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Atmospheric Chemistry and Physics Discussions

Interactive comment on "OH in the coastal boundary layer of Crete during MINOS: Measurements and relationship with ozone photolysis" *by* H. Berresheim et al.

Anonymous Referee #1

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I enjoyed this paper very much. It is quite a novel paper. Although there have been several campaigns in which OH has been measured and compared to the calculations of zero-dimensional models Ű this paper does something different. The relationship between OH and J(O1D) is analysed for 3 different periods during the MINOS campaign, and an empirical fit made to the data, of the form OH = a J(O1D) ** b. The parameter a depends upon the local levels of sources and sinks (e.g. CO), whereas the b parameter is constant (0.68) throughout the campaign. The parameter reflects the dependence of [OH] on J(O1D) itself, and also on other J values, that themselves have a dependence upon J(O1D) of the form J = J(O1D) ** c. The data are fit very well by this expression, and it is shown that almost all of the variability in OH can be explained by the variation in J(O1D) (and some experimental precision).

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The best fit for OH is then compared to the diurnal profile for the 3 periods, the best fit is close to the measured OH concentrations. The authors then try to understand the empirical relationship that fits OH well. A simple CO-CH4 model is used, that shows a similar expression a [OH](model) J(O1D) **b. However, there are some significant deviations from this on some days.

This paper is part of a series of papers from the MINOS campaign. Thus it does contain some details that are covered elsewhere. Certainly it would be interesting to see how the more detailed model compares to the OH measurements. Although this is discussed in detail in other papers, some summary of this would be worthwhile in this paper.

Looking at the entire dataset and fitting it to an empirical form in this manner has not in general been done before, and is an interesting exercise that could be well applied to other field campaigns. There is some discussion of a similar analysis applied to the POPCORN OH dataset. If the expression a [OH] = J(O1D) **b is generally found to fit data, and the values of a and b can be related to different types of environments (levels of NOx, NMHC etc.), then it may be possible to get a good estimate of OH fairly quickly without either measurements or detailed modelling. However, this does not mean that OH measurements or detailed modelling are not required!

The detection limit and the temporal resolution is very impressive, and as good as other instruments used for the measurement of OH.

Specific comments:

There is a new value of the rate coefficient for O(1D)+N2 quenching, see: A.R. Ravishankara, E.J. Dunlea„ M.A. Blitz, T.J. Dillon, D.E. Heard, M.J. Pilling, R.S. Strekowski, J.M. Nicovich and P.H Wine, ŞRedetermination of the rate coefficient for the reaction of O(1D) with N2, Geophys. Res. Lett., 29, 1745-1748 (2002). This may make a slight difference to the modelled value and of P(OH)

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Is R7, OH+HO2 really a dominant reaction Ű even in clean air?

There have been measurements of OH and HO2 made in Greece during the AEROBIC campaign in 1999. See :D. J. Creasey, D. E. Heard, J. D. Lee, ŞOH and HO2 measurements in a Forested region of north-Western GreeceŤ, Atm. Environ., 35, 4713-4724 (2001).

N. Carslaw, D.J. Creasey, D. Harrison, D.E. Heard, M.C. Hunter, P.J. Jacobs, M.E. Jenkin, J.D. Lee, A.C. Lewis, M.J. Pilling, S.M. Saunders and P.W. Seakins, ŞOH and HO2 radical chemistry in a forested region of north-western GreeceŤ, Atm. Environ., 35, 4725-4737 (2001).

These should perhaps be referenced in the context of the current study in the Greece/Eastern Mediterranean region, similar time of year.

DWD should be defined when first used in section 2.1.

Section 2.1. The correction factor of 0.82, what are the upper and lower ranges of this Ű 0.82 is presumably an average value. Does the value of the correction change as the levels of CO, O3 etc. change?

The 8% error in the UV photon flux and the flow velocity measurement for the calibration seems rather good Ű is this realistic

Section 3.1. It should read Şlowest local solar zenith angleŤ

The individual spikes of OH at 2.4 x 10E7 are some of the highest I have seen reported. Any comment on this?

J(O1D) was measured in Greece during AEROBIC using a filter radiometer (see references above). So it is not strictly true that the results of Balis et al (2002) were the first measurements in this region.

Does the summit station, being some metres higher than the OH sampling position, block the flow of air for one particular flow direction (off-shore winds)?

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Page 7. What was the percentage loss of OH by reaction with NMHC? Is the CO-CH4 only approach likely to be accurate? Even in fairly clean airflows, NMHC and o-VOCs can be significant for the budget of OH.

The absence of HCHO, HONO and H2O2 measurements is bound to cause some error in the model calculated OH, and in the parameterised relationship between OH and J(O1D). At Cape Grim, even in very clean air, H2O2 and HCHO are significant for the OH budget.

Only 1% of the total variance in OH remains unexplained. Wow, that is quite a result.

Page 9. Second paragraph, the section on the relationship between [OH]norm and [OH]cims etc. could be made clearer.

Although there is a full model comparison with the measurements presented in a separate paper, I think it would make the discussion in this paper better if the major conclusions from the full modelling study were reproduced here. In the conclusions, start of second paragraph, Şclose agreementŤ with these studies is stated, the average % difference between the MINOS model studies and the OH data should be given.

Acknowledgements Ű Şfor his excellent jobŤ should be reworded.

How constant is [H2O]? RH is given.

Fig 5 could be explained slightly better in the text

Fig 7, there are some quite big empirical model underpredictions, comment?

Interactive comment on Atmos. Chem. Phys. Discuss., 3, 1183, 2003.