

Nitrous acid in the urban area of Rome

Karin Acker^{a,*}, Antonio Febo^b, Sebastian Trick^{c,1}, Cinzia Perrino^b, Paolo Bruno^{b,2},
Peter Wiesen^d, Detlev Möller^a, Wolfgang Wieprecht^a,
Renate Auel^a, Marco Giusto^b, Andreas Geyer^{c,3}, Ulrich Platt^c, Ivo Allegrini^b

^aBrandenburgische Technische Universität Cottbus (BTU), Lehrstuhl für Luftchemie und Luftreinhaltung, 03013 Cottbus, Germany

^bC.N.R. Consiglio Nazionale delle Ricerche, Istituto Inquinamento Atmosferico, Rome, Italy

^cUniversität Heidelberg (UHEI), Institut für Umweltphysik, Germany

^dBergische Universität Wuppertal, Physikalische Chemie, Germany

Received 23 June 2005; accepted 13 January 2006

Abstract

Nitrous acid (HNO_2) and a large variety of other components were simultaneously measured in the city centre of Rome (Italy) during the NITROCAT ground based field experiment in May/June 2001. The highest HNO_2 concentrations were found under high-pressure conditions with high nocturnal atmospheric stability and high values of pollutants. After night time formation and accumulation up to 2 ppb HNO_2 were observed. The measurements confirm that during the first hours after sunrise, when hydroxyl radical (OH) production rates from other sources (photolysis of ozone and formaldehyde (HCHO)) are slow, HNO_2 photolysis is the most important primary OH source in the lowest part of the troposphere; up to $1-4 \times 10^7 \text{ OH cm}^{-3} \text{ s}^{-1}$ were estimated for that time from this source. This contributes considerably to the initiation of the photochemistry for the day. The unexpected high daytime concentrations of few hundred ppt observed by DOAS as well as by the two in situ wet collection techniques (wet denuder/IC, coil sampling/HPLC) possibly influence ozone chemistry during the entire day. The heterogeneous on-surface production of HNO_2 (and consequently of HNO_3) provides also a new-type acidity formation influencing directly the biosphere and the materials. About 20% of the total nitrite was found on atmospheric aerosols. The HNO_2 measurements agree well for the different in situ measurement techniques and the spatial integration DOAS simultaneously performed over several weeks in the real atmosphere and during reaction chamber experiments.

© 2006 Elsevier Ltd. All rights reserved.

Keywords: Air pollution; Atmospheric chemistry; Heterogeneous processes; Nitrous acid

1. Introduction

Nitrous acid is one of the most investigated species in laboratory, field and modelling studies. The HNO_2 formation process is of crucial interest and, up to now, not completely clear. The basic known properties of the HNO_2 formation are extensively summarised among others in [Stutz](#)

*Corresponding author.

E-mail address: ack@btu-lc.fta-berlin.de (K. Acker).

¹Now at: ABB Automation GmbH Frankfurt, Germany.

²Now at: Environnement S.A, Poissy Cedex, France.

³Now at: University of California Los Angeles, Department of Atmospheric and Oceanic Sciences, USA.

et al. (2004). HNO_2 is often referred to as a typical product of the polluted urban air because its amount seems to depend on the degree of pollution. The observed high HNO_2 concentration in the atmosphere cannot be explained either by homogeneous gas reactions, which are too slow, or by direct emissions from combustion processes, which are too small. Nitrous acid was detected for the first time in the ambient air by Perner and Platt (1979) and since that time its heterogeneous formation was assumed, nowadays by the heterogeneous reaction of NO_2 with water on surfaces



In the last two decades, numerous studies were carried out to investigate the heterogeneous NO_2 reactivity, e.g., on vegetated, aqueous, sea salt, carbonaceous or urban surfaces having different catalytic properties (e.g., Svensson et al., 1987; Vecera and Dasgupta, 1994; TenBrink and Spoelstra, 1998; Kalberer et al., 1999; Stadler and Rossi, 2000; Gutzwiller et al., 2002; Geiger et al., 2002; Finlayson-Pitts et al., 2003; Schimang et al., 2006). The formation of HNO_2 on aerosol surfaces, soils, cloud droplets, fog and dew was estimated to be also atmospheric relevant (e.g., Notholt et al., 1992; Harrison and Kitto, 1994; Simon and Dasgupta, 1995; Lammel and Cape, 1996; Kleffmann et al., 1998; Reisinger, 2000; Acker et al., 2001; Zhou et al., 2002; Rubio et al., 2002; Stutz et al., 2002). Nitrous acid, which accumulates in the planetary boundary-layer (PBL) at night, is photolysed during the day to form NO and the hydroxyl radical OH, which is the most important oxidizing species in the daytime atmosphere, in polluted as well as in clean areas (e.g., Crutzen and Zimmermann, 1991). Results from the Berlin-Ozone-Experiment BERLIOZ showed that the peak OH formation rate from HNO_2 photolysis is comparable to that from ozone photolysis at noon. 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., 2002, 2003). Recent estimates further suggest a continuous and non-trivial contribution towards OH-production during the day (e.g., Staffelbach et al., 1997; Zhou et al., 2002; Ren et al., 2003; Kleffmann et al., 2005; Acker et al., 2006; Aumont et al., 2003). Despite rapid photolysis of HNO_2 unexpected high values of HNO_2 (100–400 ppt) have been detected during the day in urban (e.g., Febo et al., 1996) but also rural (e.g., Staffelbach

et al., 1997; Zhou et al., 2002; Acker et al., 2005) regions. It therefore seems likely that an additional (yet unknown) HNO_2 source is present during the day. A photoenhanced surface formation of HNO_2 following the NO_2 and H_2O adsorption has been previously proposed by Akimoto et al. (1987), partly confirmed by Zhou et al. (2003) and Ramazan et al. (2004); different mechanisms have been suggested, e.g. photolysis of adsorbed HNO_3 or NO_2 -water adducts. Efficient light-dependent HNO_2 formation processes are proposed also in other recent studies (e.g., Kleffmann et al., 2005; George et al., 2005; Acker et al., 2006).

2. Experimental

The measurements were performed in Rome during the NITROCAT (NITRous acid and its influence on the Oxidation Capacity of the ATmosphere) campaign in late spring 2001 at two different sites inside the urban area of Rome. The first site was located at the northern end of the city centre inside the Villa Ada Park (west of Via Salaria, which had high traffic density throughout the day) and was defined as urban background station; all samples were taken at about 3–8 m altitude above the ground. The second one was installed on the top of the CNR headquarter building in the city centre, about 2 km south of the Villa Ada site, and all measurements were done approx. 50 m above street level. Other measurements including HNO_2 were carried out at the rural station of Montelibretti, sited about 25 km north-east of Rome. During the afternoon sea-breeze, this site was in the prevailing downwind direction from the others. Results from this site are given and discussed in Wiesen (2003) and Trick (2004). Three different measurement techniques have been used for the determination of nitrous acid in Rome.

2.1. LP-DOAS

On top of the CNR building one active long path (LP) DOAS telescope was sited (built and operated by UHEI), having one fixed light path of 3690 m (one-way) to north-eastern direction (from the city centre towards a sub-urban residential area). The light beam (from a 500 W Xe high-pressure arc lamp) was then reflected by an array of 69 retroreflectors (Quartz triple prisms) and sent to a Czerny–Turner spectrograph—1024 pixel photodiode array detector system for analysis of

characteristic trace gas absorption structures. A total spectral range of 309–390 nm was available. The principle of this LP-DOAS system including optical components and analysis procedure has been described in detail among others in Stutz and Platt (1996) and Trick (2004). The average detection limit of the HNO₂ concentration determination was 0.078 ppb, the systematic error $\pm 6\%$, the time resolution varied between 5 and 15 min.

2.2. DNPH-HPLC

A measurement technique based on aqueous scrubbing using a coil sampler (air sampling flow rate 2 l min⁻¹, liquid flow rate 0.24 ml min⁻¹, 1 mM phosphate buffer) followed by 2,4-dinitrophenylhydrazine (DNPH) derivatisation (300 μ M DNPH and 8 mM HCl at 45 °C and completed within few minutes) and reverse-phase high-performance liquid chromatographic (HPLC) analysis (UV detection at 309 nm) was run at the Villa Ada site. The precision of the instrument can be checked by comparing the signals coming from the two independent inlet lines and was estimated to be around $\pm 4\%$. The detection limit is 0.005 ppb at a temporal resolution of 5 min. More details are given in Zhou et al. (2002).

2.3. WEDD/steam jet

The principle of diffusion-based collection of trace gases on a wetted (here about 0.5 ml pure deionised water per minute) denuder surface (wet effluent diffusion denuder WEDD) with separation from their particulate counterparts was adopted e.g. from Simon and Dasgupta (1995), Khlystov et al. (1995), Neftel et al. (1996), Zellweger et al. (1999), Löflund et al. (2001) and modified (Acker et al., 2005). This technique was operated at the Villa Ada site. Behind the denuder water steam is added to the airflow and the aerosol particles grow to droplets in an aerosol chamber, later separated from the air stream using a cyclone. The solutions containing the scavenged acids and aerosol compounds are pumped peristaltically each through one of the two pre-concentration columns. Alternately, one of these columns is used for pre-concentration while the other is eluted by the elutant for direct ion chromatographic analysis (IC). Using 30 min sampling time at an air flow of 10 l min⁻¹, the detection limit for HNO₂ (HNO₃) is 0.002 ppb, for aerosol nitrite (nitrate) 5 ng m⁻³.

A large variety of other components was measured in the urban centre of Rome simultaneously. Additional measurements included NO₂, HCHO and O₃ by DOAS and CO, PAN (peroxyacetyl nitrate), NO₂, NO, NO_y, O₃ and SO₂ by continuous analysers. Total suspended particles (TSP) were collected on filters installed in a high volume sampler (DIGITEL). A spectroradiometer (Bentham, typ DTM300) was operated to measure the actinic flux in the range of 280–425 nm, from which the photolysis frequencies $J(\text{NO}_2)$, $J(\text{HNO}_2)$, $J(\text{O}^1\text{D})$, and $J(\text{HCHO})$ were calculated. A set of meteorological parameters was measured using commercial analysers. Natural radioactivity measurements were carried out by means of an automatic sampler that draws air through a filter which was hourly analysed for the total beta activity of the short-lived radon progeny.

2.4. Chamber experiments

Within the extension of the NITROCAT project a set of chamber experiments was carried out in April 2002 in the building of the UHEI. The NO₂ conversion and the HNO₂ formation was studied both, on Teflon and on real asphalt surfaces by addition of gaseous NO₂ to a wet or dry atmosphere inside the chamber. Details are discussed elsewhere (Wiesen, 2003; Trick, 2004), here only few data are used to show quality and comparability of HNO₂ data from different techniques. The reaction chamber (based on Volkamer, 1996) mainly consists of a Teflon tube of 15 m length with a diameter of 0.5 m. Two Aluminium boxes containing the mirrors of the UHEI DOAS White multi-reflection system (Trick, 2004) closed each end of the chamber. Therefore the DOAS integrated the trace gas concentrations of NO₂, HNO₂, O₃, and HCHO in the whole chamber. Additional HNO₂ was measured by the LOPAP instrument (LP absorption photometry after wet chemical sampling and production of an azo dye; Heland et al., 2001; Kleffmann et al., 2002) with a time resolution of 0.5 min at one end of the chamber. At the other end the WEDD (Acker et al., 2004) with a time resolution of 10 min and a NO/NO₂ monitor were placed, also to characterise the background level of HNO₂, NO₂ and NO and mixing conditions.

3. Results

Compared to other capital cities in Europe the industrial sector in Rome is small. The pollution

levels (e.g., particulate matter and nitrogen oxides) are mainly due to public and private energy consumption (~30%) and transport (~60%, mainly private), see Kirchmayer et al. (2005).

During the late spring 2001 campaign, the atmosphere of Rome can be generally described as polluted: up to 90 ppb NO (30 min average), 55 ppb NO₂ (30 min average), 75 μg m⁻³ TSP (12 h average), but on average only 2 ppb SO₂, were detected. Only in low pressure conditions (e.g., on 3–4 June 2001) significantly reduced values of pollutants were found due to the strong mixing of the atmosphere and to the absence of atmospheric nighttime stabilisation, as can be seen for example for the HNO₂ concentration (Fig. 3), which remains low also during nights. During the high-pressure period of 27–31 May 2001 a strong build-up and break-up of ground inversions occurred. This was detected by the study of the time pattern of the natural radioactivity due to the short-lived progeny of radon, an inert trace gas emitted only by the soil that can be used as a tracer for atmospheric stability (Perrino et al., 2001), see also Fig. 5 (graph 4). During the entire period of 27–31 May 2001, elevated concentrations of photochemical products like nitric acid (HNO₃) and PAN were observed (Fig. 1). It is also interesting to observe that the partition between nitric acid and particulate nitrate formed by the oxidative chain is in favour of nitrate.

That is not surprising because in the first hours of the morning much ammonia (up to 7–8 μg m⁻³ at the Villa Ada site, but 15–20 μg m⁻³ at traffic sites, Perrino et al. (2002)) is available in the atmosphere (emission from catalytic converters) for the reaction with nitric acid. Later on, the dilution of the lower atmosphere causes a fast decrease of the concentration level of nitrate. Most of the atmospheric nitrite (~80%) is present as HNO₂ in the gas phase. The amount of aerosol nitrite found (~20% of the total, see also Fig. 1) indicate that aerosols should be taken into consideration as a surface for the heterogeneous formation of HNO₂, although formation on the ground surface is expected to be the main source of HNO₂ (e.g., Neftel et al., 1996; Veitel 2002). Anyway, daytime HNO₂ concentrations of more than 500 ppt found on cloudy days in Rome, e.g. entire 24 May 2001 (Figs. 2 and 3) may support the idea of a wet aerosol-related HNO₂ formation (a mechanism which adds to the reduced photolysis rates occurring in cloudy conditions and in winter-time atmospheres (e.g., Reisinger, 2000)). Altogether the measured species HNO₂, HNO₃, nitrite, nitrate and PAN contribute on average to 15% to the total reactive nitrogen budget NO_y, ranging from 3% when fresh emissions affected the site, to 50% for more aged air masses (around noon). Deposition of nitrogen acids, but also of NO_x and PAN can cause stress for plant organisms,

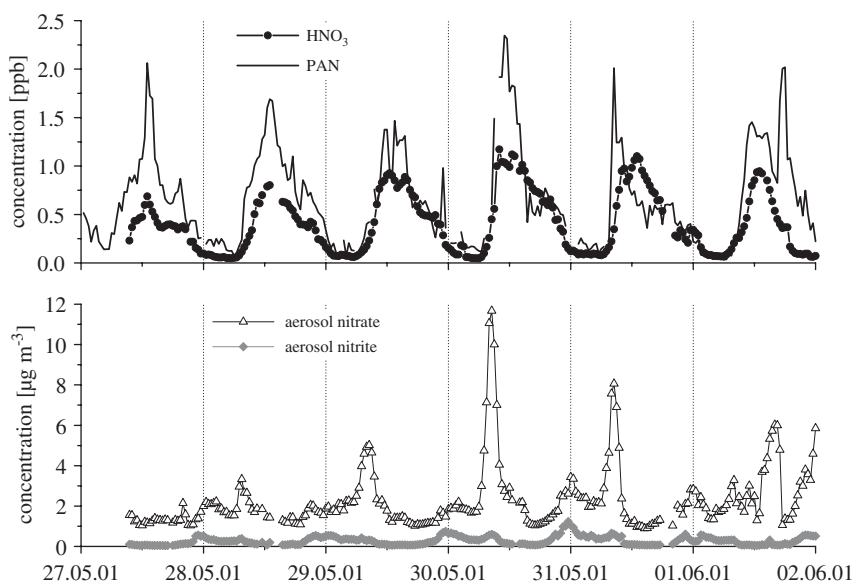


Fig. 1. Temporal variation of nitric acid (upper graph, closed circles), PAN (upper graph, solid line), aerosol nitrite (lower graph, grey closed diamonds) and aerosol nitrate (lower graph, open triangles) observed between 27 May and 01 June 2001 at the site Villa Ada, Rome.

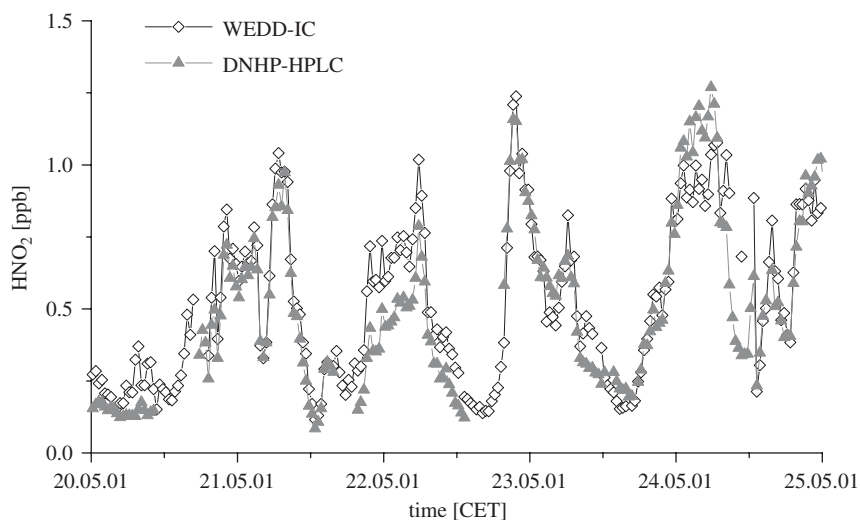


Fig. 2. HNO_2 concentration measured by the WEDD (open diamonds) and DNHP-HPLC (closed grey triangles) instruments for 5 days at the Villa Ada site.

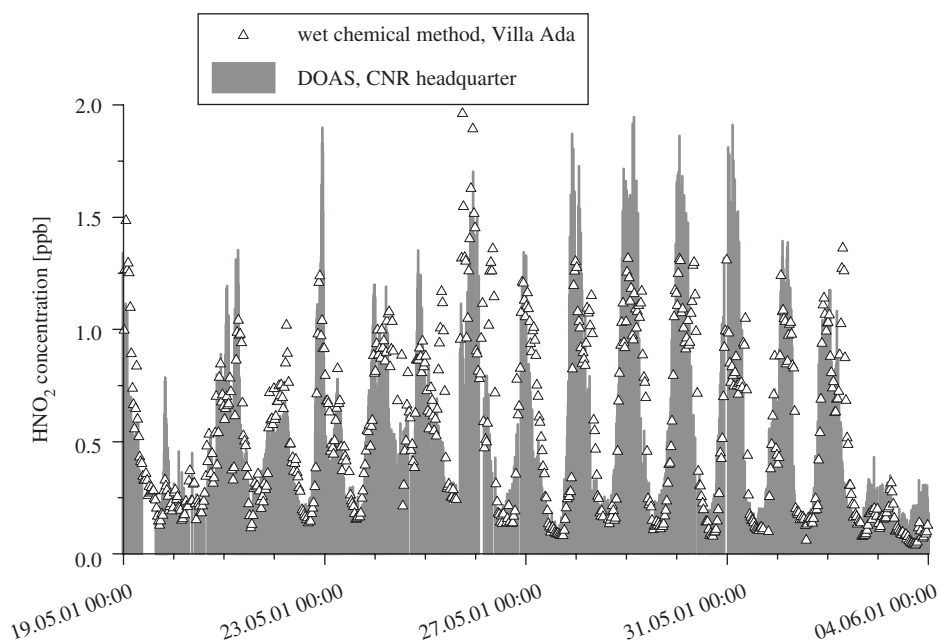


Fig. 3. Nitrous acid in the centre of Rome measured by LP-DOAS (grey area) and wet chemical methods (open triangles) from 19 May to 03 June 2001.

HNO_2 is also a precursor to harmful pollutants (nitrosamines, nitroaromatic compounds).

Mixing ratios of nitrous acid in Rome showed a typical strong diurnal cycle. The concentration levels and the temporal structures of the HNO_2 data obtained by the three independent methods are in good agreement. In Fig. 2 the HNO_2 concentra-

tion measured by WEDD-IC as well by DNHP-HPLC during 5 days of the NITROCAT campaign at the Villa Ada site are compared. The correlation analysis of 30 min data from both wet chemical methods over the whole campaign leads to a coefficient of $r = 0.89$ ($N = 563$; $y(\text{HPLC}) = 1.22x(\text{WEDD}) - 0.045$). In Fig. 3 the time series

of the Villa Ada HNO_2 (mean of both data sets) are shown in comparison to that derived from LP-DOAS at the CNR headquarter building. To our knowledge for the first time such an experimental data set over few weeks of simultaneous HNO_2 measurements using DOAS and wet chemical instruments under ambient conditions is presented. Comparison studies for different continuous wet denuder measurements are described among others in Genfa et al. (2003) and Acker et al. (2004). Despite the spatial distance of the DOAS and wet chemical measurements in Rome (see experimental chapter) and the fact, that here data from in situ point-sampling instruments are compared with trace gas concentrations averaged over the length of a light path of 3.7 km, the HNO_2 data agree well. During well mixed atmospheric conditions (because the methods were operated at different heights above the ground) the following linear regression parameters were obtained for $N = 114$ data from 1000–1600 CET on 20, 22, 25–31 May, 01 and 04 June: $y(\text{wet}) = 0.009 + 0.92 x(\text{DOAS})$ ($r = 0.7$). This indicates that at low atmospheric HNO_2 concentrations and under urban pollution conditions the wet chemical methods show no systematic interference to higher values. A similar good agreement between HNO_2 data measured with a wet technique (LOPAP) and a DOAS White system during the formaldehyde as a tracer of oxidation in the troposphere (FORMAT) campaign in Bresso/Milan (Italy) in summer 2002 is reported for few days in Trick (2004). During the NITROCAT reaction chamber experiments (Wiesen, 2003; Trick, 2004),

WEDD, LOPAP and DOAS White system were used simultaneously. Fig. 4 shows the data for one case study when the whole inner surface was the Teflon tube only and NO_2 was added (180 ppb) after flushing the reaction chamber three times with synthetic air cleanliness 5.0. The NO_2 is converted partly into HNO_2 , and after reaching the maximum HNO_2 concentration a first order loss process of HNO_2 is observed. A good mixing of the air mass inside the reaction chamber is confirmed by the NO_2 data from DOAS and the NO_2 monitor at the end of the chamber. The concentration time profiles of HNO_2 are found to be in good agreement for the three measurement techniques also at high NO_2 levels. Even though spectroscopic methods can have some clear advantages when dealing with reactive molecules, also the different wet chemical methods can successfully measure atmospheric HNO_2 with high time resolution and with high detection sensitivity.

During the NITROCAT campaign, the HNO_2 concentrations were positively correlated with those of NO_2 , but different meteorological and air chemical regimes cause significant differences in the source-receptor relationship. The HNO_2 -to- NO_2 ratio is a useful parameter in discussing the diurnal cycle of HNO_2 because it is less influenced by transport processes than individual concentrations. On average, a ratio of 0.033 was observed, significantly higher than the value known for direct emission from combustion sources which was found to be ~ 0.008 (e.g., Kurtenbach et al., 2001).

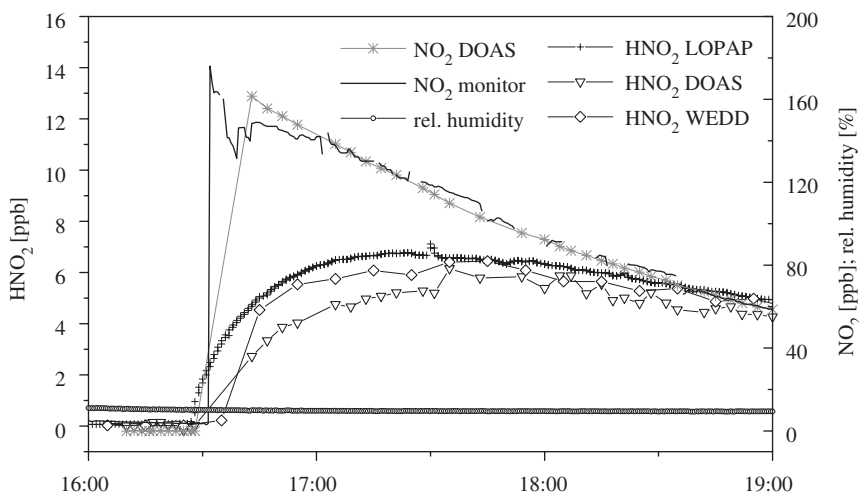


Fig. 4. The concentration time profiles of NO_2 (DOAS: stars; NO_2 monitor: solid line) and HNO_2 (DOAS: open triangles; WEDD: open diamonds; LOPAP: crosses) during a reaction chamber (teflon tube) characterisation experiment at low humidity (open circles).

In the following the period with photochemical smog conditions (27 May–01 June 2001; high pressure system over Italy, clear skies) is discussed. Generally, sun irradiation was high; photolysis frequencies for NO_2 , HNO_2 , $\text{O}(^1\text{D})$ and HCHO peaked for example at noon on 30 May 2001, at 1×10^{-2} , 2×10^{-3} , 7×10^{-5} and $1 \times 10^{-4} \text{ s}^{-1}$, respectively. The nocturnal pattern of HNO_2 (Fig. 5) is similar to those observed at many other urban sites reflecting the nocturnal heterogeneous formation (assuming a pseudo-first order rate concerning NO_2) after sunset until midnight. Simultaneously, NO_2 starts to increase: due to the build-up of an inversion layer, in fact, ozone at the ground is decoupled from the upper reservoir layer,

the concentration of NO , as well as of all primary pollutants, increases, and thus the titration reaction reaches its maximum (Fig. 5). The increase of NO_2 concentration stops when the surface O_3 amount is run out. NO_2 concentration decreases after midnight likely by removal processes onto surfaces. The concentration of HNO_2 reaching a maximum around midnight is then slightly decreasing until 0800, possibly due to the dry deposition which counterbalance the HNO_2 surface formation. As a consequence of the above mechanisms, the $[\text{HNO}_2]/[\text{NO}_2]$ ratio increases steady from ~ 0.015 at 1900 (sunset) to ~ 0.04 at 0430 (sunrise) (accumulation of HNO_2 relatively to NO_2). However, a maximum in the $[\text{HNO}_2]/[\text{NO}_2]$ ratio is found between 0500 and

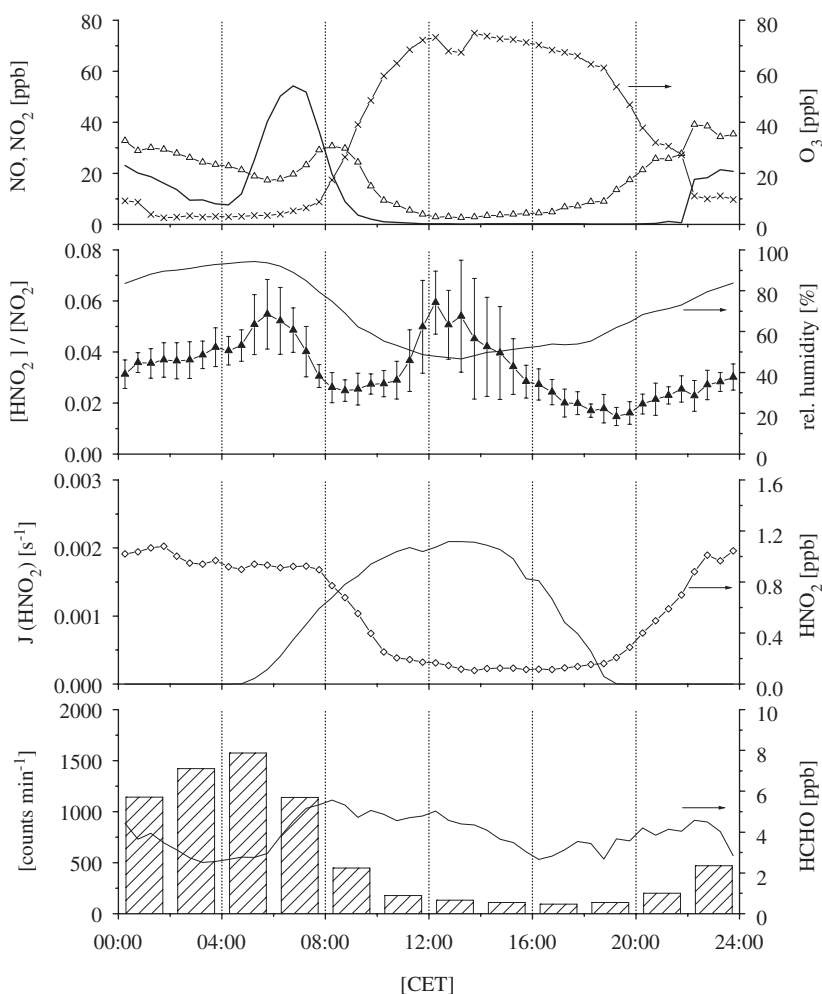
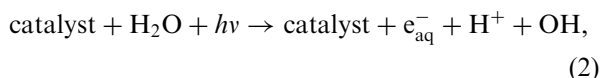


Fig. 5. Diurnal variation of different parameters in the centre of Rome (averaged over the high pressure period 27 May–01 June 2001). Graph 1 shows the NO (solid line), NO_2 (open triangles) and O_3 (crosses) concentrations. The graph 2 presents the HNO_2 to NO_2 ratio (closed triangles) and the relative humidity (solid line). In graph 3, the HNO_2 mixing ratio (open diamonds) and the photolysis frequency $J(\text{HNO}_2)$ (dashed line) are given. The lowest graph shows the variation in natural radioactivity (columns) and in HCHO concentration (solid line). Data from Villa Ada site, only $J(\text{HNO}_2)$ and HCHO from CNR headquarter site.

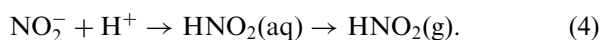
0600 (~0.055) just before NO₂ increase. This NO₂ increase is due to many concurrent processes: the slow increase in the height of the mixed layer which permits a slow intrusion of ozone from the upper layers and the production of HO₂, starting after sunrise, which allows the emitted NO to be oxidised to NO₂. This early morning phase of the oxidative process is crucial for determining the strength of the photochemical smog episode in the lower boundary layer during the rest of the day. During the same period, HNO₂ concentration decreases because of both the increasing height of the mixed layer and the beginning of the photolytic process. From the above, it follows that the [HNO₂]/[NO₂] ratio decreases to a minimum between 0800 and 1000 and that NO₂-HNO₂ relationship is shifted into a different photostationary state (PSS). The increase of the vertical mixing leads to “dilution” of all surface produced species. NO reaches concentration values close to zero as a result of the titration reaction. The [HNO₂]/[NO₂] ratio rises again after 10:00 until noon suggesting (as also the increase by about 50% in less than 1 h with the first sun radiation) an effective daytime HNO₂ source which is much stronger than the nocturnal heterogeneous formation. An effective (radiation and surface dependent) photocatalytic process could be a possible explanation. The HNO₂ concentration remains constant between 1100 and 1800 (~200 ppt) as a result of the stationary state between all the sink and the source processes (beside the “new-type” HNO₂ formation the “classical” nocturnal formation is active). The decrease of the [HNO₂]/[NO₂] ratio after 1200 (minimum around 1900) may be attributed to a lowering of the additional HNO₂ source—which we assume to be radiation dependent—and to the reduced surface wetness which is a precondition (e.g., Lammel, 1999; Finlayson-Pitts et al., 2003; Stutz et al., 2004) for the heterogeneous HNO₂ formation on surfaces. With sunset (after 1900) the [HNO₂]/[NO₂] ratio increases again due to increasing NO₂ concentration and “classical” surface formation, amplified by the stabilisation of the lower atmosphere as well as to increasing humidity and missing HNO₂ photolysis.

The NITROCAT data reinforce the assumption of the existence of a strong daytime HNO₂ source. A photocatalytic enhancement of HNO₂ formation already has been proposed by Akimoto et al. (1987) based on smog chamber studies. They found a photoenhancement factor of about 7 comparing to the “dark” reaction (1) which would explain the

nature of the extra OH radical flux in smog chamber experiments. Our likely explanation could be given by assuming a very fast electron transfer to NO₂ which may lead to the direct formation of nitrite anions. The formation of free electrons in aqueous phase is well known via different photocatalytic initial processes, following described by a schematic net process (2):



With the subsequent e-transfer to adsorbed NO₂ as proposed above



Similar e-transfers onto O₂ and O₃ have been already described elsewhere.

As a final result acidity is produced and, even when HNO₂ is not emitted into the atmosphere, a surface acidification occurs. Deposition of HNO₂ was found to be particularly efficient on vegetation (e.g., Neftel et al., 1996; Harrison and Kitto, 1994) and wet sandstone (Behlen, 1996); it was also suggested (e.g., Lammel and Metzger, 1998) and experimentally shown (Trick, 2004) for urban surfaces. The release of deposited or of on-surface heterogeneously formed nitrous acid into the gas phase is a strong function of pH (dissociation equilibrium).

The heterogeneous nocturnal and daytime HNO₂ formation processes are especially important for the OH budget. As already mentioned, the mechanisms producing OH radicals constitute the most important processes influencing the oxidation capacity and ozone formation in the atmosphere. Starting from the measured photolysis frequencies and concentrations the radical production rates P(OH) from the photolysis of HNO₂, HCHO, and O₃ were calculated on the basis of the reactions and equations described among others in Aliche et al. (2003), and will not be revised here. For the period 29–31 May 2001 of the NITROCAT campaign these values are given below in [10⁶ cm⁻³ s⁻¹]:

Time [CET]	0600	0900	1200	1500
HNO ₂ photolysis	9.1–10.7	27.8–40.6	7.1–10.9	4.9–6.4
HCHO photolysis	0.96–2.03	8.3–15.5	11.2–14.5	4.6–10.7
O ₃ photolysis	0.03–0.05	2.5–4.3	18.3–27.3	11.7–16.2

Because of its lower dissociation threshold, the photolysis of HNO_2 accumulated during the night in Rome started immediately after sunrise (Fig. 5), followed by the photolysis of formaldehyde. The HCHO mixing ratios followed the same temporal trend as the O_x ($\text{O}_3 + \text{NO}_2$) variable (not shown here), suggesting that HCHO is mainly of secondary origin. The oxidative process occurred very early in the morning when ozone photolysis was almost negligible. At the time when the oxidation was at its maximum rate (about 0830 CET, Fig. 5), the ozone mixing ratio was still below 20 ppb and the OH production rate from O_3 was still not significant. The photolysis of O_3 became important later in the day (see values given above), when the actinic fluxes in the low UV (below 319 nm) increased sufficiently.

A detailed quantitatively estimation of different OH production and removal processes to the total daytime production of OH in Rome was done by Trick (2004) using a combination of the highly resolved one-dimensional “Nocturnal Chemistry And Transport” model with its altitude-dependent calculation of vertical trace gas fluxes and the established gas-phase “Regional Atmospheric Chemistry Mechanism” (RACM). It also includes variable biogenic and anthropogenic emissions, dry deposition, and surface chemistry. 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 HNO_2 photolysis is very important only in the lowest few hundred metres of the atmosphere.

4. Conclusion

Measurements were performed in the urban area of Rome indicating that the heterogeneous formation (on urban surfaces, vegetation, aerosols) is a significant source of nitrous acid during the night (up to 2 ppb were found), but also throughout the day, possibly intensified by photocatalytic reactions. The HNO_2 -to- NO_2 ratio varied in a wide range (0.015–0.1) and showed a diurnal pattern with maxima in the night and around noon. High daytime HNO_2 concentrations of few hundred ppt were observed by DOAS as well as by the in situ wet collection techniques used in this study. Referring for example to the lowest 100 m of the PBL, it was found that during the first hours after sunrise the photolysis of HNO_2 is the dominant primary OH source (~80%). Its contribution decreases over the

morning to ~30% at noon. At this time of the day, O_3 photolysis (~30%) and HCHO photolysis (~30%, secondary source) contribute similar amounts (Trick, 2004). The data confirm earlier results from Staffelbach et al. (1997), who found in the southern part of Switzerland that HNO_2 would account for about 30% of the radical production in air close to the ground. Therefore, HNO_2 photolysis not only acts as starter of photochemistry in the early morning hours, but also plays a significant role as precursor of photo-oxidants throughout the day. An impact of the HNO_2 heterogeneous formation process on the surface of biological and non-biological materials could be assumed and should be object of further investigations, also the search for an effective daytime HNO_2 source. For it under ambient conditions optical as well as wet chemical measurements can provide satisfied HNO_2 data.

Acknowledgements

The NITROCAT programme was a European initiative and supported by the European Commission (EC framework 5 project NITROCAT EVK2-1999-00207). We would like to thank all colleagues for excellent co-operation in the project, especially J. Kleffmann for LOPAP measurements and many helpful discussions.

References

- Acker, K., Möller, D., Wierecht, W., Auel, R., Kalaß, D., Tschervenka, W., 2001. Nitrous and nitric acid measurements inside and outside of clouds at Mt. Brocken. *Water, Air and Soil Pollution* 130, 331–336.
- Acker, K., Spindler, G., Brüggemann, E., 2004. Nitrous and nitric acid measurements during the INTERCOMP2000 campaign in Melpitz. *Atmospheric Environment* 38, 6497–6505.
- Acker, K., Möller, D., Auel, R., Wierecht, W., Kalaß, D., 2005. 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. *Atmospheric Research* 74 (1–4), 507–524.
- Acker, K., Möller, D., Wierecht, W., Meixner, F., Bohn, B., Gilge, S., Plass-Dülmer, C., Berresheim, H., 2006. Strong daytime production of OH from HNO_2 at a rural mountain site. *Geophysical Research Letters* 33, L02809.
- Akimoto, H., Takagi, H., Sakamaki, F., 1987. Photo-enhancement of the nitrous acid formation in the surface reaction of nitrogen dioxide and water vapour: extra radical source in smog chamber experiments. *International Journal of Chemical Kinetics* 19 (6), 539–551.
- Alicke, B., Platt, U., Stutz, J., 2002. Impact of nitrous acid photolysis on the total hydroxyl radical budget during the

- limitation of oxidant production/Pianura Padana Produzione di Ozono study in Milan. *Journal Geophysical Research* 107 (D22), 8196.
- Alicke, B., Geyer, A., Hofzumahaus, A., Holland, F., Konrad, S., Pätz, H.W., Schäfer, J., Stutz, J., Volz-Thomas, A., Platt, U., 2003. OH formation by photolysis during the BERLIOZ experiment. *Journal Geophysical Research* 108 (D4), 8247.
- Aumont, B., Chervier, F., Laval, S., 2003. Contribution of HONO sources to the $\text{NO}_x/\text{HO}_x/\text{O}_3$ chemistry in the polluted boundary layer. *Atmospheric Environment* 37, 487–498.
- Behlen, A., 1996. Reaktive Stickstoffverbindungen in der Atmosphäre—Konzentrationsbestimmung und trockene Deposition auf Natursteine Ph.D. Thesis, Universität Hamburg, Schriftenreihe Angewandte Analytik, vol. 29, pp 207.
- Crutzen, P.J., Zimmermann, P.H., 1991. The changing photochemistry of the troposphere. *Tellus* 43, 136–151.
- Febo, A., Perrino, C., Allegrini, I., 1996. Measurement of nitrous acid in Milan, Italy, by DOAS and diffusion denuders. *Atmospheric Environment* 30, 3599–3609.
- Finlayson-Pitts, B.J., Wingen, L.M., Sumner, A.L., Syomin, D., Ramazan, K.A., 2003. The heterogeneous hydrolysis of NO_2 in laboratory systems and in outdoor and indoor atmospheres: An integrated mechanism. *Physical Chemistry Chemical Physics* 5 (2), 223–242.
- Geiger, H., Kleffmann, J., Wiesen, P., 2002. Smog chamber studies on the influence of diesel exhaust on photosmog formation. *Atmospheric Environment* 36, 1737–1747.
- Genfa, Z., Slanina, S., Boring, C.B., Jongejan, P.A.C., Dasgupta, P.K., 2003. Continuous wet denuder measurements of atmospheric nitric and nitrous acids during the 1999 Atlanta Supersite. *Atmospheric Environment* 37, 1351–1364.
- George, C., Strekowski, R.S., Kleffmann, J., Stemmler, K., Ammann, M., 2005. Photoenhanced uptake of gaseous NO_2 on solid organic compounds: a photochemical source of HNO_2 . *Faraday Discussion* 130, 1–16.
- Gutzwiller, L., Arens, F., Baltensperger, U., Gaggeler, H.W., Ammann, M., 2002. Significance of Semivolatile Diesel Exhaust Organics for Secondary HONO Formation. *Environmental Science & Technology* 36, 677–682.
- Harrison, R.M., Kitto, N., 1994. Evidence for a surface source of atmospheric nitrous acid. *Atmospheric Environment* 28, 1089–1094.
- Heland, J., Kleffmann, J., Kurtenbach, R., Wiesen, P., 2001. A new instrument to measure gaseous nitrous acid (HONO) in the atmosphere. *Environmental Science & Technology* 35, 3207–3212.
- Kalberer, M., Ammann, M., Arens, F., Gaggeler, H.W., Baltensperger, U., 1999. Heterogeneous formation of nitrous acid (HNO_2) on soot aerosol particles. *Journal Geophysical Research* 104 (D11), 13825–13832.
- Khlystov, A., Wyers, G.P., Slanina, J., 1995. The steam-jet aerosol collector. *Atmospheric Environment* 29, 2229–2234.
- Kirchmayer, U., Michelozzi, P., Forastiere, F., Perucci, C., 2005. Rome city report. Department of Epidemiology, Local Health Authority RM/E in <http://www.apheis.net/apheisnewcityreports1.pdf>.
- Kleffmann, J., Becker, K.H., Wiesen, P., 1998. Heterogeneous NO_2 conversion processes on acid surfaces: possible atmospheric implications. *Atmospheric Environment* 32, 2721–2729.
- Kleffmann, J., Heland, J., Kurtenbach, R., Lörzer, J., Wiesen, P., 2002. A new instrument (LOPAP) for the detection of nitrous acid (HONO). *ESPR—Environmental Science & Pollution Research Special. Issue 4*, 48–54.
- Kleffmann, J., Gavriolaiei, T., Hofzumahaus, A., Holland, F., Koppmann, R., Rupp, L., Schlosser, E., Siese, M., Wahner, A., 2005. Daytime formation of nitrous acid: a major source of OH radicals in a forest. *Geophysical Research Letters* 32, L05818.
- Kurtenbach, R., Becker, K.H., Gomes, J.A.G., Kleffmann, J., Lörzer, J.C., Spittler, M., Wiesen, P., Ackermann, R., Geyer, A., Platt, U., 2001. Investigations of emissions and heterogeneous formation of HONO in a road traffic tunnel. *Atmospheric Environment* 35, 3385–3394.
- Lammel, G., 1999. Formation of nitrous acid—parameterisation and comparison with observations. Report 286, MPI für Meteorologie Hamburg, 36pp.
- Lammel, G., Cape, N.J., 1996. Nitrous acid and nitrite in the atmosphere. *Chemical Society Review* 25, 361–369.
- Lammel, G., Metzger, G., 1998. On the occurrence of nitrite in urban fog water. *Chemosphere* 37, 1603–1614.
- Löflund, M., Kasper-Giebl, A., Tschewenka, W., Schmid, M., Giebl, H., Hitzinger, R., Reischl, G., Puxbaum, H., 2001. The performance of a gas and a aerosol monitoring system (GAMS) for the determination of acidic water soluble organic and inorganic gases and ammonia as well as related particles from the atmosphere. *Atmospheric Environment* 35, 2861–2869.
- Nefel, A., Blatter, A., Hesterberg, R., Staffelbach, T., 1996. Measurements of concentration gradients of HNO_2 and HNO_3 over a semi-natural ecosystem. *Atmospheric Environment* 30, 3017–3025.
- Notholt, J., Hjorth, J., Raes, F., 1992. Formation of HNO_2 on aerosol surfaces during foggy periods in the presence of NO and NO_2 . *Atmospheric Environment* 26A, 211–217.
- Perner, D., Platt, U., 1979. Detection of nitrous acid in the atmosphere by differential optical absorption. *Geophysical Research Letters* 6, 917–920.
- Perrino, C., Pietrodangelo, A., Febo, A., 2001. An atmospheric stability index based on radon progeny measurements for the evaluation of primary urban pollution. *Atmospheric Environment* 35, 5235–5244.
- Perrino, C., Catrambone, M., Di Menno, A., Allegrini, I., 2002. Gaseous ammonia in the urban area of Rome and its relationship with traffic emissions. *Atmospheric Environment* 36, 5385–5394.
- Ramazan, K.A., Syomin, D., Finlayson-Pitts, B.J., 2004. The photochemical production of HONO during the heterogeneous hydrolysis of NO_2 . *Physical Chemistry Chemical Physics* 6, 3836–3843.
- Reisinger, R.A., 2000. Observations of HNO_2 in the polluted winter atmosphere: possible heterogeneous production on aerosols. *Atmospheric Environment* 34, 3865–3874.
- Ren, X., Harder, H., Martinez, M., Leshner, R.L., Olinger, A., Simpas, J.B., Brune, W.H., Schwab, J.J., Demerjian, K.L., He, Y., Zhou, X., Gao, H., 2003. OH and HO_2 Chemistry in Urban Atmosphere of New York City. *Atmospheric Environment* 37, 3639–3651.
- Rubio, M.A., Lissi, E., Villena, G., 2002. Nitrite in rain and dew in Santiago city, Chile. Its possible impact on the early morning start of the photochemical smog. *Atmospheric Environment* 32, 293–297.
- Schimang, R., Folkers, A., Kleffmann, J., Kleist, E., Miebach, M., Wildt, J., 2006. Uptake of gaseous nitrous acid (HONO) by several plant species. *Atmospheric Environment* 40, 1324–1335.

- Simon, P.K., Dasgupta, P.K., 1995. Continuous automated measurement of Gaseous Nitrous and Nitric Acids and Particulate Nitrite and Nitrate. *Environmental Science & Technology* 29, 1534–1541.
- Stadler, D., Rossi, M.J., 2000. The reactivity of NO₂ and HNO₂ on flame soot at ambient temperature: The influence of combustion conditions. *Physical Chemistry Chemical Physics* 2, 5420–5429.
- Staffelbach, T., Neftel, A., Blatter, A., Gut, A., Fahrni, M., Stählerin, J., Prévôt, A., Hering, A., Lehning, M., Neining, B., Bäumle, M., Kok, G.L., Dommen, J., Hutterli, M., Anklin, M., 1997. Photochemical oxidant formation over Southern Switzerland, 1. Results from summer 1994. *Journal of Geophysical Research* 102 (D19), 23345–23362.
- Stutz, J., Platt, U., 1996. Numerical analysis and estimation of the statistical error of differential optical absorption spectroscopy measurements with least-squares methods. *Applied Optics* 30, 6041–6053.
- Stutz, J., Alicke, B., Neftel, A., 2002. Nitrous acid formation in the urban atmosphere: Gradient measurements of NO₂ and HONO over grass in Milan, Italy. *Journal Geophysical Research* 107 (D22), 8192.
- Stutz, J., Alicke, B., Ackermann, R., Geyer, A., Wang, S., White, A.B., Williams, E.J., Spicer, C.W., Fast, J.D., 2004. Relative humidity dependence of HONO chemistry in urban areas. *Journal Geophysical Research* 109, D03307.
- Svensson, R., Ljungström, E., Lindqvist, O., 1987. Kinetics of the reaction between nitrogen dioxide and water vapour. *Atmospheric Environment* 21, 1529–1539.
- TenBrink, H.M., Spoelstra, H., 1998. The dark decay of HNO₂ in environmental (SMOG) chambers. *Atmospheric Environment* 32, 247–251.
- Trick, S., 2004. Formation of Nitrous Acid on Urban Surfaces—a physical-chemical perspective. Ph.D. Thesis, Universität Heidelberg, Fakultät für Naturwissenschaften und Mathematik, 290pp.
- Vecera, Z., Dasgupta, P.K., 1994. Indoor nitrous acid levels. Production of nitrous acid from open-flame sources. *Intern. Journal Environmental Analytical Chemistry* 56, 311–316.
- Veitel, H., 2002. Vertical profiles of NO₂ and HNO₂ in the planetary boundary layer. Ph.D. Thesis, Universität Heidelberg, Fakultät für Naturwissenschaften und Mathematik, 270pp.
- Volkamer, R., 1996. Absorption von Sauerstoff im Herzberg I System und Anwendungen auf Aromatenmessungen am European Photo Reactor (EUPHORE), Diploma Thesis, University of Heidelberg.
- Wiesen, P. (scientific coordinator), 2003. Nitrous acid and its influence on the oxidation capacity of the atmosphere (NITROCAT). Final EU project report (EVK2-CT-1999-00025), 198pp.
- Zellweger, C., Amman, M., Hofer, P., Baltensperger, U., 1999. NO_y speciation with a combined wet effluent diffusion denuder—aerosol collector coupled to ion chromatography. *Atmospheric Environment* 33, 1131–1140.
- Zhou, X., Civerolo, K., Dai, H., Huang, G., Schwab, J., Demerjian, K., 2002. Summertime nitrous acid chemistry in the atmospheric boundary layer at a rural site in New York State. *Journal Geophysical Research* 107, 4590.
- Zhou, X., Gao, H., He, Y., Huang, G., Bertman, S., Civerolo, K., Schwab, J., 2003. Nitric acid photolysis on surfaces in low-NO_x environments: significant atmospheric implications. *Geophysical Research Letters* 30 (23), 2217.