

## Responses (bule) to Reviewer's comments (black)

The authors addressed most of the two reviewers' comments adequately. Meanwhile I still have reservations about two remaining issues as follows. I support the publication of this paper if they can be further addressed.

1. I agree that UVAI can be used as a proxy of aerosol absorption and OH abundance to some extent, but please further explain 1) why is the absolute value of UVAI used in the analysis (Figure 11, negative UVAI implies aerosol scattering, not absorption); 2) should some absolute abundance of aerosol also be used (e.g., AOD) since UVAI is more of an indicator of relative absorption vs. scattering?

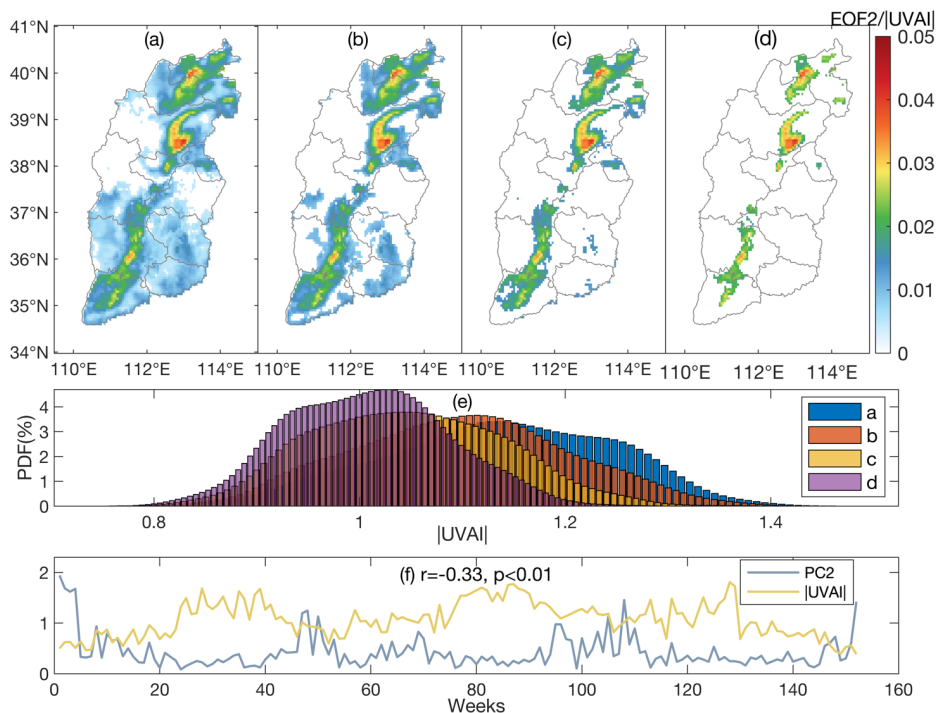
Large negative values of UVAI (especially more negative than -0.5) correspond to high AOD values (larger than 0.5) and concurrent SSA values generally ranging from 0.92 to 0.98, as observed at multiple AERONET stations (Figs 1, 6, 8 from Penning et al., 2009). While these values are not as absorbing as large positive values of UVAI (especially more positive than 1.0) which correspond to SSA values less than 0.9 (Torres et al., 2020), both are still absorbing due to the high AOD values present (1.0 to 3.0 or possibly even more). Analyzing all of the data from 2019 through 2021 on a grid-by-grid basis, there are found to be 357171 grids (5.0%) with positive values and 6740079 (94.4%) grids with negative values. The negative UVAI values observed over Shanxi are found to be very negative, as shown in the results before, consistent with and even stronger than the AERONET conditions reported by Penning et al. (2009).

There is a statistically significant correlation between the negative UVAI and EOF2 in both the spatial and temporal dimensions, although it is slightly smaller than the correlation shown in Figure 11 of the paper, and of the opposite sign, since the majority of values of UVAI which are far from zero are negative. The PDFs of the UVAI values over each of the subregions as EOF2 is increased are also recalculated using the negative UVAI values only, and demonstrate that the results are again nearly the same as in the original Fig.11 in the paper, but found to just be of the opposite sign.

We conclude that in this case, the use of the absolute value of UVAI is most appropriate and reasonable, since given the relatively high AOD levels found on average, even particles with a small amount of absorption still will have a significant

impact on the UV radiation. For these reasons, the analysis using the absolute value of UVAI was explained more in depth, and the following changes have been made in the paper:

Second, it is asserted that EOF2 is related to TROPOMI measured UVAI, which physically makes sense, since satellite observations of UVAI are sensitive to aerosol extinction in the UV, with very large values indicating large amounts of highly absorbing aerosol (SSA less than 0.9) and very large negative values indicating large amounts of partially absorbing aerosol (SSA between 0.92 and 0.98) (Penning et al., 2009; Torres et al, 2020). There have been numerous studies reporting that absorbing aerosols affect the downwelling surface radiative forcing in the visible (and therefore the actinic flux) (Léon, 2002) as well as OH concentrations (Hammer et al., 2016). Therefore, UVAI is an indirect proxy of an aspect contributing to the chemical decay capacity of NO<sub>x</sub> in-situ. Applying four different cutoffs to EOF2, it is observed that as the EOF2 domain increases in magnitude, that the 3-year mean measured absolute value of TROPOMI UVAI becomes smaller in magnitude, as demonstrated in Fig. 11. Since values of UVAI closer to zero imply less atmospheric extinction (absorption for positive values and a mixture of scattering and absorption for negative values), it therefore also scales inversely with surface UV radiation, implying that when the UVAI is lower, that there is more available UV radiation, and hence implicitly faster chemical decay of NO<sub>x</sub>. This is consistent with the UV radiation being responsible for the second mode of the maximized variance. The negative correlation observed between absolute values of UVAI weighted by high absolute values of EOF2 (EOF2>0.02) grid-by-grid in the same EOF2 region is anticorrelated with PC2 ( $r=-0.33$ ,  $p<0.01$ ). While  $r$  in this case is a lot smaller, it is also consistent with theory, since in order to significantly affect the OH levels, the changes in UV radiation and hence UVAI must be very large, which is found to not occur frequently in time, but when it does occur, it makes a significant impact.



**2<sup>nd</sup> Response Figure 1 (new Figure 11):** Four different cutoffs of EOF2 are used to set the spatial domains. The maps in (a-d) are plots of EOF2/|UVAI| where the cutoffs are given as (a) EOF2 >0.005, (b) EOF2 >0.01, (c) EOF2 >0.015, (d) EOF2 >0.02. (e) Histograms of |UVAI| over the domains given respectively in a-d. (f) Time series of weekly PC2 and |UVAI| in the (d) domain.

Your suggestion to use an absolute abundance of aerosol (e.g., AOD or AAOD) would provide an interesting point for future work. This is in our planned set of future work, as we have already used AAOD in previous works elsewhere in the past (i.e., Cohen and Wang, 2014; Wang et al., 2021), although at the present time this is not easy to do over Shanxi, since there are no AERONET stations available over this region for validation. There is a Chinese SONET station which was recently installed, and perhaps it can provide the validation required for this as future work.

2. I still disagree that the alpha1 can really be used to distinguish the source categories. 1) Response Figure 2: the anti-correlation between O<sub>3</sub> and NO<sub>2</sub> exactly suggests strong conversion from NO to NO<sub>2</sub> by O<sub>3</sub>. I do not understand the way the authors used this example to indicate insufficient conversion?

There are a few points that we use to guide our response to this interesting point. First of all, surface observations clearly demonstrate that there are frequently observations found where there is little to no ozone at the surface. Therefore, during these times of day, the conversion from NO to NO<sub>2</sub> by O<sub>3</sub> will not occur or will occur so slowly as to not impact the ratio of the emissions occurring at these times of the day. Hence, during this fraction of the day, the ratio of emissions is almost 100% controlled by the thermodynamic relationship from  $\alpha_1$ . This is particularly so for emissions from large sources observed by CEMS, which tend to run roughly evenly throughout the 24-hour day. Second, there is an even longer period of time where the concentration of ozone is not zero, but is still much lower than NO<sub>2</sub>, indicating that even if it is exerting some control on the NO to NO<sub>2</sub> conversion, that it is not dominant when compared with the thermodynamic relationship from  $\alpha_1$  on freshly emitted NO<sub>x</sub> during these times of the day. Third, due to the buoyancy from the heat co-emitted with the NO<sub>x</sub> from these large sources, a significant amount of these fresh emissions will be lofted into the free troposphere, wherein the ozone values are even lower than at the surface, and therefore the impacts will also be less.

In order to quantify the relationship between O<sub>3</sub> and NO<sub>2</sub>, we have conducted a one-year long (2019) analysis of surface observations in Taiyuan City, which is both in the domain of this work, and located near one of China's largest individual iron and steel sources. We use 5 $\mu\text{g}/\text{m}^3$  and 25 $\mu\text{g}/\text{m}^3$  of O<sub>3</sub> concentration as the dividing line to separate almost no ozone available to titrate NO<sub>x</sub> and as there being some ozone but insufficient to fully titrate to chemical equilibrium over the hour-long time period of the observations. There are four months in which every day has more than 3 hours that the O<sub>3</sub> concentration smaller than or equal to 5 $\mu\text{g}/\text{m}^3$  and four months with at least half of the days under similar ozone levels. There are five months during which every single day has more than 3 hours during which the O<sub>3</sub> concentration is relatively low (smaller than or equal to 25 $\mu\text{g}/\text{m}^3$ ), while the remaining 7 months have at least 1/3 of all days with a similar ozone level. We recognize that NO<sub>2</sub> and NO conversion processes via O<sub>3</sub> do occur, but given that there is a substantial amount of time in which there is insufficient surface O<sub>3</sub>, changes in NO<sub>2</sub> and NO concentrations that do occur must be contributed to more so by emissions, meteorology, transport, other chemical processes, and their thermodynamic conditions at the point of emissions, hence  $\alpha_1$ .

On top of this point, the geospatial distribution of heavy industrial enterprises in Shanxi are mostly clustered, so they may face similar atmospheric chemical environments and may influence each other, which would lead to those enterprises downwind of the first one having even less ozone available to undergo any titration reactions (Cohen et al., 2011; Cohen and Prinn, 2011). This has been found to be very important, especially so at night time or under heavy aerosol loading conditions when there is insufficient UV to restart such chemical processes, which is commonly observed in the region and consistent with the observations shown.

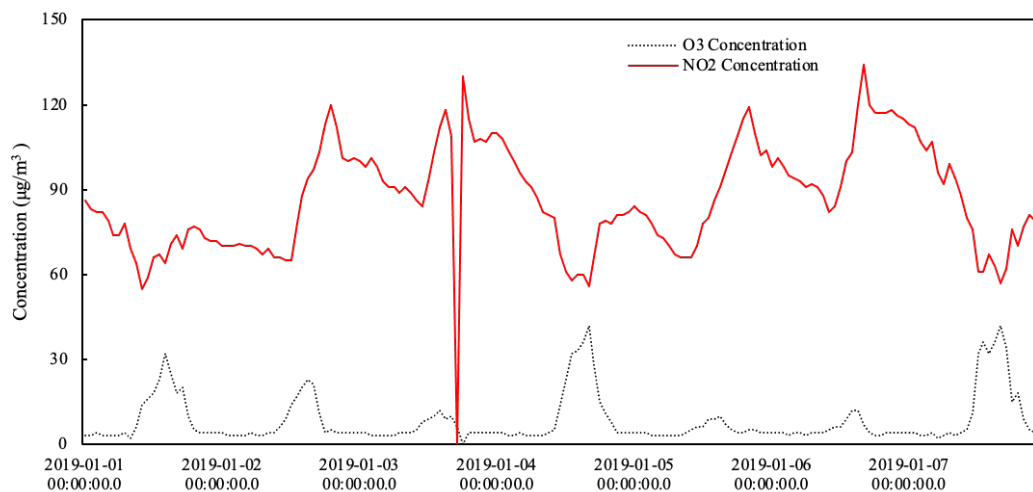
On top of this, we believe that the data speaks for itself in this case. We have shown the statistics of the distributions of  $\alpha_1$  and believe that they are significantly different from each other. We do understand that some ozone titration occurs, but also do not believe it is fair to merely assume that it is important in the context of this work, just because in other places it is dominant, and do not feel it is fair to state that the thermodynamic contribution is not important, when clear statistical differences are observed in the computed PDFs. We also believe that a more careful analysis of the data will show that changes in the  $\text{NO}_2$  and  $\text{O}_3$  are not always correlated or anti correlated, with it being clear that there are other processes which occur, including by not limited to transport and changes in aerosol induced UV, as demonstrated in the 2<sup>nd</sup> Response Figure 2, and as included in other parts of the emissions equations that this work is using.

Thank you for the suggestion to investigate in more detail the issues surrounding upslope winds, plume rise, and differences under different times of the year and different climatological conditions. We believe that this future work will provide interesting insights to better understand at high frequency and spatial resolution the relative importance of all of these driving factors, such as those which are first order, second order, etc.

**2<sup>nd</sup> Response Table 1.** Ozone concentration statistics from ambient air quality monitoring stations near an iron and steel factory in Taiyuan City of 2019

Month	Days in which have more than 3 hours that $\text{O}_3$ concentration $\leq 5\mu\text{g}/\text{m}^3$	Days in which have more than 3 hours that $\text{O}_3$ concentration $\leq 25\mu\text{g}/\text{m}^3$
January	27	31

February	4	20
March	10	23
April	15	22
May	10	19
June	0	7
July	0	9
August	6	13
September	13	28
October	24	28
November	26	27
December	27	29



**2<sup>nd</sup> Response Figure 2.** Time series of hourly concentration of O<sub>3</sub> and NO<sub>2</sub> from ambient air quality monitoring stations near an iron and steel factory in Taiyuan City.

There are many observations in this area that demonstrate at times there is insufficient ozone present at the surface to convert NO to NO<sub>2</sub> even on days which have a high surface temperature, which should be the times with the largest surface O<sub>3</sub> concentration (Response Figure 2). Statistics of the two figures (2<sup>nd</sup> Response Table 2) show that more than 56% of the days have at least 3 hours of O<sub>3</sub> less than 5µg/m<sup>3</sup>, and more than 89% if the days have at least 3 hours of O<sub>3</sub> less than 20µg/m<sup>3</sup>. Hence, even in summer there are insufficient ozone time.

**2<sup>nd</sup> Response Table 2. Ozone concentration statistics for Response Figure 2**

Day	Hours that O <sub>3</sub> concentration ≤5μg/m <sup>3</sup>	Hours that O <sub>3</sub> concentration ≤25μg/m <sup>3</sup>
Sep. 11 <sup>th</sup>	0	5
Sep. 12 <sup>th</sup>	3	14
Sep. 13 <sup>th</sup>	10	13
Sep. 14 <sup>th</sup>	4	13
Oct. 3 <sup>rd</sup>	4	12
Oct. 4 <sup>th</sup>	0	2
Oct. 5 <sup>th</sup>	0	0
Oct. 6 <sup>th</sup>	0	5
Oct. 7 <sup>th</sup>	7	15

2) Response Figure 4: are the PDFs from the six sources really that different? It reads to me like the PDFs of four sources (Cement, Power, Iron&Steel and Alumina) are very similar, and the PDFs of the other two are close to each other. So are the derived alpha values really "distinguishing these sites from each other"?

We have calculated the statistical distribution of  $\alpha_1$  and have presented the results of the 10<sup>th</sup>, 25<sup>th</sup>, 50<sup>th</sup>, 75<sup>th</sup>, and 90<sup>th</sup> percentile values in the 2<sup>nd</sup> Response Table 3. We hope that the table below makes the differences clearer for the reader to follow. Cement, power and iron/steel have higher  $\alpha_1$  at almost all the percentile values than the other three types of sources, with cement factories having the highest values, while boilers clearly have the lowest values. Further details between more closely related sources are also demonstrated. For example, power and iron/steel have significant differences across different parts of the distribution with power having larger values from the 25<sup>th</sup> through 75<sup>th</sup> percentiles and steel having higher values at the 90<sup>th</sup> percentile level. This is consistent with the fact that iron and steel use several different processes, one of which contains very high temperature combustion (blast furnace based) and the other which contains a lower temperature process (sinter bed based). Other such differences are shown within the table and in the plots in the paper.

**2<sup>nd</sup> Response Table 3.** Distribution of  $\alpha_1$  (10<sup>th</sup>, 25<sup>th</sup>, 50<sup>th</sup>, 75<sup>th</sup>, and 90<sup>th</sup> percentile values) calculated based on CEMS using MFIEF at different industry sources.

Industry Sources	$\alpha_1$				
	10 <sup>th</sup>	25 <sup>th</sup>	50 <sup>th</sup>	75 <sup>th</sup>	90 <sup>th</sup>
Cement	1.4	2.2	3.7	6.3	10.3
Power	1.4	2.0	3.3	5.9	8.6
Iron/Steel	1.3	1.8	3.2	5.4	9.4
Coke	1.2	1.5	2.2	3.8	6.6
Aluminum oxide	1.3	1.4	2.6	3.5	5.0
Boiler	1.1	1.3	1.7	2.3	3.9

I think the other parts of this study is excellent, and I retain the suggestion to greatly reduce the amount of discussion of this part.

Thank you again for helping us to improve how we both interpret and explain the results. We have made updates in the paper accordingly.

## References

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