**Atmospheric
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Interactive comment on "Two-years of NO$_3$ radical observations in the boundary layer over the Eastern Mediterranean" by M. Vrekoussis et al.

Anonymous Referee #1

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General Comments:

This paper presents one of the few seasonal observations of nitrate radicals (NO3) available to date, and the only one in the Mediterranean. Three others have been done in northern Europe, two of which were at coastal locations (Rugen on the Baltic Sea (Heintz, 1996) and Weybourne on the North Sea (Allan, 1999)) and one of which was at a continental location near Berlin (Geyer, 2001). The location of this study is in area impacted alternately by relatively more polluted air masses from Europe and cleaner air masses from the Atlantic or north Africa. The long-term database (spanning June 2001 - September 2003) shows the dependence of the nocturnal chemistry of the nitrate radical on season and on air mass origin. The NO3 measurements are by long path DOAS. Additional measurements include NO2 by long path DOAS, O3 using an

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in-situ instrument, Rn gas as a tracer, and meteorological data.

The results and analysis show that the mixing ratio of NO3 is quite variable and that the mechanism by which it is lost has a seasonal dependence. Although monthly mean mixing ratios of NO3 are in the range 1-8 pptv, the peak values in summer frequently exceed 100 pptv. Analysis is done to show that the very large NO3 mixing ratios occur either as a result of transport at low level from polluted areas, or as the result of downward mixing of NO3 from aloft. The latter implies that mixing ratios of NO3 are generally lager aloft than in the boundary layer, a result consistent with several recent studies of vertical profiles of NO3. NO3 mixing ratios also show seasonality, being lower in winter than in summer. Analysis of the loss processes in different seasons is carried out by two methods. The first is the correlation of NO3 with its production rate, P(NO3). Such a correlation is expected if the "direct" loss of NO3 via reaction with VOC is important. This correlation is most evident in summer seasons. The other analysis method is the correlation of the logarithm of the NO3 lifetime with the logarithm of measured NO2 concentration. A correlation with a slope of -1 indicates that "indirect" NO3 loss is most important - i.e., formation of N2O5, followed by hydrolysis. This correlation is most evident in winter. These trends are generally consistent with measurements from other locations.

Specific Comments:

I have a few comments that would help to clarify the manuscript and that may correct several possible errors.

1. Page 9522, 22-25. Comparison is made to results from other locations, apparently to make the point that the observed maximum NO3 concentrations at the Finokalia site are large in comparison to other observations. However, the 100 pptv value of Brown et al. refers to an autumn measurement and is not directly comparable to the summertime maxima observed at Finokalia. Much larger NO3 mixing ratios, up to 300 pptv, have been observed at continental sites in California (e.g. Platt & Perner, Geophys. Res.

Lett, 7 89-92 (1980)).

2. Page 9526, section 3.2.1. A figure showing the correlations, rather than a list of correlation coefficients, between NO3 and O3, NO2, RH, temperature and wind speed, would make the argument clearer. Also, on line 5, the r^2 value of -0.18 does not make sense (i.e., the square of a number should not be negative). Are the values given actually R, rather than R^2? Also, it is not clear what "deseasonalized" ozone values mean in the context of this correlation. Again, a plot might make this clearer. Finally, why choose NO2 as a controlling factor for NO3 rather than O3 based on the argument that NO2 and O3 are themselves correlated?

3. Section 3.2.2: For equation R3, NO3 should probably be determined as a function of NO2 in pptv (rather than ppbv, so that the units on NO3 and NO2 are the same), and T in K (rather than C). The term "total variance" should be defined. Finally, the plots of NO3 against the variables in the equation (see above) would be useful to the reader.

4. Page 9527, section 3.3: An expression is given for P(NO3), but not for f(NO3). Presumably f(NO3) = P(NO3)/NO3, where f(NO3) is the sum of direct and indirect NO3 losses. This should be clarified in equations or text. Line 13, reference to equation (3) is really to (R5)? Some renumbering of equations and reactions appears to be needed. Similar error on page 9528, line 2, in the reference to equation (2), which appears to reference (R4)?

5. Page 9528, line 15: Was NO really 0.02 ppbv, 25 x smaller than NO2 (given as 0.5 ppbv). What time of day does this refer to, and how is the NO value arrived at (no reference given to actinic flux measurements or to NO measurements). Also, production rates for NO3 are given initially in pptv hr-1, then later in molecules cm-3 s-1. Consistent units should be used throughout.

6. Page 9529, lines 9-11. Not clear what the wording "further extracted per unit" means. Does this sentence mean that the data have been binned?

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7. Section 3.3.2: The discussion surrounding the data in Table 2 should be clarified, and possibly some figures should be added. First, it is difficult to interpret the quantitative meaning of the slopes of NO3 against P(NO3). It appears that the authors are making an argument primarily based on the correlation coefficients. In any case, plots of NO3 against P(NO3) should be given rather than just numbers in a table resulting from these plots. Second, the data that stand out in the table are spring time values only. Should not the direct sinks of NO3 also be readily apparent in summer? Can the authors make some comment about the biogenic VOC seasonality to corroborate the argument here that these correlations actually represent chemistry of NO3 in the atmosphere? Finally, summer and autumn are separated into two distinct populations based on the correlation between NO3 and P(NO3). Is there any justification for the separation other than the behavior of the data themselves? Do these distinct populations show any dependence on some other variable, such as predicted biogenic VOC abundance, relative humidity, wind direction, back trajectories, etc?

Similar comments apply to the second two columns in Table 2. Here, the slopes of ln[tNO3] vs ln[NO2] are often more negative than -1, which is the "ideal" slope for purely indirect loss of NO3 via. N2O5 hydrolysis. Is there any significance to this? Again, only the springtime data stand out in the analysis, whereas the largest contrast might be expected between summer and winter, which have similar slopes (-1.5 and -1.1, respectively). What is the significance of this?

8. Figure 7: The RH dependence of the slope of ln[t(NO3)] vs ln[NO2] is a nice indication of the increasing importance of N2O5 hydrolysis with increasing RH. A plot of this slope vs. RH would be helpful. The statement on page 9530, line 11, is not supported, however, because the seasonal dependence of RH is not shown in the figure. Quite independently of RH, one would expect N2O5 hydrolysis to be important in winter because colder temperature shift the equilibrium between NO3 and N2O5 toward N2O5, increasing the importance of N2O5 losses over those of NO3. In this context, some presentation of the seasonal variation of N2O5 calculated from these data would be

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useful.

9. Section 3.4: A few of the conclusions here are laid out too briefly to be really clear, although most of the points are valid. For example, daytime O3 loss by reaction 2b ought to have a chemical mechanism showing the individual reactions and the net O3 loss that results. Numbers should be given from the Gerasopoulos reference for the "calculated tropospheric ozone destruction in the area." The argument about VOC oxidation should be supported with numbers for OH radical concentrations and levels of DMS and monoterpenes.

Typographical error:

Page 9520, line 15, "thought" should probably read "though"

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

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