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Comment

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.

Anonymous Referee #1

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General Comments

A solar eclipse is a rare phenomenon, in which the ambient radiation decreases to zero, or is significantly depleted, for a fairly short period, and is decoupled from many of the meteorological changes that are associated with sunrise and sunset. Hence it represents a unique opportunity to study rapid changes in photochemical pathways that are largely controlled by sunlight, and allows the chemistry to be studied under fairly constant meteorological conditions. In this paper, events surrounding a solar eclipse in Greece in 2006 are described. Measurements of O₃, NO and NO₂ were measured at 4 sites, one almost in the path of totality, the other 3 are varying distances

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from this region. The measurements are compared with the results of a chemical box model, which contains a reasonably detailed description of the chemistry, and also with the predictions of a regional air quality model, which has a much simpler chemical scheme. The paper focuses on the observations themselves, and also the level of agreement with the 2 models for the various sites, and consider both eclipse events and non-eclipse days either side. Two of the sites are described as clean and unpolluted, whereas 2 are polluted sites. An eclipse event is quite rare, and these measurements and model comparisons provide some insight into how key processes differ during an eclipse event. Although very interesting, the advances in understanding from this study are limited, and the manuscript is confusing in several places. For example there are apparently contradictory statements about whether there is a real effect on O₃ during the eclipse for the unpolluted sites. Some more quantitative measure is needed for comparison of the observations and model results for eclipse/non-eclipse days to quantify the difference in air quality during an eclipse. Also, a key earlier reference has been omitted. However, subject to a revision addressing the points below, I would like to see this paper published in ACP.

Specific comments

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.

Introduction. There is a description of expected changes during an eclipse, and HO_x 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

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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.

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 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 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.

Results. It is very difficult to see ozone and NO in the plots (e.g. Fig 1). Suggest

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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.

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 seem confused.

The paper states that the changes in O₃ for some sites are masked by transport effects. Can this be 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.?

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 of the plot (very near for NO).

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.

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 of 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 aver-

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age 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 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.

Aegean -See-

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

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

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's 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?

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

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.

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

Fig 5. The panels are pretty small, make bigger.

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