

**Two-years of NO₃
radical observations**

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Two-years of NO₃ radical observations in the boundary layer over the Eastern Mediterranean

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Abstract

This is the first study that investigates the seasonal variability of nitrate (NO_3) radicals in the marine boundary layer over the East Mediterranean Sea. An extensive data set of NO_3 radical observations on the north coast of Crete for more than two years (June 2001–September 2003) is presented here. NO_3 radicals follow a distinct seasonal dependency with maximum mixing ratios in summer (5.6 ± 1.2 pptv) and minimum in winter (1.2 ± 1.2 pptv). Episodes with high NO_3 mixing ratios have been encountered mainly in polluted air masses originating from mainland Greece, Central and East Europe, and Turkey. Ancillary measurements of ozone, nitrogen dioxide (NO_2) and meteorological parameters have been conducted and used to explain the observed NO_3 variability. The acquired NO_2 nighttime observations provide the up-to-date most complete overview of NO_2 temporal variability in the area. The data show that the NO_3 nighttime mixing ratios are primarily dependent on NO_2 (positive correlation) and relative humidity (negative correlation) and to a lesser extent on temperature (positive correlation). As inferred from these observations, on average the major sink of NO_3 radicals in the area is the heterogeneous reaction of dinitrogen pentoxide (N_2O_5) on aqueous particles whereas the homogeneous gas phase reactions of NO_3 are most important during spring and summer. NO_3 chemistry in the area significantly contributes to VOC oxidation and to the nighttime formation of peroxy radicals, nitric acid and particulate nitrate.

1 Introduction

The self-cleaning efficiency of the troposphere is important for air quality, and depends on the oxidation and deposition of trace constituents. The most important oxidants in the atmosphere are the hydroxyl radical (OH) during daytime, the nitrate radical (NO_3) during nighttime, and ozone (O_3) during the entire day. In the presence of nitrogen dioxide (NO_2) and ozone (O_3), NO_3 radicals are mainly formed in the lower troposphere

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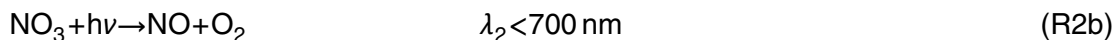
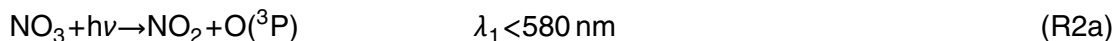
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via Reaction (R1):



During daytime NO_3 radicals do not build up to detectable levels because they have a short lifetime of about 5 s (Orlando et al., 1993) due to the radiation absorption in the visible band of the solar spectrum (maximum absorption at 662 nm) and consequent photodissociation to NO_2 and to a lesser extent NO (R2b).



Besides its role in the formation of NO_3 radicals, NO_2 also acts as a sink for NO_3 to form N_2O_5 via the equilibrium (3, -3) (Atkinson et al., 2004):



The equilibrium (3, -3) depends strongly on temperature and therefore N_2O_5 can act as a reservoir or as a sink for the nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$ depending on ambient temperature. Gas-phase N_2O_5 might contribute to nitric acid formation via reaction with water vapor, a process that is probably slow though uncertain (Wahner et al., 1998; Atkinson et al., 2003). Most importantly, N_2O_5 undergoes heterogeneous reactions with water (and water dimers) on aerosol or/and in clouds to form HNO_3 and nitrate (NO_3^-) anions, thus leading to a net loss of NO_3 and NO_x . Reported uptake coefficients of N_2O_5 (the ratio of the number of gas molecules removed by the condensed phase divided by the number of gas molecules colliding with the particle) $\gamma_{\text{N}_2\text{O}_5}$ on different aerosol surfaces vary from $2 \cdot 10^{-4}$ to 0.04 depending on temperature and surface composition with the lowest values observed for aerosols containing organics (Schutze et al., 2002; Zetsch et al., 1992; Hu and Abbatt, 1997; Badger et al., 2006; Brown et al., 2006). The direct hydrolysis of NO_3 radicals is slow with γ_{NO_3} equal $4.4 \cdot 10^{-4}$ at 273 K (Rudich et al., 1996). In the aqueous phase NO_3 can also react with anions like Cl^-

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to produce NO₃⁻ anions with $\gamma_{\text{NO}_3} \geq 2 \cdot 10^{-3}$ at 293 K (Thomas et al., 1998). NO₃ radicals also react rapidly in the gas phase with NO to form NO₂. In polluted areas this reaction might dominate the sink of NO₃ during daytime. At night, NO levels are low, especially in areas far from primary NO_x emissions. This in addition to the absence of light, which dissociates NO₃ radicals, allows the build up of significant NO₃ mixing ratios during night. The NO₃ radicals undergo gas phase reactions with Volatile Organic Compounds (VOCs) (Atkinson, 2000) and form peroxy (RO₂) and hydroxyl (OH) radicals (e.g. Platt et al., 1990; Carslaw et al., 1997 a, b; Salisbury et al., 2001). They also contribute to the conversion and subsequent removal of NO_x to reactive nitrogen (Allan et al., 1999) forming nitric acid (HNO₃) and particulate nitrate (NO₃⁻) during night (Brown et al., 2004; Vrekoussis et al., 2006). Although for most VOCs, the rates of reactions with NO₃ are lower than those with OH (Atkinson et al., 2004), there are several VOCs that are very reactive towards NO₃; for example, dimethylsulfide (DMS), isoprene, monoterpenes, some alkenes and aromatics. NO₃ reactions with VOCs proceed either via H-abstraction, forming HNO₃ (e.g. with aldehydes, higher alkanes and DMS) or NO₃ addition, forming nitrated organic peroxides, which is the case of alkenes and other unsaturated VOCs. During night NO₃ mixing ratios can be 10–100 times higher than of hydroxyl radicals during the day. In these cases NO₃ radicals can be the main atmospheric oxidant for species with similar reactivity towards NO₃ and OH radicals (for instance various pinenes, Atkinson et al., 2004). Therefore, atmospheric processes driven by NO₃ radicals, involving both gas phase and heterogeneous chemistry, may be of importance for the oxidizing capacity of the atmosphere and for nutrient nitrate formation. To our knowledge only two studies have addressed the role of NO₃ on a seasonal basis (Heinz et al., 1996; Geyer et al., 2001a). Seasonal NO₃ radical measurements are challenging because of the low mixing ratios and high spatial and temporal variability involved. The present study aims to investigate the seasonal variability of NO₃ radicals and the controlling factors in the marine planetary boundary layer over the East Mediterranean Sea. This region attracts attention as it is a cross point of various air masses of different origin. Depending on the wind direction, polluted

air masses with important loading of NO_x and anthropogenic aerosol are alternate with cleaner air originating from the Atlantic Ocean and Sahara, e.g. with low O_3 and significant dust loading (Mihalopoulos et al., 1997; Kouvarakis et al., 2000; Lelieveld et al., 2002).

2 Location of the station and experimental setup

Nitrate radicals were measured by a long path differential optical absorption spectroscopy (DOAS) instrument (Platt and Perner, 1983) along a 10.4 km light beam at Finokalia station (35.3' N, 25.3' E) on the island of Crete in the East Mediterranean for more than two years (June 2001–September 2003). The sampling station characteristics and the experimental device used for NO_3 measurements have been described in detail elsewhere (Mihalopoulos et al., 1997; Kouvarakis et al., 2000; Vrekoussis et al., 2004). NO_3 radicals are detected via its two significant absorption bands at 623 and 662 nm in the visible region of the solar spectrum. To eliminate influences such as water bands, NO_2 and lamp structures, the proper reference spectra are fitted simultaneously to derive the NO_3 signal, as described by Martinez et al. (2000) and Vrekoussis et al. (2004). Finally, the optical density of NO_3 is quantified through the 662 nm peak using the absorption cross section reported by Yokelson et al. (1994). The sampling time ranged from 10 to 30 min depending on the visibility through the light path. Note that a single measurement is the average of several individual absorption spectra over a long optical path in the atmosphere of 10.4 km, thus reducing the influence of small-scale variability. The detection limit (signal to noise ratio $S/N=3$) for the NO_3 radicals has been estimated to 1.2 ± 0.3 pptv. Nitrogen dioxide has been measured in parallel with NO_3 by changing the region of the light spectrum and by periodically shifting between the visible (VIS) for NO_3 and the ultraviolet (UV) region for NO_2 detection. NO_2 quantification has been achieved by using the optical density of the 405 nm peak and the cross section provided by Yoshino et al. (1997). Unfortunately, the NO_2 data set is not as extended as the NO_3 observations due to the increased noise in the UV region

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caused by a malfunction of the Photo Diode Arrays. Only good quality spectra (signal to noise ratio larger than 3) are used for the present analysis. The mean detection limit for NO₂ mixing ratios was 0.18±0.04 ppbv. Short path UV absorption instrument (Dasibi 1008) has been used for the continuous 5 min O₃ measurements during these two years. The instrument has a detection limit equal to 1 ppbv as indicated by the manufacturer. An extensive 5 min O₃ record since 1997 has been reported and analysed by Kouvarakis et al. (2000, 2002) and Gerasopoulos et al. (2005, 2006). The radioisotope Radon-222 has also been measured for this study with a 2-hour sampling time and detection limit better than 1 mBq/m³, and is used as a tracer of continental air masses (see details in Gerasopoulos et al., 2005). The 5 min mean meteorological parameters (temperature, relative humidity, wind speed and direction and solar irradiance) have been recorded by an automated meteorological station. Local time (LT) is used for the presentation and the discussion of the results hereafter.

3 Results and discussion

3.1 NO₃ variability and impact of transport

Measurements were performed during a total of 392 nights from June 2001 to September 2003. During 336 nights, NO₃ radical mixing ratios were above the detection limit of 1.2 pptv (Fig. 1) and in 8 cases exceeded 100 pptv. The maximum observed NO₃ value was 139 pptv (June 2001) and the 2-year period nighttime average was 4.2±2.3 pptv (arithmetic average±standard deviation). As shown in Table 1, the average NO₃ observations compare fairly well with data reported earlier for various locations and similar time periods. In addition, the maximum NO₃ values of 100 pptv in the continental boundary layer and 98 pptv in the marine boundary layer reported by Brown et al. (2003) and Heintz et al. (1996), respectively, are by 40% lower than those observed at Finokalia during summer. Since O₃ and NO₂ are precursors to NO₃ radical formation (R1), examination of their levels and variability is essential for understanding the chem-

istry of NO_3 . Figures 2a–c show the monthly mean (and maximum) nighttime mixing ratios of NO_3 radicals, NO_2 and O_3 , observed during the studied period. NO_3 radical levels are high in spring (seasonal average 3.7 ± 0.9 pptv) and summer (5.6 ± 1.2 pptv) and low during winter (1.2 ± 1.2 pptv) and follow those of its precursors, NO_2 and O_3 .

The NO_2 data series acquired with the DOAS instrument and presented here (Fig. 2b) provides the most complete overview of NO_2 temporal variability at a coastal area in the Eastern Mediterranean since only few NO_2 measurements have been reported in the literature for the area (Kourtidis et al., 2002; Vrekoussis et al., 2004). The annual mean NO_2 mixing ratio is 0.31 ± 0.13 ppbv whereas the individual NO_2 measurements range from below the detection limit (0.18 ppbv) up to 5 ppbv. The lowest monthly average of 0.24 ppbv was observed in winter and the highest (about 0.60 ppbv) in spring and summer. Similarly to NO_2 and NO_3 , O_3 minimum levels were registered in winter (seasonal average value equals 37 ± 6 ppbv) while the highest levels were observed in late spring-mid summer (summer seasonal average of 56 ± 10 ppbv) (Fig. 2c). For the studied 2-year period, the annual mean mixing ratio of O_3 is 48 ± 9 ppbv with the 5 min observations ranging from 23 ppbv to 83 ppbv. Details on the seasonal variation of O_3 at Finokalia are given by Gerasopoulos et al. (2005). The impact of the air mass origin on the levels of NO_3 radicals and other chemical species of interest for the present study has been investigated for the 2-year period. The rose diagrams shown in Figs. 3a–f have been constructed by averaging within each 10 degrees of wind direction interval all data acquired during the 2-years of the study. They have to be interpreted in conjunction with the various source areas that surround Finokalia station, notably mainland Greece, central Europe (N, NW), east Europe, Turkey (NE, E), Italy and the western Mediterranean region (W), and Africa (SW, S, SE). Note also that during winter air originates mainly from the Atlantic region and during summer from polluted Europe and Turkey (Lelieveld et al., 2002). The wind speed and Radon (Fig. 3a, b) highest values were associated with the northwest sector, indicative of air mass transport from polluted continental areas. High levels of ozone (Fig. 3c) were observed for wind directions from the north-west (Greece and central Europe) and north

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to north-east (east Europe, Turkey). NO₂ (Fig. 3d) was also slightly enhanced when the air masses originate from the northwest sector, compared to southerlies. As shown in Fig. 2e, NO₃ radicals were 50% higher when the air masses are of north-westerly origin in comparison to all other source regions. This dependency of the NO₃ mixing ratios on the wind direction has been further analysed for all NO₃ levels exceeding 30 pptv (in total 32 cases) during the period June 2001–September 2003 (Fig. 1). Back trajectories of the air masses reaching the sampling location, calculated by the HYSPLIT program (<http://www.arl.noaa.gov/ready/hysplit4.html>), are used to characterise the origin of these peaks. A high percentage (90%) of these elevated NO₃ cases is related to air masses from the northwest-northeast sectors, while the remaining 10% has a local-mixed origin. For these 32 cases, the observed NO₃ radical mixing ratios per wind sector average 64±37 pptv (northwest), 50±38 pptv (north), 55±24 pptv (north-east) and 48±13 pptv (local and mixed). To examine the importance of the individual chemical and meteorological factors for NO₃ radicals in detail, two characteristic cases of high NO₃ levels have been selected. Each of the 32 high NO₃ episodes observed during this study can be classified within one of these two categories (12 in case one and 20 in case two shown below).

3.1.1 Intrusion into the boundary layer

During the night of 4–5 June 2002 a rapid increase in NO₃ levels has been observed from 3 pptv to 102 pptv within 2.5 h (Fig. 4). Shortly before the NO₃ increase, the relative humidity dropped from 75 to 55%, Radon declined by about 0.8 Bq m⁻³ while ozone and NO₂ increased by about 7 ppbv and 0.2 ppbv, respectively. These observations support an intrusion event during which dry air from the free troposphere subsided into the nocturnal marine boundary layer, as identified by the trajectory analysis (Fig. 4). The air masses originated from polluted continental areas in Central Europe. The enhanced NO₃ radical mixing ratios in the free tropospheric subsiding air masses, may result from the high levels of NO₃ precursors in conjunction with depressed NO₃

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losses, in particular via the N_2O_5 reaction with water vapour.

3.1.2 Transport from pollution sources

During the night of 11–12th May 2003 NO_3 radicals mixing ratio increased from 4 pptv to 104 pptv within less than 1.5 h (Fig. 5). This rise was associated with the progressive increase in wind speed and changes in the wind direction. The back trajectory analysis reveals that these air masses had crossed the south-west coast of Turkey before reaching the sampling station. Note that under these conditions the station is receiving air masses rich in NO_2 and Radon. The relative humidity in this case did not change but remained at rather low levels (20–30%); in parallel the temperature was almost constant decreasing by only 1°C throughout the night. The clear anti-correlation observed between O_3 and NO_2 indicates titration of O_3 by NO leading to NO_3 production. Therefore, in contrast to the earlier case when air was transported in the free troposphere and then penetrated into the boundary layer at Finokalia, in this case the air mass originated from the polluted boundary layer and was transported at lower altitudes.

3.2 Correlations between NO_3 radicals and related species

Single and multiple regression analyses have been deployed to investigate the specific role of each of the factors that control the levels of NO_3 radicals such as NO_2 , O_3 , Radon-222, temperature (T), relative humidity (RH), wind direction and wind speed. The analysis is confined only to nighttime hours during which NO_3 radical mixing ratios exceed the detection limit. Specifically, more than 11 000 data points were used for the following analyses. A moving average has been additionally applied to the data series in order to subtract the seasonality (where existed) thus removing possible covariance between variables, which is due to their seasonal dependence.

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3.2.1 Single regression analysis

Linear regression analysis has been performed using both original and deseasonalised data. Significant correlations with NO₃ radicals at the 99% confidence level are apparent with O₃ (R²=0.13, N=9845), NO₂ (R²=0.21, N=8008), temperature (R²=0.26, N=9737), relative humidity (R²=-0.18, N=9737) and wind speed (R²=0.10, N=9737). When deseasonalised ozone and temperature values are used, their correlation coefficients are lower (0.08 and 0.17 respectively). This corroborates that a significant part of both O₃ and temperature correlation with NO₃ radicals is due to their common seasonality. Therefore, the single regression analysis indicates NO₂ (positive correlation) and RH (negative correlation) as the most important factors controlling NO₃ levels.

3.2.2 Multiple regression analysis

To evaluate the relative importance of each parameter for the NO₃ mixing ratios a multiple regression analysis has been performed. Based on the single regression analysis results, NO₂, O₃, T, RH and wind speed have been chosen as individual variable-parameters. Among them, O₃ and wind speed have been rejected by the model at the 95% confidence level (alpha=0.05). This result is not surprising since as shown by Gerasopoulos et al. (2005) a large part of ozone variability in the area can be explained by nitrogen oxides, RH and T changes and therefore O₃ can not be considered as an independent parameter. The analysis has been repeated with NO₂, RH and T, after eliminating the extreme values. These outliers have been identified via residual analysis between the predicted and initial NO₃ values with the criterion of the ±2 sigma. The best linear correlation that expresses the NO₃ variability is:

$$\text{NO}_3 = (0.80 \pm 0.04) \cdot \text{NO}_2 + (0.17 \pm 0.01) \cdot T + (-0.037 \pm 0.004) \cdot \text{RH} + (3.1 \pm 0.4) \quad (\text{R3})$$

where NO₃ in pptv, NO₂ in ppbv, T in °C and RH in %. The predictors in this case, NO₂, T, RH, contribute relative to 8, 7 and 5, respectively, and the explained total variance is 12%. This value is significant taking into account the total number of data used

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(N=8217). The results of both single and multiple regression analyses show that the NO₃ radicals are very sensitive to changes in NO₂ and in relative humidity and, to a lesser extent to temperature variations. Relative humidity is the only parameter anti-correlated with NO₃ due to the indirect removal via heterogeneous reactions of N₂O₅, as will be discussed below.

3.3 Factors controlling NO₃ levels

Under steady state conditions the NO₃ levels are in equilibrium between production (P_{NO₃}) and losses (f_{NO₃}). The production rate of NO₃ radicals by Reaction R1 is given by:

$$P_{NO_3} = k_{NO_2+O_3} \cdot [NO_2][O_3] \quad (R4)$$

where $k_{NO_2+O_3}$ is the rate of this reaction. The losses of NO₃ radicals (f_{NO₃}) are the sum of direct (f_A) and indirect loss rates (f_B). The indirect losses of NO₃ (f_B) are related to the loss of N₂O₅ (f_{B'}) as shown below in Eq. (3) that is derived assuming steady-state conditions for N₂O₅, NO₃ (Geyer et al. 2001b):

$$[NO_3] = \frac{P_{NO_3}}{f_A + [NO_2] \cdot k_{eq} \cdot f'_B} \quad (R5)$$

where

$$k_{eq} = \frac{k_{NO_2+NO_3}}{k_{-(N_2O_5)}} = \frac{[N_2O_5]}{[NO_2] \cdot [NO_3]} \quad (R6)$$

The N₂O₅ levels can be calculated based on the observed NO₃ and NO₂ levels, and the temperature dependent equilibrium constant k_{eq} of the reversible Reaction 3,-3. For the whole sampling period monthly averages for N₂O₅, P_{NO₃}, and f_{NO₃} are shown in Fig. 6.

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If the indirect losses are negligible ($f_B \approx 0$), (NO_3) should be directly proportional to the P_{NO_3} and, then, the slope of the linear relationship between (NO_3) and P_{NO_3} equals the lifetime of NO_3 radicals (τ_{NO_3}) and is f_A^{-1} . On the other hand, if the direct losses are negligible ($f_A \approx 0$) and the indirect NO_3 loss predominates, the above equation leads to

$$\tau_{\text{NO}_3} = \frac{1}{[\text{NO}_2] \cdot k_{\text{eq}} \cdot f_B} \quad (\text{R7})$$

Then τ_{NO_3} is proportional to the inverse of the NO_2 mixing ratio (or $\ln(\tau_{\text{NO}_3}) = -\ln(k_{\text{eq}} f_B / [\text{NO}_2])$).

Below the production and loss rates of NO_3 will be examined in detail.

3.3.1 Production rate of the NO_3

Based on Eq. (2) and the temperature dependence of the reaction rate $k_{\text{NO}_2+\text{O}_3} = 1.4 \cdot 10^{-13} \cdot \exp\left[-\frac{2490}{T}\right]$ (T in K; Atkinson et al., 2004), under typical conditions in the Mediterranean area during summer ($\text{NO}_2 = 0.5$ ppbv, and (O_3) = 50 ppbv, $T = 298$ K), the production rate of NO_3 (P_{NO_3}) equals 72 pptv NO_3 per hour. Assuming dynamic equilibrium of NO_3 (i.e. that the production by Reaction R1 equals the loss by photo-dissociation (R2a) and (R2b) and reaction with NO, for (NO) = 0.02 ppbv and $k_{\text{NO}_3+\text{NO}} = 1.8 \cdot 10^{-11} \cdot \exp\left[\frac{110}{T}\right] = 2.6 \cdot 10^{-11}$, the steady-state daytime concentration of NO_3 is calculated to be about 0.1 pptv. Maximum temperature differences of 40°C that have been observed between summer and winter can change P_{NO_3} by a factor of 3.5 (higher P_{NO_3} during summer) assuming that the levels of NO_2 and O_3 do not change significantly. However, the monthly mean temperatures differ by about 14°C between summer and winter (Vrekoussis et al., 2006). In addition, NO_2 and O_3 mixing ratios are higher during summer than during winter. Thus, the overall effect is that the nitrate radical production (P_{NO_3}) is about 4 times faster during summer than during winter. The annual mean P_{NO_3} derived from the monthly averages equals $(2.6 \pm 1.4) \cdot 10^5$

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molecules $\text{cm}^{-3} \text{s}^{-1}$ (Fig. 6). Note that P_{NO_3} calculated over the 5 min sampling time shows two orders of magnitude variability, ranging from $5.0 \cdot 10^4$ molecules $\cdot \text{cm}^{-3} \text{s}^{-1}$ to $5.5 \cdot 10^6$ molecules $\cdot \text{cm}^{-3} \text{s}^{-1}$.

3.3.2 Losses of NO_3

5 Direct removal of NO_3 concerns the NO_3 reactions mainly with VOC, including DMS naturally emitted by the ocean, and with peroxy (RO_2) radicals. The indirect removal of NO_3 occurs via N_2O_5 formation and subsequent heterogeneous reactions.

For the following analysis, to reduce the high scatter in the NO_3 data set (more than 15 000 measurements), NO_3 averages have been further extracted per unit of P_{NO_3} equal to $1 \cdot 10^5$ molecules $\cdot \text{cm}^{-3} \text{s}^{-1}$ and τ_{NO_3} (equal to $1/f_{\text{NO}_3}$) has been averaged per unit of NO_2 equal to 100 pptv. The interpretation of all data, according to the above analysis for the direct sinks, leads to a linear regression

$$10 \quad [\text{NO}_3] = 300 P_{\text{NO}_3} \quad (r^2 = 0.41) \quad (\text{R8})$$

whereas the derived equation for the indirect sinks is:

$$15 \quad \ln(\tau_{\text{NO}_3}) = -1.02 \ln[\text{NO}_2] + 4.6 \quad (r^2 = 0.93) \quad (\text{R9})$$

The above indicate relatively strong indirect losses in this region during the 2-years period.

However there is also significant seasonal variability in the importance of the direct versus the indirect NO_3 loss pathways as indicated by the seasonally resolved correlations (Table 2). During winter the direct sinks of NO_3 radicals are of little importance whereas during spring the data reveal a strong linear correlation ($r^2 = 0.96$) between NO_3 radicals and their production rate, most probably due to increased VOC concentrations from biogenic emissions, indicating dominance of direct NO_3 losses.

For summer and autumn, a closer examination of the dataset reveals two sub-sets. For both seasons, the one sub-set corresponds to a higher linear regression slope and

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a significant correlation between P_{NO_3} and NO_3 , whereas the second one does not present any significant correlation between P_{NO_3} and NO_3 (Table 2). The first one, with a high production rate P_{NO_3} and high NO_3 mixing ratios, corresponds to steady-state conditions in the area where the direct sinks of NO_3 are important. The second subset is linked to high P_{NO_3} , high NO_2 and low NO_3 mixing ratios pointing to indirect sinks for the NO_3 radicals.

To further investigate the importance of the heterogeneous chemistry in NO_3 removal via the reactions of N_2O_5 , the logarithmic correlation between the NO_3 lifetime and the NO_2 concentration is considered for 7 different ranges of relative humidity from 20 to 90% every 10% (Fig. 7). It is found that the slope approaches the “ideal” value of -1 at high relative humidity, which explains why heterogeneous processes peak in winter.

3.4 Implications of the observations

Based on our observations, during nighttime the annual median steady-state NO_3 lifetime is estimated to be about 5 min. During daytime NO_3 is rapidly destroyed via photodissociation and can be involved in O_3 titration through Reaction R2b that contributes by about 10% to the total photodissociation of NO_3 . Thus based on the range of the P_{NO_3} estimated in Sect. 3.3.1, Reaction R2b could provide a sink of up to 70 pptv O_3 per hour that is at most 10% of the calculated tropospheric ozone destruction in the area (Gerasopoulos et al., 2006).

Taking into account the observed levels of NO_3 radicals, several VOC species are subject to important nighttime chemistry initiated by NO_3 , i.e. of similar relevance as daytime chemistry driven by OH radicals (Vrekoussis et al., 2004). Indeed, for the studied area, based on the observed NO_3 levels and the OH radicals observed during summer 2001 (Berresheim et al., 2003) and calculated for the other seasons (Vrekoussis et al., 2006), the NO_3 initiated nighttime VOC oxidation appears to be more important than the daytime oxidation by OH radicals for a number of VOCs, particularly for monoterpenes and DMS. VOC oxidation can lower NO_3 levels and shorten NO_3 lifetime. These results agree with recent observations of a positive NO_3 radical vertical

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gradient in the mid-latitude coastal marine boundary layer during summer (Saiz-Lopez et al., 2006). These authors have explained their observations by a potentially efficient removal of NO_3 radicals by DMS.

In addition, the NO_3 initiated oxidation of VOCs contributes to the nighttime formation of OH and peroxy radicals (Platt et al., 1990; Vrekoussis et al. 2006, in preparation) Finally, our results underscore that nighttime chemistry initiated by NO_3 radicals is as important as daytime chemistry for the formation of nutrient, nitrate as discussed in detail by Vrekoussis et al. (2006).

4 Conclusions

This paper presents the first long-term NO_3 radical observations performed by a DOAS instrument in the marine boundary layer in the eastern Mediterranean region for a two-year period. The observed nighttime NO_3 levels vary between the detection limit of the instrument (about 1.2 pptv) and 139 pptv with seasonal averages that have a maximum in summer (5.6 ± 1.2 pptv) and a minimum in winter (1.2 ± 1.2 pptv); and an annual mean value of 4.2 ± 2.3 pptv.

Single and multiple component regression analyses on the large number of simultaneous observations ($n=8217$) demonstrate NO_2 (positive correlation) and relative humidity (negative correlation) as the most important factors controlling NO_3 levels, and to a lesser extend temperature that is strongly linked to the seasonal variation of NO_3 levels.

Further data analysis points to the indirect loss of NO_3 via conversion to N_2O_5 , followed by heterogeneous reactions as the major loss process for NO_3 year-around. Direct losses of NO_3 are shown to be important in spring and some summer and autumn periods with high biogenic emissions. Our results also indicate that NO_3 radicals can be important for nighttime VOC oxidation, contributing to the nighttime formation of peroxy radicals, nitric acid and particulate nitrate.

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Acknowledgements. The authors acknowledge valuable help with the DOAS instrument logistics by D. Perner and T. Kluepfel. MV has been supported by a PENED grant. Presentation of the work has been facilitated by the ACCENT EU Network of Excellence. At its latest stage this project has been supported by European Social Funds and National Resources EPEAK II-PYTHAGORAS. This paper is dedicated to the memory of G. Hönninger from the University of Heidelberg, who performed the first DOAS measurements at Finokalia station during the ELCID campaign (June 2000).

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Table 1. NO₃ radical measurements for different environments and seasons reported in the literature. L: total path of the used DOAS instrument.

Location	Latitude-Longitude	NO ₃ Average (pptv)	NO ₃ Max (pptv)	L (km)	Time/Season	Year	Ref	
Continental Boundary Layer								
Lindenberg, Germany	52°13'N-14°07'E	4.6	85	10	Feb.-Sept.	1998	Geyer et al. (2001a)	
		5.0	-	10	March-April	1998	"	
		5.7	-	10	May-Sept.	1998	"	
Pabstthum, Germany	52°51'N-12°56'E	-	70	12.6	July-Aug.	1998	"	
Boulder, Colorado, US	40°6'N-105°16'W	-	100	-	Oct.-Nov.	2001	Brown et al. (2003)	
Marine Boundary Layer								
Kap Arkona (Rügen Island), Germany	54°30'N-13°30'E	7.8	98	7.3	April 1993-May 1994	1993/94	Heintz et al. (1996)	
Izana, Tenerife, Spain (2003m)	28°40'N-16°05'W	8.0	20	9.6	May	1994	Carslaw et al. (1997a)	
		-	20	9.3	June/July	1997	Allan et al. (2000)	
Wayborne, England	52°57'N- 1°08'E	9.7 SP*	-	5	Winter (4 nights)	1994	Allan et al. (1999)	
		10.0	25	5	Spring (4 nights)	1994	Carslaw et al. (1997b)	
		6 CL*	-	5	Summer (4 nights)	1995	Allan et al. (1999)	
		11.1	-	5	Autumn (1 night)	1994	Carslaw et al. (1997b)	
Mace Head, Ireland	53° 19'N-9°54'W	1-5 CL*	40	8.4	July/August	1996	Allan et al. (2000)	
		1-40 SP*	-	-	-	-	-	-
		1-5 CL* 1-40 SP*	40	8.4	April/May	1997	idem	
Helgoland, island	54 °2'N-7°9'E	3 CL* 13 SP*	25	8.4	July/August	2005	Saiz -Lopez et al. (2006)	
			40	3.6	October	1996	Martinez et al. (2000)	
Finokalia, Greece	35°30'N-25°7'E	4.5	37	10.4	July/August	2001	Vrekoussis et al. (2004)	
		5.6	139.3	10.4	Summer	2001	This work	
		3.4	64.1	10.4	Autumn	2001	"	
		1.0	6.0	10.4	Winter	2002	"	
		2.9	75.2	10.4	Spring	2002	"	
		5.3	119.2	10.4	Summer	2002	"	
		4.7	31.5	10.4	Autumn	2002	"	
		2.2	11.1	10.4	Winter	2003	"	
		5.1	101.4	10.4	Spring	2003	"	
		7.2	127.7	10.4	Summer	2003	"	
7.8	62.9	10.4	September	2003	"			

* CL=Clean conditions; SP=Semi-polluted conditions; P=Polluted conditions

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Table 2. Indicators of direct **(a)** and indirect **(b)** NO₃ losses and corresponding lifetimes (τ_A and τ_B , respectively). (a) Linear correlation of the NO₃ radicals mixing ratio with the NO₃ production rate (P_{NO_3}), and (b) linear correlation of the logarithm of the NO₃ lifetime (τ_{NO_3}) with the logarithm of the NO₂ mixing ratio. The linear slope of the direct sinks represents the NO₃ lifetime, $\tau_A\tau_B$ is calculated from the seasonal (or annual) NO₂ values and the corresponding logarithmic equation presented in the table. NO₃ values are expressed in molecules·cm⁻³, P_{NO_3} in molecules·cm⁻³·s⁻¹, NO₂ in ppbv, τ_{NO_3} in s.

Period	[NO ₃]=f(P_{NO_3}) Slope (r^2)	τ_A (min)	$\ln[\tau_{\text{NO}_3}]=f(\ln[\text{NO}_2])$ $y=ax+b(r^2)$	τ_B (min)
Year	300* (0.41)	5.0	$y = -1.0 x + 4.6$ (0.93)	5.4
Winter	174 (0.08)	2.9	$y = -1.5 x + 2.8$ (0.78)	2.3
Spring	520 (0.96)	8.6	$y = -0.8 x + 5.1$ (0.38)	7.5
Summer	203 (0.10*)	3.4	$y = -1.1 x + 4.9$ (0.88)	6.1
Summer_1	321 (0.99)	5.4	$y = -0.6 x + 5.5$ (0.95)	7.1
Summer_2	106 (0.10)	1.8	$y = -1.2 x + 4.9$ (0.78)	6.7
Autumn	200 (0.25)	3.3	$y = -1.4 x + 3.3$ (0.92)	2.3
Autumn_1	649 (0.75)	10.8	$y = -0.8 x + 4.6$ (0.97)	4.2
Autumn_2	128 (0.35)	2.1	$y = -1.6 x + 3.7$ (0.94)	4.4

*experimentally deduced see text.

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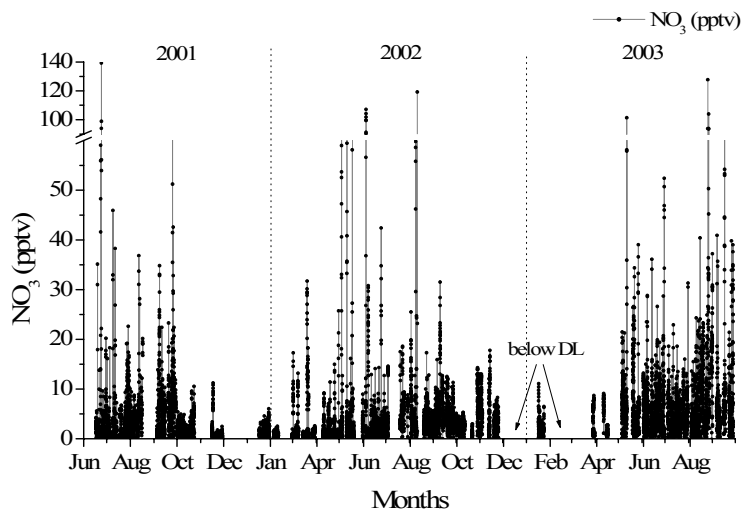


Fig. 1. NO₃ observations (in pptv) at Finokalia during 2 years of sampling (June 2001–September 2003).

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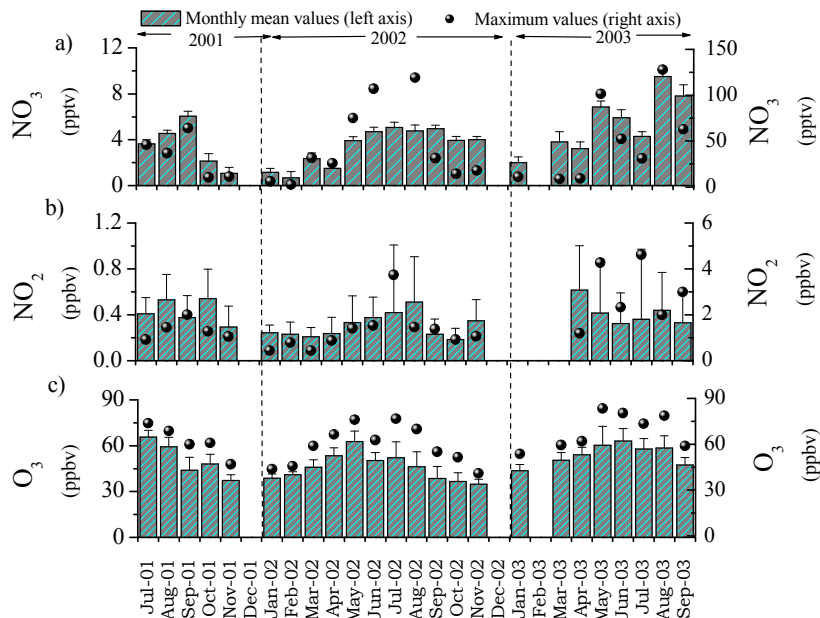


Fig. 2. Monthly mean mixing ratios (left axis) of (a) NO_3 , (b) NO_2 and (c) O_3 and their standard deviations (nighttime observations only). Black squares, circles and triangles depict the maximum values per month (right axis) of NO_3 , NO_2 and O_3 respectively.

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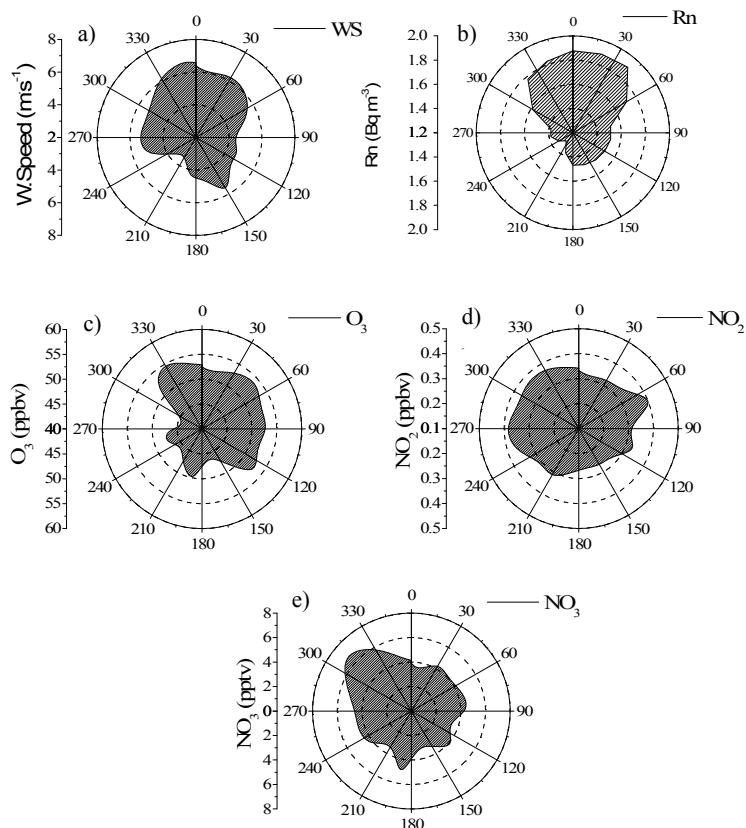


Fig. 3. Rose diagrams of the (a) Wind speed, (b) radon-222, (c) O_3 , (d) NO_2 and (e) NO_3 as a function of wind direction at Finokalia, based on all nighttime observations integrated per 10 degree intervals of wind direction.

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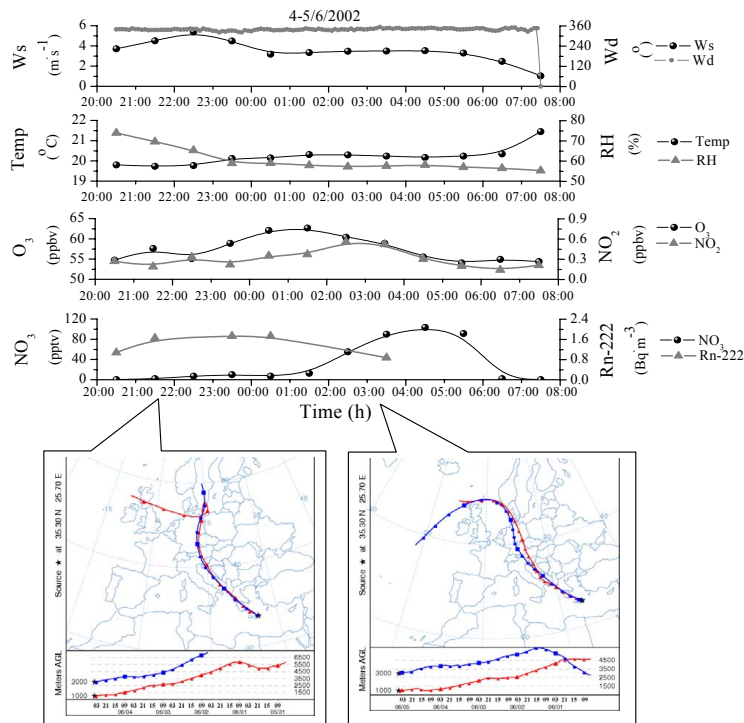


Fig. 4. Variation of wind speed, temperature, O_3 and NO_3 radicals during an intrusion of free tropospheric air masses associated with a decrease in Radon and relative humidity and increases of O_3 and NO_3 radicals (time expressed in local time), and 5-day back trajectories of air masses arriving at Finokalia on the 4th of June 2002 at 21:00 LT and on the 5th of June 2002 at 03:00 LT.

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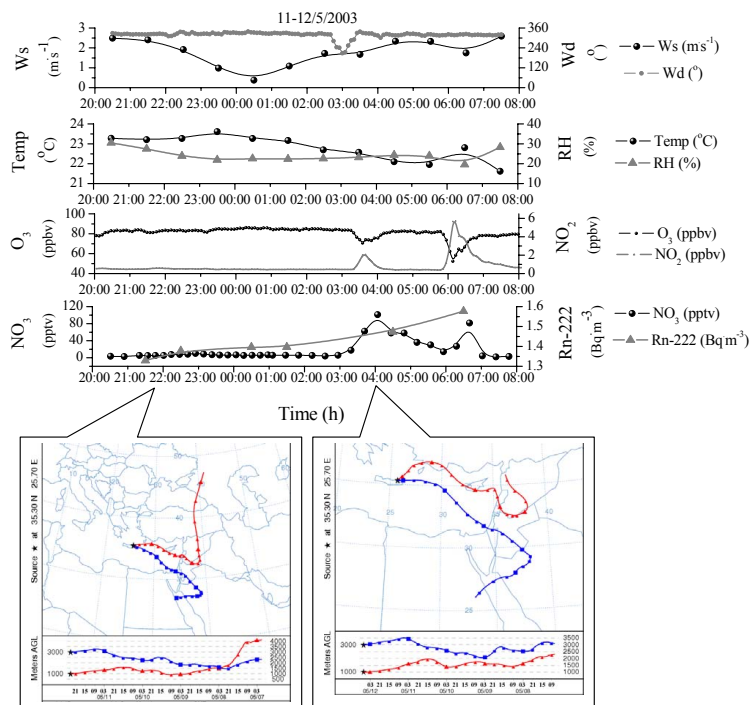


Fig. 5. Variation of wind speed, temperature, O_3 and NO_3 radicals during transport of polluted air masses as indicated by an increase in Radon, and wind speed, change in wind direction followed by an increase in NO_2 and depletion of O_3 , an increase in NO_3 radicals (time expressed in local time) and 5-day back trajectories of air masses arriving at Finokalia on the 11th of May 2003 at 22:00 LT and on the 12th of May 2003 at 04:00 LT.

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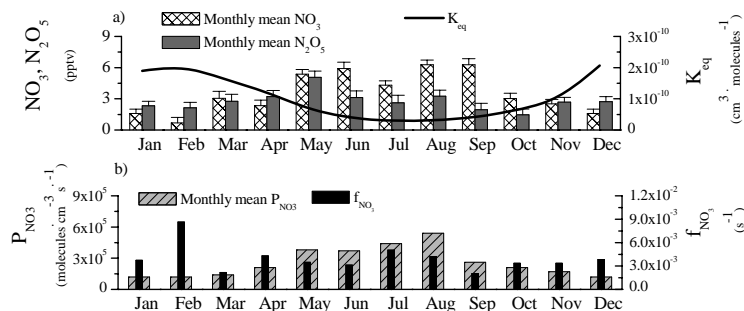


Fig. 6. Annual cycle (a) of observed NO_3 and of N_2O_5 (left axis) calculated assuming steady-state conditions and no heterogeneous losses and of the equilibrium constant K_{eq} of the Reactions (3,-3) (right axis) given by $k_{\text{eq}} = 3 \cdot 10^{-27} \exp(10990/T)$ (Sander et al., 2003) (b) of P_{NO_3} (left axis) and f_{NO_3} (right axis); monthly mean values and standard deviations based on the June 2001 to September 2003 observations.

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Two-years of NO_3 radical observations

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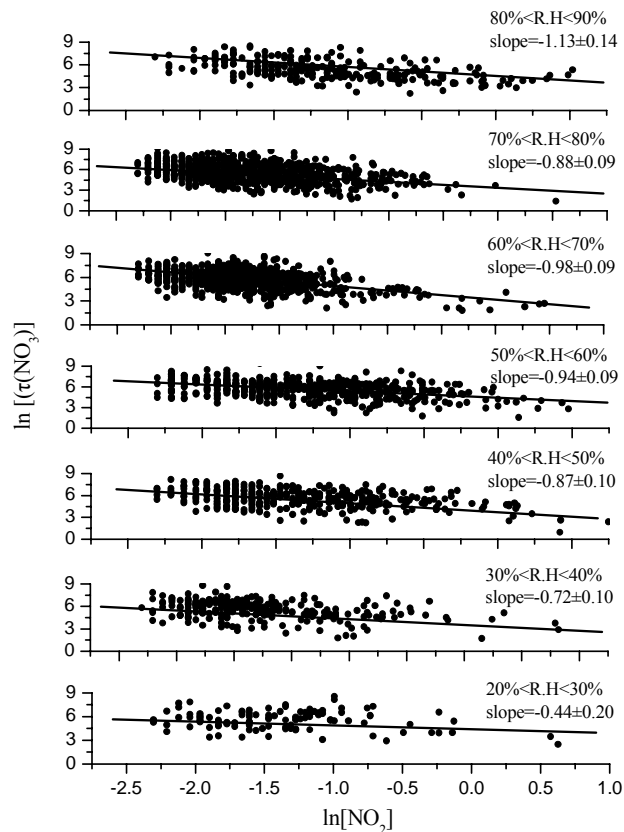


Fig. 7. Correlation of the logarithm of the lifetime of NO_3 radicals as deduced from observations and the logarithm of NO_2 mixing ratios at 7 different relative humidities ranges (from 20% to 90% every 10%). Slopes closer to -1 indicate higher involvement of the indirect losses of NO_3 .

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