both recommend also major modifications. We especially appreciate one of the reviewers' comment that Colombia is an interesting study area due to its various emission sources and isolated regions but also having the large diversity in biogeochemical regimes and complex topography. All comments greatly help in further improving the manuscript. Below, we address each comment individually. Referee comments are given in *italic*, author response are given in normal font, changes made to the text are given in blue. This document is finalized by a markdown version of the manuscript including all the changes.

Review #1:

Summary of review:

This paper is well written from a technical point of view and the science is solid, but I recommend this current manuscript be split into two (or maybe even three) papers. It appears that the authors are combining several complementary papers into a single manuscript. One that is evaluating the sources and sinks of NO_2 using WRF-Chem and OMI and its effects on ozone, one that is trying to resolve a discrepancy in PBL height, and perhaps even another on the role of lightning NO_x in the Amazonia. In my opinion, the authors have two options here: 1) either significantly shorten Section 4 & Discussion and add a stronger focus on the SCM model or 2) to exclude Section 5 entirely. I would prefer option 1, but I will leave that decision up to the authors. I also think option 1 better fits the scope of ACP. I recommend publication, but only after the scope of the paper is narrowed.

We thank anonymous referee #1 for the critical review and constructive comments. The idea of the paper was to apply and evaluate WRF-Chem by comparison with remote sensing and few available in situ observations to study air quality in regions/countries with a limited in situ network such as Colombia. We decided to limit the presented study to identification of some of the main issues in this assessment of Colombian AQ such as the lightning NO_x parametrization of WRF-Chem but also how the model performs regarding simulations of observed sub-grid scale levels of urban pollution. The proposed more detailed analysis of NO_x lightning, should be focus in follow-up studies since, as also indicated by reviewer, this analysis would be more than sufficient for another dedicated study. According to the reviewer, the same holds for evaluation of the boundary layer dynamics relative to the (mis)representation of emissions introducing application of the SCM simulations. Based on the reviewers comments, we have considered to indeed completely remove Section 5 but have now decided to handle the raised comments by 1) substantially shortening this section (5) on the SCM results, 2) to be less quantitative regarding the SCM results and, 3) merging these results with section 4.3. So, we still would like to make this specific point in this paper on a misrepresentation of emissions relative to the role of boundary layer dynamics in explaining discrepancies between simulated and observed concentrations. But we revised the text to stress more explicitly that the SCM exercise was not to propose a new modelling strategy with an improved representation of BL dynamics, but mainly aimed to conduct a sensitivity experiment to complement the evaluation of WRF-Chem simulated urban area pollutant concentrations. Consistent with these changes in Section 4 & 5, the abstract, discussion and conclusions have been modified accordingly.

Major comments:

Ln 260: I am uneasy with attributing the high model bias in the Amazonia to lightning NO_x*, primarily because the boundary of your domain is fairly close to this region and that climatological winds are generally from the east. I do not think it is correct to automatically assume lightning* NO_x *is the reason for the discrepancy. I believe that boundary conditions could be playing a role here. Additionally, you may only be using <10 days of OMI data in the comparison (Figure 2), which is particularly an issue here since the* NO_2 *measurements are near the lower limit of the OMI's capability. In general, a long discussion on the lightning NOx is not warranted because it is a small sample size near the instrument's detection limit. Please also revise the later parts of the manuscript when lightning* NO_x *is discussed.*

Also based on the comments by Reviewer #2 and re-reading the text, we realize that we might have been to explicit in our statements regarding overestimation of the lightning NO_x emissions. We have addressed the issue that only a small number of measurements are available over these regions although we have already taken January 2014 as simulation month, but this does not outweigh the statements on the overestimation of the emissions. Based on the reviewers comments, we have once more again carefully evaluated especially the model's eastern boundary conditions, but in general, very little NOx is advected over the domain boundary (also visible in the eastern most grid cells in fig. 5a). We agree that OMI is operating here near the detection limit. We have updated the manuscript in many sections, mostly reducing the statements on the overestimation of lightning NO_x emissions.

Ln 295-298: After looking at Figure 6, I am confused how the authors are implying that there is good agreement between the modeled NO_x/O_3*/CO and surface monitors at any hour. Perhaps I am misinterpreting something, but if not, these sentences should be modified.*

The text was referring to Figure C1 in the Appendix. The point we wanted to stress is that WRF-Chem generally represents the lower limit in observed NO_x mixing ratios and the upper limit of observed O_3 mixing ratios during daytime. However, WRF is not able to simulate the high NO_x ratios found during rush hour or the low nocturnal O_3 (< 5 ppb) mixing ratios of the individual stations. We have modified the text such that it should be clear that we are discussing those upper and lower limits found in the individual (and not the average diurnal cycle) measurements.

Ln 354 How is the boundary layer constrained in the single column model? This seems to be key information, but it is left out. In general, Section 5 is lacking specifics. As emphasized above, I think this could be a either a great follow-up paper or Section 4 should be shortened and this could be a larger focus of the paper.

Boundary layer (BL) dynamics in the SCM are calculated in a similar manner compared to WRF-Chem in online calculations involving surface and boundary layer exchange of momentum, energy, moisture (and tracers) but then using different BL schemes (YSU in WRF-Chem, ECHAM4 climate model BL scheme in SCM). The details can also be found in previous references on SCM studies (e.g., Ganzeveld et al., 2002b). We might have though not been clear enough that, in contrast to offline models that prescribe the BL depth, the SCM calculates this BL dynamics in an online set-up similar to WRF-Chem. We have further stressed this essential feature: e.g., Section 4.3 "The SCM simulates online, similar to WRF-Chem, atmospheric chemistry processes, including anthropogenic and natural emissions, gas-phase chemistry, wet and dry deposition and turbulent and convective tracer transport as a function of meteorological and hydrological drivers, surface cover, and land use properties (Ganzeveld et al., 2002b, 2008)". However, rather providing the details of BL dynamics in the SCM (and WRF-Chem) in a more elaborated Section 5, we decided to strongly shorten and merge this section with Section 4.3. Furthermore, also being less quantitative we refrain from any claim that the SCM performs better regarding BL dynamics and which is also not possible not having BL depth/structure measurements. If such measurements would be available then it would definitely be worthwhile to further investigate the representation of urban boundary layer dynamics in the SCM and WRF-Chem also motivated by the presented simulated large differences in pollutant diurnal cycles. Throughout the manuscript we have modified the description of the purpose and main findings of the supporting experiments with the SCM.

Minor comments:

Ln 101: What initial conditions are used?

The ECMWF ERA-Interim and CAMS data products used for the boundary conditions are also used for the initial conditions. This is updated in the text.

Ln 142: The words "on the large-scale" are probably unnecessary.

We have removed "large scale"

Ln _190: Silvern et al., 2018 should at least be mentioned at this point in the manuscript. It suggests that the NO_2/NO partitioning may not be good in the upper troposphere. The paper shows that NO_2 in upper atmosphere is often too low in global models. This is important when calculating the AMF and could affect it significantly when NO_2 is generally low such as the Amazonia region. Silvern, R. F., Jacob, D. J., Travis, K. R., Sherwen, T., Evans, M. J., Cohen, R. C., Laughner, J. L., Hall, S. R., Ullmann, K., Crounse, J. D., Wennberg, P. O., Peischl, J., and Pollack, I. B.: Observed NO/NO2 Ratios in the Upper Troposphere Imply Errors in NO-NO2-O3 Cycling Kinetics or an Unaccounted NOx Reservoir, Geophys. Res. Lett., 45, 4466–4474, https://doi.org/10.1029/2018gl077728, 2018.âˇA´C

This can indeed be an explaining factor. We have added the reference.

Figure 2: Borders are hard to see. Perhaps change them to white? Also for clarity, perhaps change the values to % of the month instead of number of measurements.

We have changed the values and borders.

Figure 4b: The units are unclear. Please clarify

The figure indicates the spatial distribution of the dominant emission source. The saturation of the color indicates the % of the total flux coming from the dominant emission source going up to 100% for the darkest colors. We have updated the caption to make it more clear.

Ln 250 & Ln 257: Insert the word "model" before "overestimation"

Added model twice.

Ln 273: Is Figure 5d necessary? It does not seem to add any helpful information.

We have removed figure 5d, also combining the colorbar of 5a and 5b.

Ln 296: Should clarify to "morning rush hour"

Added morning.

Ln 359: Discussion section should be more concise.

We have reduced the information in the discussion. Especially also removing a section where we discuss in detail the representativeness of EDGAR anthropogenic emissions above Bogota (Colombia) and Caracas (Venezuela) due to a decrease in economic activity. This analysis extra was not directly supporting the main goal/message of the manuscript.

Ln 376 - 390: I'm not sure how many overarching conclusions about lightning NO_x can be made from this study. I suggest this paragraph be removed.

We realize that these points have indeed been addressed before (methods/results/beginning of discussion) and come back later in the discussion. We have removed this section for the large part (thereby making the discussion section more concise) and moved Further attention is required no only regarding the lightning NO_x parametrization scheme, but also the model representation of convection and clouds, in follow-up studies on atmospheric NO_x over Colombia, or other regions where lightning is a dominant source of NO_x. further down in the discussion.

Review #2:

In their paper, Barten et al. provide an evaluation of atmospheric chemistry over Colombia using WRF-Chem modelling evaluated with satellite and surface observations. The paper is very well written, contains a good and balanced set of references, has an appropriate length and amount of detail and I could not discover any obvious flaws. Colombia is a complex and interesting country with isolated regions and various climate zones where the dominant emissions may vary from anthropogenic, biomass burning to lightning. The approach is of wider interest, because similar studies may be conducted for other countries with limited air-quality monitoring networks. Figure 4-b is a central figure in the paper and starting point to discuss the different regions in more detail. I am in favour of publishing this work, but I have four major general comments, provided below, which will require a major revision.

We thank anonymous referee #2 for her/his review of our manuscript and the very constructive feedback. We already mentioned previously that we really acknowledge the comment what makes Colombia being an interesting study area regarding meteorology and AQ but also appreciate the comment by this reviewer that the selected approach is of wider interest.

General comments:

1. The authors present only one month of simulations (January 2014) but the seasonal dependence of NO_x *and ozone is not discussed. There are good reasons to focus on January because it is the dry season, but the country experiences wet and dry seasons where the relative importance of sources of NO may change. The diurnal variability as well as the multi-annual variability in the satellite data are discussed, but the seasonality is missing. Would it be possible to extend the simulations to a couple of months to sample the yearly cycle in emissions? It would be interesting to present also the seasonality of the satellite (and surface) observations.*

One of the goals of this manuscript was to present a concise method to study air quality in complex regions like Colombia with a limited monitoring network in rural areas. The goal was not necessarily to study the capability of WRF-Chem to simulate these NO_2 (and O_3 urban) column/mixing ratios over the whole year. We decided to focus on January (2014) mainly because of the larger availability of remote sensing data with the generally reduced cloud cover. We have also added the yearly trend to indicate some features relevant to Colombia (El Nino) and to put it in perspective. We appreciate the reviewers comment and agree that a seasonal analysis of the OMI data would finalize this, without the need to conduct extra WRF-Chem simulations. We have added a subfigure, to figure A1, that shows the seasonality of the NO_2 columns above dominant emission sources including the spread (standard deviation) in the years 2005-2019. We discuss this figure in the Discussion section.

2. The authors show that the lightning source is the dominant source for 63% of the grid cells and is also the largest source in terms of total amount. Therefore lightning is a key aspect for Colombia, and, given also the major uncertainty in the modelling of this process, deserves special attention. The uncertainty in the lightning source is e.g. demonstrated by the adjustments made to the default settings of WRFchem, which scaled down lightning by a factor 20. However, the authors (if I understood correctly) have used only the clear-sky observations of OMI. It has been shown in several publications that lightning source estimates may be derived using the observations over high clouds. Because the resolution of WRF is comparable to OMI, it would be interesting to include a comparison between these cloud covered observations and WRF-Chem, to test the capability of the model to describe major thunderstorms. See for instance: Beirle, S., Huntrieser, H., and Wagner, T.: Direct satellite observation of lightning-produced NOx, Atmospheric Chemistry and Physics, 10, 10 965–10 986, https://doi.org/10.5194/acp-10-10965-2010, 2010. Pickering, K. E., Bucsela, E., Allen, D., Ring, A., Holzworth, R., and Krotkov, N.: Estimates of lightning NOx production based on OMI NO2 observations over the Gulf of Mexico, Journal of Geophysical Research: Atmospheres, 121, 8668–8691, https://doi.org/10.1002/2015JD024179, 2016.

It was not necessarily the goal of the paper to put more emphasis on the representation of lightning NO_x emissions. However, in analysing the results (and from other literature) it became clear that this is indeed a very uncertain process in regional air quality modelling and the region focus of our study. It was also not the goal to arrive at more quantitative estimates of (lightning NO_x) emissions but rather use the satellite data, besides the limited in-situ observations, to study regional air quality and define the different source regions. We concede to the comment of Referee #1 that the paper is already potentially too 'broad'. We also agree that an analysis like you mention is a very insightful tool to look at the lightning NO_x emissions in more depth and suggest that it would be a very interesting follow-up research. We have updated the manuscript with the following statement in the discussion: This study does not aim to provide comprehensive estimates of any of the emission sources using OMI data. Rather, we show the potential use of satellite data in a region with a limited air quality monitoring network in determining the regional scale air quality and NO_x source regions. The use of cloud covered OMI observations to get a more comprehensive estimate of lightning NO_x emissions (Beirle et al., 2010; Pickering et al., 2016) would make a very interesting follow up study.

3. The discussion of soil biogenic emissions is very limited. The regions where these emissions are dominant are identified. Therefore the comparison with OMI could be extended: are there indications that soil emissions are under (over) estimated? Where and by what amount?

We realize that soil emissions can potentially be underestimated by MEGAN, especially in regions with land management practises such as fertilizer application also after we found out in a recent other application of WRF-Chem for Europe (Visser et al., 2019) that this contribution to soil NO emissions is not considered in MEGAN/WRF-Chem. However, the OMI-WRF comparison indicates no clear under- or overestimation of biogenic emissions. In the discussion section we have added a comparison with the global chemistry-climate model EMAC. The MEGAN biogenic emissions in this study seem to be in line with the estimates by EMAC for the same region. Also, the contribution of fertilizer to the total soil NO flux seems to be very limited (~1.3%).

4. The differences between the single-column model and WRF-Chem should be more clearly described. Why does WRF-Chem produce so much lower concentrations in the city?

The differences appear to be mostly associated with the representation of the nocturnal inversion layer with the SCM simulations being nudged (e.g., Ganzeveld et al., 2006) with the WRF-Chem meteorology resulting a shallower nocturnal inversion layers compared to WRF-Chem. It is both the depth of the nocturnal inversion layer but also the timing of the onset of turbulent mixing relative to the onset of the morning rush hour and associated emissions that explains the large differences. But (see also previous comments), we have substantially shortened that section also aiming to present this more as a sensitivity analysis also given the fact that we cannot proof which of the different simulations are more realistic not having detailed BL dynamics observations. Throughout the manuscript we have modified the description of the purpose and main findings of the supporting experiments with the SCM.

Detailed comments:

Abstract, l15: "averaged difference of 0.02Â°u10ˆ15". How significant is this number?

We have included the 90% Confidence Interval to the text to indicate the spread around the mean. We have also changed it to a mean bias (WRF-Chem minus OMI) to make it more clear that it is about the bias between OMI and WRF.

l19: "WRF-Chem was unable to capture NO_x and CO urban". For which cities?

The urban comparison was done for all four cities (Cali, Bogota, Medellin, Bucaramanga) with air quality monitoring data. Therefore, the statement is in general for all Colombian cities with air quality monitoring data. Because the comparison showed similar results for the different cities we decided to only show the results for Bogota since they are most robust due to the presence of multiple measurement stations.

l80: "air quality in Colombia concerns are generally" Replace by "concerns about air quality in Colombia are generally"

Updated

l101: The spin-up time is very short? How is the model initialised?

The model is initialized with ECMWF ERA-Interim (meteorology) and CAMS (chemistry). For the surface mixing ratios, the signal of the initialization seems to be gone after 24 hours due to the local emissions and advection.

l103: "in Appendix A we show how the selected study period can be deemed being representative for the baseline state of air quality in Colombia. " This claim is not very clear to me. Figure A1 shows the year-to-year mean variation in January. Why is it representative? I would like to see also a seasonal variation, e.g. linked to the wet and dry seasons. Only showing results for January is a weak point of the paper that should be better motivated. Also, a seasonal mean could be more representative because of the limited number of OMI pixels in a month, see Fig.2.

See reply to general comment #1

l107: " ... (ECMWF) .. meteorological boundary conditions." Is this the operational dataset or reanalysis?

As stated above, this is the ERA-Interim product. We have updated this accordingly in the text.

l158: "data filtering recommendations by the QA4ECV": What is the filtering criterion for clouds? I assume cloud-covered pixels are not used?

The criterion for clouds is: cloud radiance fraction > 0.5. We have added this to the text. This is by far the strictest criterion for the selected study period.

l161: "limiting the quality of and which increases the uncertainty". Please reformulate.

We have changed the sentence to This limits the quality of the measurements and which increases the uncertainty in the averaged tropospheric NO_2 column.

l184: "mostly decreases in AMF". Please replace by "increases in the VCD" because not all readers will be familiar with the AMF concept. This remark applies to the whole section: please refer to VCD only.

We have updated this in the manuscript.

l190: "This reflects a higher abundance of NO_2 higher up in the troposphere". It is not fully clear to me how this can be concluded. The whole profile will be important. Are lightning emissions modelled higher in the atmosphere in WRF compared to the TM5-MP? Was this checked? Also, cloud-covered observations are removed from the OMI dataset by the filtering?!

In this specific case, we have checked the individual and average TM5/WRF-Chem profiles with valid observations (not filtered out by clouds).

l196: "In this research, we focus on tropospheric NO_2 columns." This line can be removed.

Removed.

Sec. 3.2 in-situ data: please provide information about the instruments used. Is the data publicly available?

The data and information on the instruments is publicly available at http://sisaire.ideam.gov.co/ideam-sisaire-web/

Fig. 4a: Unit? Is this per grid cell, per square km, or something else?

The unit was initially per grid cell as indicated in the caption. We realize that a flux per unit area (square km) is easier to interpret. We have changed this in the figure, text and caption accordingly.

l232-237: The numbers in the table are repeated in the text. This paragraph may be shortened therefore. I would suggest to add the % of land where the source is dominant (as given in the text) as extra column in the table.

We have reduced the text and remove the numbers from this paragraph.

l241: "very low VCD over Caribbean". What is the influence of the (free troposphere) boundary conditions?

We are analysing here the complete modeling system (so WRF-Chem including emission inventories and the boundary conditions). The prevailing winds are easterlies. So this is not the region where we would expect the largest influence of the boundary conditions.

l248: "northeastern part". Please provide a more detailed explanation where these high values come from.

These high VCDs are mostly caused by a lot of NO_2 close to the surface in the CAMS boundary conditions advected into the WRF-Chem domain by easterly winds. We have updated this in the manuscript.

l257: "Even though the overestimation is small in absolute terms". Could a possible bias in the satellite observations contribute to the difference observed?

We realize that OMI is operating here at its detection limit and that only clear-sky observations are considered. We have updated the text on Lightning NO_x in several sections also based on Review #1.

l261: "This further confirms the finding that lightning NO_x emissions are overestimated". Maybe this conclusion should be weakened. As explained by the authors in l262-265, the comparison with OMI is only performed in OMI clear-sky conditions. Therefore the comparison may be biased.

See previous comment.

l290: "These results confirm the application of the recalculated OMI data." It should be noted that the differences in mean, median, 90% confidence interval is not very large. So it is questionable if the confirmation is significant.

Since this was also not the main goal of the procedure we have decided to leave out the analysis on the reduction of the bias using the recalculated OMI columns. We have also revised this in earlier and later parts of the manuscript.

p14: I was wondering if the authors have analysed the precise location of the surface stations in Bogota? Closeness to major sources/roads could perhaps explain the difference with WRF-Chem?

We have done this, we think that all the surface stations should give a representative signal for the (Bogota) urban mixing ratios. The spread of the mixing ratios measured at the stations can be seen in Figure C1 (Appendix).

l341: "nudging the concentrations of long-lived tracers such as O_3, NO_x and CO above the boundary layer using the CAMS data". Why not use the WRF-Chem data for this?

Based on this comment we have conducted once more again the experiments with the SCM applying, instead of the CAMS data, the WRF-Chem simulated free tropospheric mixing ratios of O_3, NO_x and CO. Also, the initially indicated numbers were not properly updated to the selected values of the actual simulation set-up presented in the paper. The new setup and results are now included in the revised document in Figure 6 and presented in the modified Section 4.3.

l342: "used the same emissions, including diurnal cycle, as in the WRF-Chem simulation." I find it conceptually difficult to understand why the SCM works better than WRF-Chem with such similar inputs. From the previous section I understood that the local (traffic) emissions at the surface stations are underestimated. But the SCM apparently uses the same emissions as WRF-Chem. Why are *concentrations of NO_x/CO so much higher in the SCM than in WRF-Chem? Which aspect of the SCM is responsible for this difference?*

See previous reply regarding the differences between the SCM and WRF-Chem simulated diurnal cycles in inversion/boundary layer depth

l367: "VCD analysis for January 2014 is representative for the NOx emissions for the larger study domain". I find this not well justified. The A1 plot only shows January. In particular the seasonal variability would be of interest while the study is limited to one year and January only.

See reply to general comment #1

l389: "still overestimates NO_x emissions". Please explain why? The domain studied is a very active lightning region. What fraction of the global lightning total is expected to come from this area? E.g. the comparison with Miyazaki is quite close.

The domain in Miyazaki et al. (2014) covers a larger domain of South-America including the complete Amazon region where lightning is very active. Also based on other comments, we have restructured and rewritten results, discussion and conclusions on lightning NO_x emissions.

l400: "urband"

Changed to urban.

l415: "which explains part of the overestimation by WRF-Chem". It should be mentioned that there is a strong variability from year to year, most likely related to other reasons than changes in emissions which are expected to result in more gradual changes. See next line.

We have chosen to remove this section entirely also based on Reviewer #1 comment to reduce the content in the Discussion. We see that this section made the manuscript more 'broad' then intended especially since it does not support the main goal of the manuscript.

l423: "we found that WRF-Chem does not systematically underestimate urban VCDs". What is this statement based on? Do the authors refer to studies over other regions with the same setup?

We have chosen to remove this section entirely also based on Reviewer #1 comment to reduce the content in the Discussion. We see that this section made the manuscript more 'broad' then intended especially since it does not support the main goal of the manuscript.
The statement was based on the OMI-WRF comparison specifically for urban regions (similar to the OMI-WRF comparison for lightning and biomass burning regions, but not explicitly mentioned in the manuscript)

l434-436:"overestimations of VCDs ... in contrast with ... there is an overestimation " ? Please reformulate.

We have changed the second 'overestimation' to underestimation. We have also added modeled to make it easier to read.

l445; l457 : "indicating that all surface monitoring stations are located at or near busy roads", "EDGAR emissions integrated in a relatively simple Single Column Model, can represent the averaged diurnal cycles of O_3, CO and NO_x reasonably well.". This is confusing and should be explained more clearly. The SCM concentrations also match quite well in absolute amount the surface observations, which seems to suggest that EDGAR is OK and that the surface network is representative for larger areas?!

We think that all the surface stations (especially the averaged diurnal cycle) should give a representative signal for the (Bogota) urban mixing ratios. We have removed the (incorrect) statement that all measurement stations are located near busy roads but still indicated that single measurements do not rarely exceed 150 ppb NO_x (to indicate the spatial variability).

There is a repetition of concluding remarks when comparing the discussion and conclusion sections. This repetition should be removed. Maybe the two sections can be merged (and thereby shortened a bit)?

Also based on the remarks by the other reviewer we have strongly reduced the length of the discussion section and also tried to minimize the repetition of concluding remarks.

The close agreement of the mean/median is a bit over-emphasised to my taste. In the different source sectors there are major differences with compensating effects on the mean or total.

In both the abstract and conclusion we have changed the text such that we indicate the mean bias, but shortly after indicate that there are over- and underestimations in regions with lightning and biomass burning respectively.

l489: "showed that the selected simulation period is representative for the baseline state of air quality in Colombia". Is this a statement for January only?

See reply to general comment #1. We have updated this statement also to include the seasonal variability.

l497: "evaluate the impact of a modified representation of emissions based on the observed to WRF-Chem simulated CO mixing ratio". The description of the SCM, section 5, says: "and used the same emissions, including diurnal cycle, as in the WRFChem simulation". This is confusing. Please explain more clearly the setup of the SCM and explain why e.g. the CO/NO_x concentrations have increased substantially compared to WRF-Chem.

Initially, the hypothesis was that a modified representation of the emissions (based on the observed to WRF-Chem simulated CO mixing ratio) would lead to a better agreement between model and observations. However, it appeared that the choice of the modelling system alone (with different advection and mixing conditions) already resulted in a much better agreement as indicated in l497: "This was actually achieved using the EDGAR emissions as also applied in WRF-Chem and mainly due to especially a different representation of advection and (nocturnal) mixing conditions.". For clarity, we have removed "to evaluate the impact of a modified representation of emissions based on the observed to WRF-Chem simulated CO mixing ratio"

l507: "It may provide as a base for more local studies or the application towards future predictions". Please re-write.

Done.

Evaluation of nitrogen oxides sources and sinks and ozone production in Colombia and surrounding areas

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Abstract. In Colombia, industrialization and a shift towards intensified agriculture have led to increased emissions of air pollutants. However, the baseline state of air quality in Colombia is relatively unknown. In this study we aim to assess the baseline state of air quality in Colombia with a focus on the spatial and temporal variability in emissions and atmospheric burden of nitrogen oxides (NO_x = NO + NO_2) and evaluate surface NO_x, ozone (O_3) and carbon monoxide (CO) mixing ratios. We quantify the magnitude and spatial distribution of the four major NO_x sources (lightning, anthropogenic activities, soil biogenic emissions and biomass burning), by integrating global NO_x emission inventories into the mesoscale meteorology and atmospheric chemistry model WRF-Chem. The model indicates the largest contribution by lightning emissions (1258 Gg N yr^{-1}), even after already significantly reducing the emissions, and the lowest contribution by biomass burning emissions (104 Gg N yr^{-1}) to total NO_x emissions within the WRF-Chem domain. The comparison with in situ measurements is bound to urban areas whereas the use of remote sensing data allows to also evaluate air quality in remote regions. WRF-Chem was set up for a domain centered over Colombia ~~with a similar resolution as~~ at a similar (∼25km) resolution as the OMI observed NO_2 vertical columns as well as the EDGAR anthropogenic emission inventory~~, both providing information on a ∼20 km resolution~~. However, this apparently poses a challenge regarding comparison with ~~these urban observations~~urban air quality measurements. Air mass factors were recalculated based on the vertical distribution of NO_2 within WRF-Chem, with respect to the coarse (1°x1°) a priori profiles because WRF-Chem is expected to better resolve spatial contrasts in NO_2 profiles. The main reason for recalculation is a more consistent satellite-model comparison~~but it also reduced the mean bias . WRF-Chem was, on average, able to provide good estimates for~~. The mean bias of tropospheric NO_2 columns ~~with an averaged difference of~~ over the whole domain (WRF-Chem minus OMI) is 0.02 (90% CI: [-0.43, 0.70])·10^{15} molecules cm^{-2}, which is <5% of the mean column. However, the simulated NO_2 columns are overestimated ~~in regions with abundant modeled lightning emissions~~ and underestimated in regions where ~~biomass burning emissions dominate in the model. This result reflects the high contribution by lightning emissions (1258 Gg N yr^{-1}), even after already significantly reducing the emissions, and the low contribution by~~ lightning and biomass burning emissions ~~(104 Gg N yr^{-1}) to total NO_x emissions within the WRF-Chem domain~~dominate, respectively. WRF-Chem was unable to capture NO_x and CO urban pollutant mixing ratios, both in timing and magnitude. Yet, WRF-Chem was able to simulate the urban diurnal cycle of O_3 satisfactory but with a systematic overestimation of 10 ppb due

to the equally large underestimation of NO mixing ratios and, consequently, titration. This indicates that these city environments are in the NO_x-saturated regime with frequent O_3 titration. We ~~also applied~~ conducted sensitivity experiments with an online meteorology-chemistry single column model (SCM) to evaluate how ~~enhanced emissions and different representation of advection and mixing conditions~~ WRF-Chem subgrid scale enhanced emissions could explain an improved representation of the observed O_3, CO and NO_x diurnal cycles. ~~The SCM appears to indeed better represent~~ Interestingly, the SCM simulation, showing especially a shallower nocturnal inversion layer, results in a better representation of the observed diurnal cycle of urban pollutant mixing ratios ~~. But, interestingly, this result did not require~~ without an enhancement in ~~the emissions, indicating thatthe role of~~ emissions. This stresses that, besides application of higher-resolution emission inventories and model experiments, the diurnal cycle in boundary layer dynamics ~~and advection should be considered besides the use of high-resolution models and emissions inventories to realistically simulate~~ (and advection) should be critically evaluated in models such as WRF-Chem to assess urban air quality. Overall, the presented approach shows a concise method, integrating in situ and remote sensing observations, to quantify air quality in regions with a limited measurement network. This study not only identifies four distinctly different source regions, but also shows the interannual and seasonal variability of these sources during the last one and a half decade. Furthermore, this study shows that with a critical consideration of advection and (nocturnal) boundary layer mixing, relatively coarse anthropogenic emission inventories can give reasonable results regarding the diurnal cycle of urban pollutant mixing ratios. It serves as a base to assess scenarios of future air quality in Colombia, or similar regions with distinct contrasting emission regimes, complex terrain and a limited air quality monitoring network, as a function of further industrialization and land use changes.

1 Introduction

Nitrogen oxides ($NO_x = NO + NO_2$) are one of the main precursors of lower atmospheric ozone (O_3). Exposure to NO_x has an adverse effect on human health on acute and long-term basis (Panella et al., 2000; Wolfe and Patz, 2002). Likewise, O_3 is toxic to humans (WHO, 2003) and can also reduce agricultural yields (Ashmore and Marshall, 1998). Therefore, accurate monitoring and predictions of surface concentrations of these air pollutants are key. Especially in densely populated regions air pollution has been a major concern and is expected to even have larger impacts in the future due to the continuous urbanization and increasing emissions from for example traffic.

Anthropogenic NO_x is produced in combustion processes and is an indicator of industrial activity and transportation as well as other anthropogenic activities like biomass burning and agricultural activities. Anthropogenic sources add up to ∼70% (∼50% industrial activity/transportation, ∼20% biomass burning) of the total global annual NO_x emissions (Lamarque et al., 2010). In addition to anthropogenic sources, natural sources contribute to total nitrogen budgets. NO emissions from soils add up to ∼12-20% of the global NO_x emissions on a yearly basis (Bradshaw et al., 2000; Ganzeveld et al., 2002a; Jaeglé et al., 2005; Vinken et al., 2014). Lightning emissions are estimated to attribute on average 10-18% to the global yearly NO_x emissions (Pickering et al., 2016). In the tropics (35°N - 35°S), anthropogenic activities (7.81 Tg N yr^{-1}), biomass burning (8.28 Tg N yr^{-1}), soil emissions (5.44 Tg N yr^{-1}) and lightning discharges (6.33 Tg N yr^{-1}) all contribute an approximately equal fraction to the total NO_x emission budget (Bond et al., 2002). A modeling study in the tropics must therefore provide accurate estimates of all these source categories.

In Colombia, where economy is thriving after a period of civil war (Vargas et al., 2015), further industrialization and intensified agriculture have already resulted in- and are expected to further increase- NO_x emissions (Ganzeveld et al., 2010). Previously, Grajales and Baquero-Bernal (2014) aimed to assess the air quality of Colombia with a relatively coarse (2.5°x2.0°) 3D global model (GEOS-Chem), whereas other studies focused mostly on air pollution of other compounds in cities using local emission inventories (Zárate et al., 2007; Kumar et al., 2016; González et al., 2018). Currently, there is a lack of understanding of the baseline state of air quality in Colombia on regional scale. Following from this, an application of inventories of the different sources of NO_x (and other pollutants) and covering both Colombia and its surrounding, upwind, areas can give valuable information about the current state of air quality in Colombia. This is also essential to determine how air quality might change in the future, e.g., due to further urbanization and land use changes such as the conversion to oil palm (Vargas et al., 2015).

Up until now, Colombia does not have an air quality monitoring network covering the entire country. Current measurement sites are mainly located in or close to the major cities. The rural areas, which are now undergoing rapid land use changes, do not have air quality stations nearby. This makes air quality monitoring for the whole country a challenging task. The use of satellite data, to observe species like NO_2 and formaldehyde (CH_2O), is a valuable tool to fill the gaps and evaluate air quality in remote regions (Bailey et al., 2006; Kim et al., 2009; Webley et al., 2012). However, satellite retrievals in the tropics are often limited by the presence of clouds.

During the last decades, computational advances have increased the possibility to conduct more detailed meteorology and air quality studies (Bauer et al., 2015). The recognition of the effects of chemical composition of the atmosphere on meteorology have stimulated the development of online coupled meteorology/chemistry models (Baklanov et al., 2014). Nowadays, these models can be run for a large range of temporal and spatial scales. Not only the models, but also global emission inventories have considerably improved in spatial resolution during the last decades (González et al., 2018). Even though they may not provide enough spatial detail and heterogeneity for local scale (< 1 km) studies, e.g. to compare with in situ observations, they have provided essential information regarding emissions for regional scale (∼20 km) studies (Saide et al., 2012; Ghude et al., 2013). In this study, rather than using high resolution urban emission inventories (e.g. González et al., 2018), we will demonstrate the importance of boundary layer mixing and advection in the comparison of simulated and observed in situ measurements.

The primary objective of this study is to assess the current baseline state of air quality in Colombia, diagnosed with a focus on NO_x, using global emission inventories in a regional atmospheric chemistry model resolving the atmospheric chemistry and meteorology at a resolution comparable to that of the emission inventories as well as the remote sensing observations. Furthermore, we evaluate surface NO_x, O_3 and CO mixing ratios in urban regions. We are aware that concerns about air quality in Colombia ~~concerns~~ are generally not limited to smog photochemistry mainly involving O_3-NO_x-VOC chemistry. Actually high concentrations of particulate matter might pose the largest risk to public health in many Colombian urban areas (Kumar et al., 2016). However, in this study we focus on NO_x as an insightful metric to assess the spatial and temporal patterns in air quality in this region given its role in O_3 photochemistry as well as the availability of remote sensing observations to be integrated with a bottom-up model analysis. In this study we use the Weather Research and Forecasting model coupled with Chemistry (WRF-Chem) (Grell et al., 2005). The model outcomes will be compared to in situ measurements and satellite retrievals to address the performance of the model both at the surface and integrated over the troposphere. This evaluation of surface and total column —using a highly resolving coupled meteorology-air quality model including the identification of different NO_x sources— seeks to fill the gaps between local scale (González et al., 2018; Zárate et al., 2007; Kumar et al., 2016) and larger scale studies (Grajales and Baquero-Bernal, 2014). This study also includes an evaluation of the interannual and seasonal variability of air pollution for the different source regions during the last one and a half decade. This analysis is not only useful to address the representativeness of the performed simulation and to identify the baseline state of air quality in Colombia but also justifying potential use of the modeling system such as WRF-Chem to assess future changes in air quality using future anthropogenic emission and land use change scenarios (e.g. Ganzeveld et al., 2010).

2 WRF-Chem & its emission inventories

2.1 Model: WRF-Chem

In this study we use ~~the~~ WRF-Chem (Grell et al., 2005) version 3.7.1. WRF is a non-hydrostatic mesoscale numerical weather prediction model used for operational and research purposes. Figure 1 shows the WRF-Chem domain including cities and regions that we refer to in this research.

The simulation was set up for one domain with a spatial resolution of 27 km centered at 4.89 °N, 71.07 °W. The entire domain consists of 100 grid points in both the North-South and the East-West direction with 60 vertical levels —in a sigma coordinate system— up to 50 hPa. The simulation length is one month (also given technical constrains on conducting much longer integrations with WRF-Chem), with a spin-up time of 24h, covering the whole month of January 2014. Selection of this study period is motivated by the fact that January is the dry season in Colombia where loss of remote sensing data due to presence of clouds is minimized (see Sect. 3.1.1). In addition, in Appendix A we show how the selected study period can be ~~deemed being representative for~~ put into context of the baseline state of air quality in Colombia using the interannual and seasonal variability in emission sources inferred from the remote sensing observations. A more detailed analysis on this is presented in Sect. 5.

The European Centre for Medium-range Weather Forecasting (ECMWF) ERA-Interim product provides us with the meteorological initial and boundary conditions. The chemical initial and boundary conditions are constrained with the Copernicus Atmosphere Monitoring Service (CAMS) near-real-time dataset. The boundary conditions are updated every six hours on a spatial resolution of 0.4° (∼44 km) with 60 vertical model levels. For January 2014, boundary conditions of O_3, NO_x, CO, SO_2 and CH_2O are available. For tropospheric chemistry, the Carbon-Bond Mechanism version Z (CBM-Z) chemical scheme (Gery et al., 1989; Zaveri and Peters, 1999) is used here because it has been successfully implemented and tested in similar studies (Gupta and Mohan, 2015). Additional parametrization schemes used in this research are listed in Table 1.

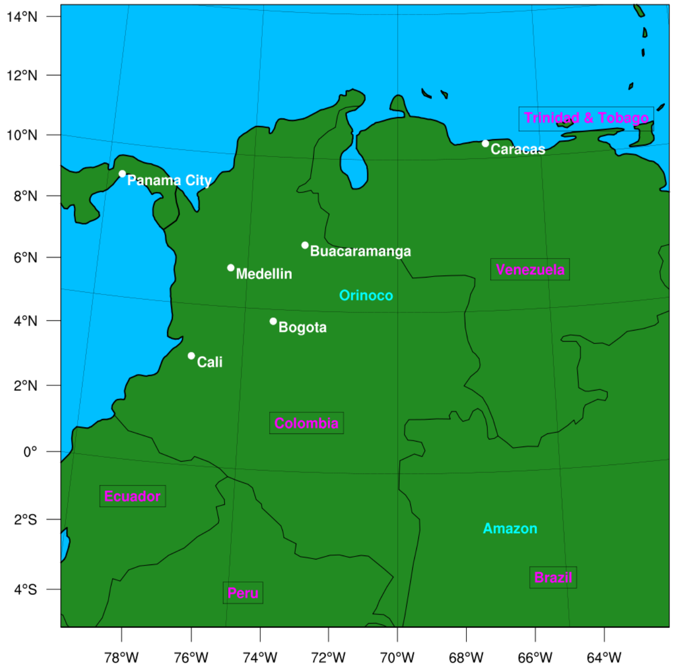

Figure 1. WRF-Chem domain including countries (pink), major cities (white) and regions (blue).

Table 1. WRF-Chem physical and chemical parametrization schemes.

WRF-Chem option	Configuration
Physical parameterizations	
Microphysics	Morrison 2-moment (Morrison et al., 2009)
Long wave radiation	RRTM (Mlawer et al., 1997)
Short wave radiation	Dudhia (Dudhia, 1989)
Surface layer	Monin-Obukhov (Janić, 2001)
Land surface	Noah (Chen and Dudhia, 2001)
Boundary layer	YSU (Hong et al., 2006)
Cumulus	Grell 3D (Grell and Freitas, 2013)
Lightning option	P&R neutral buoyancy (Price and Rind, 1992)
Chemical options	
Gas-phase	CBM-Z (Gery et al., 1989; Zaveri and Peters, 1999)
Photolysis	F-TUV (Tie et al., 2003)
Lightning chemistry	Single-mode vertical distribution (Ott et al., 2010)

2.2 Emission inventories

Anthropogenic emissions are described by the Emission Database for Global Atmospheric Research (EDGAR) dataset for greenhouse gases (Janssens-Maenhout et al., 2017) and Non-Methane Volatile Organic Compounds (NMVOCs) (Huang et al., 2017). Emission estimates are gridded on a 0.1°x0.1° resolution. EDGAR emissions are monthly estimates implying constant emissions over the whole simulation. In this study we use the EDGAR-HTAP emission inventory updated for 2010. EDGAR-HTAP uses nationally reported emissions combined with regional scientific inventories. For this research we assumed that 95% of the total anthropogenic emission of NO_x is emitted as NO and 5% as NO_2 (Carslaw, 2005). VOC (Volatile Organic Compounds) speciation is according to Archer-Nicholls et al. (2014). In densely populated urban areas the anthropogenic emissions are dominated by vehicular emissions (Dodman, 2009). These emissions have a clear diurnal and weekly variation in contrast to emissions from the industry sector (Streets et al., 2003). Zárate et al. (2007) estimated traffic emission factors for Bogotá using in situ measurements and inverse modeling techniques. To account for this diurnal and weekly variation we multiply the EDGAR emissions with the hourly and daily emission factors presented by Zárate et al. (2007).

The Global Fire Emissions Database version 4 (GFEDv4) dataset (Randerson et al., 2015) provides us with the biomass burning emissions. GFED is available on a spatial resolution of 0.25°x0.25°, approximately the same size as the WRF-Chem grid cells. Biomass burning NO_x emissions are assumed to be completely in the form of NO.

Natural emissions of VOCs from terrestrial ecosystems are considered in this study using the Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGANv2.1) (Guenther et al., 2012). Biogenic emissions are updated on-line using the WRF-Chem simulated surface temperature, soil moisture, leaf area index and photosyntetically active radiation. MEGAN also provides estimates of soil biogenic NO emissions.

The lightning-NO_x parametrization scheme (Price and Rind, 1992), embedded in WRF-Chem, is used to account for NO_x emissions by lightning. For this study we used an IC:CG (intracloud:cloud-to-ground) ratio of 2:1 constant over the whole domain with a flashrate factor of 0.1. Per lightning flash (both for IC and CG strikes), it is assumed that 250 moles of NO are emitted (Miyazaki et al., 2014). It has to be noted that in an initial simulation, using standard WRF-Chem settings (flashrate factor = 1.0 & 500 moles of NO per strike), resulted in a significant overestimation of the lightning emissions (see Sect. 4.1) (Bradshaw et al., 2000; Miyazaki et al., 2014; Murray, 2016)~~and the~~. The settings we used resulted in a twentyfold decrease of lighting emissions compared to standard WRF-Chem settings.

3 Observations of atmospheric composition

3.1 Satellite retrievals

Observational data on the ~~large scale~~ distribution of NO_2 is retrieved from the Ozone Monitoring Instrument (OMI) onboard the National Aeronautics and Space Administration (NASA) Aura satellite (Levelt et al., 2006). OMI measures, among other pollutants, NO_2 column densities (Boersma et al., 2007) with daily, global coverage. The pixel size of 24x13 km^2 may be coarse for particular applications, such as assessing urban pollution, but is suitable to assess contrasts in regional-scale air quality with apparent contrasting emission regimes. In addition, the resolution of the OMI observations is also comparable to the resolution of the anthropogenic emission inventory.

In this research we use the Quality Assurance for Essential Climate Variables (QA4ECV) NO_2 data product (Boersma et al., 2018). The measured slant columns —the tilted path directly from sun through the atmosphere to surface back to satellite— are converted to vertical columns using Air Mass Factors (AMFs) [-] by

$$VCD = \frac{SCD}{AMF}, \tag{1}$$

where VCD and SCD are the Vertical Column Density and the Slant Column Density [molecules cm^{-2}], respectively. The AMFs define the relation between slant column and the vertical column above a pixel based on external information on e.g. surface albedo, scattering, clouds and the vertical distribution of NO_2 (Boersma et al., 2011). The vertical distributions of NO_2 in the QA4ECV product, which are used to calculate the AMFs, are simulated by the TM5-MP global chemistry transport model at a resolution of 1°x1° (Williams et al., 2017).

3.1.1 Filtering

We follow the data filtering recommendations by the QA4ECV consortium. Presence of clouds (cloud radiance fraction > 0.5) led to omission of 63% of OMI NO_2 data. Figure 2 shows the amount of OMI data per WRF-Chem grid cell after filtering the observations of January 2014. Especially above mountainous regions, where we also find the main urban areas of Bogotá and Medellín, there is a lack of available data due to the continuous presence of clouds~~limiting~~. This limits the quality of the measurements and which increases the uncertainty in the averaged tropospheric NO_2 column (Boersma et al., 2018). On average 9 data points per grid cell are available for this specific domain in January 2014, but with a large spatial heterogeneity. Some areas have >20 data points and other only two valid observations in this month.

3.1.2 AMF recalculation

The AMF dependens on assumptions of the state of the atmosphere and surface (e.g. surface albedo, cloud fraction, vertical distribution of NO_2) at the specific moment and location of a satellite observation (Lorente et al., 2017). This vertical sensitivity is described by an averaging kernel, which describes the relationship between the true column and the estimated, or retrieved column (Boersma et al., 2016). High-resolution models such as WRF-Chem are expected to better represent spatial gradients in NO_2 profiles compared to coarse-scale global models such as GEOS-Chem or TM5-MP. Consqeuently, we can expect WRF-Chem to better resolve strong enhancements in tropospheric NO_2 VCDs in densely populated areas. Using grid sizes comparable to the size of such large urban areas is a major advantage of this procedure (Krotkov et al., 2017). The application of the averaging kernel is shown to reduce systematic representativeness errors for a satellite-model comparison (Boersma et al., 2016). We can recalculate the AMF based on the a priori concentration profile x_a (from the TM5-MP model) and the

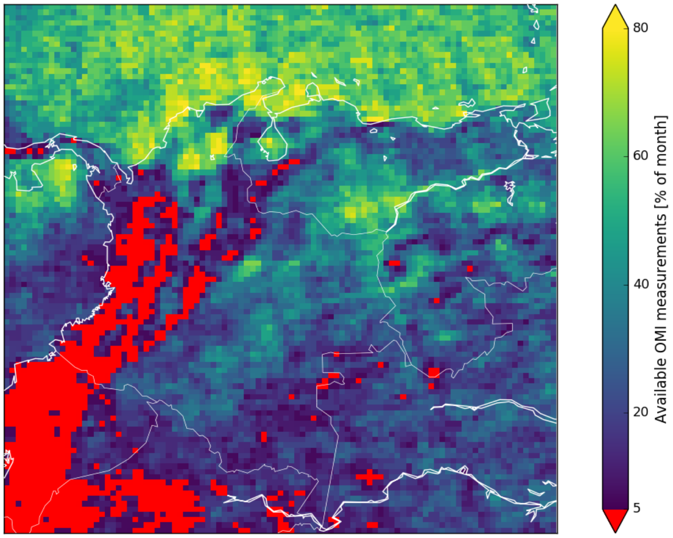

Figure 2. Spatial distribution of the available OMI measurements in January 2014 after filtering has been applied.

concentration profile in the high-resolution model x_m, in this study WRF-Chem (Boersma et al., 2016):

$$M'(x_m) = M(x_a)\frac{\sum\limits_{l=1}^{L} A_l x_{m,l}}{\sum\limits_{l=1}^{L} x_{m,l}}, \tag{2}$$

where $M(x_a)$ is the tropospheric AMF used in the retrieval, A_l are the elements of the averaging kernel for each l^{th} vertical layer and $M'(x_m)$ is the recalculated AMF. In a next step, the new VCDs can be calculated by dividing the SCDs (retrieved by the satellite) with the recalculated AMFs (Eq. (1)).

Fig. 3 shows the difference in AMFs and the subsequent effect on the tropospheric NO_2 columns for the WRF-Chem domain. On average, we find a mean decrease in AMF of 0.05 with a standard deviation of 0.15. Regarding inferred changes in the VCD due to this recalculation of AMF, we find a mean increase in the VCD of $0.02 \cdot 10^{15}$ molecules cm^{-2} ($\sim$3% of the average VCD) and a standard deviation of $0.07 \cdot 10^{15}$ molecules cm^{-2}. Above cities (e.g. Caracas, Bogotá, Medellín), we find mostly ~~decreases~~ a decrese in AMF (Fig. 3a)~~.~~, and, consequently an increase in VCD (Fig. 3b). This indicates that there is more NO_2 present near the surface in WRF-Chem compared to TM5. This is consistent with our expectation that WRF-Chem better captures the sub-1°x1° processes that are not resolved by TM5, such as the localized urban emissions. Furthermore, we find ~~pronounced decreases in AMF above the Amazon region. However, these large decreases in AMF (up to -1) lead to an increase in the VCD of~~ increases in VCD (0.5·10^{15} molecules cm^{-2}~~which is equal or even smaller than the increase in VCD due to the much smaller decrease in AMF over cities (Fig. 3b) because of the large VCDs over cities compared to over the~~) above the Amazon region. ~~Increases in AMF~~ Decreases in VCD (Fig. 3~~a~~b) are found mostly across the border from Colombia to Venezuela, better known as the Orinoco region (Fig. 1). This reflects a higher abundance of NO_2 higher up in the troposphere from lightning sources,

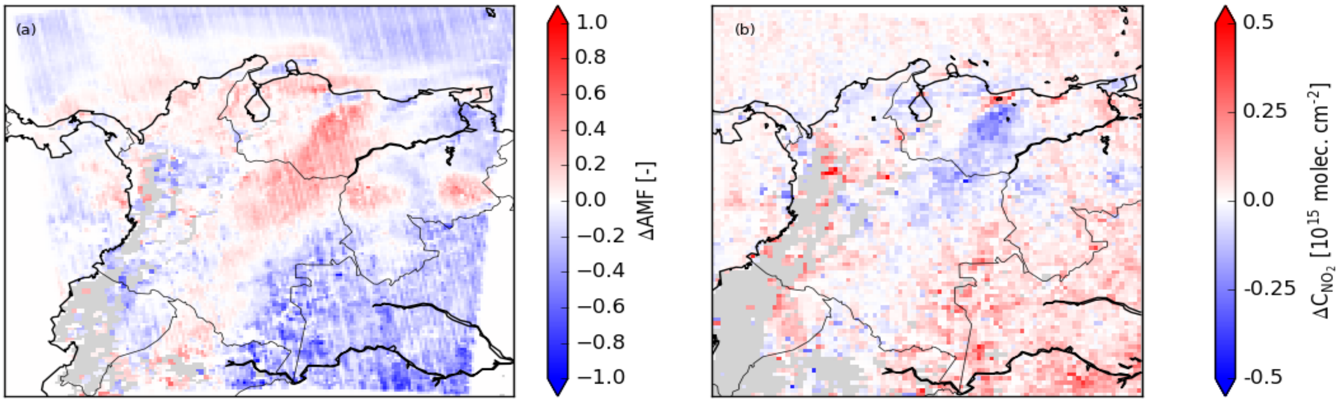

Figure 3. Spatial distribution of (a) the AMF difference (recalculated minus QA4ECV standard product, ΔAMF [-]) in January 2014 based on the WRF-Chem simulation and (b) the subsequent effect on the NO_2 column difference (recalculated minus QA4ECV standard product, ΔC_{NO_2} [10^{15} molecules cm^{-2}]) on the WRF-Chem grid.

which are potentially underestimated by the global TM5 model (Silvern et al., 2018), combined with less NO_2 near the surface. We also find two isolated hot spots of ~~increases in AMF (∼0.3)~~ decreases in VCD in southern Venezuela which correlate well with topography within the WRF-Chem domain which is less well resolved in the coarser resolution of TM5. Despite locally significant changes in VCDs, a domain average of $0.6 \cdot 10^{15}$ molecules cm^{-2} indicates that the difference in the NO_2 a priori profiles of TM5 compared to those in WRF-Chem does not lead to domain-wide significant changes in VCDs.

3.1.3 Comparison of OMI and WRF-Chem

In ~~this research, we focus on tropospheric NO_2 columns. In~~ WRF-Chem we calculate the tropospheric NO_2 column by integrating from the surface to the tropopause, determined to be approximately the 50th model level (∼90 hPa, ∼17km). This level is determined based on the average temperature profile (from surface to 50 hPa) of the complete simulation. Furthermore, to assess the daily differences in total NO_2 columns from OMI and WRF-Chem we need to co-sample their data points. For Colombia, OMI passes around 17-19 UTC (1:00 PM local time). Grid points with none or only one measurement after filtering (see Fig. 2) will be completely discarded. In this way we aim to get a reliable comparison between WRF-Chem and OMI, which enables us to determine systematic biases in the regions dominated by different emission sources.

3.2 In situ data

To further ~~validate~~ evaluate the model, ~~besides the comparison with OMI observations,~~ observational data from air quality monitoring stations in Colombia are used. These include 30 stations confined to four cities in Colombia: Bogotá, Bucaramanga, Cali and Medellín (see Fig. 1). Observational data consists of 1-hourly averaged CO, NO, NO_2 and O_3 concentrations. The complete availability and locations of the station within the WRF-Chem domain can be found in Table B1. The data and information on the measurements is publicly available at http://sisaire.ideam.gov.co/ideam-sisaire-web/ (last access: March

2020). In this paper we only show the results of Bogotá also ~~sincethe comparisons in~~ because the comparisons for the other cities show similar results. Even on the still coarse resolution of the current WRF-Chem simulations, we expect that the evaluation of the temporal variability in simulated and observed concentrations indicates how well the model captures some of the key drivers of atmospheric pollution.

4 Results

4.1 Nitrogen emission budgets and distribution

First of all, we identify the major sources of NO$_x$ within the domain of this study. The anthropogenic and biomass burning emissions are prescribed using their inventories whereas soil NO and lightning NO$_x$ emissions are explicitly simulated in WRF-Chem. Some large cities contribute dominantly to the total NO$_x$ emissions (Fig. 4a). Total emissions are in the order of ~~$\sim10^2$-10^3 Mg N month^{-1} per grid box~~ 200-1000 kg N km^{-2} month^{-1} for the Colombian cities. However, largest NO$_x$ emissions, according to the EDGAR inventory, are found in and around Caracas, Venezuela. All these emissions can be attributed to anthropogenic emissions as reflected by a $\sim$100% contribution of anthropogenic emissions to the total emissions shown in Fig. 4b. Another major source of NO$_x$ is found in the south-east of the domain with values ranging up to ~~70 Mg N month^{-1} per grid box~~100 kg N km^{-2} month^{-1}. In this region, with land cover dominated by rainforest, large convective systems are present generating thunderstorms with associated lightning NO$_x$ emissions. They appear to be the most important emissions in this region (Fig. 4b) also because anthropogenic and biomass burning emissions are mostly absent (with some exceptions near rivers). Biomass burning and soil biogenic emissions seem to be the most prominent sources of NO$_x$ across the Colombian-Venezuelan border (Fig. 4b), in the Orinoco region, in our model study. This region is dominated by savanna type grasslands which emit a relatively high amount of soil NO$_x$ but also have a high probability of catching fire. NO$_x$ emissions in these regions are up to ~~$\sim10^1$-10^2~~ one or two orders of magnitude smaller compared to anthropogenic emissions, but, on the other hand, cover a larger area.

Lightning NO$_x$ emissions ~~seem to be~~ is the most dominant emissions source over land in 63% of all grid cells~~the most dominant emission source~~, followed by anthropogenic- (22%), biomass burning- (9%) and biogenic (6%) emissions (Fig. 4b). Since we use four different emission inventories, all with their own estimates and uncertainties, the distinct contrasts in the spatial distribution of emission sources will be key to determine spatially heterogeneous biases in satellite retrievals compared to WRF-Chem. From budget calculations integrating over the whole domain, and using these January emissions to infer a NO$_x$ emission budget expressed per year (see Table 2) ~~, we~~ we also find that lightning NO$_x$ ~~emissions add up to 1258 Gg N yr^{-1}, with a distinct diurnal cycle. Anthropogenic NO$_x$ emissions add up to 933 Gg N yr^{-1}. Biogenic NO$_x$ emissions add up to 187 Gg N yr^{-1} with daytime emissions being $\sim$2 times larger compared to nighttime emissions (mostly regulated through temperature). Biomass burning NO$_x$ emissions —according to the emission inventory— provide the smallest contribution to the domain with a total NO$_x$ emission strength of 104 Gg N yr^{-1}~~is the largest source in absolute terms, followed by anthropogenic, biogenic and biomass burning respectively.

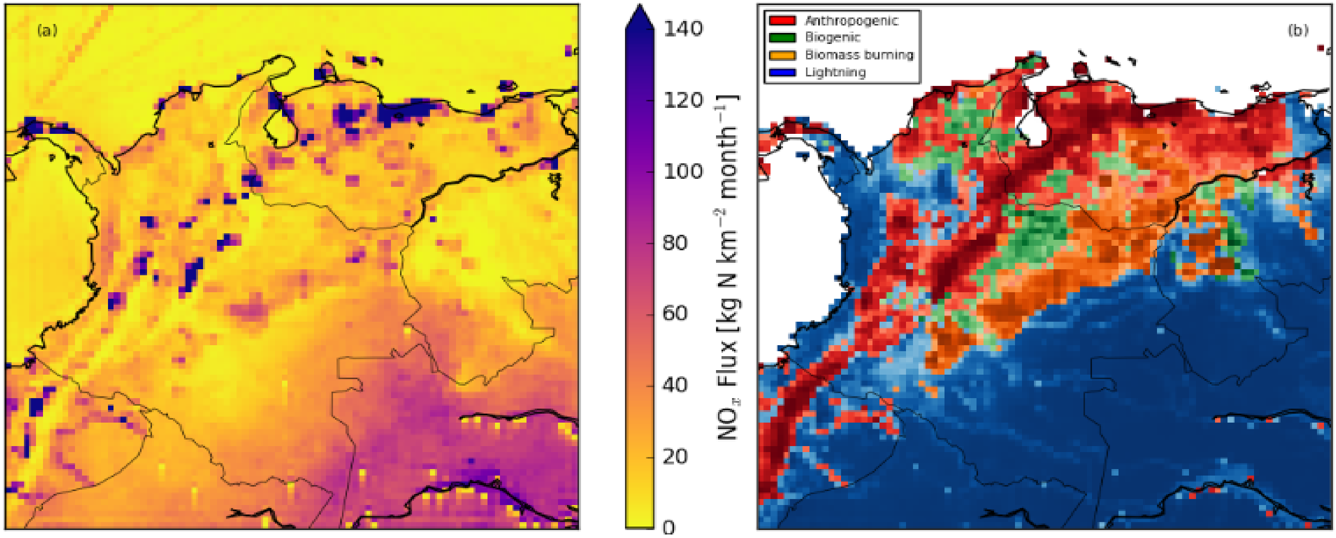

Figure 4. Spatial distribution of (a) the total NO_x flux [~~Mg~~ kg N km^{-2} month^{-1}] ~~per grid cell~~ in January 2014 and (b) the ~~largest contributor %of the four~~ dominant emission ~~inventories~~ source per grid cell over land. ~~More saturated colours indicate a larger maximum fractional contribution~~ In (b), the saturation of the color indicates the % of the total NO_x flux coming from the dominant emission source going up to 100% for the darkest colors.

Table 2. Total NO_x emissions in the WRF-Chem domain per source category using January 2014 emissions to infer yearly total NO_x emissions [Gg N yr^{-1}]. The percentage surface area over land where the emission source is dominant is also indicated.

NO_x source category	Emission [Gg N yr^{-1}]	Surface area [% of total land surface area]
Lightning	1258	63%
Anthropogenic	933	22%
Biogenic	187	6%
Biomass burning	104	4%
Total	2482	

4.2 WRF-Chem & OMI comparison

To assess whether WRF-Chem is able to reproduce filtered and recalculated NO_2 VCDs satisfactorily we check for the spatial and frequency distributions for both WRF-Chem and OMI (see Fig. 5). For WRF-Chem we find a wide range of column densities (Fig. 5a). We find very low VCDs ($\sim 0.3 \cdot 10^{15}$ molecules cm^{-2}) over the Caribbean sea and across the eastern border of Colombia into Venezuela. High VCDs in WRF-Chem are simulated above the major Colombian cities and the northeastern part of the domain ($\sim 5 \cdot 10^{15}$ molecules cm^{-2}) while the highest VCDs are simulated above the city of Caracas with values up to $8 \cdot 10^{15}$ molecules cm^{-2}. Similar to WRF-Chem, we find the lowest VCDs over the Caribbean sea in OMI (Fig. 5b). Also, we find the highest VCDs above major cities —most pronounced for Caracas and Medellín— but the magnitude of the OMI observed VCD ($\sim 2.5 \cdot 10^{15}$ molecules cm^{-2}) is much smaller compared to WRF-Chem. In OMI we find low VCDs above the Amazon rainforest.

The large WRF-Chem VCDs ($\sim 5 \cdot 10^{15}$ molecules cm^{-2}) we find in the northeastern part of the domain (Fig. 5c) seem to reflect mostly the role of the imposed ~~boundary conditions which is~~ CAMS boundary conditions. High mixing ratios of NO_2 are found in the lowest CAMS model layers advected into the WRF-Chem domain by the prevailing easterlies. High VCDs are not seen in the OMI retrievals where we only find a small plume coming from Trinidad & Tobago transported westward~~due to the prevailing easterly wind. The overestimation~~. The model overestimation of the VCD above Caracas might be due to an overestimation of anthropogenic emissions but this is not supported by a systematic major overestimation above cities (for example, we find no overestimation above Panama City or Bucaramanga). However, the EDGAR emission inventories are based on the year of 2010, when Venezuelan economy was still at its maximum (Wang and Li, 2016). After 2010, Venezuelan economy and oil production have declined strongly (Wang and Li, 2016) and therefore also emissions of pollutants have ~~been decreasing. In Sect. 5 we provide a more detailed overview of these findings regarding temporal changes in Venezuelan emissions.~~ likely also decreased substantially. Lastly, we find a systematic overestimation in the WRF-Chem simulated VCD above the Amazon rainforest. Even though the model overestimation is small in absolute terms ($\sim 0.5 \cdot 10^{15}$ molecules cm^{-2}) it is quite substantial relative to the background mixing ratios. In this region, soil NO_x release is small, anthropogenic activities are hardly present and there are no known sources of biomass burning during January 2014. Also the role of advection from outside the model domain by the prevailing easterly winds seems to be limited indicated by lower VCDs at the eastern most grid cells. Consequently, overestimation in the simulated VCDs ~~can be attributed~~ is most likely due to the simulated major influence of lightning NO_x emissions in this region (Fig. 4b)~~. This further confirms the finding that lightning NO_x emissions are overestimated in WRF-Chem~~, even though they have already been significantly reduced relative to the standard settings (see Sect. 2.2). However, we have to take into account that the OMI retrievals used for this comparison are near the detection limit and reflect those conditions when cloud formation, and therefore lightning production, is less active resulting in very low VCDs. In contrast, the co-sampled WRF-Chem columns might reflect simulated cloud cover resulting in production of NO by lightning. Nonetheless, the question whether lightning production was actually present or that it could not be picked up by OMI, being less sensitive to the presence of NO_2 below clouds, remains unanswered.

Remarkably, we find a region with systematic underestimations ranging from the center of Colombia to the northeastern border with Venezuela (the Orinoco region). In this region, there is no presence of major cities and lightning NO_x emissions are small. The discrepancy we find might be due to missing agricultural- or biomass burning emissions. Localized enhancements observed in OMI ($\sim$2.5$\cdot 10^{15}$ molecules cm^{-2}) might also be caused by biomass burning emissions since enhanced soil NO_x are expected to result in a more homogeneous enhancement of VCDs over a larger area with smaller intensities. We find that this intensity of biomass burning is not picked up by the WRF-Chem simulation using the GFED biomass burning inventory.

Figure 5d ~~and Fig. 5e show~~shows, for both WRF-Chem and OMI, the ~~scatter and~~ frequency distribution in the NO_2 VCD. We find that both model simulated and observed VCDs show similar distributions, peaking at approximately the same VCD. However, WRF-Chem shows more outliers especially regarding the simulation of high NO_2 VCDs. The 90% confidence interval of the WRF-Chem simulated VCDs is (0.33,1.33)$\cdot 10^{15}$ molecules cm^{-2} while for OMI the 90% confidence interval is (0.32,1.06)$\cdot 10^{15}$ molecules cm^{-2}, with medians of 0.59$\cdot 10^{15}$ and 0.56$\cdot 10^{15}$ molecules cm^{-2}, respectively.

We find the median and mean of the absolute overestimation by WRF-Chem to be 0.02$\cdot 10^{15}$ and 0.09$\cdot 10^{15}$ molecules cm^{-2} respectively (Fig. 5~~f~~e). The 90% confidence interval equals (-0.43,0.70)$\cdot 10^{15}$ molecules cm^{-2}. The distribution is approximately Gaussian with a standard deviation of 0.53$\cdot 10^{15}$ molecules cm^{-2} but somewhat left-skewed indicating an overestimation by WRF-Chem. This confirms the finding that WRF-Chem is able to produce on average good estimations for vertical NO_2 columns above Colombia. However, over- and underestimations can be significant, e.g. larger than the $\sim$10% uncertainty in monthly averaged OMI VCD over polluted regions (Boersma et al., 2018), due to numerous factors in both the model setup and the characteristics of the retrievals. ~~The use of the recalculated AMFs and VCDs, for a consistent model-satellite comparison (Sect. 3.1.2), also reduced the overall bias of the WRF-Chem simulated VCDs. We conducted the same analysis for the original OMI data. In this analysis we find that the 90% confidence interval for OMI VCDs changes to (0.30,1.06)$\cdot 10^{15}$ molecules cm^{-2} and the median and mean of the absolute error increase to 0.05$\cdot 10^{15}$ and 0.11$\cdot 10^{15}$ molecules cm^{-2} respectively. Overall we get slightly larger columns (reflected by a increased 5th percentile) using recalculated columns and a reduction in absolute error between model and observations. These results confirm the application of the recalculated OMI data.~~

4.3 Surface mixing ratios

We retrieve January averaged diurnal cycles ~~for the month of January shown in~~ in O_3, NO_x and CO surface mixing ratios (Fig. 6) by removing the significant spread in observed surface mixing ratios and by averaging the day-to-day variation in both the model and observations. We also compare the model simulated and observed temporal evolution ~~over~~ in NO_x and O_3 over the whole simulation period (see Fig. C1, Appendix C). WRF-Chem ~~is able to represent the lowest~~ represents the lower limit (generally mid-day) of observed NO_x mixing ratios~~of individual stations quite well~~, but is unable to simulate the observed maxima (generally morning rush-hour) up to 200 ppb for particular events. Regarding O_3, WRF-Chem ~~captures~~ resembles the upper limit of observed mixing ratios ($\sim$40 ppb) during daytime but is unable to reproduce the observed low (<5 ppb) nighttime mixing ratios~~in the surface measurements~~.

Regarding simulated NO_x~~we find an averaged diurnal cycle of~~, the average nocturnal mixing ratios are 20 ppb~~during nighttime~~, with some day-to-day variation (standard deviation = 10 ppb), and a minimum of 2 ppb during daytime but with less day-to-day variation (Fig. 6a). The observations reach peak mixing ratios around 7:00 local time where vehicular emissions during rush

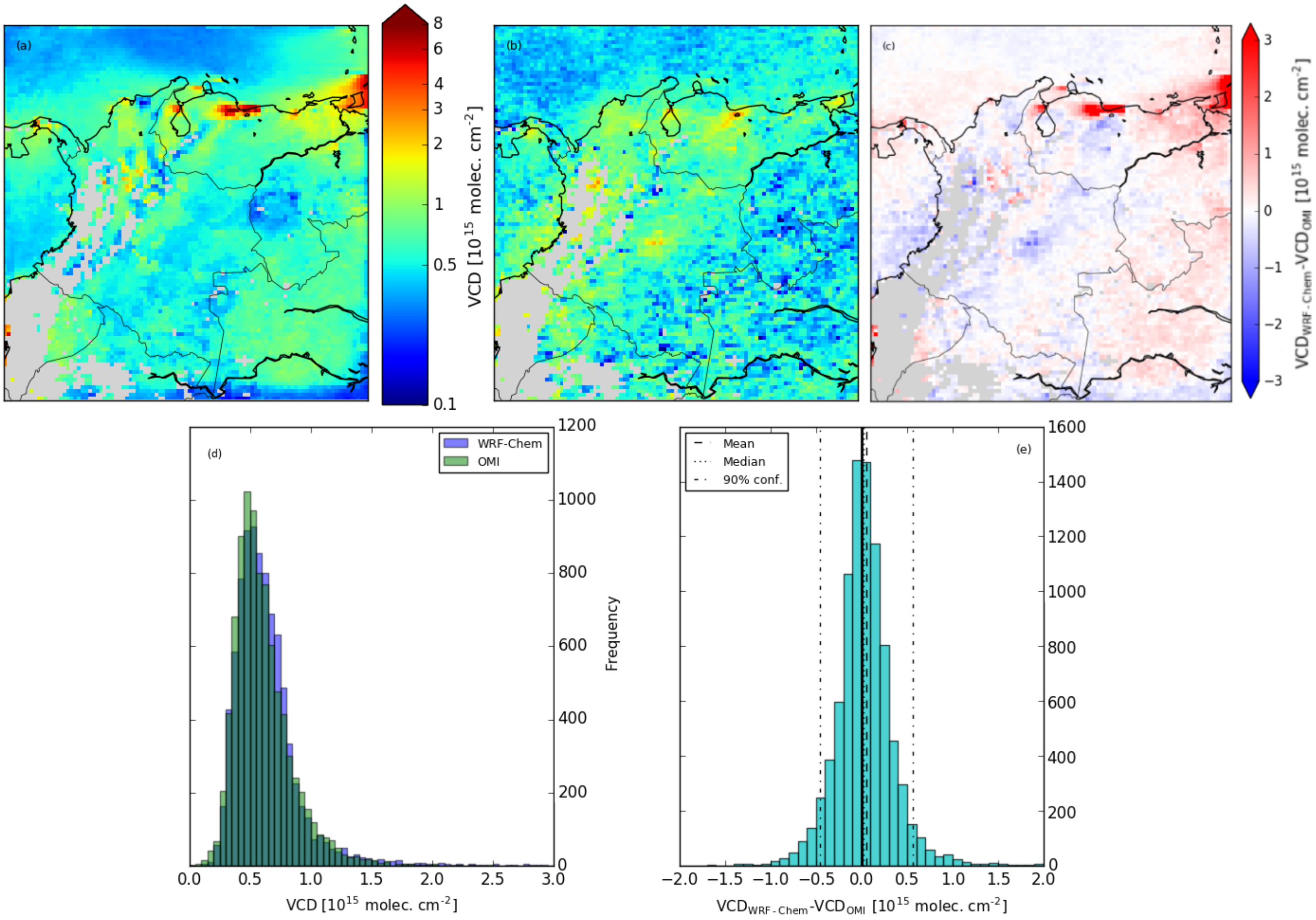

Figure 5. Spatial distribution of averaged co-sampled Vertical Column Densities (VCD) [10^{15} molecules cm^{-2}] for (a) WRF-Chem, (b) OMI recalculated retrievals and (c) the absolute difference between the two as well as (d) ~~scatter plot, (e)~~ frequency distribution of both WRF-Chem and OMI over the whole domain and (~~f~~e) the distribution of the absolute difference between the two per grid point including mean (dashed line), median (dotted line) and 90% confidence interval (dashed-dotted line).

hour are mixed in a shallow boundary layer increasing NO$_x$ mixing ratios to 85 ppb on average. After rush hour mixing ratios decrease due to decreasing emissions, increasing boundary layer height and decreasing NO$_x$ lifetime. It is interesting to note that there does not seem to be a clear signal of evening rush hour in the NO$_x$ measurements and simulation.

The averaged diurnal cycle of CO in WRF-Chem shows a similar pattern to that of NO$_x$ (Fig. 6b). WRF-Chem shows daytime mixing ratios of $\sim$150 ppb (well above rural background mixing ratios of 100 ppb) and $\sim$350 ppb during nighttime while the surface measurements show a significantly larger variation. Averaged surface measurements during rush hour exceed CO mixing ratios of 1500 ppb~~indicating that the measurement stations are located above or near busy roads~~. Some measurement stations even report mixing ratios above 3000 ppb. Even though nighttime emissions are mixed over a smaller boundary layer ~~they appear to be considerably smaller so that surface mixing ratios remain lower. We~~ we find that WRF-Chem underestimates surface mixing ratios of CO by a factor of 4 during rush-hour and by a factor of 2 for nighttime conditions. These ratios are similar to the NO$_x$ ratios in Fig. 6a. Since CO has a relatively long lifetime compared to that of NO$_x$ we argue that observed differences regarding simulated and observed CO mixing ratios reflect issues regarding the representativity of the WRF-Chem grid simulated pollutant levels, including the representation of emissions and online simulated meteorological conditions, relative to the footprint of the surface observations.

We find that for WRF-Chem most of the NO$_x$ is present as NO$_2$ with NO mixing ratios being very close to 0 ppb (Fig. 6c). In contrast, the observations show that most of the NO$_x$ is present as NO. For WRF-Chem we find a [NO]/[NO$_2$] ratio of $\sim$0.32 ($\pm$0.13) during daytime and $\sim$0.07 ($\pm$0.04) during nighttime while for the surface measurements these ratios are $\sim$1.11 ($\pm$0.40) and $\sim$0.89 ($\pm$0.38) respectively. ~~This dominance of NO in the NO$_x$ observations further indicates that the measurement stations are situated very close to the main~~ The observations that show a high [NO]/[NO$_2$] ratio might be indicative of a location close to local sources, e.g. roads. The abundant fresh NO emissions at these locations quickly react with O$_3$ forming NO$_2$. The surplus NO, however, pushes the [NO]/[NO$_2$] ratio up. Indeed, a simulated underestimation by WRF-Chem of 10 ppb NO during nighttime is consistent with a simulated overestimation of 10 ppb O$_3$ (Fig. 6d). We also find that in WRF-Chem, the formation of O$_3$ immediately starts at 6:00 local time (sunrise) while for the observations we find the lowest mixing ratios at 7:00 local time due to the extra NO titration caused by rush hour. Nonetheless, it seems that chemical production and destruction rates of O$_3$, as well as other processes contributing to the overall magnitude and diurnal cycle in O$_3$, e.g., entrainment and deposition, are well captured by WRF-Chem considering the similar shape and amplitude of the diurnal cycle.~~Averaged diurnal cycle of (a) NO$_x$, (b) CO, (c) NO and (d) O$_3$ mixing ratios ppbin Bogotá for the WRF-Chem output (black solid line) and averaged observational data (red solid line). The black and red shading indicate the 30-day standard deviation of WRF-Chem and observations respectively. The vertical lines, blue (night) and yellow (day) shading indicate daytime and nighttime.~~

5 ~~Single Column Model~~

To test the hypothesis that the model-data mismatch over Bogatá is caused by a too coarse model resolution~~and representation~~, or a misrepresentation of emissions, we ~~apply~~ conducted additional experiments with a Single Column chemistry-meteorological Model (SCM)~~. This SCM has been~~, also being previously applied for an analysis of observations of the plume of pollution downwind of the city of Manaus (Brasil) (Kuhn et al., 2010). ~~In contrast to that study, conducting so-called Lagrangian simulations with the SCM, we used here the SCM setup for a fixed location resembling the city of Bogotá. The SCM explicitly considers~~ The SCM simulates online, similar to WRF-Chem, atmospheric chemistry processes, including anthropogenic and natural emissions, gas-phase chemistry, wet and dry deposition and turbulent and convective tracer transport as a function of meteorological and hydrological drivers, surface cover, and land use properties (Ganzeveld et al., 2002b, 2008). For these urban area simulations with the SCM we have modified the surface cover properties by prescribing surface roughness at ~~2 meters~~1 meter, assuming a ~~small~~ reduced vegetation fraction of ~~0.25~~0.6, using a city area albedo of ~~0.1 and assuming reduced evapotranspiration (through a reduction of soil moisture which limits transpiration). We~~ 0.18 and nudged the SCM meteorology with wind speed, moisture, and temperature profiles from the WRF-Chem simulation. ~~In order to simulate the chemistry in the SCM we constrained these simulations also nudging the concentrations of~~ The SCM is also nudged with long-lived tracers such as O_3, NO_x and CO above the boundary layer using ~~the CAMS data and~~ WRF-Chem mixing ratios. Finally, we also used the same emissions, including diurnal cycle, as in the WRF-Chem simulation.

Using these settings in the SCM ~~leads to a generally good~~ results in simulated January average diurnal cycles in NO_x, NO and CO, quite different from WRF-Chem but, in better agreement with the observations in terms of 30-day average diurnal cycles, maximum early morning peak and daytime minimum mixing ratios of CO, NO_x and NO (Fig. ~~??~~6). The ~~SCM overestimates the rush-hour peak NO and NO_x mixing ratios but is within the spread of the observations. Especially during daytime, the simulated mixing ratios (∼5-10 ppb NO and ∼20 ppb NO_x) agree very well with the observations. Regarding CO, the magnitude of the rush-hour peak is well represented (∼1500 ppb). For both the modeled and observed NO_x mixing ratios we find maximum values at 7AM. For CO, the modeled maximum values are also at 7AM, but the observations show a maximum at 8AM. The~~ skewed O_3 diurnal cycle is also ~~much~~ better reproduced compared to WRF-Chem although the overestimation of the maximum afternoon mixing ratios ~~are equally overestimated. This SCM analysis shows that the observations in Bogotá seem to be mostly governed by the interplay between emissions, boundary layer dynamics, and chemistry, and that advection likely plays a limited role. With simulated substantially smaller wind speeds, the SCM simulates almost every night the presence of an inversion. In contrast,~~ is larger. Interestingly, the SCM simulation, showing especially a shallower nocturnal inversion layer compared to that simulated in WRF-Chem~~simulations appear to also have quite efficient mixing during the night due to simulated relatively high wind speeds preventing the build-up of a strong nocturnal inversion . In the SCM, the simulated average nocturnal boundary layer height is in~~ , results in a better representation of the observed diurnal cycle of urban pollutant mixing ratios without requiring the hypothesized enhancement in emissions. This stresses that, besides application of higher-resolution emission inventories and model experiments, the ~~order of ∼90 meters while in the WRF-Chem simulation this is ∼200 meters. This additional model analysis indicates how in such direct comparisons of model simulated and in situ urban area pollution levels, there should be a critical consideration of both the representation of spatial and temporal variability in emissions as well as~~ diurnal cycle in boundary layer dynamics ~~and advection~~(and advection) should be critically evaluated in models such as WRF-Chem which, however, would then also require urban boundary layer structure measurements.

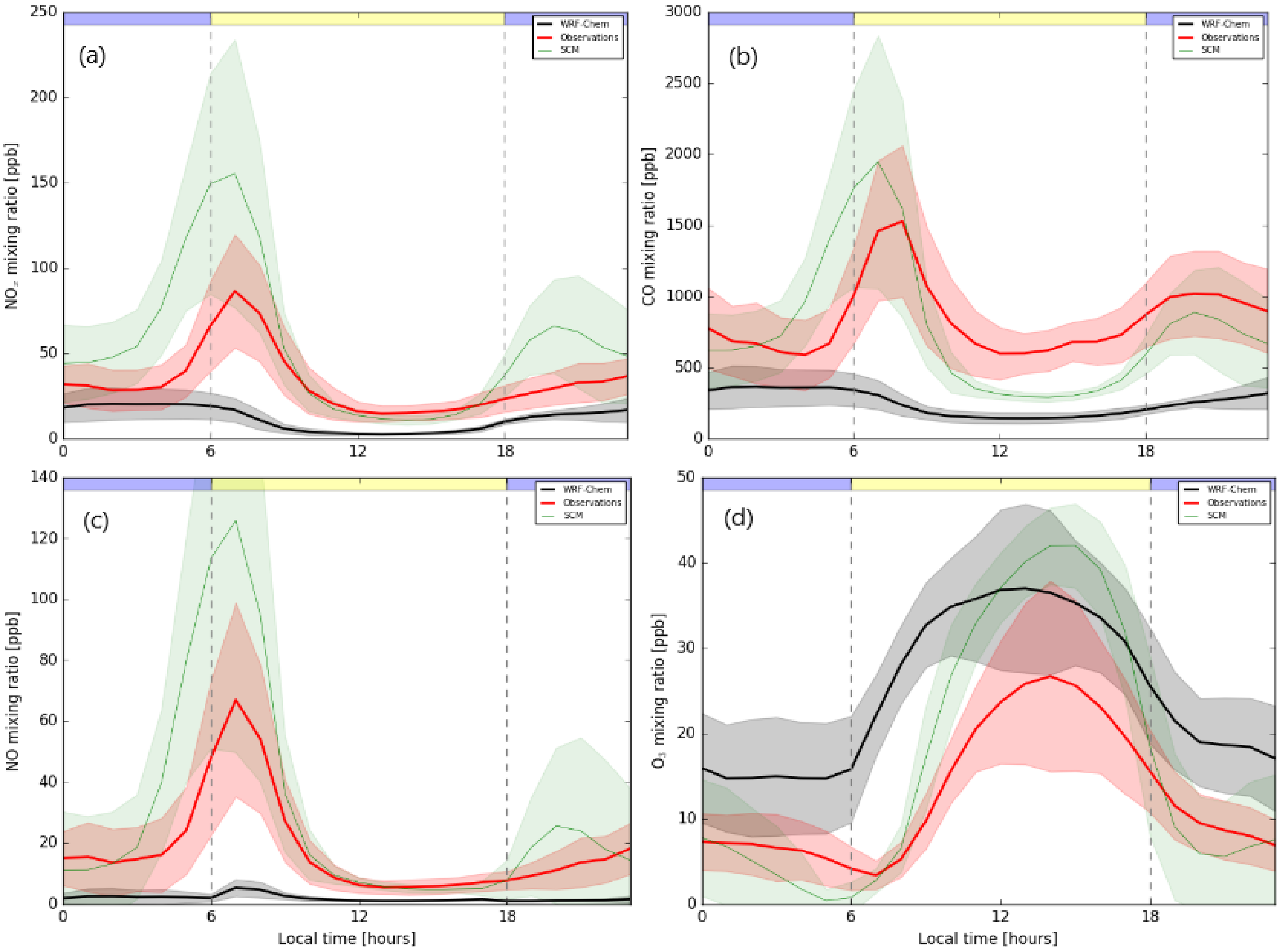

Figure 6. Averaged diurnal cycle of (a) NO_x, (b) CO, (c) NO and (d) O_3 mixing ratios [ppb] in Bogotá for ~~the~~ WRF-Chem (black solid line), averaged observational data (red solid line) and ~~the~~ SCM ~~runs~~ (green solid line). The black, red and green ~~shading~~ shadings indicate the 30-day standard deviation of WRF-Chem, observations and SCM respectively. The vertical lines, blue (night) and yellow (day) shading indicate daytime and nighttime.

5 Discussion

The integration of global emission inventories in a highly resolved coupled meteorology-air quality model (WRF-Chem), with roughly the same spatial scale, allowed us to assess the state of- and contribution by different sources to the air quality in Colombia and neighbouring countries, diagnosed with a focus on NO$_x$. We identified four major sources of NO$_x$ in Colombia which were implemented in WRF-Chem partly through emission inventories (anthropogenic and biomass burning) and partly through emission models (soil NO and lightning). Using January emissions to infer a NO$_x$ emission budget expressed per year we found that lightning NO$_x$ emissions are the main source for the domain applied in this study, with 1258 Gg N yr^{-1}. These are followed by respectively anthropogenic (933 Gg N yr^{-1}), soil biogenic (187 Gg N yr^{-1}) and biomass burning (104 Gg N yr^{-1}) emissions. Figure A1 shows the averaged VCDs over the regions dominated by one of the four emissions classes (Fig. 4b)~~to further evaluate how the presented combined WRF-Chem~~. Figure A1a shows the yearly trends in OMI NO$_2$ ~~VCD analysis for January 2014 is representative for the NO$_x$ emissions for the larger study domain~~VCDs. The domain averaged anthropogenic or lightning dominated regions seem to have relatively low interannual variability. The biogenic and biomass burning dominated regions show most interannual variability which also seem to correlate with El Niño years (https://origin.cpc.ncep.noaa.gov/products/analysis_monitoring/ensostuff/ONI_v5.php, last access: ~~30~~ October 2019), with the exception of 2015. Colombia is relatively warm and dry during El Niño years (Córdoba-Machado et al., 2015). Figure A1a indicates that biogenic- and biomass burning emissions might have increased during El Niño years reflected by higher January monthly mean VCDs above those regions. ~~Based on this further analysis of the long-term trends in~~ To further put the findings of the combined WRF-Chem and OMI VCDs for January 2014 in context, Figure A1b shows the seasonal variability in OMI NO$_2$ VCDs~~, we can argue that the 2014 simulation is a reasonably good approximation of the baseline state of air quality in Colombia. Using standard settings for the lightning NO~~. We find that biogenic, biomass burning and anthropogenic emissions show a maximum at the end of the dry season (March). For biogenic and biomass burning this is most likely caused by increased emissions while for the domain dominted by anthropogenic emissions this is most likely caused by advection of NO$_x$~~parametrization scheme (Ott et al., 2010) in WRF-Chem, emissions would be 20 times higher compared to the settings used in this study. In this research we reduced the predicted number of flashes tenfold and also reduced the number of moles NO emitted per lightning flash —which is still a major factor of uncertainty (Murray, 2016; Pickering et al., 2016)— from 500 to 250. Miyazaki et al. (2014) provides an overview of estimates of the amount of moles NOemitted per lightning flash based on satellite, laboratory, theoretical and field studies. Estimates range mostly from 10 to 650 moles NO per flash and rectify the use of 250 moles NO per flash in this study. Miyazaki et al. (2014) also estimated total lightning NO~~, emitted by biogenic or biomass burning sources, located upwind. For lightning NO~~$_x$~~$_2$ ~~emissions for a subdomain of South-America of 1.21 Tg N yr^{-1}, comparable to our results. However, these emissions are for a larger domain (38°x45°) covering a larger~~ VCDs we find a maximum in August/September. We find that this is caused by an increase in NO$_2$ VCDs in the south-eastern part of the ~~Amazon rainforest compared to this study (23°x20°). In contrast, this study uses January emissions which are ~50% larger than yearly averages for this region (Miyazaki et al., 2014), because of the dry season in Colombia generating more vigorous convection. The estimate of lightning produced NO~~domain (Amazon region), not shown here. The large standard deviation in the biomass burning $NO_{\cancel{x}2}$ ~~emissions for the small domain used in this study (1.26 Tg N yr^{-1}) already makes up a significant portion of the estimated worldwide lightning NO~~VCDs again indicates the large interannual variability. Based on this further analysis of the long-term trends in OMI $NO_{\cancel{x}2}$ ~~emissions (2-12 Tg N yr^{-1} (Murray, 2016; Bond et al., 2002; Bradshaw et al., 2000)) indicating that the lightning NO~~VCDs, we argue that the 2014 simulation and remote sensing data analysis is a reasonably good approximation of the baseline state of air quality in Colombia, at least regarding NO_x~~parametrization scheme, despite the introduced significant decrease in flashes and amount of NO produced, still overestimates NO_x emissions. Further attention is required regarding the lightning NO_x parametrization scheme in follow-up studies on atmospheric NO_x over Colombia, or other regions where lightning is a dominant source of~~. However, we have to take into account the interannual and seasonal variability in NO_x emissions in interpreting the OMI data and WRF-Chem results.

~~Another noticeable outcome of this research is that biogenic and biomass burning emissions are ∼6 to 10 times smaller compared to lightning and anthropogenic emissions while other studies suggest that they would be of comparable magnitude in the tropics (Bond et al., 2002; Holland et al., 1999). Since all the emission inventories have been performing well in similar or larger scale studies (Ghude et al., 2013; González et al., 2018; Jiang et al., 2012; Zhong et al., 2016) we can not draw strong conclusions regarding a misrepresentation of the biogenic and biomass burning emissions as they also heavily depend on the investigated domain. However, the spatial distribution and the relative importance of each emission inventory within the domain (Fig. 4b) provided us with valuable information for both the bottom-up validation using in situ data as well as the top-down validation approach using remote sensing data .~~The top-down validation approach, using satellite retrievals, is a valuable tool to evaluate air quality in remote regions (Bailey et al., 2006; Webley et al., 2012) with a missing network of air quality monitoring in both ~~urband~~ urban and rural sites. The daily global coverage and retrievals of NO_2 by OMI (Levelt et al., 2006) were used to assess the quality of all emission inventories over the whole domain. However, 63% of the data is lost for this specific model setup mainly due to the continuous presence of clouds. Thus, longer simulation times have to be considered in the tropics compared to mid-latitudes. The vertical distribution of NO_x within a modeling environment is key to identify discrepancies for a top-down validation approach using satellite retrievals. It has to be recognized that the satellite sensitivity is reduced towards the surface (Boersma et al., 2016), inducing enhanced differences between observed and modeled profiles. However, this can be overcome by replacing a priori TM5 profiles with those from the applied model (Boersma et al., 2016)~~that results in reduced the mean biases in this particular case as well~~.

~~WRF-Chem simulated VCDs showed the largest overestimation with respect to OMI above Caracas. This can be explained by a decrease of industrial activity in 2014 —with respect to 2010 EDGAR estimates— due to the decrease in economy and oil production in Venezuela (Wang and Li, 2016). This is further illustrated in Fig. **??** which shows the January monthly averaged VCDs for OMI from 2005 to 2019 over both the urban area of Bogotá and Caracas. We find an OMI observed January monthly averaged NO_2 column above Caracas of $2.1\cdot10^{15}$ molecules cm^{-2} which agrees with the findings of Fig. 5b. However, the EDGAR anthropogenic emission inventory is based on the year 2010. For 2010 we find a January monthly averaged NO_2 column above Caracas of $3.4\cdot10^{15}$ molecules cm^{-2} which explains part of the overestimation by WRF-Chem. This is supported by an estimated reduction in Venezuelan CO_2 emissions of ∼197 Tg CO_2 in 2010 to ∼183 Tg CO_2 in 2014 (, last access: 30 October 2019). The reduction in CO_2 emissions, as a proxy for NO_x emissions, is mostly caused by a~~

~~reduction in the industrial sector. From 2012 onwards, we find a clear declining trend in NO$_2$ columns caused by a decline in economic activity (Wang and Li, 2016). For Bogotá, the discrepancy between 2010 and 2014 columns is lower also indicated by a smaller bias found in Fig. 5 and indicate that the 2010 EDGAR emissions should reflect the baseline state of air pollution in Colombia reasonably well. January monthly averaged NO$_2$ vertical column densities 10^{15} molecules cm^{-2}retrieved from OMI for 2005-2019 for the cities Bogotá (brown) and Caracas (cyan) including their mean (dashed) over the whole period. The grey vertical bars highlight the 2010 and 2014 years indicating the years of the EDGAR emissions and WRF-Chem simulation, respectively.~~ In contrast to the bottom-up validation approach, where WRF-Chem showed a significant underestimation of NO$_x$ compared to the in situ measurements, we found that WRF-Chem does not systematically underestimate urban VCDs. This suggests that the problem is indeed bound to representativeness of WRF-Chem with respect to sub-grid scale emissions and other processes and not so much to the magnitude of anthropogenic emissions. The underestimation by WRF-Chem in the Orinoco region, where biogenic and biomass burning emissions make up a great part of the emission budget, indicate an underestimation of biomass burning emissions. Biogenic emissions are expected to show a more homogeneous distribution over a larger area with less pronounced peak emissions~~although the role of enhanced emissions by pulsing and fertilizer application should not be ruled out (Ganzeveld et al., 2002a).~~. Therefore, they are also not expected to explain VCDs over 2·10^{15} molecules cm^{-2} we found in OMI retrievals. This connects to the findings of Grajales and Baquero-Bernal (2014) who concluded that high VCDs in this region are most likely related to biomass burning, which is apparently underestimated by the emission inventory we applied in this study. ~~Castellanos et al. (2014) discussed that small fires could add up to 55% more burned area and that agricultural biomass burning NO $_x$ emissions may be significantly underestimated .~~Soil NO emissions might be underestimated due to the missing anthropogenic term (fertilizer and manure application) (Visser et al., 2019). However, enhanced soil NO emissions due to the use of fertilizer is estimated to only contribute ~1.3% to the total soil NO flux in the global chemistry-climate model EMAC (~2.8°) for this domain (Ganzeveld et al., 2010). Furthermore, the simulated soil biogenic NO flux (187 Gg N yr^{-1}) from MEGAN is in the range between the total soil NO flux (230 Gg N yr^{-1}) and the NO flux at the top of the canopy (105 Gg N yr^{-1}) estimated by EMAC.

~~Connected to the budget calculations we~~ We find a large area with overestimations of modeled VCDs in the region dominated by lightning NO$_x$ emissions. These findings are in contrast with Grajales and Baquero-Bernal (2014) who found in their study with the GEOS-Chem modeling system that in remote regions without biomass burning there is an ~~overestimation of OMI~~ underestimation of modeled VCDs. Our study indicates that lightning NO$_x$ emissions are ~~the~~ a major source of NO$_x$ ~~that explains~~ which might explain the discrepancy in the study by Grajales and Baquero-Bernal (2014) in which this source was not considered. Also, the use of WRF-Chem, having a spatial resolution approximately the same size as the OMI observations, can be advantageous over coarser models such as GEOS-Chem used by Grajales and Baquero-Bernal (2014). Further attention is required not only regarding the lightning NO$_x$ parametrization scheme, but also the model representation of convection and clouds, in follow-up studies on atmospheric NO$_x$ over Colombia, or other regions where lightning is a dominant source of NO$_x$. This study does not aim to provide comprehensive estimates of any of the emission sources using OMI data. Rather, we show the potential use of satellite data in a region with a limited air quality monitoring network in determining the regional scale air quality and NO$_x$ source regions. The use of cloud covered OMI observations to get a more comprehensive estimate of lightning NO$_x$ emissions (Beirle et al., 2010; Pickering et al., 2016) would make a very interesting follow up study.

The air-quality monitoring network in Colombia is limited to four major cities. This implies that the validation is limited to urban areas where anthropogenic emissions are the dominant source of pollution. A comparison with in situ data showed that WRF-Chem systematically underestimates urban surface mixing ratios of NO$_x$ and CO. ~~All the~~ The surface observations showed a clear signal of morning rush-hour emissions with average observed NO$_x$ mixing ratios up to 90 ppb and single observations not rarely exceeding 150 ppb~~indicating that all surface monitoring stations are located at or near busy roads. We do not find any evidence of evening rush-hour which is supported by Zárate et al. (2007) who estimated the temporal variability of vehicular emissions in Bogotá~~. Similar to González et al. (2018), who focused on O$_3$ dynamics in Manizales (medium sized Andean city), we find an overestimation of O$_3$ by WRF-Chem both during nighttime and daytime. For Manizales, NO$_x$ measurements were not available (González et al., 2018) and were proposed to explain most of ~~inferred the~~ the inferred discrepancies between the observed and simulated O$_3$ mixing ratios. In this study we found that the underestimation of NO by $\sim$10 ppb translates to an overestimation of $\sim$10 ppb O$_3$. Even though O$_3$ production and destruction ~~is~~ seems to be well captured by WRF-Chem, local emission inventories, including a more detailed spatial resolution around cities, can provide the extra detail needed for sub-grid scale analysis of the interactions between local-scale emissions, chemistry, mixing and resulting pollutant concentrations (González et al., 2018). ~~But~~However, as shown in Sect. ~~??~~4.3, a nested domain with local, high-resolution emission inventories ~~is not always needed to resolve~~ might not be the main solution to properly simulate urban pollutant concentrations. ~~With a different representation of advection and (nocturnal) mixing conditions, EDGAR emissions integrated in a relatively simple Single Column Model, can represent the~~ EDGAR emissions as included in WRF-Chem but then applied in the SCM simulations resulted in averaged diurnal cycles of O$_3$, CO and NO$_x$ ~~reasonably well~~that agreed reasonably well with the observed diurnal cycles. The main difference being that the SCM simulations were especially showing differences regarding the nocturnal inversion compared to WRF-Chem.

One of the regions that is currently undergoing major land-use changes is the Orinoco. Its traditional agriculture and extensive grazing shift rapidly towards a more intensified production of food, biofuels and rubber (Lavelle et al., 2014). Especially oil palm, which is one of the world's most rapidly expanding crops (Fitzherbert et al., 2008), is becoming more and more dominant in the Orinoco region (Vargas et al., 2015). Also, urbanization in Colombia is continuously increasing (Samad et al., 2012). Ongoing and anticipated future transformation of both rural and urban areas, in combination with expected increases in temperature and changes in the hydrological cycle, imply changes in emission budgets affecting air quality in the future. Further consistent coupling of land-use classes with emission representations ~~, such as~~ may provide valuable information of future predicted air quality in Colombia. This includes anthropogenic-, biomass burning-, biogenic-, and lightning emissions apparently all having a generally dominant role in atmospheric NO$_x$ cycling in different regions of Colombia~~, may provide valuable information of future predicted air quality in Colombia~~.

6 Conclusions

This study presented an analysis of the baseline state of air quality in Colombia, focusing on NO_x as main metric. Using a highly resolved coupled meteorology-air quality model (WRF-Chem), with roughly the same scale as both global emission inventories as well as satellite retrievals (OMI), allowed us to identify sources of pollution and the baseline state of air quality in Colombia. The main findings illustrate that, within the modeling domain, lightning (1258 Gg N yr^{-1}), anthropogenic (933 Gg N yr^{-1}), soil biogenic (187 Gg N yr^{-1}) and biomass burning emissions (104 Gg N yr^{-1}) all contribute to the total nitrogen emission budget. Especially the spatial distribution, clearly identifying regions with different dominating NO_x sources, shows the importance of providing good estimates of ~~every individual source of NO_x on its own~~each individual NO_x source.

The top-down validation approach, using OMI retrievals, ~~showed that WRF-Chem was able to produce on average estimates~~ indicated a mean bias of NO_2 Vertical Column Densities (VCDs) ~~close to that observed. We found the mean and median of the difference between model and observations to be~~ of $0.02 \cdot 10^{15}$ ~~and 0.09~~molecules cm^{-2}, which is <5% of the mean column, with a 90% confidence interval of (-0.43, 0.70)$\cdot 10^{15}$ molecules cm^{-2}~~, respectively. However, we found an overestimation of the lightning NO_x production within~~. The VCDs in the Amazon region are overestimated in WRF-Chem~~depicted by an overestimation of the vertical columns in the Amazon region ,~~, even after an already strongly reduced production efficiency, with respect to the low cloud free VCDs in OMI which is operating near the detection limit. This is a region where lightning NO_x emissions are the only significant source of NO_2. Additionally, the comparison indicates that GFED biomass burning emissions are ~~underestimated in WRF-Chem~~ potentially underestimated for January 2014 since OMI showed some strong enhancements in NO_2 not being reproduced by WRF-Chem. The biomass burning emission inventory shows some presence of wildfires in that region but the model only produces estimates of VCDs of $\sim 1 \cdot 10^{15}$ molecules cm^{-2}, compared to OMI VCDs up to $2 \cdot 10^{15}$ molecules cm^{-2}, in regions where it is known to have significant biomass burning sources. Air Mass Factors (AMFs) were recalculated based on the vertical distribution of NO_2 within WRF-Chem with respect to the coarse (1°x1°) a priori profiles ~~. The AMF recalculation procedure, necessary to obtain a consistent comparison between WRF-Chem and OMI NO_2 columns, also resulted in a better agreement between model and satellite . Using recalculated AMFs decreased the median of the difference between WRF-Chem and OMI from $0.05 \cdot 10^{15}$ molecules cm^{-2} to $0.02 \cdot 10^{15}$ molecules cm^{-2} even though this was not the main reason for the recalculation.~~ for a more consistent model satellite comparison. An analysis of the past one and a half decade of OMI NO_2 VCD data showed that the selected simulation period is representative for the baseline state of air quality in Colombia but ~~also that the~~ that interannual and seasonal variability has to be taken into account in interpreting the OMI data and WRF-Chem simulations. The interannual variability in NO_2 columns over the different source regions can be attributed to specific events such as ENSO whereas the seasonal variability shows a strong enhancement of NO_2 VCDs above biogenic and biomass burning regions at the end of the dry season.

The bottom-up validation approach using air quality monitoring stations in urban areas showed that WRF-Chem, at the relative coarse resolution, does not reproduce these observations given the role of large heterogeneity in the emissions and other processes determining pollution levels. Application of the anthropogenic EDGAR emission inventory (0.1°x0.1° resolution) in WRF-Chem resulted in a ~~clear~~ simulated underestimation of NO_x and CO mixing ratios with respect to the local urban surface measurements. However, WRF-Chem was able to simulate the diurnal amplitude in O_3 reasonably well for all urban locations. It seems that the underestimation of ∼10 ppb O_3 both during day- and nighttime can be attributed to the underestimation of NO by ∼10 ppb. ~~Application of~~ Additional sensitivity simulations were performed with a Single Column Model (SCM) ~~, to evaluate the impact of a modified representation of emissions based on the observed to WRF-Chem simulated CO mixing ratio, showed a much better agreement between observed and simulated surface mixing ratios. This was actually achieved using the EDGAR emissions as also applied in WRF-Chem and mainly due to especially a different representation of advection and (nocturnal) mixing conditions~~showed especially a shallower nocturnal inversion layer compared to that simulated in WRF-Chem. This resulted in a better representation of the observed diurnal cycle of urban pollutant mixing ratio without the hypothesized enhancement in emissions. This indicated that besides the use of local emissions inventories in highly resolved modeling systems, it is also essential to carefully assess the role of boundary layer dynamics, in ~~partiuclar~~ particular the representation of nocturnal mixing conditions, to evaluate simulations of pollutant concentrations.

In this study we presented a concise method, integrating both in situ and remote sensing observations with a mesoscale modeling system, to arrive at a quantification of air quality in regions with a limited measurement network to cover the large spatial heterogeneity in air pollution source distribution. Results obtained in this study provide insight in the baseline state of air quality in Colombia ~~. The findings add new information about uncertainties related to emission inventories and their application in regional air quality modeling. It may provide as a base for more local studies or the application towards future predictions of air quality in Colombia, due to~~ and which is essential to apply the presented combined modeling and measurement approach also to assess how air quality will further change due to future industrialization and land use changes~~, or comparable regions not having air quality monitoring networks with national coverage~~.

Code and data availability. OMI data, in situ data and WRF-Chem output are available upon request as well as scripts to recalculate the tropospheric AMF.

Author contributions. JGMB and LNG designed the experiment. JGMB performed the WRF-Chem simulations. LNG performed the single column model simulations. JGMB performed the analysis and wrote the manuscript, with contributions from all co-authors.

Competing interests. The authors declare no competing interests.

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Appendix A: Long term analysis of OMI VCD

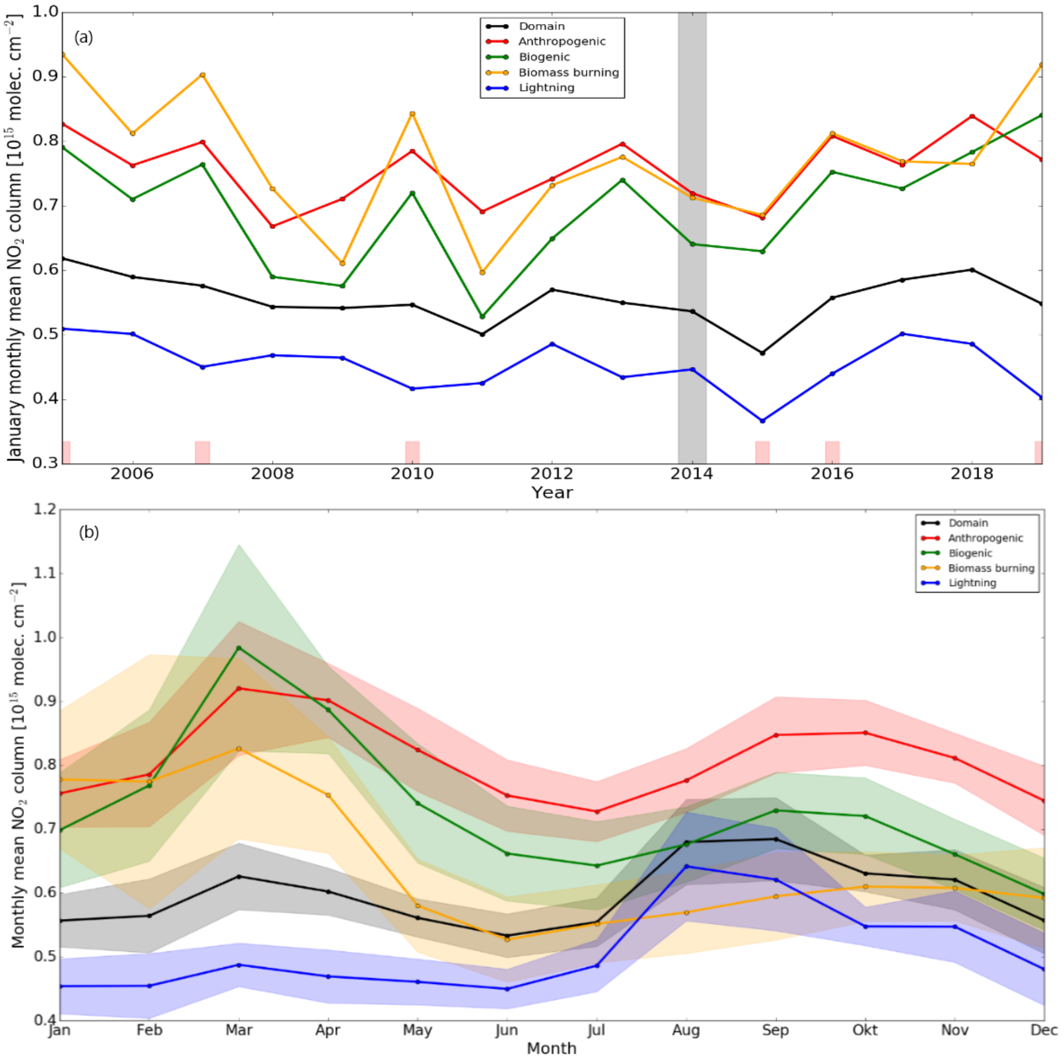

Figure A1. (a) January monthly averaged NO_2 vertical column densities [10^{15} molecules cm^{-2}] retrieved from OMI for 2005-2019 for the whole domain (black), regions with dominating anthropogenic (red), biogenic (green), biomass burning (yellow) and lightning (blue) emissions. The grey vertical bar highlights the WRF-Chem simulated year 2014. The red bars indicate El Niño years (2005, 2007, 2010, 2015, 2016, 2019). (b) Monthly averaged OMI NO_2 vertical column densities [10^{15} molecules cm^{-2}] for 2005-2019. The shadings indicate +/- 1 standard deviation.

Appendix B: Complete overview in situ data

Table B1. Available air quality monitoring stations including city, location and measured compounds.

Station name	City	Latitude	Longitude	CO	NO	NO_2	O_3
Pance	Cali	3.305	-76.533				✓
Universidad del Valle	Cali	3.378	-76.534			✓	✓
Compartir	Cali	3.428	-76.467				✓
C. Alto Rendimiento	Bogotá	4.658	-74.084	✓			✓
Carvajal - Sevillana	Bogotá	4.596	-74.149	✓			✓
Fontibon	Bogotá	4.670	-74.142	✓			✓
Kennedy	Bogotá	4.625	-74.161	✓	✓	✓	
Las Ferias	Bogotá	4.691	-74.083	✓			✓
MinAmbiente	Bogotá	4.626	-74.067				✓
Puente Aranda	Bogotá	4.632	-74.118	✓	✓	✓	✓
San Christobal	Bogotá	4.573	-74.084				✓
Tunal	Bogotá	4.576	-74.131	✓	✓	✓	✓
Guaymaral	Bogotá	4.784	-74.044		✓	✓	✓
Suba	Bogotá	4.761	-74.094		✓	✓	✓
Usaquen	Bogotá	4.710	-74.030				✓
CAL-Corp. Lasallista	Medellín	6.102	-75.642				✓
ITA-Casa Justicia	Medellín	6.188	-75.601		✓	✓	
ITA-Col. Concejo	Medellín	6.171	-75.648				✓
MED-Politecnico JIC	Medellín	6.212	-75.581		✓	✓	
MED-Politecnico JIC (S)	Medellín	6.212	-75.581		✓		
BEL-U.S. Buenaventura	Medellín	6.331	-75.569		✓	✓	✓
MED-Museo Antioquia	Medellín	6.253	-75.570	✓			
MED-UN Fac. Minas	Medellín	6.274	-75.593		✓	✓	
MED-UN Nucleo Volador	Medellín	6.266	-75.580		✓	✓	✓
MED-Univ. Medellín	Medellín	6.256	-75.559				✓
MED-Villahermosa	Medellín	6.256	-75.559				✓
BAR-Parque Las Aguas	Medellín	6.409	-75.417				✓
Cabecera	Bucaramanga	7.113	-73.111	✓			
Centro	Bucaramanga	7.119	-73.127	✓	✓	✓	
Ciudadela	Bucaramanga	7.106	-73.124	✓			

Appendix C: O_3 and NO_x mixing ratios in Bogotá for January 2014

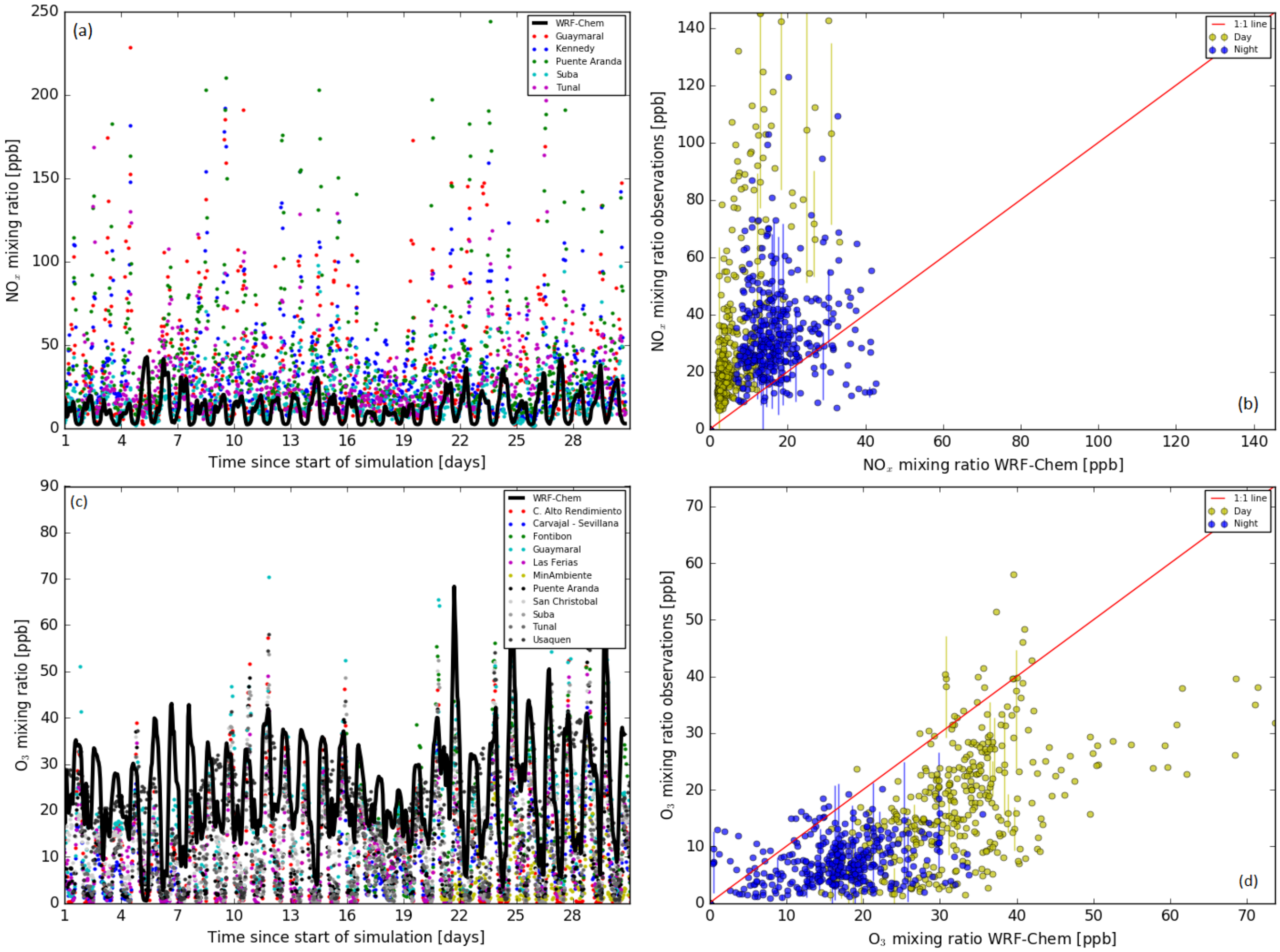

Figure C1. Temporal evolution of (a) NO_x and (c) O_3 mixing ratios [ppb] in Bogotá for WRF-Chem (black solid line) and all available observational stations (coloured points). Scatter plots of the WRF-Chem output compared with averaged (b) NO_x, (d) O_3 mixing ratios [ppb] from the stations are split up in day (yellow) and night (blue). The error bars indicate the standard deviation of the observational data from randomly sampled points (not all standard deviations are shown for visual purposes).

References

Archer-Nicholls, S., Lowe, D., Utembe, S., Allan, J., Zaveri, R. A., Fast, J. D., Hodnebrog, Ø., Denier van der Gon, H., and McFiggans, G.: Gaseous chemistry and aerosol mechanism developments for version 3.5. 1 of the online regional model, WRF-Chem, Geoscientific Model Development, 7, 2557–2579, 2014.

Ashmore, M. R. and Marshall, F.: Ozone impacts on agriculture: an issue of global concern, in: Advances in Botanical Research, vol. 29, pp. 31–52, Elsevier, 1998.

Bailey, J. E., Dean, K. G., Dehn, J., Webley, P. W., Power, J., Coombs, M., and Freymueller, J.: Integrated satellite observations of the 2006 eruption of Augustine Volcano, The, pp. 481–506, 2006.

Baklanov, A., Schlünzen, K., Suppan, P., Baldasano, J., Brunner, D., Aksoyoglu, S., Carmichael, G., Douros, J., Flemming, J., Forkel, R., et al.: Online coupled regional meteorology chemistry models in Europe: current status and prospects, Atmospheric Chemistry and Physics, 14, 317–398, 2014.

Bauer, P., Thorpe, A., and Brunet, G.: The quiet revolution of numerical weather prediction, Nature, 525, 47, 2015.

Beirle, S., Huntrieser, H., and Wagner, T.: Direct satellite observation of lightning-produced NOx, Atmospheric Chemistry and Physics, pp. 10 965–10 986, 2010.

Boersma, K., Eskes, H., Veefkind, J., Brinksma, E., Van Der A, R., Sneep, M., Van Den Oord, G., Levelt, P., Stammes, P., Gleason, J., et al.: Near-real time retrieval of tropospheric NO 2 from OMI, Atmospheric Chemistry and Physics, 7, 2103–2118, 2007.

Boersma, K., Eskes, H., Dirksen, R., Veefkind, J., Stammes, P., Huijnen, V., Kleipool, Q., Sneep, M., Claas, J., Leitão, J., et al.: An improved tropospheric NO2 column retrieval algorithm for the Ozone Monitoring Instrument, Atmospheric Measurement Techniques, 4, 1905, 2011.

Boersma, K., Vinken, G., and Eskes, H.: Representativeness errors in comparing chemistry transport and chemistry climate models with satellite UV-Vis tropospheric column retrievals, Geoscientific Model Development, 9, 875, 2016.

Boersma, K. F., Eskes, H. J., Richter, A., Smedt, I. D., Lorente, A., Beirle, S., Van Geffen, J. H., Zara, M., Peters, E., Roozendael, M. V., et al.: Improving algorithms and uncertainty estimates for satellite NO 2 retrievals: results from the quality assurance for the essential climate variables (QA4ECV) project, Atmospheric Measurement Techniques, 11, 6651–6678, 2018.

Bond, D. W., Steiger, S., Zhang, R., Tie, X., and Orville, R. E.: The importance of NOx production by lightning in the tropics, Atmospheric Environment, 36, 1509–1519, 2002.

Bradshaw, J., Davis, D., Grodzinsky, G., Smyth, S., Newell, R., Sandholm, S., and Liu, S.: Observed distributions of nitrogen oxides in the remote free troposphere from the NASA global tropospheric experiment programs, Reviews of Geophysics, 38, 61–116, 2000.

Carslaw, D. C.: Evidence of an increasing NO2/NOx emissions ratio from road traffic emissions, Atmospheric Environment, 39, 4793–4802, 2005.

Castellanos, P., Boersma, K., and Van Der Werf, G.: Satellite observations indicate substantial spatiotemporal variability in biomass burning NOx emission factors for South America, Atmospheric Chemistry and Physics, 14, 3929–3943, 2014.

Chen, F. and Dudhia, J.: Coupling an advanced land surface–hydrology model with the Penn State–NCAR MM5 modeling system. Part I: Model implementation and sensitivity, Monthly Weather Review, 129, 569–585, 2001.

Córdoba-Machado, S., Palomino-Lemus, R., Gámiz-Fortis, S. R., Castro-Díez, Y., and Esteban-Parra, M. J.: Influence of tropical Pacific SST on seasonal precipitation in Colombia: prediction using El Niño and El Niño Modoki, Climate Dynamics, 44, 1293–1310, 2015.

Dodman, D.: Blaming cities for climate change? An analysis of urban greenhouse gas emissions inventories, Environment and urbanization, 21, 185–201, 2009.

Dudhia, J.: Numerical study of convection observed during the winter monsoon experiment using a mesoscale two-dimensional model, Journal of the Atmospheric Sciences, 46, 3077–3107, 1989.

Fitzherbert, E. B., Struebig, M. J., Morel, A., Danielsen, F., Brühl, C. A., Donald, P. F., and Phalan, B.: How will oil palm expansion affect biodiversity?, Trends in ecology & evolution, 23, 538–545, 2008.

Ganzeveld, L., Lelieveld, J., Dentener, F., Krol, M., Bouwman, A., and Roelofs, G.-J.: Global soil-biogenic NOx emissions and the role of canopy processes, Journal of Geophysical Research: Atmospheres, 107, 2002a.

Ganzeveld, L., Lelieveld, J., Dentener, F., Krol, M., and Roelofs, G.-J.: Atmosphere-biosphere trace gas exchanges simulated with a single-column model, Journal of Geophysical Research: Atmospheres, 107, ACH–8, 2002b.

Ganzeveld, L., Eerdekens, G., Feig, G., Fischer, H., Harder, H., Königstedt, R., Kubistin, D., Martinez, M., Meixner, F., Scheeren, H., et al.: Surface and boundary layer exchanges of volatile organic compounds, nitrogen oxides and ozone during the GABRIEL campaign, Atmospheric Chemistry and Physics, 8, 6223–6243, 2008.

Ganzeveld, L., Bouwman, L., Stehfest, E., van Vuuren, D. P., Eickhout, B., and Lelieveld, J.: Impact of future land use and land cover changes on atmospheric chemistry-climate interactions, Journal of Geophysical Research: Atmospheres, 115, 2010.

Gery, M. W., Whitten, G. Z., Killus, J. P., and Dodge, M. C.: A photochemical kinetics mechanism for urban and regional scale computer modeling, Journal of Geophysical Research: Atmospheres, 94, 12 925–12 956, 1989.

Ghude, S. D., Pfister, G. G., Jena, C., van der A, R., Emmons, L. K., and Kumar, R.: Satellite constraints of nitrogen oxide (NOx) emissions from India based on OMI observations and WRF-Chem simulations, Geophysical Research Letters, 40, 423–428, 2013.

González, C., Ynoue, R., Vara-Vela, A., Rojas, N., and Aristizábal, B.: High-resolution air quality modeling in a medium-sized city in the tropical Andes: Assessment of local and global emissions in understanding ozone and PM 10 dynamics, Atmospheric Pollution Research, 2018.

Grajales, J. F. and Baquero-Bernal, A.: Inference of surface concentrations of nitrogen dioxide (NO 2) in Colombia from tropospheric columns of the ozone measurement instrument (OMI), Atmósfera, 27, 193–214, 2014.

Grell, G. A. and Freitas, S. R.: A scale and aerosol aware stochastic convective parameterization for weather and air quality modeling., Atmospheric Chemistry & Physics Discussions, 13, 2013.

Grell, G. A., Peckham, S. E., Schmitz, R., McKeen, S. A., Frost, G., Skamarock, W. C., and Eder, B.: Fully coupled "online" chemistry within the WRF model, Atmospheric Environment, 39, 6957–6975, 2005.

Guenther, A., Jiang, X., Heald, C., Sakulyanontvittaya, T., Duhl, T., Emmons, L., and Wang, X.: The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2. 1): an extended and updated framework for modeling biogenic emissions, 2012.

Gupta, M. and Mohan, M.: Validation of WRF/Chem model and sensitivity of chemical mechanisms to ozone simulation over megacity Delhi, Atmospheric Environment, 122, 220–229, 2015.

Holland, E. A., Dentener, F. J., Braswell, B. H., and Sulzman, J. M.: Contemporary and pre-industrial global reactive nitrogen budgets, Biogeochemistry, 46, 7–43, 1999.

Hong, S.-Y., Noh, Y., and Dudhia, J.: A new vertical diffusion package with an explicit treatment of entrainment processes, Monthly weather review, 134, 2318–2341, 2006.

Huang, G., Brook, R., Crippa, M., Janssens-Maenhout, G., Schieberle, C., Dore, C., Guizzardi, D., Muntean, M., Schaaf, E., and Friedrich, R.: Speciation of anthropogenic emissions of non-methane volatile organic compounds: a global gridded data set for 1970-2012, Atmospheric Chemistry and Physics, 17, 7683–7683, 2017.

Jaeglé, L., Steinberger, L., Martin, R. V., and Chance, K.: Global partitioning of NO x sources using satellite observations: Relative roles of fossil fuel combustion, biomass burning and soil emissions, Faraday discussions, 130, 407–423, 2005.

Janić, Z. I.: Nonsingular implementation of the Mellor-Yamada level 2.5 scheme in the NCEP Meso model, US Department of Commerce, National Oceanic and Atmospheric Administration, National Weather Service, National Centers for Environmental Prediction, 2001.

Janssens-Maenhout, G., Crippa, M., Guizzardi, D., Muntean, M., Schaaf, E., Dentener, F., Bergamaschi, P., Pagliari, V., Olivier, J., Peters, J., et al.: EDGAR v4.3.2 Global Atlas of the three major Greenhouse Gas Emissions for the period 1970–2012, Earth Syst. Sci. Data Discuss, 2017.

Jiang, F., Liu, Q., Huang, X., Wang, T., Zhuang, B., and Xie, M.: Regional modeling of secondary organic aerosol over China using WRF/Chem, Journal of aerosol science, 43, 57–73, 2012.

Kim, S.-W., Heckel, A., Frost, G., Richter, A., Gleason, J., Burrows, J., McKeen, S., Hsie, E.-Y., Granier, C., and Trainer, M.: NO2 columns in the western United States observed from space and simulated by a regional chemistry model and their implications for NOx emissions, Journal of Geophysical Research: Atmospheres, 114, 2009.

Krotkov, N. A., Lamsal, L. N., Celarier, E. A., Swartz, W. H., Marchenko, S. V., Bucsela, E. J., Chan, K. L., Wenig, M., and Zara, M.: The version 3 OMI NO 2 standard product, Atmospheric Measurement Techniques, 10, 3133–3149, 2017.

Kumar, A., Jiménez, R., Belalcázar, L. C., and Rojas, N. Y.: Application of WRF-Chem Model to Simulate PM10 Concentration over Bogota, Aerosol and Air Quality Research, 16, 1206–1221, 2016.

Lamarque, J.-F., Bond, T. C., Eyring, V., Granier, C., Heil, A., Klimont, Z., Lee, D., Liousse, C., Mieville, A., Owen, B., et al.: Historical (1850–2000) gridded anthropogenic and biomass burning emissions of reactive gases and aerosols: methodology and application, Atmospheric Chemistry and Physics, 10, 7017–7039, 2010.

Lavelle, P., Rodríguez, N., Arguello, O., Bernal, J., Botero, C., Chaparro, P., Gómez, Y., Gutiérrez, A., del Pilar Hurtado, M., Loaiza, S., et al.: Soil ecosystem services and land use in the rapidly changing Orinoco River Basin of Colombia, Agriculture, ecosystems & environment, 185, 106–117, 2014.

Levelt, P. F., van den Oord, G. H., Dobber, M. R., Malkki, A., Visser, H., de Vries, J., Stammes, P., Lundell, J. O., and Saari, H.: The ozone monitoring instrument, IEEE Transactions on geoscience and remote sensing, 44, 1093–1101, 2006.

Lorente, A., Boersma, K. F., Yu, H., Dörner, S., Hilboll, A., Richter, A., Liu, M., Lamsal, L. N., Barkley, M., De Smedt, I., et al.: Structural uncertainty in air mass factor calculation for NO 2 and HCHO satellite retrievals, Atmospheric Measurement Techniques, 10, 759–782, 2017.

Miyazaki, K., Eskes, H., Sudo, K., and Zhang, C.: Global lightning NOx production estimated by an assimilation of multiple satellite data sets, Atmospheric Chemistry and Physics, 14, 3277–3305, 2014.

Mlawer, E. J., Taubman, S. J., Brown, P. D., Iacono, M. J., and Clough, S. A.: Radiative transfer for inhomogeneous atmospheres: RRTM, a validated correlated-k model for the longwave, Journal of Geophysical Research: Atmospheres, 102, 16 663–16 682, 1997.

Morrison, H., Thompson, G., and Tatarskii, V.: Impact of cloud microphysics on the development of trailing stratiform precipitation in a simulated squall line: Comparison of one-and two-moment schemes, Monthly Weather Review, 137, 991–1007, 2009.

Murray, L. T.: Lightning NOx and impacts on air quality, Current Pollution Reports, 2, 115–133, 2016.

Ott, L. E., Pickering, K. E., Stenchikov, G. L., Allen, D. J., DeCaria, A. J., Ridley, B., Lin, R.-F., Lang, S., and Tao, W.-K.: Production of lightning NOx and its vertical distribution calculated from three-dimensional cloud-scale chemical transport model simulations, Journal of Geophysical Research: Atmospheres, 115, 2010.

Panella, M., Tommasini, V., Binotti, M., Palin, L., and Bona, G.: Monitoring nitrogen dioxide and its effects on asthmatic patients: Two different strategies compared, Environmental monitoring and assessment, 63, 447–458, 2000.

Pickering, K. E., Bucsela, E., Allen, D., Ring, A., Holzworth, R., and Krotkov, N.: Estimates of lightning NOx production based on OMI NO2 observations over the Gulf of Mexico, Journal of Geophysical Research: Atmospheres, 121, 8668–8691, 2016.

Price, C. and Rind, D.: A simple lightning parameterization for calculating global lightning distributions, Journal of Geophysical Research: Atmospheres, 97, 9919–9933, 1992.

Randerson, J., van der Werf, G., Giglio, L., Collatz, G., and Kasibhatla, P.: Global Fire Emissions Database, Version 4,(GFEDv4), ORNL DAAC, Oak Ridge, Tennessee, USA, 2015.

Saide, P., Spak, S., Carmichael, G., Mena-Carrasco, M., Yang, Q., Howell, S., Leon, D., Snider, J. R., Bandy, A. R., Collett, J. L., et al.: Evaluating WRF-Chem aerosol indirect effects in Southeast Pacific marine stratocumulus during VOCALS-REx, Atmospheric Chemistry and Physics, 12, 3045, 2012.

Samad, T., Lozano-Gracia, N., and Panman, A.: Colombia urbanization review: amplifying the gains from the urban transition, World Bank Publications, 2012.

Silvern, R., Jacob, D., Travis, K., Sherwen, T., Evans, M., Cohen, R., Laughner, J., Hall, S., Ullmann, K., Crounse, J., et al.: Observed NO/NO2 Ratios in the Upper Troposphere Imply Errors in NO-NO2-O3 Cycling Kinetics or an Unaccounted NOx Reservoir, Geophysical Research Letters, 45, 4466–4474, 2018.

Streets, D. G., Bond, T., Carmichael, G., Fernandes, S., Fu, Q., He, D., Klimont, Z., Nelson, S., Tsai, N., Wang, M. Q., et al.: An inventory of gaseous and primary aerosol emissions in Asia in the year 2000, Journal of Geophysical Research: Atmospheres, 108, 2003.

Tie, X., Madronich, S., Walters, S., Zhang, R., Rasch, P., and Collins, W.: Effect of clouds on photolysis and oxidants in the troposphere, Journal of Geophysical Research: Atmospheres, 108, 2003.

Vargas, L. E. P., Laurance, W. F., Clements, G. R., and Edwards, W.: The impacts of oil palm agriculture on Colombia's biodiversity: what we know and still need to know, Tropical Conservation Science, 8, 828–845, 2015.

Vinken, G., Boersma, K., Maasakkers, J., Adon, M., and Martin, R.: Worldwide biogenic soil NO x emissions inferred from OMI NO 2 observations, Atmospheric Chemistry and Physics, 14, 10 363–10 381, 2014.

Visser, A. J., Boersma, K. F., Ganzeveld, L. N., and Krol, M. C.: European NO x emissions in WRF-Chem derived from OMI: impacts on summertime surface ozone, Atmospheric Chemistry and Physics, 19, 11 821–11 841, 2019.

Wang, Q. and Li, R.: Sino-Venezuelan oil-for-loan deal–the Chinese strategic gamble?, Renewable and Sustainable Energy Reviews, 64, 817–822, 2016.

Webley, P., Steensen, T., Stuefer, M., Grell, G., Freitas, S., and Pavolonis, M.: Analyzing the Eyjafjallajökull 2010 eruption using satellite remote sensing, lidar and WRF-Chem dispersion and tracking model, Journal of Geophysical Research: Atmospheres, 117, 2012.

WHO: Health aspects of air pollution with particulate matter, ozone and nitrogen dioxide: report on a WHO working group, Bonn, Germany, 2003.

Williams, J. E., Boersma, K. F., Sager, P. L., and Verstraeten, W. W.: The high-resolution version of TM5-MP for optimized satellite retrievals: description and validation, Geoscientific Model Development, 10, 721–750, 2017.

Wolfe, A. H. and Patz, J. A.: Reactive nitrogen and human health: acute and long-term implications, Ambio: A journal of the human environment, 31, 120–125, 2002.

Zárate, E., Belalcazar, L. C., Clappier, A., Manzi, V., and Van den Bergh, H.: Air quality modelling over Bogota, Colombia: Combined techniques to estimate and evaluate emission inventories, Atmospheric Environment, 41, 6302–6318, 2007.

Zaveri, R. A. and Peters, L. K.: A new lumped structure photochemical mechanism for large-scale applications, Journal of Geophysical Research: Atmospheres, 104, 30 387–30 415, 1999.

Zhong, M., Saikawa, E., Liu, Y., Naik, V., Horowitz, L. W., Takigawa, M., Zhao, Y., Lin, N.-H., and Stone, E. A.: Air quality modeling with WRF-Chem v3. 5 in East Asia: sensitivity to emissions and evaluation of simulated air quality., Geoscientific Model Development, 9, 2016.