

Reply to Dr. A. Kourtidis (Referee #1)

We thank the reviewer for the careful reading of the manuscript and helpful comments. We have revised the manuscript following the suggestion, as described below.

(1) General comments

In general I found the paper fairly well written and the results well-explained. Further, the methodology is sound and well-explained. The paper contains a lot of modeling work on the photochemistry of Mexico City and its relation to aerosols. The only thing I might be missing is one (preferably large) paragraph in the conclusions, summarizing and generalizing the implications of the presented work to other world megacities apart from Mexico City. I believe the presented work has such implications, and I would like to suggest to the authors to try to deliver such a paragraph, briefly discussing what the possible differences in location, climate, emission fingerprints etc. would mean in interpreting more generally the presented work.

We have added the following discussions in Section 4: *“There are several implications to the present study. In Mexico City, a large amount of BC and POA are emitted to the atmosphere (Zavala et al., 2009), causing strong absorption of UV radiation during daytime. However, high levels of non-absorbing aerosols, such as SOA, sulfate, nitrate and ammonium, efficiently scatter UV radiation. Aerosols can enhance photolysis frequencies when UV scattering dominates UV absorption by aerosols or vice versa. In most of the megacities and large urban complexes in the United States, the observed BC concentrations are lower (Murphy et al., 2011), so the change in photolysis frequencies due to aerosols is likely to be positive. In contrast, very high POA and BC emissions in the megacities in China have caused the reduction of photolysis frequencies and ozone concentrations (Bian et al., 2007). In addition, the aerosol radiative module developed in the present study is based on the aerosol modal approach in CMAQ, which is now widely used in air pollution simulations. Considering its efficiency and accuracy demonstrated in the present study, the module provides a powerful tool for evaluating the aerosol impact on the photochemistry in megacities.”*

Specific minor comments

(2) Abstract

“aerosol size, composition and mixture”: I do not understand what the authors mean by “mixture”. “aerosols can slightly enhance photolysis rates”: please add “at the lower-most model layer” or specify altitudes. “lead to about 2-17% surface ozone reduction”: please add either “depending on time and location” or “with generally higher reductions in the early morning hours near the city center” “resulting in a further decrease of other chemical species”: Please either specify the species or remove, as for some species the reductions in photolysis rates would mean slower removal rates.

We have changed “mixture” to “mixing”.

We have added “at the lower-most model layer”.

We have added “with generally larger reductions during early morning hours near the city center”.

We have removed “resulting in a further decrease of other chemical species”.

(3) Introduction

“particular matter” change to “particulate matter” “are chemical mixture” change to “are a chemical mixture” “0.63 Dobson unit” change to “0.63 Dobson units” end of 2nd paragraph: In the discussion on the impact of aerosols on photolysis frequencies please add the works of Balis et al. (2002a), Johnson et al. (2000) and Zanis et al. (2002), which, to my opinion, are very relevant. “which provides a unique opportunity” change to “which provide an opportunity”. I do not agree that the opportunity for studying aerosol/photochemistry interactions is unique; other campaigns have also resulted in large datasets. “at T0 supersite” change to “at theT0 supersite” “Barnard et al. (2009)”: in the reference list it is Barnard et al. (2008).

We have changed “particular matter” to “particulate matter” in Section 1.

We have changed “are chemical mixture” to “are a chemical mixture” in Section 1.

We have changed “0.63 Dobson unit” to “0.63 Dobson units” in Section 1.

We have included the works of Balis et al. (2002), Jonson et al. (2000) and Zanis et al. (2002) in Section 1:

“Jonson et al. (2000) found small effects on monthly averaged ozone with the inclusion of aerosols in the simulations of a regional-scale photochemistry model. Zanis et al. (2002) concluded that increasing absorbing aerosol (Sahara dust) content could reduce net ozone production rate in box model calculations constrained by the measurements. Balis et al. (2002) reported the reduction of the photolysis rates during a Sahara dust event by radiative transfer model calculations and aircraft measurements.”

We have changed “which provides a unique opportunity” change to “which provide an opportunity” in Section 1.

We have changed “at T0 supersite” change to “at theT0 supersite” in Section 1.

We have changed “Barnard et al. (2009)” to “Barnard et al. (2008)” in Section 1.

(4) 2.2 aerosol and cloud radiative module

The 48 bins of the aerosol spectrum are with a constant step? Please specify. D’Almeida et al., 1991, appears as de Almeida et al., 1991 in the reference list.

We have specified in Section 2.2: *“When the bin’s radius is less than 0.1 μm , the interval of bins ranges from 0.001 to 0.005 μm . When the bin’s radius is greater than 0.1 μm , the interval is increased to 0.025 to 0.25 μm .”*

We have changed “D’Almeida et al., 1991” to “d’Almeida et al., 1991” in Section 2.2.

(5) 2.3 model configuration

Please briefly explain the “typical O₃-convection south/north” meteorological conditions in Mexico City.

We have added explanations in Section 2.3: *“O₃-Convection South takes place when there is a weak northerly wind component aloft with rain in the southern part of the Mexico City basin. O₃-Convection North takes place when there is a weak southerly wind component aloft with a gap flow and rain in the northern part of the basin.”*

(6) 3.1 aerosol simulations

“. . .SOA. . . formed from the chemical production of gaseous precursors” change to “. . .SOA. . . formed from the atmospheric processing of gaseous precursors” De Foy et al., 2009, mentioned twice in the text: This is missing from the reference list. “during dry season” change to “during the dry season” “observation for nitrate” change to “observations for nitrate”

We have changed “The secondary aerosols, such as nitrate and SOA, are mainly formed from the chemical production of gaseous precursors” to “The secondary aerosols, such as nitrate and SOA, are mainly formed from the atmospheric processing of gaseous precursors” in Section 3.1.

We have added the reference for “de Foy et al. (2009)”.

We have changed “during dry season” to “during the dry season” in Section 3.1.

We have changed “observation for nitrate” to “observations for nitrate” in Section 3.1.

(7) 3.2 aerosol optical properties

“due to the cloud impacts” change to “due to cloudiness” “averaged in the model domain” change to “averaged over the modeling domain” “the model reasonably reproduces” change to “the model reproduces reasonably well” “in spite” change to “in spite”

We have changed “due to the cloud impacts” to “due to cloudiness” in Section 3.2.

We have changed “averaged in the model domain” to “averaged over the model domain” in Section 3.2.

We have changed “the model reasonably reproduces” to “the model reproduces reasonably well” in Section 3.2.

(8) 3.3 aerosol impacts on photolysis frequencies

In the discussion about the vertical profiles of photolysis frequencies, the experimental and modeling works of Balis et al. (2002b) and Hofzumahaus et al (2002) are to my opinion worth mentioning here.

We have added discussions in Section 3.3: *“Along the aircraft flight track, aerosols increase or decrease $J[O_3(^1D)]$ and $J[NO_2]$, dependent on the domination of UV scattering or UV absorption by aerosols. During the Photochemical Activity and*

Ultraviolet Radiation campaign, radiative transfer model calculations and airborne measurements have shown that the absorbing dust aerosols reduce actinic flux (280–420 nm) and photolysis rates (Balis et al., 2002; Hofzumahaus et al., 2002)."

(9) 4 conclusions

See in general comments above.

Please see the reply in (1).

(10) Reference (please change to References)

De Foy et al., 2008: This reference is duplicated. Lane et al., 2008: This reference is not mentioned in the text.

We have changed "Reference" to "References".

We have removed one of de Foy et al. (2008) and Lane et al. (2008).

(11) Figures

Figure 5: The numbering in the x-axis in both parts of the figure is by no means optimal.

For reading convenience, we have kept the numbering in the x-axis in both parts of Figure 5.