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Environmental Chemistry 2006, *4*, pp. 242–255. doi:10.1071/ EN07023

The editor wishes to alert readers of the following technical error:

Page 247, 2nd column, *x*-axis of Fig. 5: $(J(NO_2) (10^{-3} \text{ s}^{-1}))$ should read $(J(NO_2) (\text{s}^{-1}))$.



Fig. 5. Correlation of $J(NO_2)$ against the extra (missing) daytime source.

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Atmospheric variation of nitrous acid at different sites in Europe

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Environmental context. Nitrous acid (HNO₂) is an important source of the hydroxyl radical (OH[•]), the most important daytime oxidising species that contributes to the formation of ozone as well as of other secondary pollutants in the troposphere. Understanding the sources and sinks of HNO₂ is of crucial interest for accurately modelling the chemical composition of the troposphere and predicting future trace gas concentrations.

Abstract. Nitrous acid and several other atmospheric components and variables were continuously measured during complex field experiments at seven different suburban and rural sites in Europe. HNO₂ is mainly formed by heterogeneous processes and is often accumulated in the nighttime boundary layer. Our results confirm that the photolysis of HNO₂ is an important source of the hydroxyl radical, not only in the early morning hours but also throughout the entire day, and is often comparable with the contribution of ozone and formaldehyde photolysis. At all research sites unexpectedly high HNO₂ mixing ratios were observed during the daytime (up to several hundred ppt, or pmol mol⁻¹). Moreover, surprisingly, the HNO₂ mixing ratios during the night. Assuming a quickly established photo-equilibrium between the known significant gas phase reactions, only a few ppt HNO₂ should be present around noon. The ratio of known sources to sinks indicates a missing daytime HNO₂ source of 160–2600 ppt h⁻¹ to make up the balance. Based on these values and on production mechanisms proposed in the literature we hypothesise that the daytime mixing ratio levels may only be explained by a fast electron transfer onto adsorbed NO₂.

Additional keywords: atmospheric chemistry, heterogeneous processes, hydroxyl radical, nitrous acid, photochemistry.

Introduction

Nitrous acid has been an object of research for a long time and previous results indicate its great importance in environmental chemistry. Concentrations have been measured at a wide range of locations, as reviewed by Harrison et al. and Lammel and Cape.^[1,2] In addition, HNO₂ is considered to be an indoor pollutant and is of toxicological relevance as a precursor of different carcinogenic species.^[2–4] HNO₂ contributes to the oxidation efficiency of the atmosphere through its photolytic production of the hydroxyl radical, OH[•], at wavelengths \leq 400 nm:

$$HNO_2 + h\nu \rightarrow OH^{\bullet} + NO$$
 (R1)

The hydroxyl radical is accepted to be the most important oxidising species in the daytime atmosphere (e.g. review by Crutzen and Zimmermann^[5]), and is often referred to as the 'detergent of the atmosphere'. Ozone formation in both polluted and clean areas is based on this central compound. Major chemical processes that form OH' in the troposphere have been summarised by Finlayson-Pitts and Pitts.^[6]

For a long time, the dominant source of hydroxyl radicals was believed to be the photo-dissociation of ozone and formaldehyde (HCHO) by actinic UV radiation in sunlight. In the late 1970s, reaction (R1) was proposed to be a significant source of OH[•] in the troposphere,^[7–9] and in the following years was assumed by many authors and checked using models.^[10–18] However, accurate experimental determinations of OH[•] production as a result of HNO₂ photolysis were first reported by Staffelbach

et al. for photochemical pollution events occurring over Southern Switzerland and by Alicke et al. for conditions of a heavily polluted urban atmosphere.^[14,19] The authors found that 17–34% of the total OH[•] is produced by HNO₂ photolysis in a 24-h period. Recently performed studies confirmed the significance of the contribution of HNO₂ to the integrated OH[•] production in urban as well as in rural regions.^[20–27,42]

Gaseous HNO₂ in ambient air was measured for the first time by Perner and Platt using differential optical absorption spectroscopy (DOAS).^[8] More sophisticated DOAS devices also allow for detection of HNO₂ in the lower ppt range (the limit of detection (LoD) is typically in the range of 100– 200 ppt).^[19,22–24,28] A variety of other methods have been developed for the sensitive detection (LoD 1–50 ppt) of HNO₂ in the atmosphere with a high time resolution. Most of them make use of wet chemistry techniques. After quantitative scrubbing of the reactive gas using wet effluent denuders, mist chambers or mixing coils, the nitrite content of the solution can be analysed, for example, directly by ion chromatography^[29–33] or after derivatization to an azo complex by high-performance liquid chromatography (HPLC),^[21,34,35] long-path absorption photometry,^[15,25,89] or fluorescence detection.^[36] Existing techniques to detect HNO₂ were recently reviewed by Genfa et al., Clemitshaw and Liao et al. (2005).^[37–39]

Generally, the HNO_2 mixing ratios are found to be higher in (polluted) urban than in rural areas and are often found to scale with mixing ratios of NO_2 ; on average the HNO_2 -to- NO_2 ratios reach a few percent. Nitrous acid mixing ratios mostly show a diurnal variation dominated by nighttime accumulation and photolytic decay during the day.^[1,2,13,19,24,28,40] Despite the effective photolysis, up to several hundred ppt HNO₂ were found during the daytime in urban and suburban regions.^[22,24,26,42] Recent measurements indicate that HNO₂ also plays a much larger role for the reactive nitrogen budget of rural sites than previously expected; values around 100 ppt and higher were also observed in rural regions.^[14,21,25,27,41] The main sink of atmospheric HNO₂ is the photolysis reaction (R1). HNO₂ can also be removed by deposition processes or by direct reaction with OH[•] (see reaction (R2)), to a few percent:

$$HNO_2 + OH^{\bullet} \rightarrow NO_2 + H_2O$$
 (R2)

An important source of atmospheric HNO₂ is the homogeneous formation, see reaction (R3), in the gas phase from NO and OH[•].^[43] But reaction (R3) and other proposed gas phase reactions (e.g. NO₂ with peroxy or alkoxy radicals) are too slow to account for the observed atmospheric HNO₂ mixing ratios.^[12,24]

$$OH^{\bullet} + NO \rightarrow HNO_2$$
 (R3)

Several studies have been carried out to estimate the source strength of nitrous acid from direct emissions such as combustion engines.^[44,45] On average 0.3 to 0.8% of the total NO_x (NO + NO₂) emitted from combustion processes was observed to be direct nitrous acid emission, but these observations may be overlapped by heterogeneous HNO₂ formation on soot, asphalt and walls (see below). In the atmosphere significantly higher HNO₂-to-NO₂ ratios are mostly observed, even in Milan and Rome.^[22,26] Therefore, the contribution of direct emission to the measured atmospheric HNO₂ levels was found to be only very locally relevant (e.g. in urban canyons, traffic channels).

Accordingly, different heterogeneous formation pathways have been postulated. Numerous field and laboratory studies as well as chamber experiments have been designed and carried out to characterise the heterogeneous NO₂ reactivity on various environmental and artificial surfaces (e.g. aqueous films, polytetrafluoroethylene (PTFE), glass, asphalt, soot, aerosols).^[24,46–53] For example, HNO₂ may be formed from NO₂ suspended on a reducing soot surface as indicated by Ammann et al.^[47] However, only a very small fraction of the surface of fresh soot particles acts to reduce species, which leads to a high reaction probability, and a very fast termination of the reaction was found (e.g. see discussion by Trick).^[24] In addition, a proposed heterogeneous reaction of NO and NO₂ on surfaces^[12,28,57] and the reaction of NO with adsorbed nitric acid (HNO₃)^[50] were found to be unimportant as a potential HNO₂ source.^[24,49,55,65] A more important HNO₂ source is supposed to be the heterogeneous conversion of NO2 adsorbed on humid surfaces:^[e.g. 2,10,18,19,24–27,52,65,82]

$$NO_{2(ads)} + NO_{2(ads)} \xrightarrow{H_2O} HNO_{2(aq)}$$
$$+ HNO_{3(aq)} \rightarrow HNO_{2(g)} + H^+ + NO_3^- \qquad (R4)$$

The nitrous acid is released to the gas phase and can accumulate during the night; the nitric acid remains adsorbed on the surface. Although formation on ground surfaces is expected to be the main source,^[1,15,54,55] it seems likely that under circumstances when atmospheric aerosol or fog droplets provide sufficient surface area, they could also supply an additional surface for the heterogeneous formation of HNO₂.^[28,49,52,56–58]

During their study in Milan, Stutz et al. found that the conversion of NO₂ into HNO₂ is less efficient over grass (about a factor of 10 lower) than expected from laboratory results on artificial surfaces.^[22] Schimang et al. studied the uptake of gaseous HNO₂ by several plant surfaces and their data imply that plant surfaces represent a sink for HNO2.^[96] The number of HNO_2 molecules formed per NO₂ molecule deposited on the surface seems to depend on the surface type.^[1,24] But the exact mechanism of reaction (R4) is not known. Recently a process with dinitrogen tetroxide (N₂O₄) after adsorption of NO₂ and steric rearrangement as a key intermediate has been proposed by Finlayson-Pitts et al.^[52] The authors found that measurements of HNO₂ at different relative humidities may be affected both by the dependence of reaction (R4) on water and by the displacement of HNO₂ from the surface through preferential adsorption of water. Whereas the interpretation of observed nighttime HNO₂ formation rates is mainly based on reaction (R4), this 'classical' heterogeneous HNO₂ formation by NO₂ disproportionation is too slow to account for the observed atmospheric daytime HNO2 mixing ratios.^[25,27] From midday measurements above a mixed deciduous forest canopy near Jülich (Germany) Kleffmann et al. calculated a missing daytime source of $\sim 500 \text{ ppt h}^{-1}$. For the potential candidate, reaction (R4), the authors estimated a mean HNO₂ source strength of 8 ppt h^{-1} , 64 times less efficient than required.^[25]

Several alternative formation path-ways to reaction (R4) have been suggested. Akimoto et al.^[60] has observed a photoenhanced formation of HNO2 during smog chamber experiments. Evidence was found by Ramazan et al. for the generation of gas phase HNO₂ by photolysis of adsorbed nitric acid (HNO₃) formed during the heterogeneous hydrolysis of NO₂ (reaction (R4)).^[59] In several reports from field studies the nitrate/HNO₃ photolysis on wet surfaces as a daytime source of nitrous acid is also proposed.^[20,21,61–64] However, in atmospheric simulation chamber experiments by Rohrer et al. the latter process was found to be negligible.^[53] George et al.^[65] found that a photoinduced conversion of NO2 into HNO2 on various surfaces that contain photosensitive organic substrates may exceed the rate of reaction (R4) by more than one order of magnitude, depending on the substrate. A high conversion yield for the NO₂ reduction by photo-chemically activated electron donors, see reaction (R5), that are present in films of humic acid was observed by Stemmler et al.^[66] and the authors discussed that this photo-chemically driven conversion is common to many surfaces 'rich' in partly oxidised aromatic structures and is, therefore, a major candidate for a daytime HNO₂ source.

$$NO_{2(ads)} \xrightarrow{e^{-}} (NO_{2}^{-} \xrightarrow{H^{+}} HNO_{2})_{(aq)}$$
 (R5)

A non-negligible new HNO₂ source was proposed by Bejan et al. for the urban atmosphere during the day, based on their irradiation experiments with *ortho*-nitrophenols.^[67] The authors excluded a formation of HNO₂ by heterogeneous NO₂ photochemistry and proposed a homogeneous HNO₂ formation initiated by intra-molecular hydrogen transfer from the phenolic OH group to the nitro group. Nitrophenols strongly absorb in the atmospherically relevant UV range of 300–400 nm, their sources are mainly combustion processes and thus their photochemistry might be of importance for the atmosphere.

In Fig. 1 a simplified picture of the HNO₂ chemistry is shown. In the present study, measured diurnal HNO₂ variations from various ground-based sites are presented and compared. The data



Fig. 1. Schematic of the chemistry of HNO₂.

Region	Site	Study period (HNO ₂)	Refs
Harz Mountains, Germany	Mt. Brocken 51°48'N, 10°37'E 1142 m a.s.l.	19 Jun-4 Jul 1999	[56,68,69,83]
Saxonia, Germany	Melpitz, 40 km NE of Leipzig 51°32'N, 12°54'E 87 m a.s.l.	3–14 Apr 2000 11–30 Jun 2006	[32,70,71]
Rome, Italy	Villa Ada Park 41°54'N, 12°30'E	18 May-5 Jun 2001	[24,26,72,85]
Southern France	46 m a.s.l. Realtor, 30 km N of Marseille 43°29'N, 5°20'E 208 m a s l	13 Jun–13 Jul 2001	[33,73,74]
Thuringian Forest, Germany	Goldlauter 50°38'N, 10°45'E 605 m a.s.l.	3 Oct-7 Nov 2001	[75–77]
Rhine Valley, France	Rossfeld, 30 km S of Strasbourg 48°20'N, 7°37'E 167 m a.s.l.	22 May-16 Jun 2003	
Southern Bavaria, Germany	ern Bavaria, Germany 47°48'N, 11°01'E 985 m a.s.l.		[27,78,79,92]

Table 1. Nitrous acid sampling sites

indicate that to date the sources and sinks of atmospheric HNO_2 are still not completely understood. Results from recent studies concerning a photo-catalytic formation pathway are included in the discussion.

Experimental

Measurements of nitrous acid were carried out at different places in Germany, France and Italy within national and international joint projects. Detailed descriptions of the experimental sites, research aims, measured compounds, equipment used and quality assurance assessments can be found in the papers referred to in Table 1. Site elevations range from near sea level to more than 1100 m above sea level (a.s.l.). At all these field sites, sampling of HNO₂ was done using a continuously wetted denuder system that allows for diffusion-based collection of the trace gases with separation from their particulate counterparts (a big advantage compared to mixing coils or bubbling absorption methods).^[33,36] The collection surface is constantly renewed with ~0.5 mL min⁻¹ pure deionised water (the use of carbonate in the denuder liquid as proposed by Zellweger et al.^[30] leads to an incomplete capture of nitrite and nitrate ions during the pre-concentration step). The analysis of the scavenged acids can be continuously performed on-line with a suitable analyser/detector, in our case an ion chromatograph (IC, DIONEX DX500) after pre-concentration of the trace species (on TAC-LP1 columns). The approach for our wet effluent diffusion denuder system (WEDD) in parallel-plate design was adopted,^[29–31,41] and modified; a report by Acker et al. gives details including a schematic diagram.^[33] The airflow through the denuder is 10 L min⁻¹ and is kept constant by calibrated mass flow controllers. The sample air residence time in the WEDD is very short (below 0.5 s) and the solution residence time is also short (below 2 min). Using 30-min sampling time (pre-concentration), mixing ratios of 5 ppt HNO₂ can be reliably recorded (limit of quantification). The calibration in the field was done using injected liquid standards instead of the denuder effluent, in the laboratory gas-standards (range 2-20 ppb) were used in zero air generated by a HNO3 permeation source or a HNO₂ generation system.^[33] Our system is combined with an uninterruptible power supply and operated in an air-conditioned environment at ~20°C (container or laboratory truck) with a very short PTFE inlet outside (20 cm; opaque, wall thickness 0.5 cm, inner diameter 2 cm like the denuder fitting unit) altogether \sim 3 m above earth. The data completeness for nitrous acid measurements over the study times given in Table 1 was greater than 90%. During several field experiments DOAS as well as other wet chemistry techniques were used in parallel to determine nitrous acid concentrations, and despite any interference discussion, the results agree very well.^[26,32] Generally, the quality of our laboratory work (rain, aerosol and cloud water analysis) is checked by participation (twice a year with excellent results) in international intercomparison studies within the WMO-GAW program (http://www.gasac-americas.org).

Various other components (trace gases, aerosols, meteorological variables) were simultaneously measured during the field studies using commercial analysers. Before every field experiment measurements of NO, NO₂, O₃ and SO₂ were checked against available transfer standards. Depending on the aim and the size of the field experiments additional measurements were performed, e.g. including formaldehyde, peroxides, peroxyacetyl nitrate (PAN), photolysis frequencies (from spectroscopic actinic flux measurements, mainly *J*(NO₂)) and natural radioactivity. The photolysis frequency of HNO₂ was directly measured in Rome and at Hohenpeissenberg, and in the other cases estimated from a measured photolysis frequency of NO₂ following the approach by Kraus and Hofzumahaus:^[80]

$$J(\text{HNO}_2) = 0.189 \times J(\text{NO}_2) + 8.433 \times 10^{-2} \times [J(\text{NO}_2)]^2$$
(1)

No photolysis frequency data are available for the 1999 Mt. Brocken field study, but the UV_A radiation (maximum sensitivity of the used sensor at 360 nm) was measured.

Mixing ratios given for NO₂, SO₂, O₃, HNO₃ and HNO₂ are 30 min averages and are expressed in the units ppb and ppt (or nmol mol⁻¹ and pmol mol⁻¹, respectively). For the mass concentrations of aerosol particles with aerodynamic diameter smaller than $10 \,\mu m$ (PM₁₀), 24-h averages are reported. Concurrent measurements of the hydroxyl radical concentration are available only from the Hohenpeissenberg site. Chemical ionization mass spectrometry based on complete titration of OH with ³⁴SO₂ and detection of the corresponding gaseous bisulfate anion $(H^{34}SO_4^-)$ was used in this case.^[81] When the Mt. Brocken summit was inside clouds, their liquid water content was detected using a forward scattering laser spectrometer (PVM100). To separate the cloud droplets from the interstitial air during cloud events an active cloud water collector (Winklertype) was installed in front of the denuder and continuously in operation (air sample flow rate $2 \text{ m}^3 \text{ min}^{-1}$) to avoid reactions on the sampler surface, for more details see Acker et al.[56] All data presented here are related to Central European Time (CET). The diurnal variations of HNO2 averaged for the corresponding periods of study are given as medians together with the matching 0.25 and 0.75 quartiles. Backward trajectories calculated by the HYSPLIT (Hybrid Single Particle Langrangian

Integrated Trajectory) model were applied in order to identify the origin of air masses that reached the experimental area (www.arl.noaa.gov/ready/hysplit4.html). For detection of frontal processes, synoptic scale advection and air mass classification in the lower troposphere, synoptic charts from the German Weather Service were analysed.

Overview of field campaigns, results and findings

More than 200 diurnal profiles of nitrous acid (measured by identical equipment, measurement and personal conditions) under different pollution and meteorological conditions were obtained from the measurement campaigns presented in Table 1. For each site average diurnal cycles were derived, and partly found to be similar to those previously reported consistent with heterogeneous formation and accumulation of HNO₂ overnight and a rapid decrease after sunrise because of efficient photolysis by reaction (R1) and vertical mixing processes.^[1,13,19,41] In addition to the expected diurnal cycles at the flat country station, surprising results were obtained for the mountain sites.

In many studies the kinetics of the heterogeneous NO₂ conversion by reaction (R4) has been found to be first order in NO₂,^[2,15,52,82] (d[HNO₂] = k[NO₂]dt). As the exact mechanism of reaction (R4) is unknown, the source strength may be estimated from the measured increase of the HNO₂ to NO₂ ratio with time in the late evening hours as well as from the assumption that the rate is independent of the time of day (see described approaches in Kleffmann et al. and Alicke et al.),^[15,19] which results in the expression of the rate constant *k*. Values between 0.006 and 0.027 h⁻¹ (or 1.7×10^{-6} to 7.5×10^{-6} s⁻¹) were obtained from our data, which is in good agreement with other studies.^[15,18,19,23,25]

Mt. Brocken (Harz Mountains)

In early summer 1999, measurements were made at Mt. Brocken (surrounded by coniferous forest, but with the summit above the timberline) in the National Park Hochharz to study the interactions between the different phases (gaseous species, aerosol particles and liquid droplets) in cloudy atmospheres in detail. The phase partitioning of reactive trace species was investigated using different kinds of impactors and the denuder method.^[56,68] Low polluted air masses reached this highest peak of the Harz Mountains as a result in part of heavy rain on the air mass back trajectory first from northerly (19-24 June) and later from southwesterly directions. On average 2.4 ppb NO₂ were observed. The complete time series of HNO2, HNO3 and NO2 were reported earlier by Acker et al.^[56] Cloudy conditions (also see Fig. 2) occurred for $\sim 21\%$ of the study time. Based on measured droplet spectra, the surface-to-volume ratio in the clouds at Mt. Brocken has often been estimated to be between 0.4 and $0.7 \,\mathrm{m}^{-1}$, which is significantly higher than that known for the Earth's surface $(0.2-0.02 \text{ m}^{-1})$ and even aerosol (urban 0.02; rural $0.0002 \,\mathrm{m}^{-1}$). During cloud events, in addition to gaseous HNO₂, the amount of nitrite dissolved in the cloud water was also determined (100–5700 nmol L^{-1}). As expected, the distribution between (interstitial) gas and the liquid phase was found to be a function of the pH. In most cases cloud water pH was below 5 and bulk samples were supersaturated with respect to the atmosphere from which the samples were drawn (for more details see Acker et al.^[84]). Super-saturation could result in outgassing of weak acids from the samples, if such an exchange is allowed.



Fig. 2. Time series of the gas phase HNO₂ mixing ratio, the liquid water content (LWC) of clouds (upper graph) and the HNO₂-to-NO₂ ratio (lower graph) at Mt. Brocken.



Fig. 3. Average diurnal variation of HNO_2 at different mountainous rural sites (averaged over the study times, based on Central European Time (CET)), given as median and 25 and 75 quartiles. (a) Mt. Brocken (19 June–04 July 1999), (b) Goldlauter (03 October–07 November 2001), and (c) Hohenpeissenberg (29 June–14 July 2004).

To summarise, in all Mt. Brocken HNO₂ data, no marked diurnal variation was found. On average over the whole day \sim 0.060 ppb of HNO₂ was measured (Fig. 3a), mainly because of high horizontal advection at the isolated summit, which is often above the planetary boundary layer (PBL) during nights. A steady increase in the HNO₂ mixing ratio (up to 0.152 ppb) was observed during four days from the late evening hours till a few after midnight, and HNO₂-to-NO₂ ratios between 0.016 and 0.031 were found. An average nighttime conversion rate constant for reaction (R4) was determined from the increase in the HNO₂-to-NO₂ ratios: $0.008 \pm 0.004 h^{-1}$. On a few occurrences around noon, the HNO₂ mixing ratios showed either a broad maximum or several distinct peaks (see Fig. 2). For example, the maritime-influenced air masses sampled on 20 June contained a high amount of uncondensed humidity and aerosols whose chemical composition was dominated by sea salt, but also nitrate and organic carbon; the HNO₂ mixing ratios tend to correlate with radiation (UV_A, $r^2 = 0.41$). During and after cloudy episodes often higher HNO₂-to-NO₂ ratios (0.01–0.06) were found, see Fig. 2. The data obtained at Mt. Brocken underline the evidence for heterogeneous formation of nitrous acid on cloud droplets and wet aerosols at least partly causing the observed great deviations from Henry's law.

Goldlauter (Thuringian Forest)

Aerosol-cloud interaction field experiments were designed and carried out at a mountain ridge in the Thuringian Forest. Trace gases, aerosol particles and cloud droplets were probed at three sites upwind, downwind and within orographic clouds to study the budgets and conversions of gas and particle phase con-stituents, especially organics.^[75–77] The Goldlauter station was located outside the village at the entrance of a valley. In a southwesterly wind, Goldlauter is windward of Mt. Schmücke (937 m a.s.l.) and the air masses that reach this site were characterised in detail before cloud processing. The site is surrounded by coniferous forest (mostly spruce, with a distance of a few meters), the nearest town is Suhl (\sim 5 km). During the study time in autumn 2001 (day time temperatures 7-14°C, radiation intensity ($J(NO_2)$) up to $2.7 \times 10^{-3} \text{ s}^{-1}$), medium or low polluted air masses reached this valley site, and on average mixing ratios of SO₂ below 1 ppb, NO₂ below 10 ppb and PM₁₀ mass concentrations between 8 and $17 \,\mu g \,m^{-3}$ were observed. The investigated organic species (formic and acetic acid, dicarboxylic acids as well as carbonyl compounds) showed increasing mixing ratios from night to midday in connection with a slight increase of the photochemical activity.[77]

In autumn, under rural conditions the mixing ratios of nitrous acid were expectedly low but showed unexpected diurnal cycles. Only in a few cases (6 days), an increase of HNO₂ was observed in the evening hours. For a nighttime formation by reaction (R4) an average rate constant of $0.006 \pm 0.006 \,h^{-1}$ was calculated from the linear increase of the HNO2-to-NO2 ratio, which varied between 0.015 and 0.04 on average. Few days did not show any clear structure in diurnal HNO₂ variation. But surprisingly often a daytime HNO2 maximum was found between 0900 and 1500 hours CET with values between 0.1 and 0.43 ppb. The average diurnal variation given in Fig. 3b reflects this behaviour. On sunny days (e.g. on 11-20 October) the daytime HNO2 mixing ratio tended to positively correlate with photolysis frequencies of $J(NO_2)$ ($r^2 = 0.33$). Unfortunately, no measurements of aromatics (e.g. phenolic derivatives), which can be oxidised by NO2, are available so as to consider the hypothesis of a photochemically driven NO₂ conversion on the surface of soils or spruce needles (which contain, for example, p-hydroxyacetophenone, which was used in the laboratory study by George et al.^[65]). Cloud droplets that formed during the study time at Mt. Schmücke were relatively acidic (pH 3.3-5.1) and the aqueous-phase nitrite concentrations were low; on average the concentration was only one tenth of the aerosol nitrite in the air masses before cloud formation (for details see Acker et al.^[84]). Therefore, a release of heterogeneously formed or scavenged HNO2 from wetted aerosols or plant surfaces seems to have occurred.

Hohenpeissenberg (South Bavaria)

Measurements of nitrous acid were made by our group in the summers of 2002, 2003 and 2005 at the Meteorological Observatory Hohenpeissenberg at \sim 300 m above the surrounding countryside (mainly forest and pastures) and $\sim 18 \text{ m}$ above ground level, which roughly corresponds to the canopy level of the closest trees on the steep slopes of Hohenpeissenberg. At this observatory the German Weather Service operates its Global Atmosphere Watch program (GAW), which features the monitoring of a broad range of meteorological and atmospheric chemical variables, hence providing a platform for detailed research studies.^[78,79] There are no significant industrial sources in the vicinity, the nearest major city is Munich \sim 70 km NE, and the dominating wind direction is SW. Measurements of the hydroxyl radical have been continuously carried out at this site for many years, which is a big advantage for studying HNO₂ formation processes.^[92] The time series of mixing ratios of HNO₂ and OH[•] for the 2004 summer campaign are partly presented in Acker et al. and completely in Fig. 4.^[27] Peak daytime hydroxyl radical concentrations in the range of $(5-10) \times 10^6$ molecule cm⁻³ were measured, which are comparable to results of $(2-10) \times 10^6$ molecule cm⁻³ obtained at other ground level sites at mid-latitudes during summer.[86-88]

To our surprise the highest HNO₂ mixing ratios were consistently measured during daytime in all campaigns (for 2002 and 2004 see Acker et al.;^[27] for 2005 a paper is in preparation), which show a broad maximum occurring between 0800 and 1600 hours CET. The average diurnal cycle of nitrous acid measured in June/July 2004 at Hohenpeissenberg is shown in Fig. 3c. The noontime levels reached 0.110 ppb on average whereas nighttime values were significantly lower (~ 0.040 ppb). During the night the observatory is mostly out of the stable nocturnal boundary layer (see also Fig. 9a, where the diurnal ozone variation of two different altitudes is given). Nighttime measurements at this hilltop site are, therefore, more characteristic for the so-called residual layer, which resembles the fully mixed convective (daytime) boundary layer of the day before. Low to moderately polluted air masses reached the site during the 2004 experiment: means for the NO₂ and SO₂ mixing ratios are 1.5 and 0.05 ppb, respectively. Only during a few nights an increase in HNO2 mixing ratios was



Fig. 4. Time series of HNO₂ mixing ratios (a) and OH[•] concentrations (b) measured simultaneously during the 2004 experiment at the Meteorological Observatory Hohenpeissenberg.

observed and from the increase of the HNO₂/NO₂ ratio an upper limit of the rate constant for the heterogeneous NO₂ conversion (reaction (R4)) of 0.007 h⁻¹ was estimated. The HNO₂-to-NO₂ ratio varied then between 0.007 and 0.05. It was summery warm (14–24°C around noon at the mountain top) during the campaign. A linear correlation coefficient $r^2 = 0.48$ was obtained for HNO₂ with regard to $J(\text{HNO}_2)$ around noon in 2004 with $J(\text{NO}_2)$ maxima of (8–9) × 10⁻³ s⁻¹. Much more meaningful is a correlation of the extra HNO₂ daytime source against $J(\text{NO}_2)$, which was found to be very significant ($r^2 = 0.81$), see Fig. 5.

Melpitz (Saxonia)

In spring 2000 as well as in summer 2006, field studies including HNO₂ measurements were performed near Leipzig, at the research station Melpitz. The site is surrounded by agriculturally used land, mainly grassland for hay harvest, and mixed forests.

During the 2000 campaign the air masses reaching the field site were predominantly non- or slightly polluted (from North Atlantic or Western Europe; PM_{10} 7–20 μ g m⁻³; SO₂ ~0.7 ppb, NO₂~3 ppb). Only on 10 to 11 April, Eastern Europe influenced and moderately polluted air (PM₁₀ up to $35 \,\mu g \,m^{-3}$; SO₂ up to 3 ppb, NO₂ up to 7 ppb) reached the site. Complete time series can be found in Acker et al. and Müller et al., which include meteorological variables and nitrous acid whose mixing ratios varied between 0.02 and 0.35 ppb.^[32,71] From the evening increase of the HNO₂-to-NO₂ ratio observed on most of the campaign days the source strength of reaction (R4) could be estimated and the calculated rate constant was found to be $(0.010 \pm 0.006 \text{ h}^{-1})$. The HNO₂-to-NO₂ mixing ratios were then between 0.013 and 0.085; values in the upper range were observed for the night from 10 to 11 April, but also in the morning hours of 7 April under hazy conditions. The mean diurnal HNO2 variation is shown in Fig. 6a. In the morning hours, the HNO₂ mixing ratio reached a maximum because of overnight accumulation and local formation during the traffic rush hours, before photolysis caused a significant decrease. On average, daytime mixing ratios of ~0.050 ppb (0.02–0.15 ppb) were measured.

The 2006 campaign was carried out in June, which was warm and dry above average (e.g. daytime temperatures from 20 to 34°C). The investigated air masses mainly originated from the Baltic or North Sea (10 to 18 June; 28 to 30 June) and Southwest Europe/Atlantic (19 to 27 June). On average, the air masses were medium polluted, especially when mainly transported over land with NO₂ up to 15 ppb (mean 3 ppb), SO₂ up to 4 ppb (mean 1 ppb) and PM₁₀ mass concentration up to 30 μ g m⁻³ (mean 19 μ g m⁻³). The HNO₂ mixing ratios increased more or less every night reaching up to 1.4 ppb, followed by effective



Fig. 5. Correlation of J(NO₂) against the extra (missing) daytime source.

photodecomposition after sunrise until minimum values (0.03–0.2 ppb) were reached at ~1600 hours CET. Fig. 6b shows the average diurnal variation, which is similar to the 2000 campaign, but much more pronounced. Increasing HNO₂-to-NO₂ ratios during the nights are evidence for heterogeneous formation (reaction (R4)). For single events average values between 0.017 and 0.10 were found and on average a nighttime conversion rate of $0.027 \pm 0.012 \, h^{-1}$ was calculated from the increasing HNO₂-to-NO₂ ratio. Besides very high solar irradiation (*J*(NO₂) (6–10) × 10⁻³ s⁻¹) and HNO₂ values much higher than can be expected from the photo-stationary state (see below), no correlation could be found between *J*(NO₂) and nitrous acid ($r^2 = 0.06$) around noon.



Fig. 6. Average diurnal variation of HNO₂ at the flat country site Melpitz under early spring as well hot summer conditions (averaged over the study times, based on Central European Time (CET)), given as median and 25 and 75 quartiles. (a) 4–14 April 2000 and (b) 11–29 June 2006.

Rossfeld (Rhine Valley)

Within the border-crossing INTERRREG III project 'Common information and evaluation system about the air quality in Upper-Rhine Region' a complex field experiment was performed with numerous field sites around Strasbourg (France) in late spring 2003. Our group participated with different kinds of measurements (including HNO₂) which were done at the Rossfeld station, south of Strasbourg. The field site was located outside the village and mainly surrounded by agriculturally used land. On average, air masses reaching the site were medium polluted: NO₂ up to 20 ppb (mean 5.6 ppb); SO₂ up to 7 ppb (mean 0.8 ppb) and PM₁₀ mass concentration up to $35 \,\mu g \,m^{-3}$ (mean $23 \,\mu g \,m^{-3}$). Mostly it was very warm and dry with clear skies $(23-35^{\circ}\text{C}; J(\text{NO}_2) (9-10) \times 10^{-3} \text{ s}^{-1})$, and only a few thunderstorms occurred. Ozone and nitric acid mixing ratios of up to 105 and 2.7 ppb, respectively, were measured on 12 June as a result of photochemical pollution. In the boundary layer air masses travelled more or less along the Rhine Valley and the station was sometimes upwind of Strasbourg (Figs 7a, 7b), and sometimes downwind of Strasbourg (Figs 7c, 7d), which resulted in different patterns of nitrous acid and HNO2-to-NO2 ratios. Higher pollution levels were observed when air masses travelling over Strasbourg reached the site.

During this study, nighttime HNO₂ mixing ratios of up to 1.3 ppb were observed – mainly caused by heterogeneous formation processes and accumulation of HNO₂ in the night-time boundary layer (see also Fig. 7c). From the increasing HNO₂-to-NO₂ ratio on average a conversion rate constant of $0.022 \pm 0.017 \,h^{-1}$ was determined. During the monotonic increase of nitrous acid in the evening hours, average HNO₂-to-NO₂ ratios of 0.016-0.06 were found for the single periods. The mean diurnal variation is shown in Fig. 8a and was found to be very similar to those of the Melpitz 2006 experiment (Fig. 6b).

Realtor (Southern France)

The experiment ESCOMPTE took place in summer 2001, and was aimed at estimating the photochemical production of pollutants within and around an urbanised area. Five pollution



Fig. 7. Time series of HNO₂ mixing ratios (stars), HNO₂/NO₂ ratios (open circles), NO mixing ratios (closed triangles), NO₂ mixing ratios (closed circles) and wind direction (open diamonds) measured simultaneously at the Rossfeld site on 22 May 2003 (a, b) and on 27 May 2003 (c, d).

events were characterised by a network of ground stations, ship-borne, balloon-borne and airplane measurements within a $120 \times 120 \text{ km}^2$ domain.^[73,74] Measurements of nitrous acid (and numerous other components) were carried out by our group at the Realtor station, located \sim 30 km north of the urban environment of Marseille and east of the industrial centre Berre Pond.^[33] Measurement equipment was installed on top of a hill covered by Mediterranean natural landscape. Noontime temperatures varied between 25 and 35°C. On average medium to polluted air masses reached the station: NO₂ up to 35 ppb (mean 6 ppb); SO₂ up to 40 ppb (mean 4 ppb) and PM₁₀ mass concentration up to $72 \,\mu g \,\mathrm{m}^{-3}$ (mean $32 \,\mu g \,\mathrm{m}^{-3}$). Time series of HNO₂ (and HNO₃) throughout the complete campaign are given in Acker et al.^[33] Lowest mixing ratios were observed when air masses connected with strong NW winds (Mistral situation) reached the Realtor site and caused high turbulence (e.g. 16 to 19 June) and HNO₂ mixing ratios of ~ 0.1 ppb over the whole day. The highest HNO₂ mixing ratios (up to 1.2 ppb) were observed during episodes of strong pollution accumulation when a sea breeze transported industrial, traffic and urban pollution land-inwards, e.g. from 21 to 26 June. High mixing ratios in ozone were observed in the whole domain. At the Realtor site, 118 ppb O₃ on 24 June and 130 ppb O₃ on 27 June were measured at noon. Increasing nitric acid mixing ratios (at ~1200 hours CET on 21 June, 1.5 ppb HNO₃; on 24 June, 3.5 ppb HNO₃) are another indication of an intensive episode of photochemical pollution.

Except for the few days under Mistral conditions, the nitrous acid mixing ratios increased steadily after sunset and for the conversion from NO₂ into HNO₂ by reaction (R4) an average rate constant of $0.020 \pm 0.019 \,h^{-1}$ could be estimated. HNO₂to-NO₂ ratios between 0.015 and 0.08 were observed during the night. The average diurnal pattern of HNO₂ for the whole experiment time is given in Fig. 8b. On average, HNO₂ accumulates during the night until a maximum level (~ 0.5 ppb) is reached. The photolysis of HNO2 then starts to cause a significant decrease in HNO₂ mixing ratio at the latest at ~0600 hours CET. In addition, the morning break up of the mixing layer causes dilution of HNO2-rich air by entrainment of fresh air from layers above the boundary layer. The high scattering around the nighttime maximum is caused by different levels of pollution (e.g. aerosols, NO₂) and by differences in meteorological conditions (e.g. stability of the boundary layer, relative humidity). The photolysis frequency of NO2 was measured from 28 June till the end of the experiment and was found to be $(6-8) \times 10^{-3} \text{ s}^{-1}$ around noon without any correlation ($r^2 = 0.04$) to HNO₂.

Rome

Our group was involved in the European research program NITROCAT to study the influence of nitrous acid on the oxidation capacity of the atmosphere, and the city of Rome was chosen for a complex field experiment in an urban environment.^[24,26,85] Here we report measurements of HNO₂ made at the northern end of the city centre inside the Villa Ada Park (west of Via Salaria, which had a high traffic density throughout the day) and which was defined as an urban background station. During the late spring 2001 campaign, the atmosphere of Rome can be generally described as polluted: up to 90 ppb NO, 55 ppb NO₂, 75 mg m⁻³ TSP (total suspended matter), but on average only 2 ppb SO₂, were detected. Only in low pressure conditions (e.g. from 2 to 4 June 2001) were significantly reduced values of pollutants found because of the strong mixing of the atmosphere and the absence of atmospheric nighttime stabilisation; HNO₂ also remains low



Fig. 8. Average diurnal variation of HNO₂ at different flat country urban and suburban sites (averaged over the study times, based on Central European Time (CET)), given as median and 25 and 75 quartiles. (a) Rossfeld (22 May–16 June 2003), (b) Realtor (13 June–13 July 2001), and (c) Rome (19 May–05 June 2001). In addition, for the Villa Ada site, the variation in natural radioactivity (columns) and in the HNO₂ to NO₂ ratio (stars) are shown.

during nights as well as concentrations of natural radioactivity. The inert gas Radon emitted only by soil may be used as a tracer for the build-up and break-up of ground inversions, as shown by Perrino et al.^[72] The radon activity constantly increases as long as the inversion layer is stable and as generally during the campaign, the nocturnal atmospheric stabilities were high, often a significant decrease in radon concentration was observed not before 0800 hours CET in the morning, see Fig. 8c. The reduced horizontal advection (winds below 1 m s⁻¹ from NW directions) led to enhanced levels of primary pollutants.^[24,26,85]

The complete time series of HNO2 and numerous other variables for the whole campaign are presented elsewhere, [24,26,85] the mixing ratios of nitrous acid in Rome indicated a typical strong diurnal cycle, see Fig. 8c. Heterogeneous formation on ground, urban and aerosol surfaces seems to be a significant source of nitrous acid during the night; up to 2 ppb were found and a mean NO2-to-HNO2 formation rate constant of $0.01 \pm 0.003 \,h^{-1}$ was derived. On average, the HNO₂-to-NO₂ ratio increased during the nights from 0.02 to 0.05. The road traffic in Rome was low during the later part of the night, and while HNO₂ levels were still increasing, direct emission of HNO₂ was concluded to be of minor importance as a HNO₂ source. The 'intermediate' dip in HNO₂ between 0300 and 0500 hours CET may be a result of effective dry deposition of HNO₂ and increasing pollution levels from the morning rush hour, when the vertical atmospheric stability was still high. In Fig. 8c, the average diurnal variation in the corresponding HNO2-to-NO2 ratio and in natural radioactivity is also given. After sunrise (~0430 hours CET), after the initial onset of photolytic reactions, and

a destabilisation of the nighttime boundary layer (~0800 hours CET, Fig. 8c), HNO₂ levels decrease over several hours and stabilise at ~0.200 ppb during the day (temperatures ~30°C, easterly winds ~2.5 m s⁻¹, high sun radiation, $J(NO_2)$ (10–12) × 10⁻³ s⁻¹ at noon). The correlation between HNO₂ and $J(NO_2)$ (noontime data) is very poor and even negative. On the other hand, daytime HNO₂ mixing ratios of more than 0.5 ppb found on cloudy days in Rome (e.g. the whole of 24 May) may support the idea of a heterogeneous HNO₂ formation on wet surfaces like aerosols; a mechanism which adds to the reduced photolysis rates.

Discussion

The diurnal patterns of HNO2 presented above may be explained by the processes described in the following. At night, a pool of HNO₂ can accumulate mainly by reaction (R4) and because of missing destruction by photolysis and reduced vertical dilution. Our atmospheric measurements suggest a HNO2 formation rate with respect to NO₂ of ~0.6–2.7% h⁻¹, which is in agreement with values obtained in other field studies.^[1,2,19,22–24,54,55,82] Remarkably, formation rates at urban as well as rural sites were found to be very similar, proposing an identical reaction mechanism at night. The HNO2-to-NO2 ratio, which reaches a few percent at all sites, is significantly higher than that on average observed at high traffic density (found to be below 1%), thus suggesting that in relation to on-site chemical HNO₂ formation the contribution from emission and transportation is less important.^[24,44,45] The level of observed nighttime HNO₂ mixing ratios seems to depend on the degree of pollution. Winds from regions with high emissions (industrial complexes, highways, cities) tended to bring higher mixing ratios of pollutants, such as NO_x and perhaps nitrates/HNO₃, to the sites where HNO₂ is assumed to be formed locally from its precursors on surfaces. Since ground surfaces provide most of the surface area for the heterogeneous NO₂ conversion (reaction (R4)), the stability of the atmospheric boundary layer becomes an important factor in controlling HNO2 mixing ratios near the ground surface.

Later in the night heterogeneous formation on surfaces often seems to compete with the deposition of HNO₂ on these surfaces. Based on gradient measurements of NO₂ and HNO₂ over grass in Milan, Stutz et al. explained the observed behaviour of these trace gases by a combination of deposition of NO₂ and HNO₂ and a conversion of NO₂ into HNO₂ at ground level.^[22] The influence of relative humidity on the reaction probability for the NO₂ into HNO₂ conversion and the loss of HNO₂ was studied recently by Stutz et al.^[82] In the morning, within a few hours following sunrise, the accumulated HNO₂ is depleted by increasing photolysis and simultaneous convective mixing. As at all sites, some minutes after sunrise the photolysis frequency increased from ~10⁻⁴ s⁻¹ to more than 10⁻³ s⁻¹ three hours later, it was, therefore, the dominant sink process during this part of the day.

Around noon, the HNO₂ pool, which had accumulated during the night, is completely removed and more or less low mixing ratios of HNO₂ were observed. Surprisingly at mountain sites the HNO₂ mixing ratios during the day time showed a broad maximum (Hohenpeissenberg, Goldlauter) or several distinct peaks (Brocken). A similar behaviour was also observed at Whiteface Mountain (1483 m a.s.l., USA) by Huang et al.^[34] and near Mt. Zugspitze (2650 m a.s.l.) by Kleffmann et al.^[89] during the onset of sunny conditions. The positive correlation between HNO₂ and solar radiation as observed at the Hohenpeissenberg (Fig. 5) and at the Goldlauter site may suggest a substantial radiation-induced production of HNO_2 . Thus, during daytime we possibly have a competing process, namely light-induced production and destruction of HNO_2 .

At all of our measurement sites the measured noontime mixing ratios of nitrous acid were 'unexpectedly' high: on average from 0.06 to 0.300 ppb (see Figs 2, 3a-c, 4a, 6a-b, 8a-c), despite effective photolysis (the main sink of HNO₂, reaction (R1)). Another HNO₂ sink is reaction (R2). The significant daytime source of HNO₂ in the gas phase is the homogeneous recombination of hydroxyl radicals and NO (reaction (R3)). Under full sun conditions HNO₂ is relatively short-lived (around 10 min), and one could assume that around noon the photo-stationary state (PSS) was reached rapidly. This PSS is dominated by an equilibrium between photodecomposition (reaction (R1)) and back reaction of OH[•] with NO (reaction (R3)), with little net effect on OH[•].^[12,25] Based on measurements of OH, HNO₂, NO, NO2, J(HNO2) or J(NO2) and meteorological variables (temperature, pressure, relative humidity) the photo-stationary HNO₂ mixing ratios can be calculated for the time around noon using the following equation:

$$[\text{HNO}_2]_{\text{PSS}} = \frac{k_3[\text{OH}^{\bullet}][\text{NO}]}{J(\text{HNO}_2) + k_2[\text{OH}^{\bullet}]}$$
(2)

The corresponding rate constants for $k_2 = 6.0 \times 10^{-12}$ cm³ s⁻¹ reaction (R2) and $k_3 = 9.8 \times 10^{-12}$ cm³ s⁻¹ reaction (R3) were taken from Atkinson et al.^[90]

During the nitrous acid measurement campaigns all variables needed for this calculation were simultaneously measured at the Hohenpeissenberg site only. Based on these values, the photostationary HNO₂ mixing ratios were calculated, see also Table 2. On average, daytime maximum PSS levels of ~12 ppt would be expected for bright sunny days ($J(NO_2) > 6 \times 10^{-3} \text{ s}^{-1}$; $J(HNO_2) > 1 \times 10^{-3} \text{ s}^{-1}$) at Hohenpeissenberg, which is more than one order of magnitude smaller than the measured HNO₂ levels of ~0.1–0.2 ppb (see also Fig. 3c). Our findings confirm results from Kleffmann et al. obtained in July 2003 above a mixed deciduous forest canopy near Jülich (Germany), and also based only on experimental observation.^[25]

Estimations for the photo-stationary HNO₂ mixing ratios were also performed for our other sites for sunny conditions (with the exception of Mt. Brocken, where no photolysis frequency data were obtained), but using OH[•] concentrations based on assumptions (Table 2). Prinn et al.^[91] reported a global mean for OH[•] to be 0.7×10^6 molecule cm⁻³; under mid-latitudes during summer (2–10) × 10⁶ molecule cm⁻³ were measured.^[42,86–88,92] From their long-term measurements (1999–2003) of atmospheric OH[•] concentrations at Hohenpeissenberg, Rohrer and Berresheim found that the concentration of OH[•] can be described by a surprisingly linear dependence on solar ultraviolet radiation ($J(O^1D)$, $J(NO_2)$) throughout the measurement period, despite the fact that OH[•] concentrations are influenced by thousands of reactants.^[92]

All examples presented in Table 2 clearly show daytime maximum PSS levels of a few ppt, which are significantly lower than the corresponding HNO₂ levels observed. The ratio of the gas phase HNO₂ source to sinks, reactions (R3/(R1 + R2)) varied between 0.01 and 0.46 around noon, which indicates that a major additional HNO₂ source is required to close the balance. Higher source-to-sink ratios were found on days with elevated noontime NO mixing ratios, possibly because of increased homogeneous formation through reaction (R3).

Site/date	O ₃ (ppb)	$OH^A \times 10^6$ (cm ⁻³)	$J(\text{HNO}_2)^{\text{B}} \times 10^{-3}$ (s ⁻¹)	[NO] (ppb)	[HNO ₂] _{PSS} (ppb)	[HNO ₂] _{meas.} (ppb)	Source/sinks R3/(R1 + R2)
Goldlauter 2001							
12, 13, 20 Oct	26-40	0.5	0.4	0.6-0.8	0.007-0.010	0.125-0.135	0.05 - 0.08
16 Oct	30	0.5	0.4	3.1	0.038	0.224	0.17
19 Oct	11	0.5	0.4	11	0.134	0.296	0.45
Rossfeld 2003							
07, 12 Jun	70-85	7	1.76	0.07 - 0.1	0.003-0.004	0.222-0.228	0.01-0.02
29 May	45	5	1.6	0.55	0.016	0.344	0.05
27, 28 May	35-50	5	1.6-1.7	1.45	0.039-0.051	0.320-0.460	0.09-0.16
Melpitz 2000							
6 Apr	41	5	1.5	0.45	0.014	0.05	0.29
11 Åpr	48	5	1.2	0.82	0.032	0.145	0.22
Melpitz 2006							
28, 29 Jun	57	5	1.1	0.07-0.1	0.003-0.005	0.056-0.061	0.06-0.09
16, 20 Jun	74	7	1.6-1.8	0.34-0.39	0.015	0.187	0.08
27 Jun	64	7	1.75	0.32	0.012	0.068	0.18
Rome 2001							
27 Jun	72	7	2.1	0.1	0.003	0.107	0.03
3 Jul	55	5	1.7	0.24	0.007	0.083	0.08
28 Jun-01 Jul	70	7	2-2.1	0.21-0.34	0.007-0.012	0.137-0.224	0.03-0.08
20, 22 Jun	34	5	1.3	2-2.3	0.071-0.093	0.209-0.259	0.34-0.36
Realtor 2001							
30 Jun	86	7	1.5	0.19	0.009	0.102	0.08
2, 3, 4 Jul	72–99	7	1.4	0.2-0.3	0.010-0.014	0.124-0.164	0.08-0.1
9, 10 Jul	80-84	7	1-1.1	0.3	0.018-0.020	0.136-0.17	0.12-0.13
Hohenpeissenberg 2004							
30 Jun, 4 Jul	47-67	5.7-7.8	1.5	0.08-0.11	0.003-0.004	0.099-0.130	0.03-0.04
8 Jul	40	5.6	1.3	0.66	0.028	0.144	0.19

Table 2. Measured and calculated variables at different sites between 1100 and 1300 hours CET

^AMeasured directly at Hohenpeissenberg, other OH' values are assumptions.

^BMeasured directly in Rome and at Hohenpeissenberg, other values were calculated from measured J(NO₂).

A contribution to the daytime HNO₂ source is also expected from the heterogeneous hydrolysis of NO₂ (reaction (R4)), which is believed to occur with the same mechanism during the day as during the night. The surfaces of soil, buildings, roads and vegetation provide similar solid supports and should also hold water in sufficient amounts to promote heterogeneous reactions during the day. The source strength was estimated from the nighttime increase of the HNO₂-to-NO₂ ratio (see information to single stations given above). Using upper limits of determined rate constants k_4 and reactions (R1–R4) in daytime conditions, the total HNO₂ source-to-sink ratios increase only slightly. Apparently the heterogeneous HNO₂ production according to reaction (R4) (3 to 50 ppt h^{-1} from our data) is of minor importance as a daytime source under sunny conditions. However, the rate constant k_4 for NO₂ conversion will critically depend on the convective mixing and NO2 deposition velocity, which is much higher during the day.^[24] Thus, the rate could be higher than estimated here from our nighttime data.

Overall, a missing daytime HNO₂ source of $(1-17) \times 10^6$ molecule cm⁻³ s⁻¹ (corresponding to 160–2600 ppt h⁻¹) is calculated from a simple reaction (R1–R4) balance equation under sunny conditions. However, the nature of this source remains unknown. One possible source mechanism may involve heterogeneous formation on organic films on ground and vegetation surfaces with directly photo-catalysed electron transfer to NO₂, as recently suggested by George et al. and Stemmler et al.^[65,66] However, yet unconsidered photochemical processes in the gas phase leading to HNO₂ formation cannot be excluded, as recently proposed by Bejan et al.^[67] These authors estimated an upperlimit for the photolytic HNO₂ formation rate of 100 ppt h⁻¹ for a maximum $J(NO_2)$ value of 10^{-2} s^{-1} , in the presence of 1 ppb of phenolic aromatic hydrocarbons (with a nitro-group in the *ortho* position). But at suburban as well as at rural sites, much lower mixing ratios than used in this laboratory study were observed.^[83,93] For example, the sum of measured mono- and dinitrophenols in the gas phase and liquid phase at Mt. Brocken was ~50 ppt.^[83] Adopting much lower mixing ratio figures, the rates then obtained seem to be an order of magnitude less than needed for balancing the daytime 'new-type' HNO₂ formation. We assume that only a fast electron transfer according to reaction (R5) can account for formation rates this high.^[27] It is well known (e.g. Faust et al.^[94]) that aquated free electrons are photocatalytically produced in the aqueous phase under atmospheric conditions and form O₂⁻ from dissolved O₂.

The evidence for a radiation-dependent HNO₂ source was completely constrained by measured variables and parameters needed to determine the daytime budget of HNO₂. At Hohenpeissenberg a correlation of the extra HNO₂ daytime source against $J(NO_2)$ (calculated by subtracting the known sources, reactions (R3,R4), from the known sinks reactions (R1,R2)) was found to be very significant ($r^2 = 0.81$, Fig. 5).

The heterogeneous nocturnal and daytime HNO_2 formation processes are especially important for the OH[•] budget. As already mentioned, the mechanisms that produce hydroxyl radicals constitute the most important processes that influence the oxidation capacity and ozone formation in the atmosphere.^[6,14,19,25,27] In the following, the primary production of OH[•] was compared for different radical sources, here the photolysis of O₃, HNO₂ and HCHO. Another chemical process that forms OH[•] in the troposphere is the ozonolysis of



Fig. 9. Hohenpeissenberg data of the 4 July 2004: (a) Diurnal variation of ozone at the Hohenpeissenberg summit (closed circles) in comparison with ozone at a foothill site 270 m lower (open diamonds); (b) HO_x radical production rates $P(HO_x)$ at Hohenpeissenberg from the photolysis of HNO₂ (closed diamonds, after subtracting the rate for reaction (R3)), HCHO (open triangles), O₃ (solid line), and HNO₂ (closed circles) calculated from PSS neglecting the unknown daytime source.

unsaturated volatile organic compounds (alkenes, terpenes) and this was found to contribute to the primary OH[•] production by $\sim 4-10\%$,^[24,25] or even more.^[95]

From the simultaneously measured photolysis frequencies and mixing ratios of O_3 , HNO₂, and HCHO the total production rate of HO_x (= OH + HO₂) radicals can be calculated as:

$$P(\text{HO}_x) = J(\text{O}^1\text{D})[\text{O}_3]\Phi_{\text{OH}} + J(\text{HNO}_2)[\text{HNO}_2] + 2 \times J(\text{HCHO})_r[\text{HCHO}]$$
(3)

(with $\Phi_{OH} = OH^{\bullet}$ yield of the $O({}^{1}D) + H_{2}O$ reaction under the measurement conditions; $J(O{}^{1}D) =$ the photolysis frequency of $O_{3} \rightarrow O({}^{1}D)$ and $J(HCHO)_{r} =$ the photolysis frequency of HCHO \rightarrow H + HCO).

The total net OH[•] production rate will be obtained after subtracting the loss rate of OH[•] as a result of reaction (R3). But this was only possible for the Hohenpeissenberg site, were OH was also measured. In Fig. 9b, results from similar estimations are shown for the Hohenpeissenberg site on 4 July 2004. The diurnal profiles of ozone (Fig. 9a) simultaneously measured at 980 m and 710 m a.s.l., respectively, demonstrate the strength of nighttime decoupling and effective daytime mixing between foothill and hilltop layers. Clearly, the important role of HNO2 is evident. The photolysis of HNO₂ starts at larger solar zenith angles compared to photolysis of HCHO and O₃, and particularly in the morning contributions from HNO₂ photolysis are even higher than those from O₃ photolysis. If the HNO₂ mixing ratio is calculated from a PSS, its HO_x production rate would be substantially underestimated. Based on Eqn 3, the contribution of HNO₂ photolysis to the integrated HO_x formation at the top of Hohenpeissenberg was calculated to be in the order of 42% for the 2004 campaign. Also based only on experimental observation, Kleffmann et al. found a contribution of 33% to the primary OH[•] production during noon at the top of a forest canopy.^[25]



Fig. 10. In-situ OH[•] production rates from $J(\text{HNO}_2) \times [\text{HNO}_2]$ from six different campaigns calculated for single sunny days: Rome 29 May 2001 (crosses), Melpitz 27 June 2006 (closed stars), Rossfeld 07 June 2003 (closed circles), Realtor 3 July 2001 (solid line), Hohenpeissenberg 4 July 2004 (open diamonds), Melpitz 6 April 2000 (closed triangles), and Goldlauter 16 October 2001 (closed quadrangle).

Table 3. The OH[•] formation rates from the photolysis of HNO₂ (in-situ), O₃ and HCHO for the period from 29 to 31 May 2001 of the Rome campaign

Time (hours,	Reaction rates $\times 10^6$ (molecule cm ⁻³ s ⁻¹)				
CET)	HNO ₂ photolysis	HCHO photolysis	O ₃ photolysis		
600	9.1-10.7	0.96-2.03	0.03-0.05		
900	27.8-40.6	8.3-15.5	2.5-4.3		
1200	7.1-10.9	11.2-14.5	18.3-27.3		
1500	4.9–6.4	4.6–10.7	11.7–16.2		

Calculated in-situ OH[•] formation rates from nitrous acid alone (no correction for reaction (R3)) for the single sites are compared in Fig. 10. The level of formed OH[•] depends on the accumulated HNO₂ pool, pollution situation, atmospheric stability conditions and radiation intensity. At the Goldlauter site the radiation measurements in the morning hours were influenced by the very nearby stock of trees. For the period from 29 to 31 May 2001 of the Rome campaign, the in-situ OH[•] formation rates from HNO₂ and the rates for the photolysis of O₃ and HCHO are given in Table 3.

Referring, for example, to the lowest 100 m of the PBL, it was found that during the first hours after sunrise the photolysis of HNO₂ is the dominant primary OH[•] source (\sim 80%) in Rome. Its contribution decreases over the morning to \sim 30% at noon, when the ozone mixing ratio and the actinic fluxes in the low UV (below 319 nm) increased significantly. At this time of the day, O₃ photolysis (~30%) and HCHO photolysis (~30%, secondary source) contribute similar amounts.^[24] The data confirm earlier results from Staffelbach et al. who found in the southern part of Switzerland that HNO₂ would account for \sim 30% of the radical production in air close to the ground.^[14] Therefore, HNO₂ photolysis not only acts as a starter for photochemistry in the early morning hours, but also plays a significant role as precursor of photo-oxidants throughout the day. However, because of interaction of nitrous acid and its precursor with the ground (heterogeneous formation, deposition) and a well mixed and much higher daytime boundary layer it should be noted that HNO₂ photolysis is very important only in the lowest few hundred meters of the atmosphere.

Conclusions

Results from seven ground-based field experiments – which took place at different sites in Europe following different objectives in environmental research - were put together concerning their findings in HNO2 chemistry. Average diurnal HNO2 cycles were derived from the data and found to be typical for the location (pollution situation) during the investigated time of the year. Surprisingly, at the three mountain sites the HNO2 mixing ratio often showed a broad maximum or several distinct peaks at midday and lower mixing ratios during the night. In the morning hours, the photolysis of nitrous acid represents the dominant OH source and initiates the daytime photochemistry. HNO2 accounts for \sim 30–42% of the radical production in air close to the ground, similar to contributions from photolysis of HCHO and O3. From the nighttime increase in HNO2 more or less observed at all sites, a rate constant for the heterogeneous formation through reaction (R4) could be estimated to be in the range of 0.006- $0.027 \, h^{-1}$. But despite considering reaction (R4) as a HNO₂ source also during the daytime (in addition to the homogeneous formation, reaction (R3)), a big discrepancy is still observed at all sites between measured HNO2 mixing ratios around noon (up to few hundred ppt) and values expected when assuming PSS conditions. Overall, a missing daytime HNO₂ source of 160–2600 ppt h^{-1} is calculated from a simple balance equation. For the Hohenpeissenberg site, this calculation (\sim 450 ppt h⁻¹) is completely based on measured quantities and is in agreement with results observed elsewhere.^[25] The high correlation of the extra HNO2 daytime source against J(NO2) observed there, also gives evidence for a radiation dependent source. In the literature different light-dependent processes are proposed, but we hypothesise that only a fast electron transfer onto adsorbed NO₂ may explain the measured daytime HNO2 mixing ratio levels. The key question is the electron source, which is likely to be from organic compounds. Understanding the formation of nitrous acid as an important trace species in the tropospheric oxidant chemistry is clearly a critical area for future research.

Acknowledgements

This work combines results from different joint research studies supported by the German Ministry of Education and Research (BMBF), the Deutsche Forschungsgemeinschaft (DFG) and the European Commission (EU). We thank all colleagues involved in the projects for excellent co-operation and the two anonymous reviewers for their careful revision of the manuscript.

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Manuscript received 26 February 2007, accepted 30 May 2007