

Formation of HNO₃ and NO₃⁻ in the anthropogenically-influenced eastern Mediterranean marine boundary layer

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Received 2 November 2005; revised 31 January 2006; accepted 3 February 2006; published 9 March 2006.

[1] To investigate the seasonal behaviour of nitrate radicals (NO₃) as a source of nitric acid (HNO₃) and particulate nitrate (NO₃⁻) in the eastern Mediterranean atmosphere, we conducted NO₃ measurements on the island of Crete for more than two years. Ancillary measurements of chemical compounds and meteorological parameters were used to analyse the observations. Nighttime production of HNO₃ plus NO₃⁻, as initiated by NO₃ radicals, accounts for about 50–65% of the total production rate depending on season. The remainder is produced by the hydroxyl radical (OH) reaction with nitrogen dioxide during daytime. On a yearly mean basis, about 17% of the HNO₃ plus NO₃⁻ formation results from the reaction of NO₃ radicals with dimethylsulfide of marine origin. This shows important interactions between biogenic and anthropogenic compounds contributing to nutrient deposition to the sea. **Citation:** Vrekoussis, M., E. Liakakou, N. Mihalopoulos, M. Kanakidou, P. J. Crutzen, and J. Lelieveld (2006), Formation of HNO₃ and NO₃⁻ in the anthropogenically-influenced eastern Mediterranean marine boundary layer, *Geophys. Res. Lett.*, 33, L05811, doi:10.1029/2005GL025069.

1. Introduction

[2] The biogeochemical cycling of nitrogen (N) is of a great importance for atmospheric photochemistry and biological productivity. Reactive nitrogen species regulate the production of tropospheric ozone, a noxious pollutant and a key atmospheric oxidant. They are, to a large extent, removed from the atmosphere via the formation of water soluble HNO₃ and particulate NO₃⁻ and subsequent wet and dry deposition on the Earth's surface. The deposition of these species provides nutrients to the marine biosphere. On a global scale riverine and atmospheric inputs of dissolved inorganic nitrogen (DIN, mainly in the form of HNO₃ and NO₃⁻) to the oceans have been estimated to be of similar significance [Duce *et al.*, 1991; Jickells, 1998].

[3] Studies with a focus both on the western and eastern Mediterranean basins [Loye-Pilot *et al.*, 1990; Kouvarakis *et al.*, 2001] have indicated that the uptake of atmospheric N by the sea largely accounts for the new marine biogenic nitrogen production. Based on speciated nitrogen measurements, Kouvarakis *et al.* [2001] concluded that up to 75% of the DIN originates from atmospheric deposition of HNO₃

and NO₃⁻ (i.e., 0.3 to 0.4 g-Nm⁻²y⁻¹). Understanding the formation of these species in the Mediterranean atmosphere is thus of great relevance.

[4] Heterogeneous reactions of HNO₃ on sea-salt or dust particles have been identified as main pathways of NO₃⁻ formation in the area [Markaki *et al.*, 2003]. During daytime, the main formation pathway of HNO₃ is the reaction of OH radicals with nitrogen dioxide (NO₂). During nighttime reactions with NO₃ radicals, being produced via the reaction of NO₂ and ozone (O₃), are an important source of HNO₃. NO₃ radicals abstract an H atom from Volatile Organic Compounds (VOCs), including dimethylsulfide – DMS – and to a lesser extent aldehydes and higher alkanes, to form HNO₃. Heterogeneous reactions of NO₃ radicals on particles [Heintz *et al.*, 1996] also lead to NO₃⁻ formation although this is only a minor pathway in the production of NO₃⁻. Dinitrogen pentoxide (N₂O₅), formed via (NO₃ + NO₂ + M ⇌ N₂O₅ + M), also contributes to nighttime HNO₃ formation via the reaction of N₂O₅ with H₂O on particles [Atkinson *et al.*, 2004]. The gas phase reaction of N₂O₅ with water vapor is considered to be very slow [Atkinson *et al.*, 2004] and only the upper limit of their rates has been determined [Wahner *et al.*, 1998]. They are, therefore, neglected in the present study.

[5] Field campaigns have indicated a significant contribution of nighttime chemical mechanisms to the formation of HNO₃ and NO₃⁻ [Brown *et al.*, 2004; Vrekoussis *et al.*, 2004]. However, the seasonal dependence of the relative contribution of the day- and nighttime mechanisms to the HNO₃ plus NO₃⁻ formation in the anthropogenically influenced marine atmosphere has not been previously addressed. In addition, only few studies have addressed the seasonal variation of NO₃ radicals [Heintz *et al.*, 1996; Allan *et al.*, 1999].

[6] Here we present a comprehensive time series, including the seasonality of the NO₃ radical abundance over the eastern Mediterranean Sea, acquired during more than 2 years. We use this data in conjunction with additional information on ozone (O₃), photodissociation rates, nitrogen oxides and a number of ancillary compounds and meteorological parameters to investigate the role of NO₃ chemistry in the formation of HNO₃ plus NO₃⁻ and thus in the seasonal deposition of DIN to the eastern Mediterranean Sea.

2. Method Description

2.1. Experimental Devices

[7] The NO₃ radical mixing ratio has been monitored continuously by a long path DOAS instrument (10.4 km) at Finokalia (35.3N, 25.7E), Crete, Greece, from June 2001 to

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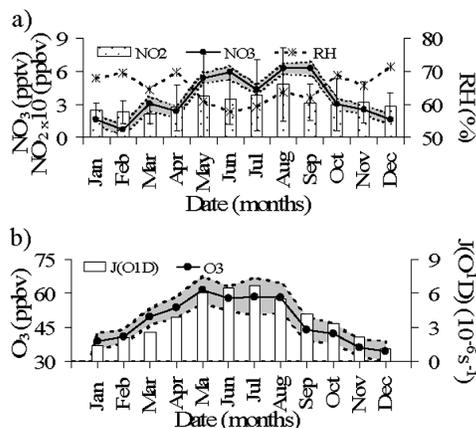


Figure 1. Monthly averages and standard deviations (bars) of (a) NO₃ radicals, NO₂ (concentrations multiplied by a factor of 10 for clarity), and RH and (b) O₃ (mean, minimum and maximum values) and O₃ photolysis to O¹D (mean values for the period of June 2001–Sept 2003).

September 2003. Details about the station, the instrumentation and the data processing (based on absorption at 623 and 662 nm) are given by *Vrekoussis et al.* [2004].

[8] NO₂ was measured using the same DOAS instrument, operated in the UV spectral region. The mean instrumental noise (σ) has been estimated to be 0.4 and 80 pptv, which leads to a detection limit (3σ) of 1.2 and 240 pptv, for NO₃ and NO₂ respectively. Nitrogen monoxide (NO) was monitored every 5 min with a chemiluminescence (Thermo 42C analyser) instrument and was calibrated by a 300 pptv standard.

[9] Photolysis frequencies of O₃ (JO¹D) and of NO₂ (JNO₂) were measured continuously since 2001 by filter radiometers (Meteorologie Consult, Germany). The sensors were calibrated annually against a spectral radiometer at the Research Centre Juelich, Germany (B. Bohn, personal communication, 2001, 2004). The accuracy is 15% and the precision is better than 3%.

[10] O₃ was measured using a Thermo Analyser Model 49C, calibrated regularly by a UV Photometric calibrator. CO was monitored every 20 min by a Thermo Analyser Model 48C based on IR detection, corrected for baseline drift and water vapour interference and calibrated by a 10 ppmv standard [*Kouvarakis et al.*, 2002].

[11] Discontinuous gaseous HNO₃ and particulate NO₃⁻ measurements were performed using a filter pack technique. At Finokalia, NO₃⁻ exists exclusively as sodium and calcium salts, so that this technique can successfully separate HNO₃ and NO₃⁻ without artifacts.

[12] The air temperature, relative humidity (RH), wind speed and direction and the direct solar radiation were measured and recorded by an automatic meteorological station.

2.2. Model Description

[13] Observed seasonally and hourly mean values of O₃, CO, NO, NO₂, JNO₂ and JO¹D are used as input to the chemical box model [*Vrekoussis et al.*, 2004] used for the present study. Nighttime NO₂ values, used as input to the model, were taken from the DOAS data set, whereas

daytime NO₂ levels were simulated by the model. Isoprene, ethene, propene, ethane, propane and butane mixing ratios were based both on measurements performed in the area during an 8-month period (February to October 2004, unpublished data) and in the western Mediterranean [*Plass-Dülmer et al.*, 1992]. Seasonally mean wet aerosol surfaces have been derived from SMPS observations at Finokalia from July 2004 to January 2005 complemented by one-year size-segregated aerosol mass and ambient RH observations (July 2004 to 2005). They vary from about 200 to 280 $\mu\text{m}^2\text{cm}^{-3}$ in winter and summer, respectively. Details on the parameterizations of heterogeneous losses are given by *Vrekoussis et al.* [2004]. DMS fluxes derived from the seawater DMS concentration and wind speed have been used to drive the model. Seasonally varying seawater DMS concentrations were taken from the DMS data base established by our laboratory for the eastern Mediterranean since 1998 [*Kouvarakis et al.*, 2002].

3. Results and Discussion

3.1. Seasonal Variation of NO₃, NO, NO₂, O₃, N₂O₅

[14] Measurements of NO₃ were performed during 392 nights from June 2001 to September 2003. During 336 nights, NO₃ radicals mixing ratios exceeded the detection limit (1.2 pptv). Figure 1a shows monthly mean and Table 1 seasonal mean nighttime NO₃ concentrations. During winter, NO₃ levels were significantly lower than during the other seasons. This is due to lower temperatures and higher RH and precipitation (see indicative seasonality of meteorological parameters in Table 1) that favour the removal of reactive nitrogen species via dissolution of N₂O₅ in water droplets and subsequent removal by precipitation, and especially via heterogeneous reactions of N₂O₅ on aerosols.

[15] NO, NO₂ and O₃ seasonal variations during the studied period are shown in Figures 1a and 1b. For the

Table 1. Seasonal Variation of O₃, NO₂, NO, N₂O₅, NO₃, OH, HNO₃, NO₃⁻ at Finokalia, Crete, Greece

Mean Mixing Ratio	Winter	Spring	Summer	Autumn
nighttime length (hours)	13.7	11.3	10.3	13.0
Temperature (°C) ^a	10.8 ± 3.6	14.8 ± 4.2	24.4 ± 2.9	19.8 ± 4.3
RH ^a	68.5 ± 13.3	64.0 ± 18.2	59.8 ± 15.3	64.4 ± 14.8
O ₃ (ppbv)	37.4 ± 6.4	49.7 ± 9.6	55.5 ± 9.5	43.4 ± 9.0
NO ₂ (ppbv) ^a	0.20 ± 0.16	0.42 ± 0.49	0.56 ± 0.60	0.37 ± 0.25
NO (pptv)	25 ± 42	27 ± 38	33 ± 46	41 ± 61
N ₂ O ₅ (pptv) ^{a,b}	2.4 ± 2.0	3.7 ± 2.3	3.0 ± 2.5	2.0 ± 1.0
N ₂ O ₅ (pptv) model ^a	2.6 ± 0.9	2.3 ± 1.5	2.2 ± 1.5	2.2 ± 1.6
NO ₃ (pptv) ^a	1.2 ± 1.2	3.7 ± 0.9	5.6 ± 1.2	4.6 ± 1.1
NO ₃ (pptv) model ^a	2.5 ± 0.9	2.8 ± 1.6	7.6 ± 4.5	5.1 ± 3.2
OH (cm ⁻³) model	1.3 ± 0.7 · 10 ⁶	2.0 ± 1.4 · 10 ⁶	3.7 ± 2.8 · 10 ⁶	2.5 ± 1.7 · 10 ⁶
HNO ₃ + NO ₃ ^{-c} (ppbv)	0.39	0.67	1.02	0.53
HNO ₃ + NO ₃ ⁻ (ppbv) model	0.4 ± 0.01	0.58 ± 0.03	0.88 ± 0.01	0.64 ± 0.03

^aNO₂, N₂O₅, NO₃, RH, and temperature refer to nighttime averages; all others are diel averages.

^bCalculated values based on observations and neglecting heterogeneous loss, see text.

^cMedian values.

entire study period, the diel mean mixing ratios of NO₂, NO and O₃ were 0.35 ± 0.31 ppbv, 0.033 ± 0.020 ppbv and 48.4 ± 8.9 ppbv, respectively. The seasonal variation of these species is summarized in Table 1.

[16] Previous studies [Vrekoussis *et al.*, 2004], using measured JO¹D, CO and water vapour, showed that OH radical observations at Finokalia can be successfully simulated by the model. Figure 1b presents monthly mean JO¹D during the studied period, and Table 1 the seasonal variation of the calculated OH radicals concentrations.

[17] The concentrations of N₂O₅ were estimated for the entire period using measured mixing ratios of NO₃ and NO₂ and the air temperature, considering the temperature dependant reaction $\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5$ and its equilibrium constant of $K_{\text{NO}_3 + \text{NO}_2} = 3.010^{-27} \exp\left[\frac{10990}{T}\right] \text{cm}^3 \text{molecules}^{-1}$ [Wängberg *et al.*, 1997]. The importance of N₂O₅ formation from the above reaction varies with season mainly due to changes in temperature (with extreme values from -1.5°C in winter to 43°C in summer, respectively). Table 1 shows the seasonal variation of the estimated N₂O₅ levels, being about a factor of 2 lower than NO₃ levels during summer and autumn. Contrary, during winter, N₂O₅ and NO₃ levels are quite similar. The ratio of N₂O₅ to NO₃ is very sensitive to air temperature changes as well as to heterogeneous losses. Both factors affect this ratio similarly, i.e. increasing temperature or heterogeneous losses favor NO₃ versus N₂O₅.

3.2. Model Results

[18] Atmospheric chemical box model simulations have been performed for the four seasons using the observed seasonally mean diel variations of the trace gases, meteorological parameters and photolysis rates. Nevertheless, the estimated N₂O₅ levels are in fair agreement with the model results, taking into account the associated variability and the measurement uncertainty. The model seems to underpredict by 25–40% the N₂O₅ seasonal mean values estimated from the observations of NO₃ and NO₂ during spring and summer and slightly (less than 10%) overestimates both N₂O₅ and NO₃ levels during winter and fall. However, no discrepancy reveals when the variability of measurements is taken into account.

3.2.1. Simulated Versus Observed NO₃

[19] Seasonal mean nighttime NO₃ radical concentrations simulated by the model were 2.5 ± 0.9 , 2.8 ± 1.6 , 7.6 ± 4.5 , 5.1 ± 3.2 pptv for winter, spring, summer and autumn, respectively. These results are within the range of variability of the measurements as shown in Table 1. Note that although very good agreement between model and observations exists for spring and autumn, the mean wintertime observations of NO₃ are overestimated by a factor of 2 by the model whereas N₂O₅ is nicely reproduced. Therefore, the importance of NO₃ chemistry during winter deduced by our model calculations and discussed below should be viewed with caution since it might be overestimated. The model reproduces the diel pattern of the NO₃ observations, showing increasing concentrations following the sunset, a maximum a few hours after midnight and a rapid decrease at sunrise. The correlation between simulated and measured NO₃ ($r^2 = 0.6\text{--}0.9$) is significant for all seasons.

3.2.2. Losses of NO₃ and N₂O₅

[20] Since NO₃ and N₂O₅ are tightly linked by the equilibrium reaction of NO₃ with NO₂ forming N₂O₅,

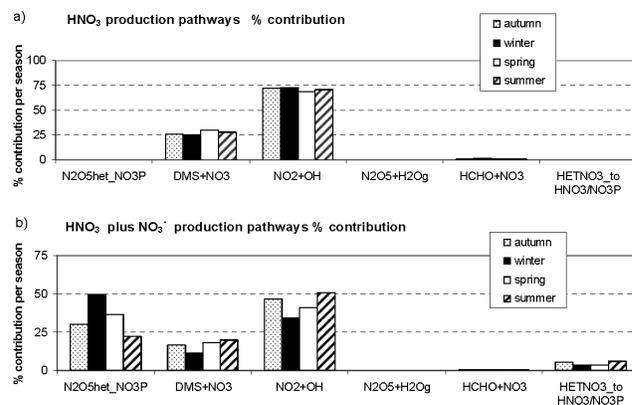


Figure 2. Percent contribution of the different pathways (a) to the production of HNO₃ (diel means) and (b) to the production of the sum of HNO₃ and NO₃⁻ (diel means). N2O5het_NO3p: heterogeneous reaction of N₂O₅ on particles; HETNO3: heterogeneous reactions of NO₃ on aerosols.

hereafter we consider NO₃ and N₂O₅ collectively of which we investigate the loss. Regarding the loss pathways of the NO₃ and N₂O₅ pool other than photodissociation, heterogeneous losses range between 57% during winter and 40% during summer when photochemistry is enhanced. With regard to the gas phase reactions, NO₃ losses both with DMS and with NO (even at very low sub-pptv NO levels, encountered during dusk and dawn) account for about 20% each, followed by that with isoprene (up to 10%). The above figures are seasonal averages and substantial variability is typical for all periods. Note that N₂O₅ loss on water drops will add to the heterogeneous loss terms, particularly during the rainy period. However, the contribution of this process can not be evaluated on the basis of the available experimental data.

3.2.3. Contribution of NO₃ to HNO₃ Formation

[21] Our model calculations show that the main production pathway of HNO₃ is the reaction of NO₂ with OH during daytime (Figure 2a). Depending on the season, this mechanism is responsible for about 68–73% of the HNO₃ formation. In addition to this reaction, the oxidation of DMS by NO₃ radicals contributes 25–30% to the diurnal mean HNO₃ formation. Another nighttime mechanism is the reaction of N₂O₅ with water vapor which may contribute up to 20% to nighttime HNO₃ formation (estimate based on the upper limit of this reaction; simulations not shown here). All other gas phase reactions appear to be of minor importance.

[22] The results show that nighttime chemistry significantly contributes to HNO₃ formation. By considering the combined production of HNO₃ and NO₃⁻, the role of nighttime chemistry is even larger (up to about 65% during winter and more than half (55%) on an annual mean basis; Figure 2b). This contribution is very sensitive to the adopted RH (seasonal mean observations). The reaction probability of N₂O₅ on aerosols, which varies with the particle chemical composition (by up to a factor of 3–4 [Thornton and Abbatt, 2005]), is the major source of uncertainty in these estimates.

[23] During periods with intensive photochemical activity, the homogeneous gas phase reaction of NO₂ with OH is the largest production pathway for HNO₃ plus NO₃⁻ (Figure 2b). It is remarkable that during the winter dark period with low OH levels the N₂O₅ heterogeneous reaction dominates, causing about half the production of the HNO₃ and NO₃⁻ pool (compare the black columns in Figure 2b). Direct heterogeneous reactions of NO₃ play a near-negligibly small role (less than 6%) in this process. Therefore, on an annual basis nighttime and daytime chemistry are of similar importance for the production of the HNO₃ plus NO₃⁻ in the area. The overall HNO₃ plus NO₃⁻ formation rates derived are 0.7, 0.5, 0.4, 0.5 ppbv/day for the summer, autumn, winter and spring, respectively.

[24] It is important to note that on a yearly mean basis about one third (15–65% depending on season) of the nighttime HNO₃ plus NO₃⁻ production at Finokalia is due to the reaction of NO₃ with DMS, a naturally emitted compound. When considering the diurnal mean HNO₃ plus NO₃⁻ production the reaction of NO₃ with DMS contributes about 17% annually. Depending on the season, NO₃ radicals are estimated to be 2.7 (summer), 3.9 (spring), 5.4 (autumn) and 8.5 (winter) times as effective as OH radicals in DMS oxidation. This points to an interesting chemical interaction between anthropogenic and biogenic gases. Emissions of DMS and the relative role of the DMS and NO₃ reaction in the HNO₃ formation maximize during summer. In winter, heterogeneous reactions leading to NO₃⁻ are more effective.

4. Conclusion

[25] Long-term observations of NO₃ radicals have been performed and analyzed in conjunction with continuous JO¹D and O₃ and discontinuous HNO₃, NO₃⁻, isoprene and DMS measurements in a remote marine area in the eastern Mediterranean. Nighttime and daytime chemistry are of similar importance in the formation of HNO₃ and NO₃⁻. They both contribute between 0.1 to 0.2 g-Nm⁻²y⁻¹ to DIN deposition to the ocean.

[26] Nighttime production of HNO₃ plus NO₃⁻, as initiated by NO₃ radicals, accounts for about 50–65% of the total production rate depending on the season. The remainder is produced by the reaction of OH with NO₂ during daytime. Several chemical pathways are responsible for the formation of HNO₃ plus NO₃⁻ during nighttime. On a yearly mean basis, 37% of the HNO₃ plus NO₃⁻ formation is due to the heterogeneous reactions of N₂O₅ and NO₃ on atmospheric particles. However, during summer and autumn, when phytoplankton blooms are frequent, a significant part (about 20%) of the HNO₃ plus NO₃⁻ formation is due to the

reaction of DMS with NO₃, pointing to an unforeseen interaction between anthropogenic and biogenic species.

[27] **Acknowledgment.** We thank T. Klüpfel and D. Perner for assistance with the DOAS instrument, the Greek GSRT for PENED grants to M. V. and E. L.

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