

Interactive comment on “Role of NO₃ radical in oxidation processes in the eastern Mediterranean troposphere during the MINOS campaign” by M. Vrekoussis et al.

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First of all we would like to thank the referee for the thorough comments that helped improving the manuscript.

A. We agree with the referee's comment that the rate of N₂O₅ reaction with water vapor is highly uncertain. The temperature dependent relation we used for the calculations is given in the Geyer PhD thesis and is based - as stated in that thesis on the Dimitropoulou and Marsh, 1997 values. Following the referee's suggestions to include a more thorough discussion on the uncertainties of these rates, we performed the computations again using:

1- the IUPAC recommendations (no temperature dependent rates)

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$\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2 \text{HNO}_3$ $2.5\text{E}-22$ (reaction 5a)

$\text{N}_2\text{O}_5 + 2\text{H}_2\text{O} \rightarrow \text{HNO}_3 + \text{H}_2\text{O}$ $1.8\text{E}-39$ ($\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$) (reaction 5b)

2- the upper limit of the reaction rate $\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3$ (of $2\text{E}-21$) given by the JPL recommendations (evaluation 14- latest available) that is about an order of magnitude higher than that of the IUPAC recommended value for reaction (5a) and not lower as mentioned by the referee.

and 3- a rate constant by a factor of 4 lower than the upper limit recommended by JPL since this is suggested as a possible uncertainty factor for the rate of the reaction (5a).

On line with these simulations, in the revised version of the paper we have added the following discussion (in page 3138 of the ACPD version): "The rates of the above reactions remain rather uncertain since the temperature dependence of these rates is not satisfactorily documented (Dimitroulopoulou and Marsh, 1997). Thus, the Wahner et al. (1998) temperature independent estimates, which are recommended by Atkinson et al. (2002), are used in the present study. Note also that Sander et al. (2003; JPL recommendations) give a slightly higher upper limit of $2\text{E}-21$ for the first order reaction (5a). They also point out the large difficulty in distinguishing between the gas phase and the heterogeneous reactions of N_2O_5 with water and mention that the rate of (5a) could be 4 times lower, as has been measured by Sverdrup et al. (1987). This fourfold uncertainty is taken into account in the following discussion."

In addition in the revised version of the paper we disregard the temperature dependent rate, earlier used, and applied the IUPAC recommended values as a reference. However, no significant differences are calculated for the studied cases between the earlier results and those derived based on IUPAC recommended values. The earlier use of temperature depend reactions rates is providing NO_3 mixing ratios lower by on the average 0.2 pptv and at most 1.2 pptv that correspond to a 2.5% (average) and 10% (upper limit) underestimate of NO_3 compared to the IUPAC recommendation based results.

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On the other hand the JPL recommended value (upper limit) results to slightly higher NO₃ levels by less than 0.5 pptv compared to the temperature dependent scheme but by up to 0.5 pptv lower NO₃ levels than calculated with the IUPAC recommendations.

In the revised version although the results of these simulations are mentioned to allow discussion on the uncertainties, however for clarity reasons, since the concentrations of NO₃ calculated by the different simulations are very close to each other (max difference of 1.2 pptv and most of the time less than 0.5 pptv), the simulations based on IUPAC recommendations are only shown and used as the base case for the budget analysis.

To discuss these uncertainties we added the following text in section 4.5.1 "The sensitivity of the NO₃ calculated levels to the rates of the reactions 5a and 5b has been studied on the basis of the IUPAC (Atkinson et al., 2003) and of the upper and lower limit JPL (Sander et al. 2003) recommendations. It has been found that the reported uncertainty in these rates can lead to up to a 0.5 pptv of uncertainty in the NO₃ calculated levels. Larger uncertainty is expected to be linked with the temperature dependence of these rates (up to 1.2 pptv) that is unfortunately not sufficiently documented (Dimitroulopoulou and Marsh, 1997)."

All figures have been updated when appropriate although this update is not evident since the calculated differences are very small. Table 4 has been removed and the calculated lifetimes of N₂O₅ are now mentioned in the discussion.

B. The reflectors are located near the sea surface (about 10m asl) so the DOAS measurements correspond to average concentrations within the first 150 m asl (text added in section 2.1.

A stable night means low wind speed. A closer look at the meteorological data shows that such conditions were relatively rare during the experiment. During most of the campaign, the wind speed was higher than 5m/s resulting in a well mixed MBL with height reaching 1000-1500m (based on the radiosoundings performed every night at 3:00 LT at the Heraklion airport). Thus with only two exceptions (on the 13th and the

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21st of August) DMS is expected to be well mixed. It is therefore reasonable to co-investigate the observed NO₃ and DMS variations. This comment has been added in section 3.4.

Direct comparison with the work by Friedeburg et al. (2002) is not possible because the conditions of the two studies are not the same. Finokalia where our study has been conducted is a coastal area and is subject to rather strong winds in particular during the studied summertime period, prohibiting the establishment of very shallow BL near the ground. On the contrary, the work by Friedeburg et al. (2002) has been conducted in a city in the middle of the continent where the PBL is expected to present strong diurnal variability and thus vertical gradient of O₃ and NO_x is possible due to existence of point sources (case of NO_x) or sinks (case of O₃). Since Finokalia is a coastal site, we could expect that sea-salt aerosol levels will present a vertical gradient reflecting their source at the sea surface and their deposition onto the surface controlled by gravity since sea-salt are mainly on coarse particles. However, this is not expected to be the case for DMS since this gas emitted from sea surface has not important deposition onto the surfaces and can thus be mixed in the boundary layer as has been observed at other marine sites (Davis et al., 1999). Since DMS is expected to be well mixed within the boundary layer the comparison between DMS and this average NO₃ value is still valid. A discussion in that direction has been added in the manuscript in section 3.4.

C. We do not exclude that NO₃ or N₂O₅ are transported to/from the sampling site from/to areas with different air temperatures. Under the experimental conditions NO₃ and N₂O₅ interconvert very fast to reach equilibrium with levels that depend on temperature and the NO₂ concentrations. For the high temperatures occurring during the MINOS experiment and for the geometric mean NO₂ levels observed during the MINOS campaign, the turnover times of NO₃ and N₂O₅ for the reactions (4) and (-4) range from 1–1.5 min and from 6–27 s respectively (Table 3). With such short turnover times, an equilibrium is reached in less than 2 min. It is worth mentioning that at temperatures as high as those observed at Finokalia, NO₃ radical is longer lived than

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N₂O₅ and acts thus as the reservoir compound contrary to what is observed for colder areas where N₂O₅ is thermally more stable (in section 3.2).

D. The factors controlling the DMS behavior during night have been discussed above. A sentence is been also added in section 3.4: "On the basis of the observed average NO₃, OH and DMS levels, DMS nighttime oxidation by NO₃ is about 75% the daytime loss by OH radical. This is determined in further detail in Kanakidou et al. (2003 paper in preparation)." This information is also given in the abstract.

E. Discussion on the importance of N₂O₅ losses has been improved following also ref#2 comments: "No significant correlation was observed during the MINOS campaign indicating that the N₂O₅ sink is regulating the NO₃ levels (Martinez et al., 2000; Heintz et al., 1996). In addition, a good negative correlation has been observed between the calculated NO₃ lifetime and the NO₂ (NO₃ lifetime = -0.94 [NO₂]+4.42, r²=0.82) as in Heintz et al. (1996) indicating that NO₃ is mainly removed via transformation to N₂O₅ and subsequent loss of N₂O₅ by reactions with water vapour and heterogeneous reactions. This conclusion is also supported by the model simulations presented in section 3.5 and by the effect of temperature and relative humidity (RH) on NO₃ levels that are discussed in detail in the following paragraphs." (section 3.2)

Concerning the temperature dependence of the NO₃ lifetime, A sentence has been added in section 3.3 referring to Geyer and Platt (2002) work.

Addressing the specific comments: 1- Text has been added in page 2: "However, the DOAS measurements average over a few minutes of time and a few kilometres of distance (see section 2.1) and thus partially integrate the time and space variability of the radical."

2- NO+NO₃ reaction: In the introduction after the 5th paragraph we added: "In the presence of NO, NO₃ is rapidly converted to NO₂ via reaction (3). At 298 K and for NO concentration of about 0.3 ppbv, the reaction (3) is equivalent to the NO₃ loss via photo dissociation J₂ in mid latitudes at noon: NO + NO₃ -> 2 NO₂ (3)" A comment

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has been added also in section 3.5.2: "The loss of NO₃ by the reaction with NO is half that due to photolysis."

3- scattered light: "After each S spectrum measurement the light is refocused on the focal point using an optimisation procedure that is computer controlled. Since a S spectrum is taken before each individual measurement, several S spectra are used for an integrated 30-min averaged measurement."

4- retrieval of NO₃ levels: We do use both NO₃ absorption bands. The corresponding sentence has been rephrased to: "In this work both NO₃ absorption bands are used for the NO₃ evaluation procedure and the band (B2E'fX2A2') at 662 nm is used for the quantification." Additional explanations are now given in section 2.1: "Note that the few negative NO₃ values that have been calculated with this procedure have absolute values are always below the detection limit of the method. These values are depicted in Figure 3 that presents NO₃ observations by the DOAS instrument integrated approximately every 30 min during the whole campaign. The negative values are not taken into account for the interpretation and discussion of the results. Missing data were due to power breakdown or to drift of the focal point of the instrument during operation." and the few negative values have been now reported in Figure 3.

5- HNO₃ measurements were performed with the Nebulisation/reflux - IC technique and the detection limit was 20 pptv for 3-h sampling time (information added in Table 1).

6- Figure 5 has been redrawn. NO₃ declines after sunrise that occurred around 6:30 local time.

7- We have modified the discussion in page 3143 (lines 20-27) as suggested by the referee, the overall idea remains the same, i.e. linking the N₂O₅, NO₃ and NO₂ levels via the rates of NO₃ to N₂O₅ conversion and of N₂O₅ decomposition. We have also took into account relevant comment of ref#2: "Indeed, the rates of the NO₃ conversion to N₂O₅ (reaction 4) and of the thermal decomposition of N₂O₅ (reaction -4) as well as the equilibrium rate (k_4/k_{-4}) strongly depend on temperature as shown in Table 3. On

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the other hand, for the range of temperatures in Table 3 the production rate of NO₃ from the O₃ reaction with NO₂ presents 2.5-3.5 times smaller temperature dependence (the rate of reaction (1) is given in Table 4)."

8- the temperature change of 9C does affect NO₃. This was indeed wrong and has been corrected.

9- The sentence on the importance of N₂O₅ as NO₃ reservoir has been rephrased to "Thus, at high temperatures as those observed at Finokalia during the MINOS campaign, NO₃ is longer lived than N₂O₅ and consequently N₂O₅ is less effective as reservoir species for NO₃ contrary to what is expected at higher NO₂ levels and/or lower temperatures."

10- Normalized DMS is calculated by dividing the hourly DMS data with the daily average of DMS. This well known technique allows representing the diurnal variability of the compound eliminating its day-to-day variability. In the caption of figure 7 and in the text, we have added the definition: "(DMS concentrations divided by the corresponding diurnal mean DMS)" The whole DMS dataset is presented in Bardouki et al. 2003 (this issue). A comment has been added in the text.

11- "Only on the 13th of August, this pattern is inversed with a N₂O₅/NO₃ ratio of 1.52 i.e exceeding unit. During this particular day the site was influenced both by biomass burning as shown on the black carbon levels (Salisbury et al., 2003) and by subsidence of air masses with low RH." (section 3.3). "When neglecting the NO₃ values observed during the nights of 11 to 12 and 12 to 13 of August 2001 that are exceptionally high for the measuring period an overall good agreement between the model results and the observations is apparent. Note that during these days biomass burning activities have affected the site as indicated by the CO observed levels and relevant compounds (Salisbury et al., this issue). In addition, the very low RH observed on the 8th and the 13th of August linked to low aerosol surfaces (Bardouki et al., this issue, 2003a) indicates subsidence of air masses from higher altitudes. This transport mechanism

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can not be reproduced by the box model." (section 3.5)

12- all technical comments are taken into account in the revised version

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