Atmospheric Chemistry and Physics Discussions

Interactive
Comment

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

M. Vrekoussis et al.

Received and published: 11 January 2007

We would thank the reviewer for the time he/she has spent on manuscript and for the pertinent comments that helped significantly improving the quality of the paper.

Reply to comment 1.- This part of the discussion has been modified: 'As shown in Table 1, the monthly or seasonally averaged NO3 observations compare fairly well with data reported earlier for various locations and similar time periods. However, the random peak levels of NO3 observed at Finokalia mainly during summer exceed by 40% earlier reported maximum NO3 values in the continental (100 pptv in autumn, Brown et al., 2003) and in the marine boundary layer, (98 pptv in spring, Heintz et al., 1996) and are significantly lower than those recorded by Platt et al. (1980) for the polluted continental area of Riverside, California (up to 300 pptv). Our values are lower than those reported by Sebastian (PhD Thesis, Univ. of Heidelberg, 2004) for Finokalia during July 2000,

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

EGU

period during which the area has been affected by exceptionally high biomass burning events.' These references have been added in Table 1.

Reply to comment 2.- We have added (new) Figures 6a-c that depict the scatter plots of NO3 versus the O3, temperature and relative humidity factors identified by the single and multiple regression analysis as the significant predictors for NO3 variability in the area. This allowed the detection of a typographic mistake during the application of the statistical software that changed our results by removing NO2 from the list of predictors for NO3 variability and maintaining O3 as a predictor. We are definitely grateful to the reviewer for giving us the opportunity to detect this mistake. We have also removed the word 'deseasonalized', corrected line 5 and rephrased the paragraph for clarity as follows:

'Linear regression analysis revealed significant correlations at the 99% confidence level between NO3 radicals and O3 (R=0.12, N=9844), temperature (R=0.23, N=9736), relative humidity (R=-0.19, negative correlation, N=9736) and wind speed (R=0.04, N=9736). No significant correlation was found between NO3 and NO2. The scatter plots of NO3 mixing ratios as function of O3, temperature and relative humidity are shown in Figures 6a-c. The averaged data (blue circles) for O3, temperature and RH with the corresponding NO3 averages do help the easier visualization of the existing relationships and fit well with the regression lines (red lines) drawn from the whole data set, obscured at first glance by the increased scattering of the values. A significant part of both O3 and temperature correlation with NO3 radicals is due to their common seasonality. This is supported by the fact that when the residuals of the ozone and temperature are used for the correlations with NO3 (residuals derived by subtraction of the annual cycle of the series simulated by fitting the sum of a sine and its first harmonic to the data), the correlation coefficients are lower and equal 0.08 and 0.17, respectively.'

Reply to comment 3. - The multiple regression analysis has been affected by the change in the single regression analysis above explained. We have now re-calculated the coefficients of equation R3 (equation 1 in the revised manuscript) with T in K, and

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

O3 in pptv. The paragraph has been modified as follows: 'The derived linear correlation that expresses the NO3 variability is: NO3 = (1.2+-0.4) 10ˆ-5 Ţ O3 + (0.18+-0.01) Ţ T + (-0.030+-0.003) Ţ RH + (-48+-3) [eq 1] where NO3 in pptv, O3 in pptv, T in K and RH in %, regression coefficients are accompanied by their respective standard errors. The Rˆ2 (0.072, N=8943) indicates that 7.2% of the variability of NO3 radicals can be explained by the above 3 variables. This explained variability is related by 60%, 30% and 10% to the T, the RH and the O3 variability respectively. The results of both single and multiple regression analyses show that the NO3 radicals are very sensitive to changes in temperature and in relative humidity and, to a lesser extent to O3 variations'

Reply to comment 4 - fNO3 has been clearly defined now by the equation 3 in section 3.3.2: [eq. 3] Equations have been renumbered as eq.# and have been separated from the reactions that are numbered as R#.

Reply to comment 5 - The NO value of 0.02 ppbv refers to early morning and later afternoon NO levels. We have changed this to the average daytime value of NO that varies around 0.05 ppbv during summer. This modification does not affect the remaining part of the discussion. In addition in section 2 (page 9522, line 7) we have added a sentence on NO measurements: 'Nitrogen monoxide is experimentally determined by a Thermo Environmental Model 42C high sensitivity chemiluminescence NOx analyzer equipped with a molybdenum converter that in addition to NO and NO2, allows detection of PAN, nitric acid, and organic nitrates.'

Reply to comment 6- We have replaced 'further extracted' by 'averaged'

Reply to comment 7- The idea behind the analysis of the slope of NO3 against P(NO3) is explained in the introduction of section 3.3 that has been further improved as suggested by the reviewers (see also comment 4). The added equations, eq. 3 (fNO3=fA+fB=P(NO3)/[NO3]) and eq. 6 (t(NO3)=1/(fA+[NO2].Keq.fB')), clearly show that the slope is the mean turnover time of NO3 considering both the direct and the

indirect losses of NO3. Significant correlation between NO3 and P(NO3) indicates that the turnover time is independent of NO2 levels and points to direct losses of NO3 as the dominant loss processes. This is now explained in the introduction of section 3.3.

In Table 2, spring values clearly indicate a direct sink for NO3 and that indirect losses are minor. However, when separating the seasonal data in two sub-sets then significant correlations between NO3 radicals and their production rate have been also determined for summer and to a lesser extend for autumn, most probably due to increased VOC concentrations from biogenic emissions, indicating dominance of direct NO3 losses (as stated in the revised manuscript).

We have looked for any justification for the separation of the two sub-sets for both the summer and the autumn data but we have failed in finding any other criteria than the behaviour of the data themselves. Unfortunately, there are no simultaneous measurements of biogenic VOC in the area that could help us clarify this point. We have enriched the discussion in section 3.3.2 based on non-simultaneous with NO3 biogenic VOC observations in the area: 'The above analysis is coherent with observations of biogenic organic compounds in the area that are reactive against NO3 radical. These observations indicate enhanced levels of isoprene during spring and summer (Liakakou et al., Atmospheric Environment 41(5),1002-1010, 2007) and of marine dimethylsulfide from spring to autumn (Kouvarakis and Mihalopoulos, Atmospheric Environment, 36, 929-938, 2002). However, lack of simultaneous measurements of NO3 radicals and biogenic organic compounds prohibits any deeper analysis of our data.'

In addition, uncertainties in the observations and data scatter prohibit a straight forward interpretation of the data. Thus, there is no significance for negative slopes with absolute values greater than 1 for the ln[t(NO3)]versus ln[NO2] correlation. Motivated by the wise comment of the reviewer, we have modified/added the following related text: 'In addition, for this subset the slope of ln[t(NO3)] versus ln[NO2] is significantly more negative than the respective of the subset one, thus, suggesting indirect sinks for the NO3 radicals. These slopes have to be viewed with caution since due to the

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

large variability of the observations the slopes are associated with high uncertainties that can generate absolute values higher than unity.' We have also added respective errors in the slopes given in Table 2.

Reply to comment 8 -As suggested by the reviewer, we have plotted the slope of ln[t(NO3)] vs ln[NO2] as a function of RH (new figure 9) although all information required for this is already available in the manuscript and the discussion has been modified as follows: 'Indeed the slope of of ln[t(NO3)] vs ln[NO2] exhibits a nice logarithmic relationship with R.H. (Figure 9; R2 =0.856, N=7) that further supports the existence of indirect sinks for NO3 that are strongly related to the presence of water vapour in the atmosphere. This clearly indicates the increasing importance of N2O5 hydrolysis with increasing RH and thus water vapour in the atmosphere.' N2O5 monthly mean levels calculated assuming steady-state conditions are shown in Figure 6 (now figure 7) together with the monthly mean variation of NO3 levels and the Keq. These calculations indicate that N2O5 maximizes in late spring and early summer. In the revised manuscript we have added discussion on this point in the section 3.3 when Figure 7 (earlier figure 6) is mentioned and adopted the comment of the reviewer: 'In winter when temperatures are low, keq (Figure 7a) is high, thus shifting the equilibrium towards N2O5 and increasing the importance of N2O5 losses over the direct losses of NO3. In addition, our wintertime observations indicate a very efficient loss of NO3 (fNO3: sum of direct and indirect losses; Figure 7b) that drastically suppresses the bulk NO3 and N2O5 pool levels and as will be discussed in section 3.3.2 is related to the indirect sink of NO3 radicals. Therefore, N2O5 monthly mean levels calculated assuming steady-state conditions (Figure 7a) present maxima in late spring and early summer.'

Reply to comment 9 - Discussion on O3 loss by reaction 2b has been removed. On the contrary, we have now extended the discussion on the interactions of VOC with NO3, mainly isoprene and dimethylsulfide (DMS) that have been measured in the area (Liakakou et al., 2007 and Kouvarakis and Mihalopoulos, 2002). For these two volatile

organic compounds of biogenic origin the degradation frequencies have been calculated based on the observed seasonally averaged NO3, O3 and temperature levels and the modelled OH for the area (Vrekoussis et al., 2006). The derived annual mean degradation frequencies for the area indicate that NO3 radicals are almost 6 times more efficient than OH radicals in destroying DMS. For isoprene degradation, OH radicals are almost 4 times more efficient than NO3 and 10 times more efficient than O3 that contributes by about 8% to the degradation frequency of isoprene on an annual basis. In turn, our model calculations (Vrekoussis et al., 2006; Liakakou et al., 2007) indicate that in the area in the marine boundary layer DMS and isoprene contribute by about 5% and 20%, respectively, to the annual mean NO3 degradation frequency.

Typographical error has been corrected.

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

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

EGU