

Interactive comment on “The impact of aerosols on photolysis frequencies and ozone production in urban Beijing during the four-year period 2012–2015” by Wenjie Wang et al.

Anonymous Referee #1

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The work by Wang et al. studies the reducing impact of aerosols on photolysis frequencies $j(\text{O1D})$ and $j(\text{NO}_2)$ during a four-year measurement period in Beijing. Aerosol optical depths (AOD) were taken from AERONET measurements and photolysis frequencies were derived from co-located radiometric measurements of spectral actinic flux. Based on these measurements, polynomial parametrizations were derived describing empirically the influence of AOD on photolysis frequencies $j(\text{O1D})$ and $j(\text{NO}_2)$ in Beijing (under clear-sky conditions). The parameterizations were then used to estimate the effect of aerosol-diminished photolysis frequencies on photochemical ozone production in a chemical box model and compared to hypothetical aerosol free conditions. A 25% reduction of the monthly mean ozone production was predicted for a

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selected summer month of the year 2012.

The work describes an interesting data set and comes to interesting conclusions. However, although the text excessively describes many details, some important information is missing and the data analysis is in part not satisfying. The manuscript needs major revision before publication can be recommended. The text should be widely shortened and focused. Moreover, the specific comments listed below should be addressed.

Specific comments

Abstract

Line 30: “In addition, the slopes are equal to ...” 1) The wording: “In addition, ...” is awkward. 2) Why there is a range of slopes for $j(\text{O1D})$ and a single value for $j(\text{NO2})$ is unclear at this point, and what the slopes refer to in the first place when the relationships are non-linear. 3) The slopes should be negative in any case. 4) The authors should take into account significant digits (throughout the paper). The precision of the data does not justify a statement “4.21-6.93”. I would say “4.2-6.9” at the very most. 5) AOD has to be specified here, i.e. AOD (380 nm)?

Line 32: “... larger than those observed in the Mediterranean.” I would say: “... than those observed in a similar, previous study in the Mediterranean.”

Line 33: “...have a stronger extinction on ...” Please reword.

Line 38, 39: “... $j(\text{NO2})$ by 24.2% and 30.4% for summer and winter, ... $j(\text{O1D})$ by 27.3% and 32.6%...” 1) The meaning of these numbers is unclear. I assume they refer to some kind of seasonal mean of the photolysis frequencies that needs to be specified. 2) The precision implied by three digits is misleading.

Line 42: “... the monthly average net ozone production is reduced by 25%.” By looking at Fig. 10, I assume the 25% refers to a monthly mean daytime net ozone production that needs to be specified.

Introduction

Lines 54, 59, 63, 65, 66: Use consistent notations for O(3P) and O(1D).

Line 60: "...the only significant chemical source..."

Lines 68-71: Remove the symbol "S" in the brackets. It may be added as an index to "sigma" and "phi" but "S" is no variable like "lambda" or "T".

Lines 78-79: "Scattering aerosols can enhance..., while absorptive aerosols reduce ...throughout the boundary layer." These statements are unclear and certainly do not apply for all conditions.

Line 91: "Therefore it is necessary to quantitatively evaluate the effect of aerosols on photolysis frequencies for the purpose of ozone prevention". I would say: "... for a better understanding of ozone formation under highly polluted conditions."

Line 98: "... are compared with the observed value to test the simulation effect." Unclear: If radiative transfer models are used there are usually no measurements available. And what is the "simulation effect"?

Line 100: "... due to complicated environmental conditions...". Clarify.

Line 123-136: Use the term "photolysis frequencies" consistently throughout the text.

Lines 134, 135: Mind significant digits, see abstract by Li et al., 2011.

Line 143ff: "Our overall goal..." It should be made clear that this study was strongly informed by a similar work by Gerasopoulos et al., 2012 which is not adequately referred to in the Introduction.

Measurements

Line 155: The exact measurement period should be given here. Was it exactly four years?

Line 163: What absorption cross sections and quantum yields were used to calculate

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the photolysis frequencies?

Line 163: I assume the $j(\text{O1D})$ were calculated temperature dependent according to Eq. 1 (and a statement in lines 302-304). That should be clearly stated. However, is it useful, if a common parameterization as a function of AOD is later used for summer and winter $j(\text{O1D})$? There may be arguments to include temperature but the influence should be mentioned and quantified in Section 3 (see below).

Line 164: “Shetter and Müller , 1999”

Line 169: The studies by Shetter and Müller, 1999, and Hofzumahaus et al., 1999 describe double-monochromator based instruments with somewhat different properties. The authors should state what type of detector was used and how regular calibrations of the instrument were performed during the four-year period. Moreover, it is unclear if the 10% uncertainty comes from the calibration uncertainty or is attributed to the uncertainties of absorption cross sections and quantum yields.

Line 175: “... close to the PKUERS site” should be specified in km.

Line 184: “This wavelength (380 nm) was chosen as it is more representative of $j(\text{NO}_2)$ ” Why wasn’t the AOD at 340 nm used as well to estimate AODs more representative for $j(\text{O1D})$ (around 300 nm), e.g. by the Angstrom equation? You can argue with better comparability with Gerasopoulos et al. , 2012 but that should be made clear.

Line 185: SSA measurements during a period of one month are hardly representative for four years. Since the AOD-SSA relationship becomes important later to explain the steep decrease of j -values with AOD, I wonder why AERONET based SSA are not consulted for the whole period.

Line 191: The source of the ozone column data should be specified and a citation included.

Line 198: “... under cloudless conditions.” Was there an additional cloud screening performed or was any period marked cloud-free by AERONET taken? Because of the

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distance between the sites there were certainly some cases when clouds were present at PKUERS and no clouds at the AERONET site? Moreover, to assess the importance of this work, it would be interesting to learn what fractions of daytimes were identified as clear-sky during the four years. This could be included in Table 2 for the different seasons.

Line 203: “Global irradiance” is a different quantity than actinic flux.

Line 204: Explain “AE”. Were the AE taken from AERONET, was a constant AE used, or was AE set to zero to simulate with a wavelength-independent AOD? This is important later for the model measurement comparisons in Fig. 5.

Line 205: Were mean Earth-Sun distances used in the calculations or were time, date and location specified? If not, were the measured j -values scaled to a common mean Earth-Sun distance?

Line 205: Were the same absorption cross sections and quantum yields used to calculate $j(\text{O1D})$ and $j(\text{NO2})$ from TUV-derived spectra? What temperatures were used?

Line 230-234: Equations E2, E3 are not self-explaining. At least give a citation where these formulas are rationalized and explain “ θ ”.

Results and discussion

Lines 239-278: “In order to evaluate the extinction capacity...” The motivation to look into the relationship between PM_{2.5} and AOD should be made clearer and the results shown in Fig. 1 and Fig. 2 should be reassessed. Obviously, PM_{2.5} is not a good proxy to estimate AOD. Moreover, the summer-winter differences in the slopes in Fig. 1 are probably explainable by the different heights of the boundary layers alone and there is no basis to speculate about seasonal differences of aerosol optical properties unless you consult AERONET data. My conclusion of Sect. 3.1 and the first paragraph of Sect. 3.2 would be that PM_{2.5} is not suitable to estimate AOD (and consequently, PM_{2.5} data are not used in the remainder of the text). On the other hand, did you

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check the relationship between PM_{2.5} and e.g. $j(\text{NO}_2)$ directly? I assume it looks much poorer than the relationship between $j(\text{NO}_2)$ and AOD which would confirm the assumption that AOD is a more relevant parameter.

Line 249, Table 2: Table 2 should be mentioned in Section 2.1, not here. Please consider significant digits in Tab. 2 and specify season periods in the caption.

Figs. 2-3: Specify what is shown here. Averages, medians? The periods defined as “spring”, “summer”, “autumn” and “winter” should be defined clearly somewhere. Are the PM_{2.5} data in Fig. 2b also from clear-sky days only? Specify “AOD (380 nm)” in the caption of Fig. 2.

Lines 285-292: 1) What do the stated differences in photolysis frequencies refer to? Mean daily maxima? Please specify. 2) What are the uncertainties of these differences? 3) Does the TUV-derived difference refer to aerosol-free conditions? 4) What role plays the temperature, certainly lower in Beijing during the winter compared to conditions in Crete?

Fig. 4: Specify in the caption what the full lines show. Averages, medians? What AOD bin size was used? Indicate AOD (380 nm).

Fig. 5: Add standard deviations to the measured values. Otherwise the relevance of the differences compared to the model calculations cannot be assessed. Specify the ozone column range of the measured data in the caption. Indicate AOD (380 nm) for the measured data and $\text{AOD} \neq f(\lambda)$ for the model calculations (if that applies).

Line 319-326: Here the question again arises, what AE was used in the TUV calculations, what temperatures and if the annual changes in Sun-Earth distances were considered.

Lines 327-341 and lines 341-347: These sections are too speculative without consulting AERONET data. As already mentioned, the 1-month data in Fig. 6 is probably not representative for the average aerosol over the four year measurement period.

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Lines 357-361 and Table 3: Consider significant digits.

Figure 7: What do the full lines show?

Line 397: Equation E5 should appear here.

Lines 397-406, Tables 5 and 6: 1) If ozone columns have no significant influence on $j(\text{NO}_2)$, why does Tab. 5 give four different parametrizations for four different ozone column ranges? A single parametrization should be given here to make things easier for readers who want to use these formulas. 2) What is the nature of the error limits of the parameters a_1 - a_6 and are they of any relevance to estimate the quality of the parameterizations? Please note that for $j(\text{NO}_2)$ most parameters vary more strongly if different ozone column ranges are compared than indicated by the errors of the parameters. So these errors have no relevance and pretend an accuracy that is not real. 3) Did you systematically test if simpler parameterizations give satisfactory results as well by taking out single parameters? 4) For $j(\text{O}_1\text{D})$ the parametrization appears arbitrary: parameters show no clear trend with ozone column although this would be expected even for an empirical formula. It would be more convincing to use a parameterization that contains SZA, AOD and ozone columns in a single formula. 5) Given that the data were probably (i) not normalized to a common Sun-Earth distance, nor (ii) to the same temperature; (iii) the AOD (380 nm) used does not apply strictly to the $j(\text{O}_1\text{D})$ wavelength range, (iv) only 30 DU wide ranges of ozone columns were merged, and (v) cloud-sceneing cannot be perfect, the obtained $r^2 > 0.95$ is remarkable, also compared to Tab. 3 and 4, and should be rationalized.

Lines 407-409: What do the percentage reductions refer to? See also abstract and conclusions.

Line 411: "... and lower SSA in winter" Was not shown.

Lines 431-433: As mentioned above, this statement is not justified and the use of $\text{PM}_{2.5}$ would most likely lead to no improvement of estimated $j(\text{O}_1\text{D})$ or $j(\text{NO}_2)$ unless

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you can show it directly.

Line 460, Figure 8: I assume what is shown in Fig. 8, and the 25% reduction stated in the text, refer to mean daytime ozone productions. Please specify time period.

Figure 9: How were the data shown derived, i.e. what periods of time do single data points represent?

Figure 10: Indicate in the caption that the data represent mean values over a period of one month (or n clear-sky days) in August 2012.

Figure 11: In the caption refer to Table 7 to explain the meaning of day A and day B.

Table 7, 8: Mind significant digits.

Conclusions

Conclusions 1) and the first part of 2) are speculative.

Specify meaning of percentage reductions in 3).

Line 559: Measurement campaign in August 2012 or 2014?

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