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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Role of NO_3 radical in oxidation processes in the eastern Mediterranean troposphere during the MINOS campaign" *by* M. Vrekoussis et al.

Anonymous Referee #2

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The NO3 radical plays an important role for the oxidation capacity in polluted and semipolluted environments. As it is difficult to measure, only a limited amount of observations exist. The manuscript by Vrekoussis et al. presents such measurements taken during the MINOS campaign and discusses the role of NO3 for VOC oxidation and production of HNO3, comparing the results with previous studies. It therefore offers a substantial contribution to current knowledge.

However, the paper is difficult to read due to poor use of the English language. It is also quite chaotic in structure. Some statements are made in the text which are not supported by figures, on the other hand some tables provide information on every single step of a calculation when only the final result would be needed. Comparison with

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other studies should be done more systematically, and the model calculations need more discussion (see below). I therefore recommend publication of this manuscript after major revisions.

Detailed comments:

Page 3137: Replace kNO2O3 for kNO2+O3. J4 should be J2.

Page 3138: Contribution to HNO3 formation by the NO3 radical has been studied in many publications.

Page 3139: How big are Heraklion and Agios Nikolaos, and how much did they influence the site ? Replace the sentence decribing the scattered light spectra for "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".

Page 3140: Are the daytime spectra used as reference spectra also treated according to the equation "N=..." ? First it says that the daytime reference spectra are "fitted and subtracted Ě to derive the spectrum containing only NO3 radical data" (should be signature instead of data), then it says "in practice the reference spectra are for H2O and NO3 are fitted simultaneously". This is confusing. It is important that all references are fitted simultaneously, as otherwise the fitting procedure is likely to compensate absorption structures from one species for which no information is available to the fitting procedure, with the available structure from another species.

Page 3142: The text is misleading in that table 2 does not compile all available measurements. Correct "Heinz et al., 1998" with "Heintz et al., 1996". The OH maxima seem to occur at 12:30, not 13:30, according to Fig. 4. OH and NO3 are compared, but the mean and standard deviation are only given for OH and not for NO3.

Page 3143: How does the NO3 lifetime correlate with NO2 ? A negative correlation would point to loss through N2O5. Contrary to the text, temperature is expected to

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affect NO3 variability through the thermal equilibrium with N2O5, as explained in the text. What is probably not much affected is NO3 formation from O3 and NO2, but this should also not be just stated but quantitatively commented. Equilibrium between NO3 and N2O5 is reached in any case, as reaction 3 and -3 are fast, but not necessarily at equal concentrations of NO3 and N2O5. To make the point that there was more NO3 than N2O5, I suggest to calculate the equilibrium N2O5/NO3 for the measured ranges of NO2 and temperature, instead of giving all the other related but less useful information in table 3. NO2 seems to be higher than 0.4 ppb on average according to Fig. 5b.

Page 3144: "The high NO3 concentrations observed near 12 August 2001 point to elevated temperature as the main cause due to thermal dissociation of N2O5." Why ? Was the temperature especially high on this day ? A figure should be provided to support such statements. In any case, Fig. 6a provides more convincing evidence, as the whole dataset is used instead of a single night. The reaction rate for the homogeneous reaction of N2O5 and water is higher than that given in the JPL and IUPAC recommendations. Where does it come from ? References should be given for all rate constants used. Even if the homogeneous reaction is this fast, it is still an order of magnitude too slow to explain the lifetimes of 40-300 s given in Fig. 5c. Therefore the negative correlation with relative humidity cannot be explained by the homogeneous reaction alone, and heterogeneous reactions should be included in the quantitative discussion. Table 4 is superfluous, only the resulting range of N2O5 lifetimes should be given in the text. How does the NO3 lifetime correlate with RH and temperature ? If the correlations are due to loss mechanisms, a correlation of the NO3 lifetime would be more meaningful than a correlation of NO3, which could also be due to influences of RH and temperature on NO3 production.

Page 3145: What is "normalized DMS" in Fig 7, what are the units ? "During sunset DMS decreases ... when NO3 radicals build up, reflecting significant DMS night time oxidation by NO3 leading to HNO3 and possibly lower DMS fluxes during night due to

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dilution by continental air." So how much could dilution by continental air contribute ? Please discuss using wind data. It takes longer for DMS to decrease then for the sun to set. While DMS is of minor importance for the NO3 budget, NO3 is very important for the DMS budget. These two aspects are scrambled together in this section. The conclusion about what causes the DMS decrease should come last but is given first ("reflecting significant DMS night time oxidation by NO3"), the evidence is presented later by discussing the NO3 lifetime. The lifetime of DMS due to reaction with measured NO3 concentrations would be a better argument than the NO3 lifetime to reach this conclusion.

Page 3147: While the model NO3 compares well with the average levels of NO3, it does not seem to follow the variability in the data. I would therefore not speak of an "overall good agreement". As the model does not succeed in reproducing the NO3 variability but only the mean concentration level, this indicates to me that only the average total NO3 loss is similar in the model, whereas probably loss partitioning is often wrong in the model. Therefore I am not convinced that the model accurately represents the different HNO3 production mechanisms via NO3 and N2O5. The role of NO3 for HNO3 production is investigated using the model only for a 4-day time period out of the whole campaign (28 July to 1 August) because the agreement between measured and modeled sum of gaseous HNO3 and particulate NO3- is stated to be best for these days. No figure is provided to support this statement. Furthermore, the agreement between measured and modeled NO3 does not seem to be particularly good in this time period, according to Fig. 9.

Page 3175: According to the JPL recommendations, 0.1 is an upper limit for the uptake coefficient of N2O5.

Interactive comment on Atmos. Chem. Phys. Discuss., 3, 3135, 2003.