

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_{f1} 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.

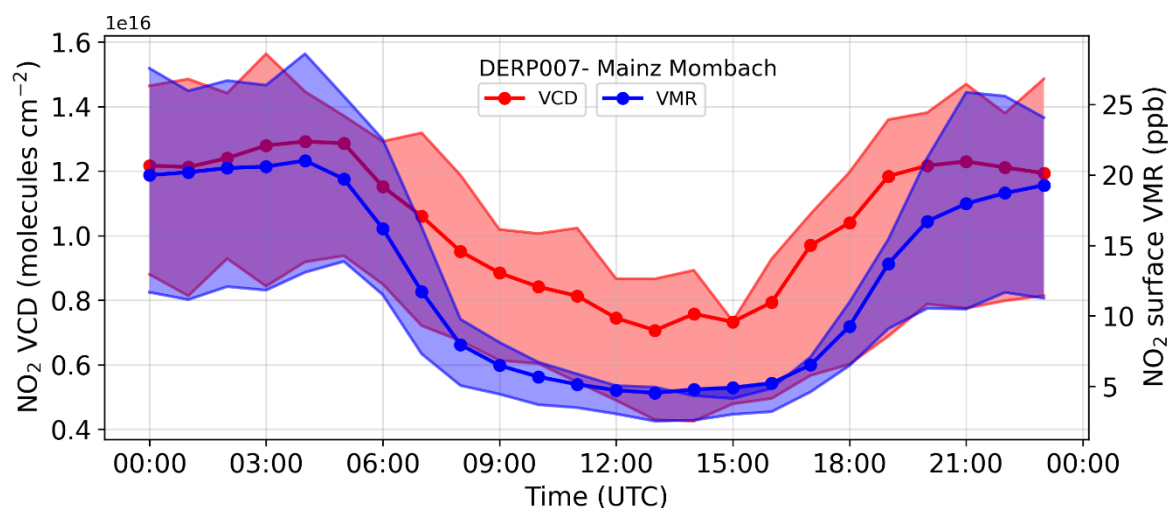


Figure 1: Mean hourly diurnal profiles of simulated NO_2 tropospheric VCDs (red) and surface volume mixing ratios (blue) at a background site Mainz Mombach (8.02°E , 50.02°N) for the model set up UBA_{fl} (diurnal variability of road transport and non-industrial combustion sectors not considered). The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