

## ***Interactive comment on “Role of NO<sub>3</sub> radical in oxidation processes in the eastern Mediterranean troposphere during the MINOS campaign” by M. Vrekoussis et al.***

### **Anonymous Referee #1**

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#### General comments:

The paper presents nighttime data of the NO<sub>3</sub> radical concentration during the MINOS campaign in 2001 in Crete, Greece. The interpretation of the data concentrates on the analysis of the role of NO<sub>3</sub> for DMS oxidation and NO<sub>x</sub> to HNO<sub>3</sub> conversion in Crete. Simultaneous measurements of OH allow a comparison of the contribution of NO<sub>3</sub> and OH to the oxidation of DMS (missing in text, see below) and HNO<sub>3</sub> formation.

NO<sub>3</sub> chemistry is an important part of the diurnal oxidation cycle in anthropogenically influenced areas and the analysis aspects discussed in this paper are of interest and significance for the scientific community. Therefore I suggest publishing this paper after major revisions.

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My main critique on the paper is that it does not critically discuss the justification of its assumptions and the effect of uncertainties in our present view of nighttime chemistry and physics on the results. Here are some examples:

1. Homogeneous loss of  $\text{N}_2\text{O}_5$  with water vapor: The kinetic rate constants are highly uncertain. The IUPAC suggests using the relatively high values and second order term found by Wahner et al. 1996; 1998. However, the large uncertainty of the data (only one experiment found this values) is also pointed out in the IUPAC publications. JPL recommends a much smaller value of the rate constant for this reaction. I also could not find a temperature dependence of the rate constants and wonder where the function in Table 5 comes from? Dimitroulopoulou and Marsh, 1997 suggest a temp function of this reaction. The interpretation of field data in their publication is, however, somewhat questionable. I suggest including a more thorough discussion of the effect of the uncertainty of this reaction rate in the paper and not using a temperature dependence of the reaction rate constant.

2. Assumption of wellto mixed nocturnal boundary layer: The DOAS light path measured the average concentration of  $\text{NO}_3$  in the lowest 150 m of the atmosphere (the authors do not mention the altitude of the retroreflectors, from fig. 1 it seems near sea level). All other measurements were performed at 150 m asl. Is the assumption of a wellto mixed NBL justified in stable nights? Is it possible that the DMS concentration measured at the station is considerably lower than the DMS concentration near the retroreflectors? Is it possible that  $\text{NO}_3$  has a vertical profile with high levels at 150 m asl but very low levels near the sea level (because of higher DMS and aerosols)? If  $\text{NO}_3$  actually has a vertical profile (as for example measured by Friedeburg et al., 2002), is the interpretation of the paper still valid or is in reality  $\text{NO}_3$  in 150 m much higher than the measured values? I suggest discussing this point in the paper and possibly state the consequences of a  $\text{NO}_3$  profile.

3. You assume pseudo steady state for  $\text{NO}_3$ . I agree that  $\text{NO}_3$  probably is in chemical steady state. But why is it justified that  $\text{NO}_3$  or  $\text{N}_2\text{O}_5$  are not vertically or horizontally

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transported thus changing the steady state of NO<sub>3</sub>. For example, a temperature gradient can lead to a N<sub>2</sub>O<sub>5</sub> gradient and thus to N<sub>2</sub>O<sub>5</sub> vertical transport. Why can you exclude this? Please discuss this topic shortly!

4. The lower DMS levels at night are interpreted as indicator for NO<sub>3</sub> oxidation (or wind direction changes). However, there are other possibilities for this behavior, for example it may be possible that DMS emitted at the sea level does not reach 150 m asl in stable nights.

I also miss a section about the comparison of the role of NO<sub>3</sub> and OH for DMS oxidation.

The paper should be better organized with respect to your main results. Here an example: One result of the paper is that NO<sub>3</sub> in Crete is mostly removed by N<sub>2</sub>O<sub>5</sub> losses. This result was concluded by the modeling study at the end of the paper. But already earlier in the analysis, there are two indications for this result. You state on page 3143 that NO<sub>3</sub> is not correlated with PNO<sub>3</sub>. Consequently, NO<sub>2</sub> must be a source and a sink. This points to N<sub>2</sub>O<sub>5</sub> losses being important. The temperature dependence of the NO<sub>3</sub> lifetime is another indicator for N<sub>2</sub>O<sub>5</sub> loss dominance. This topic is discussed in detail in Geyer A. and U. Platt (2002), The temperature dependence of the NO<sub>3</sub> degradation frequency  $\bar{U}$  a new indicator for the contribution of NO<sub>3</sub> to VOC oxidation and NO<sub>x</sub> removal in the atmosphere, J. Geophys. Res., doi: 10.1029/2001JD001215. Maybe you should mention this paper in the text.

Specific comments:

Page 3136: Line 21: Change to: its concentration is in most situations negligible.

Page 3137 Line 1: high spatial variation? Can DOAS be used then? Line 2: why consequently? I miss discussion of NO<sub>3</sub>+NO reaction. According to your data you have ca. 0.2 ppb NO at day. This limits the lifetime of NO<sub>3</sub> to 10 s! I do not believe you can neglect this here.

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Page 3139 Altitude of retroreflectors is missing, DOAS averages over  $x$  to 150 m altitudes. Why can you assume that the scattered light is not changing if you refocus at the fiber? Figure 1: Is the bracket on the map indicating the light path too long? It seems like larger than 5 km.

Page 3140 Line 5: What are adjacent border spectral trends? Please explain to the reader Just a comment: generally I do not recommend to use only one NO<sub>3</sub> absorption band because the measurements are rather sensitive to interferences with lamp emission bands and H<sub>2</sub>O absorptions. Does your fit result in any negative NO<sub>3</sub> values? It is ok as long the absolute value is below the detection limit. Since you do not show negative values in Fig 3 and no data is shown during many periods at all, did you simply not plot data, which is negative? Please shortly comment on this topic (in particular why you have only few data points in many nights).

Page 3141 Line 1: You mention in Table 1 that the detection limit of NO<sub>3</sub> is 1.5 ppt? The detection limit for HNO<sub>3</sub> would be interesting here Table 1: HNO<sub>3</sub> is missing

Page 3142 Figure 5: When was sunrise? Why is NO<sub>3</sub> declining already before sunrise? Please discuss this question.

Page 3143 Line 12 to 16: This part is not clear to me: If NO<sub>3</sub> is not correlated with its production rate, N<sub>2</sub>O<sub>5</sub> loss is the dominant sink of the NO<sub>3</sub> to N<sub>2</sub>O<sub>5</sub> system. Line 20 to 27: This part is not clear to me: Change here and in Table 3 the term equilibrium  $K_{3eq}$  with a NO<sub>3</sub> to N<sub>2</sub>O<sub>5</sub> ratio of one. Equilibrium is also reached if NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> are different. State that  $K_{3eq}$  is extremely dependent on temperature (see your data in Table 3: factor 3 during MINOS). Your sentence that the temperature change of 9C does not affect NO<sub>3</sub> is wrong and must be changed!

Page 3144 Line 6: Your argument is unclear: Explain that at higher temperatures, the importance of N<sub>2</sub>O<sub>5</sub> as NO<sub>3</sub> reservoir decreases. Therefore N<sub>2</sub>O<sub>5</sub> sinks are less important NO<sub>3</sub> sinks at high temperatures (Geyer and Platt 2002) Table 4: Where does RN<sub>2</sub>O<sub>5</sub>H<sub>2</sub>O come from? From the function in Table 6? As already mentioned above,

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the temperature dependence of this reaction is completely unclear at the moment. You cannot simply use this function without detailed discussion of its uncertainty! I suggest using a temperature independent value of  $k_{N_2O_5+H_2O}$  and mention that the temperature dependence is unclear at the moment.

Page 3145 Caption of Figure 7: Define normalized in the text. Why do you not show the real DMS data?

Page 3146 You mention Heinz et al., 1996 as reason for the temperature dependence of the  $N_2O_5 + H_2O$  reaction. First, it is Heintz et al., 1996. Second: I could not find anything about a temperature dependence in this paper. Correct this error please!

Page 3147 Why does the model predict too high  $NO_3$  sinks at high temperatures? I would wish to have a little more discussion about this problem.

Technical comments:

The use of English could be improved in several parts of the paper, in particular the use of word the is not always correct.

Title: Change to: Role of the  $NO_3$  radical in oxidation processes in the eastern Mediterranean troposphere during the MINOS campaign

Page 3136: Line 16: Change to: The quality of the air and climate depends Line 19: Change to: are the OH radical, the  $NO_3$  radical, and ozone.

Page 3137 Line 21: Change to: dependent Line 22: Change to: Waengberg et al., 1997

Page 3142 Line 15: Change to: Heintz et al., 1996 Table 2: Change Rugen to: Ruegen  
Caption of Figure 4: Change to: of the  $NO_3$  concentration during OH radical data

Page 3143 Line 2: Change to: diagnostic tool Line 5: Change K1 to:  $k_{NO_2+O_3}$  as on page 3137 Line 17: Change to: and their impact Table 3: Change to: Rate constants for the reactions xy and the equilibrium constant

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Page 3144 Caption of Figure 6: Change to: (b) Time series of NO<sub>3</sub> and relative humidity

Page 3145 Line 6: Change to: NO<sub>x</sub> to NO<sub>y</sub> partitioning (The title of this paper has a typo)

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