Atmos. Chem. Phys. Discuss., 7, S7111–S7124, 2007
www.atmos-chem-phys-discuss.net/7/S7111/2007/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Effects on surface atmospheric photo-oxidants over Greece during the total solar eclipse event of 29 March 2006" *by* P. Zanis et al.

P. Zanis et al.

Received and published: 22 November 2007

Reply to Reviewer #1

We would like to thank Reviewer #1 for the constructive and helpful comments. It follows our response point by point.

1) "Abstract. Suggest splitting up the sentence -At the relatively unpolluted — masked by transport-. I would like to see some more quantitative statements in the abstract. What are the expected uncertainties in the models which make the conclusions valid? What does -clearly revealed- mean; what is the quantitative measure here; perhaps in the form of a correlation or average model/meas ratio across the eclipse period for key species, and also the same ratio for the non-eclipsed period."

A few statements have been added in the abstract concerning the lifetime of ozone at the different sites as well as the correlation of global radiation with O3, NO and NO2 to support our findings. Concerning the uncertainties in the model and a quantitative measure of these we calculated the mean bias between modelled and observed values from the formula (1/N) ∑(modi-obsi) for the time window 9:30 -12:00 UTC. The results are shown in Table 1 and they are discussed in Section 3.3.

2) "Introduction. There is a description of expected changes during an eclipse, and HOx budget modifications are mentioned, and also a discussion of papers from the August 1999 eclipse. However, there is a previous publication (Abram et al., GRL, 2000) which describes field measurements of OH radicals, together with J(O1D) and ozone, during an eclipse in 1999, together with a discussion of how the fast photochemical cycles are perturbed. For some reason this reference is not mentioned at all, which I found surprising. Its major points should be included in this paper."

We thank the reviewer for pointing out this omission. We now refer to the work by Abram et al. 2000. The major findings of the Abram et al., paper have been added in the introduction (Page 4, lines 22-28) as well as in Section 3.2 (Page 12, lines 25-27).

3) "Data and methods. Although these are mentioned in stages during the paper, I would have found a clear statement saying that the % obscuration of the sun is for each of the 4 sites. -contacted- measurements cannot be right The uncertainty in the field measurements of O3, NO and NO2 should be listed. Also, although more difficult to estimate, the uncertainty in the model predictions for these species should also be given."

The maximum sun obscuration for each site have been added in Table 1 while a statement for the average sun obscuration in the time window 10:30-11:00 UTC was added in Section 3.1 (page 11, lines 21-23). Contacted has been changed to conducted. Statements for the uncertainties and detection limits of the measurements O3, NO2 and NO have been added in Section 2.1 (page 5, lines 21-24 and page 7, lines 4-5).

ACPD

7, S7111–S7124, 2007

Interactive Comment

4) "The box model, although containing a condensed mechanism, has a significant number of reactions and includes up to C5 chemistry, with isoprene. How has the condensed model been validated; by comparison with (presumably) a much large model? Field measurements are mentioned for O3, NO, NO2, radiation and some other parameters, but it is not clear how the VOCS are used in the model , these will impact on the calculated OH shown in Figure 2(b)."

The condensed chemistry scheme of the box model has been evaluated for its ability to compute oxidant fields by comparison to a detailed chemistry scheme for C1-C5 chemistry as shown in Poisson et al. (2001) as well as to several field observations under different conditions in the boundary layer (Poisson et al., 2001; Sciare et al., 2000; Tsigaridis and Kanakidou, 2002; Vrekoussis et al., 2004; 2006). Ethene, propene, ethane, propane and butanes diurnal mean mixing ratios, measured at Finokalia, Crete, in 2004 (Liakakou, 2007), are adopted in the model as initial conditions for all stations due to the absence of VOC data for the other locations. Formaldehyde (HCHO) mixing ratios have been initialised to 1 ppbv (Lelieveld et al., 2002). This model version has been previously applied to evaluate on a seasonal basis the impact of isoprene chemistry on the oxidizing capacity of the area (Liakakou et al., 2007). Additions have been made in Section 2.2 (page 7, lines 26-30 and page 8, lines 1-7).

5)"The regional air quality model has been -modified accordingly to reproduce the event of eclipse-. Although details of this are in a sister publication in this issue, it would seem crucial to give the main points here. Otherwise the statement suggests some tuning of the model to reproduce the current results has been done! Also the CB-4 mechanism is used for this model, and a note about the validation of this mechanism compared with more detailed mechanisms for the conditions encountered in this study would give confidence on the output. Can an uncertainty be assigned to its predictions? How is the vertical cloud attenuation factor calculated separately for above and within/below clouds? How are details of the cloud coverage known (satellites?). This should be explained."

ACPD
7, S7111–S7124, 2007

EGU

Statements to clarify these points of the reviewer have been added in Section 2.3 (page 9, lines 26-31 and page 10 lines 1-15). The cloud fraction is introduced into the CAMX model by the input of WRF meteorological fields

6) "Results. It is very difficult to see ozone and NO in the plots (e.g. Fig 1). Suggest blowing up the vertical axis so this is easier to see, otherwise one has to believe the text that there is significant change in these concentrations for the various case studies."

New Figure 1 was done.

7) "Page 11408, last 5-10 lines. There is a seemingly contradictory statement. First no major changes during the eclipse in O3 (and other species) are stated in the text, then it is stated that a decline of ozone of 9 ppb was observed?? This needs to be resolved as otherwise the conclusions on the paper seen confused. The paper states that the changes in O3 for some sites are masked by transport effects. Can this made more specific. Transport from local pollution sources which depend on local wind direction, or changes in air masses over a wider region? Entrainment/ deposition which can vary from day to day due to changes in wind speed etc."

The reviewer is right that the statement of ozone decline of 9 ppbv is rather confusing and may lead to misinterpretations. We removed this statement. Concerning that transport effects may mask eclipse effects we calculated the ozone lifetime at the four sites. It become that at the unpolluted sites the lifetime of ozone is a few days and hence it is sensible to anticipate that in this timescale local to regional scale transport effects may mask the eclipse effects. Furthermore comparing the simulated from CAMx eclipse effect on ozone (less than 1 ppbv) with the short-term observed ozone variability (a few ppbv) it is easily conceived why a clear evidence of the solar eclipse on O3 cannot be supported by the observations at both Kastelorizo and Finokalia.

8)"Page 11409. Line 7, it is stated that NO2 at Thessaloniki change during the eclipse (Fig 1d). It is very hard to see this from the current plot, and more vertical resolution on the plot is needed. Likewise for the NO and O3 which can be quite near the bottom

ACPD

7, S7111–S7124, 2007

of the plot (very near for NO)."

New Figure 1 was done.

9) "3.2. Box model results. OH is calculated and seen to decrease markedly during the eclipse. The Abram ref can be used to show that this is observed experimentally. The increase in NO3 is interesting for the clean site, where NO levels are low in order that NO3 levels can be sustained. How does the chemical processing ability of 4 pptv of NO3 compare with the OH levels that are removed during the eclipse. Such a comparison would enable the net effect of less OH and more NO3 on the production of secondary VOCs during the eclipse to be estimated."

See our reply to point 2. We added a few statements for the work by Abram et al. 2000. For the other point we compared the loss rates of DMS and isoprene due to reaction with OH and NO3 respectively. According to our box model simulations for Kastelorizo, during day, outside the eclipse period, OH radicals are 40 times and almost 3 orders of magnitude more effective than NO3 radicals in oxidizing DMS and isoprene, respectively. During the eclipse this pattern is reversed and NO3 radicals are the most efficient oxidant being 70 times and 4 orders of magnitude more efficient than OH in oxidizing DMS and isoprene respectively. The related statements have been added in Section 3.2 (page 13, lines 12-16).

10) "Page 11411, good level of agreement is noted for J(NO2) between model (Fig 4a) and observed (Fig 2a); this would be easier to see if plotted together. One the averaging periods used in the analysis is the -time window of maximum total solar obscuration (10:30-11:00)-. I think it would be useful to state what the average reduction in light levels is during this period compared with the non-eclipse event. Clearly at the actually point of maximum eclipse, the obscuration will be much higher than during the 30 minute period."

A new Figure 4 was done in which observed J(NO2) values for Finokalia were plotted together with the modeled values as suggested by the reviewer.

ACPD

7, S7111–S7124, 2007

11) "A conclusion is that at the unpolluted sites the eclipse events observed are masked by transport effects. Some further discussion of this is needed as it is rather vague as presented, and is one of the main results. What is the lifetime of O3, NO, NO2 during the eclipse? NO2 lifetime will get longer as the eclipse progresses, what sort of transport event has a lifetime that is then similar to this. What sort of lifetime for a species is required before one would be expected to see the effect of the eclipse at the unpolluted site? What is the ozone variability above which the effect of the solar eclipse cannot be observed? What is the level of NO required, that destruction of O3 from O3+NO can be observed above the O3 variability from day to day? Clearly it is not high enough at two of the sites, but plenty high enough at the 2 polluted sites to see the change in O3 induced by the eclipse."

We added a discussion especially for the ozone lifetime as calculated from CAMx at the four sites with and without eclipse. The role of the O3+NO reaction is also discussed for the lifetime. The lifetime of any chemical species in equilibrium can be defined by the concentration of this chemical species divided with its destruction or production rate. In the background atmosphere the ozone gas phase destruction rate is basically determined from fractional ozone photolysis in reactions (R4) and (R5) as well as reactions of ozone with HOx (HO2+OH) radicals in reactions (R8) and (R9). The chemical process analysis in CAMx calculates the ozone destruction rate due to the above mentioned processes and other ozone destruction pathways including ozone titration by NO and ozone reaction with alkenes. We calculated the ozone lifetime based on CAMx simulated fields for the four sites for both the eclipse and non-eclipse conditions. For the two relatively unpolluted sites, Kastelorizo and Finokalia, the ozone lifetime is about 2.7 days for non-eclipse conditions and becomes around 6.5 days for eclipse conditions. The first point to be mentioned is that for such ozone lifetimes it is sensible that we do not clearly see and abrupt and major signal of solar eclipse on surface O3 as in this timescale local to regional scale transport effects may mask the eclipse effects. The second point to be noted is that the ozone lifetime increases as we move from non-eclipse to eclipse conditions which can be explained by the fact that in the rela-

ACPD

7, S7111–S7124, 2007

tively unpolluted atmosphere (far from high NOx emission areas) the ozone loss terms are reduced during the eclipse as both HOx and JO1D levels are reduced. For the polluted sites, Thessaloniki and Pallini, the ozone lifetimes are much smaller being 1.3 hours and 3 hours for eclipse conditions and 1.9 hours and 7.8 hours for non-eclipse conditions, respectively, which can be explained by the fact that in high NOx emission areas there is rapid ozone destruction by NO-titration dominating over the other ozone loss terms (CAMx version 4.40, 2006). In contrast to the relatively unpolluted sites, at the two polluted sites we note that the ozone lifetime decreases as we move from non-eclipse to eclipse conditions. This can be attributed to fact that ozone during the eclipse continues to be removed by its reaction with NO (R3) without being efficiently reproduced by NO2 photolysis in reaction (R1). This discussion was added in Section 3.3 (page 17, lines 7-31 and page 18, lines 1-3).

12) "Aegean -See-" Corrected

13) "Table 1. Can the % obscuration of the sun at max eclipse be stated also in the Table."

Done as suggested by the reviewer.

14) "Table 2. The number of significant figures changes in the table, should these be consistent?"

Done.

15) "Figure 1. The NO is so close to the y=0 axis that it is impossible to really see how [NO]is changing. Suggest that this is blown up considerable in the y direction. Likewise for NO2 for (b), (c) and (d). It is also hard to see O3 clearly. Is it possible to see the days either side of the eclipse, to see what NO, NO2 and O3 behaviour (observed) is like on these days?"

New Figure 1 was done. Unfortunately, for Kastelorizo (the site with 100% sun obscuration) there are no data available the day before and the day after the eclipse. Hence

ACPD
7, S7111–S7124, 2007

EGU

we thought for consistency reasons among the four sites of the study not to show three days of data.

16) "Fig 2 , the OH profile is very similar to that measured in Abram et al (GRL, 2000)."

This has been commented in Section 3.2 (Page 12, lines 25-27).

17) "Fig 3 , for Finokalia, why not put the measured J(NO2) on the plot also? It would be interesting to see if the small dip before the eclipse is reproduced."

A new Figure 4 was done in which observed J(NO2) values for Finokalia were plotted together with the modeled values as suggested by the reviewer.

18) "Fig 4. The 4 dots are not that clear (white dot better?)"

Done.

19) "Fig 5. The panels are pretty small, make bigger."

Done.

Reply to Reviewer #2

We would like to thank Reviewer #2 for the constructive and helpful comments. It follows our response point by point.

1) "The presentation of the measurements could be made clearer. In figure 1 the chosen scale makes it difficult for the reader to see any change in ozone at any of the sites. The scale for ozone should be changed to something more appropriate. I would also suggest changing the figure to also show data from the day before and day after the eclipse (such as is plotted for the photochemical model results), with a second part showing the zoomed-in eclipse period."

New Figure 1 was done. Unfortunately, for Kastelorizo (the site with 100% sun obscuration) there are no data available the day before and the day after the eclipse. Hence we thought for consistency reasons among the four sites of the study not to show three

ACPD

7, S7111–S7124, 2007

days of data.

2) "In the description of the measurements at the Finokalia unpolluted site, a statement is made saying there is no drastic change in O3,NO2 and NO due to the solar eclipse, then the next sentence describes a 9ppb decline in ozone that can be partially associated with the eclipse. These statements would appear to contradict each other."

The reviewer is right that the statement of ozone decline of 9 ppbv is rather confusing and may lead to misinterpretations. We removed this statement.

3) "A correlation between O3, NO2 and NO with radiation during the eclipse period for all of the sites would give a more rigorous analysis of how the sudden change in radiation is affecting concentrations."

As suggested by the reviewer such an analysis has been carried out and it is discussed now in the revised manuscript. Furthermore a new Table 2 with the correlations between O3, NO2 and NO with radiation during the eclipse period for all of the sites was introduced. Specifically, at the polluted sites we note a positive correlation of O3 and NO with GR and a negative correlation of NO2 with GR. This can be attributed to the fact that during the evolution of the solar eclipse the decrease of solar radiation is associated with a decrease in O3 and NO and an increase in NO2 in accordance with theoretical expectations from the perturbation of the photostationary state of O3, NO and NO2. The only exception is the lack of correlation between NO2 and GR at Thessaloniki. In contrast at the two relatively unpolluted sites we note a negative correlation of O3 with GR which means that the decrease of solar radiation during the eclipse is surprisingly associated with an increase in O3. Furthermore we note a lack of statistical significant correlation (at the 95% confidence level) of NO and NO2 with GR. These results do not corroborate with our expectations from the perturbation of photostationary state of O3, NO and NO2 during the eclipse and point to longer lifetimes of these species and local to regional transport effects masking the eclipse effects. This discussion has been added in Section 3.1 (page 11, lines 29-31 and page 12, lines

ACPD

7, S7111–S7124, 2007

1-15), and in Section 4 (page 20, lines 6-13).

4) "Table 3 shows how O3, NO2 and NO change between eclipse and non-eclipse periods by using time periods before and after the event. The authors should also consider looking at average data for the identical time periods to the eclipse on other, non-eclipse days."

Unfortunately, for Kastelorizo (the site with 100% sun obscuration) there are no data available the day before and the day after the eclipse. There are only measurements specifically carried out there for the eclipse day only. Hence we thought for consistency reasons among the four sites of the study not presenting such a comparison.

5) "The section presenting the box modelling results could be expanded to describe the box model results from all 4 sites. It is stated that the simulations have been performed so it would be interesting to see how the ozone production budget is affected at the 2 polluted sites as well as the rural sites described in the paper. This could also be shown in figure 2 which currently only shows results from one site."

Instead of expanding Figure 2 we introduced a new Table (Table 3) which shows the concentrations of NO3, HO2 and OH for eclipse and non-eclipse conditions in box model simulations at the time of maximum solar obscuration for all four sites. Specifically during the eclipse maximum, OH radicals decrease by about 99% at Kastelorizo and Finokalia, 94% at Pallini, and 98% at Thessaloniki while HO2 radicals decrease by about 91% at Kastelorizo and Finokalia, by 58% at Pallini and by 69% at Thessaloniki. Finally the NO3 radicals increase at the time of maximum solar obscuration by 3.8 pptv at Kastelorizo, 0.8 pptv at Finokalia, 0.6 pptv at Pallini and 2.5 pptv at Thessaloniki. At Table 3 we also note that HOx (HO2+OH) levels are lower at the polluted sites than at the relatively unpolluted sites as HOx levels are suppressed at high NOx conditions. These comments have been added in Section 3.2 (page 13, lines 1-11). Furthermore in Table 5 we added box model calculations of net ozone productions for the two polluted sites as well and there is new discussion of Table 5 in Section 3.3 (page 18, lines

ACPD
7, S7111–S7124, 2007

EGU

12-31).

6) "OH radicals are calculated by the model and for the Finolkalia rural site show the expected result with concentrations dropping rapidly. Reference should be made to the paper Abram et al. (Hydroxyl radical and ozone measurements in England during the solar eclipse of 11 August 1999; GRL, vol 27, page 3437), which presented measurements of OH and ozone during a near total eclipse at a semi polluted site near London, UK. "

We thank the reviewer for pointing out this omission. We now refer to the work by Abram et al. 2000. The major findings of the Abram et al., paper have been added in the introduction (Page 4, lines 22-28) as well as in Section 3.2 (Page 12, lines 25-27).

7) "When looking at the O3 loss term (QO3) was the reaction of O3 with NO included? I would guess that even at the relatively rural sites this would be a significant factor in the O3 loss and certainly would be for the polluted sites."

In the background atmosphere the ozone gas phase destruction rate is basically determined from fractional ozone photolysis in reactions (R4) and (R5) as well as reactions of ozone with HOx (HO2+OH) radicals in reactions (R8) and (R9). The chemical process analysis in CAMx calculates the ozone destruction rate due to the above mentioned processes and other ozone destruction pathways including ozone titration by NO and ozone reaction with alkenes. We added a discussion especially for the ozone lifetime as calculated from CAMx at the four sites with and without eclipse. The role of the O3+NO reaction is also discussed for the lifetime. This discussion was added in Section 3.3 (page 17, lines 9-31 and page 18, lines 1-3).

8) "My other concern with this section is the input parameters for the model. In the experimental details section the model is described as taking into account the oxidation chemistry of C1-C5 hydrocarbons including isoprene but no mention is made of how these species are constrained in this study. Presumably, the amount of hydrocarbons present (especially fast reacting species like isoprene) will have an effect on the be-

ACPD
7, S7111–S7124, 2007

EGU

haviour of ozone during the changes in photolysis rate. If not this should at least be stated."

The condensed chemistry scheme of the box model has been evaluated for its ability to compute oxidant fields by comparison to a detailed chemistry scheme for C1-C5 chemistry as shown in Poisson et al. (2001) as well as to several field observations under different conditions in the boundary layer (Poisson et al., 2001; Sciare et al., 2000; Tsigaridis and Kanakidou, 2002; Vrekoussis et al., 2004; 2006). Ethene, propene, ethane, propane and butanes diurnal mean mixing ratios, measured at Finokalia, Crete, in 2004 (Liakakou, 2007), are adopted in the model as initial conditions for all stations due to the absence of VOC data for the other locations. Formaldehyde (HCHO) mixing ratios have been initialised to 1 ppbv (Lelieveld et al., 2002). This model version has been previously applied to evaluate on a seasonal basis the impact of isoprene chemistry on the oxidizing capacity of the area (Liakakou et al., 2007). Additions have been made in Section 2.2 (page 7, lines 26-30 and page 8, lines 1-7).

9) "In the description of measurements (section 2.1) it would be useful to have information about the accuracy of the measurements. Later on in the paper, NOx data is described as having dropped to below the instrument detection limit but there is no information as to what this is."

Statements for the uncertainties and detection limits of the measurements O3, NO2 and NO have been added in Section 2.1 (page 5, lines 21-24 and page 7, lines 4-5).

10) "P11404 line 24: should read have been carried out" Done.

11) "P11403 line 21: a better term would be nitrogen oxides (NO and NO2); as is used later in the paper"

Done.

12) "Section 2.3: Is there a reference where the CAMx model is described in more detail?"

ACPD

7, S7111–S7124, 2007

The most details about CAMx can be found in the CAMx manual which is cited.

13) "P11409 line 27: Fig 2a cited twice"

Corrected.

14) "P11410 line 2: should read are increasing"

Corrected.

15) "P11410 line 6: should be sudden not sadden"

Corrected.

16) "P11414 line 6: should be Sea not See"

Corrected.

17) "P11414 line 16: remove with"

Done.

18) "Tables 1 and 2 could be combined so the reader can more easily see the difference between observed and modelled species."

Tables 1 and 2 have been combined in table 1 as suggested by the reviewer.

19) "Table 4: Only contains data for 2 sites - the caption and text indicate that data from all four sites are shown"

We added data for all 4 sites.

20) "Figure 4: I am not sure this figure is necessary. If it is kept, then the measurement of JNO2 from Finokalia could be included to show the level of agreement."

A new Figure 4 was done in which observed J(NO2) values for Finokalia were plotted together with the modeled values as suggested by the reviewer.

21) "Figure 6: It may be useful to add a 4th panel showing the non eclipse NOx con-

ACPD

7, S7111–S7124, 2007

centration to allow the reader to see where the areas of high pollution are and thus compare with the changes in O3, NO and NO2 during the eclipse."

A new Figure 6 was done in which we added a 4th panel showing the non eclipse NOx concentration as suggested by the reviewer.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 11399, 2007.