

Dear Editor,

We thank you for agreeing to serve as editor for our submission and your evaluation to find the manuscript titled "Evaluation of the coupled high-resolution atmospheric chemistry model system MECO(n) using in situ and MAX-DOAS NO₂ measurements" (amt-2021-23) suitable for publication in AMTD. We also thank the two anonymous reviewers for their thorough evaluation, suggestion for improvement and recommendation for publication after minor revisions.

Through the interactive discussion, we have addressed all the concerns raised by the reviewers and incorporated their feedback in the revised submission. We would like to mention that we overlooked the contribution of Prof Holger Tost and Marc Barra from the Johannes Gutenberg University Mainz in the original submission. They extended their support for setting up the region model MECO(n) used in the study. In the revised manuscript, we have included them as co-authors.

For convenient perusal, we have also appended the response to both the reviewers as well as the revised manuscript with marked changes with respect to the original submission below. We hope that you find the revised manuscript suitable for publication in Atmospheric Measurement Techniques.

Kind regards,

Vinod Kumar

(on behalf of all the co-authors)

Reviewer #1

This is a nice piece of work, I enjoy reading it. This work provide a comprehensive evaluation of NO_x high-resolution simulation over Germany. NO_x is one of the most important tracer gases in the atmosphere, which largely impacts photochemistry and generate secondary pollutants, including ozone and nitrate. High resolution simulation is critical to improve the non-linear photochemical processes and heterogeneous processes, the latter of which is also important for both air quality and climate, eg. (Chen et al., 2020). The work uses a broad surface observation network and DOAS column observations of NO_x to provide a valuable evaluation of the high-resolution results using different emission inventories, and help us understand the uncertainties in model and inventories. I am more familiar with modelling and possibly not the best person to comment on the observation part, while, I have collaborated with MPIC a few years ago, I trust the data is of high quality from their rigorous research style. And authors have described the observation method in details and it looks convincing for me. This manuscript is well organized and written. I am happy to recommend it for publishing.

Thanks a lot for the encouraging remarks and highlighting the importance of this work. We have noted the relevance of high resolution modelling for non-linear photochemical processes and heterogeneous processes and accordingly modified lines 20-22 of the original manuscript as follows:

“The high spatial resolution of these models allows us to resolve localized emissions (e.g., industrial and urban clusters), quantify their impacts on non-linear photochemical processes, e.g., ozone production (Vinken et al., 2014; Visser et al., 2019; Mertens et al., 2020) as well as on heterogeneous processes e.g., particulate nitrate production (Chen et al., 2020).”

A few minor comments may help improve the discussion.

We have undertaken the revision suggested by this reviewer. The questions and suggestions are marked in blue color while our responses are shown in black color.

1) line 39, “secondary chemistry”, may be better using secondary pollution?

Done.

2) A little more information on the emission inventory would be helpful. Such as, the resolution of TNO and UBA inventory, and how does seasonal variation considered? What does “fl” subtitle mean, better introduce it.

Thanks a lot for the suggestion. We have added the following text in lines 131-132 of the revised manuscript to provide information about the spatial resolution of TNO and UBA inventory

“The spatial resolution of TNO MACC III and UBA emissions are 0.0625° (latitude) \times 0.125° (longitude) and $1\text{km} \times 1\text{km}$, respectively.”

In appendix A (line 558-560) of the original manuscript, we provide the information about how we considered the monthly variability.

“Both TNO MACC III and UBA emissions are available at a temporal resolution of one year. The monthly profiles of the anthropogenic emissions depend on the emitted species, emissions sectors and the country. For Europe, these factors are also provided by Builtjes et al. (2002), and, are used to create monthly resolution emissions.”

We have modified lines 132-134 of the original manuscript as follows to introduce the “fl” and “di” subscripts:

The subscript “di” in Table 1 indicates the use of the diurnal and day-of-the-week variability in NO_x and CO emissions from the road transport and residential and non-industrial combustion sectors (see appendix A for further details). Similarly, the subscript “fl” (e.g. in the TNO_{fl} and UBA_{fl} set ups) indicates that constant anthropogenic emissions (and a “flat” diurnal pattern) are used for the complete month.

3) In conclusion, up to 50% higher human emission of NO_x only have a minor effect on ambient VMRs and dSCDs, and authors think this possibly stem from the short lifetime of NO_x. I feel we may want a more careful discussion here, because, no matter what time scale it is for NO_x lifetime, NO_x concentration is a result of the equilibrium between sources and sinks. And 50% higher of anthropogenic source has a minor impact on surface concentration, I feel it could due to two reasons: 1) anthropogenic emission is a minor source in afternoon, clearly this cannot be true over Germany, or 2) boundary layer vertical mixing is high in afternoon, this maybe more likely to be the reason. You may want to take a look of the column NO_x value, VCDs. If there is a clear increase of VCDs, it could be an evidence of vertical mixing.

Thanks a lot for the feedback and the suggestion. Indeed the boundary layer height plays an important role in governing the surface volume mixing ratios (VMR) of NO₂, as indicated in lines 489-491 of the original manuscript:

“NO₂ has a short lifetime of a few hours in the daytime, which together with a strong mixing in the daytime boundary layer compensates even for ~ 50% higher emissions (an increase in emissions from the transport sector by a factor of two would translate to an overall increase of ~ 50% in NO_x emissions)”

We agree with the reviewer that, during the daytime, the minor effect of increased emissions on ambient VMRs and VCDs is not entirely due to the short lifetime of NO₂. We also feel that the use of the word “compensate” is not appropriate here, and we correct this in the revised manuscript.

Furthermore, as suggested by the reviewer, in order to disentangle the effect of vertical mixing in the daytime boundary layer from that of photochemistry, we compare the mean diurnal patterns of both the tropospheric VCD and surface VMR of NO₂ at the background site Mainz Mombach for the UBA_{fl} simulations. This set up was chosen because it does not consider any diurnal modulation in emissions and observed diurnal patterns are due to chemical and meteorological effects. We observe that the diurnal variability is much stronger for the surface VMRs (363% peak to peak) as compared to tropospheric VCDs (83 % peak to peak).

This further confirms the stronger impact of boundary layer evolution as compared to the lifetime on the surface mixing ratios of NO₂.

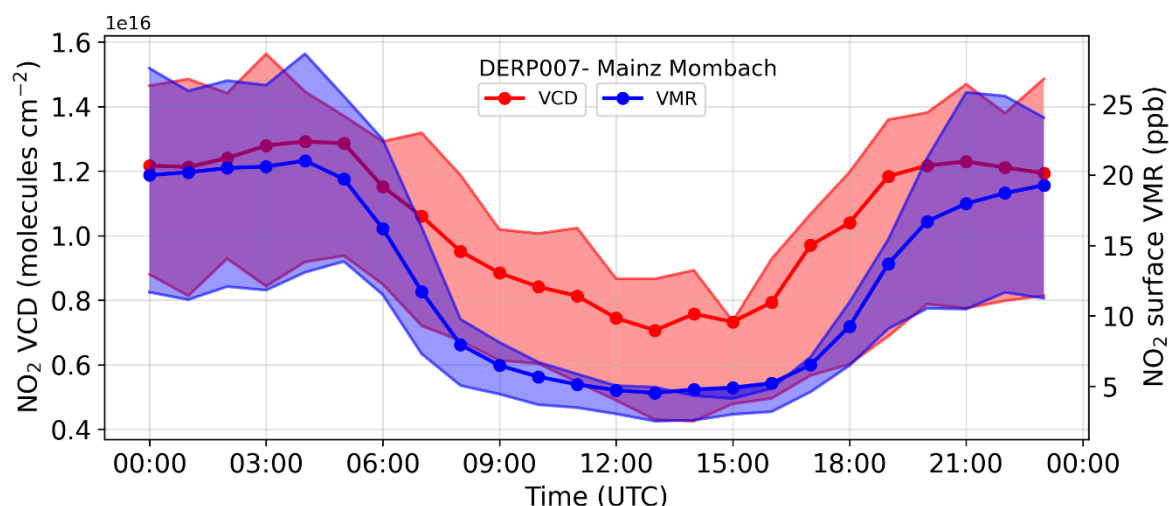


Figure 1: Mean hourly diurnal profiles of simulated NO_2 tropospheric VCDs (red) and surface volume mixing ratios (blue) at a background site Mainz Mombach (8.02°E , 50.02°N) for the model set up UBA_{fl} (diurnal variability of road transport and non-industrial combustion sectors not considered). The solid line and markers represent the mean while the shaded region shows the inter-quartile variability range.

Considering these points, we have added Figure 1 shown above in the appendix of the revised manuscript and modified lines 489-492 of the original manuscript as follows:

“Concerning the diurnal variation, both UBA_{fl} and UBA_{di} show smaller NO_2 dSCDs and surface VMRs during the daytime which agrees reasonably well with the measurements in both set ups. However, stronger discrepancies are observed during early morning and late evening for UBA_{fl} . The discrepancy is even larger for the UBA_{fl} surface concentration at night-time (Figure 13). While emissions primarily drive the surface VMRs during night-time, dilution in the higher boundary layer and chemical loss due to OH in the daytime counters the stronger emissions. We further investigated the diurnal patterns of VCDs and surface VMRs in the UBA_{fl} set-up (Figure C4), and found that the magnitude of diurnal modulation in the hourly mean was $\sim 350\%$ peak to peak, while the same was $\sim 80\%$ for VCDs. This difference in the magnitude of diurnal variability indicates a stronger role of the boundary layer height evolution as compared to the chemical loss due to short lifetime towards off-setting the effect of higher NO_x emissions during the daytime.”

This has also been updated in the abstract (lines 16-18 of the original manuscript) and conclusion (line 537-538 of the original manuscript).

“Accounting for diurnal and daily variability in the monthly resolved anthropogenic emissions was found to be crucial for the accurate representation of time series of measured NO_2 VMR and dSCDs and is particularly critical when vertical mixing is suppressed and the atmospheric lifetime of NO_2 is relatively long.”

“For the afternoon hours, however, even up to 50% higher anthropogenic NO_x emissions only have a minor effect on ambient VMRs and dSCDs due to enhanced dilution in the high daytime planetary boundary layer and its short atmospheric lifetime.”

References:

Chen, Y., Cheng, Y., Ma, N., Wei, C., Ran, L., Wolke, R., Größ, J., Wang, Q., Pozzer, A., Denier van der Gon, H. A. C., Spindler, G., Lelieveld, J., Tegen, I., Su, H., and Wiedensohler, A.: Natural sea-salt

emissions moderate the climate forcing of anthropogenic nitrate, *Atmos. Chem. Phys.*, 20, 771-786, 10.5194/acp-20-771-2020, 2020.

Reviewer #2

Kumar et al. present a confrontation of NO₂ simulations performed with a high-resolution atmospheric chemistry model, set up over southwest Germany, with surface mixing ratio observations and ground-based MAX-DOAS observations of NO₂ vertical column densities and differential slant column densities. The simulations are performed using two emission inventories with different spatial resolutions and emission totals. An additional simulation is performed where sector-specific temporal emission profiles are applied for the high-resolution inventory. The authors report the best model performance using the high-resolution inventory with temporal variation in emissions. Next, the authors derive differential slant column densities from the model simulations and compare these to MAX-DOAS observations under different viewing angles. This allows an evaluation of the spatial and vertical distribution of NO₂ in the vicinity of the MAX-DOAS instrument.

The evaluation of the atmospheric chemistry model is comprehensive and detailed. The evaluation of dSCDs to evaluate the spatial and vertical distribution of NO₂ in the lower atmosphere seems innovative and reproducible in other model evaluation studies (from my atmospheric chemistry modelling perspective). The overall quality of the presented figures and tables, as well as their discussion in the text, is of good quality. Therefore, the manuscript is suitable for publication in AMT after addressing the following questions.

Thanks a lot for assessing our study and the constructive comments. In this document, we address the individual comments and questions of this reviewer. Our responses are presented in black color while the questions are presented in blue color. The revisions in the manuscript are shown in *italics*.

- The difference between the TNO-MACC-III and UBA anthropogenic emission inventories (70%) is remarkable and deserves further discussion.
 1. Can anything be concluded regarding the agreement per source sector?

Thanks a lot for highlighting this point. Here we admit that there was a mistake related to the selection of country mask in the calculation of total emissions from the TNO-MACC-III. In the original manuscript, the total NO_x emissions from the TNO-MACC-III inventory within Germany was 214 Gg(N) for 2011, while the correct value is 288 Gg(N). We have corrected it at lines 128 and 276-280 of the original manuscript. The actual difference in the NO_x emissions between the two NO_x emission inventories is 21% with respect to UBA emissions (27% with respect to TNO MACC III emissions).

We also show the sector-wise difference in figure 1 below. The individual sectors are Agriculture (AGR), Energy industries (ENE), Other Industries (IND), Residential and non-industrial combustion (RCO), Fossil fuel production and distribution (REF), Water navigation (SHP), Solvent and other product use (SOL), Road transport (TRA) and Waste collection, treatment and disposal activities (WST). TNO MACC III deviates most from the UBA dataset in the road transport, energy industries and other industries sectors towards lower estimates, while ship emissions are higher in TNO MACC III. It should also be noted that agricultural emissions are not included in TNO MACC III inventory (Kuenen et al., 2014), while these are included in UBA inventory. Here we would like to point out that in our simulations using UBA emission inventory, emissions due to the use of organic and inorganic fertilizers are doubly counted within Germany, as these are also calculated online using the ONEMIS submodel. We have checked the contribution of these two sources in the total NO_x emissions within Germany, and these are 8% of the total. However, this is within the uncertainty of the NO_x emissions in the inventories, which are in the order of 20% (Solazzo et al., 2021).

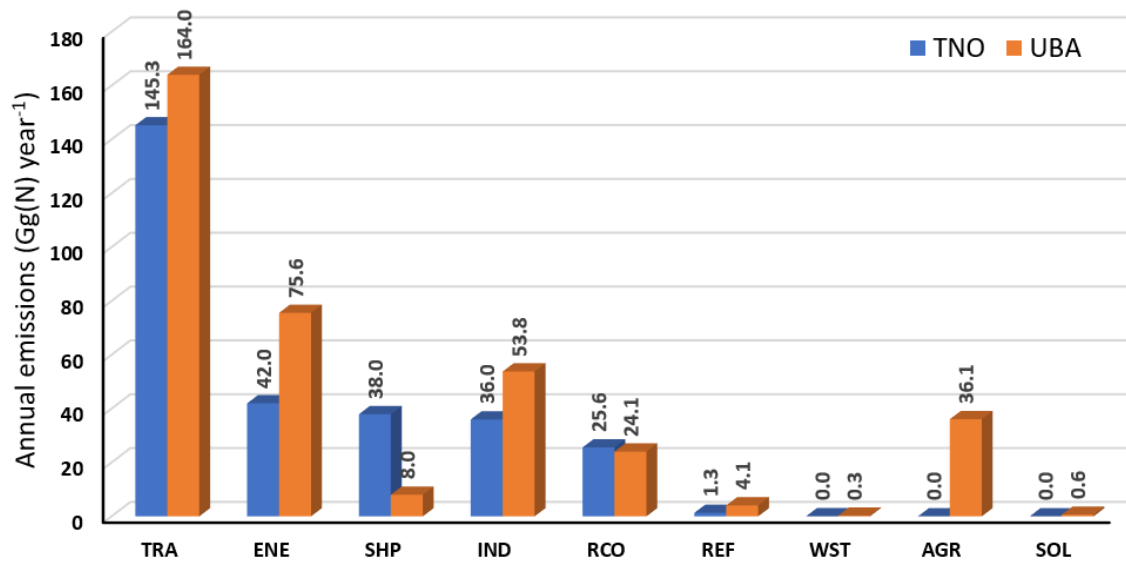


Figure 1 Contribution of individual sectors towards the total NO_x emissions within Germany for TNO MACC III emission inventory for 2011 (blue) and UBA emission inventory for 2018 (orange).

This information and Fig. 1 are now included in Appendix A of the revised manuscript.

2. How do EDGAR emission totals compare to both inventories (as an independent estimate)?

We have calculated the EDGAR version 5.0AP (https://edgar.jrc.ec.europa.eu/dataset_ap50) total NO_x emissions for years 2011 and 2015 for Germany. These are 389.2 and 366.9 Gg(N) per year respectively. We have also added this information in the revised manuscript (line 161).

3. I believe TNO-MACC-III distinguishes between gridded sources (which have unit mass per grid cell per year) and point sources (which have unit mass per year). The latter should be added after interpolation to the destination model grid in order to conserve the mass balance. Not accounting for this leads to inaccurate representations of local emission peaks, and may affect domain emission totals. Please further discuss the strategy to interpolate emission data.

Thanks a lot for highlighting this issue. We apprehended this issue and have carefully checked the TNO MACC III emission inventory. There point sources are distinguished during the preparation stage and are subsequently distributed in the grid as suggested by the reviewer. In this context, we would like to cite the excerpt from the TNO MACC emissions inventory description paper (Kuenen et al., 2014).

“Point sources were spatially distributed using the specific location of the point source”

4. It would be good to embed this finding in the context of the literature: e.g. Travis et al. (2016) suggest sector-specific emission reductions of 30-60% over the Southeast US, and Visser et al. (2019) report European satellite-derived emission totals of $\pm 50\%$ higher compared to TNO-MACC.

Thanks for the suggestions. We have modified lines 282-285 of the original manuscript as follows to include the additional discussion:

“Top down emission estimates using OMI NO₂ measurement also indicated an underestimation of NO_x emission by more than 50% over western Germany and other parts of Europe by the TNO MACC III emission inventory (Visser et al., 2019). It should be noted that the exclusion of soil NO_x emissions from the TNO MACC III inventory also contributed towards the large underestimation in the estimates by Visser et al. (2019). The underestimation of the a priori NO_x emissions is the most important factor for the large negative bias in the TNO_{fl} set-up. Getting up to date emission inventories is difficult, and we could only get this data for Germany, but for future studies with simulation involving larger domains, which include more countries, it is recommended to use more up-to-date emission inventories. The situation of underestimation of NO_x emissions over Germany (and most parts of Europe) is different from that observed in the USA, where national emissions inventories are biased high by as much as 30-60% (Travis et al., 2016)”

- Based on the model comparison with MAX-DOAS observations, can anything be concluded regarding the representativeness of surface emissions from different sources in relation to the model-observation agreement (e.g. T2 in direction of Mainz (anthropogenic footprint), vs. T4 in direction of agricultural areas).

Thanks for the question. In lines 437-439 of the original manuscript, we mention that we did not observe a large difference in the measured and simulated dSCDs along the four viewing directions. One of the plausible explanation of this observation could be the prevailing wind directions (panel (a) of Figure 6), as for most of the time, easterly winds bring the air mass from the urban locations to the agricultural lands.

However, we have evaluated the spatial patterns of the NO_x emissions from the UBA inventory for the individual sectors classified as Agriculture (AGR), Energy industries (ENE), Other Industries (IND), Residential and non-industrial combustion (RCO), Fossil fuel production and distribution (REF), Water navigation (SHP), Solvent and other product use (SOL), Road transport (TRA) and Waste collection, treatment and disposal activities (WST). These spatial patterns are shown in the figure below and the four viewing directions of the MAX-DOAS instrument are overlaid on the maps. While it is difficult to estimate the accuracy of the emissions quantitatively, qualitatively, we can infer that the emissions sources are represented reasonably. For example, while anthropogenic emissions sources (e.g. RCO, IND and ENE) are concentrated towards T2 and T3, agricultural emissions sources are more abundant along T4 and west of T3. Ship emissions are along the Rhine river while the road transport emissions follow the motorways as well as are concentrated in the urban regions.

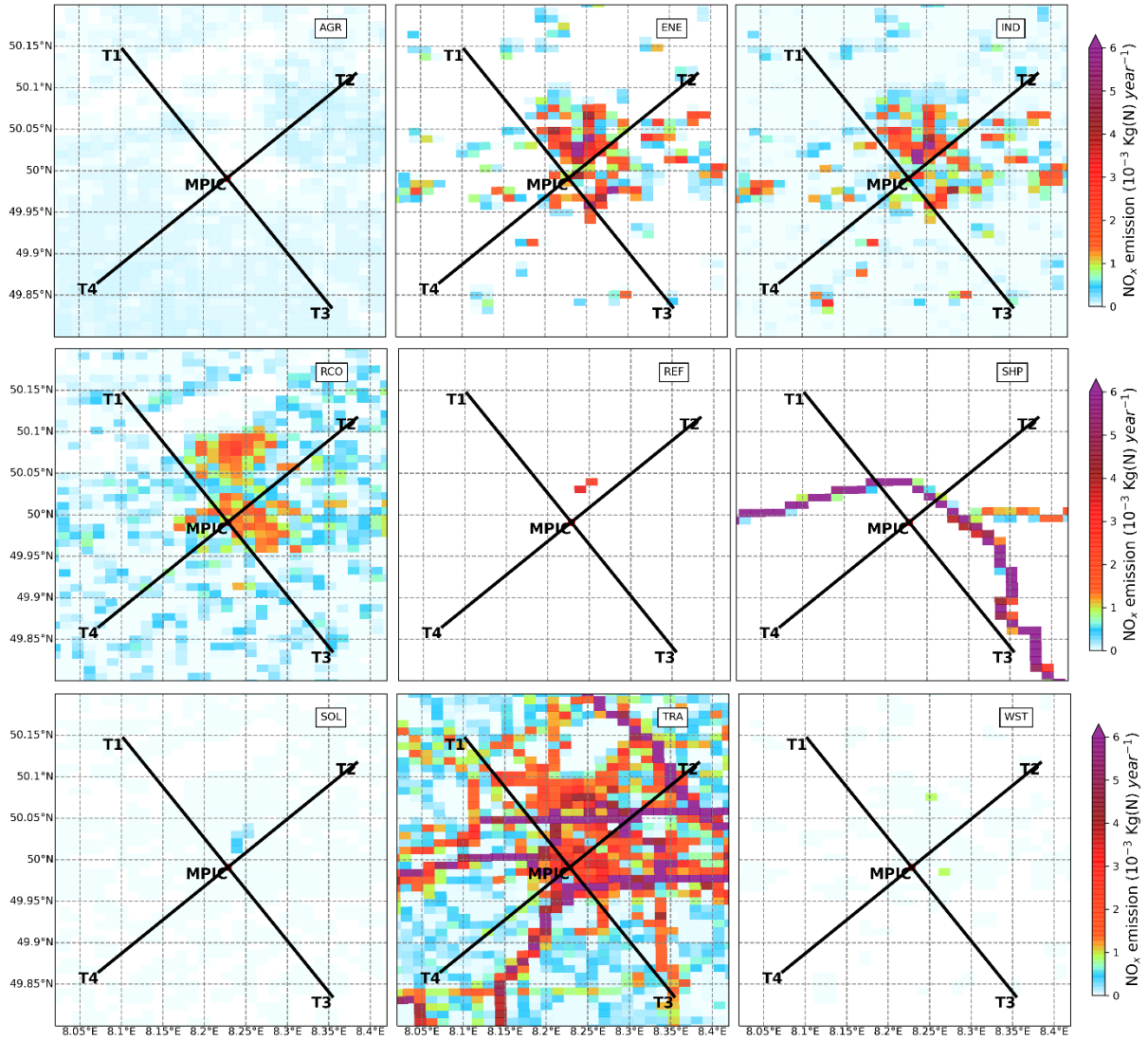


Figure 2 Spatial patterns of NO_x emissions from the UBA inventory for 2018 around the MAX-DOAS measurement location. The viewing directors of the four telescopes are overlaid on top of the emissions maps. Broadly, the telescopes T2 and T3 point towards the city centre and urban areas, T4 points towards the agricultural lands and T1 points towards anthropogenic sources (in the near vicinity) and small forests.

- Appendix B: this is a highly relevant discussion, and most (if not all) models struggle to accurately capture the diurnal cycle in O_3 . I believe this section can be strengthened by pointing this out, for example by referring to regional model intercomparison efforts with similar results (e.g. Solazzo et al. 2012; Im et al., 2015). Why are O_3 simulations only moderately sensitive to substantial NO_x emission differences? Can you detect an effect of model resolution on O_3 mixing ratios (e.g. by comparing domains CM07 and CM02)?

Thanks a lot for indicating the importance of this section and the relevant discussion. We have extended the discussion in appendix B by adding the following lines to the manuscript (lines 622-628):

“Over the European region, regional models usually struggle to capture the diurnal variability of surface O_3 VMRs as indicated by AQMEII (Air Quality Model Evaluation International Initiative) studies (Solazzo et al., 2012; Im et al., 2015). For example, in WRF-CHEM, the night-time overestimation of surface O_3 was found to be due to an underestimation of O_3 titration by NO_x , while that in COSMO-MUSCAT was due to relatively weaker dry deposition fluxes and inaccurate representation of vertical mixing. A night-time overestimation over central Europe was also observed

for global model EMAC, though the bias was smaller as compared to MECO(n) (Mertens et al., 2016).”

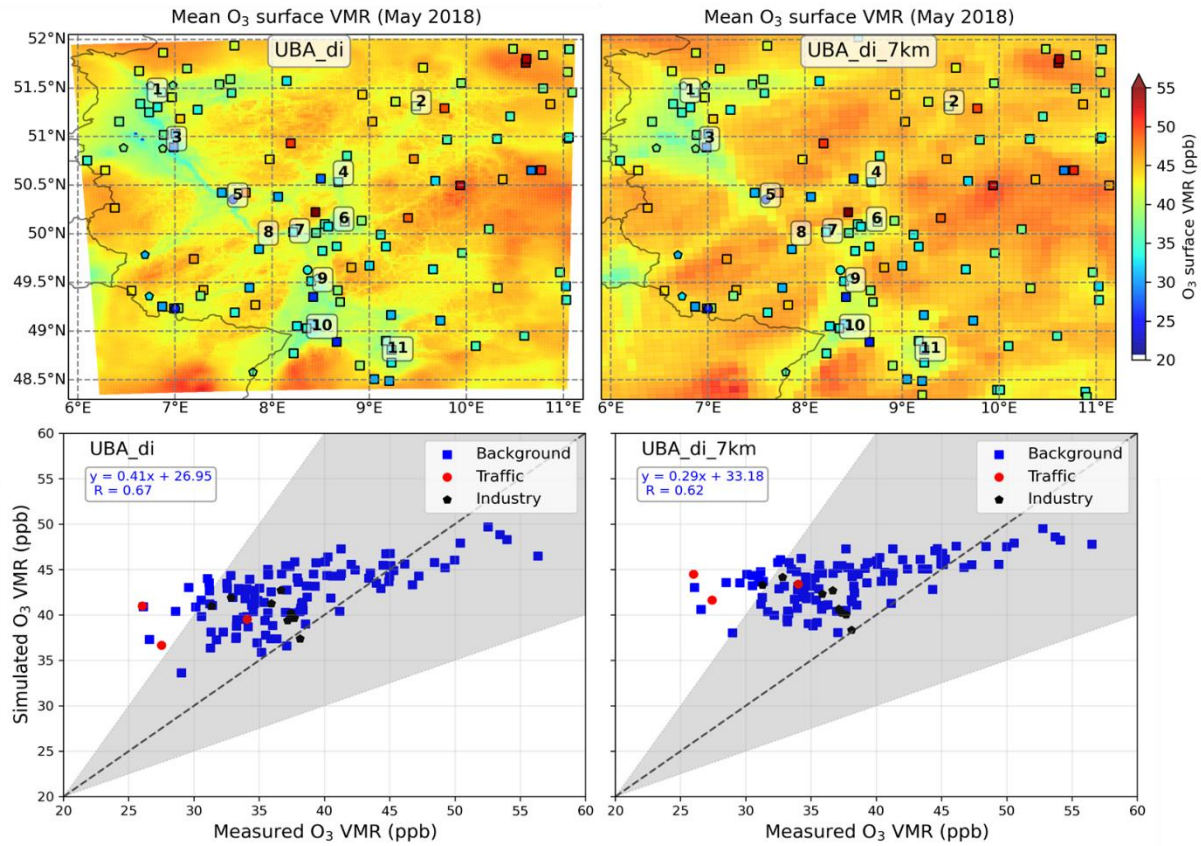


Figure 3 Top) Spatial patterns of monthly mean O₃ volume mixing ratios for the UBA_{di} set up for CM02 domain (left panel) and CM07 domain (right panel). The corresponding monthly mean measured O₃ VMRs are shown as markers overlaid on the map. The numbers in the map show major cities similar to that in Figure 4 of the original manuscript. The bottom panel shows the linear regression between the measured and simulated monthly mean O₃ VMRs at various measurement stations.

For the UBA_{di} setup, we compared the spatial patterns and mean ozone surface volume mixing ratios (VMR) at various measurement stations in the CM07 and CM02 domain (Figure 3). From the spatial patterns, we could conclude that the fine resolution model (left panel) simulates the spatial patterns in greater detail. Its improved spatial variability is obvious from the scatter plot, where we could find better accountability (slope) corresponding to the measured values. At coarser resolution, we observe moderately higher (~2ppb) domain mean ozone mixing ratio (Figure 4). This further supports our hypothesis of a NO_x saturated ozone production regime (lines 600-601 of the original manuscript); as the NO₂ mixing ratios are lower by ~0.2 ppb in the 7 km resolution domain as compared to the 2.2 km

resolution domain.

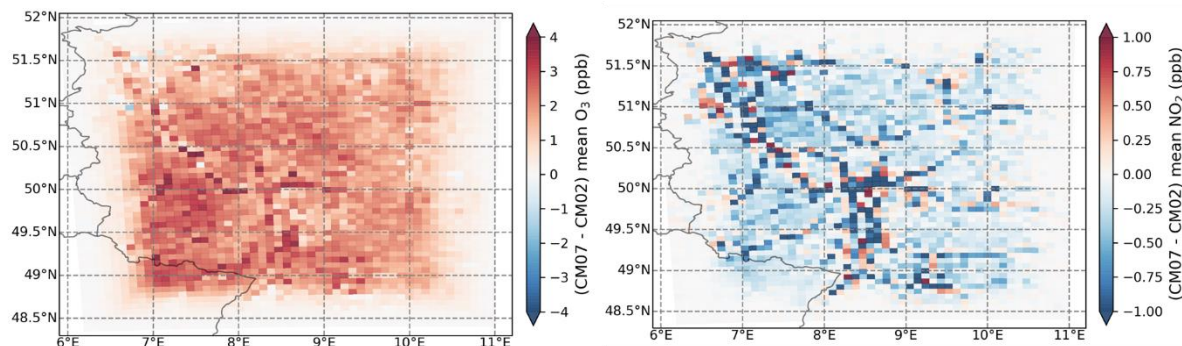


Figure 4 Spatial patterns of difference in simulated monthly mean O_3 surface VMRs (left panel) and mean NO_2 surface VMRs (right panel) between CM07 and CM02 domains of the UBA_{di} set up.

In mid-Europe, the non-anthropogenic sources (e.g. biogenic, methane oxidation, stratospheric intrusion) contribute to > 55% of the surface ozone production in the summertime (Mertens et al., 2020). The contribution is even higher for the CM02 domain region presented in the study. The stronger difference in NO_x emissions between the TNO and UBA emissions are with respect to the road transport emissions, energy industries and other industries (see Figure 1). The contribution of road transport emissions towards surface ozone in the summertime are 12-14%, while that for all other anthropogenic sources, including energy industries is >30%.

Hence, we believe that a relatively weaker contribution of anthropogenic emissions as well as a NO_x saturated ozone production regimes are the reason behind the moderate sensitivity of surface ozone towards NO_x emissions in our study.

We have added the following lines in the revised manuscript to discuss the above-mentioned points (lines 639-642 of the revised manuscript):

“It is interesting to note that an increase of ~27% anthropogenic NO_x emissions by using the UBA emission inventory shows little change in surface O_3 VMRs. In addition to the NO_x saturated ozone production regime, a relatively weaker contribution of anthropogenic emissions towards the ozone production in summertime (Mertens et al., 2020b) could also be a plausible reason for this weak effect.”

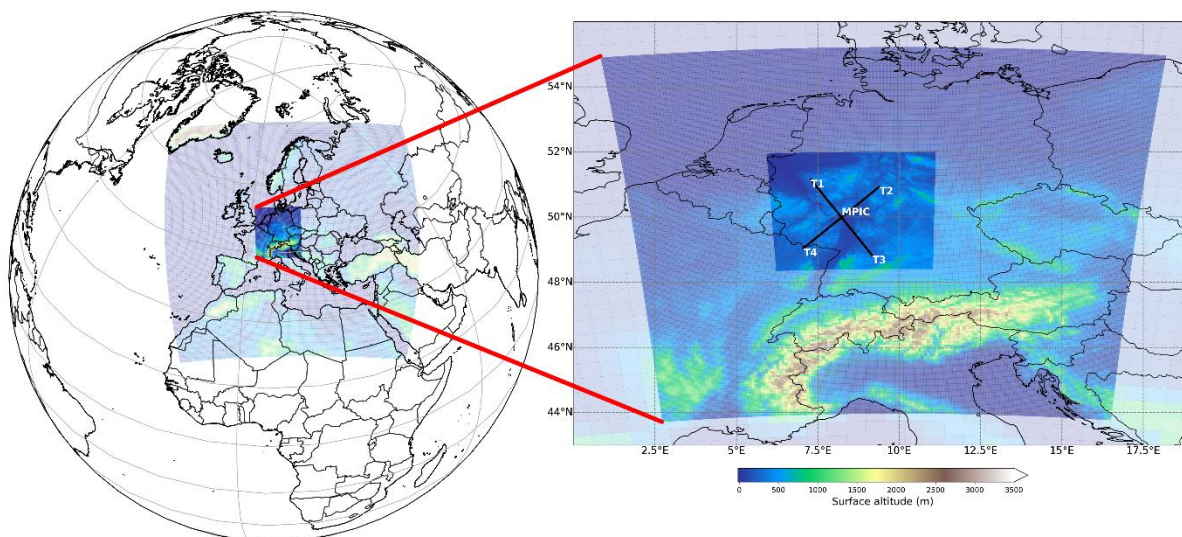
Specific comments

- Line 96: change ‘6 hourly’ to ‘6-hourly’

Done

- Figure 1: Please increase the font size of the annotated text in the zoomed panel for increased legibility

Done. The new figure is also shown below.



- Line 151-154: I suggest to give some more context to the soil NO_x emission totals and how they compare to other estimates. This is especially relevant in the context of the increasing importance of soil NO_x due to decreasing anthropogenic NO_x sources (see e.g. Skiba et al. 2020)

Thanks a lot for suggesting this point. The soil NO_x emissions are highly variable as these are dependent on various meteorological factors including ambient temperature and rainfall. Since we have performed model simulations only for one month (May 2018), it is difficult to accurately compare with other estimates, which provide annual soil NO_x emissions estimates. However, we attempt to do so by considering the monthly temporal profiles of agricultural soil NO_x emissions prescribed by Crippa et al. (2020). Upon application of the monthly factors, the 5.9 Gg(N) soil NO_x emissions over complete Germany in the CM07 domain scales to ~33.7 Gg(N) annually. For reference, the soil NO_x emissions combined due to the application of inorganic nitrogen fertilizers and animal manure was 30.1 Gg(N) for the year 2018, according to the UBA emission inventory. However, for EDGAR version 5.0, the total soil NO_x emissions directly from agricultural soils and Manure management combined for May 2015 for Germany were 19 Gg(N).

In the revised manuscript, we have added the comparison with respect to the EDGAR version 5.0 soil NO_x emissions in lines 160-161:

“The soil NO_x emission calculated online are smaller as compared to the estimated 19.0 Gg(N) for May 2015 from agricultural soils and Manure management sectors combined by EDGAR v5.0 (Crippa et al, 2020)”

- Line 370-371: The reference to Figure C1 now refers to the cloud classification figure, and I cannot find the figure showing Pi-MAX VCDs elsewhere in the text. Please include this figure.

Thanks for pointing this out. This was a mistake in figure labels. The π-MAX VCD are shown as black markers in Figure 6 of the original manuscript. Accordingly, we have corrected the reference in the text as well.

- Line 589: change ‘deposited’ to ‘deposition’

Done

References

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Evaluation of the coupled high-resolution atmospheric chemistry model system MECO(n) using in situ and MAX-DOAS NO₂ measurements

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Abstract. We present high spatial resolution (up to 2.2×2.2 km²) simulations focussed over south-west Germany using the online coupled regional atmospheric chemistry model system MECO(n). Numerical simulation of nitrogen dioxide (NO₂) surface volume mixing ratios (VMR) are compared to in situ measurements from a network with 193 locations including background, traffic-adjacent and industrial stations to investigate the model's performance in simulating the spatial and temporal variability of short-lived chemical species. We show that the use of a high-resolution and up-to-date emission inventory is crucial for reproducing the spatial variability, and resulted in good agreement with the measured VMRs at the background and industrial locations with an overall bias of less than 10%. We introduce a computationally efficient approach that simulates diurnal and daily variability in monthly resolved anthropogenic emissions to resolve the temporal variability of NO₂.

MAX-DOAS measurements performed at Mainz (49.99 °N, 8.23 °E) were used to evaluate the simulated tropospheric vertical column densities (VCD) of NO₂. We propose a consistent and robust approach to evaluate the vertical distribution of NO₂ in the boundary layer by comparing the individual differential slant column densities (*dSCDs*) at various elevation angles. This approach considers details of the spatial heterogeneity and sensitivity volume of the MAX-DOAS measurements while comparing the measured and simulated *dSCDs*. The effects of clouds on the agreement between MAX-DOAS measurements and simulations have also been investigated. For low elevation angles ($\leq 8^\circ$), small biases in the range of -14 to +7% and Pearson correlation coefficients in the range of 0.5 to 0.8 were achieved for different azimuth directions in the cloud-free cases indicating good model performance in the layers close to the surface. Accounting for diurnal and daily variability in the monthly resolved anthropogenic emissions was found to be crucial for the accurate representation of time series of measured NO₂ VMR and *dSCDs* and is particularly critical when [vertical mixing is suppressed and](#) the atmospheric lifetime of NO₂ is relatively long.

Regional atmospheric chemistry and transport models are important for the study and forecasting of atmospheric processes at fine spatial resolutions. The high spatial resolution of these models allows us to resolve localized emissions (e.g., industrial and urban clusters) and, quantify their impacts on non-linear photochemical processes, e.g., ozone production (Vinken et al., 2014; Visser et al., 2019; Mertens et al., 2020a) as well as on heterogeneous processes e.g., particulate nitrate production (Chen et al., 2020). Various studies have shown that significant improvements in satellite retrievals can be achieved through the incorporation of highly resolved a priori trace gas and aerosol fields calculated by high-resolution regional models (Valin et al., 2011; Liu et al., 2020; Ialongo et al., 2020).

Regional models achieve high resolution by employing nesting around the location of interest, in which a fine-resolution model domain receives meteorological and chemical boundary conditions from a coarser resolution model spanning a broader area. The MECO(n) (MESSy-fied ECHAM and COSMO models nested n times) regional model system developed by Kerkweg and Jöckel (2012b) allows online coupling between different nests and in this way facilitates frequent updates of meteorological and chemical boundary conditions. The use of MESSy submodels for this coupled system also ensures consistent treatment of chemical speciation, chemistry and several other relevant processes governing the concentration of chemical species among various nests. A chemical evaluation of MECO(n) over Europe was performed by Mertens et al. (2016) for a set up at $\sim 12 \times 12 \text{ km}^2$ spatial resolution for nitrogen dioxide (NO_2), ozone (O_3) and carbon monoxide (CO). The main strength of MECO(n), i.e., the online coupling with the COSMO model, makes it suitable for performing very high resolution (e.g. $< 3 \times 3 \text{ km}^2$) simulations. For example, the operational COSMO model is already being used for weather forecasts at a spatial resolution of $2.8 \times 2.8 \text{ km}^2$ by the German weather service (Deutscher Wetterdienst) and at $1 \times 1 \text{ km}^2$ by the Federal Office of Meteorology and Climatology, Switzerland (MeteoSwiss). Similar high-resolution model simulations including chemistry have been shown to better represent local maxima (e.g., isolated point sources, road networks and ship tracks) and facilitate understanding of sector-specific impacts on secondary chemistry-pollution (e.g., ozone production) (Colette et al., 2014; Mertens et al., 2020a). However, comparison with in situ measurements showed that these gains could only be quantitatively determined up to a resolution of $\sim 7 \times 7 \text{ km}^2$, beyond which major improvements were not observed (Colette et al., 2014). In most of the cases, the improvement was limited by the resolution of the input emission inventory used in these studies, which are available at a much coarser resolution than that of the model set up. Apart from the coarse resolution, further limitations in such comparisons are imposed by the availability of mostly outdated anthropogenic emissions inventory and limited information about short-term temporal variability (e.g., day of the week or hour of the day) (Kuik et al., 2018). In most cases, input emission inventories are available at temporal resolutions of months to years, but in reality, emissions from several sectors (e.g., road transport, residential combustion) vary markedly depending on the hour of the day and day of the week. From a modelling perspective, however, incorporating high temporal resolution input emissions can be computationally inefficient due to the high readout time and subsequent requirement for interpolation on the model grid.

The evaluation of high-resolution mesoscale models is even more challenging due to the limited availability (in situ measurements) and unavailability (e.g. satellite observations) of reference datasets. The TROPOMI instrument aboard the Sentinel-5P

satellite (Veefkind et al., 2012) has a high spatial resolution (up to $3.5 \times 5.5 \text{ km}^2$) and is in principle well suited for comparison
55 of the tropospheric vertical column densities (VCDs) simulated by the model. However, the limited temporal information –
generally measurements from one overpass per day – precludes an evaluation of diurnal profiles, and hence TROPOMI is not
well suited to demonstrating the advantages of considering diurnally varying input emissions. Besides VCDs, conventional
model evaluation studies are often restricted to the evaluation of concentrations at discrete layers (most often at the surface)
using in situ measurements which are limited with respect to the temporal and spatial coverage. Evaluations of model vertical
60 profiles are even rarer due to the paucity of vertically resolved measurements (e.g., balloon-based and aircraft measurements),
which are technically very challenging. For example, discrepancies between regional models (WRF-Chem and CHIMERE)
and measurements were proposed to arise due to inappropriate parametrization of the turbulent diffusion constant; however,
this could not be verified due to the lack of vertically resolved NO_2 measurements (Kuik et al., 2018; Schaap et al., 2015).
Mertens et al. (2016) evaluated the vertical profiles of O_3 simulated by MECO(n) using ozone sonde data, but this provides
65 little information about the variability within the boundary layer which is masked by that in the upper troposphere (above 400
hPa or $\approx 7 \text{ km}$).

In this regard, MAX-DOAS measurements (Hönninger et al., 2004) provide a unique opportunity for model evaluation
for a larger representative area (a few square kilometers), and over long temporal scales. To our knowledge, regional model
comparison studies with MAX-DOAS are very limited (e.g. Shaiganfar et al. (2015); Vlemmix et al. (2015); Blechschmidt
70 et al. (2020)), and mostly focus on the tropospheric VCDs. These studies have shown moderate correlations between MAX-
DOAS and regional model calculated VCDs with major differences arising due to inappropriate representation of anthropogenic
emissions, differences between model-simulated and actual wind vectors, the presence of clouds and uncertainties related to
the MAX-DOAS VCD retrieval. Further limitations in these comparisons arise due to assumptions of horizontal homogeneity
and the challenges associated with accurately defining the area/volume for which the MAX-DOAS measurements are sensitive.
75 In addition to the VCDs, there is additional information content in the MAX-DOAS measurements (e.g. spatial distribution
of trace gases), which comes from scans performed at different elevation angles, thus probing the atmosphere along different
light paths. This information can be utilized to evaluate the performance of regional models in accurately simulating the spatial
distribution within the boundary layer.

In this paper, we present high-resolution up to ($2.2 \times 2.2 \text{ km}^2$) MECO(3) simulations of NO_2 over south-west Germany
80 using a high spatial resolution and up to date input emission inventory. We also effectively account for the day-of-the-week
and diurnal variability in anthropogenic emissions in the model simulations by applying sector-specific hourly scaling factors
to the monthly-resolved anthropogenic emissions. The model description, details of MAX-DOAS measurements and analyses
and other reference data are provided in section 2. We evaluate the model performance with respect to two input emission
inventories and temporal resolution of emissions through comparison with in situ measurements in section 3.2 and MAX-
85 DOAS tropospheric NO_2 VCDs in section 3.3. The TROPOMI comparison will be the focus of a future study. In this paper, we
introduce a sophisticated and consistent approach for MAX-DOAS comparison, which overcomes the limitations of previous
such comparisons. We also evaluate the performance of the model in reproducing the vertical distribution of NO_2 within the
boundary layer.

2 Methods

90 2.1 Model description

We use the one way coupled model system MECO(3) (Kerkweg and Jöckel, 2012a, b) based on MESSy version 2.54 (Jöckel et al., 2010), which couples the global chemistry climate model EMAC (Jöckel et al., 2006) one way to the regional model COSMO-CLM/MESSy (called COSMO/MESSy hereafter). COSMO-CLM is the community model of the German regional climate research community jointly further developed by the CLM-Community (Rockel et al., 2008). The core driving model
95 for EMAC is ECHAM5 version 5.3.02 (Roeckner et al., 2003) and for COSMO/MESSy it is COSMO 5.00_clm10 (Rockel et al., 2008; Steppeler et al., 2003). EMAC is configured with T106L31ECMWF spectral resolution corresponding to a grid resolution of $\sim 1.1^\circ \times \sim 1.1^\circ$, extending up to 10 hPa (≈ 30 km over Europe) vertically in 31 vertical layers and time step of 360 s. The global model meteorology (temperature, vorticity, surface pressure and divergence) is nudged to ~~6hourly~~hourly ECMWF ERA-Interim reanalysis data. Model simulation are performed for May 2018, i.e., from 01-05-2018 00:00:00
100 until 01-06-2018 00:00:00. The initial chemical conditions for the regional model instances are provided by an EMAC simulation starting three years before the MECO(n) simulations start, i.e. on 01-03-2015.

The three instances of the COSMO/MESSy model are coupled online one way from coarser resolution to finer resolution. The first instance of COSMO/MESSy has a spatial resolution of $0.44^\circ \times 0.44^\circ$ ($\sim 50 \times 50$ km²; referred to as CM50 hereafter), the second one at $0.0625^\circ \times 0.0625^\circ$ ($\sim 7 \times 7$ km²; referred to as CM07 hereafter) and the third one at $0.02^\circ \times 0.02^\circ$ (~ 2.2
105 $\times 2.2$ km²; referred to as CM02 hereafter). All three COSMO/MESSy domains are set up in a rotated coordinate system with the location of the north pole at 40° N and -170° E. The CM07 domain is focussed around Germany, and CM02 further zooms in to south-west Germany, as shown in Figure 1. CM50 and CM07 have 40 terrain-following vertical levels extending up to 22.7 km while CM02 has 50 terrain-following vertical levels extending up to 22 km. In all the three domains, the lowermost atmospheric model layer has a thickness of 20 m, while the lowest 1 km is split into 11 levels for CM50 and CM07 and 12
110 levels for CM02. The thickness of the vertical layers increases with altitude. The time steps for CM50, CM07 and CM02 are 120 s, 60 s and 20 s, respectively. The online coupling enables the specification of boundary conditions at each time step by the respective driving model and is particularly advantageous for complex atmospheric chemistry modelling involving hundreds of chemical tracers. Convection is parametrized according to the Tiedtke-Bechtold scheme for both CM50 and CM07 domains, while for the CM02 domain, only shallow convection is parametrized according to the Tiedtke scheme (Bechtold et al., 2001;
115 Tiedtke, 1989).

The MECO(n) model set up achieves a very high consistency within the model chain, as all four model instances (EMAC and three times COSMO/MESSy) use MESSy and thus imply the very same chemical speciation and process formulations for the chemical processes (e.g., online/offline emission of chemical tracers (ONEMIS/OFFEMIS), chemistry (MECCA), dry deposition (DDEP), wet scavenging (SCAV) and photolysis (JVAL)) (Jöckel et al., 2010; Tost et al., 2006; Kerkweg et al.,
120 2006a; Sander et al., 2014; Kerkweg et al., 2006b). Since deep convection is resolved in the CM02 domain, the MESSy submodel CVTRANS (Tost et al., 2010) used to calculate the tracer transport due to convection is not used in this domain. Consequently, convective scavenging and convective rain flux are also disabled in the CM02 domain when using the SCAV

submodel (Tost et al., 2006). For the chemical mechanism in MECCA, we use the Mainz Isoprene Mechanism (MIM 1) (Pöschl et al., 2000), including 142 gaseous chemical species involved in 236 gas and multiphase reactions and 74 photochemical reactions.

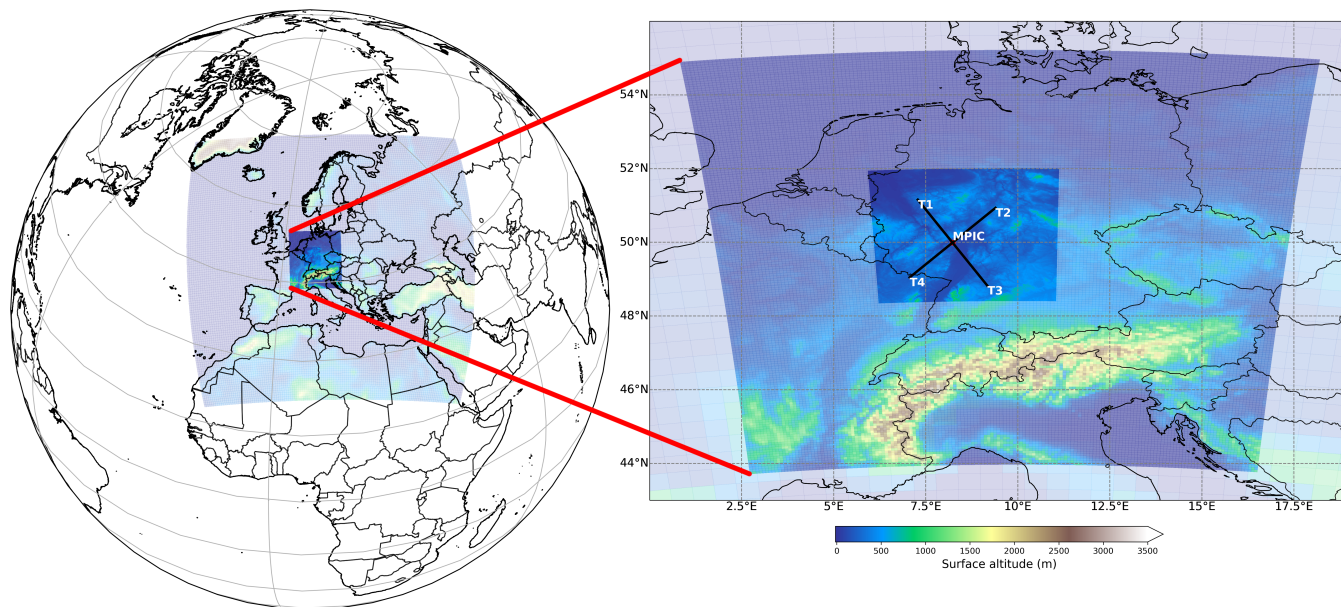


Figure 1. MECO(3) domains in the left panel colour-coded according to the surface altitude. A close up of the map in the right panel shows the CM07 and CM02 domains. The location of MPIC is shown as the red dot in the right panel with the arrows pointing in the viewing direction of the four telescopes.

For the global model and the CM50 domain, EDGAR 4.3.2 anthropogenic emissions ($0.1^\circ \times 0.1^\circ$ globally) (Crippa et al., 2018) have been used, while for the CM07 and CM02 domain, two different anthropogenic emission scenarios, namely TNO MACC III (Kuenen et al., 2014) (available for Europe, until 2011) and UBA (Strogies et al., 2020) (Umweltbundesamt; available for Germany, until 2018) have been employed. Total annual anthropogenic emissions of NO_x within Germany are 366 Gg(N) and 214–288 Gg(N) for UBA (for 2018) and TNO MACC III (for 2011), respectively. To put these estimates in perspective, EDGAR v5.0 (Crippa et al., 2020) annual anthropogenic NO_x emissions for 2011 and 2015 for Germany are 389.2 and 366.9 Gg(N). The spatial resolution of TNO MACC III and UBA emissions are 0.0625° (latitude) \times 0.125° (longitude) and $1\text{ km} \times 1\text{ km}$, respectively. For the TNO MACC III and UBA emissions, NO_x was originally expressed as ~~and~~ kg year^{-1} and kt year^{-1} , respectively, of NO_2 , which were further converted as $\text{molecules m}^{-2} \text{s}^{-1}$ for use in model simulations. In Appendix A and Figure A3, we also compare the contribution of individual sectors towards the total anthropogenic NO_x emissions in the TNO MACC III and UBA inventory.

Three MECO(3) simulations were performed with differing fine temporal variation for the TNO MACC III and UBA anthropogenic emissions, as summarized in Table 1.

Table 1. Model set ups

Simulation id	Anthropogenic emissions (in CM07 and CM02 domains)	Temporal resolution of emissions
TNO _{fl}	TNO MACC III	Monthly
UBA _{fl}	UBA (for Germany) and TNO MACC III (outside Germany)	Monthly
UBA _{di}	UBA (for Germany) and TNO MACC III (outside Germany)	Hourly

The subscript “di” in Table 1 indicates the use of the diurnal and day-of-the-week variability in NO_x and CO emissions from the road transport and residential and non-industrial combustion sectors (see appendix A for further details). ~~For the~~ Similarly, the subscript “fl” (e.g. in the TNO_{fl} and UBA_{fl} set ups) indicates that constant anthropogenic emissions (and a flat diurnal pattern) are used for the complete month. The sector-wise anthropogenic emissions are imported via the IMPORT submodel (Kerkweg and Jöckel, 2015). For specifying the temporal profiles (diurnal and day-of-the-week) in the anthropogenic emissions, we first created hourly resolved time series of scaling factors to be applied to the monthly mean values using the factors shown in Figure A1. Please note that the factors have a weekly cycle, and these are normalized such that the total emission over a week is conserved for a given sector. Individual hourly time series of emission scaling factors are imported via IMPORT_TS (Kerkweg and Jöckel, 2015). The scaling factor for a specific model time step is calculated by interpolating the time series and applying to the monthly emissions and subsequently, the emissions flux and tendency (change in VMR per model time step) are calculated using the ONEMIS submodel (Kerkweg et al., 2006b). The MESSy OFFEMIS submodel (Kerkweg et al., 2006b) updates the tendencies for emissions from the sectors for which a finer temporal profile is not necessary (e.g., agriculture, waste management, refineries).

The anthropogenic emissions are vertically distributed depending on the source sectors according to the recommendation by Pozzer et al. (2009) except that the lowest injection height is reduced to 10 m as opposed to 45 m. This was necessary because the lowest level of COSMO extends from the surface to 20 m altitude, while the median lowest level height of EMAC (as used by Pozzer et al. (2009)), is about 60 m. Lightning NO_x is calculated for the global model according to the parametrizations by Grewe (2009) and transferred to the subsequent instances of COSMO using the Multi-Model-Driver (MMD) coupling of MMD2WAY submodel (Kerkweg et al., 2018). The lightning frequency was scaled to produce 2.5 Tg(N) year⁻¹ globally. Soil NO_x and biogenic emissions (e.g., isoprene and monoterpenes) are calculated online using the ONEMIS submodel separately in EMAC and individual COSMO/MESSy instances. For May 2018, soil NO_x emissions were calculated to be 17.8 and 2.4 Gg(N) for the CM07 and CM02 domains, respectively. Soil NO_x emission over entire Germany in the CM07 domain was 5.9 Gg(N) for May 2018. The soil NO_x emission calculated online are smaller as compared to the estimated 19.0 Gg(N) for May 2015 from agricultural soils and manure management sectors combined by EDGAR v5.0 (Crippa et al., 2020). Non-methane volatile organic compounds (NMVOCs) emissions were also provided as lumped group of species, which were speciated according to the recommendation by Huang et al. (2017).

Multiple AXis Differential Optical Absorption Spectroscopy (MAX-DOAS) measurements were performed using a custom-built instrument installed at the rooftop of the Max Planck Institute for Chemistry (MPIC) building (49.99 °N, 8.23 °E, 150 m amsl; the red dot in Figure 1). The instrument consists of 4 telescopes (T1, T2, T3 and T4 pointing at azimuth angles of 321, 51, 141, and 231°, respectively clockwise from the north). The intersecting arrows in Figure 1 indicate the azimuth direction of the four telescopes. Individual optical fibre bundles transmit the light from the respective telescopes to a temperature-controlled spectrograph. The spectrograph consists of a 2-dimensional (1023 × 255) CCD detector array. The incoming light of the four telescopes is projected to different row regimes of the CCD. This set up reduces the instrumental differences between the measurements to a minimum. The measurements are performed along the four viewing directions simultaneously such that all the telescopes (T1-T4) point towards the same elevation angle (EA). One complete measurement sequence for each telescope involved measurements at eight off-axis elevation angles (1, 2, 3, 5, 8, 10, 15 and 30°) and in the direction of the zenith. The field of view at 1° elevation angle was blocked partially for the different telescopes and hence was discarded from the subsequent analyses. We applied the DOAS principle (Platt and Stutz, 2008) to the measured spectra to retrieve the elevation angle dependent differential slant column densities ($dSCD$) of NO₂ and the oxygen dimer (O₂-O₂ or O₄) adapting to the fit setting described in Table C1. The $dSCDs$ can be regarded as the difference between the concentration integrated along the light path at a chosen elevation angle and the concentration integrated along the direction of the zenith. This approach is used to eliminate the stratospheric information and retrieve the tropospheric contribution.

In order to retain only the highest quality DOAS fit results, we discarded all retrievals with fit rms (root mean square) values greater than 1.0×10^{-3} . NO₂ VCDs are retrieved using the geometric approximation on the measured $dSCDs$ at 30° elevation angle. Since MECO(3) was configured to write the output for the CM02 domain at an hourly frequency as mean values, we also average the MAX-DOAS retrieved quantities (see section 2.2.2) at a similar frequency while discarding retrieval with high spectral analysis rms values.

2.2.1 Cloud classification

A cloud classification was performed using MAX-DOAS measurements of the colour index (CI; the ratio of measured signal at 330 nm and 390 nm) and the O₄ $dSCDs$ according to the method described by Wagner et al. (2016). In order to generate robust thresholds for the cloud classification, one month of data is not sufficient, and hence we used a longer time series of MAX-DOAS measurements from 27.03.2018 until 14.09.2018. We performed cloud classification separately using measurements performed by the four telescopes. Figure C1 summarizes the cloud conditions for all the days of May 2018 for telescope T2. Briefly, clear sky conditions were observed from 05-05-2018 until the afternoon of 09-05-2018. On other days, cloudy conditions were observed for several hours with sky conditions alternating between broken clouds, continuous clouds and optically thick clouds. The cloud classification results for the other telescopes were similar to that of T2.

2.2.2 Retrieval of differential box air mass factors using 3D aerosol profile inversion

As mentioned above, the $dSCDs$ retrieved from MAX-DOAS measurements depend on the differential light path between the off-axis ($EA = \alpha$) and zenith measurements. $dSCDs$ are related to the VCDs via the differential air mass factors ($dAMFs$) according to the following equation:

$$VCD = \frac{dSCD_{\alpha}}{dAMF_{\alpha}} \quad (1)$$

The O_4 mixing ratio is almost constant throughout the troposphere and its VCD only depends on the atmospheric temperature and pressure profile. Hence, using measured O_4 $dSCDs$ and the knowledge of O_4 VCDs, the corresponding $dAMFs$ can be calculated. If we visualize the atmosphere in several discrete layers, the partial $dSCD$ in a specific layer (k) would be related to the partial VCD (V_k) and the differential box air mass factor ($dbAMF_{\alpha,k}$) would be specific for the layer k in a similar way as in equation 1. $dAMF$ can be reconstructed from the $dbAMF_{\alpha,k}$ according to equation 2:

$$dAMF_{\alpha} = \frac{\sum_k V_k \times dbAMF_{\alpha,k}}{\sum_k V_k} \quad (2)$$

The presence of aerosols can change the light path, and hence the $dSCDs$ (and consequently the $dAMFs$). Profile inversion algorithms can find the optimal aerosol extinction profiles corresponding to the measured O_4 $dSCDs$ for a sequence of elevation angles (Wagner et al., 2004; Cl  mer et al., 2010; Wagner et al., 2011). This can be subsequently used to calculate the $dbAMF_{\alpha,k}$ in the discrete atmospheric layer indexed by k . In addition to the O_4 VCDs and measured $dSCDs$, the profile inversion algorithms require an offline look-up table of O_4 $dAMFs$ corresponding to various combinations of measurement geometry and aerosol extinction profiles calculated using radiative transfer models (e.g., McArtim; Deutschmann et al. (2011)).

We used the profile inversion algorithm π -MAX (Parameterized profile Inversion for MAX-DOAS measurements) (Remmers et al., in preparation), for the retrieval of the $dbAMFs$. In comparison to the traditional parametrized profile inversion algorithms (e.g., MAPA; (Beirle et al., 2019)), which only parametrizes the aerosol optical depth (AOD) and vertical profiles of aerosol extinction (e.g. shape (s) and height (h) of the profile) for a 1D retrieval (along altitude), π -MAX includes additional parameters related to the horizontal gradients in the viewing direction. Figure 2 shows the schematic of a traditional profile inversion for an example case of $AOD = 1.0$, $h = 1$ and various parametrizations of s representing the respective profile shapes as well as additional parameters g and l for π -MAX. These additional parameters describe the linear aerosol extinction change (g) from the telescope location to a specific distance (l). Hence, they allow retrievals of 2D $dbAMFs$ (and aerosol extinction profiles) as a function of distance from the telescope and altitude from the instrument, if measurement in only one azimuth direction is considered. If measurements in several azimuth directions are combined, 3D retrievals can be performed. In the current π -MAX set up, l is fixed to 10 km. The $dSCD$ measurements in all four directions are used simultaneously with the constraint that the profile at the origin (location of the instrument) is the same for all the telescopes.

The quality of the profile retrieval from π -MAX can be qualified using the rms of the $dSCD$ fit corresponding to each complete elevation sequence. In order to retain only the highest quality profile inversion results, we have retained retrievals corresponding to rms values less than 0.04 times the O_4 VCDs.

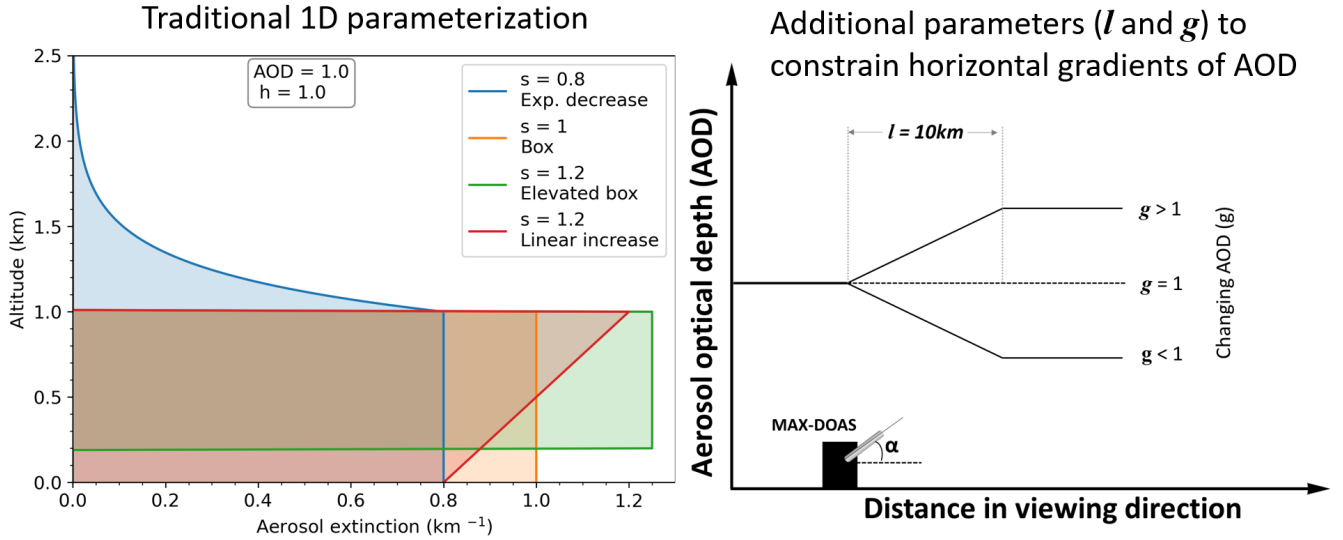


Figure 2. Left) Schematic illustration of traditional 1D parametrized profile inversion which constrains AOD, height (h) and shape (s) of the profile. The example shown here correspond to a scenario with $\text{AOD} = 1.0$, $h = 1.0$ and four different profile shapes representing exponential decrease, box profile, elevated box profile and linearly increasing profiles. Right) Additional parameters l and g further constrain the horizontal gradients of AOD for 2D profile inversion. Here, g denotes a linear change in AOD for a distance l along the viewing direction of the MAX-DOAS instrument.

2.3 In situ chemical and meteorological measurement data

We used the surface temperature, relative humidity and wind measurement data from the climate data centre of the German Weather Service (Deutscher Wetterdienst) for meteorological evaluation in the CM02 set up (DWD, 2019). Hourly measurements of surface temperature, relative humidity and wind speed are available for 304, 501 and 283 stations, respectively, in Germany for May 2018; out of these 178, 197 and 95, respectively, fall within the CM02 domain.

In situ measurements of NO_2 and O_3 are available from the German Environment Agency (Umweltbundesamt) (Minkos et al., 2019) from 410 and 266 stations, respectively, across Germany for May 2018. Among the 410 NO_2 measurement stations, 193 fall within the CM02 domain, out of which 119, 60 and 14 stations represent background, traffic and industrial locations, respectively. For O_3 , 120 stations are within the CM02 domain, out of which 109, 3 and 8 stations represent the background, traffic and industrial locations, respectively. For most of the stations within the CM02 domain, NO_2 is measured online using the chemiluminescence method, in which NO_2 is reduced to NO using a heated molybdenum converter prior to its detection (Eickelpasch and Eickelpasch, 2004). Only at Schmücke (DEUB029), a photolytic converter is used in place of the molybdenum converter, whereas at Pfälzerwald-Hortenkopf (DERP017), a CAPS (Cavity Attenuated Phase Shift Spectroscopy) instrument is used for measurement of NO_2 (<https://www.env-it.de/stationen/public/downloadRequest.do>). O_3 is measured online using UV absorption technique at all the stations. The measured in situ data are available at 1-hour resolution.

3 Results and Discussion

3.1 Meteorological evaluation: surface temperature, relative humidity and wind speed

In the online coupled MECO(n) system, COSMO/MESSy instances are not nudged directly towards the reanalysis dataset. Rather, these receive the meteorological boundary conditions from EMAC for the first instance and from the antecedent COSMO/MESSy for each subsequent instance on the four sides of the domain and the damping layer (ca. 11 km for CM50 and CM07 and 10.7 km for the CM02 domain). Hence individual COSMO/MESSy instances of MECO(n) can develop their own dynamics, which might result in a deviation from the actual meteorology. Hofmann et al. (2012) have evaluated the MECO(n) meteorology and demonstrated comparable performance with respect to a similar model with offline coupling. Here, we briefly evaluate the performance of MECO(n) in the CM02 set up with respect to the measured surface temperature, relative humidity and wind speed close to the surface.

The ability of the model to reproduce the temporal variability at multiple measurement stations can be evaluated using Taylor diagrams (Taylor, 2001), where we show the Pearson correlation coefficient (R), relative root mean square difference (RMSD) and relative standard deviation (RSD) with respect to the hourly resolution measured data. The Taylor diagrams for these parameters are shown in Figure 3.

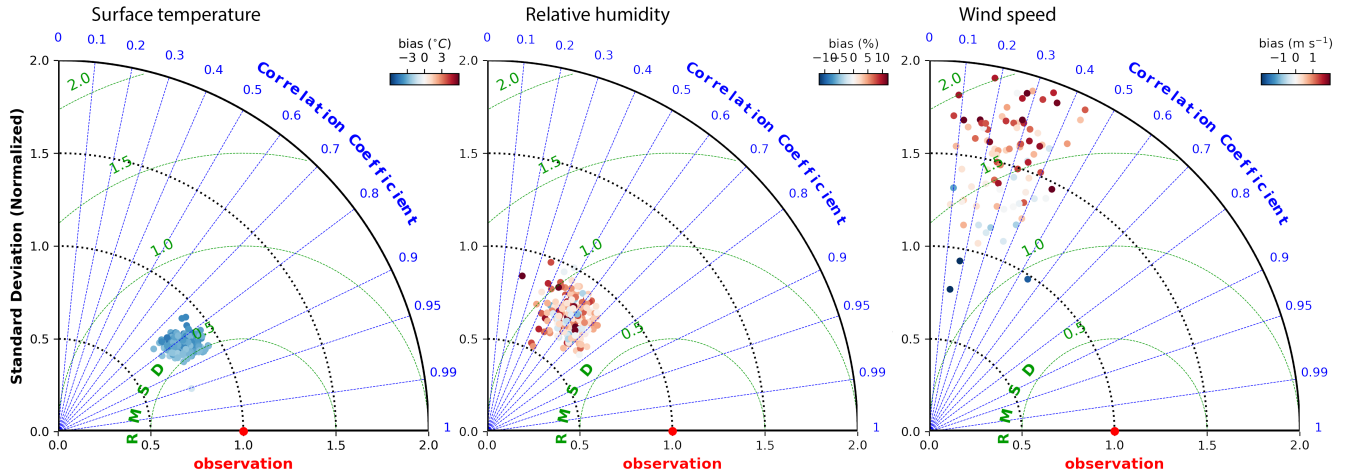


Figure 3. Taylor diagrams showing the agreement between measured and model-calculated surface temperatures (left) and relative humidity (centre) and wind speed (right). Each data point corresponds to an individual measurement station, with a total of 178, 197 and 95 stations for surface temperature, relative humidity, and wind speed, respectively

For surface temperature, the trends in the hourly resolved time series agree quite well with Pearson correlation coefficients generally between 0.8 and 0.9. The spatial patterns of the surface temperatures are also represented very well as inferred from small and precise RMSD values of circa 0.5. RSD values of less than 1 indicate that observed temporal variability in the model has a smaller amplitude than that of the measurements. There is a cold bias of ~ 3 °C across the domain, which is similar to

that observed by Mertens et al. (2016) for Germany in summer. Previous long term evaluation of the COSMO-CLM model has shown a cold bias of 2 – 2.5 °C compared to observation of the annual mean surface temperature over Germany, which increases in the summertime (Böhm et al., 2006). This bias is most probably due to inaccurate representation of root depth and soil temperature damping in the soil model. For relative humidity, the trends in the hourly resolved time series agree reasonably well with Pearson correlation coefficient generally between 0.5 and 0.7. Both positive and negative mean biases are observed for the different stations. For wind speeds, the Pearson correlation coefficients are generally between 0.2 and 0.5, but the bias was generally small and in the range of $\pm 1 \text{ m s}^{-1}$.

3.2 Evaluation of surface mixing ratios of NO₂

In this section, we present the model results for simulated NO₂ surface volume mixing ratios (VMR) and compare with the in situ observations for May 2018. Figure 4 shows the spatial distribution of monthly mean NO₂ VMRs in the lowest vertical layer (0-20 m) for the CM02 domain for the three model set ups listed in Table 1. The monthly mean VMRs from the in situ measurement stations are depicted as square, circle and pentagon markers for background, traffic-adjacent and industrial sites, respectively, overlaid on the maps using the same colour scale as that for simulated VMRs.

Overall, the spatial distribution of NO₂ VMRs is as expected, such that the high values are observed in densely populated areas, e.g., the Ruhr area, Luxembourg, around Frankfurt, Mannheim, Karlsruhe and Stuttgart. For the simulation with the high-resolution UBA emissions, we observe many details in the NO₂ surface concentration with higher values coinciding with the major motorways of Germany which were not so obvious with TNO_{fl} (e.g., A61 motorway between Köln and Bingen, A3 between Frankfurt and Bingen, A48 and A1 connecting Koblenz and Luxembourg and A4 and A9 between Gießen and Leipzig). The performance of the model in reproducing the spatial variability can be quantitatively described using the root mean square deviation (RMSD) between the monthly mean measured and simulated NO₂ VMRs for all the measurement stations combined. We note that using the high-resolution UBA emissions improves the RMSD for background locations from 3.3 ppb ($\sim 45\%$ of the measured mean) for TNO_{fl} to 2.7 ppb ($\sim 37\%$). Since UBA emissions are up to date and are available for the same year as that of simulation, the mean bias for the background locations also improves from -2.0 ppb (-27%) for TNO_{fl} to -0.5 ppb (-7%) for UBA_{fl}. At locations near heavy traffic, the bias improved from -12.5 ppb (-63%) for TNO_{fl} to -10.4 ppb (-52%) for UBA_{fl}.

Even though the anthropogenic NO_x emissions have reduced by $\sim 15\%$ over Europe from 2011 (the most recent year for which TNO emissions are available) to 2017 (EEA, 2019), total NO_x emissions over Germany are $\sim 40\%$ lower in TNO MACC III as compared to UBA. For the TNO MACC III, NO_x emissions are lower across all the sectors except for ship transport and comparable for residential and non-industrial combustion. For the two-three strongest NO_x emission sectors, e.g. road transport and energy industries, energy industries and other industries, TNO MACC III NO_x emissions (for 2011) are $\sim 30\%$ and 58% lower, 34% and 18%, respectively, lower than the UBA NO_x emissions (for 2018) (see Figure A3). Recent top-down emissions estimates over urban centres in Germany have also pointed towards an underestimation of as much as a factor of 2 from the transport sector and 1.5 overall (Kuik et al., 2018) by the TNO MACC III emissions, even by considering a conservative approach. Top down emission estimates using OMI NO₂ measurements also indicated an underestimation

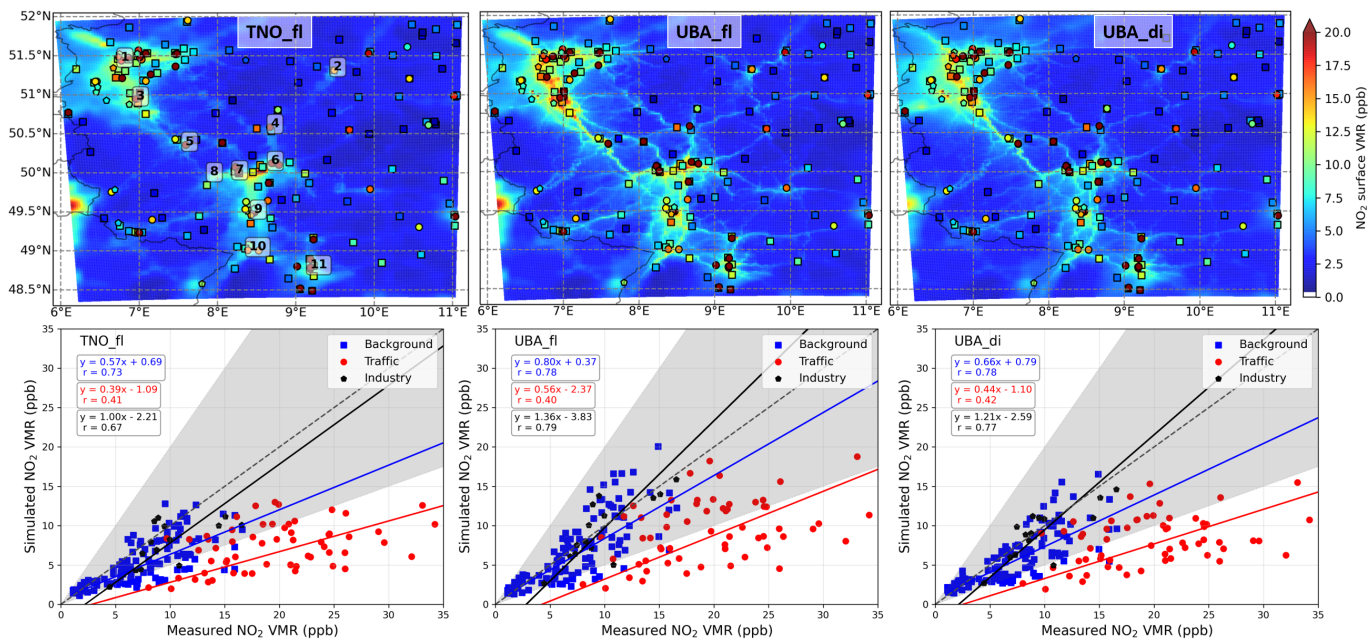


Figure 4. Top) Spatial distribution of monthly mean NO_2 surface VMRs for the three simulations using different emission inventories (left: TNO, middle: UBA without diurnal variations, right: UBA with diurnal variations) for CM02 for May 2018. The square, circle and pentagon markers overlaid on the maps represent the monthly mean measured NO_2 VMRs for background, traffic and industrial locations, respectively. The numbers on the top left panel correspond to the following German cities in decreasing order of latitude coordinate values, i.e., 1: Duisburg, 2: Kassel, 3: Köln, 4: Gießen, 5: Koblenz, 6: Frankfurt, 7: Mainz, 8: Bingen, 9: Mannheim, 10: Karlsruhe 11: Stuttgart. Bottom) Scatter plot and orthogonal distance regression weighted by the inverse of the square of the standard deviation of simulated monthly mean NO_2 surface VMRs with respect to the in situ measured values for different station types (background: blue square; traffic: red circle, and industrial: black pentagon).

of NO_x emission by more than 50% over western Germany and other parts of Europe by the TNO MACC III emission inventory (Visser et al., 2019). It should be noted that exclusion of soil NO_x emissions from the TNO MACC III inventory also contributed towards the large underestimation in the estimates by Visser et al. (2019). The underestimation of the a priori NO_x emissions is the most important factor for the large negative bias in the TNO_{fl} set up. Getting up to date emission inventories is difficult, and we could only get this data for Germany, but for future studies with simulation involving larger domains, which include more countries, it is recommended to use more up-to-date emission inventories. The situation of underestimation of NO_x emissions over Germany (and most parts of Europe) is different from that observed in the USA, where national emissions inventories are biased high by as much as 30-60% (Travis et al., 2016).

Unlike for the background locations, we do not observe a major improvement for the traffic-adjacent locations using the UBA emissions. Even at such high spatial resolution ($2.2 \times 2.2 \text{ km}^2$), the spatial smoothing leads to insufficient reproduction of peaks for locations close to strong emission sources as also documented by Shaiganfar et al. (2015). Another factor which

could contribute to the differences between measured and simulated NO_2 is related to the chemiluminescence principle used for measurements: NO_2 is first reduced to NO before subsequently reacting with O_3 generated within the analyser. This is known to overestimate the actual NO_2 , because the molybdenum converter within the analyser also reduces the NO_x reservoir species (e.g., HNO_3 , PAN) to NO prior to detection (Dunlea et al., 2007). PAN and HNO_3 are more abundant at the traffic and urban locations with a combined monthly mean mixing ratio of between 0.9 and 1.1 ppb in the UBA_{di} set up. This could account for 3 – 10% of the measured NO_2 at the traffic-adjacent locations.

Figure 5 shows a comparison of measured and the simulated NO_2 surface VMRs in the CM02 domain as Taylor diagrams for the three different simulations. Both for TNO_{fl} and UBA_{fl} , we observed rather poor agreement of the hourly temporal

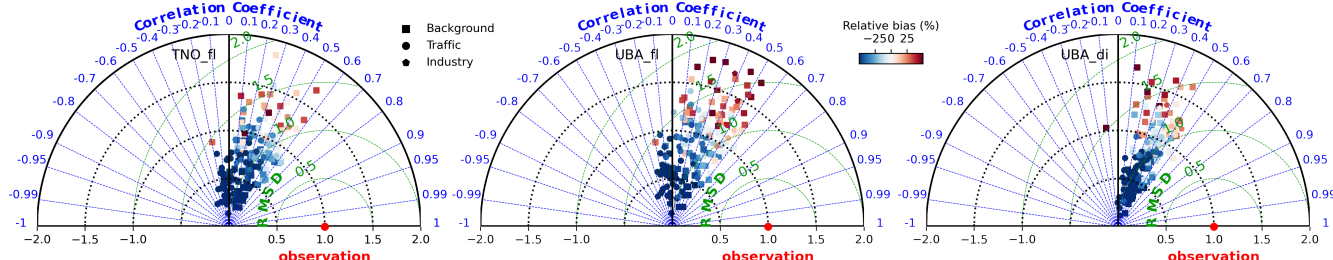


Figure 5. Taylor diagrams showing the Pearson correlation coefficients, normalized standard deviation and normalized root mean square difference corresponding to hourly resolution measured and simulated NO_2 VMRs (in CM02 domain) for background, traffic, and industrial sites represented as square, circle and pentagon markers, respectively. The left, middle and right panels correspond to the TNO_{fl} , UBA_{fl} and UBA_{di} set ups, respectively.

variations of the measured VMRs with several stations even showing negative values of R . In Germany, transport emissions account for > 45% of the total NO_x emissions, which show a large diurnal variability (greater than 200 % peak to peak; see Figure A1). These variabilities are generally not taken into account for regional model simulations and have shown to cause larger bias during peak traffic hours on weekdays (Kuik et al., 2018). In the UBA_{di} set up, accounting for diurnal and day-of-the-week variability in the anthropogenic emissions shows significant improvement with R values of between 0.3 and 0.6, smaller RMSD values and more consistent agreement for different stations. However, we also note that overall negative bias is increased for the UBA_{di} set up compared to UBA_{fl} . The diurnal profiles of emissions in the transport sector increase the NO_x amount to more than twice as much during the daytime when the atmospheric lifetime is lower and decreases to less than one quarter during the night when lifetime is high. Hence, overall, the monthly mean surface NO_2 VMR decreases when a diurnal profile is applied to NO_x emissions. The normalized standard deviation (relative to the standard deviation of measured VMRs) improves by inclusion of diurnal profiles, as we observe more stations with values in the 0.5 – 1.5 range.

Using the different COSMO/MESSy instances of the MECO(3) system, we are able to investigate the importance of model resolution if the same emission inventory is used for different model resolutions. Figure C2 shows the spatial distribution of simulated NO_2 surface VMRs and the agreement with measurements for the CM07 set up in a similar way as Figure 4 for CM02. We note that for TNO_{fl} , there is only very little further detail in the spatial distribution for CM02 as compared to

CM07. Meteorology (e.g. wind patterns) might be better resolved using a fine model resolution on individual days. Still, when
330 averaged over several days, these will be smoothed, and the spatial patterns would be limited by the resolution of the input
emissions inventory. Consequently, we also did not observe any significant improvement in the RMSD (45%) between the
monthly mean measured and simulated NO₂ VMRs as compared to the CM07 simulation (RMSD = 48%) using the TNO
MACC III emission inventory. In contrast to this, using the high-resolution UBA emissions, the spatial details as depicted in
CM02 smear out in the CM07 instance. For both, UBA_{fl} and UBA_{di} set ups, the RMSD improves from ~ 45% for the CM07 to
335 ~ 37% for CM02, showing the added value of the higher resolution simulation. Hence, for studies where small scale variability
is crucial, it is important to use a high-resolution model together with an input emission inventory of similar resolution.

Further reasons which could account for the lower bias of the NO₂ VMR in the model could be related to stronger advection
and vertical mixing. The vertical distribution of NO₂ is evaluated in section 3.3.2. Regarding advection, the wind speeds at 10
m altitude in the CM02 domain have been compared with measurements at 95 stations located within the CM02 domain (see
340 section 3.1). A small positive bias of ca. 0.5 m s⁻¹ was found. A cold bias of ~ 3 °C (a general feature of COSMO in summer
over western Europe (Böhm et al., 2006)) was observed across the CM02 domain, but that should not cause a lower bias in the
simulated NO₂ VMRs.

An evaluation of surface O₃ VMRs with respect to the in situ measurements in a similar way as that for NO₂ is discussed in
Appendix B.

345 3.3 Comparison of tropospheric columns

3.3.1 Vertical column densities

The general approach involving an evaluation of model VCDs involves summing up simulated NO₂ partial columns (concentration times height of individual model grid boxes) vertically. The same approach can be applied both for evaluation of VCDs
with respect to satellite and MAX-DOAS observations. However, different inferences can be drawn from these comparisons
350 owing to the difference in sensitivity volumes. When compared to satellite observations, a larger weight is assigned to NO₂ at
higher altitudes where satellite sensitivity is higher. Mertens et al. (2016) evaluated the NO₂ VCDs from the MECO(2) system
using SCIAMACHY observations and found that the model performed well in reproducing the spatial variability. In contrast
to the satellite observations, MAX-DOAS measurements have higher sensitivity within the boundary layer. From the CM02
domain of all three set ups, we learn that the partial column in the lowest 1 km accounts for ~ 80% of the tropospheric NO₂
355 column.

However, a generalized vertical integration on a regular model grid can introduce artefacts, because MAX-DOAS measurements are rather sensitive to air mass in the viewing direction for distances of up to a few kilometres. The artefacts increase
with increasing spatial heterogeneity. In order to consider NO₂ only in the viewing direction of the four telescopes, we first
linearly interpolated the simulated concentrations along the respective viewing directions of the telescopes (see, e.g., Figure 1).
360 The tropospheric VCDs are calculated in the following two steps: (1) summing up the partial VCDs vertically up to a height
of 4 km and (2) taking the mean of VCDs up to a fixed distance (3 km as a first estimate) only in the line of sight of the

telescope. An example time series of the simulated VCDs for the UBA_{di} set up is shown in Figure 6 along with the measured MAX-DOAS VCDs.

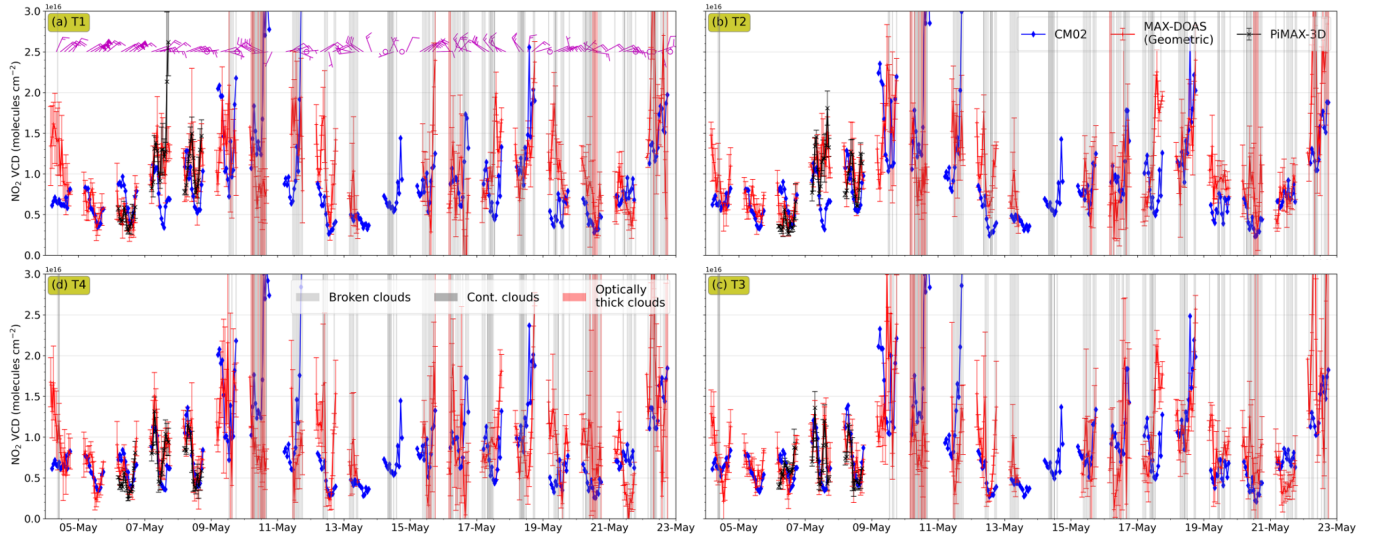


Figure 6. Comparison of NO₂ VCDs along the viewing directions of the four telescopes (T1-T4) simulated using the UBA_{di} set up in the CM02 domain. MAX-DOAS VCDs are retrieved using geometric approximation (red markers) for the complete measurement period and using π -MAX for three days (black markers). The error bars represent the hourly 1σ standard deviations. The shaded regions in the time series represent various categories of clouds as described in the legend. The purple barbs in the panel A) show the measured wind speed and wind directions, with half arrows, full arrows and flags corresponding to wind speeds of 1, 2 and 5 m s⁻¹, respectively.

Figure 7 shows the agreement between the MAX-DOAS geometric VCDs and the simulated VCDs as scatter plots for the three different set ups in different panels. The frequency distribution of the measured and the simulated VCDs are also shown next to the corresponding panels.

We observe a large scatter between the MAX-DOAS and simulated VCDs in all three model set ups, but the best agreement was observed for the UBA_{di} set up with 78% of the simulated VCDs no less than half and no greater than twice the magnitude of the measured VCDs and the best Pearson correlation coefficients ($R = 0.33$) among the three. For TNO_{fl}, large underestimation of VCDs was observed, as also seen for surface VMRs in section 3.2. The markedly lower bias (see Table C2 and C3) can be attributed to significantly lower input NO_x emissions (e.g., $\sim 40\%$ lower compared to UBA emissions over Germany for 2018). Using UBA emissions reduces the bias from 37 – 47 % to 9 – 21 % for the different telescopes. Adding diurnal variability to emissions reduces the bias further ($-1 - 13\%$), as it increases the emissions during the daytime (see Figure A1 and Table C2). While the model was able to capture the general trend in day-to-day variability, the intra-day variability could not be reproduced on most of the days. The agreement was much better on the days with clear sky conditions (4–9 May) and periods of other days with cloud-free conditions. From Tables C2 and C3 we note that the R and RMSD values improve from 0.27–0.39 and 57–67 %, respectively in the UBA_{di} set up for all measurements of all four telescopes to 0.37–0.52 and 50–53%

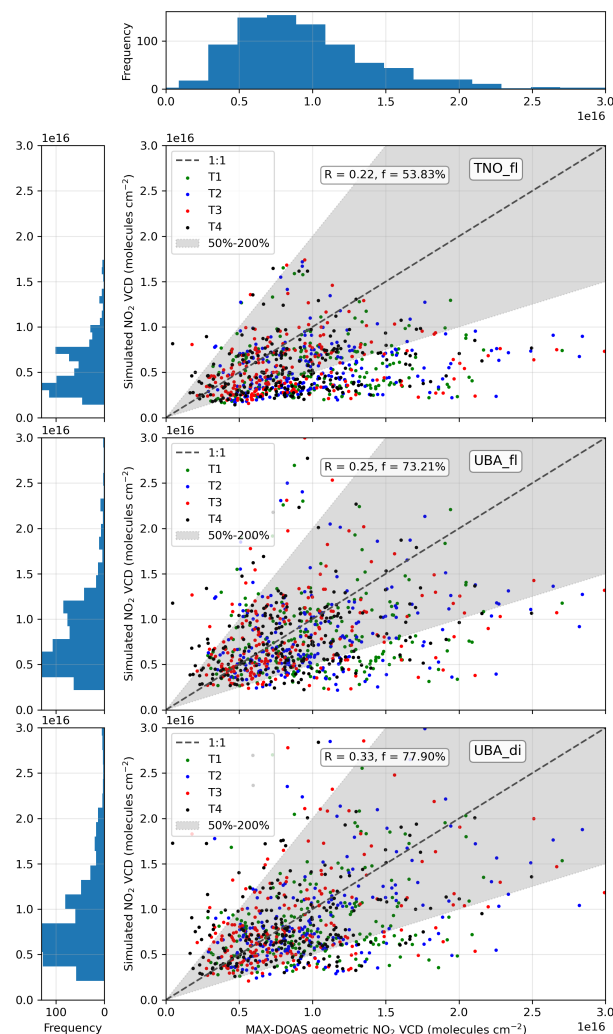


Figure 7. Scatter plot of simulated VCDs against measured VCDs for all four telescopes combined for 30° elevation angle. Individual points correspond to the hourly mean VCD values. The top, middle and bottom panels correspond to TNO_{fl} , UBA_{fl} and UBA_{di} , respectively. R represents the Pearson correlation coefficient, and f represents the fraction of simulated NO_2 VCDs no less than half and no greater than twice the magnitude of geometric VCDs. The frequency distribution of the measured VCDs are shown above the first panel and those for the simulated VCDs from the three set ups are shown on the left of the respective scatter plots.

if the analysis is restricted to cloud-free conditions. Between 5 and 9 May, the simulated VCDs matched almost exactly to the MAX-DOAS VCDs for the telescopes T3 and T4, but for T1 and T2 the agreement was not as good. Several factors can contribute to the observed differences, but there are at least two shortcomings related to VCD comparison, which hinder a conclusive assessment.

- The MAX-DOAS VCDs are calculated using the geometric approximation which assumes a single scattering event of the incoming photons above the trace gas layer. This yields reasonable VCDs for clear sky conditions with a low aerosol load scenario (Shaiganfar et al., 2011; Kumar et al., 2020). More accurate VCDs can be retrieved using the profile inversion approach, which also accounts for aerosol extinction profiles and the relative sun geometry. For the three clear sky days with low aerosol load, we also performed trace gas profile inversion using the sophisticated π -MAX approach, which also considers a linear change in NO_2 concentration along the line of sight. The VCDs retrieved using π -MAX (shown in Figure C4b) agree quite well with the geometric VCDs for these days. For most of the profile inversion algorithms used currently (Frieß et al. (2019) and references therein), it is assumed that trace gases are homogeneously distributed and that MAX-DOAS is equally sensitive within the horizontal sensitivity distance; this can be an additional source of error. Previous studies (e.g. Blechschmidt et al. (2020) and Vlemmix et al. (2015)) used the optimal estimation based profile inversion approach, which also requires an a priori estimate of the NO_2 vertical profile and can bias the model evaluation if the assumed a priori profile is similar to that simulated by the model. The averaging kernels (A_k) can be applied on the model partial column (V_k) to calculate the modified VCD (VCD_{corr}), using the a priori profile V_k^a according to equation 3, which can be directly compared to the MAX-DOAS VCDs.

$$VCD_{corr} = \sum_k \widehat{V}_k = \sum_k V_k^a + A_k(V_k - V_k^a) \quad (3)$$

For high A_k (i.e., close to 1), \widehat{V}_k is limited by the simulated V_k , whereas for low A_k (i.e., close to 0; where MAX-DOAS sensitivity is limited), \widehat{V}_k is limited by the a priori profile. Hence, the choice of the a priori profiles can impact the comparison in the latter scenario.

- While calculating the simulated VCDs, model NO_2 fields are given equal weights up to a distance of 3 km in the viewing direction and 4 km altitude. As mentioned previously, distances in both dimensions were only a first estimate and the actual MAX-DOAS sensitivity distances in both dimensions might vary according to the aerosol load, trace gas distribution, viewing geometry with respect to the sun, and presence of clouds. Moreover, even within the actual sensitivity volume, the sensitivity might vary as a function of distance from the telescope. Blechschmidt et al. (2020) have previously demonstrated that accounting for vertical sensitivity of MAX-DOAS (via averaging kernels) does not noticeably affect the simulated VCDs, because most of the NO_2 is located within the boundary layer and the averaging kernel profile has a similar shape as the model NO_2 vertical profiles. Hence, vertical sensitivity was not an issue where most of the NO_2 is located. However, if the profile is elevated, then this may no longer hold true. Nevertheless, sensitivity in the horizontal direction still needs to be accounted for, as large heterogeneity is expected close to the emission sources for short-lived species like NO_2 . The studies by Blechschmidt et al. (2020) and Vlemmix et al. (2015) proposed the relatively coarser model resolution of up to $7 \times 7 \text{ km}^2$ as one possible reason for this discrepancy. For comparison with ground-based measurements (e.g., MAX-DOAS), it is crucial to have model simulations with a grid resolution finer than or the same as the typical sensitivity ranges of the measurements. If that is not the case, spatial heterogeneity within the model grid box would result in underestimation of the enhancement and overestimation of the background values due to

415 spatial smoothing. For MAX-DOAS measurements at 30° elevation angle, the horizontal sensitivity distance (HSD) can be approximated using the boundary layer height (BLH) ($HSD = BLH / \sin \alpha$), which would be in the range of 1-3 km in the daytime. However, the exact HSD also depends on the aerosol conditions, which can vary significantly over time and should be retrieved from measurements.

In the next section, we will address these shortcomings by calculating the differential slant column densities ($dSCDs$) using the
 420 simulated NO₂. Simulated $dSCDs$ can be directly compared to the corresponding quantities derived from the DOAS analyses while also avoiding several assumptions and approximations discussed earlier. The $dbAMFs$ used for $dSCD$ calculation inherently account for the aerosol conditions and hence also address issues related to spatial sensitivity (see section 2.2.2). This also provides a way for quantification of the horizontal sensitivity distances of MAX-DOAS measurements.

3.3.2 Slant column densities

425 Calculation of simulated $dSCDs$

For calculation of $dSCDs$ from the model simulated NO₂ fields, we mimic the viewing geometry and sensitivity volume corresponding to MAX-DOAS measurements using the differential box air mass factors as described in section 2.2.2. Using MAX-DOAS, we probe the vertical and horizontal variation of NO₂ concentrations by measuring at various elevation angles. The sensitivity of the MAX-DOAS measurements at a given elevation angle (EA) is described by the differential box air mass
 430 factors ($dbAMFs$). An example of the $dbAMFs$ along the viewing direction of telescope T1 for 09-05-2018 14:00 UTC for EAs ranging from 3 to 30° is shown in Figure 8. In each viewing azimuth (corresponding to T1-T4) and for each EA (α ; between 2 and 30°) we perform a two-dimensional summation of partial VCDs ($V_{i,k}$) weighted by the differential box air mass factors ($dbAMF_{\alpha,i,k}$)(unit-less), along the distance from MAX-DOAS (indexed as i) and altitude above the instrument (indexed as k):

$$435 \quad dSCD_{\alpha} = \sum_{i,k} V_{i,k} \times dbAMF_{\alpha,i,k} \quad (4)$$

with

$$V_{i,k} = c_{i,k} \times dh_{i,k} \quad (5)$$

Where, $c_{i,k}$ and $dh_{i,k}$ represent the concentration (molecules cm⁻³) of trace gas in the grid with a thickness of $dh_{i,k}$ (cm).

Using equation 4, we can estimate the EA dependent horizontal sensitivity distances (HSD) in the viewing direction of the
 440 MAX-DOAS as the distance from the instrument which accounts for 90% of the simulated $dSCDs$. Fig C3 shows the HSD for all the off-axis elevation angles for the four telescopes. The mean HSD increases from 3-4 Km for 30° EA to 8-9 Km for 3° EA. In contrast to the comparison of the geometric VCDs in the previous section, which is limited to only one EA, we can evaluate the $dSCDs$ at various EAs with varying sensitivity volume from the location of the instrument. Additionally, while calculating the $dSCDs$, we also account for the horizontal heterogeneity and varying sensitivity within the sensitivity volume
 445 in the viewing direction.

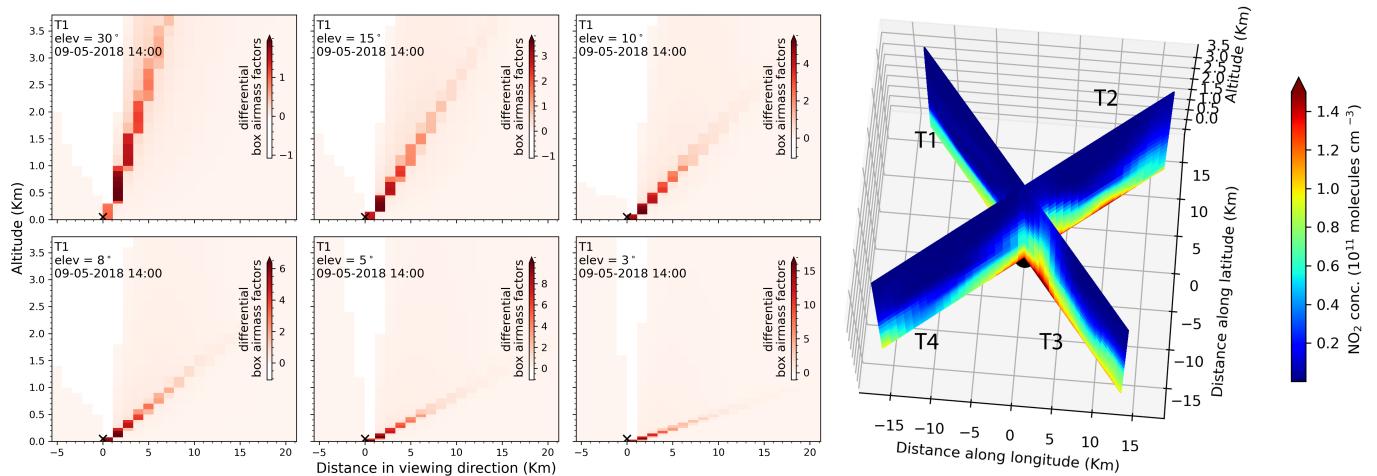


Figure 8. Left) The differential box air mass factors ($dbAMFs$) for 30, 15, 10, 8, 5 and 3° elevation angles retrieved using 3D profile inversion of measured O_4 $dSCDs$ along the direction of telescope T1 . Please note the different colour scales of differential $dbAMFs$ used for the different elevation angles. Right) Simulated NO_2 concentrations from the UBA_{di} set up in the CM02 domain from surface up to an altitude of 2.5 km along the viewing directions of the four telescopes T1, T2, T3 and T4 on 09-05-2018 14:00 UTC.

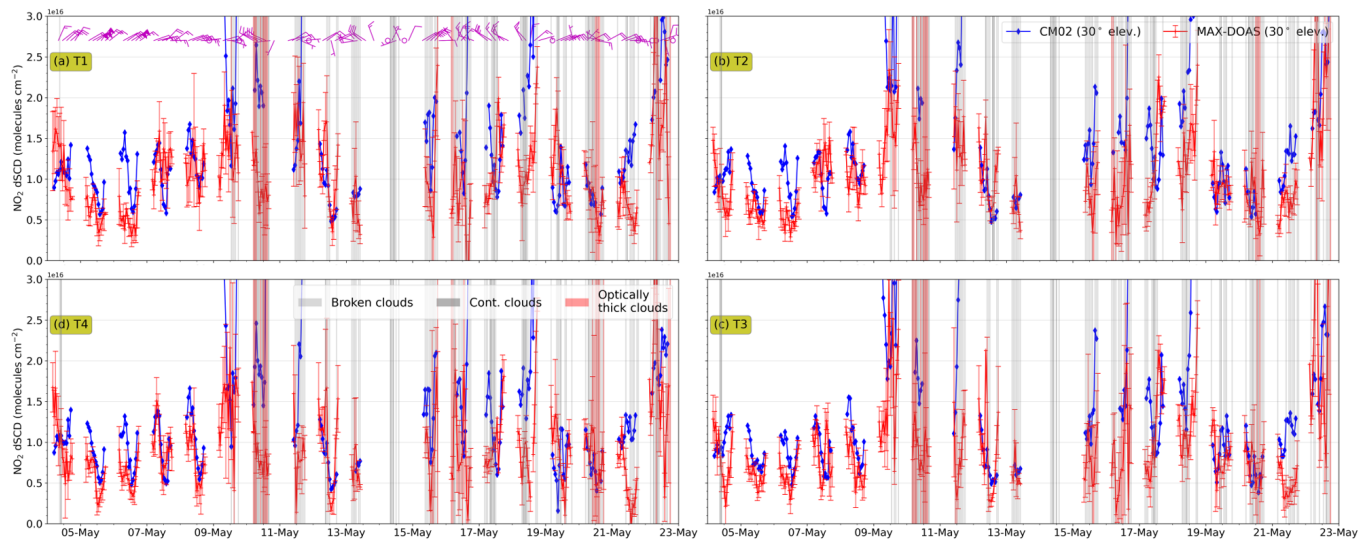


Figure 9. Comparison of NO_2 differential slant column densities at 30° elevation angle of the four telescopes simulated using UBA_{di} in the CM02 domain. The shaded regions in the time series represent various categories of sky conditions as described in the legend.

Figure 9 shows an example time series of measured and simulated $dSCDs$ for UBA_{di} for 30° EA. Comparing these values to the VCDs shown in Figure 6, we observe that the simulated $dSCDs$ are higher than the calculated VCDs as shown in the

previous section, implying $dAMFs$ at 30° EA are larger than 1. This is also observed under the cloud-free conditions, which corroborates the drawback in the geometric approximation and assumption of spatial homogeneity in the viewing direction.

450 Evaluation of simulated $dSCDs$

Figure 10 shows the distribution of measured and simulated $dSCDs$ (different colours for the different model set ups described in Table 1) for the various elevation angles as box and whiskers plots for the four telescopes in separate panels. Measurements performed at low EAs have large light paths and are more sensitive to air mass close to the surface (higher $dbAMFs$; see Figure 8), and hence larger $dSCDs$ are observed for the low EAs. Surprisingly, we did not observe major differences in the

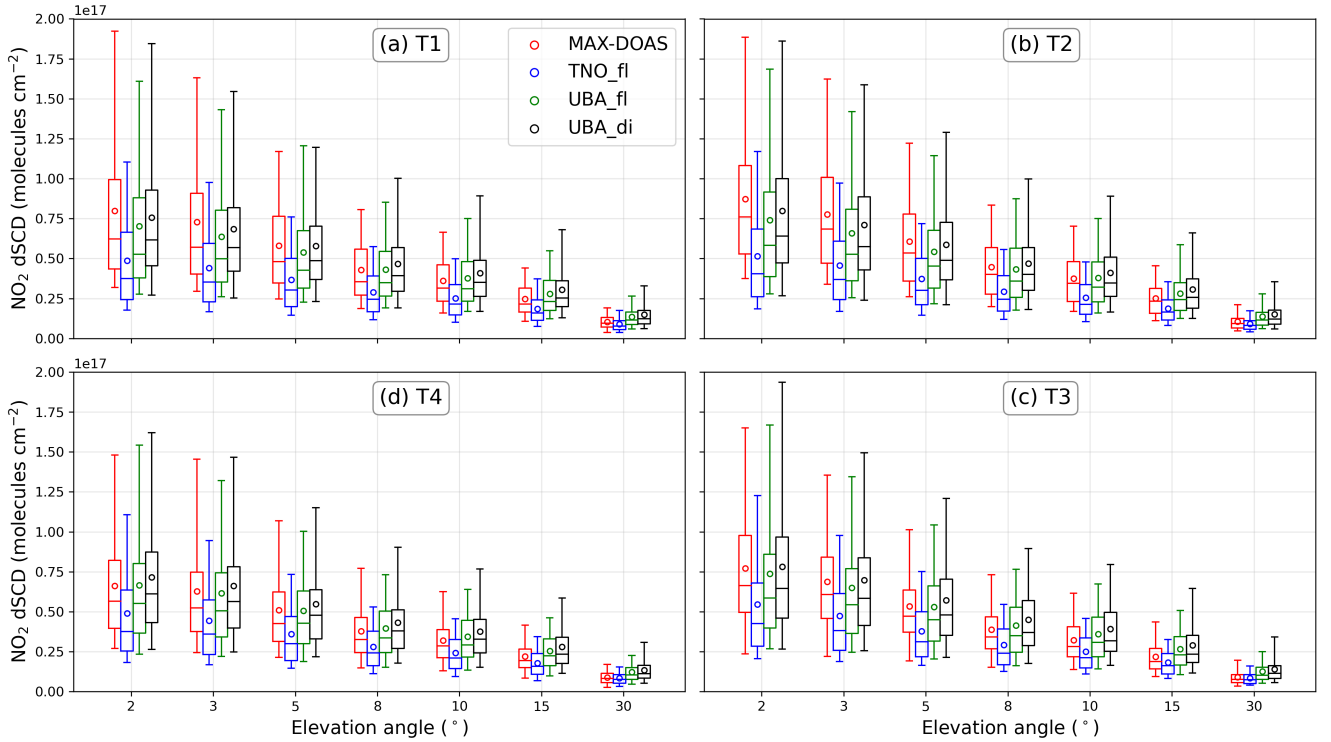


Figure 10. Box and whiskers plots for the different telescopes (panel a - d) showing the distribution of measured and simulated $dSCDs$ for the three different model set ups (depicted in different colours) for various elevation angles (2° , 3° , 5° , 8° , 10° , 15° and 30°).

455 measured as well as simulated $dSCDs$ among the four telescopes, besides slightly higher values for T2, which points towards the city centre of Mainz and lower values for T4, which spans mostly agricultural lands for a distance of 10 km. This can partially be explained by the prevailing wind directions (panel (a) of Figure 6), as for most of the time, easterly winds bring the air mass from the urban locations to the agricultural lands.

Figures 9 and 11 show example time series of measured and simulated $dSCDs$ (for UBA_{di}) for 30° and 3° EAs, respectively.
 460 Various statistical parameters corresponding to the agreement between MAX-DOAS and model simulation for individual tele-

scopes and EAs are summarized in Table C2 for all measurements and in Table C3 for cloud-free cases only. For 30° EA we did not observe any significant change in the agreement of temporal variability (i.e. R) between model and MAX-DOAS, whether we compare $dSCDs$ or VCDs. However, significantly more information is gleaned with respect to the available $dSCDs$ corresponding to all the off-axis EAs at which measurements were performed. Instead of comparing only one VCD value for a complete elevation sequence, we include $dSCDs$ corresponding to each of the elevation angles. For example, in Figure 11, we observe a much better agreement between the measured and simulated $dSCDs$ at 3° EA, especially on the cloud-free days. In Figure 12, we show the comparison of measured and simulated $dSCDs$ for the three different model set ups in different

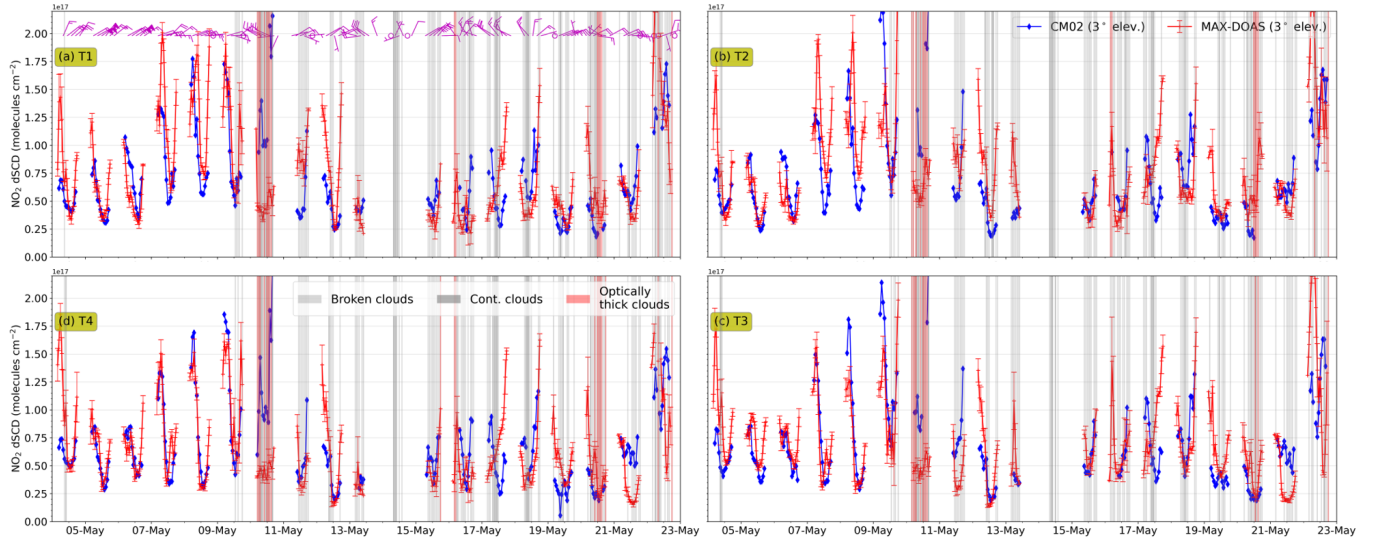


Figure 11. Same as Figure 9 but for 3° elevation angle

panels for all the EAs and all the telescopes. The frequency distribution of the measured $dSCDs$ at various EAs are shown above the top panel, while those for the simulated $dSCDs$ are shown in the panels left of the scatter plot of the corresponding model set ups. We observe a good correlation between the measured and simulated $dSCDs$ ($R = 0.63, 0.62$ and 0.67 for TNO_{fl} , UBA_{fl} , and UBA_{di} , respectively), which further improves ($R = 0.66, 0.65$ and 0.74) if the comparison is restricted to cloud-free cases only. Similar to the VMR and VCD comparisons, the best accountability was observed for UBA_{di} , with $\sim 82\%$ for the simulated $dSCDs$ no less than half and no greater than twice the magnitude of the measurements for cloud-free cases. The frequency distribution of the measured $dSCDs$ follows a right-skewed normal distribution for all the EAs, which is also represented best by the UBA_{di} set up. The width of the peak of the frequency distribution broadens from high to low EAs, representing a larger scatter in the measurements at low EAs. For UBA_{fl} , the extreme values (less than half or more than double of measurements) were mostly observed for cloudy sky conditions. Since clouds are not considered in the radiative transfer simulations and therefore also not in $dAMF$ retrieval, these only affect the measured $dSCDs$. The improved agreement between simulated and measured $dSCDs$ for the cloud-free conditions are more obvious for the individual EAs (see Tables C2 and C3) with significantly higher Pearson correlation coefficients and smaller RMSD values.

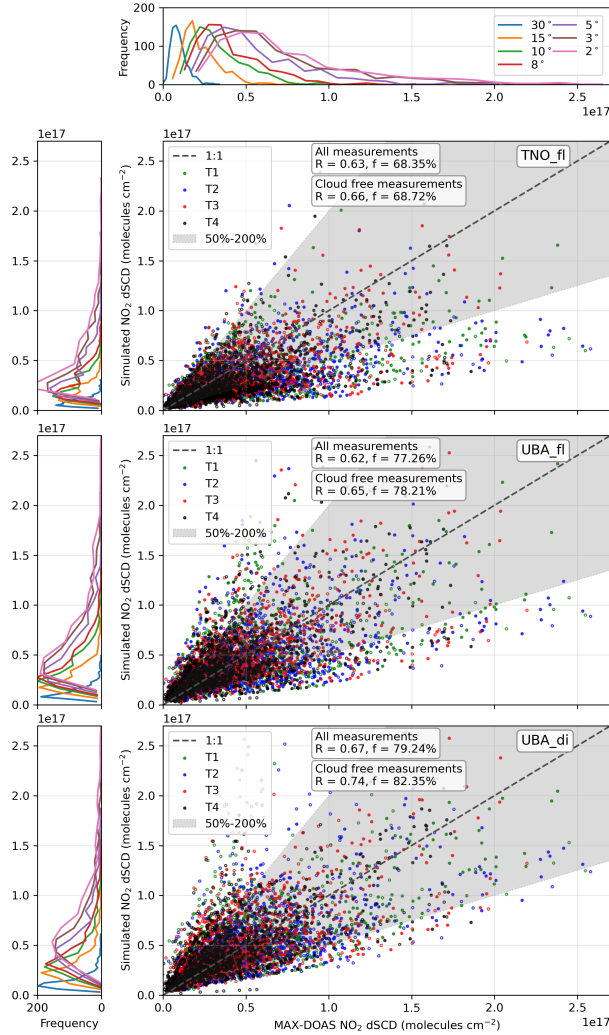


Figure 12. Scatter plot of simulated $dSCDs$ against measured $dSCDs$ for all the four telescopes combined for the elevation angles 2, 3, 5, 8, 10, 15 and 30°. The filled circles correspond to the cloud-free scenarios, while the empty circles correspond to the cloudy conditions. The Pearson correlation coefficient (R) and the fraction of simulated $dSCDs$ within 50-200% of the measurements (f) are annotated in the respective panels in grey for all measurements and in black for cloud-free conditions only. The top, middle and bottom panels correspond to TNO_{fi}, UBA_{fi} and UBA_{di} respectively. The frequency distribution of the measured $dSCDs$ is shown above the first panel, and those for the simulated $dSCDs$ from three set ups are shown on the left of the respective scatter plots.

From Tables C2 and C3, it can be inferred that the agreement between measured and simulated $dSCDs$ improves at lower EAs, which also indicates a better performance of the model in the layers close to the surface. For example, both for the UBA_{fi} and UBA_{di} set ups, a large positive bias in the range 27 – 42% was observed at 30° EA, but for low EAs (e.g. $\leq 8^\circ$) small biases in the range of +7 and -15% were observed for all the azimuth directions in the cloud-free cases. However, more pronounced

negative biases were observed for TNO_{fl} simulation even at low elevation angles. A positive bias at 30° EA is most likely due to the stronger vertical mixing in COSMO/MESSY as also indicated by Mertens et al. (2016). Due to the stronger mixing, a large fraction of NO_2 reaches at higher altitudes in the model, which has a strong weight for the $dSCD$ calculation at high EAs.

Previous studies in which models were compared with MAX-DOAS indicated that the major disagreements arise due to weekday and weekend differences and inappropriate representation of the diurnal cycle of emissions (Blechschmidt et al., 2020; Vlemmix et al., 2015). We use the measurements at a low elevation angle (e.g. 3°) to investigate if the model can reproduce the measured diurnal profiles and weekday-weekend differences of NO_2 $dSCDs$. A low elevation angle was chosen because the corresponding measurements have higher sensitivity close to the ground where a major fraction of NO_x is emitted from sectors which show strong diurnal variability.

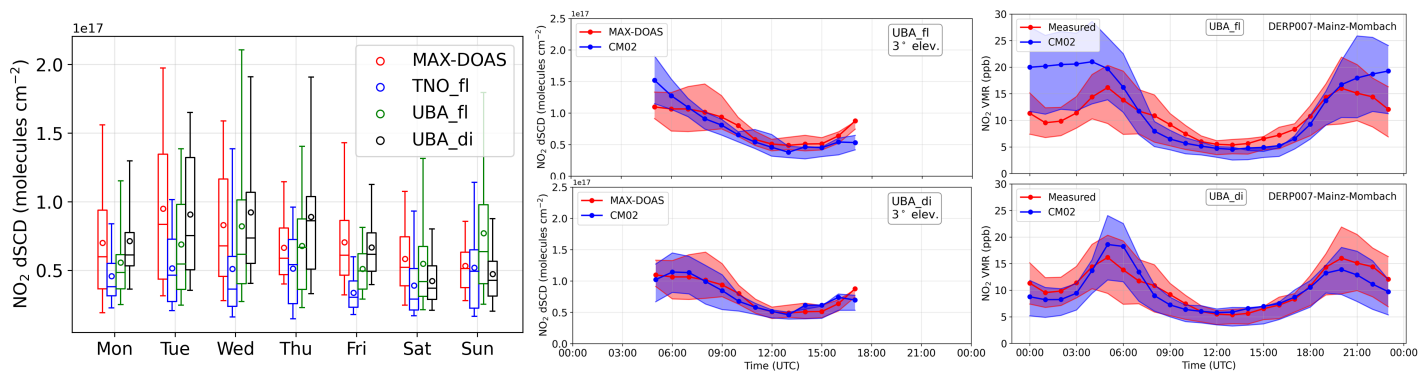


Figure 13. Left) Box and whiskers plot showing the distribution of NO_2 $dSCDs$ at 3° elevation angles for MAX-DOAS and the three different model set ups for different days of the week. Centre) Mean hourly diurnal profiles of measured and simulated NO_2 $dSCDs$ at 3° elevation angle for T1 for UBA_{fl} (top) and UBA_{di} (bottom) set ups. The shaded region above and below the mean line denote the 75th and 25th percentiles, respectively. Right) Diurnal profiles of measured and simulated NO_2 surface VMRs measured at a background site Mombach (~ 3.5 km north of MPIC) for UBA_{fl} (top) and UBA_{di} (bottom) simulations.

The left panel in Figure 13 shows the distribution of measured and simulated NO_2 $dSCDs$ at 3° EA, for all telescopes combined, binned according to the day of the week. The diurnal profiles of the measured and simulated $dSCDs$ are shown in the middle panel of Figure 13 for UBA_{fl} in the top panel and for UBA_{di} in the bottom panel. A similar plot for NO_2 surface VMR at the background site Mombach (~ 3.5 km north of MPIC) is shown in the right panel. The lowest measured $dSCDs$ are observed on the weekends. However, such a distinct weekday-weekend difference was not observed for TNO_{fl} and UBA_{fl} simulations, supporting the fact that the observed differences were primarily because of change in emissions and not due to varying meteorological conditions. Smaller weekend $dSCDs$ were only for the UBA_{di} set up which also accounts for weekday and weekend differences in NO_x emission from the transport and residential combustion sectors. Concerning the diurnal variation, both UBA_{fl} and UBA_{di} show ~~similar $dSCDs$~~ smaller NO_2 $dSCDs$ and surface VMRs during the daytime which ~~also agrees~~ agrees reasonably well with the measurements in both set ups. However, stronger discrepancies are observed

505 during early morning and late evening hours. Comparison of surface VMRs provide further information about the for UBA_{fl}. The discrepancy is even larger for the UBA_{fl} surface concentration at night-time, where even a larger difference is observed between the two model set-ups, has a short lifetime of a few hours in the daytime, which together with a strong mixing in the daytime boundary layer compensates even for (Figure 13). While emissions primarily drive the surface VMRs during night-time, dilution in the higher boundary layer and chemical loss due to OH in the daytime counters the stronger emissions.

510 We further investigated the diurnal patterns of VCDs and surface VMRs in the UBA_{fl} set-up (Figure C4), and found that the magnitude of diurnal modulation in the hourly mean was ~50% higher emissions (an increase in emissions from the transport sector by a factor of two would translate to an overall increase of ~350% peak to peak, while the same was ~50% in ~80% for VCDs. This difference in the magnitude of diurnal variability indicates a stronger role of the boundary layer height evolution as compared to the chemical loss due to short lifetime towards off-setting the effect of higher NO_x emissions). The use of

515 diurnal emission profiles has the strongest effect on the simulated VMRs and dSCDs when the atmospheric lifetime of is longer emissions during the daytime. From Figure 13, it is evident that the use of diurnally varying emissions is necessary to reproduce the observed diurnal variability of NO₂. For the complete time series of dSCDs, we also observe much improved Pearson correlation coefficients in the range of 0.5 and 0.8 if diurnal and day-of-the-week variability in emissions are considered in UBA emissions as compared to those simulated using “flat” emission profiles (see Table C3). For model studies concerning

520 satellite measurement having afternoon overpasses (e.g. OMI, TROPOMI), consideration of these factors for the anthropogenic emissions will have a relatively weak effect in our study domain or similar urban environments. For the biomass burning regions (e.g. tropical forests, southern Africa), strong NO_x emissions are typically observed during mid-day, which results in a diurnal profile of NO₂ columns with a broad daytime peak (Boersma et al., 2008). Consideration of diurnal profiles of emissions in model simulations is crucial for comparisons with satellite observations in these regions (Miyazaki et al., 2012; Boersma et al.,

525 2008).

4 Conclusions

We performed high spatial resolution (up to 2.2×2.2 km²) regional model simulations focused on south-west Germany to evaluate the short-lived pollutant NO₂ using MAX-DOAS and a network of in situ measurements. Three different MECO(3) simulations were performed in order to investigate the importance of model spatial resolution and the influence of spatial and

530 temporal resolution of input emission inventories. Anthropogenic emission inventories generally used for model simulations (e.g. TNO MACC for Europe) do not cover the most recent periods in most of the cases and are available at spatial resolutions coarser than that of the model. We show that the spatial patterns of NO₂ are best reproduced in the UBA_{fl} set up, in which an up to date and high-resolution (1×1 km²) input emission inventory (UBA) is used. In the UBA_{di} set up, use of accurate temporal profiles (e.g. diurnal and day of the week) of the road transport and residential combustion emissions improves the

535 agreement of the temporal profiles at individual measurement stations. An improved agreement was observed at the background and industrial locations with an overall bias of less than 10% for the UBA_{di} set up. However, the model largely underestimates the NO₂ VMRs (by up to 50%) at the traffic-adjacent locations. For the background locations, the mean diurnal profiles

were accurately simulated in the UBA_{di} set up. Biases were stronger if the fine resolution emissions were used for a coarser resolution model simulation (e.g., $7 \times 7 \text{ km}^2$). In contrast, a finer resolution model employing a coarse emission inventory did not result in the addition of large spatial details.

We employed the measurements of a 4-azimuth MAX-DOAS instrument from Mainz to first compare the tropospheric NO₂ VCDs. The day-to-day variability was reasonably well reproduced by the model in the UBA_{di} set up for all four viewing directions with biases of between -10% and 2%. To further augment the surface VMR and tropospheric VCD evaluation, we apply a consistent approach of comparison of the so-called differential slant column densities (*dSCDs*), which, we suggest, comes with several advantages. Firstly, *dSCDs* are available for a number of elevation angles, each of which has distinct sensitivities to the different vertical level of the troposphere. Hence, this approach enables an evaluation of the vertical distribution of NO₂ in the model. Additionally, the horizontal sensitivity distance of the MAX-DOAS instrument also changes for different elevation angles, as described by the corresponding differential box air mass factors. Hence, when using the measurement at one single location, model evaluation can be performed for various sensitivity volumes. Secondly, as compared to the VCD comparison, which gives one comparable quantity per complete elevation sequence of MAX-DOAS measurements, *dSCDs* provide a way to evaluate the simulation against the measured values for each elevation angle. Finally, for the *dSCD* comparison, we succeed in overcoming the uncertainties introduced by the assumption of a homogeneous spatial distribution of NO₂ and in some cases a priori estimates of its vertical distribution for the retrieval of VCDs from the MAX-DOAS measurements.

We evaluated the simulated *dSCDs* in the four azimuth direction for seven elevation angles (EA) ranging from 2° to 30°. We observe a similar variation of measured and simulated *dSCDs* for various EAs indicating a reasonable vertical distribution of NO₂. The agreement between model and simulation improved for lower elevation angles indicating better accountability at near-surface layers. The agreement further improved, if only the measurements in cloud-free conditions were considered for the comparison. We did not observe large differences in the measured *dSCDs* in the four azimuth direction because of the prevailing wind direction from urban areas. We also show that the consideration of diurnal profiles of the anthropogenic emissions is crucial for comparison with NO₂ *dSCDs* and VMR measurements for early morning and night time hours. For the afternoon hours, however, even up to 50% higher anthropogenic NO_x emissions only have a minor effect on ambient VMRs and *dSCDs* due to [enhanced dilution in the high daytime planetary boundary layer and](#) its short atmospheric lifetime.

Over the last two decades, several MAX-DOAS measurements have been reported from locations across the world, which have substantially contributed to the evaluation of satellite observations. We think that the complexity and uncertainties involved in VCD retrieval from the MAX-DOAS measurements have so far hindered a similar scale application in model evaluation. The consistent *dSCD* comparison approach proposed in our study validates such usage of these valuable datasets, which can be used to evaluate the vertical distribution of trace gases within the boundary layer.

Code availability. The Modular Earth Submodel System (MESSy) is a multi-institutional project, and its license is available to the affiliates of these institutions. Affiliation to MESSy can be obtained by signing the MESSy Community End-User Licence Agreement (EULA) and accepting the MESSy Software Licence Agreement (SLA) available at www.messy-interface.org. ECHAM5 model is available under

the Software Licence Agreement of the Max Planck Institute for Meteorology, Hamburg. The COSMO model can be obtained either by institutional license provided by the German Weather Service (DWD) or individual license provided by the CLM-Community. Further details about the CLM community is available at <https://wiki.coast.hzg.de/clmcom>.

575 *Data availability.* TNO MACC III emission data (Kuenen et al., 2014) is provided by Jeroen J.P. Kuenen and Hugo A.C. Denier van der Gon at the TNO, Princetonlaan 6, 3584 CB Utrecht, The Netherlands by signing the disclaimer and conditions for data use. The UBA anthropogenic emission data is made available by the German Environment Agency (Umweltbundesamt). Further details about the UBA emissions are available at www.umweltbundesamt.de/deutschland-karten-zu-luftschadstoff-daten. The hourly resolution measured data for NO₂ and O₃ is also provided by Umweltbundesamt and can be freely downloaded via the web interface www.umweltbundesamt.de/en/data/air/air-data/stations. The meteorological data used for model evaluation are provided by the German Weather Service (DWD) via the climate data centre web interface available at <https://cdc.dwd.de/portal>.
580

Appendix A: Temporal profiles and sector contributions of emissions

Both TNO MACC III and UBA emissions are available at a temporal resolution of one year. The monthly profiles of the anthropogenic emissions depend on the emitted species, emissions sectors and the country. For Europe, these factors are also provided by Builtjes et al. (2002), and, are used to create monthly resolution emissions. Builtjes et al. (2002) and Schaap et al. (2005) also provide recommendations for sector-specific fine temporal profiles (day of the week and diurnal) of emissions (see Figure A1). The fine temporal profiles are applied only in the UBA_{di} set up using the MESSy ONEMIS submodel as described in section 2.1. The recommendation of Builtjes et al. (2002) and Schaap et al. (2005), however, do not differentiate between the diurnal profiles of emission between weekdays and weekends, which is crucial for the road transport emissions. Hence, for the road transport sector, we used the actual hourly vehicle count on the A60 motorway for 2018, and derived the temporal emission profiles assuming a direct scaling between the number of vehicles and emissions. The actual vehicle counts are provided by the automatic vehicle counter and are available at www.bast.de/BASSt_2017/DE/Statistik/statistik-node.html. From Figure A1, we note that for weekdays, the derived profiles look similar to those recommended by Schaap et al. (2005). However, for the weekend, the shape of the diurnal profiles are markedly different from the factors derived using actual vehicle counts, which show a single broad afternoon peak.
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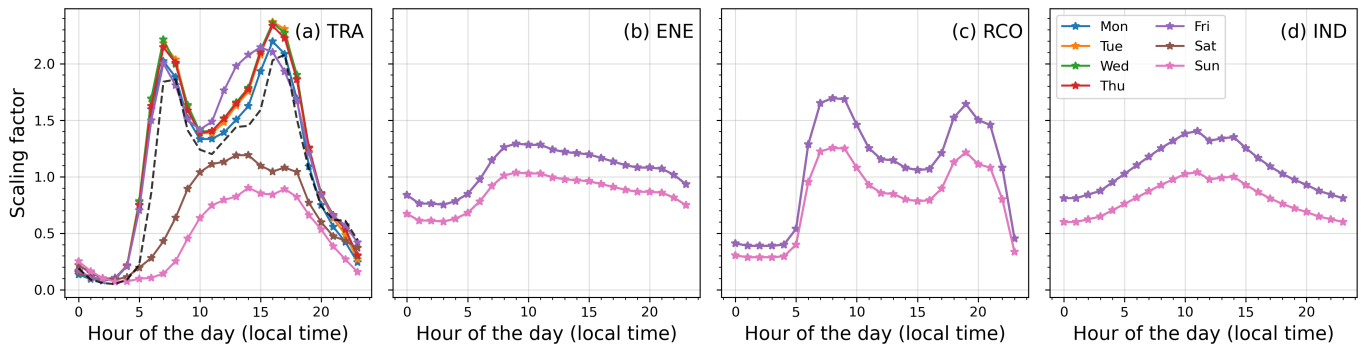


Figure A1. Temporal profiles of NO_x emissions from various sectors. “TRA”: Road transport, “ENE”: Energy generation, “RCO”: Residential and non-industrial combustion, “IND”: Industries. For “TRA”, lines and markers correspond to the profiles derived using actual vehicle count, while for others, profiles are derived according to the recommendation of Schaap et al. (2005). For “TRA”, the recommendation of (Schaap et al., 2005) are shown as the dashed line in panel (a).

595 Please note that the current implementation of incorporation of diurnal emission factors is limited to surface emissions. Since for “ENE” and “IND” sectors, a significant fraction is emitted at high altitudes, the day of the week and diurnal profiles could not be applied to these sectors. However, from Figure A1, we note that these temporal variations are not as strong as for “TRA”(> 200% peak to peak) and “RCO” (> 120% peak to peak) sectors. Moreover, for Germany, “ENE” and “IND” account for only ca. 14% and ca. 18% of the total NO_x emissions as compared to ca. 45% from “TRA” only. Hence, we only expect
600 a minor effect of including the day of the week and hourly temporal factors of emissions of “ENE” and “IND” sectors on the total NO_x emissions.

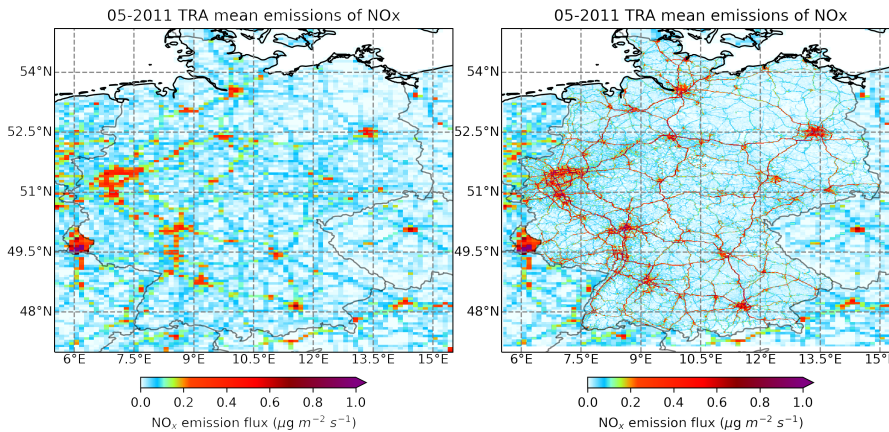


Figure A2. NO_x emission flux from the road transport sector for left) TNO MACC III emissions for May 2011 (Kuenen et al., 2014) and right) composite UBA with Germany (May 2018) and TNO MACC III emissions outside Germany (May 2011)

Figure A3 shows the contribution of different sectors to the total NO_x emissions in the TNO MACC III (for 2011) and UBA inventory (2018) for Germany. The individual sectors are Agriculture (AGR), Energy industries (ENE), Other Industries

(IND), Residential and non-industrial combustion (RCO), Fossil fuel production and distribution (REF), Water navigation (SHP), Solvent and other product use (SOL), Road transport (TRA) and Waste collection, treatment and disposal activities (WST). The major under-representations of the TNO MACC III emissions are the sectors road transport, energy industries and other industries, while ship emissions are higher in TNO MACC III. It should also be noted that agricultural emissions are not included in TNO MACC III inventory (Kuenen et al., 2014), while these are included in UBA inventory. Here we would like to point out that in our simulations using UBA emissions, emissions due to use of organic and inorganic fertilizers are doubly counted within Germany, as these are also calculated online using the ONEMIS submodel. We have checked the contribution of these two sources in the total NO_x emissions within Germany and these are 8% of the total. However, this is within the uncertainty of the NO_x emissions in the inventories which are in the order of 20% (Solazzo et al., 2021).

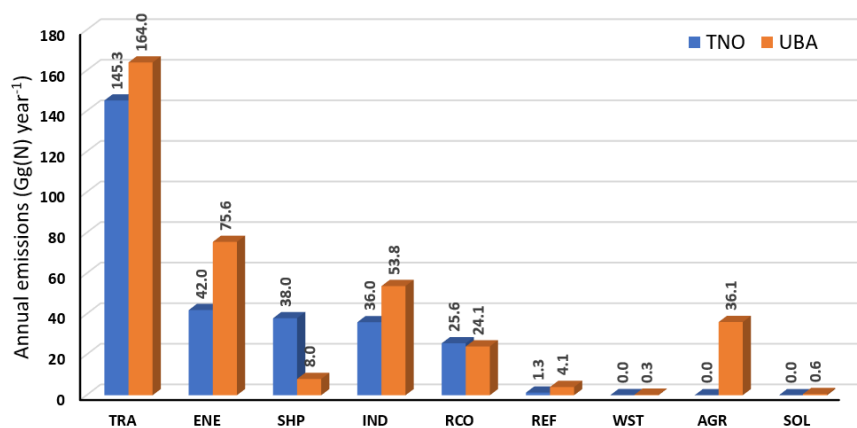


Figure A3. Contribution of individual sectors towards the total NO_x emissions within Germany for the TNO MACC III emission inventory for 2011 (blue) and UBA emission inventory for 2018 (orange).

Appendix B: Evaluation of surface mixing ratios of O_3

Figure B1 shows the spatial distribution of the monthly mean O_3 VMRs and agreement with respect to the measured values in a similar way as for NO_2 in Figure 4. We observe a rather smooth spatial distribution of O_3 as compared to that of NO_2 , with high values relatively far from the NO_2 hotspots. We observe an overestimation for smaller O_3 VMRs for all three model set ups. Since ozone is formed photochemically in the troposphere, we have further investigated the agreement separately for daytime (07:00-18:00 UTC) and night time for the UBA_{di} set up in Figure B2.

During ~~night-time~~night-time, we observe a general overestimation by $\sim 37\%$ for all the measurement stations combined. However, during daytime, we observed much better agreement with a relative bias of $\sim -5\%$. ~~This indicates a relatively weaker amplitude of diurnal variability in the simulations.~~ Mertens et al. (2016) have previously investigated the ~~positive-bias-weak amplitude~~ of simulated O_3 for-, such that night-time values are overestimated and daytime values are represented well in a coarser resolution ($\sim 12 \times 12 \text{ km}^2$) MECO(n) simulation. They have shown that COSMO/MESSy ~~simulates a relatively~~

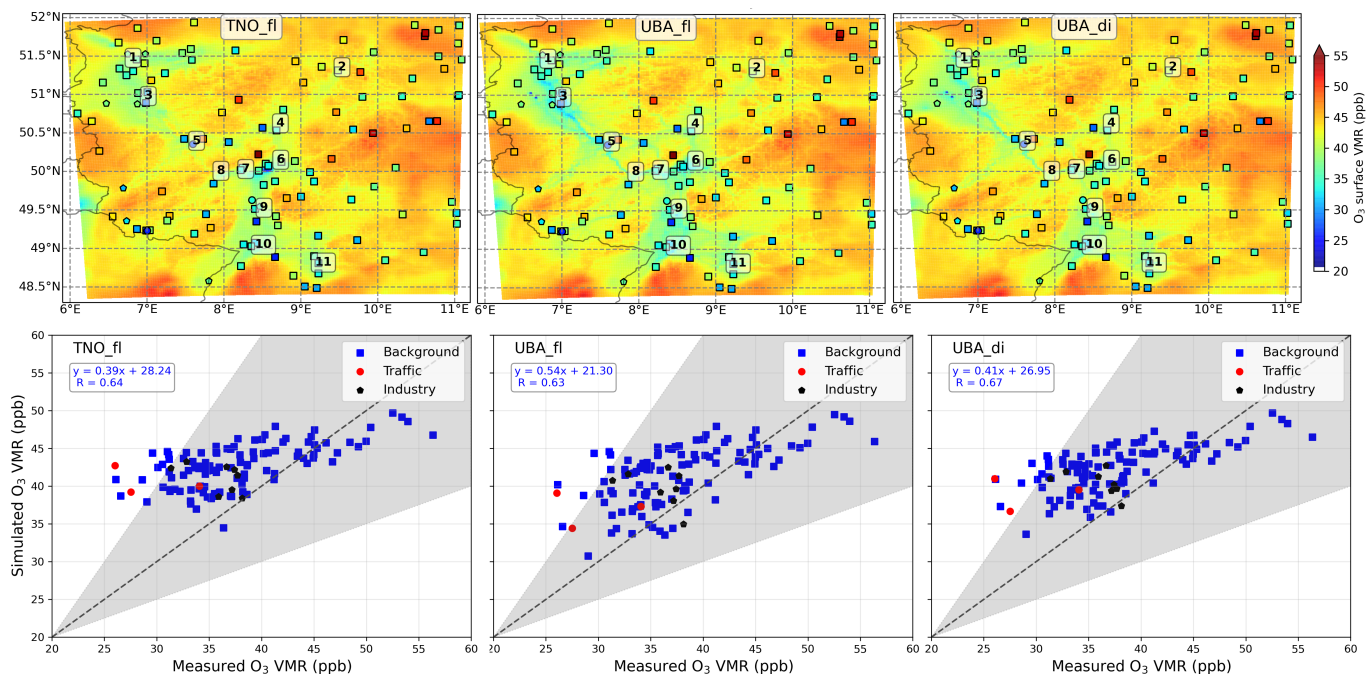


Figure B1. Spatial distribution of monthly mean O_3 surface VMRs for the three simulations using different emission inventories (left: TNO, middle: UBA without diurnal variations, right: UBA with diurnal variations) for May 2018. Bottom panel shows the scatter plot and orthogonal distance regression (ODR) weighted by the inverse of the square of the standard deviation of simulated monthly mean O_3 surface VMRs with respect to the in situ measured values. ODR was performed only for the background stations because of the low number of stations at the traffic-adjacent and industrial locations.

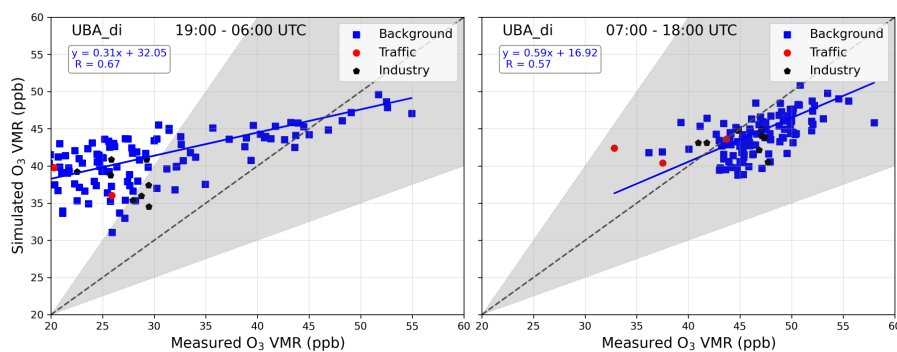


Figure B2. Scatter plot between measured and simulated O_3 for night time (left) and daytime (right) for monthly means at all the measurements stations in the CM02 domain for the UBA_{di} set up.

weaker amplitude of diurnal profiles are related to that of the planetary boundary layer height (PBLH). MECO(n) simulates a relatively weaker amplitude diurnal evolution of PBLH, such that the night-time PBLH is biased towards higher values

night-time values are biased high. This results in a large night time “reservoir” of ozone that can undergo chemical titration with NO_x or dry deposited deposition. Furthermore, a stronger vertical mixing in COSMO/MESSy brings ozone rich air, which together with a weaker dry deposition (Travis and Jacob, 2019) causes a positive bias in simulated surface ozone in the night time. The stronger vertical mixing was also confirmed by Mertens et al. (2016) using a diagnostic tracer with no atmospheric sink. Over the European region, regional models usually struggle to capture the diurnal variability of surface O_3 VMRs as indicated by AQMEII (Air Quality Model Evaluation International Initiative) studies (Solazzo et al., 2012; Im et al., 2015). For example, in WRF-CHEM, the night-time overestimation of surface O_3 was found to be due to an underestimation of O_3 titration by NO_x in the night-time, while that in COSMO-MUSCAT was due to relatively weaker dry deposition fluxes and inaccurate representation of vertical mixing. A night-time overestimation over central Europe was also observed for global model EMAC, though the bias was smaller as compared to that in MECO(n) (Mertens et al., 2016). During the daytime, the cold bias of MECO(n) could also bias the rate of ozone production from precursors via rate constants. Mertens et al. (2016) have investigated this deviation by forcing the nudged EMAC simulated temperatures in the COSMO/MESSy domain. This, however, did not explain the observed bias in O_3 .

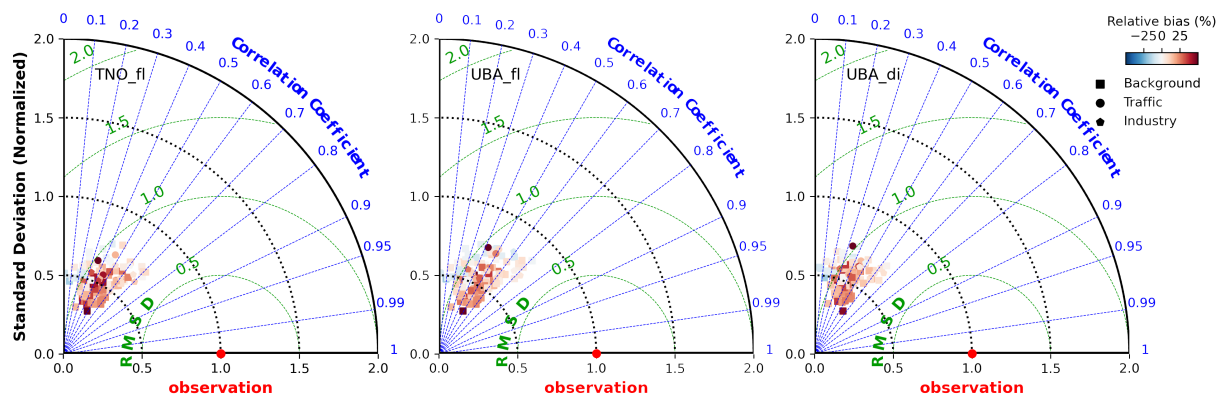


Figure B3. Taylor diagrams showing the Pearson correlation coefficients, normalized standard deviation and normalized root mean square difference corresponding to hourly resolved measured and simulated O_3 VMRs (in CM02 domain) for background, traffic, and industrial sites represented as square, circle and pentagon markers, respectively. The left, middle and right panels correspond to the TNO_{fl} , UBA_{fl} and UBA_{di} set ups, respectively.

The Taylor diagrams in Figure B3 show significantly better model performance (larger R and smaller RMSD values) as compared to that for NO_2 in section 3.2. This is due to the relatively larger lifetime of O_3 , owing to which strong spatial gradients are not observed. The temporal variability is, however, underestimated as evident by the relative standard deviations of less than 1. Using an updated and high resolved anthropogenic emission with high NO_x did not elicit further improvement in the agreement of spatial patterns of the monthly mean measured and simulated O_3 . The only improvement was a minor reduction in overestimation corresponding to the lower values. These values are observed for the sites where generally higher NO_2 VMRs were observed, thus indicating a NO_x saturated ozone production regime. It is interesting to note that an increase

of $\sim 27\%$ anthropogenic NO_x emissions by using the UBA emission inventory shows little change in surface O_3 VMRs. In addition to the NO_x saturated ozone production regime, a relatively weaker contribution of anthropogenic emissions towards the ozone production in summertime (Mertens et al., 2020b) could also be a plausible reason for this weak effect. However, there can be several discrepancies related to inappropriate NMVOC speciation, biogenic emissions and a relatively simpler chemical mechanism used in the model, due to which we are not confident about this finding. Further investigation in this direction is beyond the scope of this study and should be pursued in future works with complex chemistry.

Appendix C: Additional figures and tables

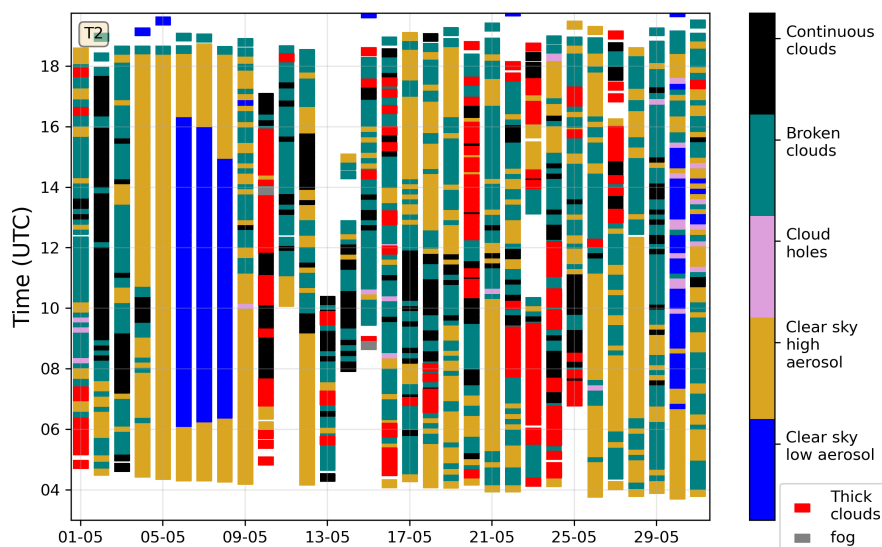


Figure C1. Daily variability of the sky conditions for May 2018 retrieved using MAX-DOAS measurements along the azimuth direction of T2. Consistent sky conditions were retrieved for the other three azimuth directions

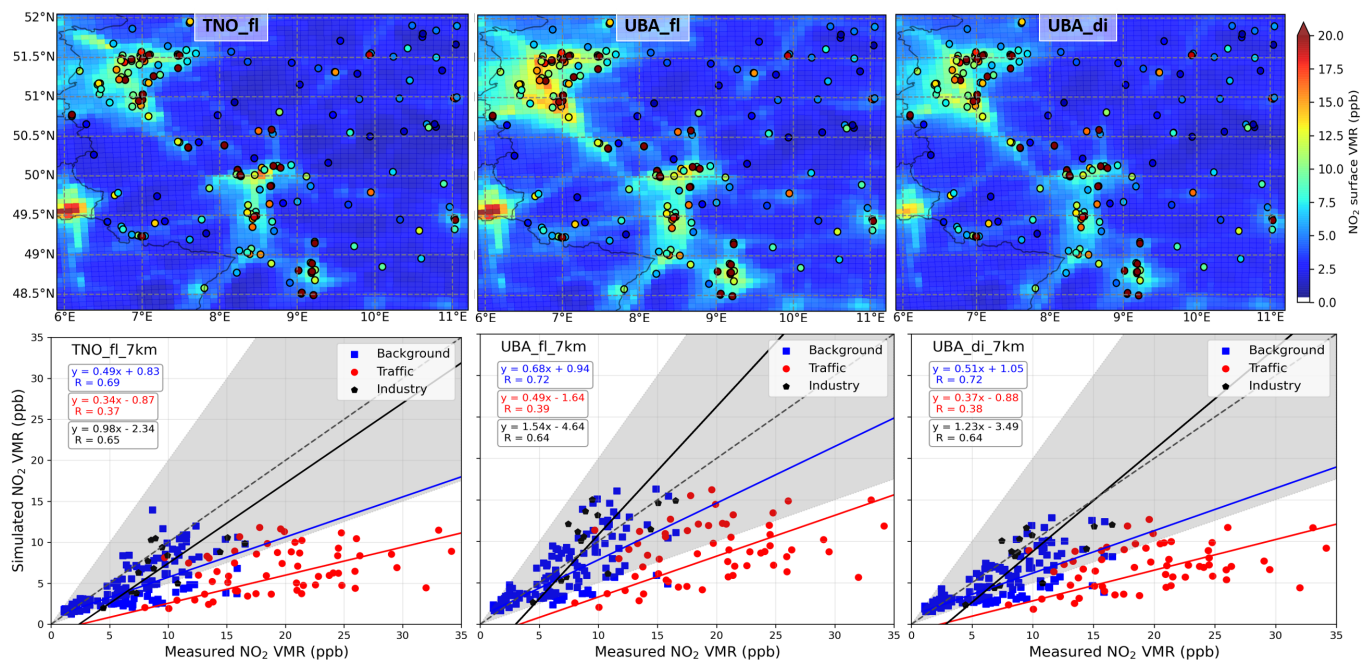


Figure C2. Same as Fig 4, but for the CM07 set up in the domain limited to that for CM02 boundaries.

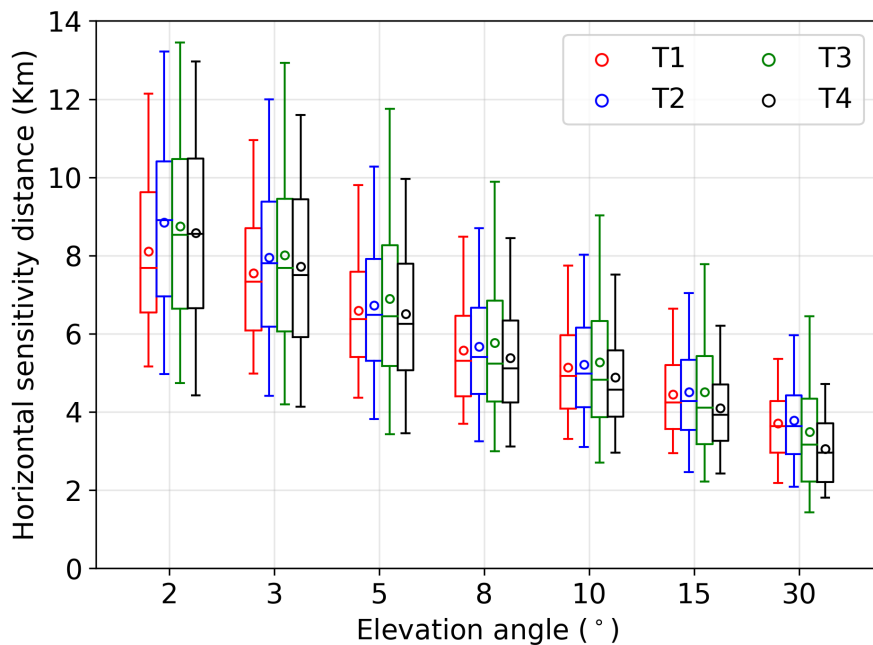


Figure C3. Typical horizontal sensitivity distances (HSD) for different elevation angles along the viewing direction of the four telescopes. The HSD for an elevation angle α is estimated as the distance along the viewing direction which accounts for 90% of simulated $dSCD_{\alpha}$.

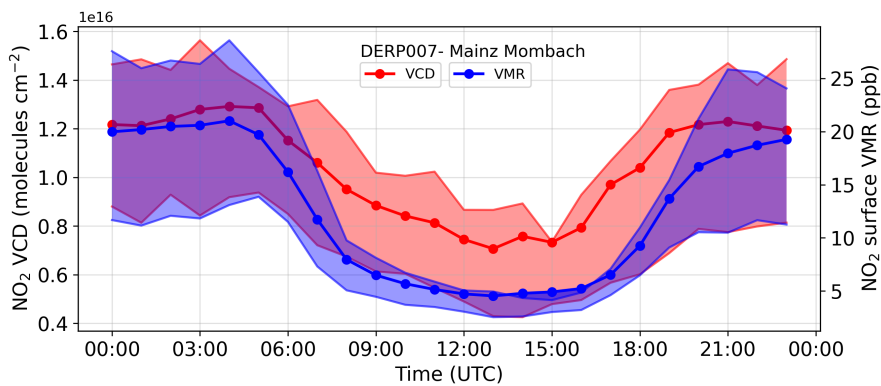


Figure C4. Mean hourly diurnal profiles of simulated NO_2 tropospheric VCDs (red) and surface volume mixing ratios (blue) at a background site Mainz Mombach (8.02 °E, 50.02 °N) for the model set up UBA_{fl} (diurnal variability of road transport and non-industrial combustion sectors not considered). The solid line and markers represent the mean while the shaded region shows the inter-quartile variability range.

Table C1. Fit settings chosen for MAX-DOAS spectral analyses

	NO ₂	O ₄
Fit window (nm)	405 - 461	352 - 387
Fitted absorption cross sections	NO ₂ (298K, I ₀ corrected) ¹ , O ₄ (293K) ² , NO ₂ (220K, I ₀ corrected, pre-orthogonalized to NO ₂ at 298K) ¹ , Ring, H ₂ O ³ , O ₃ (223K) ⁴ , C ₂ H ₂ O ₂ ⁵	NO ₂ (298K, I ₀ corrected) ¹ , O ₄ (293K) ² , HCHO (293K) ⁶ , O ₃ (223K) ⁴ , BrO(223K) ⁷ , Ring
Polynomial order	5	5
Intensity offset	Constant and first order	Constant and first order
Fraunhofer reference selection	Sequential	Sequential

¹ (Vandaele et al., 1998), ² (Thalman and Volkamer, 2013), ³ (Polyansky et al., 2018), ⁴ (Bogumil et al., 2003), ⁵ (Volkamer et al., 2005), ⁶ (Meller and Moortgat, 2000), ⁷ (Fleischmann et al., 2004)

Table C2. Summary of comparison of $dSCDs$ (molecules cm^{-2}) at various elevation angles for the three different model set ups for the CM02 domain. The values in the bracket correspond to the RMSD, bias and R of the comparison of the geometric VCDs. The geometric $dAMF$ at 30° elevation angle equals 1 and hence the geometric VCD is the same as the measured $dSCD$.

Telescope	MAX-DOAS		TNO _{fl}			UBA _{fl}			UBA _{di}		
	elev.	Mean	RMSD (%)	Bias (%)	<i>R</i>	RMSD (%)	Bias (%)	<i>R</i>	RMSD (%)	Bias (%)	<i>R</i>
T1	30	1.03E+16	60.54 (68.94)	-13.15 (-47.20)	0.17 (0.16)	82.30 (60.84)	30.62 (-20.74)	0.19 (0.17)	99.81 (60.38)	44.66 (-12.98)	0.25 (0.27)
	15	2.47E+16	59.58	-24.77	0.19	68.12	12.79	0.19	72.80	23.25	0.31
	10	3.61E+16	61.05	-30.15	0.23	64.82	4.45	0.21	64.24	13.40	0.34
	8	4.30E+16	62.51	-32.60	0.26	64.22	0.42	0.23	61.36	8.69	0.36
	5	5.81E+16	64.29	-36.96	0.38	62.07	-7.45	0.34	56.60	-0.39	0.45
	3	7.29E+16	66.52	-39.54	0.50	61.40	-12.50	0.46	55.41	-5.96	0.54
	2	7.98E+16	65.99	-38.96	0.55	61.36	-11.88	0.52	54.36	-5.28	0.60
T2	30	1.05E+16	57.45 (69.22)	-13.65 (-47.10)	0.29 (0.21)	81.72 (60.60)	30.53 (-20.51)	0.30 (0.24)	98.06 (57.14)	44.78 (-13.10)	0.39 (0.39)
	15	2.52E+16	57.40	-25.50	0.30	67.11	11.72	0.28	70.42	22.10	0.42
	10	3.74E+16	60.29	-32.00	0.30	63.92	1.18	0.27	61.41	9.92	0.43
	8	4.48E+16	61.46	-34.67	0.31	63.02	-3.38	0.27	58.15	4.67	0.44
	5	6.07E+16	63.82	-38.64	0.34	62.84	-10.57	0.29	54.69	-3.49	0.47
	3	7.76E+16	65.48	-41.19	0.41	62.92	-15.17	0.36	53.23	-8.55	0.53
	2	8.72E+16	64.46	-40.85	0.47	62.15	-15.05	0.43	52.40	-8.53	0.57
T3	30	8.95E+15	62.48 (69.16)	-4.81 (-37.48)	0.32 (0.26)	90.92 (63.25)	40.80 (-9.27)	0.35 (0.32)	113.73 (63.78)	54.64 (-0.85)	0.38 (0.39)
	15	2.17E+16	57.55	-16.03	0.32	70.84	21.89	0.36	81.04	33.58	0.40
	10	3.22E+16	59.07	-22.09	0.30	65.31	11.78	0.35	69.79	21.77	0.40
	8	3.88E+16	59.98	-24.96	0.30	63.16	6.84	0.35	65.32	16.06	0.41
	5	5.33E+16	61.32	-29.00	0.33	60.74	-0.78	0.38	60.06	7.20	0.43
	3	6.87E+16	60.41	-30.92	0.43	58.16	-5.38	0.47	56.52	1.47	0.49
	2	7.72E+16	57.21	-29.23	0.54	56.34	-4.59	0.57	55.82	1.34	0.54
T4	30	8.91E+15	62.59 (66.03)	-6.27 (-37.47)	0.24 (0.26)	85.33 (61.05)	36.39 (-9.80)	0.29 (0.28)	104.84 (66.91)	50.58 (-0.44)	0.27 (0.27)
	15	2.20E+16	57.89	-19.17	0.30	65.91	15.90	0.34	74.38	27.05	0.37
	10	3.20E+16	59.54	-24.24	0.32	62.37	7.74	0.36	66.56	17.66	0.40
	8	3.79E+16	60.49	-26.15	0.34	61.36	4.56	0.38	63.95	13.99	0.42
	5	5.09E+16	62.51	-29.25	0.39	60.41	-0.79	0.44	60.63	7.77	0.46
	3	6.27E+16	59.74	-29.22	0.50	56.92	-1.98	0.54	58.47	5.53	0.52
	2	6.62E+16	57.55	-26.12	0.50	57.55	0.59	0.54	61.24	8.02	0.47

Table C3. Same as Table C2, but for cloud-free cases only

Telescope	elev.	MAX-DOAS	TNO _{fl}			UBA _{fl}			UBA _{di}		
		Mean	RMSD (%)	Bias (%)	R	RMSD (%)	Bias (%)	R	RMSD (%)	Bias (%)	R
T1	30	9.99E+15	53.11 (64.36)	-15.61 (-47.26)	0.27 (0.22)	81.00 (59.81)	27.62 (-20.72)	0.19 (0.14)	77.95 (49.73)	33.94 (-18.11)	0.36 (0.37)
	15	2.48E+16	54.68	-25.35	0.25	69.78	12.31	0.14	57.68	16.16	0.38
	10	3.74E+16	56.33	-30.71	0.28	65.59	3.96	0.15	49.96	6.77	0.42
	8	4.52E+16	57.56	-33.14	0.31	63.99	-0.05	0.19	46.84	2.26	0.46
	5	6.39E+16	59.76	-38.27	0.43	60.09	-9.3	0.31	42.16	-8.02	0.59
	3	8.26E+16	61.72	-41.33	0.55	57.49	-15.24	0.48	40.7	-14.44	0.72
	2	9.18E+16	61.46	-41.01	0.61	57.13	-14.93	0.54	38.47	-14.33	0.78
T2	30	1.00E+16	54.01 (67.18)	-16.49 (-46.33)	0.33 (0.22)	81.72 (62.44)	26.81 (-19.24)	0.29 (0.20)	78.27 (50.64)	35.09 (-15.59)	0.50 (0.46)
	15	2.49E+16	57.55	-25.62	0.3	72.69	11.6	0.24	59.77	16.88	0.49
	10	3.80E+16	60.75	-31.67	0.29	69.54	1.52	0.22	53.45	5.59	0.49
	8	4.61E+16	61.93	-34.16	0.29	68.37	-2.89	0.22	51.36	0.64	0.5
	5	6.43E+16	64.84	-37.9	0.31	68.08	-9.93	0.24	50.08	-7.22	0.52
	3	8.44E+16	66.28	-40.48	0.39	67.36	-14.62	0.31	49.11	-12.29	0.58
	2	9.61E+16	64.61	-40.05	0.46	65.74	-14.35	0.39	47.08	-12.4	0.64
T3	30	8.91E+15	58.00 (68.07)	-9.76 (-37.79)	0.40 (0.28)	82.67 (62.54)	34.17 (-9.08)	0.45 (0.37)	84.91 (53.39)	41.66 (-6.11)	0.55 (0.52)
	15	2.24E+16	55.14	-18.98	0.36	68.32	18.32	0.42	61.5	22.44	0.55
	10	3.38E+16	56.52	-24.13	0.33	63.71	9.46	0.39	53.7	12.4	0.54
	8	4.13E+16	57.14	-26.89	0.33	61.36	4.62	0.39	50.55	7.06	0.53
	5	5.82E+16	57.95	-30.25	0.36	58.75	-2.26	0.41	47.76	-0.61	0.54
	3	7.75E+16	57.8	-32.31	0.45	56.55	-7.26	0.49	45.44	-6.37	0.6
	2	8.85E+16	53.98	-30.14	0.58	53.96	-6.01	0.61	42.91	-6.14	0.69
T4	30	8.87E+15	54.53 (61.54)	-11.96 (-39.70)	0.36 (0.35)	78.55 (56.61)	30.37 (-11.68)	0.39 (0.36)	75.34 (51.84)	35.57 (-8.34)	0.47 (0.43)
	15	2.23E+16	52.44	-21.76	0.39	63.84	14.15	0.4	54.82	17.77	0.55
	10	3.33E+16	54.88	-26.7	0.4	60.3	6.04	0.41	48.91	8.73	0.56
	8	4.01E+16	55.78	-28.73	0.41	58.76	2.6	0.43	46.69	4.91	0.58
	5	5.57E+16	56.96	-31.89	0.47	56.21	-3.01	0.48	43.61	-1.4	0.63
	3	7.33E+16	57.69	-34.05	0.55	53.86	-7.31	0.57	41.87	-6.38	0.69
	2	7.69E+16	54.18	-30.67	0.57	53.53	-4.4	0.58	41.32	-4.62	0.67

Author contributions. VK and TW prepared the manuscript with inputs from all the co-authors. JR performed the MAX-DOAS measurements, *dSCDs* and *dbAMF* retrieval with inputs from SB and TW. AK, MM, BS, MB and HT helped VK with the model set up and simulations. VK and AP pre-processed the TNO and UBA emission data so as to render it suitable for MECO(n). VK performed the cloud classification and data analyses related to model evaluation.

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