Responses to the report of anonymous referee #1

We would like to thank you for your further 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. All modifications are highlighted in the revised manuscript.

General Remarks:

Reviewer's response: I am not satisfied with the authors' reply to my first main question. I understand how the authors designed PHOT1-3 when I read their original manuscript. What I do not understand is why the authors did not calculate AOD in 1990 based on the real PM in that time. The purpose of the study is to find the reason for summer surface O3 change between 1990 and 2010 over Europe. The authors used 2010 emission to calculate 2010 AOD. So why would they not do this same in 1990? Of course, the uncertainty of the currently available emissions in 1990 is large as pointed out by the authors. However, the emissions still represent the best estimates by our scientific community. If the authors believe it is more appropriated to give a range of AOD in 1990 in this study, they should at least explain why in the paper.

In your first review you asked "why is it better to use the designed emissions in 1990 instead of using the emissions in 1990 provided directly from emission inventories". Since our intention in this study was not to design 1990 emissions, we tried to explain the reasons in our first reply. We apologize if we misunderstood your comment. We hope to clarify it better in the following.

The purpose of this study is to examine the impact of the European ARI changes between 1990 and 2010 on summer surface ozone. Therefore, we needed to isolate the ARI impact from other factors affecting ozone formation, such as precursor emissions, changes in meteorological and boundary conditions. That is why we did not simulate the actual year of 1990, but using the same input as for the base case (2010), we designed sensitivity tests (PHOT1-3) by scaling up the PM concentrations (**not emissions**) only in the AOD/radiative transfer calculations. In this way we could isolate the impact of changes in ARI on ozone from other factors. If we used a 1990 emission inventory and compared it with the base case (2010), then we would not have been able to disentangle the impact of changes in ARI on ozone from other factors, as the 1990 emissions would have influenced also the chemistry apart from the AOD/radiative transfer calculations. The method that we followed (i.e. with PHOT1-3 scenarios) ensured the isolation of the impact of ARI on ozone and its appropriateness within a realistic range of AOD conditions in 1990, was verified by comparisons of our simulated changes in AOD and SSR with the respective changes in observations (see Sections 4.3.1 and 4.3.2). We hope that the revised version now describes more clearly the purpose of this study along with the details, appropriateness and limitations of the methodology that we

used to address the study's purpose in the last paragraph of the introduction as well as in Section 2.3.1. The following sentences were modified:

From page 4, line 32 to page 5, line 1: *"Third, we modeled and compared only the initial (1990) and final year (2010) of the studied period using same model input (i.e., the one of 2010; thus the actual year 1990 was not simulated to avoid the effects from emissions and meteorology, but rather the AOD and SSR conditions representative of the 1990's were used; see Sect. 2.3) to isolate the influence of ARI on ozone from other factors."*

Page 8, lines 9-12: *"In order to quantify only the changes in ARI, we had to isolate them from other effects such as the gas-aerosol chemical interactions. For this reason, we modified the radiative transfer algorithm in CAMx (i.e. the in-line version of TUV) by applying an adjustment factor (p_f) in the AOD calculation to represent the aerosol concentrations in 1990, but without changing the concentrations themselves and thus avoiding any change due to chemistry."*

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 as in 1990."*

Reviewer's response: It is good that the authors have changed the title to address my second main question, although they do not mention it in their reply letter.

We changed the title of the paper following your suggestion but we forgot to mention it in the reply letter. We apologize for this.

Specific question 8

Reviewer's original question: Page 10 lines 4-6: the criteria III should not be listed here since all PM2.5 data in this study are estimated based on PM10, while not measured.

The authors' reply: The criteria iii is about the PM10 and PM2.5 data availability for 2010. In Sect. 2.2 we mentioned that both the PM10 and PM2.5 were provided by Airbase and NABEL networks and both products were measured at the respective sites.

Reviewer's response: It is better for the authors to point out that PM2.5 measurements may not be available in years other than 2010. Otherwise, these sentences are confusing: "they had both PM10 and PM2.5 data for 2010" (page 10 line 20) and "… the aerosol coarse mode was subtracted to estimate PM2.5 concentrations" (page 10 line 22). Readers may not be familiar with the temporal coverage of Airbase and NABEL networks.

We did the following modifications in the manuscript so that the information about the PM_{10} and $PM_{2.5}$ data availability is clearer as well as the reason for calculating the 2010 aerosol coarse mode to infer the trend in $PM_{2.5}$ concentrations:

Page 10, lines 15-16: *"… infer the $PM_{2.5}$ concentrations trend, as there are no $PM_{2.5}$ measurements available for the whole examined period (i.e. from 1990–1992 to 2010), …"*

Page 10, lines 20–22: *"... i) they covered the whole period 1990–2010 (Switzerland), or 1992–2010 (the Netherlands) for PM_{10} data, ii) they had at least 70% of daily PM_{10} and $PM_{2.5}$ data in each month, and iii) they had both PM_{10} and $PM_{2.5}$ data for 2010 in order to calculate the 2010 aerosol coarse mode ($PM_{10} - PM_{2.5}$)."*

Page 10, line 24: *"… the 2010 aerosol coarse mode was subtracted to estimate $PM_{2.5}$ concentrations as discussed above."*

Responses to the report of anonymous referee #2

We would like to thank you for your further 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. All modifications are highlighted in the revised manuscript.

The authors have taken into consideration most of my comments on the original submission. They now better explain the model set-up and the methodology employed to perturb the photolysis rates. I am also happy that they have clarified that the model simulations do not necessarily represent trends during the 1990-2010 period. Overall, the manuscript is much improved. I have a few additional minor suggestions for the authors to consider:

1) Page 5, line 17: Please clarify whether CAMx employs a modal or sectional approach to represent aerosol size distribution. I believe what the authors imply by "bimodal size distribution" is that 2 sections, nominally representing the fine and coarse aerosol, were used in the model calculations.

In our simulations with CAMx we used a static two-mode (fine/coarse) scheme. We slightly modified the sentence on page 5, lines 17-18 so that is clearer to the reader:

"… and we simulated the PM concentrations using a static two-mode (fine/coarse) scheme for the aerosol size distribution."

2) On page 5, line 25 it is stated that TUV employed a climatological aerosol profile. Does that imply that some representation of ARI is already incorporated in TUV? If so, how is this accounted for in the subsequent CAMx photolysis perturbations? Some clarification may be beneficial.

This is correct. First of all we would like to make it clear that the full-science TUV is used as preprocessor to provide CAMx with clear-sky photolysis rates. Then these rates are internally adjusted in CAMx for clouds and aerosols using a fast in-line version of TUV. Yes, there is a representation of ARI already incorporated in TUV. However, the TUV calculations (using a climatological aerosol profile) are repeated inside CAMx (using the in-line version of TUV) as its first step of radiative transfer calculations. In the second step of CAMx radiative transfer calculations, only the aerosol profile that is simulated by CAMx and clouds are taken into account. In other words, the climatological aerosol profile that is used in full-science TUV is also used in the first step of CAMx's radiative transfer calculations, but not in the second step. In general, the purpose of the 2-step calculations in CAMx is to calculate solar fluxes through the grid column for 2 cases: clear sky with default haze (i.e. climatological aerosol profile), and cloudy sky with actual haze (simulated PM). In this way, the ratio of the two solar flux profiles is applied consistently to the clear-sky photolysis rates that are pre-calculated by TUV (Ramboll Environ,

2016). Therefore, the climatological aerosol profile is used consistently between the TUV and CAMx calculations and does not influence the CAMx photolysis perturbations sensitivity tests (PHOT1-3). We did the following modifications in the text for a better clarification:

From page 5, line 24 to page 6, line 1: "*The full-science Tropospheric Ultraviolet and Visible (TUV) radiation model (NCAR, 2011) is used as a preprocessor to provide CAMx with clear-sky photolysis rates, where a climatological aerosol profile determined by Elterman (1968) is used. Then, these rates are internally adjusted in CAMx every hour for clouds and aerosols as well as for pressure and temperature using a fast in-line version of TUV (Emery et al., 2010; Ramboll Environ, 2016). The internal adjustment for clouds and aerosols inside CAMx is performed in two steps: First, the clear-sky radiative transfer calculations with in-line TUV are repeated inside CAMx. In the second step, the radiative transfer calculations are repeated including the impact of clouds and aerosols (simulated by CAMx). A ratio of cloudy- (and aerosols) to clear-sky solar radiation is derived by the aforementioned 2-step radiative transfer calculations in CAMx. This ratio is then applied to the clear-sky photolysis rates and SSR which were calculated by the full-science TUV preprocessor at the beginning. This internal adjustment (i.e., in-line TUV) is carried out only for a single representative wavelength (350 nm), …*"

3) Page 6, lines 15-17: Were the extracted SSR values from TUV and CAMx compared? How does one determine they are consistent?

In TUV we modified the code to extract the **clear-sky** SSR values. In CAMx, the radiative transfer calculations were performed by a fast in-line version of TUV in which: i) the radiative transfer calculations are performed for a single representative wavelength of 350 nm (as also stated in the manuscript), ii) the absorption from O_2, O_3, NO_2, and SO_2 was removed since it occurs in narrow UV bands compared to the broad-band influence of clouds, iii) the extraterrestrial flux cancels out in the calculation of cloudy- to clear-sky ratio, and thus was not needed (Ramboll Environ, 2016). In this way, the CAMx runtime is reduced while maintaining the accuracy of the radiative transfer calculations (Ramboll Environ, 2016). Therefore, the ratios of cloudy- (and simulated PM) to clear-sky SSR values from CAMx were applied as a multiplicative factor to the TUV clear-sky SSR values to obtain the final SSR values (also stated on page 5, lines 30-32), which were compared to the BSRN observations. In other words, the comparison between the extracted SSR values from TUV and CAMx is a comparison between clear-sky and all-sky SSR values, respectively. In addition, since the radiative transfer calculations in CAMx are essentially performed by the same TUV algorithm and the aforementioned 2-step approach has been tested and validated for a range of cloudy conditions (Emery et al., 2010), we do not believe that there are inconsistencies in the radiative transfer calculations between TUV and CAMx. We modified Sect. 2.1 (as shown above in our reply to your previous comment) and we included a clarification in the following sentence, so that is clearer that both TUV and CAMx share essentially the same radiative transfer algorithm:

Page 6, lines 15-17: *"In addition, the radiative transfer algorithms of both full-science TUV and CAMx (i.e., in-line TUV) were modified to extract the modeled AOD and SSR data."*

4) In my earlier review I had asked if the authors had examined impacts on daily maximum ozone. The authors responded that the impacts were higher by only ~0.1 ppb and explain that the maximum ARI impacts occur at times different (morning and evening transitions, as shown in earlier studies) from when the daily maximum occurs (mid-afternoon). For completeness, I think it would be useful to point this out in the manuscript discussions

We added a small discussion in the manuscript to address this, from page 14, line 31 to page 15, line 2:

"We also investigated the impact of ARI changes on daily maximum ozone, but it was higher only by up to ~0.1 ppb (not shown) compared to the daytime (10:00–18:00 LMT) average. Therefore, the ARI did not have a significantly higher impact on daily maximum ozone. The reason is that the daily maximum ozone occurs at different time (mid-afternoon) than the times the maximum ARI occurs (morning and evening), as also shown in other studies (Xing et al., 2015a, 2017)."

References

Emery, C., Jung, J., Johnson, J., Yarwood, G., Madronich, S., and Grell, G.: Improving the Characterization of Clouds and their Impact on Photolysis Rates within the CAMx Photochemical Grid Model. Prepared for the Texas Commission on Environmental Quality, Austin, TX. Prepared by ENVIRON International Corporation, Novato, CA and the National Center for Atmospheric Research, Boulder, CO (August 27, 2010). 2010.

Ramboll Environ: User's guide to the Comprehensive Air Quality Model with Extensions (CAMx). Version 6.3, http://www.camx.com, 2016.