

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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Here below we address only the comments of the referee that have not been already answered as part of our reply to referee #1 comments. Many of the major concerns of referee #2 have been addressed in that reply.

The overall presentation and discussion of the results has been improved following both referee"s comments that we found very helpful and we acknowledge them.

Figures have been improved and a new Figure (10a) has been added to support the discussion. Table 4 has been removed and the important information is now given in the text.

Table 2 does not aim to present all available literature NO₃ data. We have only pre-

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sented the marine boundary layer observations and one continental site for comparison purposes.

More references of HNO₃ formation by NO₃ radical have been added "Heintz et al. (1996), Mentel et al. (1996), Geyer and Platt (2002)" although we do not claim that the list is complete.

Information is now given on Harklion and Agios Nikolaos cities: "Heraklion (137000 inhabitants) and 25 km west of Agios Nikolaos (19000 inhabitants), the nearest big cities in the area. These cities do not have any noticeable influence on the site due to the prevailing north winds."

"S is a spectrum of the atmospheric background due to scattered light measured by mechanically shifting the focus of the collecting mirror about 1 cm away from the optical fibre." This sentence has been modified as suggested.

The text on the interpretation of the DOAS spectra has been rephrased to avoid confusion: "These reference spectra for H₂O and NO₂, were then fitted simultaneously with the NO₃ reference spectrum to derive the NO₃ radical signature using least-squares fitting routine that employs singular value decomposition."

Figure 5b has been corrected and additional comment has been added "Indeed, for the measured ranges of NO₂ and temperature, the equilibrium ratio N₂O₅/NO₃ ranges between 0.02 and below unity with average value of 0.34(+/-0.26). Only on the 13th of August, this pattern was inversed with a N₂O₅/NO₃ ratio of 1.52 i.e exceeding unit."

Following the referee's suggestion the Table 4 (of the ACPD version) has been removed and information has been added in the text: "The lifetime of N₂O₅ with respect to the gas phase reactions with water into HNO₃ is reduced by a factor of 2 (from 46 to 23 min) when relative humidity increases from 35 to 85%, which could partly explain the observed negative correlation of NO₃ with relative humidity (Figure 6c). However, a much faster removal of N₂O₅, probably by heterogeneous reactions, is needed to

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explain the calculated NO₃ lifetime of 1-6 min shown in Figure 5c."

The lifetime of NO₃ does not correlate better than its concentrations with relative humidity (RH). The correlation we are getting is: $\text{lifetime}(\text{NO}_3) = -0.02(\text{RH}) + 4.29$, $r^2 = 0.85$. Since the NO₃ concentrations are more accurate than the calculated NO₃ lifetime we decided to keep the figure 6c unchanged.

A detailed presentation on the factors controlling the behavior of DMS during the campaign has been presented in the companion paper (Bardouki et al., ACP, Minos issue). As mentioned in that work, the observed decrease of DMS during night was due to two factors: a) oxidation of DMS by NO₃ radical and b) land breeze occurrence during nighttime that resulted in a dilution of the oceanic DMS flux by 30%. A detailed modeling study of the diurnal variation of DMS will be presented in Kanakidou et al. (manuscript in preparation).

In the revised version, the sentence in question has been modified to: "During sunset DMS decreases by a factor of about 6 when NO₃ radicals build up. This DMS decrease is due to both DMS oxidation by NO₃ leading to HNO₃ and dilution by continental air resulting to about 30% lower DMS fluxes during night (Bardouki et al, this issue)." We wish to keep the discussion NO₃ oriented since this is the focus of the paper. This is reflected on the title of the section that is "Impact of DMS and other VOC on NO₃ oxidation". Thus we are interested on the impact of DMS on NO₃ and not of NO₃ on DMS oxidation that is discussed in detail in the Bardouki et al. ACP 2003 paper.

Since hourly mean data are used as input to the model, our simulations are not expected to provide reliable higher time resolution variability. We added a sentence in section 3.5.2 on this point. A figure (new figure 10a) has been added to support our statement on the choice of the 28 of July to 5 August for the analysis of the HNO₃ budget as requested by the referee.

According to the JPL recommendations, 0.1 is an upper limit for the uptake coefficient of N₂O₅: This is now mentioned in the Table.

References

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