

Interactive comment on “Two-years of NO₃ radical observations in the boundary layer over the Eastern Mediterranean” by M. Vrekoussis et al.

Anonymous Referee #2

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Comments on the Manuscript entitled:

Two-years of NO₃ radical observations in the boundary layer over the Eastern Mediterranean“ by M. Vrekoussis et al.,

The manuscript describes the first extensive long-term study of NO₃ (plus related species) encompassing more than a full annual cycle in the Mediterranean area, in fact it is only the third study of its kind (after the studies reported by Heintz et al. 1996 and Geyer et al. 2001a). Given the insight potentially to be gained by long-term studies the authors have to be commended for their accomplishment. Looking at the manuscript in detail it appears that the study methodically closely follows the earlier work quoted above, unfortunately falling behind in depth and clarity. In particular the

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concept of the NO₃ - lifetime (or loss frequency) is not applied rigorously. For instance, the authors quote (in section 3.1) a positive correlation of NO₃ levels with both, NO₂ and O₃ levels with all three species showing higher values in summer. Now it would be interesting to know whether the lower NO₃ levels in winter are due to just lower production but also higher destruction (the latter appears to be the case at least for winter of 2001/2002). Here a plot of the NO₃ lifetime (or, alternatively, its 'destruction frequency') would give much additional insight. Moreover the plot in Fig. 7 resembles very closely the corresponding plot by Heintz et al. 1996. This should (1) be acknowledged in the manuscript, and - more importantly - (2) the idea behind this type of analysis and the results need better explanation. In addition the authors present two case studies (sections 3.1.1 and 3.1.2 and Figures 4 and 5). While these are interesting it remains completely unclear whether these are the only two cases of interest encountered during the 2 year period or whether similar events occurred frequently. Here more explanation and some statistical data would be needed. In fact section 3 does not appear to be well structured. Perhaps it might be better to structure it like: - Results and statistical analysis - Case studies - Mechanistic studies (encompassing sections 3.3 ff)

Overall I strongly recommend publication of the manuscript, but only after major revisions, as outlined above and below.

In detail there are many unclear points, which sometimes make the manuscript hard to read and understand, a number of these are given in the following:

- 1) Abstract: 'maximum mixing ratios in summer (5.6±1.2 pptv)' are quoted: this is misleading in that these figures actually refer to highest monthly means (maxima were higher than 100 ppt).
- 2) Abstract, line 10: 'Ë used to explain Ë' Statistical studies do not explain data, but rather suggest relationships.
- 3) Abstract, line 13: Ë 'dependent on NO₂ Ë' this again refers to a statistical relationship

not a determined causale dependence.

4) Abstract, last sentence: The statements made here (although probably true) are not substantiated in the manuscript.

5) Page 9518, last line: Explain 'mainly'

6) Page 9519, line 3: What is the meaning of 'detectable levels'? what would be expected daytime NO₃ levels?

7) Page 9519, line 4: the authors fail to mention the reaction of NO₃ + NO, which can actually be the dominant sink during daytime (sentence on Page 9520, lines 1, 2 should be moved to here).

8) Page 9519, line 9: NO₂ + NO₃ is largely a transient sink for NO₃ only.

9) Page 9519, line 17: Is there any proof that N₂O₅ reacts with water dimers?

10) page 9520, line 14: ' some alkenes and some aromatics '

11)Page 9521 (Location ') How where the 'proper reference spectra' obtained, 'sampling time' probably means 'integration time', what is the meaning of 'peridically' (line 23 on p. 9521)? The average detection limits are given with very small variation, is this realistic?

12) Page 9522, line 10: 'the 5 min mean meteorological ' probably refers to meteorological parameters averaged over 5 minute intervals (or measured at 5 minute intervals)?

13) Page 9522, line 19: does the variation of the average night-time NO₃ levels refer to the standard deviation or the variance (the latter would make more sense)?

14) Page 9522, lines 24ff: the fact that the night-time NO₃ peak levels are 40% different than found in other studies elsewhere does not appear to be significant due to the random nature of peak levels. Rather it appears remarkable, that the levels are so similar.

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15) Page 9523, line 3: the figures appear to refer to average mixing ratios. Also it would be interesting to know lifetimes. Line 9: How are cases with NO₂ below the detection limit treated?

16) Page 9527: Define parameters f.

17) Pages 9528 and 9529: NO₃ production appears to be given and used in different units: ppt per hour (p. 9528, line 13), molecules per cm³ and second (p. 9529, line 10) which units are used in R8?

18) Page 9530, section 3.4: More detailed information on the steady state NO₃ lifetime is needed. The conclusion on O₃ destruction by NO₃ photolysis (R2b) is probably wrong, since the effect of NO + NO₃ appears to be neglected.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 9517, 2006.

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