# Responses to the comments of anonymous referee #2

We would like to thank for the comments which helped to improve our manuscript. Please find below your comments in blue, our responses in black and modifications in the revised manuscript related to technical or specific comments in italic and inside quotes. In addition, we have updated the terminology of direct and indirect aerosol effects throughout the manuscript as well as in our replies to your comments, by replacing the term "direct aerosol radiative effect (DRE)" with "aerosol–radiation interactions (ARI)" and the term "aerosol indirect effects (AIE)" with "aerosol–cloud interactions (ACI)". All modifications are highlighted in the revised manuscript.

This study reports on impacts of solar brightening on summer-time ozone levels across Europe through analysis of model simulations examining the impact of changes in radiation on photolysis rates and biogenic emissions. Several studies have previously examined the impact of aerosol induced radiation perturbations on photolysis and subsequent atmospheric chemistry (Dickerson et al., 1997; Benas et al., 2007; Bian et al., 2007; Anger et al., 2016; Wang et al., 2016; Xing et al., 2017) and similar to the current study suggest that the aerosol induced reduction in solar irradiance leads to lower photolysis rates and less O3 production. Such interactions and feedbacks are a potentially important consideration for design of multi-pollutant control strategies seeking to simultaneously reduce O3 and particulate matter pollution. Thus studies that help quantify the magnitude of these impacts relative to actual changes in composition of the atmosphere are of interest. Though the results reported are along expected lines, I think the manuscript needs to be strengthened to provide the context in which the results should be interpreted. In my assessment the current manuscript will benefit from some additional work in: (i) a clearer description of the design and methodology employed in the sensitivity experiments; (ii) clearer articulation of the assumptions and limitations of these experiments; and (iii) acknowledging that the study does not comprehensively examine the process changes induced by solar brightening between 1990 and 2010, but rather presents model sensitivity analyses that approximate the impact of aerosol burden changes on photolysis rates and biogenic emissions. The following comments and suggestions are offered:

1) The suggestion that the study examines changes in ozone between 1990 and 2010 due to solar brightening is misleading. Multiple atmospheric processes can be impacted by the direct radiative effects associated with brightening in addition to changes in photolysis rates (e.g., thermal reactions, atmospheric ventilation, changes in dry deposition). No specific simulations were conducted to fully represent conditions in 1990. Instead, AOD and surface shortwave radiation conditions "representative" of 1990's, approximated from changes in measured surface PM at a few sites, were used to perturb one component of the aerosol-radiation system, i.e., photolysis rates. Further, since no comparison of SSR changes over the time period are presented, it is difficult to ascertain whether the induced changes are actually representative of the brightening

observed during this period. Thus, I would be careful in characterizing these results as trends or changes over the two decades. The analysis is essentially a sensitivity study and should be portrayed that way, so that the results can be conveyed and interpreted in an accurate manner. In addition to changes in the text, the authors could also consider an alternate, more representative title for the manuscript.

Thank you for your suggestions. First, we would like to clarify that it was our intention not to use the emissions and meteorology of 1990 in order to isolate the impact of aerosol–radiation interactions (ARI) on photolysis rates and biogenic emissions, which cannot be the case if the emissions and meteorology of 1990 are used. Consequently, our goal was not to simulate the actual conditions of 1990, but the aerosol optical depth (AOD) and surface solar radiation (SSR) conditions representative of 1990. That is why we compared our simulated AOD and SSR changes with other modeling and observational studies, in Sections 4.3.1 and 4.3.2, to test the validity and representation of our modeling experiments. As discussed and shown in Sections 4.3.1 and 4.3.2, our simulated AOD and SSR changes are within the range of the respective changes reported by other modeling and observational studies for either the same time period or other time periods similar to the one examined in this study.

We made several changes in the text to present in a more clear way the setup and assumptions of our modeling experiments as well as the context in which these results should be interpreted. Some of these changes are listed in the replies of your next comments as well as in the replies of the 1st anonymous reviewer and some are listed below:

from page 1 line 32 to page 2 line 1: *"Finally, the role of the aerosol–radiation interactions (ARI) changes in the European summer surface …"*

page 9 line 32: *"… to assess the overall impact of the ARI changes on surface ozone"*

page 16 line 11: *"We investigated the impact of the ARI changes on European summer surface ozone between 1990 and 2010 using the …"*

page 17 line 6: *"Nevertheless, the role of the ARI changes (as quantified in this study) …"*

We also took into consideration your suggestion of modifying the title of the manuscript into a different one, which reflects more accurately the work that has been done in this study:

*"Solar "brightening" impact on summer surface ozone between 1990 and 2010 in Europe – A model sensitivity study of the influence of the aerosol–radiation interactions"*

2) The model set-up and sensitivity simulation specifics could benefit from additional clarification. From what I understand, simulations with the CAMx model driven by meteorological fields from WRF and emissions representative of 2010 were

first conducted (BASE run). Then a series of photolysis sensitivity simulations were conducted in which AOD used in the TUV photolysis code was somehow perturbed – this description currently is confusing and contradictory across the text.

a) Line 20-24 on page 5 first suggests that the TUV is used "externally" to estimate clear sky photolysis which are then adjusted in the model for clouds. It is also suggested that dry extinction efficiencies and SSA at 350nm are provided to the model. How is the AOD calculation then used to modify the already estimated clear sky photolysis rates? Line 26 on page 7 then suggests that the study used an in-line version of TUV? Which one is it? It seems that an in-line version of the TUV code in CAMx would be needed conduct the PHOT sensitivities described in Table 1, but from the current description it is not clear. Since much of the analysis focuses on these sensitivities, it is important that the model setup and the experimental design be clearly described.

The CAMx model first requires the photolysis rates in clear-sky conditions, which are calculated by the TUV model and fed as input into CAMx. In the second step, the clear-sky photolysis rates are adjusted for clouds, aerosols, temperature and pressure in one of the CAMx subroutines called "in line TUV". We modified the sentence on page 5, lines 25–26 as follows:

*"Then, these rates are internally adjusted in CAMx every hour for clouds and aerosols (simulated by CAMx) …"*

The dry extinction efficiency and single scattering albedo (SSA) values at 350 nm are provided only in the in-line version of TUV, as no aerosol species are considered in the external TUV. We modified the text on page 6, lines 2–5 as follows:

*"Inside CAMx, the COD is calculated for each model grid cell based on the approach of Genio et al. (1996) and Voulgarakis et al. (2009), while the dry extinction efficiency of the aerosol species, which is needed for the calculation of the AOD, as well as the single-scattering albedo (SSA) were provided by Takemura et al. (2002) for the wavelength of 350 nm (Table S1)."*

The internal adjustment for clouds and aerosols in CAMx is performed into two steps: First, the clear-sky shortwave solar radiation and photolysis rates are re-calculated, but this time only for a single representative wavelength of 350 nm. Then, the radiative calculations are repeated including in this second step the impact of clouds and aerosols. A ratio of clear-to-cloudy (and aerosols) sky is derived by the aforementioned radiative calculations in CAMx and then applied to the calculation of clear-sky photolysis rates and shortwave solar radiation in the TUV model. The following modification was applied in the text on page 5, lines 27–32:

*"The internal adjustment for clouds and aerosols inside CAMx is performed into two steps: First, the clear-sky shortwave solar radiation and photolysis rates are re-calculated inside CAMx, but this time only for a single representative wavelength of 350 nm. In the second step, the radiative transfer calculations are repeated including the impact of clouds and aerosols. A ratio of clear-to-cloudy (and aerosols) sky is derived by the aforementioned radiative transfer calculations in CAMx, which is applied to the clear-sky photolysis rates and shortwave solar radiation that were calculated by TUV and were given as input to CAMx."*

We hope that these clarifications describe the induced AOD perturbations within CAMx more clearly.

b) Equation 2 shows how the AOD is estimated and modified. Some parts of the text suggest that sensitivities are approximating the impact of changes in aerosol burden on radiation and photolysis, which may lead readers to assume that the aerosol concentrations in the equation are being modified. However, I believe in the PHOT experiments the AOD is solely perturbed by the adjustment factor (pf). Please clarify.

For the PHOT1–3 scenarios we adjusted the PM concentrations only in the calculation of AOD inside the CAMx model, as described in Sect. 2.3.1. In other words, the induced forcing in the PHOT1–3 scenarios lies only in the AOD calculation. For example, consider the eq. (2) from the manuscript. Let $C$ be the PM concentration species for the base case (BASE scenario) and $p_f$ the adjustment factor that is applied to each PM species concentration. The product of $C\cdot p_f$ yields a new adjusted PM species concentration (which exists only in the AOD calculation) which we denote here (referring to any of the PHOT1–3 scenarios) as $C_{phot} = C\cdot p_f$. So, the actual PM concentration $C$ does not change, except for the case of secondary aerosols due to indirect impact of changes in the chemistry originating from the changes in the photolysis rates. However, we investigated this exception and we showed that the change in secondary aerosol is small (see Figs. S3 and S4) and any subsequent change in the AOD and the photolysis rates is expected to be negligible. Therefore, the adjustment factor $p_f$ gives a pseudo-perturbation of changes in PM concentrations, since the PM concentrations do not actually change but at the same time we are able to isolate the radiative impact of PM concentration changes (as AOD is perturbed) on solar radiation and photolysis rates. This is why in some parts of the text it is suggested that the PHOT1–3 scenarios are approximating the impact of changes in aerosol burden on solar radiation and photolysis rates.

We modified the sentence on page 8, lines 9–10 as follows:

*"In order to quantify only the changes in ARI, we isolated them from other aerosol effects such as the gas-aerosol chemical interactions"*

We added a sentence on page 8, lines 15–17:

*"Hence, the product* $p_f \cdot C$ *represents the PM concentrations in 1990, but purely in AOD calculations in order to generate only AOD, solar radiation and photolysis rates in 1990."*

c) If the perturbation is only induced through the adjustment factor, then the photolysis changes are only estimating the impacts on a chemical regime representative of 2010. I would imagine if (higher) emissions representative of the 1990s were used then the estimated changes in ozone due to the corresponding changes in photolysis would have been even larger.

In Sect. 2.3 we wrote that we performed all the sensitivity runs also using a second base case with doubled $NO_x$ emissions (BASE_$NO_x$ scenario) compared to the initial base case (BASE scenario). The original motivation for this addition was a potential underestimation of ozone precursor emissions in the inventories, as discussed in Oikonomakis et al. (2018). However, the results of the scenarios using the base case with increased $NO_x$, can also give an indication of the impact of changes in ARI on photolysis rates and ozone in a chemical regime different than that of 2010. Our results (Fig. 8) indicate that using a different chemical regime leads mainly to a larger spatial coverage of the impact (of changes in ARI) on ozone, while the magnitude of those effects is influenced to a lesser degree.

d) Were photolysis rates through the model column perturbed by the same amount? Were the perturbations at the surface (or within the boundary layer) different from those in the free troposphere?

As shown in eq. (2), the AOD and hence the photolysis rates were perturbed by the relative same amount through the whole model column. However, since the PM concentrations decrease rapidly with altitude, the induced perturbation in the PM concentrations in the calculation of AOD will be higher in absolute terms closer to the surface and very small higher up in the free troposphere. In other words, since the applied perturbations in eq. (2) are in relative terms, this implies that the magnitude of these perturbations in absolute terms follows the magnitude of the PM concentrations.

3) The authors should better explain the criteria for the choice of the observation locations used in estimating the trends in PM (section 3). Why were sites only in Switzerland and Netherlands (3 each) used and how they can be considered to be representative of regional PM trends across Europe?

The first and most important selection criterion for the sites was to have available $PM_{10}$ measurements (or equivalent products) as early as possible, close to the year 1990. This was only the case for Switzerland with corrected total suspended particle (TSP) as proxies for $PM_{10}$ concentrations. In addition, we decided to include the Netherlands as well, since the data in the monitoring sites were available since 1992. Other monitoring sites in Europe did not have PM data going back to beginning of the 1990s, as reported by Airbase.

Tørseth et al. (2012) and Barmpadimos et al. (2012) have shown that the decreasing trends in both $PM_{10}$ and $PM_{2.5}$ concentrations in Switzerland were similar to other western and central European countries for the time periods 2000–2009 and 1998–2010, respectively. Furthermore, Hoogerbrugge et al. (2010) showed that the decreasing trends in $PM_{10}$ concentrations for the Netherlands were also similar to other western and central European countries (i.e. Belgium, France, Germany, United Kingdom and Denmark) for the period 1990–2006. Therefore, we believe that the results of PM trend analyses for Switzerland and the Netherlands in this study provided a good representation of the PM changes in most parts of

Europe. On the other hand, the PM changes reported in Table 2 might not be representative for southeastern Europe and the results of the sensitivity analysis might be an overestimation of the true changes, as also stated in Sect. 5.

4) Lines, 15-20 on Page 10 discuss the estimated trends in PM at the observation sites and quantify the changes to be 41-44%. How are these changes then used to estimate the 50% and 65% perturbations to the AOD for the sensitivity tests described on page 8?

The numbers 41-43% refer to annual changes in PM10. The calculated perturbations in the AOD were based on the values for PM2.5 in summer in Table 2. More specifically, 53% (for the perturbation we rounded it down to 50%) and 65% relative changes of the estimated $PM_{2.5}$ concentrations (reported in parentheses) in the summer season for Switzerland and the Netherlands, respectively. We modified the sentence on page 10, lines 15–16 as follows:

*"The adjustment factors ($p_f$) were then based on the total relative changes of the estimated $PM_{2.5}$ concentrations for the summer season (see Table 2)."*

5) Evaluation statistics for the BASE calculation are provided in Table 4, without much information on the measurements themselves -location, time, etc. Without such information it is difficult to gauge what these statistics represent. I believe correlation coefficient shown here is representative of the spatial variability captured by the model and not the "temporal evolution" as suggested on Page 10, line 30.

We revised the statistical model evaluation for $O_3$, $PM_{10}$ and $PM_{2.5}$ by reducing the data availability filter from 90% (which was used in Oikonomakis et al. (2018)) to 80% (which had already been used for AOD and SSR) in order to include some more stations, and hence increase the spatial representation of the model evaluation, but without degrading its performance. The changes are small and only in a few statistical metrics, and are highlighted in Table 4 of the revised manuscript. In addition, we added a figure in the supplement (Fig. S1) which shows the correlation coefficient for each station and for each evaluated variable in a map. The correlation coefficient for most stations in Fig. S1 is equal or higher than the overall correlation coefficient reported in Table 4, indicating that the model successfully catches most of the temporal evolution of all variables and not just the spatial variability. We made the following changes in the manuscript regarding Fig. S1 and also to provide some more information about the treatment of the measurements:

page 7, lines 6–8: *"For a better comparison between the model and the observations, we used only rural background stations due to our grid resolution. Furthermore, we evaluated the daily mean of the chemical species in order to be able to compare our results with other studies (e.g. Bessagnet et al., 2016). More details about the observational data treatment and …"*

page 11, line 8: *"… for the daily mean* $O_3$, $PM_{2.5}$ *and* $PM_{10}$ *(see also Fig. S1)."*

page 11, line 11: *"… the model can capture the observed* $PM_{10}$ *temporal evolution (Fig. S1)."*

page 11, line 20: *"… relatively high correlation (r = 0.6) between the model and the observations which is shown in more detail in Fig. S1."*

page 11, line 28: *"… inter-daily variability was captured as well (Figures 2 and S1; r = 0.8)."*

6) Section 4.3.2 and Figure 5: Please provide more details on how the SSR values are estimated. Are they from the WRF simulation or TUV? How different are the SSR from the two? Please emphasize and clarify the assumption that the changes in radiation only impact the photolysis rates and no other aspect of the modeled chemistry and transport.

In Sect. 2.1 (page 6, line 14) it is stated that the algorithms in both TUV and CAMx were modified to just extract the AOD and SSR data. Therefore, the SSR results presented in this study come from the modeling system of TUV-CAMx and were calculated with the same radiative transfer algorithm that was used for the calculation of photolysis rates (as described in detail in Sect. 2.1). The SSR originating from WRF is only used in the calculation of biogenic emissions. A consistent comparison of SSR between WRF and TUV-CAMx is not possible, as the first has instantaneous hourly output and the latter has hourly average output. However, in both cases the same cloud cover data are used in the radiative transfer calculations, and thus we do not expect significant differences in the SSR between the two models. We made the following modifications in the text to make this more clear:

page 6, lines 15–17: *"In addition, the radiative transfer algorithms of both TUV and CAMx were modified to extract the modeled AOD and SSR data. In other words, both the SSR (used in the photolysis rate calculation) and the photolysis rates were calculated according to the same parameterization that was described above."*

page 6, lines 31–32: *"… using temperature and SSR data from the WRF output (the SSR data from WRF were not used in any calculation in CAMx) as well as land use data from …"*

page 8, lines 4–7: *"Finally, it is noted that the chemistry simulated by CAMx (for any scenario) does not affect the meteorology, as it is prescribed (see Sect. 2.1), and hence the impact of ARI on atmospheric dynamics and other meteorological related effects (e.g. vertical mixing, dry deposition (Xing et al., 2017)) are excluded in this study."*

7) Page 14, lines 1-2: I think the authors should caveat the conclusion that feedback chains associated with secondary aerosol formation and subsequent aerosol burden have negligible impact on photolysis rates. Direct radiative effects on temperature

and boundary layer ventilation are also important effects that can modulate secondary organic aerosol production – since these effects are not accounted for in this study, I would caution against a broad conclusion.

We have modified that sentence to explicitly state that the presented argument about the secondary aerosol changes is relevant only to the results of this study (or similar studies within the same framework), which does not take into account any potential effects of ARI on meteorology and subsequent effects on aerosol chemistry.

page 14, lines 14–16: *"We conclude that these changes in SA have negligible impact on the photolysis rates. However, the changes in SA might not be negligible if the impact of ARI on meteorology and subsequent effects on chemistry are also taken into account (which is not the case for this study)."*

8) The impacts of photolysis changes on seasonal average ozone mixing ratios are estimated to be rather modest (a few percent). I would imagine the impacts on daily maximum ozone values will be larger and would be of greater interest. It appears the authors have analyzed those impacts also, but have not presented them here. I think many readers would be interested in impacts on daily maximum ozone.

The impact of ARI changes on daily maximum ozone is higher only by up to 0.1 ppb, as shown in Fig. 1 below, compared to the daytime (10:00–18:00 LMT) average results that we reported in the manuscript. The reason is that ozone peaks in the late afternoon hours, while the maximum impact of the ARI on ozone occurs earlier. Therefore, we think that is not necessary to include the results of Fig. 1 in the manuscript, as they do not bring any additional interesting information to our study.

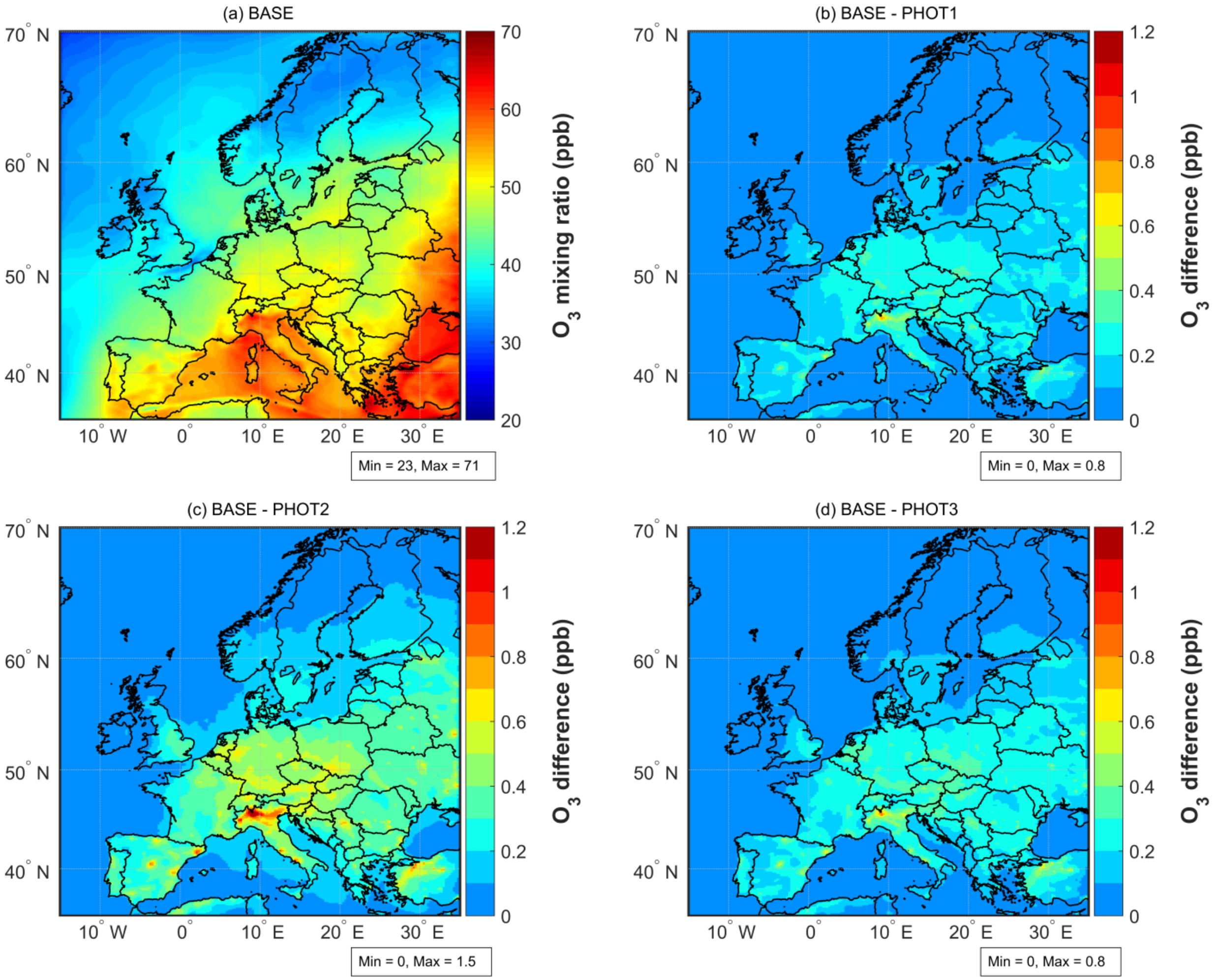

**Figure 1.** Seasonal mean of daily maximum $O_3$ mixing ratios for the BASE scenario (a) and differences in daily maximum $O_3$ between the BASE scenario and PHOT1, PHOT2 and PHOT3 scenarios (b-d), respectively, in summer 2010. Note the different color scale between panel (a) and panels (b-d).

9) The discussion in section 4.6 involving conversion of the change in ozone from the sensitivity runs to a trend over two decades and comparison with other reported trends is not convincing, especially given the range in the trends (0.06-0.16 ppb/yr). Given that the current study only examines the change induced by a single DRE process (i.e., photolysis) on a chemical state representative of 2010, I do not see how it can be converted and compared to a trend inferred from observations that have been influenced by many more chemical and physical processes that are not even approximated in this analysis.

As we explicitly stated in Sect. 4.6, we did not compare the changes in ozone reported in this study with the results of observed ozone trends with other studies. We just wanted to show a very general comparison between the orders of magnitude between our results, the total ozone concentrations and the observed ozone trends. We made the following modifications to Sect. 4.6:

page 15, line 27, section's title: *"ARI and ozone trends"*

from page 15, line 30 to page 16 line 6: *"Wilson et al. (2012) reported an annual (summer) increasing trend of 0.16 ± 0.02 (0.12 ± 0.06) ppb yr$^{-1}$ in the European ground-level ozone (stations-average) for the period 1996-2005. The total ozone difference (0.2–0.8 ppb) via both the effects on photolysis rates and BVOCs emissions (COMBO scenario) would translate (considering the full 20-year time period) to a summer trend of 0.01–0.04 ppb yr$^{-1}$. These values should not be considered for a direct comparison with the absolute values of the aforementioned observed ozone trends, not only due to differences in the data analysis like time averaging and spatial coverage, but most importantly due to the exclusion of other physical and chemical processes influencing the ozone trends. Nevertheless, the comparison of the order of magnitude between the aforementioned values and the reported ozone trends suggests a higher importance of the impact of ARI (only via photolysis rates and BVOCs emissions) on surface ozone than when just comparing to the total ozone concentrations. Therefore, this comparison indicates that the ARI (as investigated in this study) might have had an accountable impact on …"*

10) A recent study by Xing et al. (2017) analyzes the impacts of aerosol direct effects on tropospheric ozone through changes in atmospheric dynamics and photolysis rates. For summertime conditions in China they report comparatively larger impacts on ambient ozone induced by DRE impacts on atmospheric dynamics (through stabilizing of the atmosphere and modulation of dry deposition) than photolysis. Their results suggest that reducing the aerosol DRE (as would happen in a brightening scenario) will benefit the reduction of maximum O3 in summer driven both by changes in photolysis and to a larger extent atmospheric dynamics. Could similar impacts of DRE changes also have occurred over Europe during the 1990-2010 brightening period?

We have already discussed the results of other studies that included the ARI on weather or ACI and their subsequent effects on chemistry in Sect. 1 as well as in the conclusions (Sect. 5), in detail. It could be that the reduction of the ARI, via the effects on atmospheric dynamics, might have resulted in reduction in summer maximum surface ozone over Europe between 1990 and 2010, as shown by Xing et al. (2015). However, there are still a lot of uncertainties in the online models and especially in the PBL mixing processes (Baklanov et al., 2014), which were discussed in detail in Sect. 1 of the manuscript. In addition, we believe that further investigation on the topic with different models and parameterizations, as well as improvement of the models with observational and experimental information, is needed to increase our confidence in the model results in terms of agreement with the reality.

## References

Baklanov, A., Schlünzen, K., Suppan, P., Baldasano, J., Brunner, D., Aksoyoglu, S., Carmichael, G., Douros, J., Flemming, J., Forkel, R., Galmarini, S., Gauss, M., Grell, G., Hirtl, M., Joffre, S., Jorba, O., Kaas, E., Kaasik, M., Kallos, G., Kong, X., Korsholm, U., Kurganskiy, A., Kushta, J., Lohmann, U., Mahura, A., Manders-Groot, A., Maurizi, A., Moussiopoulos, N., Rao, S. T., Savage, N., Seigneur, C., Sokhi, R. S., Solazzo, E., Solomos, S., Sørensen, B., Tsegas, G., Vignati, E., Vogel, B., and Zhang, Y.: Online coupled regional meteorology chemistry models in Europe: current status and prospects, Atmos. Chem. Phys., 14, 317-398, doi:10.5194/acp-14-317-2014, 2014.

Barmpadimos, I., Keller, J., Oderbolz, D., Hueglin, C., and Prévôt, A. S. H.: One decade of parallel fine ($PM_{2.5}$) and coarse ($PM_{10}$–$PM_{2.5}$) particulate matter measurements in Europe: trends and variability, Atmos. Chem. Phys., 12, 3189-3203, doi:10.5194/acp-12-3189-2012, 2012.

Hoogerbrugge, R., van der Gon, H. D., van Zanten, M., and Matthijsen, J.: Trends in Particulate Matter. Report 500099014/2010, PBL Netherlands Environmental Assessment Agency, 2010.

Oikonomakis, E., Aksoyoglu, S., Ciarelli, G., Baltensperger, U., and Prévôt, A. S. H.: Low modeled ozone production suggests underestimation of precursor emissions (especially NOx) in Europe, Atmos. Chem. Phys., 18, 2175-2198, doi:10.5194/acp-18-2175-2018, 2018.

Tørseth, K., Aas, W., Breivik, K., Fjæraa, A. M., Fiebig, M., Hjellbrekke, A. G., Lund Myhre, C., Solberg, S., and Yttri, K. E.: Introduction to the European Monitoring and Evaluation Programme (EMEP) and observed atmospheric composition change during 1972–2009, Atmos. Chem. Phys., 12, 5447-5481, doi:10.5194/acp-12-5447-2012, 2012.

Xing, J., Mathur, R., Pleim, J., Hogrefe, C., Gan, C.-M., Wong, D. C., Wei, C., and Wang, J.: Air pollution and climate response to aerosol direct radiative effects: A modeling study of decadal trends across the northern hemisphere, J. Geophys. Res, 120, 12,221-212,236, doi:10.1002/2015JD023933, 2015.