Concentrations of nitrous acid, nitric acid, nitrite and nitrate in the gas and aerosol phase at a site in the emission zone during ESCOMPTE 2001 experiment

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Abstract

Ground-based measurements were performed at the "Expérience sur Site pour COntraindre les Modèles de Pollution atmosphérique et de Transport d'Emissions" (ESCOMPTE) field site E3 (Realtor) about 30 km north of the urban environment of Marseille and east of the industrial centre Berre pond to investigate the formation of nitrous and nitric acid and to detect the distribution of reactive N-species between the gas and particle phase during photochemical pollution events. A wet denuder sampling for gases followed by a steam jet collection for aerosols was both coupled to anion chromatographic analysis. The analytical system provided data continuously with 30-min time resolution between June 13 and July 13, 2001. Indications for heterogeneous formation of nitrous acid during nighttime and daytime on ground and aerosol surfaces were found, the average HNO_2/NO_2 ratio was 6%. Highest concentrations were observed during two episodes of strong pollution accumulation when sea breeze transported industrial, traffic and urban pollution land-inwards. After nocturnal heterogeneous formation (about 0.1 ppb_v h^{-1} were estimated corresponding to increasing HNO_2/NO_2 ratios) and accumulation processes up to 1.2 ppb_v HNO_2 were observed. Their photolysis produces up to $5–9 \times 10^6$ OH cm^{-3} s^{-1} and will contribute significantly to initiation of the daily photochemistry in the lowest part of the troposphere. For the key tropospheric species, HNO_3 daily peaks up to 4 ppb_v were detected.
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1. Introduction

A major field experiment took place in the southeast of France within the frame of "*Ex*périence sur *S*ite pour *CO*ntraindre les *M*odèles de *P*ollution atmosphérique et de *T*ransport d'*E*missions" (ESCOMPTE) from June to July 2001 to produce a relevant set of emission, meteorological and chemical data for testing and evaluating regional pollution models. The chemical and dynamical process studies were done over a 120×120-km area in the region Marseille–Berre pond with numerous industrial and urban sources of pollutants. Five pollution episodes were documented by a large set of instruments, involving ozone lidars, wind profiler, radiosonde systems, a network of ground stations, ship-borne, balloon-born and airplane measurements (Durand et al., 2002). Eighteen chemical stations were located in the emission, intermediate or remote zone to follow the pollutant plume and to investigate its chemical time evolution in a 'lagrangian mode'. The campaign strategies and experimental set up are described in detail in Cros et al. (2004). In the present paper, we focus on chemical measurements done by our group at the emission station E3 Realtor. High-pollution levels were observed there not only during periods of sea breeze, transporting coastal industrial and urban pollution land-inwards, but also under moderate wind and channelled plume regimes. This leads to intense photochemical activity, evidenced by elevated ozone concentrations, aerosol levels and photochemical active species like nitrous and nitric acid. In addition, the emission of traffic in Marseille and on the highways around is an important contributor to atmospheric pollution in open areas. Besides, NO_2 is transferred to a complex mixture of other nitrogen compounds which have great variability in their atmospheric stability. The concentration and composition of NO_y compounds show a wide variation and are dependent on meteorological and atmospheric chemical conditions. The chemistry and atmospheric behaviour of reactive nitrogen compounds is detailed and described among others in Finlayson-Pitts and Pitts (2000) and Lammel and Cape (1996).

An important mechanism for the removal of nitrogen oxides and odd hydrogen from the atmosphere is the gas phase formation of HNO_3, beside O_3 and H_2O_2 one of the most important photochemical reaction product. In reaction with ammonia. NH_4NO_3 is formed, until removal by deposition a major contributor to the degradation of visibility. The aerosol formation is affected by ambient temperature, relative humidity and the concentration of ammonia. The deposition of HNO_3 and nitrates contributes to acidification of sensitive ecosystems (e.g., Nielsen et al., 1996).

Nitrous acid is an important trace species for understanding the tropospheric oxidant chemistry and already, since more than 20 years, models have shown that HNO_2 is accumulated during nights and that after sunrise the HNO_2 photolysis can cause an "OH push" (e.g., Platt and Perner, 1980; Platt, 1986; Jenkin et al., 1988; Harrison and Kitto, 1994; Calvert et al., 1994; Staffelbach et al., 1997). Recent estimations show also a possible permanent OH-contribution during the day (Aumont et al., 2003). Results from the BERLIOZ experiment around Berlin, Germany, showed clearly that the peak OH formation rate by HNO_2 photolysis is comparable to the one by ozone photolysis at noon and the integrated OH production over 24 h showed that the photolysis of HNO_2 can contribute up to 20% of the total hydroxyl radical amount (Alicke et al., 2003). Measurements in Milan (Febo, 1999; Alicke et al., 2002) and Rome (Wiesen, 2002)

confirm that during the first 4 to 6 h after sunrise, HNO_2 photolysis is the most important OH source in the lowest part of the troposphere.

The HNO_2 formation process is of crucial interest and is not completely clear up to now. The observed high HNO_2 concentration in the atmosphere cannot be explained by homogeneous formation and direct emission from combustion processes (Kurtenbach et al., 2001). As a main source of HNO_2, the heterogeneous reaction of NO_2 with water on surfaces is assumed:

$$(NO_2 + NO_2 + H_2O)_{ads} \rightarrow (HNO_2 + HNO_3)_{ads} \rightarrow (H^+ + NO_3^-)_{aq} + (HNO_2)_{gas}.$$

(1)
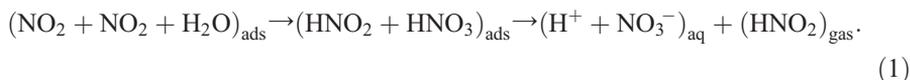
Laboratory studies and field measurements have shown that available surfaces have different catalytic properties (e.g., Svensson et al., 1987; Kleffmann et al., 1998; TenBrink and Spoelstra, 1998; Kalberer et al., 1999; Stadler and Rossi, 2000; Schurath, 2001; Gutzwiller et al., 2002; Geiger et al., 2002). Present available models (e.g., Sahm et al., 1997; Stockwell et al., 1997; Kuhn et al., 1998; Vogel et al., 2002; Aumont et al., 2003) significantly underestimate the daytime concentration of HNO_2. For a correct description of the chemical processes that lead to ozone formation, the inclusion of the heterogeneous HNO_2 chemistry in photochemical models is essential.

A variety of analytical methods for both HNO_3 and HNO_2 have been developed and an overview is given in Genfa et al. (2003). HNO_2 was first time detected in the atmosphere by Perner and Platt (1979), but methods for detection in the lower ppt_v range are developed only recently.

Research on the temporal variation in both composition and concentration and on the interaction of reactive gases and aerosols in the atmosphere requires sampling and analysis systems for the determination of gases and particles with high time resolution. An automated monitoring system, applicable for measurements at urban and rural sites and for both gases and particulate matter was developed and used in the ESCOMPTE experiment. This was based on a wet denuder and a particle collection system in combination with an ion chromatography (IC) unit which allows among others the simultaneous determination of HNO_2, HNO_3, HCl, chloride, nitrite, nitrate and sulfate.

2. Experimental

The site Realtor (43°29′ N, 5°20′ E) near the village Calas belongs to the best-equipped chemical stations located along trajectories generally followed by the air masses during meteorological conditions investigated during the ESCOMPTE campaign. Aerosol size distribution, optical, chemical and physical properties of the aerosol, peroxides and, aldehydes were measured at this site. Results will be given in Cachier et al. (2004) and Cousin et al. (2004).

From June 13 through July 13, 2001 measurements were also done by our group at the site Realtor. We measured NO, NO_2, NO_y, O_3, SO_2 (time resolution: 30 s), HNO_2, HNO_3, aerosol nitrite, nitrate, sulfate and chloride (time resolution: 30 min), meteorological parameter (wind velocity, wind direction, temperature, relative humidity (RH), photolysis

frequency of NO_2 ($J_{(NO_2)}$, starting at 28 June), global radiation/albedo with time resolution of 30 s, aerosol mass/inorganic composition of total suspended particles (TSP, time resolution: 12 h), NMHC (airmoVOC) and vertical ozone profiles (LIDAR). Beside the LIDAR van, all equipment was located on top of a hill (208 m above sea level) covered by Mediterranean natural landscape. The vertical ozone profiles and the concentrations of VOC were measured during the Intensive Observation Periods (IOPs), the data will not be discussed in this paper. For calibration of VOC measurements, a certified 74 compound standard (NCAR, USA) was used. The LIDAR data were in very good agreement with the results from ozone measurements obtained during two quality control aircraft measurements over the field site. Results will be presented elsewhere. All other parameter were recorded continuously during the whole experiment with a data completeness of 90%. All data for the IOPs had been transferred to the ESCOMPTE database.

Before the ESCOMPTE campaign, the analysers for O_3 (Dasibi Model 1108, UV absorption, detection limit 1 ppb_v), NO/NO_x (Ecophysics CLD 770 ppt and photolytical converter, detection limit 50 ppt_v), NO/NO_y (Ecophysics CLD 770 ppt and gold converter, detection limit 50 ppt_v) and SO_2 (Thermo Environmental Instruments, detection limit 50 ppt_v) had been checked and inter-calibrated against transfer standards at the IMK-IFU calibration centre, (Germany). The IFU system is calibrated against primary U.S. NIST standards. For the daily calibration procedures during the experiment, a calibrator (S 100 Environics with ozone generator) was used. The zero air was produced by Ecophysics Pure Air Generators (PAG 03). The analysers were housed in a van and operated in air conditioned environment.

The use of a denuder system allows the diffusion-based collection of trace gases with a separation from their particulate counterparts (Acker et al., 2003). Continuously wetted denuder are especially attractive because the collection surface is constantly renewed. This offers the possibility to perform the analysis continuously or semi-continuously on-line with a suitable analyser/detector. Among others available, wet denuder techniques are major reviewed in Dasgupta (2002) and Slanina et al. (1992).

A wet effluent diffusion denuder (WEDD) in the parallel plate design was operated at Realtor continuously to sample nitrous and nitric acid. The approach for this WEDD was adopted from Simon and Dasgupta (1993), Neftel et al. (1996), Zellweger et al. (1999) and Löflund et al. (2001). A silica-coated glass surface realised continuously a thin homogeneous water film (about 0.5 ml pure deionised water/min). The effluent flows down by gravity and is collected by a ring-shaped frit before transportation to the ion chromatography (IC) system (Acker et al., 2001).

In the WEDD, the sample air residence time is very short (<0.5 s) and the solution residence time is short as well (<2 min), interferences by NO_2 and SO_2 will not be expected. For artefact discussion of this denuder type, see Neftel et al. (1996) and Genfa et al. (2003). The use of pre-concentration columns necessitate the use of water as the denuder liquid, the use of carbonate in the denuder liquid (as proposed by Zellweger et al., 1999) leads to incomplete capture of desired analyte ions during pre-concentration.

The wet denuder system was extended by a steam jet chamber to detect the nitrite and nitrate (and sulphate and chloride) concentrations in the atmospheric aerosol phase also with a high time resolution. The aerosol chamber is constructed according to systems described by Simon and Dasgupta (1995), Khlystov et al. (1995) and Löflund et al. (2001).

At the top of the aerosol chamber, water steam is added to the air flow and the aerosol particles grow to little droplets. The growth chamber is spiral, hosted in a vacuum vessel to hold the temperature and followed by a tubular flow reactor and than by a cyclone to separate the droplets.

The solutions (deionised water) containing the scavenged acids and aerosol compounds are collected in flow through cells. Via a low-pressure valve, the analytes are pumped
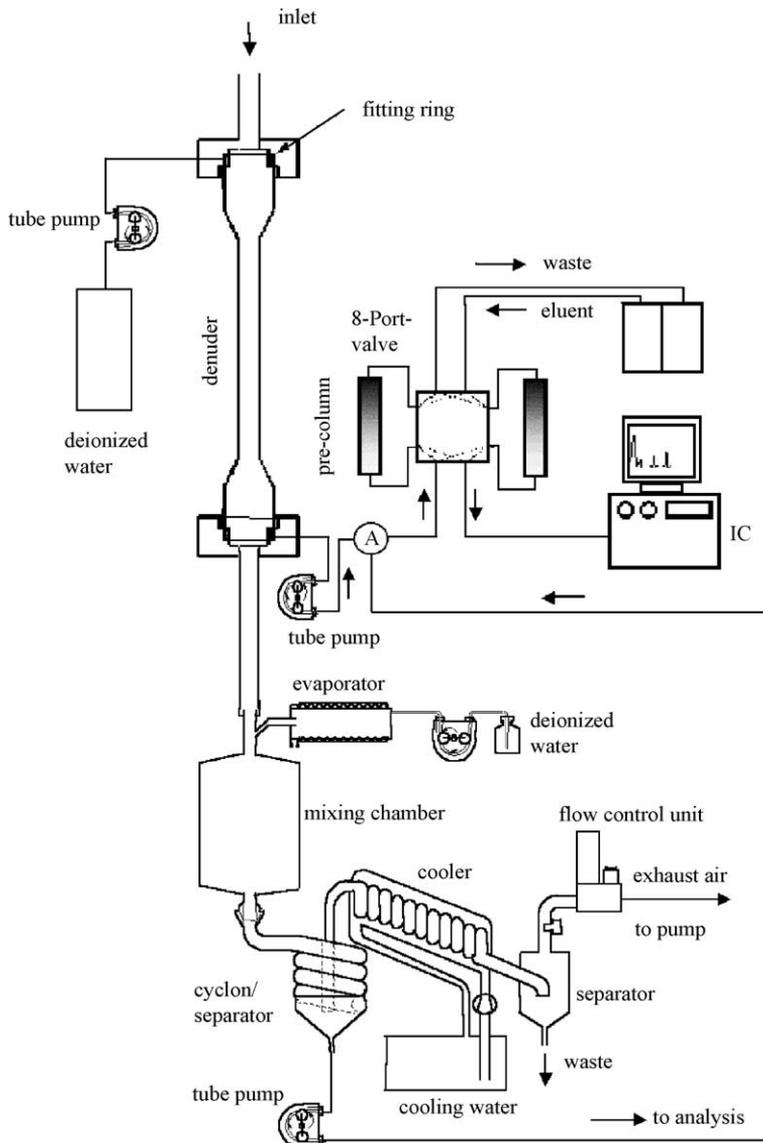

Fig. 1. Schematic diagram of the BTU-Cottbus wet effluent diffusion denuder/steam jet collector/ion chromatography system.

peristaltically through one of the two pre-concentration columns (TAC-LP1) that are connected with a high-pressure 8-port valve. Alternately, one of this pre-columns is used for pre-concentration while the other is eluted by the eluent (1.8 mM Na_2CO_3/1.7 mM $NaHCO_3$) for ion chromatographic analysis (IC, DIONEX DX500 with conductivity detection after suppression, AS4A/AG4A 4 mm columns).

The airflow through the denuder/jet steam is 10 l/min and realised constant by calibrated mass flow controllers. Using 30-min sampling time, concentrations of 0.010 µg m^{-3} of HNO_2/NO_2^- and HNO_3/NO_3^- can be reliably recorded (limit of quantification). To avoid sampling losses, our system had a very short Teflon inlet in the height of about 3 m above ground as proposed by Neumann et al. (1999). For stable analytical conditions, the whole system is operated in an air-conditioned environment at about 20 °C and combined with an uninterruptible power supply. The collection efficiency of the wet denuder was determined using gas-standards generated via a HNO_3 permeation source or a HNO_2 generation system similar to that of Febo et al. (1995). For different volume flows (5–10 l/min) of the calibration gas through the denuder, the collection efficiency was found to be between 95.6% and 99.5%. A schematic diagram of the WEDD-steam jet-IC system is given in Fig. 1.

Our WEED method was successfully proven by intercomparisons with other wet chemistry techniques: (a) rotating annular wet denuder coupled with IC (as described in Oms et al., 1996) and (b) scrubbing in mixing coils coupled with a dual channel DNPH derivatisation/High-Performance Liquid Chromatography technique (as described in Zhou et al., 2002) during international field campaigns (INTERCOMP2000 in Melpitz, Germany; NITROCAT in Rome, Italy). The very good agreement in structure and concentration levels during nighttime and daytime between our WEED HNO_2 measurements and the HNO_2 data obtained with Differential Optical Absorption Spectroscopy (DOAS, e.g., Alicke et al., 2002) during the NITROCAT Rome campaign in May–June 2001 just before ESCOMPTE is another positive result in quality assurance discussion for available atmospheric nitrous acid measurements, see Acker et al. (2004).

The High Volume Sampler (Digitel) used for TSP aerosol characteristics at the ESCOMPTE site Realtor was compared earlier with identical devices running side by side during the INTERCOMP2000 experiment and during the Berlin city aerosol project 2001/2002 with excellent results. The quality of our analytical work is certified also in reports of the laboratory intercomparisons of synthetic rain samples organized within the Global Atmospheric Watch Program of the World Meteorological Organisation (GAW WMO), in which we take part annually.

3. Results and discussion

During the ESCOMPTE experiment, different pollution episodes were observed, the meteorological conditions are described in detail in Cros et al. (2004). The concentrations of gaseous HNO_2 and HNO_3 were recorded continuously at the site Realtor with a time resolution of 30 min over a period of 4 weeks. An overview of these results of the complete campaign can be seen in Fig. 2. Daily peaks in HNO_3 were observed at noon ranging between 0.2 ppb$_v$ under mistral conditions and 4 ppb$_v$ in periods with high photo-
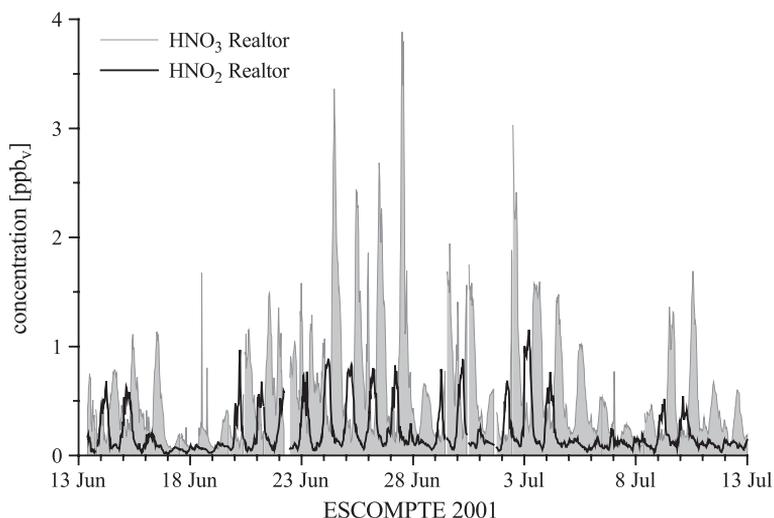
Fig. 2. Gas phase HNO_2 and HNO_3 concentrations measured with the WEDD at the site Realtor during the whole experiment time (time resolution: 30 min).

chemical activity. The concentration of HNO_2 is generally in low ppt_v levels during the day and rises to low ppb_v levels during the night. Dependent on the NO_2 concentration around the investigated site Realtor, different high values for HNO_2 were observed. A strong formation and accumulation of HNO_2 was observed after 2000 UTC until about 0700 UTC. The HNO_2 concentration is close connected with meteorological conditions (day and night chemistry, vertical mixing processes). The morning break up of the mixing layer causes dilution of HNO_2-rich air by entrainment of fresh air from layers above the boundary layer. Besides, the photolysis of HNO_2 becomes important. In Fig. 3, the average diurnal pattern of HNO_2 for the whole experiment time is given. On average, a maximum of 0.5 ppb_v between 0100 and 0600 UTC was found. The high scattering (0.15–0.85 ppb_v)
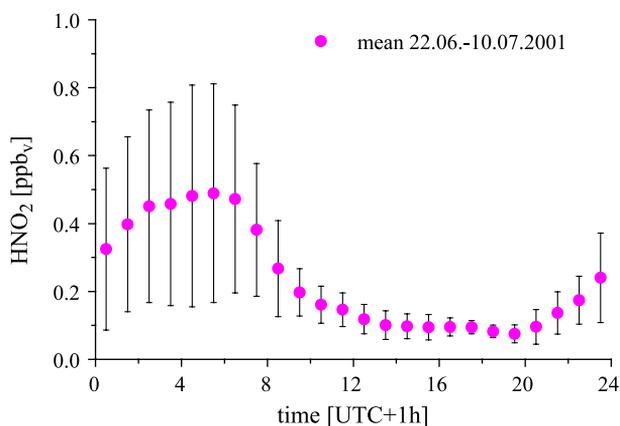

Fig. 3. Diurnal variation in HNO_2 concentration at the station Realtor averaged over 3 weeks.

around this value is caused by different levels of the precursor NO_2 (2–35 ppb$_v$) and of the relative humidity (62–100%) as well as by differences in the stability of the boundary layer (see also Fig. 4). Investigations in Milan and Rome (Febo, 1999; Wiesen, 2002) have
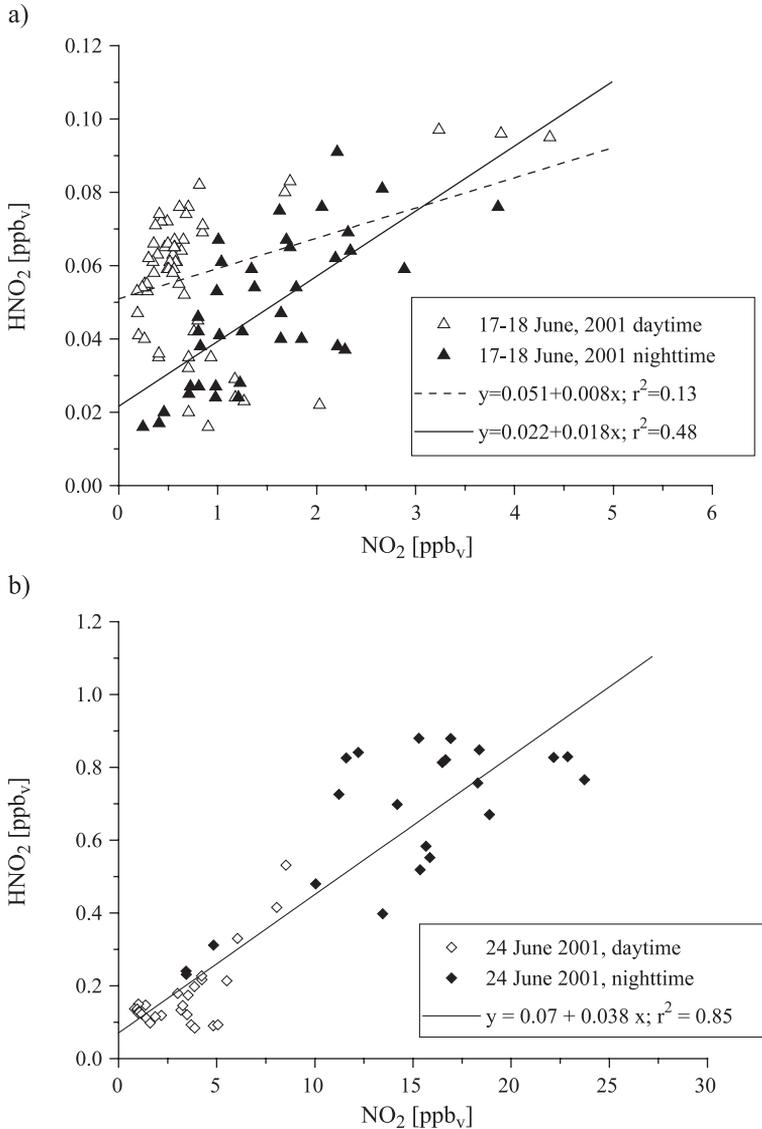

Fig. 4. (a) Correlation between nitrous acid and its precursor nitrogen dioxide at the site Realtor on 17 and 18 June 2001. Under Mistral conditions, high wind speeds occurred during day and night (5–12 m s^{-1}). The best fits for the correlation between both compounds are given as dashed (daytime) and solid (night time) line. (b) Correlation between nitrous acid and its precursor nitrogen dioxide at the site Realtor on 24 June 2001. During the pollution event (IOP2), low wind speeds occurred (0.5–4 m s^{-1}). The best fit for the correlation between both compounds (day and night) is given as solid line.

shown that the diurnal variation of HNO_2 is well correlated to the diurnal variation of the natural radioactivity element Radon.

The HNO_2 concentrations were positively correlated with those of NO_2, with $r^2=0.72$ if all data (day and night) are used. A separation of the data into sunlight and darkness hours did not improve the correlation. But different meteorological regimes cause significant differences in the source receptor relationship. Fig. 4 illustrates this behaviour. On 17 and 18 June 2001, air masses connected with strong NW winds (Mistral situation) reached the Realtor site causing high turbulence and a low correlation between HNO_2 and its precursor. The relative humidity reached only 50% and 75% during the nights. Winds of ~ 5 m s^{-1} were observed between 1900 and 0900 UTC; during the day, wind speeds were higher (~ 10–12 m s^{-1}). Much lower wind speeds were measured on June 24 and HNO_2 and NO_2 are highly correlated (night and day). Very moderate winds (~ 1 m s^{-1}) during the night reached the site from SE directions with RH between 80% and 100%; the wind direction changed to SW during the day with velocities of ~ 5 m s^{-1}.

Despite a high variation in the HNO_2 to NO_2 ratio, on average it reached few percent (6 ± 5), similar to values found by Stutz et al. (2002) in Milan (5%) but significantly higher than the contribution from direct emissions. At a high traffic density on average, a HNO_2 to NO_x ratio of 0.8% is observed (Kurtenbach et al., 2001). As expected, the influence of NO was found to be negligible on the HNO_2 formation at Realtor site (correlation between HNO_2 and NO, $r^2=0.17$).

Highest concentrations in nitrous and nitric acid and of their particulate counterparts were observed during two episodes of strong pollution accumulation when sea-breeze transported industrial, traffic and urban pollution land-inwards. One of the Intensive Operating Periods of the ESCOMPTE experiment was of 6 days duration (21 June to 26 June, IOP2) and began with a moderate NW/W wind (an end of Mistral situation), clear skies and hot temperature (>30 °C). Marseille and Berre plumes extended towards the east and over the sea. The highest surface ozone concentrations were found in the most eastern part of the ESCOMPTE domain. In the afternoon of June 23, the meteorological conditions changed significantly. Three days of very hot temperature (>34 °C) and high surface concentration in ozone (about 100 ppb$_v$ in the whole domain) were observed. On June 25, the southerly flow was well developed and an about 1-km-deep sea breeze front extends from 42°N to 44.2°N. Around noon, 30 km inland downwind Marseille, an ozone plume was clearly identified with ozone concentrations as high as 130 ppb$_v$. In the same area, a plume of NO_x and NO_y was observed. A map of the ESCOMPTE domain and more details of meteorological and pollution situation are given in Cros et al. (2004) and Cachier et al. (2004). At the Realtor site, 118 ppb$_v$ O_3 on June 24 and 130 ppb$_v$ O_3 on June 27 were found at noon. Maximum in NO_2 and NO_y occurred between midnight and noon reaching 20 and 30 ppb$_v$, respectively. Peaks in NO were found between 0500 and 0900 UTC, presenting fresh emissions from morning traffic at highways few kilometres around the site. While up to 5 ppb$_v$ NO were registered on the weekend days June 23 and 24, in the morning hours of the following workdays up to 20 ppb$_v$ were observed. In addition, a significant change in the aerosol mass (derived from High Volume TSP sampling) was found, increasing from 30 μg m^{-3} (12 h mean 0500–1700 UTC) on June 21 to 53 μg m^{-3} on June 26, 2001. The pollution situation at Realtor for this IOP2 is documented in Fig. 5.

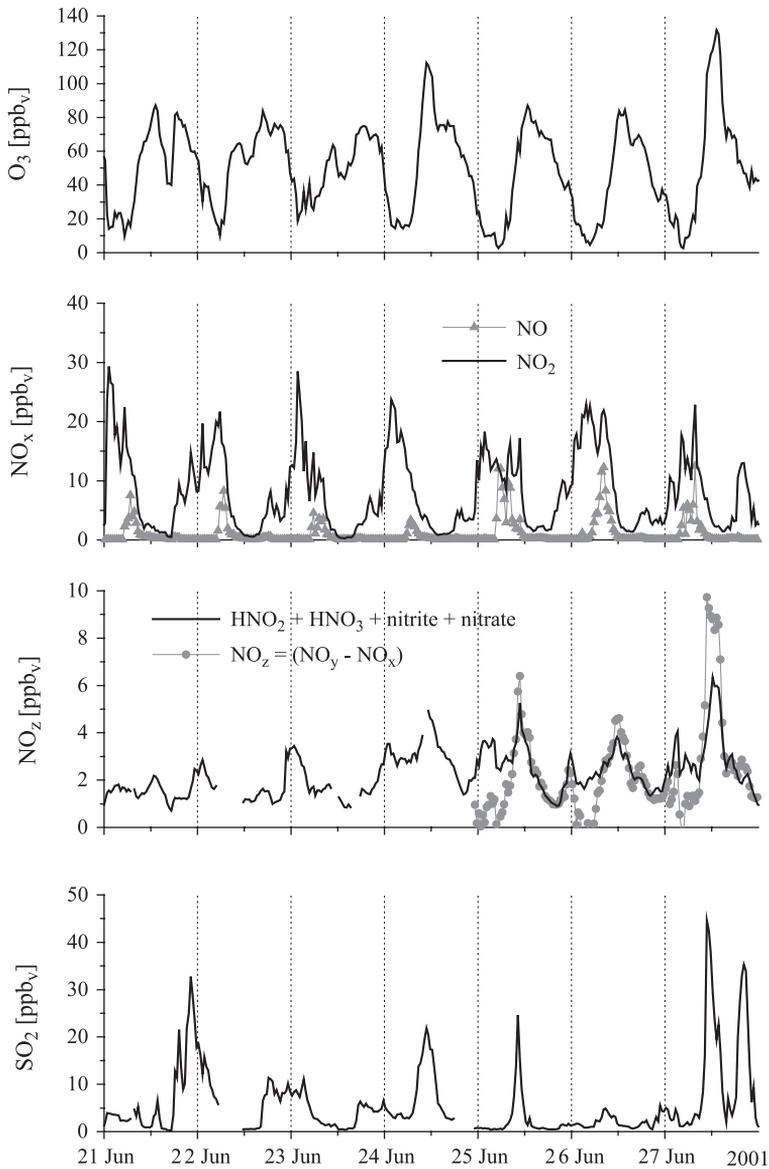Fig. 5. Time series of O_3, NO, NO_2, NO_z (calculated from $NO_y - NO_x$ and as a sum of selected measured NO_z parameters (nitrite and nitrate data were "converted" into ppb_v)) and SO_2 during a photochemical pollution event (IOP2) observed at the site Realtor.

Evidence for a photochemical episode was found also because of increasing nitric and nitrous acid concentrations, see Figs. 2, 6 and 7). While in the beginning of the event on 21 June 0.6 ppb_v HNO_2 and 1.5 ppb_v HNO_3 were measured, on June 24 concentrations of 0.9 ppb_v nitrous acid and 3.5 ppb_v nitric acid were observed at 0500 and 1100 UTC, respectively.
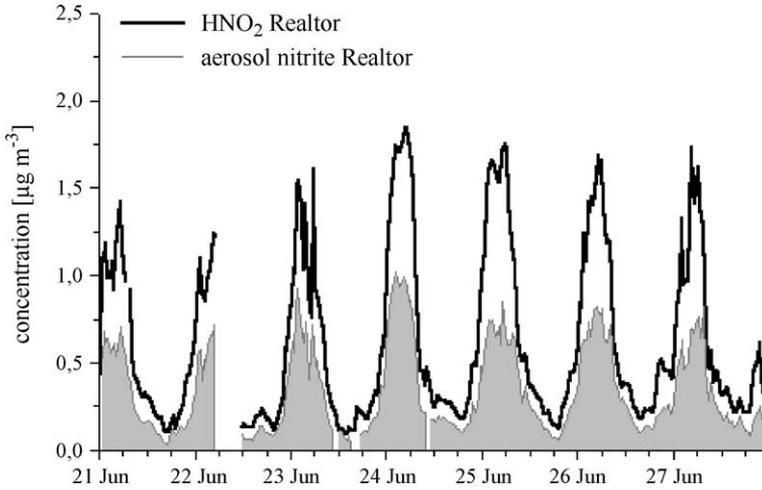
Fig. 6. Temporal variation of nitrous acid (solid line) and aerosol nitrite (grey area) during a pollution event at the site Realtor (IOP2).

For the period between 21 June and 27 June 2001, the nitrous acid mixing ratios increased steadily after sunset. In Fig. 8, this is shown for the two nights 21/22 and 25/26 June, also the corresponding increase in the HNO_2/NO_2 ratio is presented. Based on this linear HNO_2 increase during a time interval (t_2-t_1), the conversion frequency from NO_2 into HNO_2 was estimated. Since the mechanism summarised in reaction (1) is first order in NO_2, the HNO_2 formation is proportional to the NO_2 concentration. Assuming that there is
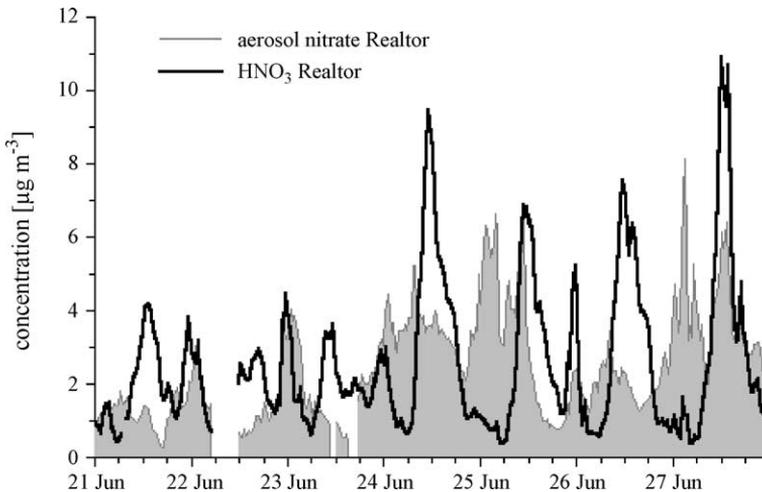

Fig. 7. Temporal variation of aerosol nitrate (grey area) and gaseous nitric acid (solid line) for a period of high photochemical activity at the site Realtor (IOP2).
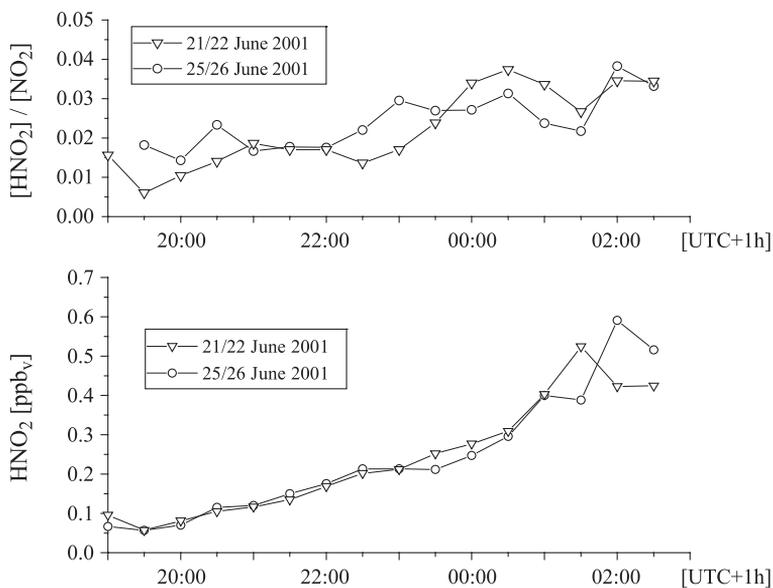
Fig. 8. Formation of HNO$_2$ during the nights of 21/22 and 25/26 June 2001 at the site Realtor. The lower graph shows the monotonic increase of HNO$_2$ from 1800 to 0100 UTC. The upper graph shows the corresponding increase in the HNO$_2$/NO$_2$ ratio.

no dependency on gas phase water as suggested by Kleffmann et al. (1998), the average nighttime conversion frequency was determined by:

$$F_{HNO2night} = ([HNO_2]_{(t_2)} - [HNO_2]_{(t_1)})/(t_2 - t_1)[NO_2]_{night}.$$

The calculated value was 0.009 (ppbHNO$_2$)/(h(ppbNO$_2$)) between 2000 and 0100 UTC. Because of very low NO concentrations (see Fig. 5), a contribution from direct HNO$_2$ emission can be neglected. The efficiency of heterogeneous NO$_2$-to-HNO$_2$ conversion found at Realtor is comparable to those observed at different other urban and rural sites (e.g., Stutz et al., 2002; Alicke et al., 2002; Acker et al., 2003).

It is assumed that nitrous acid is formed during the day by the same mechanism as during the night, but owing to the fast photolysis into OH with τ_{HNO_2} ~10 min at noon the measured mixing ratios are much lower. The lifetime of HNO$_2$ can be considerably longer during cloudy periods, or at high solar zenith angles (Stutz et al., 2000; Acker et al., 2001). Unexpected (from the photostationary state) high mixing ratios of 100–400 ppt$_v$ were found in the daytime in urban (e.g., Febo, 1999; Wiesen, 2002) as well in rural regions (e.g., Zhou et al., 2002), indicating that an effective heterogeneous HNO$_2$ formation is occurring also at daytime. Until now, it is not clear which special surface characteristics of the ground and aerosol particles may support the formation (Stutz et al., 2002). During the ESCOMPTE 2001 experiment also at noon about 100 ppt$_v$ nitrous acid were measured, 20 times higher than the quantification limit of the used WEDD method.

A sensor to measure the photolysis frequency of NO$_2$ was installed at the site Realtor on 28 June being in operation until the end of the campaign. The photolysis frequency of

nitrous acid was calculated using the measured $J_{(NO_2)}$ following the approach described in Alicke et al. (2003):

$$J(HNO_2) = 0.189 \times J(NO_2) + 8.433 \times 10^{-2} \times [J(NO_2)]^2.$$

Results for 03 July, 2001 (a day in the IOP3) are given in Fig. 9. The concentrations of HNO_2 on that day were the highest measured during the whole ESCOMPTE experiment at the site Realtor, 1.2 ppb_v were observed at 0400 UTC, as can be seen also in Fig. 9. The mixing ratios of other trace gases (NO, NO_2, O_3) are shown as well. The photolysis of HNO_2 started at about 0500 UTC, and from the measured HNO_2 concentrations and $J_{(HNO_2)}$ the OH formation rates were calculated reaching a peak around 0700 UTC. The
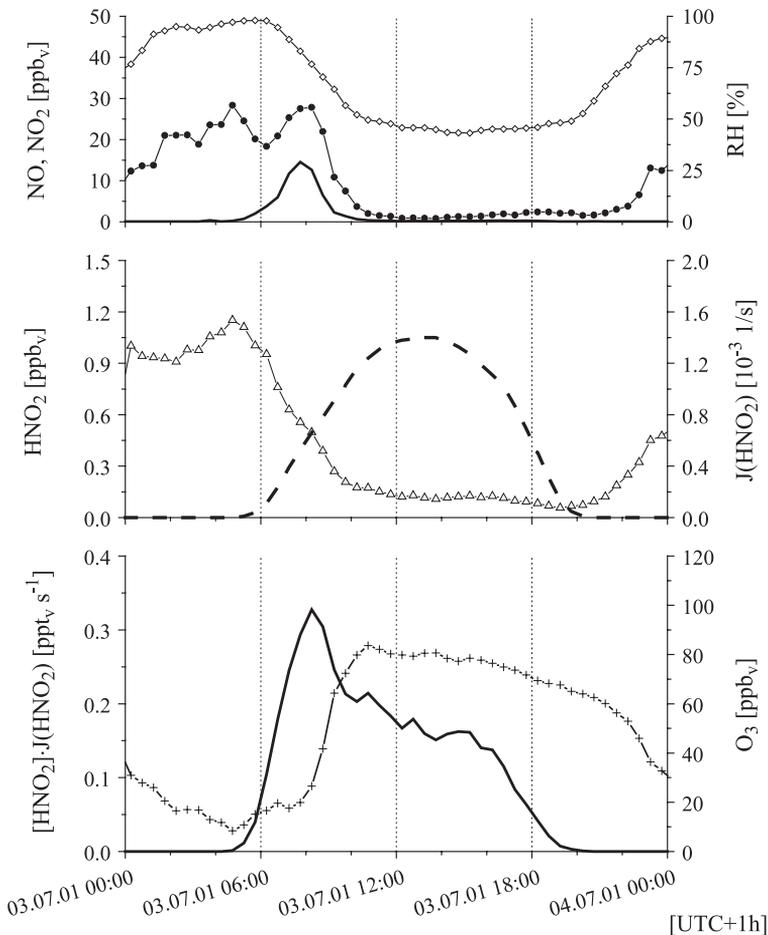

Fig. 9. Realtor data of the 03 June 2001. The upper graph shows the NO (solid line) and NO_2 (closed circles) concentrations and the relative humidity (open diamonds). In the middle graph, the HNO_2 mixing ratios (open triangles) and the photolysis frequency J(HNO_2) (dashed line; calculated from $J(NO_2)$) are given. The lower graph shows the variation in ozone concentration (line with crosses) and the calculated OH production rate from HNO_2 photolysis (solid line).

morning photolysis can form up to $5–9 \times 10^6$ OH cm^{-3} s^{-1} (in Milan $1–3 \times 10^7$ were found by Alicke et al., 2002) and lasts few hours after sunrise. Because of its lower dissociation threshold, the photolysis of HNO$_2$ accumulated during the night is the first mechanism forming OH in the morning, followed by the photolysis of formaldehyde (in polluted regions the most important source of OH, see Alicke et al. (2002); but not measured at Realtor). The photolysis of O$_3$ becomes important later in the day, when actinic fluxes in the lower UV occur. But it should also be noted that HNO$_2$ photolysis is important only in the lowest few hundred metres of the atmosphere. While morning photolysis is often restricted to the nighttime boundary layer, the fast photolysis later during the day does not permit a transport of HNO$_2$ into the upper part of the daytime boundary layer (Alicke et al., 2002). Using our 3 m HNO$_2$ mixing ratios as a representation of the whole boundary layer (at night ~100 m) will lead to an overestimation of the nitrous acid formed by about 60% (Stutz et al., 2002), and micrometeorological data should be considered when analysing trace gases that interact with the ground, because a combination of a deposition of NO$_2$ and HNO$_2$ and a conversion of NO$_2$ to HNO$_2$ at the ground is expected.

However, it is also considered that the local ozone production is a major contribution to the ozone plume concentration and the photolysis of the nitrous acid after sunrise is expected to be of major importance for initiating the daily photochemistry.

Thus, atmospheric budget research of reactive nitrogen compounds and developments of sampling and analytical methods are of big interest. Special attention was given to the distribution between nitrous and nitric acid respectively and their particulate counterparts. After separation of the acids from the gas phase—the WEED works as a selective sink—the particles were scavenged by a jet steam and aerosol nitrite and nitrate measurements have been carried out continuously.

It was observed that at the station Realtor most of the nitrite (~65%) is present as HNO$_2$ in the gas phase (see Fig. 6). The amount of aerosol nitrite found (~35% of the total) also indicated that wet aerosols have to be taken into consideration as a surface for the heterogeneous formation of HNO$_2$, although formation on the ground surface is expected to be the main source of HNO$_2$ (Veitel, 2002; Febo, 1999; Wiesen, 2002). The release of nitrous acid into the gas phase depends mainly on particle surface characteristics. The formation on atmospheric aerosols is very difficult to quantify. Under stable atmospheric conditions, the contribution is hidden by the generation flux from the ground, under strong vertical mixing by the change of the mixing height.

The results of the simultaneous measurements of gaseous nitric acid and particulate nitrate are presented in Fig. 7. A formation of HNO$_3$ parallel to that of HNO$_2$ concerning Eq. (1) could not been seen and it has to be assumed that nitric acid, because of its high solubility and adsorption ability, will remain in or scavenge into the condensed phase. The relative humidity was between 63% and 100% in the time periods 2000–0600 UTC. During the day, other production mechanisms for nitric acid are more important. On average 10 times more soluble nitrate was found in the aerosol phase compared to nitrite. The increase in nitrite during the nights is attended by a slight increase in nitrate (or adsorbed HNO$_3$), indicating the postulated heterogeneous formation reaction for nitrous acid courses.

The differences in the correlation of HNO$_2$ and HNO$_3$ to their particulate counterparts can be explained by differences in main formation mechanism (oxidation, gas-to-particle conversion, heterogeneous processes on surfaces), deposition velocities, photolysis rates,
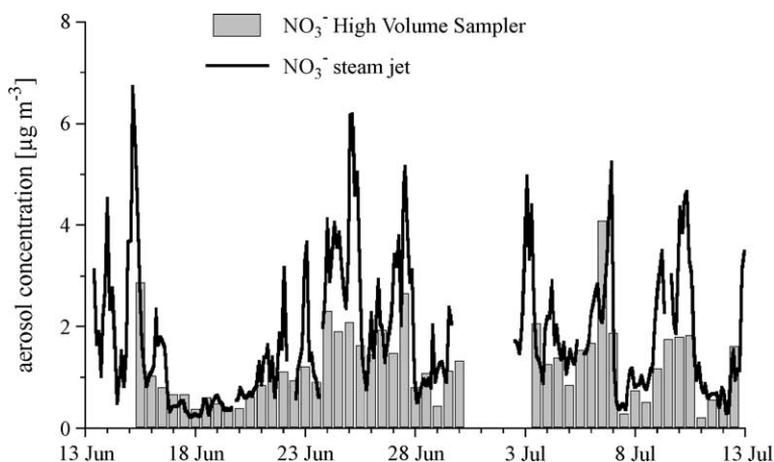
Fig. 10. Comparison of aerosol nitrate measured by high volume filter sampling (time resolution: 12 h) and aerosol steam jet collection (time resolution: 30 min) over the whole 2001 experiment time at the site Realtor.

solubility and dissociation, residence time in the troposphere and the different dependency on boundary layer meteorology. For details, see Harrison and van Grieken (1998) and Warneck (2000).

The aerosol nitrate data in Fig. 10 were derived from daily PM_{10} measurements (by Digitel high volume sampler) as well as from steam jet measurements. The latter data have a time resolution of 30 min and document the high fluctuation in aerosol composition. A comparison between aerosol nitrate scavenged by the water vapour in the steam jet and the aerosol nitrate collected on quartz fibre filters (Munktel) with the High Volume Sampler is shown in Fig. 10. Beside the different time resolution (0.5 and 12 h), the data of both methods are very well correlated in structure and concentration level. For some periods, on average, higher nitrate concentrations were detected by the steam jet, indicating possible NH_4NO_3 losses by evaporation processes during filter sampling as observed at higher temperatures (Schaap et al., 2002).

4. Conclusions

A technique to measure simultaneously atmospheric concentrations of nitrous and nitric acid in the gas phase and their counterparts in the particle phase based on wet effluent denuder–steam jet–ion chromatography combination was successfully used at the ESCOMPTE site Realtor. Episodes of strong pollution accumulation were observed at this site when emission plumes from Marseille, the industrial complex Berre-pond and the traffic on the highways were transported land-inwards. The observed high concentrations in ozone, nitric and nitrous acid are a result of transport, diffusion, chemical transformation and accumulation processes.

Our observations lead us to the conclusion that HNO_2 is formed on wet surfaces of the ground, vegetation and aerosols. On average, a HNO_2 to NO_2 ratio of 6% was found (comparable to other measurements at urban, suburban and rural sites), which cannot be

explained by homogeneous formation and direct emission. After nighttime formation and accumulation of this heterogeneous formed species (up to 1.2 ppb$_v$) and when OH production rates from other sources (photolysis of O_3 and formaldehyde) are slow, the photolysis of HNO_2 can be an OH source of greatest importance in the lowest part of the troposphere (up to 5–9×10^6 OH cm^{-3} s^{-1} were estimated for Realtor site) and will contribute considerably to the initiation of the day photo-chemistry. The diurnal variation in HNO_2 mixing ratios is dominated by NO_2 levels, photolysis, and vertical mixing. The presence of HNO_2 at concentrations higher than that predicted by most models and its low but persistent presence in the daytime require inclusion of heterogeneous HNO_2 chemistry in chemistry transport models. Our measurements are highly valuable within the frame of the ESCOMPTE campaign, which is mainly devoted to study photochemical pollution episodes.

Acknowledgement

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