Response to referee comments on acp-2020-691

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General comment

We would like to thank both referees for their constructive and useful comments, which helped to significantly improve the manuscript. We have carefully revised the manuscript according to the major concerns and the specific comments. Here, we provide our responses. In each case, we have copied the referees comments (in bold) and our responses are written in standard script. While we have tried to balance preservation of as much of the original text as possible, we have substantially modified some parts of the text to clarify and improve the presentation of the results following the suggestions of both referees. We consider that the changes made in response to the referees comments helped to improve considerably the manuscript and we hope the editor and referees find the revised version suitable for publication in ACP. We also append a marked-up version of the manuscript with the changes mentioned in our responses to the referees. Text deleted is shown as cross out sentences, and extra or new text in red script.

Response to Referee #1

The authors present an interesting study on the so called "climate penalty" i.e. the dependency of ozone concentration on temperature. They have analyzed a large observational dataset from different measurements station in Germany and estimated the changes of the climate penalty over time. Additionally they tried to interpret the data by using statistical method (general additive methods, GAMs). The manuscript is clear and well written. Despite that, it is still unclear to me what the real goal of this manuscript is. If the authors are trying to explain the causes of climate penalty changes (at least for these stations), I believe the manuscript fall short of its objective. I have the impression that the authors overlooked (voluntarily or involuntarily) the importance of many factors for a clear explanation of the climate penalty.

The primary objective of this study is to analyze how NO_x reductions have influenced the temperature dependence of O_3. As stated in the introduction, the temperature dependence of O_3 is complex and varies in space and time due to differing chemical and meteorological mechanisms that influence O_3 formation (Pusede et al. 2015). Previous studies have reported a weaker O_3 sensitivity to temperature over the past years, likely due to reduction of emissions of O_3 precursors. Here we specifically focus on the impacts of NO_x reductions that have drastically declined for last past decades in Germany. Ultimately, we aimed to infer changes in VOC accompanying NO_x reductions that might contribute to the changes in the temperature dependence of O_3. We have stressed the main objectives of the study in the revised version of the manuscript.

Here below I have listed the main concerns, followed by more specific comments, as well as few technical corrections.

Main comments:

VOC contribution: I generally miss the consideration of VOC in this paper. Together with NOx, VOC determine the dominant chemical regime which is relevant for interpreting the changes of ΔO_3 in response to decreasing NOx. For a specific time, temperature is likely a good approximation for VOC concentrations as described in the paper, but when comparing two different time periods it is important to consider the change in VOC and the resulting VOC/NOx ratio. I think some of the open questions in this paper could be solved with an evaluation of VOC data. If it is hard to find VOC data: I know most of the measurement sites

in Germany measure benzene which could be analyzed as a surrogate for anthropogenic VOC for the relative development over time.

We agree with Referee #1 that VOC changes are relevant as well as local chemical regimes, which are defined based on the VOC/NOx ratios. It was not our intention to dismiss the contribution of VOC, on the contrary, as mentioned in our earlier comment, we aim to provide further insights into changes in VOC over the past decades through the observed changes in the temperature sensitivity of O_3 under NO_x reductions.

Following the referee suggestion, we have specifically looked at long-term benzene data over Germany. We have extracted all available benzene data from 1999-2018 from Airbase ((https://www.eea.europa.eu/data-and-maps/data/aqereporting-8). Unfortunately, only two stations from the 29 sites analysed in our study presented data (Fig.R1). In Fig.R1 we show the annual averages of benzene in summertime (here defined as July-August-September) for the stations of the study. From Fig.R1 we see a downward trend for in both stations. However, it was not possible to objectively examine trends for the rest of the stations of the study.

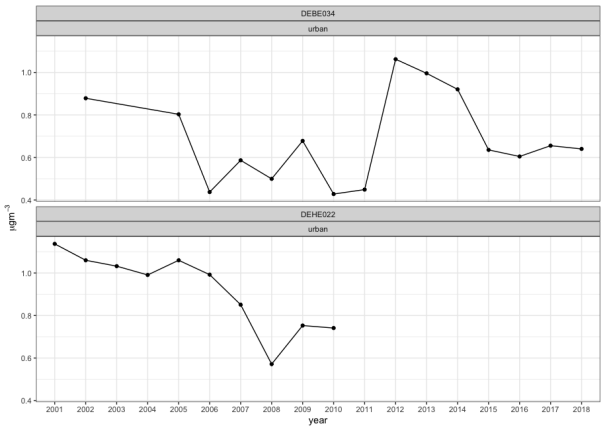

Figure R1.Annual average of benzene measurements for two urban stations included in the presented manuscript.

We have further assessed the measurements of benzene for the rest of available stations (different from the stations analysed in this study). Figure R2 shows the annual averages for the available stations and years. As in Fig.R1, it can be observed a general downward trend, but the quality of the data, in terms of both temporal and spatial coverage, was not sufficient for this study.

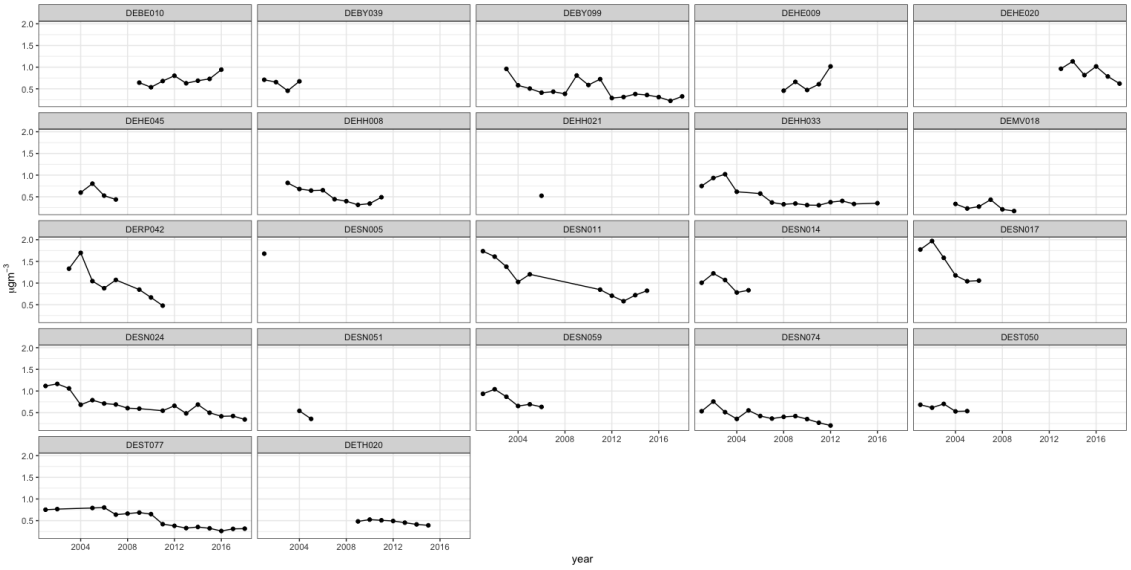

Figure R2. Annual average of benzene measurements for the rest of the stations .

Therefore, as stated in the manuscript and given that long-term records of VOC are generally not available, we used temperature that has been shown to be an useful proxy for representing VOC (LaFranchi et al. 2011, Pusede et al. 2014).

As pointed out by Referee #1 changes in the ozone chemistry due to changes in the ratio of VOC/NOx emissions is a key point when comparing two different time periods. In response to another comment from Referee #2, we have examined the weekend-weekday effect, which can be used as an indicative of the dominant chemistry regime (Steiner et al. 2006). Furthermore, we have now added the weekend-weekday effect in the revised version of the manuscript. For more details, please see our response to first comment from Referee #2 and Figs.R3 and R4.

At the urban sites it is pointed out that a VOC limited regime is dominant (at least for most NOx concentrations and temperatures). However, this doesn't fit together with the abstract where it is said that 'lowering NOx concentrations resulted in decreasing O3 production rates'. Decreasing NOx concentrations only lead to a decrease in O3 production in a NOx limited regime (Pusede et al. 2012).

Referee #1 is correct. The urban stations of this study show a dominant VOC-limited chemistry (see Fig. 4), under which decreasing VOC would be more effective in reducing O_3. We have modified accordingly the abstract.

I do additionally wonder if any changes in biogenic emissions could be expected. Although temperature (as mentioned before) can be used for VOC concentrations, I wonder if we can consider this dependency stable over the entire observed period (or even within the two periods in which the data are divided). Maybe the absolute changes are not significant, but almost certainly is their relative impact in comparison with anthropogenic VOC emissions.

We agree, and we also hypothesize that changes in biogenic emissions have contributed to the temperature dependence of O_3. In particular, soil moisture deficit is a relevant factor of stress for isoprene emissions and when soil moisture is limited plants decrease their emissions of isoprene (Guenther et al. 2006). Severe droughts might influence plant growth and limit biomass production, which can lead to a reduction of isoprene emission (Emmerson et al. 2019). Moreover, earlier studies suggested that plants have very different drought responses, and while isoprene emission tend to decrease with low levels of soil moisture below a certain value, this decreasing might be less significant under exteded severe drought (Pegoraro et al. 2004). In addition to that, recent studies have shown the regional hot and dry conditions over last decade in central Europe

(Buras et al. 2019, Ionita et al. 2017), which might have a significant impact on biogenic emissions (e.g. severe droughts reduce stomatal uptake of ozone and its precursors (Demetillo et al. 2019)). Thus, it is reasonable to expect changes in biogenic emissions. We have added some extra text in the introduction discussing the feedbacks from vegetation, including the effect of soil moisture.

Figure interpretation: Although it does make sense that the temperature sensivity of O3 production decreases for decreasing NOx, I don't think the Figures show this. For the urban site in RP (Rhineland Palatinate) I get the impression that the slope in Figure 5 right (and therefore the climate penalty) is higher for the second time period, which would indicate the opposite.

Yes, you are right, thank you. From the Figure 5 (showed in the old version of the manuscript) we see a general decrease of ΔO_3 during the second period 2009-2018 (lower NO_x) when comparing to the estimates in the first period 1999-2008. This feature is well observed in Berlin. However, in Rhineland Palatinate it can be observed that ΔO_3 tends to decrease for $NO_x > 20\ \mu gm^{-3}$ at all temperature ranges, but increases at higher temperatures ($>20\ ^{\circ}C$) when lowering NO_x ($<20\ \mu gm^{-3}$). This is likely due to changes in VOC that would also explain the differences observed in the shapes of the regression lines when comparing the prediction (green line) and GAM-P2 (blue line). We have taken note of this comment and we have stressed the influence of VOC in the case of Rhineland Palatinate.

Results representativeness: The title of the paper might be a bit too general considering that the analysis focuses on a small number of locations in Germany. Again, the response of O3 to NOx reductions can have different outcomes depending on VOC and the dominant chemical regime which varies strongly with the considered location

We would like to highlight that the selection of the area of this study was mainly motivated by the availability of long-term records of co-located data. However, we understand this comment, since the outcomes of this study are not easily extrapolated. Thus, we have decided to modify slightly the title as:

"Observed changes in the temperature dependence response of surface ozone under NOx reductions over Germany"

GAMs model: It would be great if a little more background information could be provided on how the calculations were made and how the model performance was tested. As mentioned later, the model description could be moved entirely to the electronic supplement and also enlarged to include a more exhaustive description, while on the manuscript only a small summary could be shown. Importantly, the code availability and the data source should be mentioned (best if the code could be uploaded as supplement as well).

We have used the standard tools (e.g. QQ-plot, histograms) to evaluate the model fit and we assessed the model performance by using the R^2. Following your recommendation we provide now a more detailed model description in the supplement material. We have added the code availability in the revised version of the manuscript.

Specific comments

Page 1, line 11 : nice that with the GAMs analysis you finds exactly the same results as before (see line 6) (i.e. „decreasing sensitivity of temperature" in the second period). Instead of repeating the same sentence as a new finding, you could add "the GAMs model confirm that. . . "

The sentence has been changed.

Page 1, Line 14 : Please consider the main comments: of course NOx concentration is not the only factor influencing the climate penalty. This sentence is indeed too general for explaining your 23 pages work!

We have modified the manuscript accordingly with responses and extra analysis provided here.

Page 1, line 20 : (Sillman, 1999) : The authors of this paper shown in the references are Pusede et al. (2015)

The reference has been corrected.

Page 1, lines 23-24 : What about anthropogenic VOC? Many are temperature-dependent, too. Compare Pusede et al. 2014 (also relevant for the summary)

We have added some extra text to mention the role of VOC temperature-dependent.

Page 2, line 33-34 : Jing et al. (2017) state a value of 0.43 ppb K-1 by which the climate penalty was lower in 1999-2007.

We have corrected this thank you.

Page 3, line 24 : '... variability of O3 production can explain a considerable proportion...' Do you have any reference?

We have added the corresponding reference here (Pusede et al. 2015).

Page 4, equation 1 : Please explain all variables and what the function means. To me it seems a linear regression (as you mentioned a linear model) applied for the 2 periods. Do we really need to define a mask (P) and 2 equations to explain that? I have the impression that here the readability has been somehow compromised and made difficult to follow.

Yes, we use a linear regression model. We introduced a categorical variable (period,P) to assess the significant differences between the slopes. As an alternative, a significant t-test can be applied to examine the significant differences between the coefficients (slopes). To avoid complexity, we have now simplified equation 1) and assessed differences using a significant t-test. As stated now in the revised version of the manuscript Equation 1) has the following form:

$$Y(t) = a + m_{\mathrm{O_3T}} T(t) + \epsilon(t) \tag{1}$$

with $\epsilon(t) \sim \mathcal{N}(0, \sigma^2)$, α being the constant offset and $m_{\mathrm{O_3T}}$ the slope of the linear relation.Y(t), T(t) are the time series of MDA8 and daily maximum temperature (respectively).

Page 6, line 9-31 : The description of the GAMs model is indeed difficult to follow. Most possibly is because the needed background in formations are quite large. Although the normal reader would just trust the results, I think that the results of this manuscript should be reproducible by anyone interested (I think that ACP has also a policy on that, if I'm not wrong). Therefore I would strongly suggest to move the GAMs model description to the supplement, with the goal to expand it and make it intelligible by anyone interested. Further, in the electronic supplement of the model the code used for the analysis (i.e. the GAMs algorithm) should be make publicly available, as well with an indication where to download (or obtain) the station's data.

We agree that the description of the GAM is not straightforward. After carefully revised section 3.3 we have modified some parts of the text in order to better explain the basics of GAM. Moreover, we have moved some text to the Supplement Material and following the suggestion from this referee we have also extended the model description. As stated in the data availability, the air quality data can be extracted from Airbase (https://www.eea.europa.eu/data-and-maps/data/aqereporting-8) and the meteorological variables from Climate Data Store (CDS) cloud server (https://cds.climate.copernicus.eu). The code availability has been added along with the data availability in the revised version.

Page 7, line 4 : Why did you need to fit the GAMs model if you build exactly from the dataset? I thought this information to be already used in the construction of the model.

As mentioned in the earlier comment, we have moved part of the text to the Supplement. We would like to clarify to the referee that based on the selection procedure, we selected a final GAM and then, we build a GAM individually for each station and period.

Page 7, line 19 Figure S1: I find this plot hard to analyze. Maybe it could help to add a black stroke color to all data points.

The plot has been updated in the revised version of the supplement.

Page 7, line 26 Figure 3: For Figure S3, I like that the differences between the two periods become clear on first sight, maybe this could be added to Figure 3 for a better understanding.

We have added Fig. S3 to the main text.

Page 8, line 11 Figure 4: Could you make a comparison plot similar to Figure S3 for Figure 4, too?

Figure 4 shows the deviance explained (R^2) obtained from GAM-P1 and GAM-P2 built from different datasets. Thus, it is not possible to establish a similar comparison as done for Figure S3 (old version).

Page 8, line 4 : "A final model including three interaction terms" : Again, the description of the GAMs model was not exceptional. Probably would not hurt if you list again these terms here.

We have added extra text in the revised version of the manuscript.

Page 9, line 8: '...implying a VOC-limited chemistry' If I understand the plot correctly, for DERP025 for low NOx and high temperatures the chemistry is NOx-limited for example at T=24°C for the first time period 1999-2008, ΔO_3 increases from 5 to 6 ug/m³ and then decreases again, so the change from VOC to NOx limited chemistry would occur at c(NOx)=20 ug/m³. For the second time period 2009-2018 and the same temperature T=24°C the regime change occurs already at c(NOx)=15 ug/m³. For DEBE034 it looks like an even smaller part of each plot shows a NOx limited regime. I think this could be a result from lower NOx at DEPR025 compared to DEBE034 and a more effective NOx reduction over time (as shown on the right). Maybe this could be interesting to mention or to further analyze.

Thank you for this useful comment. As Referee #1 points out, at Rhineland-Palatinate the change in the chemistry to NO_x-limited at higher temperatures occurs at lower values of NO_x for the second period. From Fig. R4 (please see in the responses to Referee #2) it can observed that the weekend-weekday effect at Rhineland-Palatinate during the second period has significantly decreased, which suggests a transition to a NO_x-limited system, while in Berlin the weekend-weekday effect is similar in both periods. Consistently, we found in Berlin a general VOC-limited regime in first and second period, which indicate that further reductions should be required for mitigating the impacts of warmer temperatures (i.e climate penalty). This results also point out VOC reductions over time. We have emphasized it in the revised version of the manuscript.

Page 9, line 9 : 'We found a stronger temperature dependence of ΔO_3 in the first period...' In Figure 5 left, I have problems to identify this, e.g. for DERP025 for c(NOx)=20 ug/m³, for a temperature increase from T1=20°C to T2=24°C, ΔO_3 increases from 2 to 6 ug/m³ for 1999-2008 and from 0 to 6 ug/m³ for 2009-2018, same for higher NOx. Figure 5 right, too, doesn't support the stronger temperature dependence in the first period: For Rhineland Palatinate I would even say that the correlation of temperature and ΔO_3 is larger for the second period when looking at the ΔO_3 for a set temperature interval, for example 20-25°C: For 1999-2008, ΔO_3 increases by approx. 6.5 ug/m³ and for 2009-2018, ΔO_3 increases by approx. 7.5 ug/m³.For Berlin, the temperature dependence could be slightly stronger for the first period, but the difference is marginal and hard to tell from the graph.

We have carefully revised the text and taken note of this comment. We agree with the referee that the dependence with temperature is not significantly larger in the first period when comparing to the second period. We have modified the text accordingly.

Page 9, lines 21-27 : What about the influence of VOC? If you look at a certain time the influence of VOC can be well represented by temperature, but between the two different time periods emission controls have decreased VOC. For the shown temperature interval and the mean NOx concentration the dominant chemical regime is VOC limited. If NOx reductions

exceed VOC reductions O3 increases which is shown by the prediction in Figure 5 left. However, if VOC reductions are larger than expected (and if I get this right the prediction only considers a change in NOx, not in VOC), this would counter run the O3 increase made by the prediction (because decreasing VOC decrease O3 in a VOC limited regime, Pusede et al. 2012) and would yield a lower curve than the predicted one. So maybe VOC reductions were more effective in Rhineland Palatinate than in Berlin – just an idea.

Yes, we agree with the referee. As mentioned in an earlier comment to this referee related to the **Figure interpretation**, from Fig. 5 (rigth) it can be noted the differences between the shapes when comparing the regression lines from the prediction and GAM-P2 in Rhineland Palatinate, which could be explained by changes in the VOC. We have stressed this in the revised verion of the manuscript, thank you.

Page 10, line 2-3 : 'This indicates that the ΔO_3 sensivity to higher NOx at moderate and high T is lower in the second period.' ... or indicates that VOC reductions at RP were more effective. (which would be consistent with the deviating prediction line for Rhineland Palatinate in Figure 5 right)

That is certainly plausible and consistent with the results showed at Fig.5. We have added some text to emphasize this in the revised version of the manuscript.

Page 10, line 5 : '... temperature dependence of ΔO_3 is stronger in the first period...' I do see this here for the rural sites, but not for the presented urban sites. Higher NOx in urban areas could be an explanation here.

As mentioned in a earlier related comment to this referee we agree that the dependence with temperature is not significantly larger in the first period at the urban stations, then this sentence has been also modified.

Page 10, line 12 : '... could partially explain the decrease in ΔO_3 estimates ...' In Berlin, for high temperatures a NOx limited regime is dominant for any NOx concentration. For lower temperatures a VOC limited regime is dominant. I think this is a good explanation for the observed plot course in Figure 8 left. The red and the blue plot intersect at around 17°C which is approximately the transition temperature for the observation of a NOx (above) and a VOC limited regime (below). For lower NOx during the second period ΔO_3 should therefore be lower in the NOx limited regime at high temperatures but higher in the VOC limited regime at low temperatures.

We have taken note of this comment and we have added some extra text in the revised version, thank you.

Page 10, line 25 : Figure 10. For high temperatures, both periods in Berlin and the earlier period in RP are dominated by a NOx limited chemistry which is also shown by Figure 8 left. Consequently, ΔO_3 increases with increasing NOx. For the second period in RP a VOC limited regime is dominant and ΔO_3 decreases for increasing NOx. I find this surprising considering the shown decrease in mean NOx in Figure 8 right from the first to the second period. Could there be an explanation? What about VOC concentrations at these sites?

Thank you for this comment. We would like to clarify that the contours shown in Fig. 8 are limited to a range of data sufficiently supported by the observations (Section 4.3). In the case of Rhineland Palatinate we did not show the contours for low NO_x concentrations. Moreover, it is important to note that by using the NO_x filter ($> 5\ \mu gm^{-3}$) we have limited the analysis to the space of higher NO_x concentrations. As stated in the manuscript, this filter was applied due to observed lack of low values of NO_x for some stations. To be consistent in our analysis among stations and periods we decided to apply the same filter to all stations.

From Fig. 8, at Rhineland Palatinate we observed for the second period that the ΔO_3 peak occurs at lower NO_x($>8\mu gm^{-3}$) than the peak observed in the first period ($<8\ \mu gm^{-3}$), which points out the effective NO_x reductions.

Page 11, Section 4.3.2 : Which parameters could have changed over time so that the plots look different for the first and the second period particularly for RP and why not for Berlin?

It might be better for the understanding of the results if the explanation of VPD was included a bit earlier, maybe at the beginning of this paragraph.

We have now introduced the VPD and its relevance for ozone production at the beginning of the section.

Technical corrections

Page 1, line 22 varies
Page 2, line 13,22,24 the United States
Page 2, line 21 photochemical
Page 3, line 7 maximum
Page 5, line 5 the latter
Page 9, line 10 the second period
Page 9, line 21 shown
Page 10, line 1/36,26 decrease
Page 10, line 2 indicates
Page 12, line 2 decrease
Page 12, line 11 lead

All technical corrections have been fixed.

Response to Referee #2

In this work the authors examine long-term O_3 data from surface stations in Germany, comparing hourly ozone changes with various ambient conditions such as temperature and NO_x levels. Using generalized additive models across two halves of the total temporal domain (1999-2018) to model and combine the influence of these driving factors, the authors conclude that these two time periods show differences in the O3-temperature relationship, driven only in part by observed NO_x emissions reductions over that period. While the topic of pollution production and its atmospheric influences is important and complex, I think this manuscript needs considerable development to be considered a novel and meaningful contribution to the existing literature on the subject. In particular, I have the following concerns:

The choice of temporal division (analyzing the full time series in two evenly divided chunks) strikes me as arbitrary and problematic. Unless the year 2009 has some special significance that is not discussed in the text, I see no reason to set up the binary comparisons between time periods as performed here. The division is ostensibly made to compare a higher NO_x time period (1999-2008) to a lower NO_x period (2009-2018), but not only is this assumption not necessarily valid for all stations during all years (see Figure 2), it also neglects the wide variety of other changes that may have occurred over the two decade span that could influence ozone and its relationships with ambient conditions. Compared to other methods of distinguishing between higher and lower NO_x conditions (for example, by leveraging the so-called weekend effect), comparing consecutive decades individually and ascribing their differences to only one factor (NO_x emissions) strikes me as flawed. The authors' observation that "decreasing NO_x concentrations are not the only factor causing the observed changes" underscores this fact, and raises the question of why they chose to dissect their long term data set in this fashion at all. I would recommend rethinking the approach here, and identifying a methodology that is less subject to non-stationarities in external variables.

As stated in the introduction, we would like to emphasize that O_3-temperature relationship varies in space and time, depending not only on the chemical but also meteorological conditions. However, the primary objective of our study is to assess how NO_x reductions influenced changes in the O_3 sensitive to temperature. Therefore, we specifically focus on the role of NO_x reductions. For that, we have divided the complete period of study (1999-2018) into two sub-periods of 10 years, which allow us to build GAMs to assess the non-linear interaction NO_x-temperature in each period. As shown in previous studies (e.g. Pusede et al 2012, Jin et

al. 2017, Solberg et al. 2017, Phalitnonkiat et al. 2016) the strategy of comparing different periods provides useful insights into the impacts of NO_x reductions in the temperature-O_3 relationship. Thus, we believe that the approach presented in this study is solid.

Nevertheless, we have taken note of this comment and we have further analyzed the weekend-weekday effect to support our results. As Referee #2 points out, the so-called "weekend–weekday" effect can be used as a marker of the dominant chemistry regime (Steiner et al. 2010; Murphy et al. 2007). Comparing changes in weekday and weekend O_3 concentrations can provide an indication of the local chemical regimes of O_3. Under a NO_x-saturated regime, O_3 concentrations tend to increase during the weekends as a result of lower NO_x (Pusede and Cohen 2012). Figure R3 shows the station type area annual averages of the "weekend-weekday" effect of daily maximum 8h average (MDA8) (i.e. difference between MDA8 concentrations during the weekends and O_3 concentrations on weekdays). The weekend-weekday effect is more pronounced at the urban stations that show positive and larger values of ΔMDA8 over most of the years. We observe a transition between chemical regimes (NO_x-saturated, NO_x-limited) in some years at rural and suburban stations. The weekend-weekday effect is more pronounced at the urban stations, consistent with a NO_x-saturated regime. However, it is noted a general decrease of the "weekend-weekday" effect during the last years of the period of study, pointing out a general transition to NO_x-limited regime.
Furthermore, to provide a general picture of the dominant regimes across the stations considered in our study, we have examined the sign and the magnitude of the weekend effect (i.e. difference between O_3 concentrations during the weekends and O_3 concentrations on weekdays) separately for each period (i.e. 1999-2008, 2009-2018) (Fig. R4). During the first period of the study 1999-2008 (left) most of the stations exhibit positive values of ΔMDA8 and the urban stations show the largest values, consistent with a NO_x-saturated regime. The weekend-weekday effect is lower across the rural stations, although we found positive values at some the rural stations over the southwest regions, which indicates a more dominant NO_x-saturated regime. On the contrary, for the second period 2009-2018 a weaker weekend-weekday effect (right) is found. The rural stations show the lowest values, consistent with a NO_x-limited chemistry. Moreover, the urban stations show a general tendency to move from a NO_x-saturated regime towards a NO_x-limited regime.

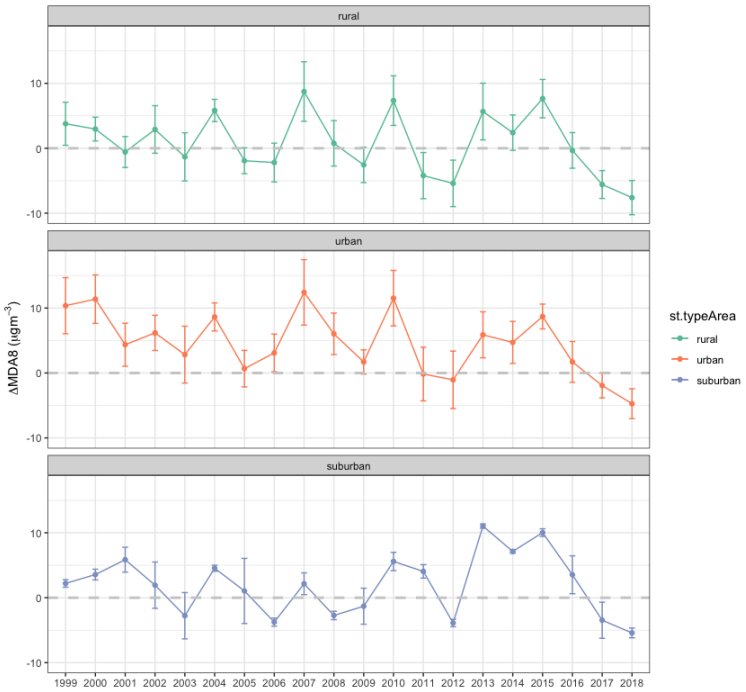

Figure R3. Annual averages of the weekend-weekday effect estimated as differences between annual weekends and weekdays averages of MDA8 over each station type area, rural, urban and suburban. Error bars represent the corresponding standard deviation.

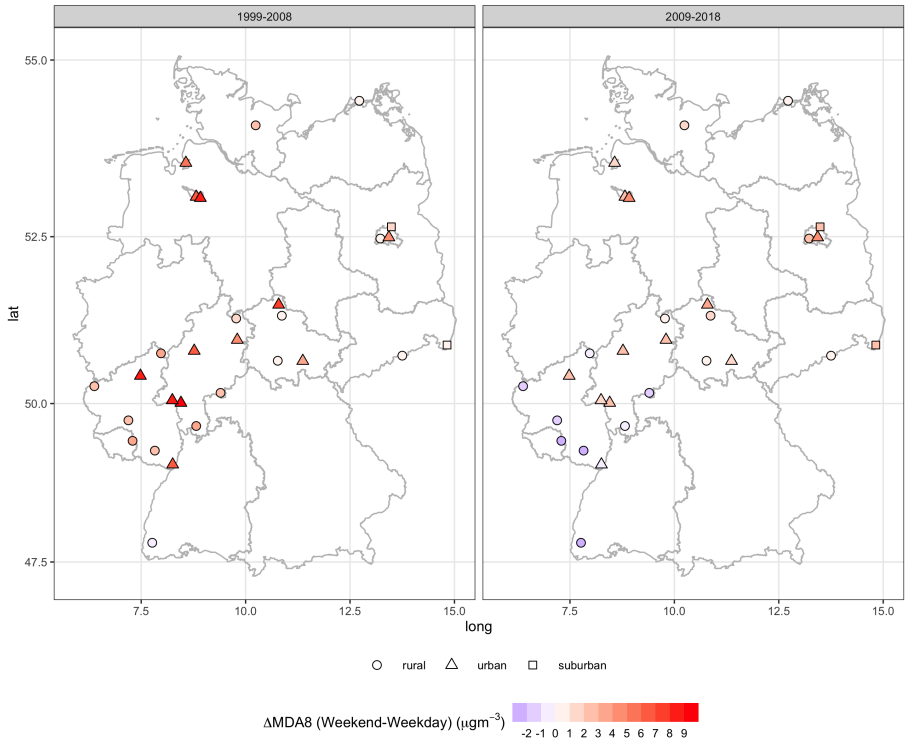

Figure R4. Spatial distribution of weekend-weekday effect calculated for each period.

We have included the analysis weekend-weekday effect (in particular, Fig. R4) in the revised version of the manuscript.

On a related note, while this study considers an assortment of ozone-influencing covariates alongside temperature and NOx, it conspicuously ignores others. For example, VPD is considered to represent dry deposition rates, and temperature is identified as a surrogate for biogenic emissions, but there is no mention of changes in the plants responsible for these effects in the first place. Changes in land cover, whether in the form of ongoing biosphere growth and aging, losses due to anthropogenic land development, or shifts in plant speciation can all have drastic impacts on biogenic emissions, their temperature dependence, and other surface/atmosphere connections such as ozone deposition velocities. It is surprising, therefore, to see no model inclusion or even mention of how changes across the temporal domain could influence O3-temperature dependence in this study.

We agree with Referee #2 that land-atmospheric interactions are an important factor for air quality. We have added some extra text in the introduction to highlight the importance of land-atmospheric interactions. We would like to emphasize that we restrict the number of covariates to those that have larger impact on ΔO_3 and might influence its temperature dependence. Here, we provide a simple approach to model ΔO_3 production rates. Examining in more detail changes in land cover, losses due to anthropogenic land development, or shifts in plant speciation would be definitively an interesting extension of this work, but it is out of scope of this study.

The primary conclusions of this paper are generally either unsurprising and under-developed. The correlation between NOx emissions and the O3 climate penalty has been consistently observed, modeled, and dissected in studies performed all over the world, and there doesn't seem to be much added to the conversation here. Furthermore, areas of potential interest, such as the observation that "NOx reductions alone can not explain the changes in the temperature dependence of O3" go largely unexplained, leaving open the questions that could lead to more

significant and meaningful answers.

As stated earlier, we have taken note of these general comments and we have accordingly modified the manuscript. In particular, we have substantially revised the section 4.3.1 (NO_x and temperature interaction) and we have modified the text according to the referees suggestions. In the revised version, we discuss in more detail the implications of NO_x reductions as shown in the GAMs, but also considering the changes in VOC.

Figure and text quality are highly inconsistent, with some glaring issues scattered throughout. Puzzling color and layout choices make it difficult to make sense of visualizations. For example, Figure 1 includes a color scheme to show station altitude, but these colors show no obvious consecutive progression, making the ready comparison of sites awkward and unintuitive. Panels of contour and ribbon plots might show features of interest, but, aside from textual description of very basic features, they don't receive much development or interpretation in the text. Grammar, spelling, and phrasing mistakes often impede manuscript fluency and flow.

Figure 1 has been updated removing the altitude colors which are not relevant for our analysis. We hope that that the modifications included in the revised version of the manuscript have helped to improve the readability of the manuscript and in particular the interpretation of the figures mentioned by this referee.

Data filtering seems to be extremely strict, and it is unclear how this filtering process may itself have resulted in spatiotemporal differences. Were there any discernable patterns with respect to the percentage of hours kept for analysis across station and year? Could changes in the frequency of removed hours over time, or between stations, confound comparisons? This seems like a potentially large source of statistical artifacts, if not examined and accounted for.

After examining the results obtained with the GAMs when using the whole data (with not previous filtering processing) we observed that in most of the stations the interaction term of temperature and NO_x representing the photochemical processes did not show a well defined pattern (see Figs. R5-R7).

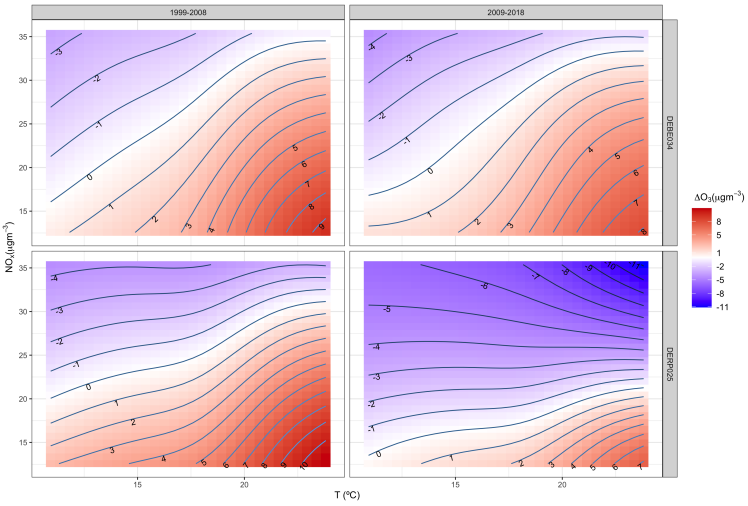

Figure R5. Countour plots obtained for the interaction term temperature and NOx from each GAMs built separetaly the selected urban stations as in the manuscript (Fig. 5, left)

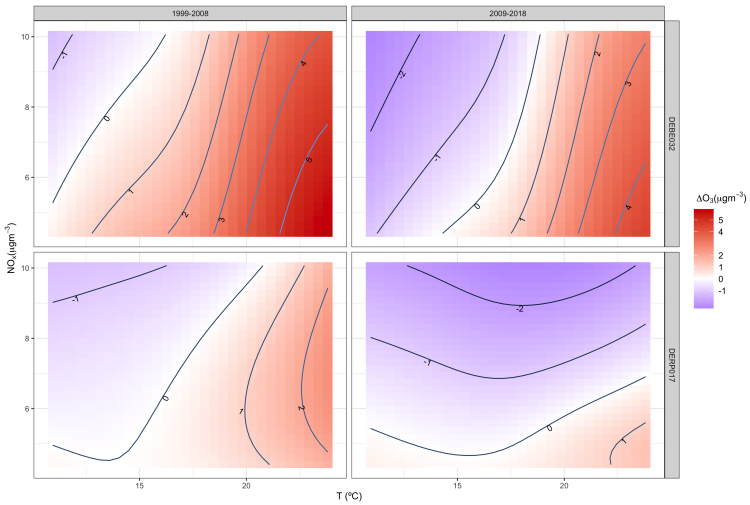

Figure R6. Countour plots obtained for the interaction term temperature and NOx from each GAMs built separetaly the selected rural stations as in the manuscript (Fig. 8, left)

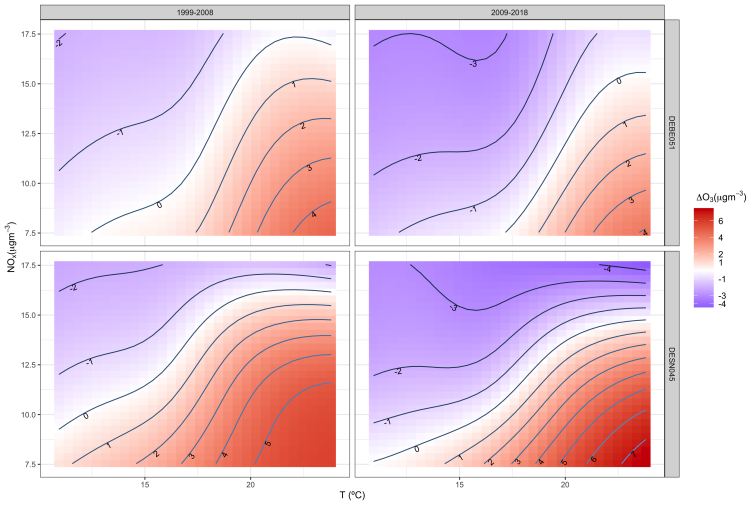

Figure R7. Countour plots obtained for the interaction term temperature and NOx from each GAMs built separetaly the selected suburban stations as in the Supplement (Fig. S10).

The filtering process was applied to assure that the photochemistry involved during the local ozone production (in our case this is represented by ΔO_3) are not masked by other meteorological factors (e.g. wind speed). Previous studies that analysed the temperature dependence of O_3 restricted the analysis to daytime (e.g. 10:00-14:00, 10:00-16:00) or afternoon (12:00-16:00) (Pusede and Cohen 2012; Abeleira and Farmer 2017; Romer et al. 2018). Here, we extend the daytime hours by filtering the data from sunrise until O_3 reaches the maximum (usually occurring in the afternoon). In addition, since we are interested in the non-linear relationship temperature-NO_x, we applied a wind speed condition to remove local meteorological effects that can influence the temperature sensitivity of O_3, but not relevant for assessing the impacts of NO_x changes.

Figure R8 shows the percentage of the data after using the filters mentioned above. After applying the second filter (i.e wind speed < 3.2), for most of the stations we use $\sim$ 15-30% of the total data (without any filter). Less data survived to the NO_x cut-off, and we noticed a major impact in some of the rural stations (i.e. DEUB029, DEUB028). However, in order to make meaningful and consistent comparisons among stations we decided to apply the same NO_x cut-off to all stations.

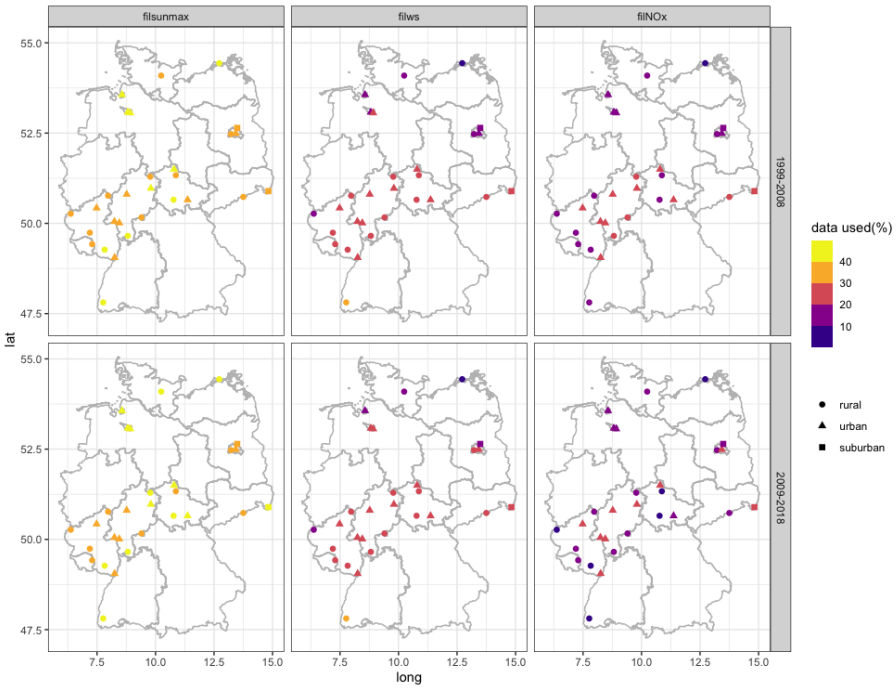

Figure R8. Percentage of survived data to the filter steps used in the analysis: from sunrise until the ozone peak (left), low winter speed (middle) and NOx above 5 ugrm-3 (right).

Most of the data used as an input for the GAMs correspond to daytime (~ 07:00-14:00) and we did not find any significant pattern with respect the hours used and years (see Fig. R9). Again, applying the NO_x cut-off decreases the percentage of the data in some stations, but we believe that for consistency it should be applied to all stations.

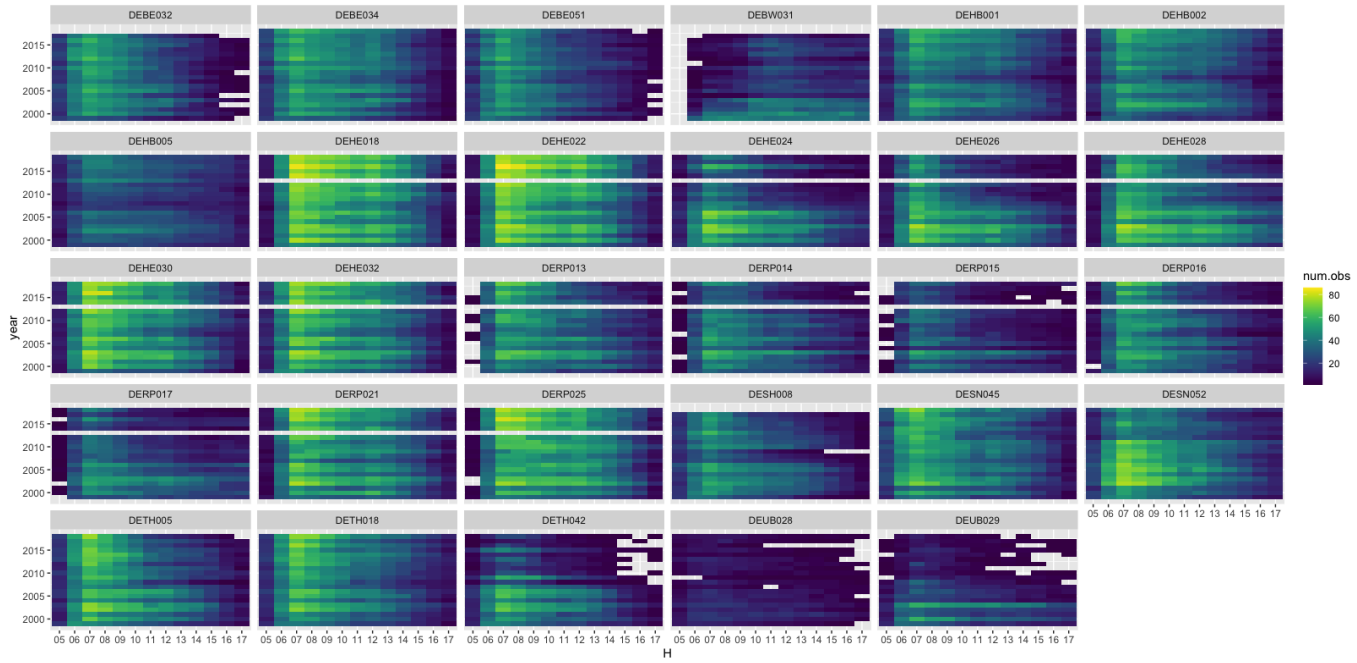

Figure R9. Hourly observations after appliying the filter applied. The empty row in some stations correspond to the missing year allowed for the study (see Section 2 in the manuscript).

Model selection deserves more attention and description. It is stated that the goal was "a common model well defined across all of the stations", but later it is mentioned that "the model selection procedure was applied separately at each station and period." Does this mean that forward selection was performed individually by station and time? If so, this is a major problem in the interpretation of model output. If not, it's unclear how these two statements are reconconciled. How was forward selection applied in a way that resulted in a common model across all stations, while also being applied separately by station and period?

This comment was also mentioned by Referee #1. Section 3.3 has been changed and a detailed model description can be found in the Supplement. We would like to clarify that the model selection procedure was individually applied to each station and period. After the selection process, we found that the best model selected at most of the stations included three interaction terms: temperature-NO_x, VPD-O_3 from the previous hour and ΔBLH-O_3 from the previous day. Therefore, we used the same model configuration (i.g. these interactions) for all the stations and both periods.

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Observed changes in the temperature dependence response of surface ozone under NOx reductions over Germany

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Abstract. Due to the strong temperature dependence of surface ozone concentrations (O_3), future warmer conditions may worsen ozone pollution levels despite continued efforts on emission controls of ozone precursors. Using long-term measurements of hourly O_3 concentrations co-located with NO_x concentrations in stations distributed throughout Germany, we assess changes in the climate penalty, defined as the slope of ozone-temperature relationship during the period 1999-2018. We find a stronger temperature sensitivity in the urban stations over the southwestern regions, especially in the first period of the study (1999-2008). We show a decrease in the climate penalty in most of stations during the second period of the study (2009-2018), with some exceptions (e.g. Berlin) where the climate penalty did not show significant changes. A key motivation of this study is to provide further insights into the impacts of NO_x reductions in the O_3-temperature relationship. For that, we propose a statistical approach based on generalized additive models (GAMs) to describe ozone production rates, inferred from hourly observations, as a function of NO_x and temperature, among other variables relevant during the O_3 production. ~~We find~~The GAMs confirm lower O_3 production rates during the second period (2009-2018) at most stations and a decreasing sensitivity to temperature. We observe that a large number of stations are transitioning to NO_x-limited chemistry, consistent with a decreasing temperature dependence of O_3 at higher temperatures as a result of sustained NO_x reductions. Our analysis indicate that emissions reductions have been effective in a number of stations, particularly in the southwestern regions. However, adional NO_x reductions should be required in a few stations (e.g. Berlin) to effectively mitigate the temperature dependence of O_3. The GAMs results showed changes in the shape of the function representing the O_3-temperature relationship when comparing the first and second decade. From these results, we infer effective VOC reductions over time that have also contributed to the observed decrease of O_3 production rates. ~~pointing out that lowering NO_x concentrations resulted in decreasing O_3 production rates. However, we also observe changes in the shape of the function representing the O_3-temperature relationship, which indicate that NO_x reductions alone can not explain the changes in the temperature dependence of O_3. Our analysis would suggest that decreasing NO_x concentrations are not the only factor causing the observed changes in the climate penalty factor.~~

1 Introduction

Tropospheric ozone (O_3) is a secondary pollutant formed from complex photochemical reactions of nitrogen oxides (NO_x), carbon monoxide (CO) and volatile organic compounds (VOCs) (J.H and Pandis, 2006). Changes in emissions of two of its major precursors, NO_x and VOCs, might alter ozone formation regimes that are controlled by the initial NO_x/VOC ratio (Sillman, 1999). Large NO_x emissions and concentrations favour a VOC-sensitive regime, which is commonly found in urban areas, while large VOC emissions and concentrations, and HO_x production rates favour a NO_x-sensitive regime, usually observed in rural environments (Sillman, 1999). The chemistry of O_3 production ~~vary~~ varies nonlinearly with temperature, which speeds up the rate of many chemical reactions. Furthermore, some anthropogenic and biogenic sources are strongly related to temperature. Pusede et al. (2014) examined changes in organic emissions by using a temperature-response framework and they found that the total organic reactivity experimented larger decreases from 2000-2010 at lower temperatures (emissions of temperature independent organic reactivity) than at higher temperatures (emissions of temperature dependent organic reactivity). Temperature is a fundamental variable that controls variations of biogenic emission of VOCs that increase with temperature and solar radiation (Pusede et al., 2015). Therefore, O_3 production is highly sensitive to meteorological parameters, and thus, changes in ambient conditions and precursor emissions are nonlinear and complex.

A wide number of studies have shown that the O_3-temperature relationship varies in space and time due to differing chemical and meteorological mechanisms that influence O_3 formation (Rasmussen et al., 2013; Bloomer et al., 2010; Steiner et al., 2010). It has been recognized the temperature dependence of biogenic VOC emissions as well as the sensitivity of O_3 production to temperature to the peroxy acyl nitrate (PAN) dissociation rates (Jacob et al., 1993; Sillman and Samsom, 1995; Jacob and Winner, 2009). Moreover, dry deposition (Wesely, 1989) and NO_x emissions (Coates et al., 2016) can contribute to the O_3-temperature relationship. Pusede et al. (2015) provides a comprehensive review of the temperature dependence of O_3 production. They pointed out that changes in O_3 precursors under a warmer climate will affect O_3 production in a predictable but complex way. For example, the continued NO_x reductions in urban areas would lead to a transition in the chemistry of O_3 production into chemical regimes typically observed in rural areas.

Romer et al. (2018) investigated the effect of temperature in O_3 production using measurements in a rural site over the southeastern ~~U.S.~~United States. They found that local chemistry were key drivers of increased O_3 concentrations on hotter days, and a large proportion of this increase was attributable to temperature-driven increases in soil emissions of NO_x. Recent modelling studies have examined the processes driving the O_3-temperature relationship. Porter and Heald (2019) used model simulations to quantify the contribution of mechanisms driving the O_3-temperature relationship. They found that a large proportion of the O_3-temperature relationship might be explained by other meteorological phenomena such as stagnation and humidity over Europe. Stagnant conditions characterised by low wind speed, allow O_3 to build up to high levels. High levels of humidity have certain scavenging effect on O_3, as higher humidity is usually associated to greater cloud cover and atmospheric instability that can inhibit ~~phochemical~~photochemical reactions and hence, decrease O_3. Similarly, Kerr et al. (2019) performed sensitivity simulations to examine the role of the processes related the to the O_3-temperature relationship over ~~U.S.~~the United States, focusing on transport, chemistry and anthropogenic emissions. They found that atmospheric transport played a significant role

in explaining the O_3-temperature relationship through out much of ~~U.S.~~the United States. Since transport is indirectly related to temperature, the authors highlighted the importance of providing a better understanding of the changes in the mechanisms linking transport and O_3 in a warmer climate.

Under future climate conditions, the benefits from control strategies of ozone precursors might be countered by temperature increases (Rasmussen et al., 2013). This effect has been termed in the literature as a "climate penalty", which has been used to quantify the additional increase of O_3 or the reduced benefits of emissions controls as a result of climate change (Wu et al., 2008; Rasmussen et al., 2013). Observational and modelling studies (Bloomer et al., 2009; Steiner et al., 2010; Rasmussen et al., 2013) have reported a decreasing sensitivity of O_3 to temperature over time reflecting the emission reductions. Using observational datasets, Jing et al. (2017) examined the climate penalty factor during three periods covering a long period of 1990-2015. They found that the climate penalty, defined as the slope of O_3 change with increasing temperature, was by average ~~0.47 ppb K^{-1}~~ $0.43\,ppb\,K^{-1}$ less in the second part of the period (1999-2007) than in the first part (1990-1998), but this decrease was not observed in the last part of the period (2008-2015), despite the NO_x reductions in most of the urban areas of the Midwest ~~U.S.~~United States. Recently, Boleti et al. (2020) showed a decreasing sensitivity of O_3 to temperature during the period 2000-2015 over some European regions. They suggested that a weaker O_3 sensitivity could be attributed to decreasing NO_x concentrations and the differences in the changes to this sensitivity across sites were driven by regional meteorological conditions. Previous studies have shown that feedbacks from vegetation worse peak O_3 episodes especially during extreme hot and dry periods over Europe (Lin et al., 2020; Gerosa et al., 2009). Moreover, soil moisture deficit is a relevant factor of stress for isoprene emissions (Guenther et al., 2006). Severe droughts might influence plant growth and limit biomass production, which can lead to a reduction of isoprene emission (Emmerson et al., 2019). Demetillo et al. (2019) found that the drought over California suppress isoprene emissions regionally and the severe drought conditions worsen the ozone climate penalty due to a decreasing biogenic activity that would favor the production of O_3 in a NO_x-saturated system. Lin et al. (2020) examined the contribution of drought to the O_3 climate penalty over the past six decades over Europe using numerical simulations. They highlight the importance of considering land-atmospheric interactions and they showed that reduced ozone removal by water-stressed vegetation due to dry conditions, exacerbate ozone air pollution over Europe.

According to the EuroDelta-Trends modelling experiment (ETC/ACM, Colette et al., 2017) the reduction of European anthropogenic emissions of O_3 precursors was the main factor in decreasing summertime O_3 peaks episodes during the period 1990-2010. Several studies have documented downward trends across European sites of different metrics of ozone concentrations, such as the 4th highest daily maximum 8-hour ozone (4MDA8) and the number of days maximum ~~maximum~~ 8-hour ozone > 70 ppb (NDGT70) (Fleming et al., 2018; Chang et al., 2017). Some studies have reported increasing levels of O_3 concentrations at urban polluted sites as a result of lower titration processes through reaction with ambient nitric oxide (Yan et al., 2019; Querol et al., 2016). Based on measurements and sensitivity analysis Yan et al. (2018) showed that emission reductions had contrasting effects on O_3 and its interannual variability was regulated by climate variability. As stated in early studies, the current regulations on emissions of O_3 precursors, in particular NO_x, establish an ideal scenario for investigating the impacts of these changes on the O_3-temperature relationship (Pusede et al., 2015). This is crucial to improve air quality regulations because mechanisms influencing the relationship between O_3 and temperature are not completely well understood, partly be-

cause it is also influenced by meteorological processes and large-scale atmospheric patterns associated with high temperatures that lead to high O_3 concentrations.

~~Our work examines long-term O_3 concentrations to investigate the observed trend in the summertime climate penalty factor.~~ The primary objective of this study is to assess the observed changes in the O_3 climate penalty and the impacts of NO_x reductions on the temperature dependence of O_3. Moreover, we aim to infer changes in organic reactivity that might have contributed to the observed changes in the O_3 sensitivity to temperature. For that, we use long-term O_3 concentrations over ~~We focus on~~ Germany where the temporal homogeneity and diversity of the data offer an unique opportunity for long-term analysis of O_3 and NO_x. We examine changes in the O_3-temperature relationship over a 20-year time period covered 1999 to 2018, for which a greater number of sites were available. Furthermore, we restrict our study to summertime when O_3 normally reaches the highest levels and the photochemical activity is higher (Pusede et al., 2015). In addition, it has been shown a stronger temperature dependence of O_3 over Germany in summertime (Otero et al., 2018). We begin our study by calculating the trends in NO_x concentrations that might lead to changes in the O_3-temperature relationship and then, we examine the climate penalty factor over the last two decades. Since the variability of O_3 production can explain a considerable proportion of O_3-temperature relationship [Pusede et al. (2015)], we propose an observational-based modelling approach to examine the nonlinear dependence of O_3 production on NO_x-temperature relationship. Within a statistical modelling framework built upon Generalized Additive Models (GAMs), we infer O_3 production (as a rate of change of O_3, ΔO_3) from hourly O_3 concentrations. Thus, we model ΔO_3 as a function of temperature and NO_x along with other critical variables during the O_3 formation. Ultimately, we aim to provide new insights into the O_3 response to changes of its precursors in different environments and the effectiveness of emission reductions.

2 Data

Hourly measurements of O_3 and NO_x concentrations were extracted from the European Environment Agency's (EEA) public air quality database "AirBase" (https://www.eea.europa.eu/data-and-maps/data/aqereporting-8). The number of sites and length of the period covered by each station for which measurements are available vary spatially and greatly by pollutant. The selection of the monitoring stations with co-located data (O_3 and NO_x) was based on the station type (background), station type area (rural, urban, suburban) and altitude (<1000m). Only the stations reporting more than 75 % of valid data out of all the possible data in each summertime were included in the study. We use the stations with at least 19 years with hourly co-located data within the whole period of study defined from 1999-2018. Here, summertime is referred to July-August-September (JAS), with a strong O_3-temperature relationship, particularly in Central Europe (Otero et al., 2018). A total of 29 stations meet the pre-processing criteria: 15 rural, 12 urban and 2 suburban stations. Despite that the spatial distribution of the measurement sites is not uniform with the largest density of stations over west and central Germany, a representative number of stations covering eastern regions are included (~~figure~~ Fig. 1). Daily means and daily maximum of the running 8-hour mean of O_3 (MDA8) were calculated following the European Union Directive of 2008 procedure (European Parliament and Council of the European Union, 2008).

The meteorology was extracted from the ERA5 (Herbach and Dee, 2016), the latest climate reanalysis produced by the European Centre for Medium Range Weather Forecast (ECMWF) that provides hourly data on regular latitude-longitude 0.25ºx0.25º spatial resolution. The variables included in the analysis are air surface 2m-temperature (°C), 10m u and v-component of wind ($\mathrm{m\,s^{-1}}$), boundary layer height (m) and relative humidity at 1000 hPa (%).

3 Methods

3.1 Climate penalty factor

A number of definitions have been used in the literature to characterise the ozone climate penalty, usually represented as the linear relationship between O_3 and temperature. Climate penalty values are normally computed using daily maximum summertime O_3 observations (1 or 8h average) and daily maximum temperature, although there is no standard definition (Pusede et al., 2015). Here, we adopted one of the most common metric to represent the climate penalty (hereinafter, m_{O_3T}) as the slope of the best fit line between long-term MDA8 concentrations and daily maximum temperature (Bloomer et al., 2009; Steiner et al., 2010; Otero et al., 2018). We first calculated the m_{O_3T} with a linear regression model applied separately for each station and each period (1999-2008, 2009-2018). The general equation for the linear model can be written as follows:

$$Y(t) = a + m_{O_3T}\,T(t) + \epsilon(t) \tag{1}$$

with $\epsilon(t) \sim \mathcal{N}(0, \sigma^2)$ being a sequence of independent Gaussian random variables with zero expectation. Y(t), T(t) are the time series of MDA8 and daily maximum temperature (respectively). We estimate the climate penalty separately for the periods 1999-2008 and 2009-2018 and the significant differences between the slopes in both periods are assessed through a t-test. ~~Then, we examined the difference between the slopes obtained for each period, introducing an interaction factor term in the linear model to quantify the slope differences:~~

~~$\mu(t)$=T(t)*P(t)~~

~~Y(t), T(t) are the time series of MDA8 and daily maximum temperature (respectively) for the whole period 1999-2018 and P is categorical variable with two categories: one representing the period 1999-2008 and another representing 2009-2018.~~

3.2 Approximation of O_3 production rates from observations

Most of the previous works have used numerical models (Steiner et al., 2006), box model (Coates et al. 2016), plume model (LaFranchi et al., 2011) or analytical models (Pusede et al., 2014; Romer et al., 2018) to analyse the temperature-dependent mechanisms affecting the O_3 production. Here, we propose a new approach based on GAMs to examine changes in the O_3 production. We approximate the ~~later~~latter by the rate of change of hourly O_3 concentrations as:

$$\Delta O_3(t) = O_3(t) - O_3(t-1) \tag{2}$$

The general O_3 budget equation can be expressed as:

$$dO_3/dt = PO_{3chem} + LO_{3chem} + MD \tag{3}$$

PO_{3chem} represents the chemical O_3 production rate, LO_{3chem} is the chemical loss rate and the last term MD represents the dynamical processes that influence O_3 concentrations, including mixing and dry deposition processes. These individual processes can vary in strength and by location throughout the day.

As we aim to assess how NO_x reductions influence the sensitivity of O_3 to temperature, we restrict our analysis to a time interval with an intense photochemical activity, which usually coincides with higher O_3 concentrations and warmer temperatures. Thus, the data was filtered to avoid including non-related photochemical processes that might mask the photochemistry in the daily O_3 production. First, we selected data after sunrise and until O_3 reaches the daily maximum value (usually in the afternoon). In order to exclude some maximum values that might occur late in the afternoon or evening and are mostly related to prevailing meteorological conditions and transport processes (Kulkarni et al., 1993), the time was restricted to 17:00 H (local time). Then, a wind speed condition was used to exclude the hourly data when wind speed was higher than $3.2\,\mathrm{ms}^{-1}$, which is the threshold value usually applied to define stagnant conditions (Horton et al., 2014). After a first inspection of the data, we found considerable differences in the minimum of NO_x concentrations across some stations and periods, likely due to the detection methods. To better establish a comparison between stations and periods, we applied an additional filter to remove NO_x values below $5\,\mu\mathrm{gm}^{-3}$. The number of observations that met these conditions varies with each station type and on average a 20%(urban), 14%(rural), 18%(suburban) of the total data was used.

3.3 Modeling O_3 production rates with GAMs

GAMs (Hastie and Tibshinari, 1990; Wood, 2006) were used to examine variations in ΔO_3(t) over the last two decades and the changes in the relationship NO_x-temperature given the observed downward trends of the O_3 sensitivity to temperature in the two periods of study 1999-2008 and 2009-2018. GAMs are useful tools for estimating non-parametric relationships whilst retaining clarity of interpretation (Wood, 2006). The relationship between the explanatory variables (henceforth covariates) and the response is described by smooth curves (splines, or potentially other smoothers). Such models have proven useful for studying the complex non-linear relationships between atmospheric chemical species and meteorological parameters (Carslaw et al., 2007; Jackson et al., 2009; Barmpadimos et al., 2011; Boleti et al., 2019).~~GAMs allow including nonlinear interactions between covariates with different smoothers assumed for each covariate. The GAM can be formally written as:~~ In the frame of GAMs a model for the expectation μ of a random variable $Y \sim \mathcal{N}(\mu, \sigma^2)$ can be written as

$$g(\mu) = \beta_0 + f_1(X_1) + f_2(X_1) + \ldots \tag{4}$$

where g is static ~~the~~ link function, X_n are the ~~explanatory variables~~ covariates and f_n are the non-parametric smoothing functions; β_0 is the intercept ~~and ϵ is an error term.~~If the response can be assumed to be normally distributed, the canonical link function is the identity. After a closer inspection of the residuals at the individual sites, we found non normally distributed residuals with problems in the tails. ~~Alternatively, we used a scaled t distribution recommended for heavy tailed response variables (Wood et al. 2016). Thin plate regression was used as smoothers to describe a nonlinear relationship between the response and 2 covariates (interaction) (Wood et al. 2016).~~ Thus we used a scaled t distribution instead, which is recommended for heavy tailed response variables (Wood et al., 2016).To include non-linear interactions between covariates, tensor products

were used as smoothers, e.g.,

$$\mu = \beta_0 + f_1(X_1, X_2) + \dots . \quad (5)$$

This describes a nonlinear relationship between the response and 2 covariates (interaction) (Wood, 2006). The smoothness of each function is controlled by the number of knots or effective number of degrees of freedom. Here, the smoothing parameters were estimated by restricted maximum likelihood (REML) (Wood, 2006).

The challenge in building a model that captures a large proportion of the variability of ΔO_3 is to select the key covariates out of a large number of potential variables. As stated in the previous section, changes in O_3 concentrations depend on local production, involving many chemical reactions that vary with temperature, loss mechanisms that are sensitive to meteorological conditions and transport processes. Therefore, we chose the variables that are expected to have a major influence on O_3 production (e.g. NO_x). The photochemical nature of O_3 production is strongly influenced by temperature. In particular, temperature increases biogenic emissions of VOCs, such as isoprene, from vegetation (Coates et al., 2016; Pusede et al., 2014). Thus, we use temperature as a surrogate to represent changes in VOC, since biogenic VOC are emitted as an exponential function of temperature (LaFranchi et al., 2011; Pusede et al., 2014).

Daytime variation in the boundary layer height (BLH) significantly contributes to changes in O_3 production rates that tend to increase with a deepening BLH during sunny and warm days. (Haman et al., 2014). In addition to chemical and mixing processes, changes in O_3 concentrations are influenced by deposition. Therefore, additional covariates are the percentage of change of the boundary layer height growth rate (ΔBLH) (in %) accounting for mixing processes, and vapour pressure deficit (VPD) as it has been recognised as a key variable for dry deposition (Kavassalis and Murphy, 2017; Otero et al., 2018). The VPD was calculated from the corresponding hourly data of air temperature and relative humidity. Moreover, we included the O_3 concentrations from the previous hour ($C_{O_3}(t-1)$) and the MDA8 concentrations from the previous day ($C_{MDA8}(t-24)$) to represent the persistence of previous chemical conditions, (Pusede et al., 2015). ~~We first started with a baseline model that included the nonlinear relationship between NO_x and temperature as follows:~~

~~$\Delta O_3 \sim f(T, NO_{x})$~~

~~$f(T, NO_x)$ represents the interaction between temperature (T) and NO_x concentrations and it is included as a tensor product (Wood et al. 2017). Observing the skewness of the NO_x data led us to introduce a modification in the baseline model using a log transformation of NO_x.Since we aim to build a parsimonious model to better explain the variability of ΔO_3, we gradually added the covariates to the baseline model through a selection procedure. During the stepwise process, we also allowed interactions between two influencing covariates: the VPD and the $C_{O_3}(t-1)$, and the ΔBLH and $C_{MDA8}(t-24)$. As in previous studies (e.g. Gong et al. 2017), we adopt a forward selection method based on the Akaike information criterion (AIC) with the goal of obtaining a common model well defined across all of the stations. AIC is a robust approach to assess the model performance and to comparing the different model structures (Pedersen et al. 2019). The model selection procedure was applied separately at each station and period. Thus, we fit a GAM for the first period 1999-2008 (GAM-P1) and a GAM for the second period 2009-2018 (GAM-P2).The model performance was assessed through standard diagnostic plots: QQ plots of the~~

~~deviance residuals, scatter plots of the residuals against the fitted values, histogram of residuals and scatter plots the response against the fitted values (Wood, 2006).~~

We use a forward selection procedure of the best set of covariates and/or its interactions that maximised the deviance explained. The model improvement was assessed with the Akaike Information criterion (AIC) (Akaike, 1974). The selection process, applied individually at each station and period, led for most of the stations to a similar model defined with three interaction terms: 1) temperature and NO_x, 2) VPD and $C_{O_3}(t-1)$, and 3) ΔBLH and $C_{MDA8}(t-24)$. Thus, a GAM with the mentioned form was built for each station and period. Here, we will refer as GAM-P1 to the GAMs built for first period 1999-2008 and similarly, as GAM-P2 to the GAMs built for the second period 2009-2018. The model selection indicated that as variables were added and the model complexity increased (i.e. more interactions), the AIC decreased and the deviance explained increased (Fig. S1). The model performance was assessed through standard diagnostic plots (Wood, 2006): QQ plots of the deviance residuals, scatter plots of the residuals against the fitted values, histogram of residuals and scatter plots the response against the fitted values (Fig. S2). More details about the GAM description and the selection procedure can be found in the Supplementary Material.

4 Results

4.1 ~~Climate penalty~~ NO_x changes and climate penalty

Before calculating the m_{O_3T}, we assess changes in the NO_x concentrations over the whole period of study (1999-2018). For that, we examine time series of the annual 5th, 50th, and 95th percentiles calculated from daily NO_x concentrations, assessing the trends (Kendall, 1975) and estimating its slope (Theil, 1950; Sen, 1968). Figure 2 shows annual 5th, 50th, and 95th percentiles calculated from daily NO_x concentrations at some example stations located in Berlin, Rhineland-Palatinate and Saxony that are representative for each station type area and will be used below to present the modelling results. The NO_x concentrations at the 95th percentile have generally declined over the overall period of study (1999-2018), but the most dramatic reduction is observed during the first part ot the period (1999-2008) in the example stations. Larger decreases are observed at the stations in Rhineland-Palatinate, specially at the urban station (DERP025) where the NO_x concentrations at the 95th percentile declined at the rate of $-4.45\,\mu g\,m^{-3}yr^{-1}$ in the first period 1999-2008 and $-3.38\,\mu g\,m^{-3}yr^{-1}$ in the second period 2009-2018 (see Fig. S3~~S1~~ in the Supplementary Material). Similar trends are observed at the urban stations located in the southwest and central regions (Fig. S3 and S4~~S1 and S2~~). The NO_x concentrations at the 95th percentile have been reduced at the urban and rural stations in Berlin during the first period 1999-2008 with decreasing rates of -2.78 and $-1.77\,\mu g\,m^{-3}yr^{-1}$, respectively, while small and non significant changes are observed during the second period (Fig. S3~~S1~~). Overall, annual 50th percentile NO_x concentrations show a steady decrease in most of the stations of the study, more pronounced during the first period, and small changes are found at the 5th percentile of NO_x especially during the second period 2009-2018 (Fig. S3~~S1~~ and S4~~S2~~).

As emissions of NO_x generally decrease on weekends, O_3 concentrations tend to be higher on weekends compared to O_3 concentrations on weekdays (Pusede and Cohen, 2012; LaFranchi et al., 2011; Murphy et al., 2007). This so-called weekend-

weekday effect has been widely used to assess the effectiveness of emission controls and it provides insights into the O_3 regimes (Abeleira and Farmer, 2017). In addition to long-term changes in NO_x, we have further examined the weekend-weekday effect calculated separately for each period as $\Delta(O_{3,\text{weekend}}\text{- }O_{3,\text{weekday}})$ to elucidate the dominant chemistry regime at each period. While a strong weekend-weekday effect during the first period (1999-2008) is observed, in the second period (2009-2018) the weekend-weekday effect significantly decrease in most of the stations (Fig.3). This analysis indicate that during the first period a VOC-limited chemistry dominated at most of the stations (including some rural stations), but during the second period a large number of stations are transitioning to NO_x-limited chemistry in which O_3 tend to decrease due to NO_x reductions. We can anticipate the effectiveness of emissions reductions in those urban stations transitioning to a more NO_x-limited chemistry.

Figure ~~3~~4 shows the spatial distribution of the m_{O_3T} for each period and the changes in the slopes (relative to the first period). The highest values are found in the southwest stations during the first period 1999-2008 with m_{O_3T} 5-6.5 $\mu g m^{-3} {}^{\circ}C^{-1}$. Among these sites, urban stations show a higher sensitivity to temperature compared to suburban and rural stations. The lowest values of m_{O_3T} during the first period are observed in the north and eastern stations (4-5 $\mu g m^{-3} {}^{\circ}C^{-1}$). Significant differences between the m_{O_3T} calculated for each period are observed in most of the stations, including some rural areas in the southern regions where the m_{O_3T} dropped $-1.2\,\mu g m^{-3} {}^{\circ}C^{-1}$ (Fig.4, right ~~S3~~). Only a few stations show similar values of m_{O_3T} in both periods (e.g. Berlin). Boleti et al. (2020) reported a general decreasing sensitivity of daily maximum of O_3 with temperature for a shorter period (2000-2015) in regional clusters defined over Europe. They found larger trends in m_{O_3T} at high and moderate polluted clusters ant they argued that it might be due to NO_x reductions. Here, we found a general decrease in m_{O_3T} obtained from long-term data across different environments (i.e. rural, urban and suburban). Our results also pointed out significant differences in the m_{O_3T} across stations, with some polluted areas where the m_{O_3T} did not show significant changes with time (e.g. Berlin). As stated in the introduction, mechanisms controlling m_{O_3T} are not well established. A priori it is not evident what the impact of NO_x reductions is in the O_3 sensitivity to temperature, in particular in rural environments. Therefore, we next examine the variability of ΔO_3 as a function of temperature and NO_x in order to provide further insights into the nonlinear temperature-dependence of NO_x and the potential impacts on the observed m_{O_3T}.

4.2 Model performance

~~A final model including three interaction terms was designed from the selection procedure as the best fit to capture the ΔO_3 variability at most stations and periods.~~ As mentioned above, the final model obtained from the selection procedure includes three interaction terms to represent: 1) photochemical processes (temperature-NO_x), 2) dry deposition (VPD-$C_{O_3}(t-1)$), and 3) mixing processes (ΔBLH-$C_{MDA8}(t-24)$). ~~The model selection indicated that as variables were added and the model complexity increased (i.e. more interactions), the AIC decreased and the deviance explained increased (Fig. S4).~~ The performance of the GAMs was assessed by the adjusted r-squared for the model (R^2), defined as the proportion of the variance explained (Fig. ~~4~~ 5). The results showed similar R^2 values in both periods over most of the stations, with some exceptions where GAM-P1 seem to perform better than GAMP-P2 (e.g. over the region of Hessen). In general, GAMs showed a better performance over urban and suburban stations and 40% of the ΔO_3 variability was captured. The models performed poorly when applied to rural stations, they showed lower values of R^2. This likely reflects that GAMs designed with the underlying

assumptions of the interactions between the selected covariates is better suited for urban and suburban areas than for rural regions.

4.3 Model interactions

Our approach is built upon a conceptual model (~~4~~3) to evaluate the effect of chemical, deposition and dynamical-mixing processes affecting the O_3 production. ~~The final GAM includes three interaction terms defined by the covariates T-NO_x, VPD-$C_{O_3}(t-1)$ and ΔBLH-$C_{MDA8}(t-24)$.~~ Given that ΔO_3 is modelled with GAMs separately at each station and period, a large number of interaction surfaces were obtained. Thus, we focus on a representative number of stations for each station type area (i.e. rural, urban and suburban). The example stations presented here were selected based on a relatively good performance of the model as well as the corresponding geographical location in order to examine the results from the previous section showing marked differences in the sensitivity of MDA8 to temperature. Figures showing the results obtained for the rest of stations are available in the Supplementary Material. Note that the contour plots presented below reflect the partial effects, which allow us to compare the effect of those covariates included in the interaction term without considering the intercept and the other covariates (e.g. Fig. ~~5~~6). The summed effects that include the intercept and constant values for the others covariates not shown in the interaction surface, presented similar shapes but with the additive effect of those constant values (not shown). To estimate the predicted surfaces within a range of data sufficiently supported by the observations, we used the first and the third quantile of the distribution of the corresponding covariates for each station type area (urban, rural and suburban).

4.3.1 NO_x and temperature

Figure ~~5~~6 shows ΔO_3 as a function of NO_x concentrations and temperature for the example urban stations located in Berlin (DEBE034) and in Rhineland-Palatinate (DERP025) (see Fig. 1). Also shown in Fig. ~~5~~6 are the estimated regression lines for temperature while holding constant NO_x concentrations (i.e. mean conditions of NO_x each period). As we aim to assess the impact of NO_x reductions in the O_3-temperature relationship, we also use the GAM-P1 to project the ΔO_3 response to temperature, as it has been estimated under the first period conditions, but using the mean NO_x concentrations of the second period 2009-2018. Examining the GAM-P1 projection for the second period 2009-2018 and the GAM-P2 estimations can provide useful insight into the changes in the ΔO_3 sensitivity to temperature when lowering NO_x concentrations.

The interaction surfaces obtained from both stations illustrate the temperature dependence of ΔO_3 with increasing temperatures, implying a VOC-limited chemistry (Fig.~~5~~6, left). The temperature dependence of ΔO_3 is observed to vary with NO_x, but also with temperature in both stations. ~~We found a stronger temperature dependence of ΔO_3 in the first period 1999-2008 (GAM-P1) compared to second period 2009-2018 (GAM-P2). This feature is more pronounced in Rhineland-Palatinate, where the mean NO_x conditions declined by 35% in the second period 2009-2018 (relative to the first period 1999-2018), while in Berlin NO_x declined only by 7.5%.~~ From Fig. 6 it can be observed that at Rhineland-Palatinate the transition to NO_x-limited chemistry at higher temperatures occurs at lower values of NO_x ($15\,\mu g\,m^{-3}$) for the second period compared to the transition observed during the first period ($20\,\mu g\,m^{-3}$). On the contrary, the VOC-limited regime observed in Berlin is dominant in both periods. This is consistent with the decreasing weekend-weekday effect observed at Rhineland-Palatinate, but not found in

Berlin (see Fig. 3), which indicates that emission reductions over time were more effective in Rhineland-Palatinate (e.g. in Rhineland-Palatinate NO_x declined by 35%, while in Berlin NO_x declined only by 7.5% in the second period).

We examine the ΔO_3 response to temperature under the mean NO_x conditions for each period using GAM-P1 and GAM-P2 along with the prediction obtained from GAM-P1 that projects the ΔO_3 response in the second period 2009-2018 (prediction line in Fig. ~~5~~6, right). In Berlin, the ΔO_3 response to temperature shows a similar increase with temperature in both periods. In this case, the GAM-P1 prediction for the second period 2009-2018 is in a good agreement with the shape obtained from GAM-P2, which suggest that a decreasing temperature sensitivity of ΔO_3 could be explained by NO_x reductions. The increase of ΔO_3 with temperature is also depicted in Rhineland-Palatinate. But, in Rhineland-Palatinate the prediction from GAM-P1 for the second period 2009-2018 reveals discrepancies at higher temperatures when comparing to the ΔO_3 response from GAM-P2. It can be noted that the prediction from GAM-P1 for the second period (prediction line, Fig.~~5~~6) does not capture the steepness at temperatures above $20°C$ showed by GAM-P2. Contrasting to the results in Berlin, the changes in the shape that represents the ΔO_3 as a function of temperature suggest that the NO_x reductions would only partially explain the observed changes in the O_3-temperature relationship, but rather an underlying effect is likely to influence the ΔO_3 at higher temperatures. We interpret that the changes in the shapes would indicate effective reductions of VOCs over time that played a significant role on controlling ΔO_3.

We found similar features in the rest of the urban stations than in the example stations, with consistent interaction surfaces in terms of the ΔO_3 response to NO_x and the temperature dependence (Fig. S5). As in Rhineland-Palatinate, the regression lines were slightly different when comparing GAM-P2 and the projected ΔO_3 response under NO_x reductions (Fig. S6), which reinforce our hypothesis of an underlying factor influencing the ΔO_3-temperature relationship.

We further assess the effect of the temperature and NO_x on ΔO_3 separately with GAM-P1 and GAM-P2 under fixed NO_x and temperature conditions determined as the 10th, 50th and 90th percentiles of the corresponding distributions over the whole period of study (1999-2018). In contrast to the contour plots (Fig. ~~5~~6), we now include the intercept and a constant value (i.e. median) for the rest of the covariates, in order to further examine the summed effects. Table 1 summarizes the values of the covariates for the selected stations. The shaded areas denote the 95% pointwise confidence intervals of the GAM estimates. It should be noted that the smooth functions show a major uncertainty in the regions with less data (i.e. in the tails of the presented ranges). Figure ~~6~~7 shows ΔO_3 as a function of temperature. ΔO_3 estimates are generally lower in the second period 2009-2018 under moderate (50th) and high (90th) NO_x concentrations at both stations. Similarly, Fig. ~~7~~8 illustrates the changes in the nonlinear relationship between ΔO_3 and NO_x. In general, at lower temperatures (10th) ΔO_3 decreases with increasing NO_x concentrations. In Berlin, the relationships are similar for both periods, but show lower ΔO_3 estimates in the second period. In Rhineland-Palatinate we found a steeper decrease~~d~~ of ΔO_3 when moving to higher NO_x concentrations during the second period. ~~This indicate that the ΔO_3 sensitivity to higher NO_x at moderate and high temperatures is lower in the second period~~

We observed a shift of the ΔO_3 peak towards lower NO_x concentrations at most of the urban stations during the second period, which indicates that those sites are near to a more NO_x-limited regime as a result continued reductions of NO_x and

concurrent VOC decreases. Ultimately, we infer effective VOC reductions that led to larger ΔO_3 decreases during the second period.

Figure 89 depicts the interaction surfaces for two selected rural stations located in the same regions than the urban stations presented above, Berlin (DEBE032) and Rhineland-Palatinate (DERP017). ~~Similarly than in the urban case, the~~The temperature dependence of ΔO_3 is stronger in the first period 1999-2008 compared to second period 2009-2018. The GAMs-P2 show a decreasing sensitivity of ΔO_3 to temperature and ΔO_3 is generally lower with increasing temperature under similar conditions of NO_x. We see similarities between the rural and urban stations in Berlin, in terms of the shape of the nonlinear relationship between temperature and NO_x, which is expected due to the proximity between both stations (Fig. 1). Moreover, in Berlin the regimes transition with temperatures is well observed in both periods: a NO_x-limited chemistry at higher temperatures and a VOC-limited chemistry at lower temperatures. We observed that at similar NO_x concentrations during the second period, ΔO_3 tends to decrease in the NO_x-limited regime (high temperatures) when comparing to the first period, while ΔO_3 increases in the VOC-limited regime (low temperatures). This suggests that NO_x reductions in the rural station of Berlin (declining by 28.8%) led to ΔO_3 decreases at higher temperatures in the second period. ~~In contrast to the urban stations, the contours obtained from GAM-P1 and GAM-P2 are significantly different, particularly in Rhineland-Palatinate.~~ Similarly than in Berlin, we observe a well defined NO_x-limited regime at temperatures > $20°C$ and a VOC-limited regime at lower temperatures in Rhineland-Palatinate. The peak of ΔO_3 occurs at lower NO_x concentrations (<$8\,\mu g\,m^{-3}$) in the second period than the peak observed in the first period (> $8\,\mu g\,m^{-3}$), due to NO_x reductions (declining by 37%). The ΔO_3 as a function of temperature under NO_x mean conditions is also shown in Fig.89(right). ~~In Berlin, NO_x concentrations declined by 28.8%, which could partially explain the decrease in ΔO_3 estimates during the second period 2009-2018. However the shapes of the regression lines obtained from the GAM-P2 and the projected ΔO_3 response from GAM-P1 differ at temperatures below $20°C$ (blue and green lines, Fig. 8). In Rhineland-Palatinate the temperature dependence is considerably lower than in Berlin and a flat regression line is shown by GAM-P2 for the second period with a 37% decrease of NO_x concentrations. The discrepancies between the projected ΔO_3 response and the ΔO_3 estimates from GAM-P2 are higher at temperatures below $20°C$.~~ For both rural stations, the shapes of the regression lines obtained from the GAM-P2 and the projected ΔO_3 response from GAM-P1 are different. In Rhineland-Palatinate the temperature dependence is considerably lower than in Berlin and a flat regression line is shown by GAM-P2 for the second period. The discrepancies found here point out that changes in VOCs have also influenced ΔO_3. This is consistent with a dominant VOC-limited chemistry found for most of the stations during the first period, including rural stations (see Fig. 3), where changes in organic reactivity would have had a major influence. Overall, we found a larger variability among the rest of the rural stations considered in the study, in terms of the interaction surfaces NO_x-temperature (Fig. S7). This is also reflected in the estimated temperature response of ΔO_3 when comparing GAM-P2 and the projected response using GAM-P1 (Fig.S8).

Figure 910 shows ΔO_3 as a function of temperature under low (10th), medium (50th) and high (90th) levels of NO_x at those rural stations. The differences between the periods are more evident in Rhineland-Palatinate where the regression line corresponding to the second period 2009-2018 becomes flat at temperatures between 18-22 $°C$ at moderate (50th) and high (90th) NO_x concentrations. In Berlin, ΔO_3 slightly decreases in the second period, and the regression lines are very similar at the

fixed NO_x conditions in both periods. The variations of ΔO_3 with NO_x at different temperature conditions are shown in ~~figure 10~~Fig. 11 . While in Berlin the relationship is similar in GAM-P1 and GAM-2 for all temperature conditions, in Rhineland-Palatinate increases of $NO_x > 7\,\mu g m^{-3}$ indicate a major decrease~~d~~ of ΔO_3 at medium (50th) and high (90th) temperatures in the second period.

Only two suburban stations were included in this study, in Berlin (DEBE051) and in Saxony (DESN045), both eastward located. The contours obtained in each period and station showed similar patterns than those found for urban stations, specially in Berlin (Fig. S9). The GAMs consistently reproduce the temperature dependence of ΔO_3 at higher temperatures and the differences between the GAM-P2 and the projected ΔO_3 response to temperature with GAM-P1 were more evident in Saxony (Fig. S9, right).

4.3.2 VPD and O_3 from the previous hour ($C_{O_3}(t-1)$)

We discuss now the interaction term from VPD and $C_{O_3}(t-1)$. VPD is crucial and controls the stomatal conductance. Its effects can be summarised as follows: under high VPD levels (associated with high temperatures), plants cannot extract sufficient moisture from dry soils to satisfy the atmospheric demand for evapotranspiration (Teuling, 2018). In this situation of drought stress, plants close their stomata to reduce water loss and limit the uptake of ozone by vegetation.

Figure ~~11~~12 reveals the nonlinear relationship between VPD and the $C_{O_3}(t-1)$ at the selected urban stations in Berlin and in Rhineland-Palatinate. In general, ΔO_3 tends to increase with higher levels of VPD (i.e. drier conditions) and low O_3 concentrations from the previous hour in both locations and periods. In the first period, the contribution of the interaction between VPD and persistent O_3 concentrations is similar at both locations, and the model shows maximum ΔO_3 at $C_{O_3}(t-1) < 30\,\mu g m^{-3}$ and VPD > $0.70\,kPa$. In Berlin, the results obtained from GAM-P2 suggest that higher levels of VPD and low $C_{O_3}(t-1)$ (~ $30\,\mu g m^{-3}$) lead to an increase of ΔO_3, but the ΔO_3 tends to decrease faster with high $C_{O_3}(t-1)$ concentrations (above $50\,\mu g m^{-3}$) when comparing to GAM-P1. The interaction surfaces obtained in Rhineland-Palatinate show small changes when comparing both periods.

The contours obtained from the GAMs built for the rural stations are shown in Fig. ~~12~~13. We see significant differences between these rural stations. ΔO_3 dependence with VPD is more pronounced in Rhineland-Palatinate, especially in the second period 2009-2018 with a larger increase of ΔO_3 with increasing VPD levels (i.e. drier conditions). In this case, GAM-P1 shows little changes in the estimated ΔO_3 ($\sim 3\,\mu g m^{-3}$) at low $C_{O_3}(t-1)$ concentrations for all range of VPD, while the GAM-P2 shows a significant increase of ΔO_3 under similar $C_{O_3}(t-1)$ concentrations when moving to higher VPD. In Berlin, $C_{O_3}(t-1)$ concentrations seems to have a major influence on ΔO_3, and ΔO_3 estimates are slightly lower in the second period 2009-2018 than in the first period 1999-2008. The interaction between VPD and $C_{O_3}(t-1)$ in the suburban stations (Berlin and Saxony) is consistent with the patterns found in the urban and rural stations and ΔO_3 increases with higher VPD and low $C_{O_3}(t-1)$ concentrations (Fig. S10).

~~VPD is crucial and controls the stomatal conductance. Its effects can be summarised as follows: under high VPD levels (associated with high temperatures), plants cannot extract sufficient moisture from dry soils to satisfy the atmospheric demand for evapotranspiration~~ (Teuling, 2018). ~~In this situation of drought stress, plants close their stomatal to reduce water loss~~

~~and limit the uptake of ozone by vegetation.~~ Our results illustrate that the combination of high VPD and lower $C_{O_3}(t-1)$ concentrations result in higher ΔO_3 (thus, less uptake of O_3). Moreover, given that O_3 concentrations are typically lower in urban environments due to the local scavenge of O_3 (NO titration), a larger contribution of the interaction of VPD and $C_{O_3}(t-1)$ to ΔO_3 in the urban and suburban stations than in the rural stations is expected.

4.3.3 ΔBLH and MDA8 from the previous day ($C_{MDA8}(t-24)$)

The effect of mixing processes was introduced in the GAMs through the ΔBLH and $C_{MDA8}(t-24)$. Figures ~~13 and 14~~14 and 15 depict the interaction surfaces between the covariates ΔBLH and $C_{MDA8}(t-24)$ at the selected urban and rural stations in Berlin and Rhineland-Palatinate. In general, ΔO_3 is mainly dependent on changes in ΔBLH and it increases at higher ΔBLH, while the influence of $C_{MDA8}(t-24)$ on ΔO_3 is negligible for ΔBLH ~ < 30%. The results obtained from most of the stations at different environments (i.e. urban and rural) showed consistent shapes with the patterns described for the selected stations (not shown). Moreover, we found similar patterns for the suburban stations(Fig. S11).

These interaction surfaces can be used to interpret the nonlinear relationship between ΔBLH and $C_{MDA8}(t-24)$ concentrations. As BLH grows, air is entrained from layers aloft and O_3 production rates can increase or ~~decrase~~ decrease depending on the O_3 concentrations in this residual layer (Haman et al., 2014). We show that a rapid development of the BLH along with high $C_{MDA8}(t-24)$ (from the previous day), likely stored at the residual layer, lead to an increase of ΔO_3. Note that $C_{MDA8}(t-24)$ concentrations seems to have an influence on ΔO_3 when the BLH rapidly changes. The effect of this interaction was slightly larger in most of the urban and suburban stations as compared to the rural stations, while small differences are observed when comparing the patterns obtained from each period.

5 Summary and conclusions

We have examined the long-term O_3 sensitivity to temperature, as well as the modulation of this sensitivity by NO_x concentrations, in a total of 29 stations over Germany during the period 1999-2018. Consistent with previous work, O_3 tends to increase strongly with temperature under high NO_x conditions due to increased in-situ photochemical production, while lower levels of NO_x leads~~~~ to a reduced O_3 sensitivity to temperature. Also consistent with previous work, we see a decreasing sensitivity of O_3 to temperature over our study period, coinciding with decreasing trends in NOx concentration.

In order to explain the trends in photochemical ozone production over our study period, we divided this period into two halves (1999-2008 and 2009-2018) and constructed sets of Generalized Additive Models (GAMs) based on hourly station observations of ozone and NO_x concentrations, along with temperature, vapor pressure deficit, and boundary layer height from a reanalysis product. We modeled the daily increase in O_3 concentrations as a function of three interaction terms accounting for phochemical production (dependent on NO_x and temperature), dry deposition (dependent on vapor pressure deficit and ozone concentrations from the previous hour) and mixing processes (dependent on the boundary layer height growth rate, and ozone concentrations from the previous day).

In most of the stations, the effect of the interaction term NO_x-temperature was larger in the first period than in the second period, resulting in higher ΔO_3 estimates in 1999-2008 compared to ΔO_3 estimates in 2009-2018. A decreasing sensitivity of ΔO_3 to temperature was shown by the GAMs built for the second period 2009-2018 when comparing with the GAMs from the first period 1999-2008, leading to lower ΔO_3 values under moderate-high temperatures in the second period. This decreasing temperature sensitivity was more pronounced in the southward urban stations (e.g. Rhineland-Palatinate). Moreover, we found that in a large number of stations the peak of ΔO_3 shift to lower NO_x concentrations in the second period, which indicates the transition to NO_x-limited chemistry, consistent with a weaker weekend-weekday effect showed in second period. The observed decreasing trend in the climate penalty over the southern stations indicates that NO_x reductions were more effective in decreasing the temperature sensitivity of O_3 at higher temperatures. This was not the case for some of the stations (e.g. Berlin) were the climate penalty did not show significant changes over time, which suggests that stronger emissions controls should be required to mitigate the temperature dependence of O_3. ~~Thus, the lower NO_x concentrations during the second period 2009-2018 resulted in a decrease in ΔO_3 as well as a lower temperature dependence.~~

~~However,our results pointed out that NO_x reductions can only partially explain the changes in the O_3-temperature relationship.~~ Using the GAMs derived from the first period 1999-2008 to project the ΔO_3 response to temperature under the mean NO_x conditions of the second period 2009-2018, we showed that the shape of the regression lines have changed in the second period for a large number of urban stations. Similar conclusions were obtained for most of the rural stations, where the shape of the projected ΔO_3 response with temperature in the second period 2009-2018 differ from the estimated ΔO_3 response from the GAMs built for that period.

We conclude that the emissions controls have been generally effective at a large number of the stations used in this study, which showed a tendency to move to a NO_x-limited chemistry. In the case of rural stations, we found more discrepancies when comparing the shapes of the regression lines of the ΔO_3 response to temperature.

~~We conclude that NO_x reductions have had an influence in the decreasing temperature sensitivity of O_3, as shown in the GAMs for the second period 2009-2018, but that such reductions alone can not explain the changes in the observed O_3-temperature relationship.~~ We interpret these discrepancies as an underlying effect influencing the ΔO_3 that has not been included in the model.

The temperature-dependence of biogenic VOC emissions is well-known. In particular, biogenic isoprene emissions have a strong temperature dependence with critical implications on O_3 production, mostly during warmer summer days. Therefore, one plausible explanation for the changes in the shapes of the ΔO_3-temperature relationship might be attributed to the accompanying effect of changes in biogenic emissions (along with NO_x) that are likely influencing the temperature-dependence of ΔO_3 and consequently the m_{O_3T}. We have shown a general decrease of ΔO_3 at higher temperatures, which may suggest that enhanced temperature-driven biogenic emissions can result in ΔO_3 being more dependent of NO_x (NO_x-limited) and thus, more sensitive to the NO_x controls. Our results have important implications for the implementation of mitigation strategies, specially when considering the effects of a warming climate. We expect that the methodology described herein can be applied to other locations with available long-term measurements to assess how NO_x reductions have influenced the temperature dependence of O_3. Consistent with previous work, we may anticipate that our approach will show changes in the climate penalty

factor as well as in the sensitivity of ΔO_3 with temperature. Further analysis to examine in more detail the effect of NO_x reductions in particular locations should be required.

In summary, the sensitivity of O_3 to temperature has decreased during the last period (2009-2018) over a great number of the German stations considered in the study, including rural areas. Even though NO_x reductions accomplished during the last decades have partially counteracted the O_3 climate penalty, our study highlights the relevance of considering the influence of additional factors controlling the O_3-temperature relationship. Since observations of long-term dataset of VOCs are lacking, further analysis including short-term measurements of a suite of VOCs would be definitively required to quantify their contribution to the observed changes in the climate penalty.

6 List of figures

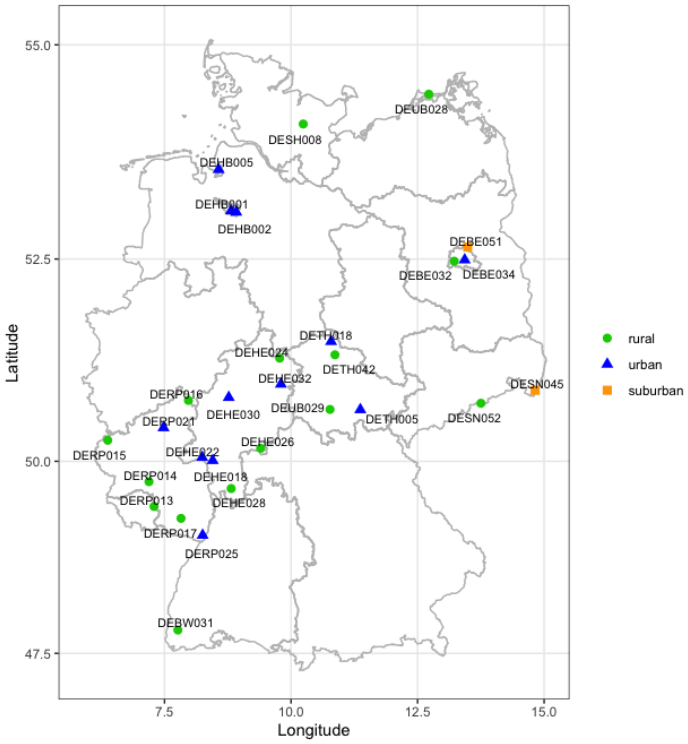

Figure 1. Spatial distribution of measurement stations. Network codes are indicated in text. Shapes indicate the station type area and color the altitude.

Figure 2. Time series of annual 5th, 50th, and 95th percentile of NOx concentrations for the whole period of study (1999-2018) at the example stations.

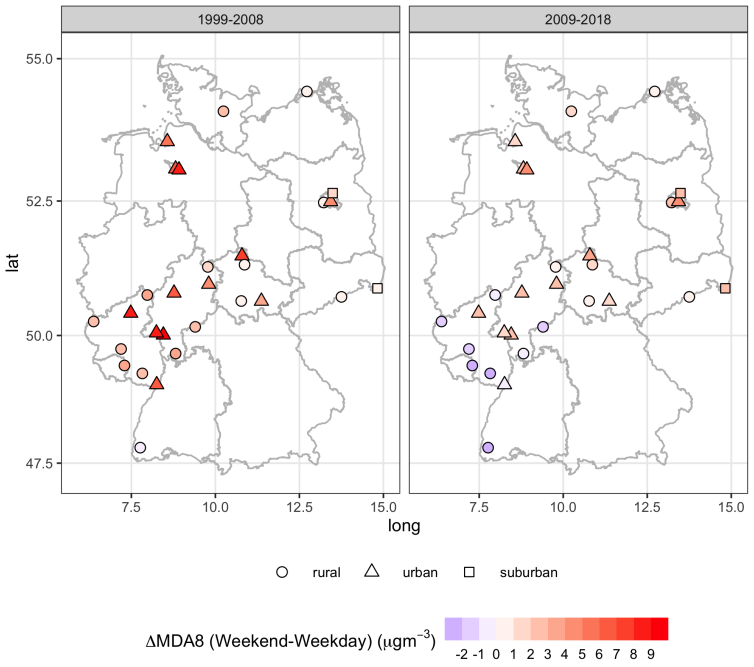

Figure 3. Spatial distribution of the weekend-weekday effect calculated for each period.

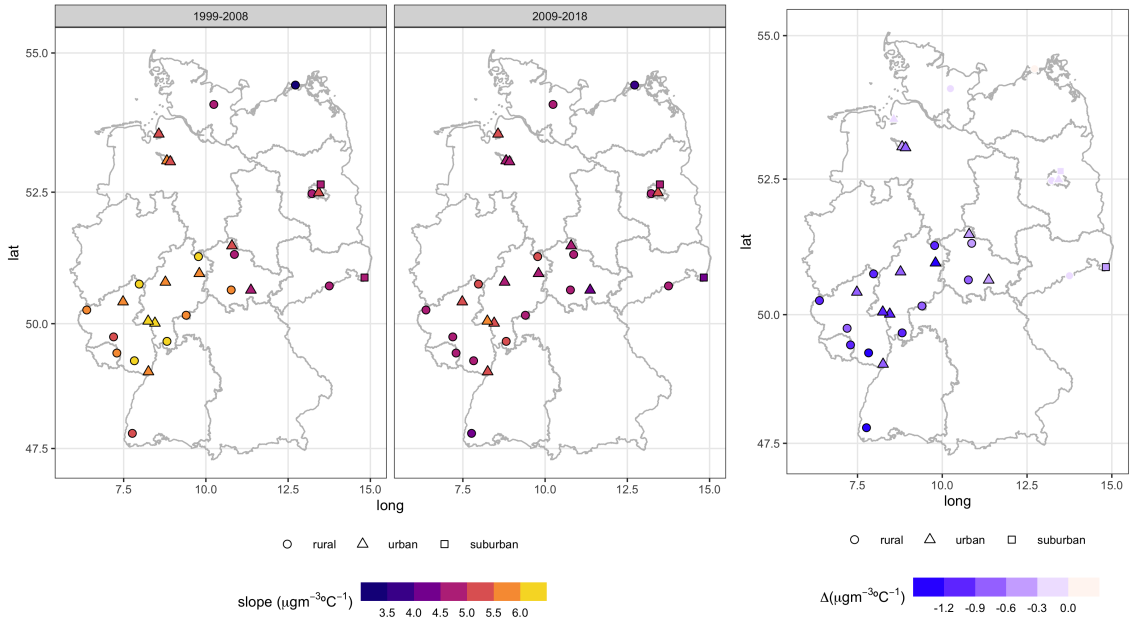

Figure 4. Spatial distribution of climate penalty factor calculated at each stations and period (left, middle) and the changes in the slopes (relative to the first period) (right).

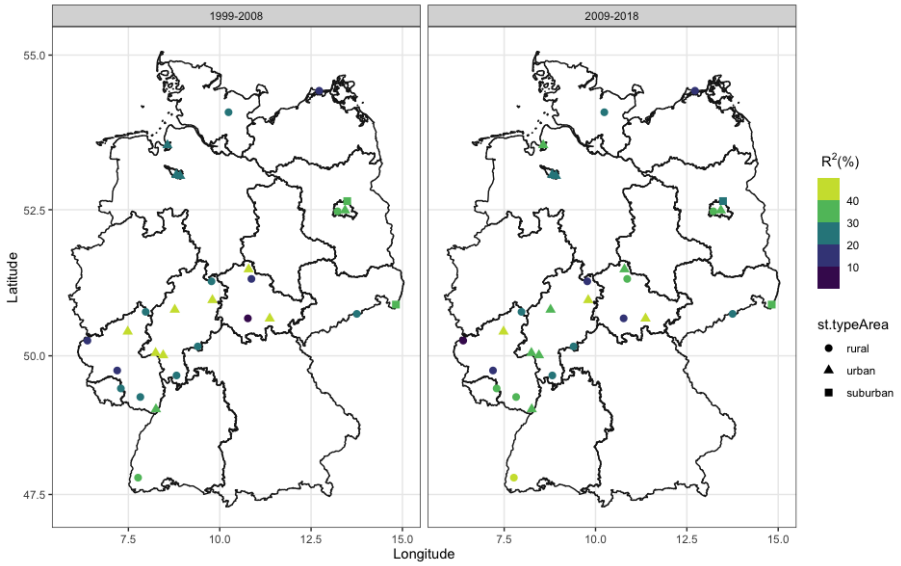

Figure 5. Spatial distribution of the adjusted r-squared for the model, R^2, for GAM-P1 (left) and GAM-P2 (right).

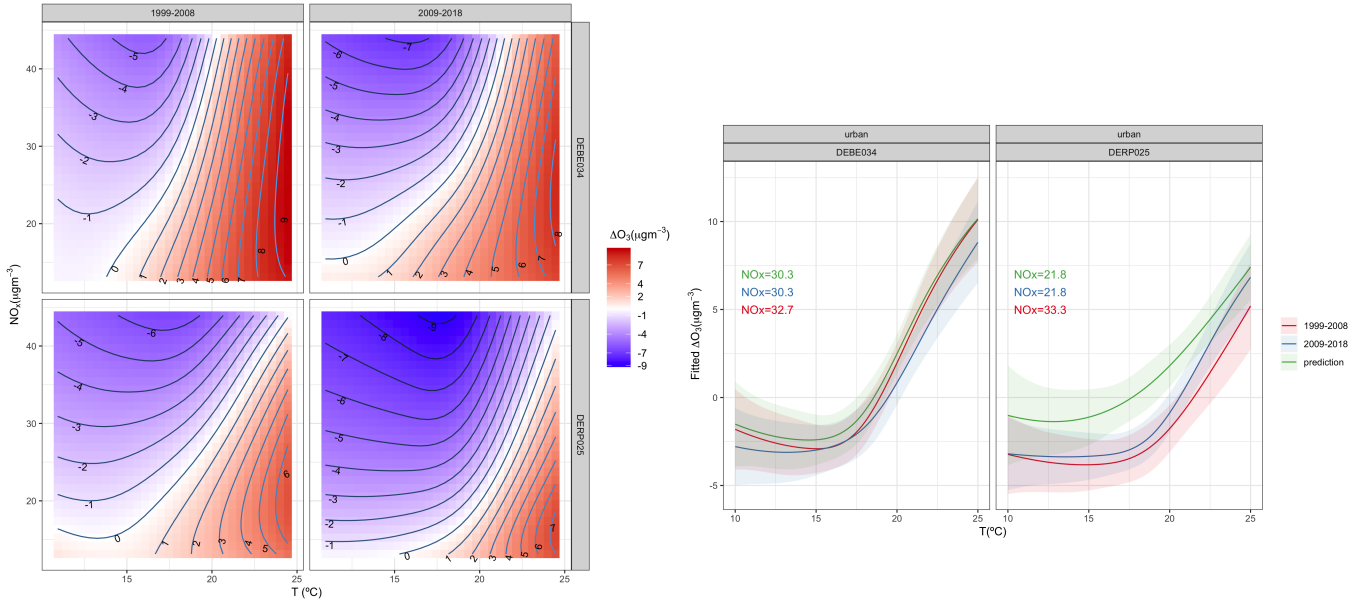

Figure 6. Contour plot for the interaction temperature-NO_x at the urban stations in Berlin (DEBE034) and Rhineland-Palatinate (DERP025) for the first period 1999-2008 and second period 2009-2018 (left). In the right panel, smooth functions representing the temperature response of O_3 production rates under mean conditions of NOx (indicated by the text numbers) obtained from GAM-P1 (red line) and GAM-P2 (blue line), along with the prediction of the O_3 response using GAM-P1 (green line). Shaded bands represent the pointwise 95% confidence interval.

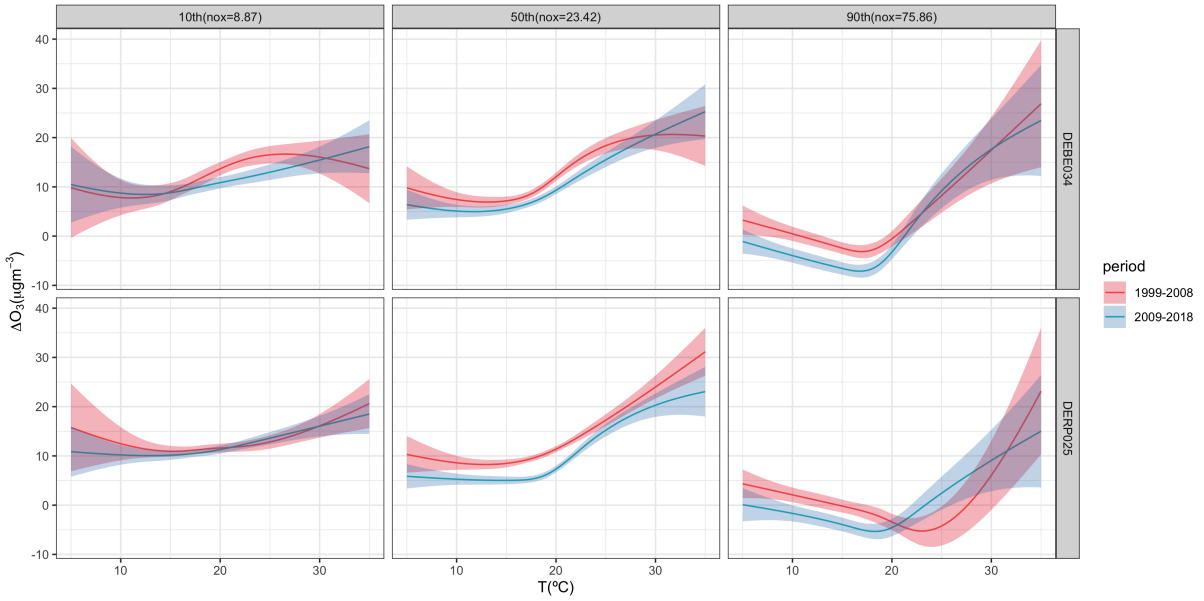

Figure 7. Smooth functions for temperature at low (10th), medium(50th) and high(90th) NO_x conditions. Shaded bands represent the pointwise 95% confidence interval.

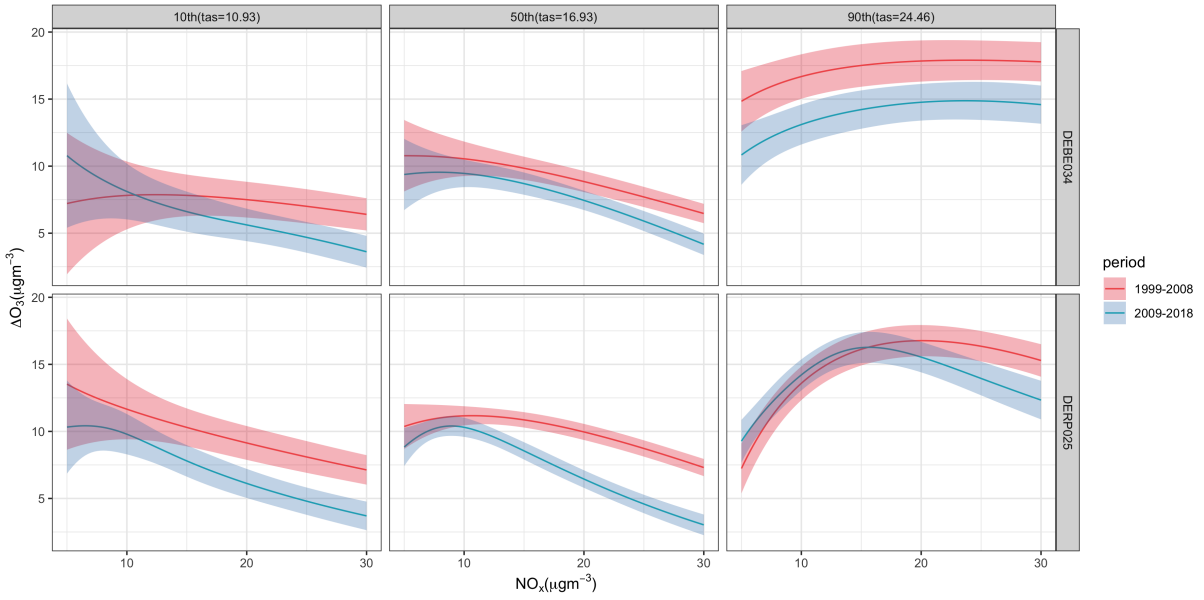

Figure 8. Smooth functions for NO_x at low (10th), medium (50th) and high (90th) temperature conditions. Shaded bands represent the pointwise 95% confidence interval.

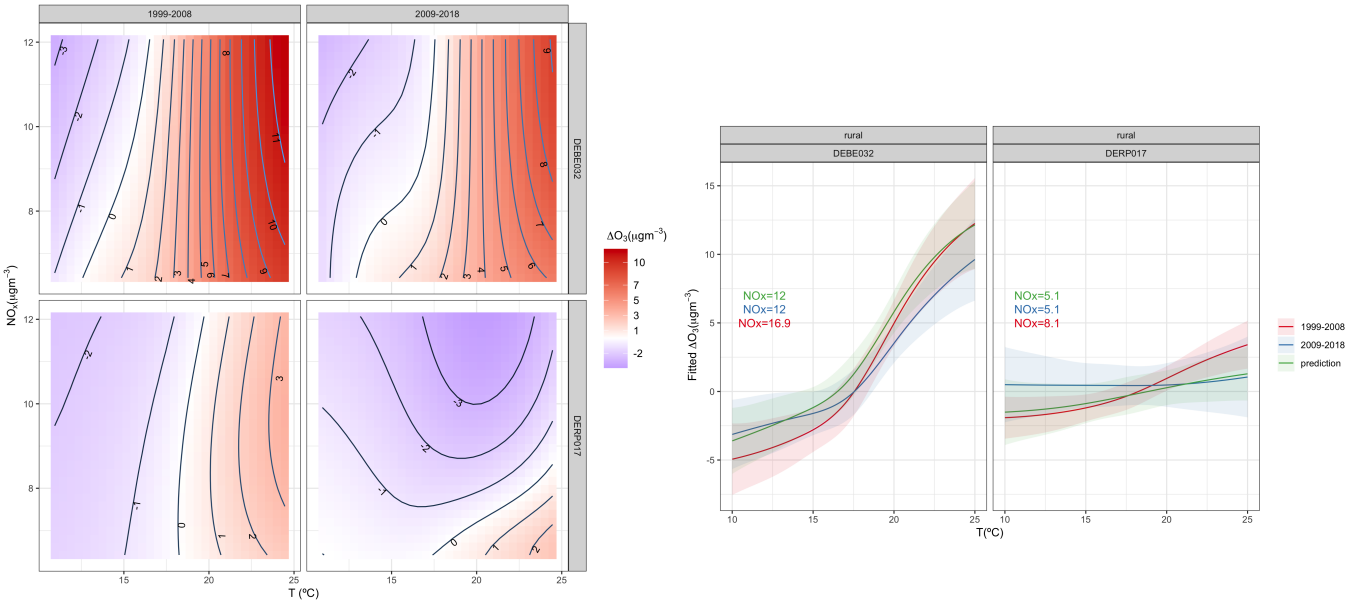

Figure 9. As figure 5, but for the rural stations in Berlin (DEBE032) and Rhineland-Palatinate (DERP017).

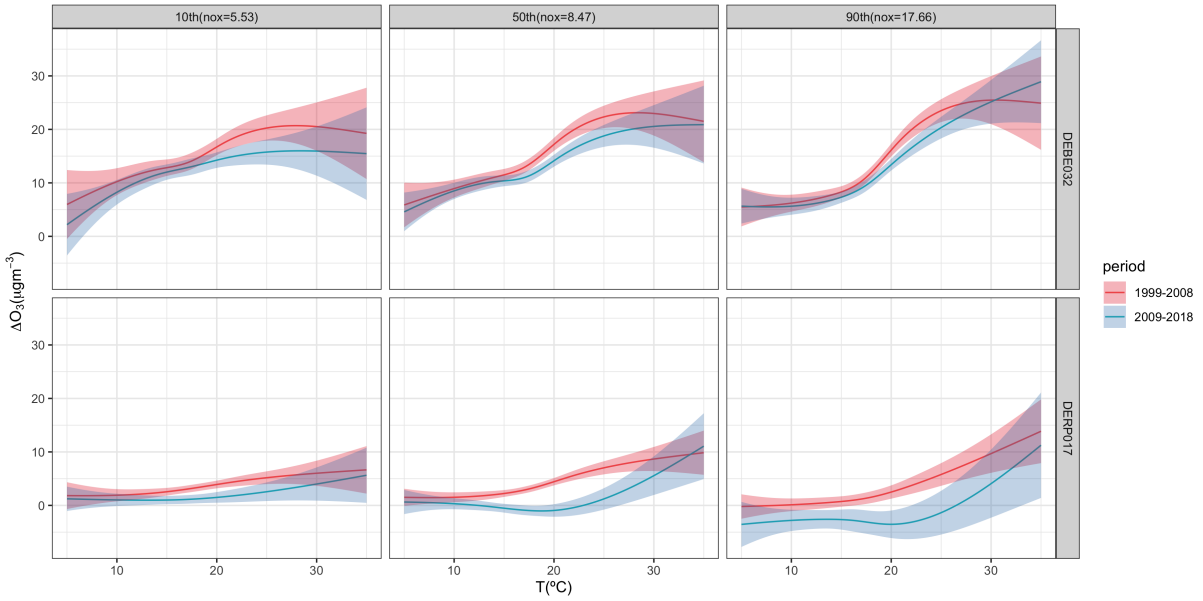

Figure 10. As figure 6, but for the rural stations in Berlin (DEBE032) and Rhineland-Palatinate (DERP017).

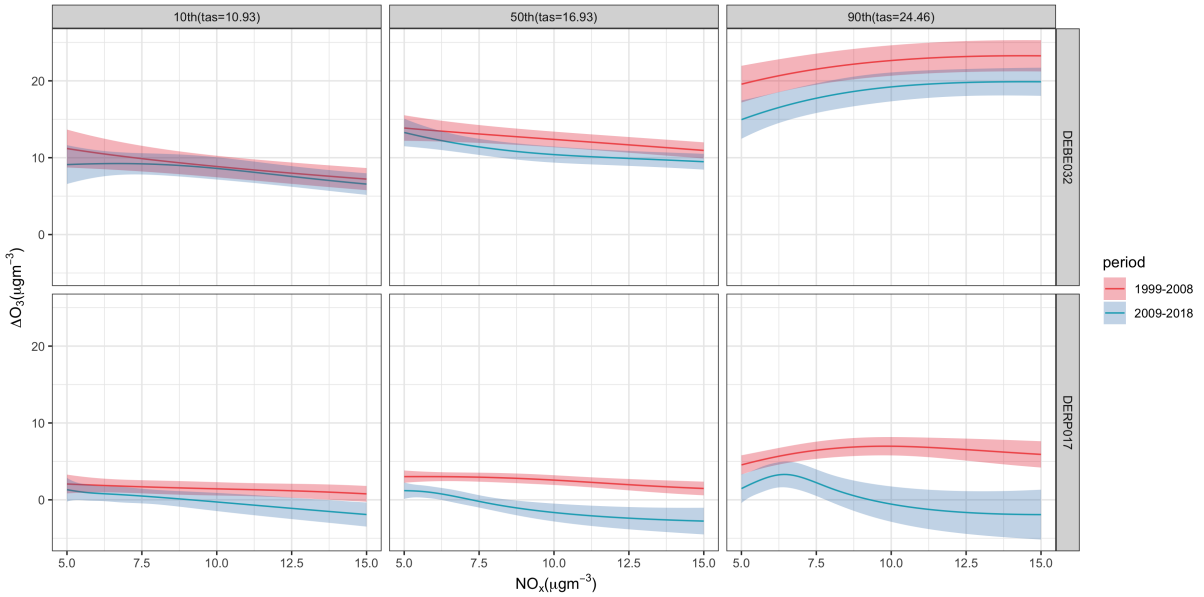

Figure 11. As figure 7, but for the rural stations in Berlin (DEBE032) and Rhineland-Palatinate (DERP017).

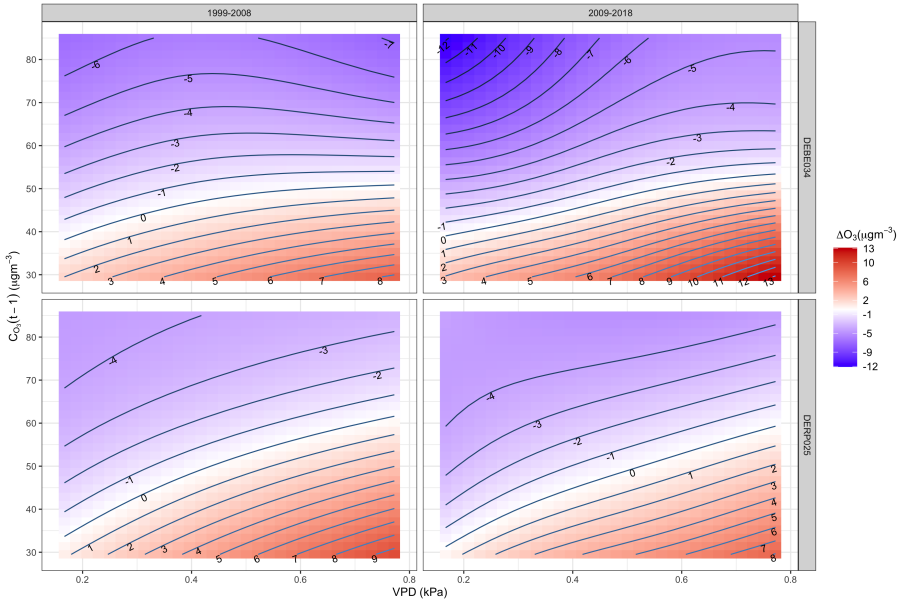

Figure 12. Contour plot for the interaction VPD-$C_{O_3}(t-1)$ at the urban stations in Berlin (DEBE034) and Rhineland-Palatinate (DERP025) for the first period 1999-2008 and second period 2009-2018.

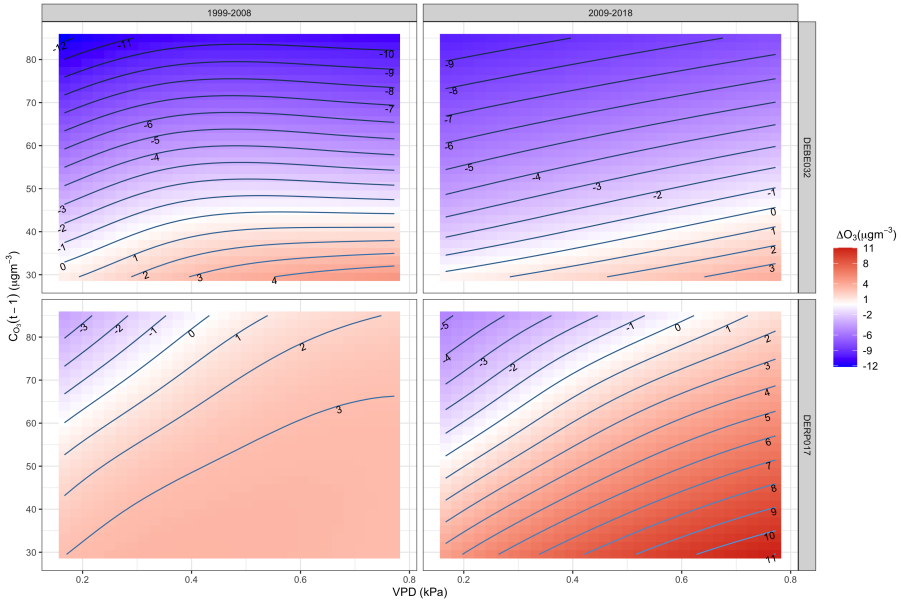

Figure 13. As figure 11, but for the rural stations in Berlin (DEBE032) and Rhineland-Palatinate (DERP017).

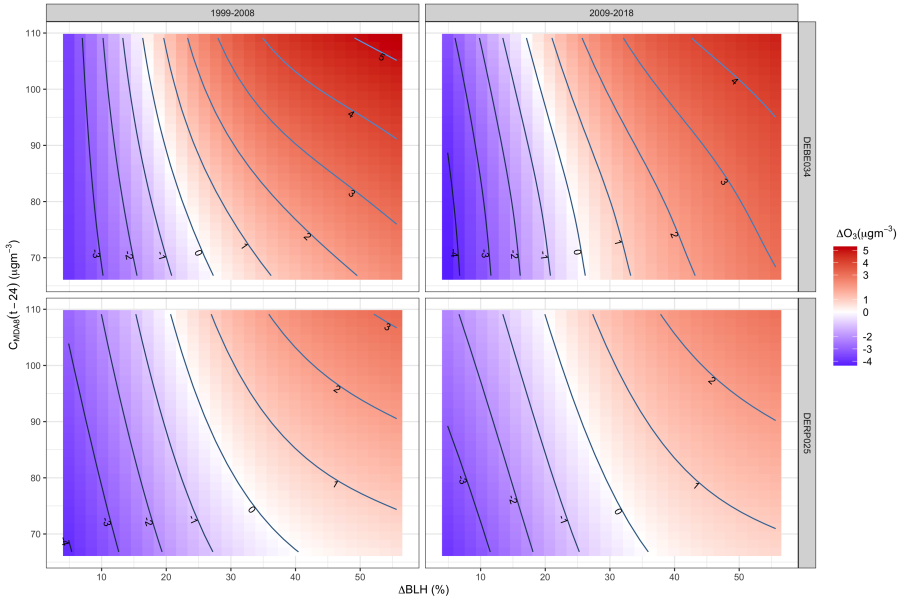

Figure 14. Contour plot for the interaction ΔBLH-$C_{MDA8}(t-24)$ at the urban stations in Berlin (DEBE034) and Rhineland-Palatinate (DERP025) for the first period 1999-2008 and second period 2009-2018.

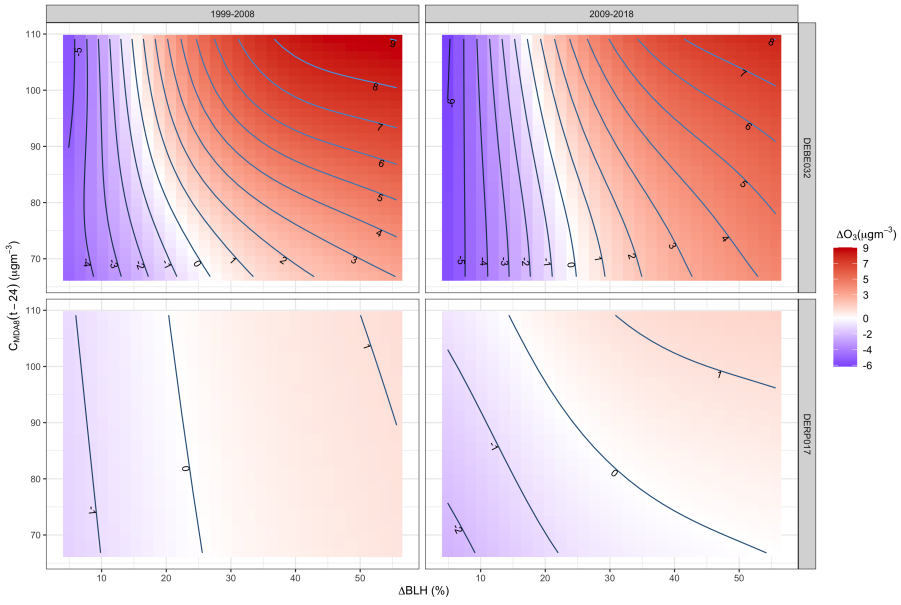

Figure 15. As figure 13, but for the rural stations in Berlin (DEBE032) and Rhineland-Palatinate (DERP017).

7 Table

Table 1. Median values of the covariates during the period first 1999-2008, and second period 2009-2018. Note that these values are obtained from the input data used for the GAMS (i.e. previously filtered).

	code	period	NOx	tas	BLh	VPD	lag	lag24	type
	DEBE032	1999-2008	14.00	17.17	23.58	0.35	30.00	74.00	rural
	DEBE032	2009-2018	12.52	17.36	24.67	0.37	27.60	73.15	rural
	DERP017	1999-2008	7.53	17.57	21.01	0.44	80.00	100.80	rural
	DERP017	2009-2018	6.39	16.33	19.49	0.36	70.90	96.26	rural
	DEBE034	1999-2008	28.00	17.71	22.65	0.39	42.50	76.12	urban
	DEBE034	2009-2018	24.26	18.41	23.36	0.46	48.84	79.11	urban
	DERP025	1999-2008	21.07	18.82	24.13	0.53	52.00	90.12	urban
	DERP025	2009-2018	15.23	19.00	24.67	0.56	51.28	85.46	urban
	DEBE051	1999-2008	16.53	16.76	22.00	0.32	40.00	81.62	suburban
	DEBE051	2009-2018	14.30	16.98	25.20	0.35	39.18	81.31	suburban
	DESN045	1999-2008	13.53	16.77	21.39	0.36	55.94	90.25	suburban
	DESN045	2009-2018	12.23	17.37	22.05	0.40	51.74	86.55	suburban

Data availability. Observational ozone data used in this study are available at the Airbase database of the European Environment Agency (EEA) data service(https://www.eea.europa.eu/data-and-maps/data/aqereporting-8). The ERA5 reanalysis products are available available on the Climate Data Store (CDS) cloud server (https://cds.climate.copernicus.eu). Code is available upon request to the corresponding author.

Author contributions. TB provided the initial study idea. NO and HR designed the statistical model with the input of TB. NO prepared the data and conducted the analysis. The manuscript was written by NO with the contributions of TB and HR.

Competing interests. The authors declare no competing interests.

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