Referee 1:

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.

We would like to thank the referee for the helpful feedback and the time to review our manuscript.

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.

We have added some text with additional citations from earlier studies regarding the NOx and O3 relationship.

Lines 40 ff.: Earlier studies on evaluating correlations of NOx and O3 in the troposphere include Liu et al. (1987), Logan et al. (1985) and Lin et al. (1988), reporting a non-linear dependence that varies with ambient levels of hydrocarbons and NOx.

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.

We have exemplarily taken the cross reaction of CH3O2 with CH3O2 as surrogate for RO2 into account. Self-reaction of CH3O2 leads to a CH3O2 loss forming HCHO. The impact can be estimated using modeled CH3O2 or calculated CH3O2 via Equation 3 and the IUPAC rate constant k(CH3O2+CH3O2)=1.03e-13*exp(365/TK). Our calculations show that the contribution of the self-reaction of CH3O2 to CH3O2 loss (and therefore to alpha as shown in Equation 1) is negligible with on average 0.4% for BLUESKY, 0.3% for HOOVER and 0.2% for UTOPIHAN. We have added text to the manuscript to point this out.

Line 53 f.: Self-reaction of CH3O2 as a contributor to CH3O2 loss forming HCHO is negligible.

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.

The cited papers report changes in pollutant concentrations during the COVID-19 lockdown. Whereas some studies find that changes in O3 mixing ratios can be (partly) attributed to meteorological changes – which we have pointed out in our manuscript – the observed changes in the abundance of primary pollutants such as NOx are not induced by meteorology and decreases are related to the lockdown regulations. To name some examples:

- Menut et al. (2020) Lines 6 ff. of Abstract:

  "This study shows that the lockdown effect on atmospheric composition, in particular through massive traffic reductions, has been important for several short-lived atmospheric trace species, with a large reduction in NO2 concentrations, a lower reduction in Particulate Matter (PM) concentrations and a mitigated effect on ozone concentrations due to non-linear chemical effects."

- Ordéñez et al. (2020) Lines 8 ff. of Abstract:

  "(…) shows that the low NO2 concentrations were mostly attributed to the emission reductions while O3 anomalies were dominated by the meteorology."

- Chossière et al. (2021) Lines 3 ff. of Abstract:

  "Using global satellite observations and ground measurements from 36 countries in Europe, North America, and East Asia, we find that lockdowns led to reductions in NO_2 concentrations globally (…)."

Most of the cited studies refer to air quality changes at the surface due to emission reductions from lockdown regulations, e.g. reduced traffic, and only very few studies consider lockdown induced changes in the free troposphere, which is why we believe our study can be an important contribution to the literature.

We have rephrased the sentence in the manuscript and now mention pollutant reductions (which is observed) instead of emission reductions (which is the origin) to avoid confusion and to emphasize that we are talking about mixing ratios, and not fluxes.

Line 75 ff.: Most of the literature on pollutant reductions during the COVID-19 lockdown focuses on near-surface air quality and only few studies consider the free troposphere.

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)

Thank you for pointing towards methanol. In fact, CH3O2 is formed from acetaldehyde and not from methanol. We have corrected this in the manuscript.

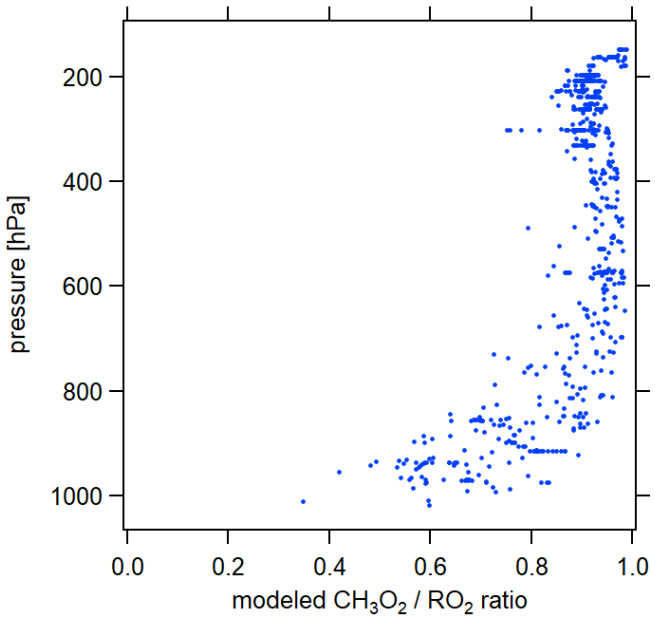
Line 49 ff.: CH3O2 formed from e.g. the oxidation of acetaldehyde (CH3CHO) or methane (CH4) …

We would like to point out that calculating CH3O2 via Equation 3 was originally derived by Bozem et al. (2017), doi: 10.5194/acp-17-10565-2017 and comparing with modeled CH3O2 shows good agreement in the upper troposphere (Figure 2g). Additionally, we have calculated ozone production via the photolysis of NO2 from model simulations and via the extended Leighton ratio (Eq. 2) using experimental data for the HOOVER campaign and find good agreement. We therefore believe this calculation to provide a reasonable estimate. We have added the vertical profiles showing the comparison of modeled and experimental NOPR for HOOVER as Figure 6 to the manuscript.

Lines 289 ff.: Modeled P(O3) via NO2 photolysis and measured P(O3) via reaction of NO with O3, OH and HO2 are in good agreement which we show in Figure 6. The only relevant deviation is observed at ground levels, where the experimental value is significantly higher compared to the modeled value. However, only three data points were available for the calculation with a 1σ standard deviation of the averaging of >100%.

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.

We agree with the referee and have investigated the proportion of CH3O2 in the overall modeled RO2 across Europe.

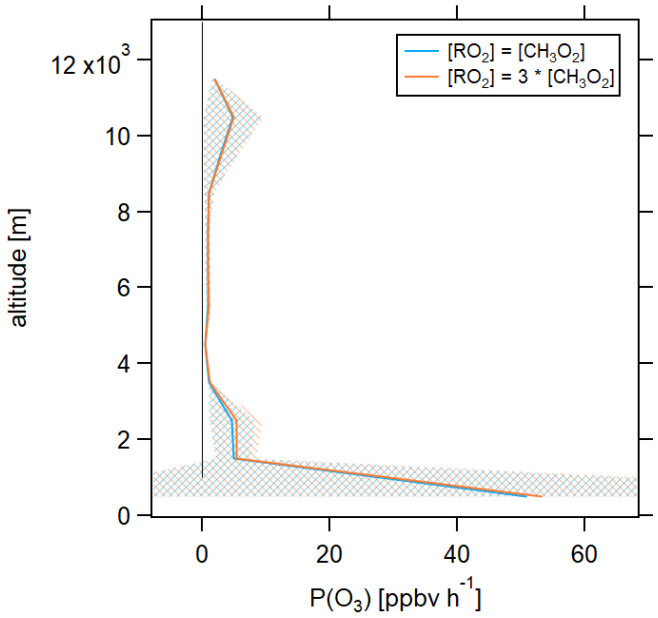


This figure shows the ratio of modeled CH3O2 and RO2 as a function of the pressure level for the BLUESKY campaign. It can be seen that above 800hPa, CH3O2 represent > 90 % of the overall modeled RO2. In the lower troposphere CH3O2 accounts for on

average ~ 70 % of RO2. We have added the figure to the Supplement and some text to the manuscript.

Lines 104 ff.: We assume RzO2 (the sum of all peroxy radicals) to be represented by CH3O2 which we find to be a reasonable approximation when comparing modeled CH3O2 to the overall modeled RO2 as shown in Figure S1 of the Supplement, exemplarily for the BLUESKY campaign. Above 800 hPa, CH3O2 represents more than 90 % of RO2. Below 800 hPa, it still accounts for more than 70 % on average.

We would additionally like to point out that this estimation of CH3O2 is only used when calculating O3 production from the measured mixing ratios. For the most part of our analysis, we use the photolysis of modeled NO2 in order to estimate ozone production. We have performed a sensitivity study of ozone production for HOOVER regarding RO2 which can be seen in the following figure. The blue profile shows ozone production when RO2 is equal to CH3O2 and the orange profile shows a case where CH3O2 represents around a third of the overall RO2. Small differences can be observed in the lower troposphere which are not significant. The error on P(O3) resulting from approximating RO2 through CH3O2 is therefore negligible.



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.

We agree with the referee that most restrictions across Europe were in place in March and April. The campaign was conducted from May 21 to June 9, which presents a time period during which emissions increased again due to for example higher traffic loads, but have not got back to the original pre-lockdown level, e.g. the Covid-19 Mobility Project (http://covid-19-mobility.org/) reported a mobility reduction of still more than 10% compared to 2019 during this time interval in Germany. This is in line with our pollutant reduction observations: we found a decrease in NOx mixing ratios at the surface which was smaller compared to findings from other studies focusing on data from March and April (Lines 218 ff. of the manuscript). We have added some text in the manuscript for clarification.

Lines 158 ff.: While most restrictions across Europe were in place in March and April 2020, May and June emissions, particularly from air travel but also from ground-based sources such as onroad traffic, were still affected by the COVID-19 lockdowns (Schlossel et al., 2020; Brockmann Lab, 2022; Hasegawa, 2022; EUROCONTROL, 2022).

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).

We do not believe the lack of VOCs to be a drawback of our study. The introduction of the measure αCH3O2 replaces the need of VOC measurements, particularly in the upper troposphere where CH3O2 is around 90% of overall RO2 (see above). However, we appreciate the literature suggestion of the referee and have added some discussion on lockdown induced VOC changes. Aircraft NOx emissions are much larger than aircraft VOC emissions (Schumann, 2002). We therefore expect a much larger decrease in NOx than VOC in the UT, which would shift the NOx/VOC ratio to smaller values and towards a NOx limited chemical regime which is line with our observations. Lamprecht et al. (2020) find that VOC reductions at the surface are similar to NOx reductions which implicates an unchanged NOx/VOC ratio and corresponds to what we report for the lower troposphere.

Lines 335 ff.: Aircraft NOx emissions are much larger than aircraft VOC emissions (Schumann, 2002). We can therefore expect reduced air traffic to effect lower NOx/VOC ratios shifting chemistry towards a NOx limited regime. Lamprecht et al. (2021) reported ground-level reductions of several aromatic VOCs during the COVID-19 lockdown to be comparable to NOx reductions in Europe, implicating a steady NOx/VOC level and therefore no changes in the dominating chemical regime, which is in line with our findings for the lower troposphere.

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.

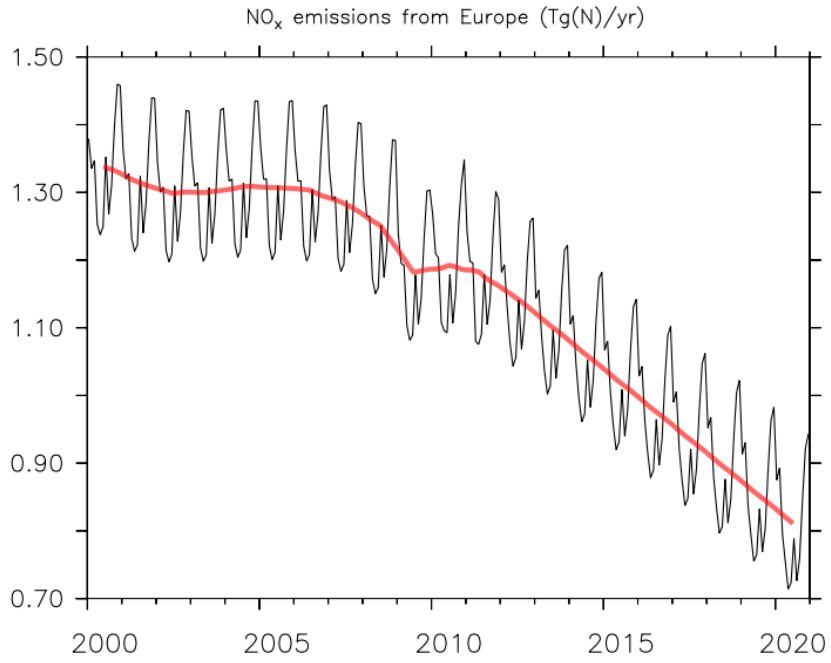
The ozone bias, the referee is pointing out, is something almost all global models suffer from and the causes of which have not been conclusively understood so far. Revell et al. (2018) found a positive O3 bias in the northern hemisphere for the models of the CCMI (Chemistry-Climate Model Initiative). Other studies reported similar observations for global models (Young et al. (2018), Jöckel et al. (2016), Parrish et al. (2014)). Regional models can be tuned to match O3 observations more easily, but lack the complexity of global models which need to encompass the entire globe. We find a model O3 overestimation by <20% for HOOVER and BLUESKY and by <10% for UTOPIHAN on average. Given the observations of Revell et al. (2018) that the O3 bias can be as large as 40-50% in the northern hemisphere, we believe our results to provide estimates at the more reasonable end. Regarding CH3O2, Figure 2g shows close agreement for calculated and modeled CH3O2 for the lower and upper troposphere which is the area which we predominantly study in this work. We have added some text to the manuscript pointing towards the O3 bias for global models.

Lines 196 ff.: Model values were approximately 20% higher compared to the measured data, but showed the same vertical shape. The observed positive O3 bias of the modeled data is an issue almost all global models suffer from in the northern hemisphere and which has not been entirely understood yet (Revell et al., 2018; Young et al., 2018; Jöckel et al., 2016; Parrish et al., 2014).

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?

We agree with the referee. We have added a Figure to the Supplement showing how NOx emissions in the model decreased over the past 20 years and rephrased our statement in the main text.



Lines 227 ff.: The differences in NO mixing ratios between the campaigns are the outcome of the general emission reduction due to legislative limitation of nitrogen oxides and other hazardous pollutants over the past decades, as the campaigns took place 15-20 years apart. We show the decrease in NOx emissions in the model over the past two decades in Figure S5 of the Supplement.

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).

We would like to point out, that this study is originally based on in-situ observations during the three field campaigns UTOPIHAN, HOOVER and BLUESKY. For consistency,

we are using the model output for the net ozone production calculations as some of the trace gas were not measured across all three campaigns, e.g. OH or HO2. The HOOVER campaign provides a full dataset of all trace gas measurements which we use as validation of the model. To our understanding the method presented by Kleinman et al. (1997) requires the knowledge on hydrocarbon concentrations which were not measured during the field campaigns. The advantage of using the described alpha value is that VOC measurements are not necessary in order to determine the dominant chemical regime. We have previously compared this method in Nussbaumer et al. (2021, doi: 10.5194/acp-21-18413-2021) to the established method of the HCHO to NO2 ratio (Sillman, 1995; Duncan et al., 2010; Martin et al., 2004) and found good agreement. We therefore believe that alpha is a powerful tool regarding the determination of dominant ozone chemistry in the troposphere.

We agree with the referee that no significant differences between the campaigns, including the BLUESKY and the BLUESKY-NL scenario, can be observed for Figure 7b (5b previously) in the lower troposphere. In contrast, for the upper troposphere in Figure 7c we do observe major differences between the campaigns. The UTOPIHAN alpha values are almost non-responsive to changing NO, reflected in the slope of 0.09 ± 0.02 $ppbv^{-1}$. In contrast, the BLUESKY alpha values change rapidly for small NO changes with a slope of 1.12 ± 0.08 $ppbv^{-1}$. Intermediate results are obtained for the BLUESKY-NL alpha values, showing a slope of 0.37 ± 0.03 $ppbv^{-1}$. These differences are mathematically significant and provide strong evidence on a changing regime in the upper troposphere in contrast to the lower troposphere where we do not make these observations. This is also shown in Figure 7a. Above ~8km the difference between the BLUESKY and the BLUESKY-NL alpha values is larger than the individual uncertainties and above ~10km even larger than the combined uncertainty. In the lower troposphere - we agree with referee – no relevant differences are observed which strongly underlines our conclusion.

We thank the referee for the suggestion of calculating OH reactivities from the model. However, we believe this to be outside the scope of this study. While VOCs and NOx are precursors to Ozone formation, we do not require the full knowledge of both in order to determine the dominant chemical regime. An example for this is the HCHO/NO2 ratio, a method well established in current literature. As HCHO can be formed by almost any hydrocarbon it can be seen as a surrogate for VOCs. Similarly, the alpha value in this study representing the HCHO yield from methyl peroxy radicals is capable of revealing the dominant chemical regime without a full set of VOC measurements.

We have added some text in the manuscript for clarification.

Lines 314 ff.: We have previously validated this method in a comparison to the established method of analyzing the HCHO/NO2 ratio (Nussbaumer et al. (2021)). HCHO can be formed by almost any hydrocarbon and is therefore a proxy for VOCs which are often not measured in their entirety. Likewise, αCH3O2 - representing the HCHO yield from methyl peroxy radicals - is capable of revealing the dominant chemical regime without the knowledge of ambient VOC levels.

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

Thank you, we have added this reference to the manuscript.

Line 30 ff.: Under the influence of sunlight, NO2 can subsequently form O3 through the reaction with molecular oxygen as shown in Reaction (R1) (Leighton, 1961; Crutzen, 1988; …).

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).

We have added the suggested reference.

Line 35 ff.: (…), which means that a reduction in ambient NOx can either increase or decrease O3 production (Calvert and Stockwell, 1983; Pusede et al., 2015).

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

Yes, the referee is correct. We have changed the word ‘share’ to ‘fraction’.

Line 46 ff.: We have recently shown that the fraction α of methyl peroxyradicals (CH3O2) forming formaldehyde (HCHO) in correlation with ambient NO concentrations (…).

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.

We meant to indicate with the empty bracket that alpha is unitless. However, we have deleted the empty brackets in the main text in order to avoid confusion.

Line 329: … $\Delta\alpha / \Delta NO = 0.09 \pm 0.02$ $ppbv^{-1}$…