Nitrite in dew, fog, cloud and rain water: An indicator for heterogeneous processes on surfaces

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Abstract

Nitrite was measured in atmospheric liquid phase samples between 1998 and 2005 to investigate the heterogeneous formation of nitrous acid in the lower atmosphere, as well as to assess the quality of water recovered from dew. The samples were collected during ground-based cloud field experiments at different German mountain sites (Brocken, Schmücke, and Hohenpeissenberg) and at a site south of the Bordeaux urban area (France). Concentrations found in Bordeaux dew samples (up to \(2800 \mu g \text{ L}^{-1}\)) are comparable to those found elsewhere in urban fog and dew water and considerably higher than those detected in cloud water or rain. Particulate nitrite (and nitrate) as well as \(\text{HNO}_2 (\text{HNO}_3)\) data in air masses from a foothill site of Mt. Schmücke, before involved in cloud processing, are also presented. In clouds at Mt. Brocken, both the interstitial \(\text{HNO}_2\) gas and the aqueous phase nitrite concentration have been measured simultaneous. Significant deviations from Henry’s law have been observed, indicating that a calculation of \(\text{HNO}_2\) from measured solute nitrite concentrations in bulk samples will overestimate the gasphase concentration. Besides the heterogeneous \(\text{HNO}_2\) production on wetted surfaces with contact to atmospheric air, a fraction of nitrite measured in cloud droplets or dew will arise from the dissolution of gasphase \(\text{HNO}_2\), the particle scavenging processes or the dissolution of surface substrates. \(\text{HNO}_2\) is a dominant hydroxyl radical source during daytime due to its effective photolysis and after water evaporation the released nitrite can significantly contribute to the total OH production and therefore to photochemical smog conditions in the lower atmosphere.

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1. Introduction

Over the past decades numerous studies have been done at many sites to improve our understanding concerning multiphase chemical, transport, and removal processes in the troposphere. In the atmospheric multiphase system, gasphase species, particulates and liquid droplets co-exist at the same time. Gas-to-particle conversion primarily involves the transformation of \(\text{SO}_2, \text{NO}_x\), and gasphase hydrocarbons; these reactions typically involve water vapour, often require solar radiation, and usually include intermediate states. Most of the water in the atmosphere is in its vapour...
phase. Condensation of humid air in the atmosphere on a substrate and transformation into liquid water can form dew, fog, clouds, and rain. Whereas for natural fog, cloud and rain condensation starts on submicron particles in a large atmospheric volume, dew formation is observed on larger surfaces at ground level.

When a humid air parcel experiences adiabatic cooling, cloud droplets may form on aerosol particles in the air by means of condensation of water as soon as the point of saturation water vapour pressure is exceeded. This process is called heterogeneous nucleation on cloud condensation nuclei (CCN) or nucleation scavenging of the particles (Pruppacher and Klett, 1997). Observed ground-based clouds on mountain summits are often the result of cloud advection related to frontal systems (preformed stratus, cumulus or stratocumulus clouds), with a history attended by turbulence, or directly formed by the orographically induced lifting of moist air. The formation and topographical propagation route of these clouds and their microphysical properties are mainly influenced by the buoyancy and the constancy of synoptic scale wind field (Arends, 1996; Tilgner et al., 2005). In fog, which is physically related to clouds, droplets are also formed on aerosol particles in supersaturated air, but the pollution of these particles is usually higher than in clouds, as fog is formed in the mixing layer of the atmosphere. Supersaturation in radiation fog (as for example observed in the Po-Valley, Italy) is achieved by cooling of air close to Earth’s surface at night by outgoing infrared (IR) radiation (Arends, 1996).

Dew formation occurs under conditions of no wind and clear night skies, accompanied with strong outgoing IR radiation, that provide efficient surface cooling with respect to ambient air and therefore larger concentrations of surface air moisture. The amount of dew water depends not only on local atmospheric humidity, but also on radiative, thermal and aerodynamical properties of the substrate and its immediate surrounding (Beysens, 1995; Nikolayev et al., 1996; Beysens et al., 2003). The nucleation of the liquid phase is controlled by surface temperature, and modified by the wetting properties of the substrate (e.g., even a monolayer of fatty acid can change the contact angle). The growth is dimensionally constrained, which gives to dew a number of original properties. Although dew cannot provide water quantities comparable to fog or rain, its presence and its chemical and biological composition may also affect many environmental processes. In addition, dew is a modest supplementary source of water, which may be essential in places where other sources of water are scarce.

Soluble gases may dissolve (after gasphase transportation onto the water surface) in the liquid phase of water and react to form new products, and existing droplets may adsorb particles (gas and particle scavenging). The chemical composition of the condensed phase of water varies as a function of droplet size because of the homogeneous chemical composition of the condensation nuclei or substrates on which the droplets grow. Substances that dissolve from the underlaying surface may contribute to the composition of dew. Drop-to-particle conversion occurs when cloud drops containing dissolved or suspended material evaporate. During evaporation processes gaseous species might also be released into the atmosphere.

The atmospheric liquid phase of water contributes to many chemical transformations that would otherwise not have taken place or would have proceeded at much slower rates (e.g., Mohnen and Vong, 1993; Fuzzi, 1995; Fuzzi et al., 2002; Pruppacher and Jaenicke, 1995; Choularton et al., 1997; Schemenauer et al., 1995; Möller, 1995; Marquardt et al., 2001; Jaeschke et al., 2001; Rubio et al., 2002; Collett et al., 2002; Herrmann et al., 2005).

A component of particular importance in the oxidant chemistry of the polluted but also of the remote atmosphere is nitrous acid (HNO₂) – see Fig. 1 – because its photolysis (reaction R1 below), which takes place at a...
high quantum yield, can be a predominant source of hydroxyl radicals (OH). Recent measurements have shown that up to 30% of the total OH is produced by HNO₂ photolysis over a 24-hour period under various conditions (Staffelbach et al., 1997; Stutz et al., 2002; Zhou et al., 2002; Alicke et al., 2003; Trick, 2004; Kleffmann et al., 2005; Acker et al., 2006a,b).

HNO₂ + hν→OH + NO
(R1)

Photolysis (R1) is an important sink of HNO₂. In addition, and at smaller scale, HNO₂ can also be removed by directly reacting with OH.

HNO₂ + OH→NO₂ + H₂O
(R2)

Furthermore deposition of nitrous acid seems to be an efficient sink, e.g. in dew water on vegetative surfaces (Zhou et al., 2002; Rubio et al., 2002; Acker et al., 2004; He et al., 2006). Chamber experiments carried out recently showed that HNO₂ absorption by several plants (sunflower, tobacco, castor, birch) contributed to at least 74% to the total HNO₂ losses observed in the chamber; compared to 22% due to photolytic processes and 4% due to wall losses (Schimang et al., 2006).

At present, the mechanisms leading to HNO₂ formation (HNO₂ sources) are still not completely understood. The observed atmospheric concentrations can not satisfactorily be explained, neither by homogeneous gas reaction (R3),

OH + NO→HNO₂
(R3)

which is too slow, nor by direct emissions from combustion processes, which are too small.

It is meanwhile accepted that HNO₂ will mainly be produced via an heterogeneous reaction (reaction R4) from NO₂ on wetted surfaces (macroscopic ground surface like asphalt and buildings, vegetation, airborne aerosol particles, soot) and a strong dependence on the properties of the surface (e.g., roughness, surface water coverage, mixture of substances) has been reported (e.g., Neftel et al., 1996; Lammel, 1999; Saliba et al., 2000; Kalberer et al., 1999; Grassian, 2001: Kurtenbach et al., 2001; Finlayson-Pitts et al., 2003; Genfa et al., 2003; Trick, 2004; Stutz et al., 2004).

NO₂(ads) + NO₂(ads) + H₂O(aq)→HNO₂(aq)
+ HNO₃(aq)→HNO₂(g) + HNO₃(ads)
(R4)

Due to high concentrations of water in the troposphere, and possible multi-layering, an aqueous phase may be established on surfaces. The rate-limiting step of the heterogeneous reaction (R4) is thereby the transition to another phase, involving several, partly reversible, processes (Kleffmann et al., 1998) that are illustrated in Fig. 2.

The efficiency of the NO₂ to HNO₂ conversion is strikingly alike at urban and rural sites (Lammel and Cape, 1996) where similar average ratios of HNO₂ to NO₂ between 0.01 and 0.1 have been observed. Although formation on ground surfaces are expected to be the main source (e.g., Harrison and Kitto, 1994; Spindler et al., 1998; Veitel, 2002; Kleffmann et al., 2003), atmospheric aerosols could also be a surface for the heterogeneous formation of HNO₂ (e.g., Kleffmann et al., 1998), especially under foggy conditions (Notholt et al., 1992) or in wintertime atmospheres (Reisinger, 2000). Gradient measurements of NO₂ and HNO₂ over a flat grass surface in the polluted atmosphere of Milan showed that the behaviour of these trace gases with respect to heterogeneous processes at ground can be explained by both a deposition of NO₂ and HNO₂ and a conversion of NO₂ to HNO₂ (Stutz et al., 2002) with the NO₂ to HNO₂ conversion rate coefficients much less efficient (about a factor of 10 lower) than found in the laboratory on artificial surfaces. Part of deposited NO₂ can be irreversibly bound to plant cuticles, as for example found by Lendzian and Kahlert (1988). Results obtained from chamber experiments with sunflower or castor exposed to NO₂ and HNO₂ showed clearly that plants can act as a sink for both compounds, that the uptake via the stomata can overcompensate other processes at the cuticula, and that HNO₂ itself or the nitrite formed from NO₂ or by HNO₂ dissociation in the apoplastic plant water could be metabolized (Schimang et al., 2006). The exposure of acid film to NO₂ in an irradiated

![Fig. 2. Schema of gas-liquid phase transfer including heterogeneous (surface) and homogeneous (droplet) reactions as well (protolytic) dissociation; for example A=NO₂ and B=HNO₂/NO₂.](image-url)
tubular gas flow reactor (Stemmler et al., 2006) indicated that soil and other surfaces containing humic acid exhibit an organic surface photochemistry that produces reductive surface species, which react selectively with NO₂ to form nitrous acid.

It was believed for a long time that nitrous acid was formed in the atmosphere (Fox, 1873; Engler, 1879) where it was called hyponitric acid, referred to be NO₂ or N₂O₄. Elements were observed in rain, during electric discharges or thunderstorms. Fox (1873) characterized nitrous acid (due to giving up oxygen to any oxidizable substance while converting in to “binoxide of nitrogen”), beside “allotropic oxygen” (ozone) and peroxide of hydrogen (H₂O₂), as one of the three greatest atmospheric agents that are engaged in destroying emanations from substances. In modern terms, we can transform this observation into the statement that these compounds are radical sources (OH).

Quantitative measurements of gas phase nitrous acid in ambient air were performed for the first time by Perner and Platt (1979) using Differential Optical Absorption Spectroscopy (DOAS). Since then a variety of measuring methods have been used at numerous sites (e.g., Genfa et al., 2003; Trick, 2004, and references therein).

As a water-soluble acid, HNO₂ can be removed from the atmosphere via wash out by rain (wet deposition), where it contributes to acid rain, or obviously by dry deposition, consisting of agglomeration on aerosols and through ground and chemical reactions. It is worthy to note that only a few ambient measurements of the aqueous phase and particulate nitrite exist to date (see Results section). In this paper we present measurements of nitrite concentrations, both in clouds and dew water, collected from the rural atmospheres of three German mountain sites, and near the urban city of Bordeaux (France), as well as data concerning the phase distribution of nitrite between gas phase and liquid or aerosol phase. This paper will emphasize that fog and cloud droplets (and possibly dew) provide an effective “surface reservoir” for heterogeneous HNO₂ production.

2. Experimental design

In October 1998 and July 1999 cloud field campaigns at Mount (Mt.) Brocken (1142 m above mean sea level (amsl), Harz Mountains) focused on nitrous and nitric acid measurements within and outside clouds (for detailed information see Acker et al., 2001, 2002). The mean liquid water content (LWC) of clouds intercepting this site between 22 September–08 October 1998 and 14 June–05 July 1999 was 470 and 250 mg m⁻³, respectively; clouds were observed during 55% (1998) and 22% (1999) of the study time.

Ground-based cloud experiments were performed also on and around the Schmücke mountain (937 m amsl, Thuringian Forest) in October 2001 and 2002 to study aerosol-cloud interactions during air flow over hills (for detailed information see Acker et al., 2003; Herrmann et al., 2005). The mountain summit was covered by clouds 40% of the study time in 2001 (02 October–05 November) and 51% of the study time in 2002 (22 September–31 October). The mean value of LWC was determined to be 220 mg m⁻³ (2001) and 190 mg m⁻³ (2002), respectively.

Measurements of nitrous acid and a large variety of other compounds and parameters (worth mentioning the OH radical concentration and the photolysis frequencies J (NO₂) and J(HNO₂)), were done in late summer 2004 and 2005 at Hohenpeissenberg (980 m amsl, Bavaria). The first results are presented in Acker et al. (2006a), and the site details are given in Mannschreck et al. (2004). Nitrite was analysed in 11 dew samples collected 1 m above grassland at the mountain top, and at a foothill site (710 m amsl) in September 2005. Some rain water samples were also collected and analysed in July 2004.

Another measurement site, selected especially for dew characterisation experiments (Beysens et al., 2005), is located south of the Bordeaux urban area (17 m amsl, within about 50 km from the Atlantic Ocean). During the one-year investigated period (15 January 2002 to 14 January 2003), dew was observed during 58% of the nights, often with a small amount corresponding to an average daily yield of 0.046 mm. Nitrite, nitrate and pH data were available for 55 samples with volumes that varied between 2 and 70 ml.

A radiative condenser as described in Beysens et al. (2003, 2004) was used for collecting atmospheric dew. The condenser was made out of plane foil (details in Nilsson et al., 1994) with a surface area of 1 m×0.318 m that was thermally isolated from below with a 20 mm thick sheet of polystyrene foam. It was located about 1 m above the ground at both the Bordeaux and Hohenpeissenberg sites. To leave the drops in contact with the support during the growth process, the plane of the condenser was installed at an angle of 15° with respect to the horizontal plain. The condenser was exposed to the outside atmosphere from sunset till sunrise (20:00 till 7:00 Central European Time (CET) is a good average), and dew water was collected in a polyethylene (PE) flask.

Separation and sampling of cloud droplets was done using a single stage active cloud water collector (Winkler, 1992). At an operational sample flow rate of 2 m³ min⁻¹, drops greater than 5 μm (50% cut-off diameter) which impacts with efficiency between 55% and 97% were collected in a PE bottle. The time interval of collection
varied between 0.5 and 2 h to obtain at least a few millilitres of water needed for chemical analysis. The LWC and droplet size and number distributions of the clouds covering the mountain tops of Mt. Brocken and Mt. Schmücke were measured by optical methods using a forward scattering laser monitor (PVM100) and spectrometer (FSSP) (Gerber, 1991, Wieprecht et al., 2005).

The amount of solute inorganic components in rain and cloud water and dew was detected by ion chromatography. Nitrite, nitrate and [H+] in cloud water were analysed immediately after sampling at the field sites. The Brocken and Schmücke nitrite data are given also as air equivalent concentrations (μg m⁻³ or ng m⁻³), obtained by multiplying the measured aqueous phase concentration by the LWC. At the Bordeaux site, dew volume and pH were measured on site, while the storage of dew samples (in sterilized PE flask at 4 °C) before analysis was not longer than 4 weeks.

The partitioning of some water soluble inorganic compounds between the gas and aerosol phase was investigated using a denuder technique which allows for the diffusion-based collection of reactive trace gases with a separation from their particulate counterparts. In this case, HONO₂ (and HNO₃) measurements were performed using a wet effluent diffusion denuder (WEDD) coupled directly with an ion chromatography unit (Acker et al., 2001, 2005). The system was extended by a steam jet unit to determine aerosol components (nitrite, nitrate, chloride, and sulfate) at a small time interval. The airflow through the denuder/steam jet chamber was 10 l min⁻¹ and by using 30 min interval sampling time, concentrations of 0.010 μg m⁻³ of HNO₂, NO₂, HNO₃ and NO₃ could be reliably recorded.

Various other chemical, physical and meteorological parameters were measured simultaneously at all sites (Beysens et al., 2005; Herrmann et al., 2005; Acker et al., 2002 and 2006a).

3. Results and discussion

In Fig. 3a to c the diurnal variations of nitrous acid at the mountain sites from which cloud and dew nitrite concentrations are presented are shown. No HNO₂ data were available from the Bordeaux station. Therefore, in Fig. 3d results from HNO₂ measurements, carried out about at 30 km north of the urban environment of Marseille (France), are given to show a typical diurnal variation at a flat country station near an urban environment in a coastal region. Different meteorological and air chemical regimes may cause significant differences in the source-receptor relationship. At all sites the HNO₂ concentrations correlated more (e.g., r² = 72) near Mar-

seille or less (e.g., r² = 0.016 at Hohenpeissenberg) with those of the precursor NO₂ (all day and night data). It seems that not the gasphase NO₂ concentrations, but the surface coverage with adsorbed NO₂ (and H₂O), is decisive for heterogeneous formation.

The HNO₂ to NO₂ ratio is less influenced by transport processes than the concentrations of the individual species. On average, low percentage values (few %) were observed at the three rural sites, as well as at the suburban site. These were significantly higher than the values known for direct HNO₂ emission from combustion sources that was found to be about 0.8% (see e.g., Kurtenbach et al., 2001), indicating heterogeneous formation.

The HNO₂ diurnal distribution observed at the three mountain sites (Fig. 3a to c) is opposite to that from the flat country station (Fig. 3d). The latter corresponds to what is
generally observed in many atmospheric measurements, i.e. accumulation of significant \( \text{HNO}_2 \) levels at night until early morning (near Marseille on average 1.0 \( \mu \text{g} \ \text{m}^{-3} \)), followed by a rapid decrease after sunrise due to efficient photolysis via reaction (R1).

Whereas average noontime \( \text{HNO}_2 \) levels of 0.2 \( \mu \text{g} \ \text{m}^{-3} \) were reached at Mt. Schmücke and Hohenpeissenberg, respectively, much lower concentrations were observed at these sites during the night (\( \sim 0.08–0.1 \mu \text{g} \ \text{m}^{-3} \)). At Mt. Brocken similar diurnal variations were observed over a few days (Acker and Möller, 2007), but on average the diurnal cycle was not very marked. \( \text{HNO}_2 \) maxima at noon (correlation of \( \text{HNO}_2 \) and solar radiation) and comparably lower concentrations at night have also been observed at other mountain stations (e.g., Kleffmann et al., 2002; Zhou et al., 2002; Huang et al., 2002). Besides turbulent transport of foothill accumulated \( \text{HNO}_2 \) to the hilltop, elevated daytime \( \text{HNO}_2 \) levels were also attributed to the evaporative release of \( \text{HNO}_2 \)/nitrite from dew that originally trapped these compounds near the ground (e.g., Zhou et al., 2002; Rubio et al., 2002; Acker et al., 2004) and to photochemical processes, such as photolysis of \( \text{HNO}_3 \), that deposit on ground surfaces (Zhou et al., 2003), heterogeneous hydrolysis of \( \text{NO}_2 \) (Ramazan et al., 2004) or photoinduced \( \text{NO}_2 \) reduction (George et al., 2005; Stemmler et al., 2006). The importance of dew in controlling the air-surface exchange of \( \text{HNO}_2 \) in rural forest environments was recently shown by He et al. (2006).

Despite differences in the diurnal variation, the observed daytime \( \text{HNO}_2 \) concentrations (0.15–0.5 \( \mu \text{g} \ \text{m}^{-3} \)) were unexpectedly high near Marseille as well as at the rural mountain sites. During midday the \( \text{HNO}_2 \) life-time with respect to photolysis should be about 10–15 min and the photo-stationary state (PSS) conditions quickly established in the gasphase. The calculated PSS-\( \text{HNO}_2 \) concentrations (homogeneous gasphase sources to sinks) amount to very few \( \mu \text{g} \ \text{m}^{-3} \) (at all sites (Acker and Möller, 2007). At Hohenpeissenberg all parameters were measured using the following calculation (Acker et al., 2006a):

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

A consideration of the heterogeneous reaction (R4) as a \( \text{HNO}_2 \) source also during daytime (for details see Kleffmann et al., 2005; Acker et al., 2006a) insignificantly reduces the large discrepancies between \( [\text{HNO}_2]_{\text{PSS}} \) and measured mid-day \( [\text{HNO}_2] \). The ratio of known sources to sinks varied for example between 0.05 and 0.34 at Hohenpeissenberg (Acker et al., 2006a). The results indicate that a major additional, but still unknown \( \text{HNO}_3 \) source, is required to make up the balance. The correlation of \( [\text{HNO}_2] \) with solar radiation, as observed at Hohenpeissenberg (\( r^2=0.48 \)), with regard to \( J(\text{HNO}_2) \) around noon, and much more meaningful the very significant (\( r^2=0.81 \)) correlation of the missing \( \text{HNO}_2 \) daytime source against \( J(\text{NO}_2) \) confirm assumptions of a substantial light-induced production of \( \text{HNO}_2 \) (Acker and Möller, 2007). Evidence of the latter was found by George et al. (2005) while studying the effect of light in the range 300–500 nm on the uptake kinetics of \( \text{NO}_2 \) on various surfaces containing photosensitive organic substrates in the laboratory.

In comparison to other solute compounds, only a few nitrite measurements in atmospheric liquid phase samples have been reported so far, mainly because concentrations are low, and nitrite ions are easily oxidised (Lammel and Cape, 1996). One of the first quantitative information was given by Okita (1968). Values of 400–1050 \( \mu \text{mol} \ \text{L}^{-1} \) were detected at Mt. Tsukuba (Japan 876 m amsl) in cloud water with pH levels of 5.7–6.5. In the acidic cloud water (pH of 3.4–4.3) collected at significant higher altitudes (much more isolated from anthropogenic and surface sources for \( \text{HNO}_2 \) formation) at Mt. Norikura (Japan 3026 m amsl) much lower nitrite values (15–104 \( \mu \text{mol} \ \text{L}^{-1} \)) were found (Okita, 1968).

Progress in analytical methods permitted Bächmann et al. (1989) to directly detect nitrite by ion chromatography. In rain and fog water samples collected in the rural Odenwald region (Germany) 1.8 and 16 \( \mu \text{mol} \ \text{L}^{-1} \) (86 and 736 \( \mu \text{g} \ \text{L}^{-1} \)), respectively, were found. In a polluted region in Germany, Lammel and Metzig (1998) measured nitrite in fogwater samples at values of 3–52 \( \mu \text{mol} \ \text{L}^{-1} \) (138–2400 \( \mu \text{g} \ \text{L}^{-1} \)) at pH > 6. Similar ranges of nitrite concentrations were found in radiation fog in the Po Valley (20–310 ng m\(^{-3} \), near Bologna, Italy) in the fall–winter season of 1998–1999 by Fuzzi et al. (2002). Analysis of water collected from orographic clouds at Great Dun Fell (Great Britain) showed much lower nitrite contents of between 0.1 and 2 \( \mu \text{mol} \ \text{L}^{-1} \) (5–92 \( \mu \text{g} \ \text{L}^{-1} \), typical 9.4 ng m\(^{-3} \)) (see Cape et al., 1992). Only a few reports on dew chemistry exist in the literature. Rather high ionic contents were found in the dew water collected in Santiago City (Chile), due to the presence of natural dust (high calcium concentrations), and of anthropogenic sources (high sulfate concentrations). Nitrite concentrations varied between 47 and 177 \( \mu \text{eq} \ \text{L}^{-1} \) (2162–8142 \( \mu \text{g} \ \text{L}^{-1} \)) during the years 1995 and 1999 (Rubio et al., 2002), with an average pH of about 6. Throughout the whole year 1997 dew was also collected in Sakai City (Japan) (Takenaka et al., 1999) where the pH varied between 5.5 and 7.3 and up to
58 μmol l\(^{-1}\) (2668 μgl \(^{-1}\)) nitrite were analysed. Zuo et al. (2006) developed a fast and sensitive reversed-phase ion-pair HPLC method for simultaneous determination of nitrite and nitrate in atmospheric liquids and found in dew samples 620–820 μg l\(^{-1}\) nitrite.

The information about nitrite concentration in the atmospheric particulate phase is also limited. For example, measurements were performed in Mainz (0.023 μg m\(^{-3}\), Lammel and Perner, 1988), in Milan (0.2–6.3 μg m\(^{-3}\), Allegrini et al., 1994), in Texas (0.04–1 μg m\(^{-3}\), Simon and Dasgupta, 1995), in Dübendorf (0.03–6 μg m\(^{-3}\), Zellweger et al., 1999) and Zurich (0.1–1 μg m\(^{-3}\), Fisseha et al., 2005) (both Switzerland), in the South of France near Marseille (up to 1 μg m\(^{-3}\), Acker et al., 2005), and in Rome (0.05–1.3 μg m\(^{-3}\), Acker et al., 2006b). Particulate nitrite tends to represent mostly local pollution. Because of the role that inorganic aerosol components play as part of CCN, this nitrite may solubilized during the cloud formation process. Most of the authors reported simultaneous measured HNO\(_2\) data.

The amount of solute nitrite in atmospheric samples varied in a wide range and dependents upon the amount of condensed water, the resulting pH, the level of pollution (concentrations of particles and trace gases), the characteristic of available surfaces for heterogeneous formation (e.g., concerning reaction R4), and possibly radiation and the presence of organic substances as e\(^-\) donors for a photochemical conversion of adsorbed NO\(_2\) into nitrite.

Measurements of HNO\(_2\) in the interstitial gasphase of clouds, and nitrite in the liquid phase were done simultaneously during cloud events observed at Mt. Brocken during the campaigns in 1998 and 1999. An active cloud water collector in front of the denuder unit (see Experimental design section) was used to separate the cloud droplets from the interstitial air (details are given in Acker et al., 2001). The nitrite concentrations in the cloud water samples of the investigated episodes were in the range of 5 to 259 μg l\(^{-1}\) (0.95–31.4 ng m\(^{-3}\); Fig. 4). Highest values were measured in the event of low acidity (pH > 5.5). Under more acidic conditions the phase partitioning changes. In Fig. 5, for a single cloud event (Brocken summit in cloud between 19:30 and 08:30 CET on 21–22 June 1999), the temporal variation of the liquid water content, the droplet number concentration, and the interstitial gasphase concentrations of HNO\(_2\) and NO\(_2\) are shown together with changes in cloud water nitrite and pH. A significant decrease in pH was observed after 02:00 CET, when advection of dryer air from the below cloud layer into the cloud caused a strong increase in the cloud droplet number. These newly formed droplets are small (2–10 μm) and contribute only a little to the LWC, although they are more acid. At the same time a decrease in cloud water nitrite and an increase in interstitial HNO\(_2\) were found.

The partition of species between gas and aqueous phases in the atmosphere is routinely described using Henry’s law. Therefore, from the measured gasphase HNO\(_2\) data (in atm), the aqueous phase nitrite
concentrations were calculated according to the effective Henry’s law coefficient at the given pH and temperature (assuming equilibrium):

$$[\text{NO}_2^-]_{\text{calculated}} = \frac{p_{\text{HNO}_2} \cdot H_{\text{eff}}}{C_{138}}$$

using the following relationships and constants:

Partial pressure \( H_{\text{NO}_2} \)

$$p_{\text{HNO}_2} = nRT/V$$

Henry-constant \( H_{\text{NO}_2} \)

$$H_{298} = 49 \text{ mol l}^{-1} \text{ atm}^{-1}$$

Dissociation constant for \( \text{HNO}_2 \rightarrow \text{H}^+ + \text{NO}_2^- \)

$$K_{298} = 0.0005 \text{ mol l}^{-1}$$

$$K_{\text{RT}} = K_{298} \exp(-1700 (1/T - 1/298))$$

Effective Henry-constant

$$H_{\text{eff}} = H_{\text{RT}} (1 + K_{\text{RT}}/[\text{H}^+])$$

The measured nitrite concentrations were divided by the calculated aqueous phase concentrations:

$$R = \frac{[\text{NO}_2^-]_{\text{measured}}}{[\text{NO}_2^-]_{\text{calculated}}}$$

These ratios present discrepancies with the Henry’s law (differences to theory). Large deviations from Henry’s law occur, in both supersaturation and subsaturation of the liquid phase (see Fig. 6). While at low pH the liquid phase is generally supersaturated, at higher pH (>5) subsaturation can be observed. A similar general trend was found for other compounds like S(IV), formic, and acetic acid in fog and clouds investigated in the Po-Valley and at the Kleiner Feldberg (Winiwarter et al., 1994; Laj et al., 1997). Samples of dew water collected by Takenaka et al. (1999) had on average pH values of 6.5 and showed for nitrite also the effect of subsaturation. The data thus indicate that it is not possible to simply extrapolate interstitial gasphase \( \text{HNO}_2 \) concentration from the measured bulk nitrite liquid phase concentrations of a cloud (the gasphase could be substantially overestimated).

Even if the individual cloud water droplets with different chemical composition are in Henry’s law equilibrium with the surrounding atmosphere, their bulk mixture is not. Using approximate quantitative calculations, a combination of different effects (e.g., no microscale equilibrium, inhomogeneity of pH and chemical composition of the individual droplets, thermodynamic shift of the equilibrium due to competing reactions, kinetic inhibition and nonequilibrium conditions due to mass transfer limitations) seems to be responsible for several orders of magnitude between theory and experiment (Pandis and Seinfeld, 1991; Cape et al., 1992; Winiwarter et al., 1992 and 1994; Laj et al., 1997). The fact that the cloud water bulk samples are supersaturated with respect to the atmosphere from which the samples were drawn will result in outgassing of weak acids from the samples, if such an exchange is allowed (Pandis and Seinfeld, 1991). The data obtained at Mt. Brocken underline the evidence for heterogeneous formation of nitrous acid on cloud droplets and wet aerosols causing at least partly the observed great deviations from Henry’s law. Already Lammel and Perner (1988) estimated from their measurements that particulate matter nitrite concentrations (assuming complete solution in water) were in excess with respect to the gasphase equilibrium.

In Fig. 4, in addition to the Brocken samples, the nitrite concentrations measured in Mt. Schmücke cloud water samples are included. They varied between 4 and 60 \( \mu g \text{l}^{-1} \) (0.75–9.62 ng m\(^{-3}\)) at pH from 3.3 to 5.1. Cloud investigations at Mt. Schmücke were completed by simultaneous characterisation of air masses at an upwind foothill site (605 m amsl) before cloud processing. There, besides many other components (Herrmann et al., 2005), the concentrations of gasphase \( \text{HNO}_3 \) (and \( \text{HNO}_2 \)) and particulate nitrite (nitrate) were measured. About one fourth of the measured nitrite in both phases occurred in the aerosol phase. The concentration of nitric acid (\( \text{HNO}_3 \)) was very low because relative humidity was nearly 100% and this gas is highly soluble in water. Up to 30 times more nitrate were found in the aerosol phase. The gas and particle concentrations before cloud formation are compared with the content of the corresponding ion found in the Schmücke cloud water samples (Fig. 7a and b; 2001 campaign). The concentration changes in the Schmücke cloud water are very well correlated with the changes observed in the upwind aerosol, as can be seen.

![Fig. 6. Ratio of measured cloud water nitrite to nitrite calculated from measured interstitial gasphase HNO\(_2\) as a function of cloud water pH for cloud water samples of the 1998 and 1999 Brocken campaigns.](image-url)
for nitrate and partly for nitrite. As expected, high scavenging coefficients were found for nitrate. The aqueous phase nitrite concentrations are low; on average the concentration is only one tenth of the aerosol nitrite in the air masses before cloud formation. Mainly due to the more or less acidic character of the cloud droplets, entrainment of particulate nitrite and gasphase HNO₂ from the sub-cloud layer was limited.

Measurable amounts of nitrite have also been observed in rainwater at Hohenpeissenberg, where simultaneous gasphase HNO₂ was measured (Fig. 8). For example, on early morning of 13 July 2004, the mountain top was in cloud (unfortunately no LWC data are available), and light drizzle was observed. The concentration of gasphase HNO₂ was low (∼0.05 μg m⁻³). After 08:00 CET the rain became stronger, and hourly rain water samples were taken. The pH was on average 4.9. The nitrite concentration was also low, and varied only little (12–15 μg l⁻¹) despite different rain intensity (0.1–1.8 mm). The rain droplets seem to be saturated with nitrite (possibly due to heterogeneous formation of HNO₂ in the cloud layer), and no decrease in gasphase HNO₂ concentration was observed in the first hours of the rain event. Later on cloud lifting processes occurred, rain stopped in between, and an increase in the gasphase HNO₂ was observed first due to advection of more polluted air masses from the foothill layer (increase of NO₂ at the hilltop from 2 to 10 μg m⁻³ between 10:30 and 12:00 CET, after that ∼3 μg m⁻³ until 20:00 CET). Finally, when the cloud disappears, the evaporative release of nitrite from cloud droplets (and later from wetted surfaces, too) into the gasphase would have contributed to the HNO₂ concentration, besides simultaneous running known and unknown, possibly light-induced HNO₂ formation processes (Fig. 8).

A number of dew samples were collected during the 2005 experiments at Hohenpeissenberg. The nitrite level varied between 30 and 220 μg l⁻¹ (Fig. 9) in dew water. Despite pH values of mostly greater than 6.2, the concentrations are low, especially when compared to dew...
samples taken at other sites as mentioned above and below (e.g., Bordeaux region, Fig. 10). Surprisingly, in all three cases where samples were taken simultaneously at the mountain top (980 m amsl) and at a foothill site (710 m amsl), higher values were observed in dew water formed at lower altitude. During night, the station of the hilltop site is indeed mostly out of the stable nocturnal boundary layer of the foothill area. In this layer a higher variability of surfaces for heterogeneous formation processes are available and HNO2 (and its precursor NO2) is more strongly accumulated.

Dew (and rain) characteristics have been investigated over longer time periods at three different sites (Bordeaux, Zadar (Croatia) and Ajaccio (France)) by Beysens et al. (2004). From the Bordeaux site results concerning chemical composition (pH, nitrate and nitrite concentrations) are available and for nitrite are shown in Fig. 10. On average the dew samples collected between January 2002 and January 2003 have a nitrite concentration of 460 μg l−1 (1–2800 μg l−1, n=55), and the pH varied between 5.3 and 6.9 (mean [H+] = 1.36 × 10−6 g l−1). As expected, the rainwater nitrite concentration was lower; on average 150 μg l−1 (0.01–1300 μg l−1, n=30), partly due to higher acidity of the samples (mean [H+] = 11.3 × 10−6 g l−1). No significant differences were found concerning the number of occurring dew events, the average amount of formed dew water and the average amount of solute nitrite (and nitrate) between summer and winter season. The nitrite concentration tends to be higher at higher pH of the formed dew droplets, but using all data the correlation is poor (r2=0.04). Unfortunately, no HNO2 and NO2 measurements were performed at this site. The high nitrite content in the dew samples seems to be mainly a result of heterogeneous formation processes (reaction (R4)) during the night. In this case deposition of HNO2 should be of minor importance.

A high variability in the dew volume per unit surface area was found on simultaneous used dew collectors having different sheet materials (Takenaka et al., 2003). The authors conclude that the dew concentration on the collector sheet as a surrogate does not necessarily represent the real dew concentration on various kinds of materials, such as leaves, cars, roofs, roads, etc. To determine the real concentration of dew on a material, the material itself has to be used as a collector. Nitrite on leaf surfaces, including maple, oak, birch and fir, was washed off with deionized water and was determined for early morning, when foliage surfaces were still moist (67 nmole m−2), and for late morning and afternoon when the leaf surfaces were dry (7–10 nmole m−2) in August 2003 at Pellston, USA. From their data He et al. (2006) estimated that if the majority of the surface nitrite is released into ambient air as HNO2 from 10 layers of tree leaves throughout the canopy, it contributes within 1–2 hour after dew evaporation to ~6×10−7 moles of HNO2 per m2 (equivalent to ~500 μg m−2 in the 50-m air column). Generally, the release of the formed nitrite into the gas phase seems to depend on surface characteristics, pH and composition of the water film or droplet. Nitrite in the aqueous phase was found to be very stable, even under solar radiation and rarely decomposes until dew dries completely (Takenaka et al., 1999). A resuspension of nitrite during dew evaporation into the boundary layer is possibly intensified due to the relative high volatility of ammonium nitrite (Rubio et al., 2002).

4. Conclusions

In fog and cloud droplets, dew and rain, collected at different rural mountain sites and in the urban area of Bordeaux, often significant amounts of nitrite have been observed. The broad variation in the concentration level is due to different available amounts of condensed water (liquid water contents of clouds, dew amount, rain intensity), the sample acidity, characteristics of the surface on which droplets grow, the local pollution situation, and the complexity of heterogeneous formation processes. From a photochemical perspective the heterogeneous uptake of NO2 and conversion to HNO2 on surfaces in contact with the atmosphere are of great interest; the influence of water, radiation, temperatures and reactant mixture there is the object of recent studies. Despite the rapid photolysis process unexpectedly high values of HNO2 (0.15–0.5 μg m−3) were detected during the day in the urban but also the rural regions and the diurnal cycles at the mountain sites surprisingly showed a broad maximum around noon, indicating a major daytime source missing in the balance of
known HNO2 sources and sinks. Recently it was found, that under humid conditions the photo-induced conversion of NO2 to HNO2 via electron transfer reactions may exceed the rate of the heterogeneous (dark) reaction (R4) by more than one order of magnitude depending on the substrate (e.g., George et al., 2005; Steimmler et al., 2006). Various ground and vegetation surfaces may contain photosensitive organic substrates and dew and fog/cloud/rain droplets (often intercepted) may be present in the atmosphere also during daytime. The atmospheric liquid phase plays an important role as a sink of HNO2, but also as a source for HNO2 upon evaporation. The released HNO2 is an additional source for OH radicals and could contribute significantly to the initiation of the daily photochemistry.

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References


Fuzzi, S., Fachini, M.C., Decearsi, S., Matta, E., Mireca, M., 2002. Soluble organic compounds in fog and cloud droplets: what have we learned over the past few years? Atmos. Res. 64, 89–98.

and nitrous acids during the 1999 Atlanta Supersite. Atmos. Environ. 37, 1351–1364.


