Atmospheric Chemistry and Physics Discussions

Atmos. Chem. Phys. Discuss., referee comment RC1
https://doi.org/10.5194/acp-2021-1028-RC1, 2021


# Comment on acp-2021-1028

Anonymous Referee #1

Referee comment on "Tropospheric ozone production and chemical regime analysis during the COVID-19 lockdown over Europe" by Clara M. Nussbaumer et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-1028-RC1, 2021

The manuscript discusses aircraft observations from three campaigns over Europe. One campaign was conducted in May/June 2020, when lockdown induced emission changes provided a unique opportunity to study changes in atmospheric chemistry. The study shows that emission changes of NOx had a profound impact on tropospheric ozone production regimes. The paper is well-written, but would benefit from further detail regarding the methodology and simplifications that represent the basis of the analysis. In this context, the fact that no accompanying VOC measurements were conducted presents a shortcoming that should be addressed in more detail.

Detailed comments:

Introduction:

The introduction would benefit from a more robust literature review on early papers that have unravelled the relationship between NOx and O3 chemistry.

Eq. 1: Why can RO2 cross reactions be ignored here? A rational should be given why these terms are omitted for the lower continental atmosphere (e.g. <4km). CH3O2 is exclusively produced from methane oxidation, however even in the remote atmosphere, methane and VOC OH-reactivity are comparable (see: Mao et al., ACP, 2009. doi: 10.5194/acp-9-163-2009). The presented simplification might work for the remote marine atmosphere, but I doubt that it is applicable to polluted continental areas in a quantitative sense as analysed here.

Line 73: The authors mention emission reduction studies were only performed at the

surface, but none of the cited papers actually investigated emission reductions. The cited studies investigated changes in ambient concentrations, which are typically subject to chemistry and meteorological / climatological differences. It is somewhat unclear what the authors try to say here. Aren't pollutants (with a few exceptions) primarily released at the surface – or do the authors rather want to refer to the impact of emissions on atmospheric chemistry? If the authors specifically mean that emissions released above the surface (e.g. from air traffic) are of importance, I would suggest to reword this paragraph and be more specific about this.

Line 100: ok here methyl peroxy radicals are simply based on methane, but earlier (line 47), methanol was also mentioned as an important precursor for a study site in Finland. In fact there could be many more precursor VOCs for methyl peroxy radicals in the upper atmosphere (e.g. the photolysis of carbonyls, or subsequent RO2 x HO2 and RO2 x RO2 reactions of most carbonyls)

Using a campaign in Africa as a reference seems a stretch here. What about the role of biogenic VOCs and oxidation products? For example Crutzen et al., (Atmos. Environ., 2000: doi: 10.1016/S1352-2310(99)00482-3) found significant amounts of BVOCs and their oxidation products in the tropics up to 10 km.

What is the bias of neglecting other RO2 sources (e.g. changes in anthropogenic VOCs and BVOCs) over Europe? Also, May / June represent seasons where biogenic emissions in Europe should play an increasing role.

Line 145: So the campaign was conducted in May/June, when most lockdown related restrictions were already easing in Europe – would the analysis presented here then be more of a reflection of the post-lockdown regime, with some restrictions (e.g. travel restrictions) still in place, others not? For example traffic volumes across Europe and elsewhere (e.g. China) largely recovered by June 2020.

Line 144 ff: No VOCs were measured during these campaigns, which presents a major uncertainty. At the minimum the authors should state something about anthropogenic VOC emission changes and estimate the potential change in VOC reactivity prior and after the lockdown relative to NOx. Observations of lockdown induced reductions of anthropogenic VOCs are sparse. In Europe there is evidence that reductions were significant, comparable to NOx (see Lamprecht et al., ACP, 2020: doi: 10.5194/acp-21-3091-2021).

Line 168: Comment on: "the model is generally capable of reproducing the experimental data": Looking at the ozone profile, it does not seem that the 3D model has a very robust predictive capability for ozone. In fact, Figure 2b shows a model offset between 10-20 ppbv for ozone concentrations around 50 – 60 ppbv (e.g. mid – troposphere), which is significant for ozone! For example regional AQ models typically reproduce tropospheric ozone within 5 ppbv when ozone concentrations are around 60 ppbv (e.g. Im et al., Atm.

Environ., 2015; doi: 10.1016/j.atmosenv.2015.02.034 ). These AQ CTMS show biases at the high (e.g. >90ppbv) and low end (<30 ppbv), but not so much in the range of 50-60 ppbv. Is there an explanation for the large model bias in the mid to upper troposphere? Both HO2 and CH3O2 are overpredicted in the mid troposphere – it appears that additional ROx losses are missing in the model, or that the simplified experimental analysis for CH3O2 has limitations. Could the representation of clouds and liquid chemistry be a limitation, or are additional losses of RO2 x RO2/HO2 type reactions missing?

There is also indirect evidence of uncertain (e.g. VOC?) chemistry. For example, in Figure 2 g a comparison between modelled and experimental CH3O2 concentration is shown. The mean difference from 3 km upward can be as large as a factor of 2! For comparison measurements and modelling by Ridley et al. (JGR, 1992, doi: 10.1029/91JD02287) showed that in the remote marine free troposphere, where CH4 and CO dominate, peroxy radicals estimated from a photo stationary state assumption can be largely reconciled with a photochemical box model.

Section 3.2

Line 212. Considering that the presented analysis in this section is exclusively based on the ECHAM/MESSy model scenarios here, why leave this statement as a possibility or "possible explanation"? It should be pretty straight forward to get the emissions data from the model and compare the model projected changes quantitatively. E.g. how much have NOx emissions in the model then changed between 2003 and 2021?

Section 3.3

While I understand that alpha could be a semiquantitative experimental measure for investigating the chemical regime of ozone production, I wonder whether this section represents a little bit of a circular argument: since the analysis is largely based on the output of a chemical Earth system model (ECHAM/MESSy) anyway, why not also use established methods (e.g. Kleinman et al., GRL, 1997; doi: 10.1029/97GL02279) to investigate net P(O3) changes prior and post lockdown. From Figure 5 b and 5c, the relationship between alpha and NO for the individual campaigns does not seem to be dramatically different. From Figure 5a the difference between BLUESKY and BLUESKY-NL seems to be smaller than the uncertainty of both. So how robust are the findings? For example, if lockdown induced changes in anthropogenic VOC and NOx are proportional, one would expect to move sideways down along ozone isopleths. In this context it would be interesting to calculate the OH reactivity from the model. From the presented results and analysis, I have the impression that it is assumed to be dominated by CH4 and CO. While perhaps plausible in the upper remote atmosphere, it is hard to believe that VOCs wouldn't play a significant role in the lower 3-5 km. Even in the remote (marine/coastal) atmosphere (e.g. Mao et al., ACP, 2009. doi: 10.5194/acp-9-163-2009) observations show that the VOC reactivity accounts for 20%. Aircraft studies have shown that models significantly underpredict VOC reactivity above North America (e.g. Chen et al., ACP, 2019: doi: 10.5194/acp-19-9097-2019), and that the VOC reactivity likely accounts for more than 40-50% in the FT over continental areas. This has been shown by many aircraft

studies (e.g. Schroeder et al., Elementa, 2020: doi: 10.1525/elementa.400; Hu et al., JGR, 2014: doi: 10.1002/2014JD022627).

In summary: Putting the analysis more into context of the above mentioned literature and performing some sensitivity analysis on VOC reactivity would help clarify uncertainties that are associated with the main findings on ozone sensitivity.

Minor comments:

Line 30: Reaction R1 has already been described by Leighton

Line 35: This has already been shown by many studies in the 70ies and early 80ies (e.g. Calvert and Stockwell, Can. J. Chem., 61, 1983).

Line 44: what is meant by share here? the authors seem to refer to a fraction or a ratio in eq. (1)

Line 300: The authors sometimes put units in brackets e.g. [ppbv], but for alpha, which is a relative quantity, an empty bracket [ ] seems somewhat arbitrary.