

# Nitrous Acid and Nitrite in the Atmosphere

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## 1 Introduction

Why is nitrous acid important as an atmospheric trace gas? It is present in very small quantities, typically up to a few parts in  $10^9$  by volume (ppbV), and usually makes up only a small fraction of the total amount of gaseous nitrogen oxides present in the atmosphere. One reason for an increasing number of recent studies into the chemistry of  $\text{HNO}_2$  is the increasing importance of nitrogen oxides as atmospheric pollutants. Unlike the emissions of sulfur dioxide, which have been decreasing markedly in recent years in Europe and North America, if not in the developing world, the emissions of nitrogen oxides are far from decreasing. In developed countries the major source of nitrogen oxides is vehicle traffic, and the steadily increasing number of cars and car journeys more than compensate, in many cases, for emission reduction measures. On a global scale the importance of  $\text{NO}_x$  pollutants ( $= \text{NO} + \text{NO}_2$ ) is on the rise too, because people produce these trace gases directly from a range of activities (e.g. fossil fuel combustion in the energy sector, biomass burning in the context of agriculture), or enhance natural sources (e.g. soil NO emission following fertilization with nitrogen).

The global significance of the nitrogen oxides in the atmosphere is in determining the production and consumption of the highly reactive hydroxyl and hydroperoxyl radicals,  $\text{HO}_x$  ( $= \text{OH} + \text{HO}_2$ ). The OH radical is the most important trace species in tropospheric chemistry, and its abundance governs the oxidation and eventual removal of most trace gases from the atmosphere. It is in this respect that  $\text{HNO}_2$  shows its importance as a trace gas; on photolysis ( $\lambda < 390$  nm)  $\text{HNO}_2$  directly produces OH. This OH source is of greatest importance during the early morning, when  $\text{HNO}_2$  concentrations may be high after night-time accumulation, and when OH production rates from other sources (photolysis of ozone and formaldehyde) are slow. Concentrations of OH radicals later in the day are also influenced by  $\text{HNO}_2$ . Apart from its role in tropospheric chemistry, nitrous acid is of toxicological relevance. It is suspected to be a precursor of carcinogens (nitrosamines) under atmospheric conditions.

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Despite this importance, nitrous acid is one of the least researched species in inorganic tropospheric chemistry. Why is this so, and why do we know so little of its major sources and sinks? The aim of this review is to unravel the puzzle of  $\text{HNO}_2$  occurrence in the atmospheric boundary layer close to the earth's surface, as far as present knowledge allows, by investigating evidence from both laboratory and field studies.

## 2 Why do we know so little?

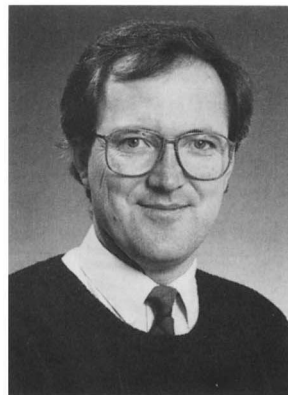
The apparent lack of information about  $\text{HNO}_2$  in the troposphere is primarily because it is very difficult to make reliable measurements of  $\text{HNO}_2$  at ambient concentrations. Conventional chemiluminescent gas analysers, which are used to measure NO (in the chemiluminescence reaction with  $\text{O}_3$ ) and  $\text{NO}_2$  (as NO after reduction), include a signal from  $\text{HNO}_2$  as part of the  $\text{NO}_2$  signal. The catalytic converters used in these instruments are designed to reduce  $\text{NO}_2$  selectively to NO, but are likely also to reduce  $\text{HNO}_2$ . In many sampling systems  $\text{HNO}_2$  may be lost to the walls of sampling lines or inlet filters before it even reaches the catalytic converter, because it appears to be a 'stickier' molecule than NO or  $\text{NO}_2$ . The potential presence of  $\text{HNO}_2$  as part of the  $\text{NO}_2$  signal from such analysers is usually ignored.

### 2.1 Gas-phase Measurement

Nitrous acid can be determined in ambient air using differential optical absorption spectroscopy (DOAS) or denuder systems (DS). Spectroscopy, as an *in situ* method, is clearly advantageous when dealing with molecules which are reactive on surfaces. Gaseous  $\text{HNO}_2$  absorbs light in the near UV with maxima at 354 and 368 nm; its absorption coefficient at these wavelengths is  $5.0 \times 10^{-19}$  and  $4.5 \times 10^{-19}$   $\text{cm}^2$  per molecule, respectively.<sup>1</sup> Most  $\text{HNO}_2$  concentration measurements have been based on earlier cross-section data,

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which led to an overestimation by *ca* 5%. Much larger discrepancies in the absorption cross-section have now been resolved.<sup>1</sup> The first unequivocal detection of HNO<sub>2</sub> in the ambient atmosphere became possible through the development of an optical absorption technique with a rapid-scanning device.<sup>2</sup> A slotted disc rotating in the focal plane allows for *ca* 100 scans of the spectrum per second. Rapid scanning of the spectrum is necessary, because atmospheric fluctuations with frequencies peaking in the range 1–10 Hz would, if resolved, dominate spectral features. Diode array detectors are coming into use now for HNO<sub>2</sub> measurements. Interfering trace species can be identified and corrected for with DOAS using simple spectral deconvolution methods. The sensitivity of the method increases with the path length, which can be up to *ca* 10 km. The method's performance is such that under favourable atmospheric conditions a detection limit of *ca* 0.2 ppbV could be achieved with a time resolution of 15–30 min with an uncertainty in the HNO<sub>2</sub> determination of *ca* ± 10%. The uncertainty of the absorption coefficient applied to calculate the concentrations introduces another *ca* ± 15% uncertainty.

In a denuder tube (usually made from glass), trace gases are separated from the aerosol in sampled air by diffusion. Gases diffuse from a laminar flow regime through the denuder to the walls, where they are absorbed by an appropriate coating, while aerosols, having very much smaller diffusion rates, pass through the denuder without being trapped. The geometry of the denuder tube, and flow rates, can be adjusted such that a high (usually close to 100%) and known collection efficiency is achieved. Alkaline surfaces, mainly sodium carbonate coatings, make effective traps for HNO<sub>2</sub>.<sup>3</sup> After collection, the material is then washed from the surface and the extract is analysed off-line by ion chromatography. DS techniques are time-consuming, but developments have been made recently in the use of automated denuders.<sup>4</sup>

No denuder system is specific for HNO<sub>2</sub>. A correction for the simultaneous collection of other trace gases, such as NO<sub>2</sub>, can be made if the interfering gas has a poor collection efficiency. With two or more denuder tubes in series, nitrite found in the second denuder can be attributed to such an interfering species and the corresponding amount would be expected as a positive artefact in the first tube. Although various sources of artefact can be identified and avoided, undetected reactions of the nitrogen oxides on the surfaces of the DS cannot be completely excluded. For instance, it has been found that at elevated levels of SO<sub>2</sub>, an interference of NO<sub>2</sub> can cause significant positive artefacts on Na<sub>2</sub>CO<sub>3</sub> coatings.<sup>5</sup> This might be the reason why high HNO<sub>2</sub> abundances during day-time, obviously not in agreement with the species' photochemical properties, have been reported on the basis of DS measurements. In principle, very low concentrations should be measurable by this method by using long sampling times. However, because some interferences tend to become more influential at long times (*e.g.* the slow diffusion of small particles to the denuder walls), the detection limit for measuring HNO<sub>2</sub> by DS is limited, too. However, DS can be applied under conditions of high humidity, when higher extinction prevents absorption measurements.

Recently, a modified chemiluminescence technique has been developed,<sup>6</sup> in which HNO<sub>2</sub> is absorbed into solution using a diffusion scrubber, then selectively reduced by ascorbic acid to NO, which can be determined using the conventional chemiluminescence technique. The use of a diffusion scrubber is claimed to avoid interferences from NO<sub>2</sub>. This technique, however, is limited by the detection limits of the NO<sub>x</sub> analyser employed, and by the need to measure the HNO<sub>2</sub> concentration in the presence of NO as the difference of two large numbers, (*c*<sub>NO</sub> + *c*<sub>HNO<sub>2</sub></sub>) and (*c*<sub>NO</sub>). The use of a diffusion scrubber, followed by the direct quantification of the nitrite ions produced in solution, by colorimetry or ion chromatography, has also been demonstrated,<sup>7</sup> but there are few published applications of this technique. Although several methods for detecting HNO<sub>2</sub> in ambient air have been developed, it is not yet possible to purchase a 'Nitrous Acid Analyser', and most of the measurements to date have been made using instrumentation developed in a research laboratory. As a result, there are few instances of long-term application of such instruments to characterising the HNO<sub>2</sub> concentration at a site over months or years.

## 2.2 Aqueous-phase Measurement

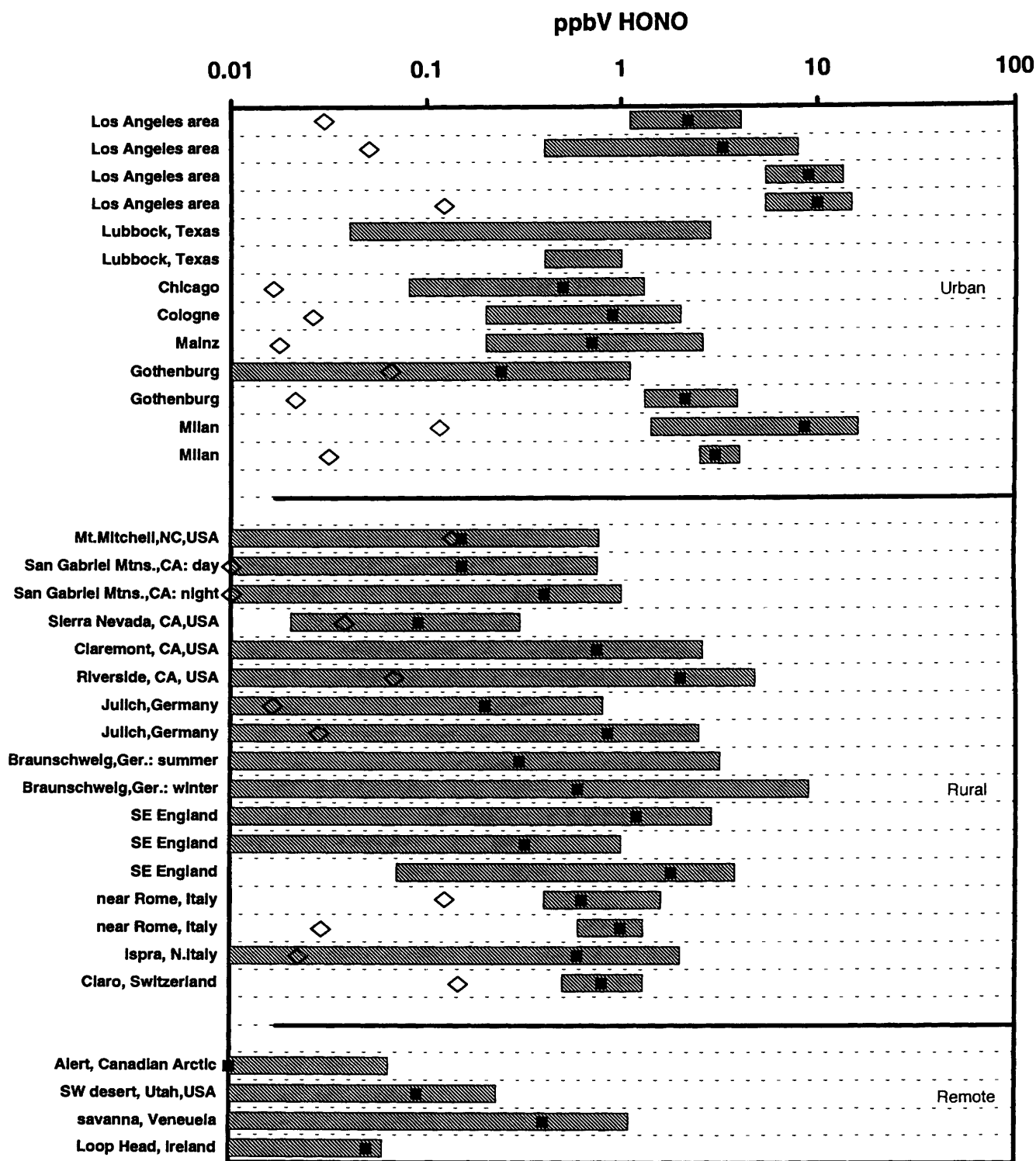
Dissolved HNO<sub>2</sub> and nitrite, N<sup>III</sup>, associated with particles, or fog and cloud droplets, is determined by wet chemical or ion chromatographic methods. A detection limit of a few ng m<sup>-3</sup> can be achieved for particles by integrating over many hours (12–24 h) and ignoring the size distribution.<sup>8</sup> An additional risk with long sampling periods is the possibility that aqueous samples might be subject to rapid oxidation. Therefore, on-line analysis or stabilization through a derivatization reaction is strongly recommended. On-line measurement of nitrite in cloud water has been achieved,<sup>9</sup> with detection limits around 10 nmol dm<sup>-3</sup>.

## 3 Observations of Nitrous Acid in the Troposphere

### 3.1 Field Measurements of Gaseous Nitrous Acid

Since the first unequivocal detection of HNO<sub>2</sub> in the atmosphere,<sup>2</sup> this species has been observed together with NO<sub>x</sub> in the night time atmosphere at both urban and rural sites, and also (at distinctly lower concentrations) during day-time. Most of the measurements have been made during winter and spring, although there are now a few sets of year-round data. Night-time HNO<sub>2</sub> concentrations up to several ppbV have been observed. Concentrations in rural areas are not necessarily lower than in regions with strong NO<sub>x</sub> sources (Figure 1). Rural concentrations over a two year period in Lower Saxony<sup>10</sup> averaged 0.6 ppbV, but with daily maxima in winter up to 8 ppbV. HNO<sub>2</sub> has also been measured inside buildings and vehicles,<sup>5,11</sup> where very much larger concentrations may be found, up to 40 ppbV.

After sunset, when photolysis ceases, concentrations of HNO<sub>2</sub> gradually increase. In many cases, the HNO<sub>2</sub> concentration stabilises (more precisely, the HNO<sub>2</sub>-to-NO<sub>2</sub> ratio stabilises) and remains constant throughout the night until, after sunrise, it starts to decay (Figure 2). During a measurement campaign<sup>12</sup> in the German city of Mainz, for instance, 38 out of 43 night-time periods of several hours were identified with a constant (insignificantly varying) or a continuously increasing HNO<sub>2</sub>-to-NO<sub>2</sub> ratio, whereas this ratio significantly decreased in only five out of 43 nights analysed. The observation of a constant HNO<sub>2</sub>-to-NO<sub>2</sub> ratio can be explained in one of two ways. It is consistent with (a) a constant reaction time relative to an upwind source as air is advected to the measuring site, or (b) the balancing of the rate of formation of HNO<sub>2</sub> by the rate of removal of HNO<sub>2</sub> in a stagnant or well mixed air mass. Source strengths at the site and upwind, together with transport and dispersion processes, need to be considered explicitly. In case (a) pollutant concentrations at the site are dominated by advection rather than local emissions and a horizontally homogeneous atmosphere is implied. This can be classified as a 'receptor site situation' where chemical species observed have the same fixed reaction time, as given by the transport time from the emission site. The closer the primary pollutants sources, the lower are the secondary pollutant levels. Dispersion processes have diluted primary pollutant concentrations since emission. Case (b) is the situation close to the emission sources, and is comparable to a smog chamber during filling. Pollutants and their secondary products accumulate through direct emission or chemical transformation processes, and inefficient mixing with outside air. This situation is common in urban areas, where primary emissions occur continuously, and mixing with cleaner air is suppressed at low wind speeds below a low night-time inversion layer. In fact, a broad distribution of reaction times (with respect to the time of emission) is then addressed, because measuring techniques integrate over a certain time period (minutes to hours). In Figure 2 the time variation of pollutants including HNO<sub>2</sub> is shown on a night when, as wind speed dropped, a shift from case (a) to case (b) occurred. The observation of decreasing HNO<sub>2</sub>-to-NO<sub>2</sub> ratios can be caused by (a) the mixing of fresh NO<sub>x</sub> emissions into the plume from the upwind source (receptor site situation), or (b) from a particularly

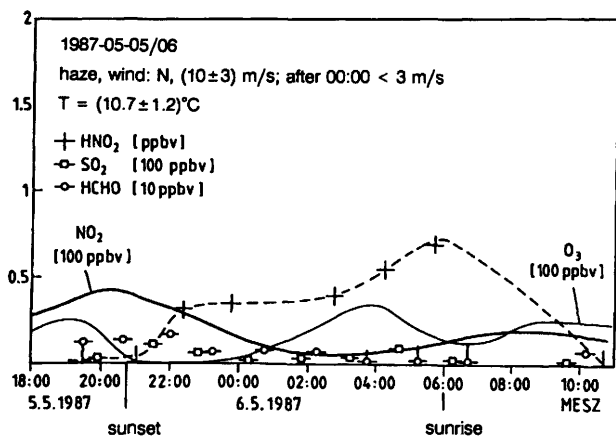


**Figure 1** Summary of published HNO<sub>2</sub> measurements in urban, rural and remote areas, shown as the average (■) and range. Data from some sites are restricted to a few hours, while at other sites the data represent continuous measurements over a year. The diamonds (◇) show the average ratio of HNO<sub>2</sub> to NO<sub>2</sub>, for sites where NO<sub>2</sub> concentrations were measured simultaneously. A detailed reference list is available from the authors.

effective HNO<sub>2</sub> decay reaction (reverse reaction producing NO<sub>x</sub>) in a stagnant or well-mixed air mass. So far, indications for the existence of a reverse reaction are sparse. In the Mainz data set, concentrations of primary pollutants (HCHO-to-NO<sub>x</sub> ratio) indicated that the decrease in the ratio was caused by an increase in primary emissions of NO<sub>x</sub>. In two nights of constant HNO<sub>2</sub>-to-NO<sub>2</sub> ratios, the concentrations of the primary pollutants indicated the advection of increasingly older emissions to the site, suggesting the influence of a mechanism which removed HNO<sub>2</sub> from the air mass.

### 3.2 Correlations with other Trace Gases

Concentrations of HNO<sub>2</sub> are often correlated with those of NO and NO<sub>2</sub>. This is partly a causal link, because NO and NO<sub>2</sub> are source gases for the formation of HNO<sub>2</sub>, or may have a common source. However, all gases in the atmosphere are subject to coincident concentration changes as the depth of the boundary layer changes (for example, under a temperature inversion in winter), or as wind directions change to bring a different mixture of trace gases past a fixed measurement point. This strong dependence on meteorological conditions has bedevilled attempts to understand the sources and sinks



**Figure 2** Measured  $\text{HNO}_2$  concentrations at Mainz, in a heavily industrialized area. Until midnight (00:00), strong winds prevailed and pollutant concentrations at the site were probably dominated by advection rather than local emission. Source strengths had decreased, and dispersion processes had diluted primary pollutant concentrations since emission. Nitrous acid was formed after sunset and disappeared during the morning. Around midnight, as wind speed dropped,  $\text{HNO}_2$  accumulated and the  $\text{HNO}_2$ -to- $\text{NO}_2$  ratio increased significantly.

of  $\text{HNO}_2$  on the basis of field measurements alone. Nevertheless, considerable effort has been made to understand the processes in the atmosphere which lead to  $\text{HNO}_2$  formation, because the amounts of  $\text{HNO}_2$  observed are often an order of magnitude larger than would be expected on the basis of reaction rates determined in the laboratory. This is a hotly debated problem in tropospheric chemistry, and will be discussed below.

### 3.3 Observations of Nitrite and Possible Chemical Formation

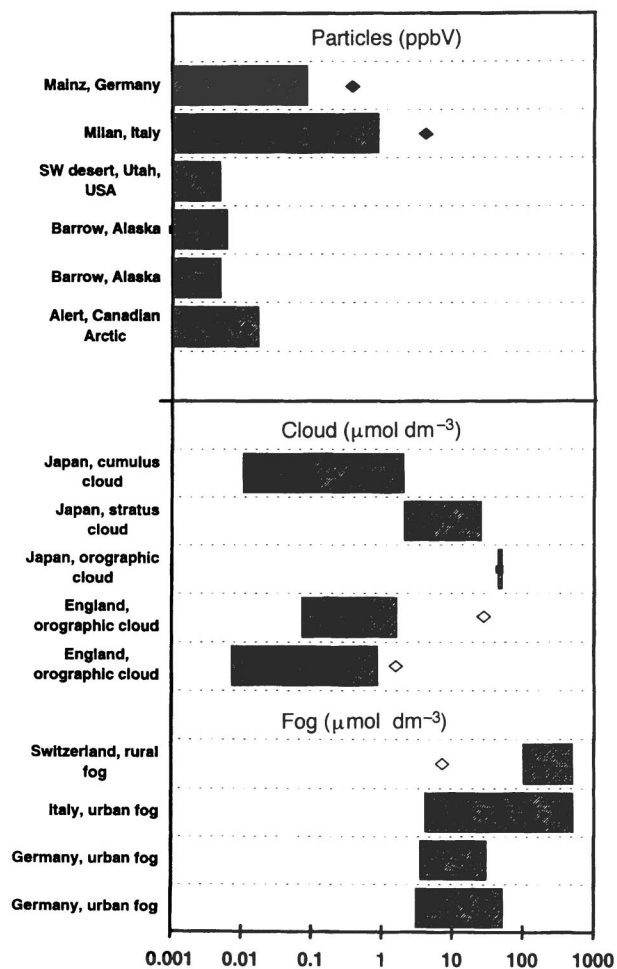
In comparison to other ions, only a few  $\text{N}^{\text{III}}$  measurements in environmental samples have been reported so far, mainly because concentrations of  $\text{N}^{\text{III}}$  are low, and nitrite ions are easily oxidised.

#### 3.3.1 Cloud and Fog Water

In the anthropogenically influenced atmosphere, cloud and fog water is usually more acidic than the natural composition of the air would suggest (which would be *ca.* pH 5.6 from carbonic acid). Acidity is produced by the oxidation of anthropogenic non-metal compounds in the atmosphere, primarily  $\text{SO}_2$  and  $\text{NO}_x$ , or in some cases by the solution of acidic gases such as HCl. Pollutant concentrations are particularly enriched in radiation fogs, as a result of the small size and long lifetime of the droplets. According to the dissociation equilibrium of  $\text{HNO}_2$  ( $\text{p}K = 3.5$ ) and its modest solubility [Henry coefficient  $H = 49 \text{ mol dm}^{-3} \text{ atm}^{-1}$  at 298 K; 1 atm  $\approx 101 \text{ kPa}$ ] only very small concentrations of  $\text{N}^{\text{III}}$  can be achieved in acidic fog or cloud water droplets. The situation is different, though, under conditions of low acidity or neutrality. These tendencies are reflected in the measured  $\text{N}^{\text{III}}$  cloud and fog water concentrations compiled in Figure 3. A partial pressure of 1 ppbV of  $\text{HNO}_2$  would lead to a concentration of  $\text{N}^{\text{III}} < 0.1 \mu\text{mol dm}^{-3}$  at pH = 3, but to  $15 \mu\text{mol dm}^{-3}$  at pH = 6. Unfortunately, so far none of the studies which addressed cloud or fog water  $\text{N}^{\text{III}}$  included co-located gas-phase  $\text{HNO}_2$  measurements to test Henry's Law equilibria in the field.

#### 3.3.2 Particulate Matter

Particulate nitrite concentrations observed are in the lower  $\text{ng m}^{-3}$  range (pptV, parts in  $10^{12}$  by volume), reaching up to hundreds of  $\text{ng m}^{-3}$  ( $> 0.1 \text{ ppbV}$ ) in the urban area of Milan (Figure 3). When measured together with gas-phase  $\text{HNO}_2$  on a short-term basis (up to a few hours), no clear relationship between the two was detected.<sup>13</sup> This is no surprise, because particulate nitrite, through its dissociation equilibrium, is in a pH-dependent phase equilibrium



**Figure 3** Summary of published measurements of nitrite in particles (expressed as equivalent mixing ratios ppbV), or dissolved in cloud and fog water (as concentrations in  $\mu\text{mol dm}^{-3}$ ). The range and average (■) concentrations are shown. For particles, simultaneous gas-phase concentrations of  $\text{HNO}_2$  (ppbV), where available, are shown as filled diamonds (◆). For cloud and fog samples, average  $\text{NO}_2$  concentrations during sampling (ppbV) are shown by open diamonds (◇). A detailed reference list is available from the authors.

with  $\text{HNO}_2$ . The atmospheric aerosol on these occasions was a source of gas-phase  $\text{HNO}_2$ , because particulate matter  $\text{N}^{\text{III}}$  concentrations were in excess with respect to the phase equilibrium. The phase equilibrium of particulate nitrite can be seen as analogous to the situation in cloud and fog water, because an aqueous layer covers atmospheric particles under ambient humidities. In the Arctic, where nitrite concentrations were measured in particles which were approximately 70% (*m/m*)  $\text{H}_2\text{SO}_4$ , the atmospheric aerosol also appeared to be a source of  $\text{HNO}_2$ , with equilibrium between gas and particulate phases.<sup>8</sup>

## 4 Atmospheric Chemistry of Nitrous Acid

Nitrous acid and nitrite are short-lived intermediates of reactive oxidised nitrogen in the atmosphere (collectively referred to as  $\text{NO}_y$ ).  $\text{NO}_y$  enters the troposphere in the form of  $\text{NO}_x$ , mainly as NO. The main fate of  $\text{NO}_x$  is to combine with the OH radical (during daytime) or to be oxidized to the nitrate radical,  $\text{NO}_3$ , by ozone, leading to nitric acid,  $\text{HNO}_3$ , or particulate or cloud- and fog-water nitrate,  $\text{N}^{\text{V}}$ .  $\text{NO}_y$  is removed from the atmosphere mostly in the form of  $\text{HNO}_3$  or particulate nitrate ions through wet and dry deposition and, by these processes, contributes considerably to acidification and eutrophication of ecosystems. The occurrence of  $\text{HNO}_2$  or nitrite, though of great significance for atmospheric chemistry, does not have any significant impact on the nitrogen balance.

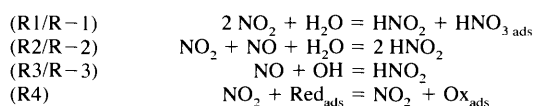
#### 4.1 Sources of Nitrous Acid

Combustion processes are a direct, but small, source of  $\text{HNO}_2$ . Emissions from vehicle exhaust pipes have a mole ratio  $\text{HNO}_2/\text{NO}_x$  of ca 0.15%, and rapid reactions subsequent to emission could lead to ratios up to 0.5%.<sup>14</sup> Measurements during the burning season in the tropical savannah suggested that  $\text{HNO}_2$  is also a by-product of biomass burning.<sup>15</sup> In both rural and urban areas, however, vehicular emission of  $\text{HNO}_2$  cannot explain the high abundances, the  $\text{HNO}_2/\text{NO}_x$  ratio typically reaches a few percent (Figure 1). Production of  $\text{HNO}_2$  is far more efficient than expected from homogeneous gas-phase reactions of the nitrogen oxides, which overnight could account for at most 0.5%  $\text{HNO}_2/\text{NO}_x$ . There is clear evidence that the formation of  $\text{HNO}_2$  in rural and urban environments is governed by heterogeneous reactions.

The initial build-up after sunset should reflect the chemical source. Formation rates,  $dc_{\text{HNO}_2}/dt$ , up to  $1.3 \times 10^{-4}$  ppbV  $s^{-1}$  and conversion rates,  $(dc_{\text{HNO}_2}/dt)/c_{\text{NO}_2}$ , up to  $4 \times 10^{-6} s^{-1}$  have been reported from a rural and an urban site in Germany.<sup>12,16</sup>  $dc_{\text{HNO}_2}/dt$  was roughly proportional to  $c_{\text{NO}_2}$ , which suggests first-order chemical kinetics.

##### 4.1.1 Possible Pathways from Laboratory Measurements

What are the possible chemical pathways? The chemistry of nitrogen oxides and nitrogen oxyacids comprises a wide variety of reaction paths. Only part of it applies to the concentration range relevant to the atmosphere. Reactions R1 to R4 (below) have been suggested to explain the formation of  $\text{N}^{\text{III}}$  in the atmosphere. As OH levels are very low during the night, channel R3 can only be significant during daytime.



Early smog chamber studies dedicated to  $\text{HNO}_2$  were stimulated by the detection of an interfering radical source. It was then shown by different laboratories that gas-phase  $\text{HNO}_2$  formation from  $\text{NO}_x$  in humid air on a wide variety of surfaces (glass, borosilicate glass, quartz, fluorinated polymers, sodium halides, oxalic acid) proceeds with a stoichiometry similar to the aqueous phase, namely via R1. The rate-determining step, however, is first order with respect to both  $\text{NO}_2$  and  $\text{H}_2\text{O}$  concentrations.<sup>17,18</sup>  $\text{N}^{\text{V}}$  remains strongly adsorbed to the surface. The same applies to  $\text{HNO}_2$  occurrence indoors.<sup>11,19</sup> Isotope studies<sup>17</sup> suggested a mechanism which includes the dissociation of  $\text{NO}_2$  but could not completely clarify the mechanisms. R1 is particularly fast on cleansed glass and on metal surfaces. In smog chambers, metal surfaces are always present in the form of end plates and mirrors of optical components. Thus, the apparent formation rate in smog chambers has to be regarded as a superposition of different surface activities and a simple increase in available surface area usually will not lead to an equal increase in the apparent rate of a surface reaction. It is nonetheless clear that the reaction rate is proportional to the surface area. The rate constants on passivated surfaces of different materials are in fairly good agreement, with a range of  $k_{1 \text{ het}} = (1.5 - 6) \times 10^{-22} \text{ cm}^4 \text{ s}^{-1}$  per molecule (for  $dc_{\text{HNO}_2}/dt = k_{1 \text{ het}} S V^{-1} c_{\text{NO}_2} c_{\text{H}_2\text{O}}$  at room temperature).<sup>5,17,18</sup> Rate constants measured in a dark, furnished mobile laboratory fall in the same range.<sup>19</sup> On alkaline surfaces, like  $\text{Na}_2\text{CO}_3$ , source reactions R1 and R2 both contribute, and R4 accounts for nitrite formation on denuders coated with guaiacol (an aromatic compound in a reduced state).<sup>20</sup>

##### 4.1.2 Possible Chemical Pathways from Field Measurements

From field investigations it is clear that  $\text{NO}_2$  is a precursor of  $\text{HNO}_2$  at both urban and rural sites (suggesting R1 or R2 or both). In many cases, R2 has been rejected because measured NO concentrations were too small<sup>21</sup> or, indirectly, through the detection of high ozone concentrations, which do not allow for NO to be present due to the very efficient 'titration' of NO by  $\text{O}_3$ . In several field studies in

urban areas, a role for NO (R2) has been claimed, and a mechanism has been proposed involving formation of  $\text{N}_2\text{O}_3$  as an intermediate.<sup>22</sup> Justification for this route has been sought on the basis of strong correlations between NO and  $\text{HNO}_2$  concentrations. NO is the predominant primary emitted  $\text{NO}_x$  molecule and  $\text{NO}_2$  is formed from NO within minutes as long as  $\text{O}_3$  is available. At a site close to sources of  $\text{NO}_x$ , however, where primary and secondary pollutants may accumulate (for example in a stagnant air mass), coincidental occurrences of NO and  $\text{HNO}_2$  are to be expected independent of any role of NO as a precursor of  $\text{HNO}_2$  (as discussed above). Thus, neither in the laboratory, nor in the field, is there any conclusive evidence of a significant contribution of R2 to  $\text{HNO}_2$  formation. With respect to water vapour, no simple relation between  $\text{HNO}_2$  build-up and humidity has been found in the ambient atmosphere.

##### 4.1.3 Heterogeneous Reactions

Two types of surface are present in the ambient atmosphere, namely the ground surfaces (the bare soil, biological surfaces, walls of buildings, paved roads) and the surface of airborne particles. Evidence for the involvement of both surface types has been found. A strong coincidence of  $\text{HNO}_2$  and radon (which has sources exclusively at the ground) concentrations in central Milan<sup>13b</sup> suggested a ground-based source of  $\text{HNO}_2$ . The surfaces of buildings and streets are substrate candidates.  $\text{NO}_2$  is known to be very efficiently absorbed by cement and building stone, both dry and moist.<sup>23</sup> The ground surface may act as both source and sink for  $\text{HNO}_2$ , over grassland in SE England an upward flux of 5–25 ng  $\text{HNO}_2 \text{ m}^{-2} \text{ s}^{-1}$  (which would correspond to tenths of a ppbV  $\text{HNO}_2 \text{ h}^{-1}$  under the influence of a low night-time boundary layer) was observed when  $\text{NO}_2$  concentrations exceeded 10 ppbV, while at lower concentrations a net downward flux occurred<sup>24</sup> (dry deposition velocity  $v_{\text{HNO}_2} = 0.2 - 1.7 \text{ cm s}^{-1}$ ).

The importance of aerosol surfaces was suggested by the observation that production of  $\text{HNO}_2$  was particularly effective under hazy conditions.<sup>16,25</sup> A correlation between  $\text{HNO}_2$  mixing ratios and particulate matter surface area (as estimated by a nephelometric method) was observed at Julich, Germany.<sup>26</sup> A clear correlation was also seen in rural air in northern Italy, where co-variation with the boundary layer depth was minimised.<sup>27</sup> Furthermore, whenever aerosol has been analysed for nitrite, it has appeared that atmospheric aerosol was a source of gaseous  $\text{HNO}_2$ .<sup>8,13</sup> It is unclear, however, whether the aerosol surface source was the only or the dominant one.

The nitrate radical,  $\text{NO}_3$ , and its adduct  $\text{N}_2\text{O}_5$ , are interesting intermediates in the atmospheric chemistry of nitrogen oxides. Laboratory and field experiments demonstrated that  $\text{N}_2\text{O}_5$  forms nitrate on sea-salts, urban particulate matter and on fly ash. In one study, however, when applying ppmV (parts in  $10^6$  by volume) concentrations, nitrite rather than nitrate formation was suggested.<sup>28</sup> By this pathway,  $\text{HNO}_2$  could be formed on the surface of sea-salt aerosol in remote regions where the lack of NO would permit the formation of  $\text{NO}_3$ , and thus  $\text{N}_2\text{O}_5$ . The relevance of this finding for ambient  $\text{NO}_x$  concentrations is not clear, particularly in the light of more recent evidence which suggests that negligible  $\text{HNO}_2$  is produced by this pathway.<sup>29</sup> The heterogeneous decomposition of pernitric acid,  $\text{HO}_2\text{NO}_2$  (PNA), or peroxyacetyl nitrate,  $\text{MeC(O)OONO}_2$  (PAN), would also lead to nitrite in the aqueous phase<sup>30</sup> (as a function of pH in the case of PNA) and then  $\text{HNO}_2$  in the gas-phase. Neither source is thought to be of any significance except perhaps at high altitudes, or at high latitudes during winter-time.

In the laboratory, reactions with model aerosols such as carbon and metal oxides have been studied. Oxides of some metals apparently enhance  $\text{HNO}_2$  formation from  $\text{NO}_2$  in humid air, while others do not, and common characteristics are not obvious.<sup>31</sup> When in contact with activated carbon and humid air,  $\text{NO}_2$  produces NO,  $\text{N}^{\text{III}}$  and  $\text{N}^{\text{V}}$ . When  $\text{NO}_2$  was bubbled through a slurry of activated carbon, much more nitrite than nitrate was produced, in clear deviation from known stoichiometries.<sup>32</sup>  $\text{NO}_2$ , under reduction to  $\text{N}^{\text{III}}$ , enhances greatly the oxidation of  $\text{SO}_2$  on freshly generated soot

and combustion aerosols<sup>33</sup> The importance of R4 in the troposphere, *ie* direct reduction of adsorbed NO<sub>2</sub>, is speculative to date NO<sub>2</sub> is a strong oxidant (potential  $E = 1.065$  V) R4 requires the presence of reductive surfaces, which appears unlikely for ground surfaces which are continuously exposed to an oxidative environment For aerosol surfaces, the reduction of ppbV levels of NO<sub>2</sub> for  $c_{\text{aerosol}} = 100 \mu\text{g m}^{-3}$  would mean the presence of reductants in the particulate phase in the percent range (by mass), which also appears unlikely However, the reductant could be fed from the gas-phase<sup>34</sup> (SO<sub>2</sub>) or recycled in the polluted aqueous phase (like M<sup>n+</sup> recycled from the reduction of M<sup>(n+1)+</sup> by dissolved SO<sub>2</sub>, M = Fe or other) The production of NO from soil and stone samples upon NO<sub>2</sub> uptake has been related to the presence of oxidizable metal ions<sup>23b</sup>

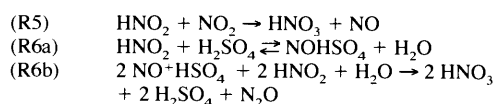
In areas with intensive agriculture, ammonia concentrations are often sufficient to completely neutralize airborne acids Because the solubility of both NO<sub>2</sub> and SO<sub>2</sub> is strongly favoured by high pH, the reduction of dissolved NO<sub>2</sub> by dissolved SO<sub>2</sub> may become important S<sup>IV</sup>, however, would be prevented from oxidation in the presence of formaldehyde (HCHO) because it forms the adduct hydroxymethane sulfonate, which is particularly stable in the pH range 3–6 Figure 4 shows the results of a model of N<sup>III</sup> concentrations in aqueous solution, representative for fog and cloud water, as a function of both gas-phase pollutants and pH under both low and high HCHO and HNO<sub>2</sub> concentrations In the absence of gas-phase HNO<sub>2</sub>, micromolar levels of N<sup>III</sup> can be expected from NO<sub>x</sub> reactions in the presence of SO<sub>2</sub>, but only if SO<sub>2</sub> is available [compare Figure 4(b) and 4(c)] Production of N<sup>III</sup> in the aqueous phase at low HCHO in the absence of gaseous HNO<sub>2</sub> [Figure 4(b)] gives concentrations within a factor of two of N<sup>III</sup> concentrations observed in the presence of gaseous HNO<sub>2</sub> at pH 6 [Figure 4(d)] In the presence of gas phase HNO<sub>2</sub>, production of N<sup>III</sup> by reactions involving SO<sub>2</sub> (in combination with HCHO) is less important, leading to differences in N<sup>III</sup> of a factor of three at most, as far as the parameter variation of Figure 4 is concerned This model suggests that part of the N<sup>III</sup> observations in neutral or almost neutral atmospheric aqueous samples could be explained without HNO<sub>2</sub> originating from the gas-phase This was the case for the Stuttgart fog events (Figure 3)<sup>35</sup>

The observation of significant concentrations of nitrite in cloud water (Figure 5) led to the suggestion that nitrite was formed in or on cloud droplets, and that this was the most likely pathway to explain the conversion of NO<sub>x</sub> into other oxidised nitrogen compounds (measured as the sum, NO<sub>y</sub>) during the passage of air through hill cap clouds in Northern England<sup>36</sup>

#### 4.2 Sinks for Nitrous Acid

Photolysis (backward reaction R-3) is the dominant sink during day-time, although photolysis of HNO<sub>2</sub> is around four times slower than NO<sub>2</sub> photolysis, and is on a timescale of tens of minutes So far, indications for the existence of a night-time removal reaction in the gas phase are sparse The frequently observed achievement of a constant HNO<sub>2</sub>/NO<sub>x</sub> ratio might be caused by transformation as well as transport processes or both (as discussed above) Dry deposition, and removal at the ground, can also deplete concentrations close to the earth's surface In smog chambers, an equilibrium of heterogeneous HNO<sub>2</sub> formation and decay reactions is established after some time NO appears as a product of this removal reaction in the gas-phase (wall materials borosilicate glass, quartz, polyethylene, fluorinated polymer surfaces)<sup>17 18</sup> This could be attributed to R-2, which is known to proceed at least partially heterogeneously Its rate is influenced by water vapour concentration and surface type

There is no evidence for R5 (below) taking place unless at high  $c_{\text{HNO}_2}$  and on activated carbon surfaces At higher humidities, NO production is enhanced, indicating a non-trivial mechanism When in contact with acid surfaces (dry quartz) or when bubbled through acidic solutions, HNO<sub>2</sub> reacts in several steps to form nitrous oxide, N<sub>2</sub>O, as well as nitrate<sup>37</sup> These findings suggest that with strong acids, such as H<sub>2</sub>SO<sub>4</sub>, HNO<sub>2</sub> acts as a base (R6)



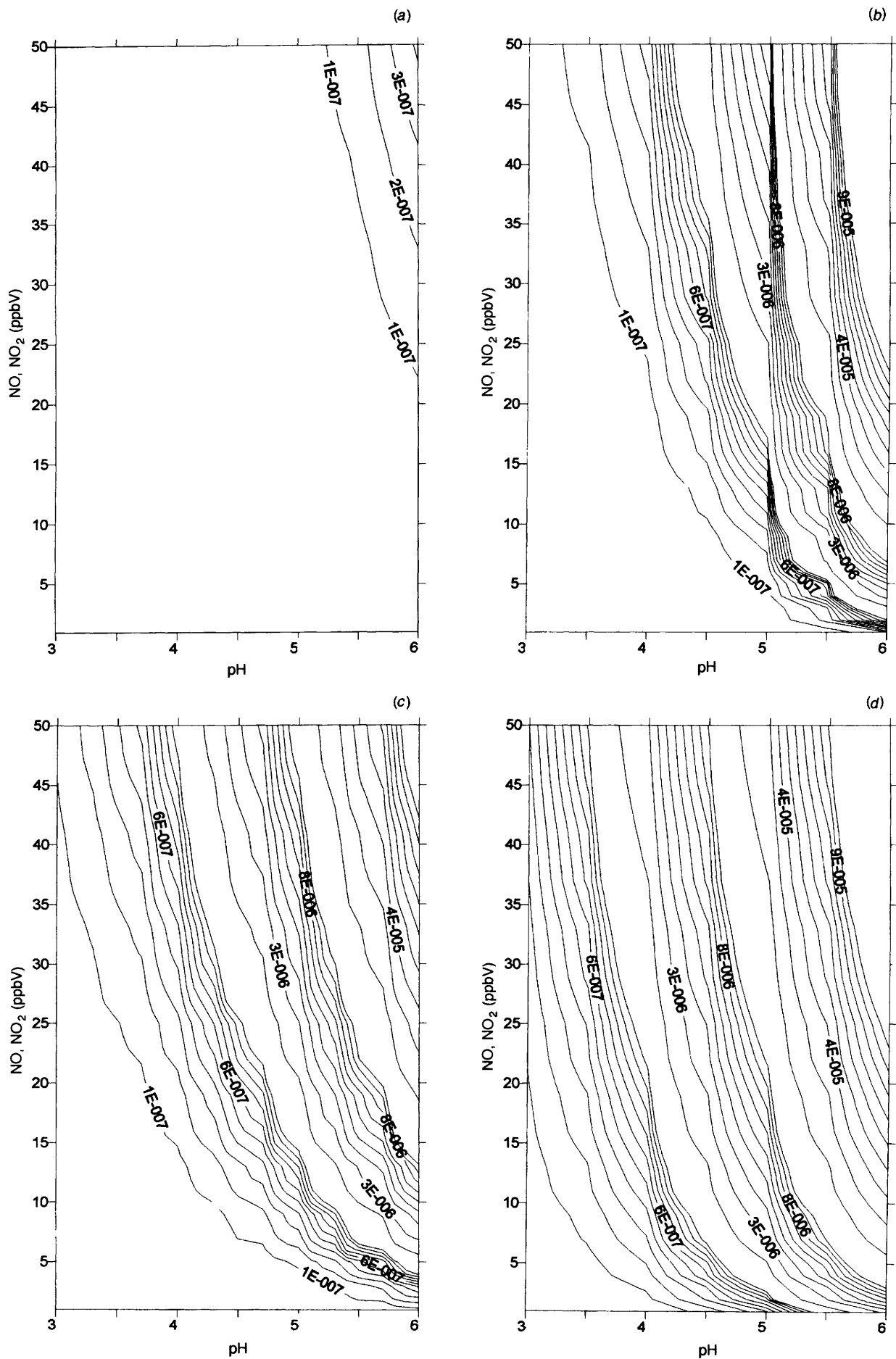
Stone surfaces, as well as acting as potential sources of HNO<sub>2</sub> from the heterogeneous reaction of NO<sub>x</sub> with water, may also act as a sink Colonies of nitrifying bacteria are frequently found on the surface of stone monuments They produce NO<sub>3</sub><sup>-</sup> from NH<sub>4</sub><sup>+</sup> deposited on these surfaces with NO<sub>2</sub><sup>-</sup> as an intermediate<sup>38</sup> The presence of gaseous SO<sub>2</sub> suppresses NO<sub>3</sub><sup>-</sup> production, which suggests that N<sup>III</sup> formed at surfaces might also have a chemical sink, besides evaporation and contribution to gas phase HNO<sub>2</sub>

### 5 Can Field and Laboratory Measurements be Reconciled?

How can we translate laboratory measurements of both homogeneous and heterogeneous reactions into the field? During the night, boundary layer heights of 50–100 m can be assumed For a column of air with a base area of 1 m<sup>2</sup>, the ground surfaces provide *ca* 10 m<sup>2</sup> from structures (a factor of 6–14 for vegetation surfaces, and *ca* 10 for urban surfaces such as buildings and roads) and the aerosol 0.005–1 m<sup>2</sup> ( $S/V = 10^{-4}$ – $10^{-3} \text{ m}^{-1}$  for rural and urban aerosols, times a factor of up to ten to account for particle porosity) leading to a specific surface to volume ratio ( $S/V$ ) between 0.1 and 1.2 m<sup>-1</sup> Applying the rate for passivated surfaces found in laboratory experiments,  $k_{\text{het}} = (1.5\text{--}6) \times 10^{-22} \text{ cm}^4 \text{ s}^{-1}$  per molecule, an apparent conversion rate ( $dc_{\text{HNO}_2}/dt/c_{\text{NO}_2}$ ) of  $(0.01\text{--}3) \times 10^{-6} \text{ s}^{-1}$  would be expected for the relevant temperatures and humidities Even the upper estimate cannot explain the highest observed conversion rates of  $4 \times 10^{-6} \text{ s}^{-1}$  Moreover, these apparent conversion rates are only lower bounds for the effective NO<sub>2</sub> to N<sup>III</sup> conversion rate in the field, because, under the influence of the cooling after sunset, HNO<sub>2</sub> desorption from surfaces to the gas phase will be suppressed

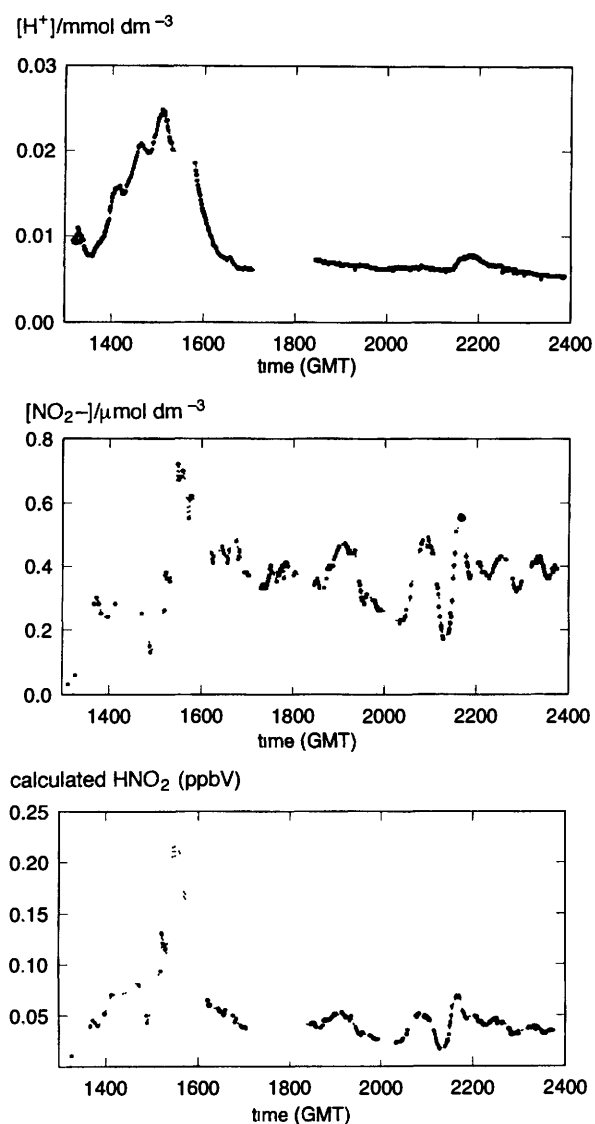
Atmospheric surfaces can be of a reactivity comparable to that of a freshly cleaned smog chamber wall (borosilicate glass)<sup>17b 25b</sup> The aerosol surface, if the site of HNO<sub>2</sub> production, must be much more efficient than laboratory surfaces studied so far At present, one can only speculate about the reasons Real surfaces, such as particles, urban surfaces and the bare soil, may be more active due to the presence of ions capable of contributing to charge-transfer type reactions, transition metal concentrations in ambient aerosols are considerable Ambient aerosols rich in carbon, although less reactive than model substances like activated carbon, are prime candidates when searching for active surfaces, they provide a high specific surface area, and carry a wide variety of functional groups and adsorbed material When newly formed, such particles are hydrophobic, but may eventually be incorporated into fog and cloud water The wetting of surfaces could mean that active sites are blocked and pores become inaccessible, resulting in a reduced specific surface area Wetting of particles occurs as a function of humidity, because they take up liquid water above the humidity of deliquescence of the predominant salt components The growth curve of ambient aerosol rises steeply above 70–75% relative humidity (*r*<sub>h</sub>) Under these conditions one might expect HNO<sub>2</sub> production to be inhibited, and this idea is supported by observations that only in very few cases could significant HNO<sub>2</sub> formation be observed at *r*<sub>h</sub> > 70–75% and then, only when advection was from a sector with a large fraction of urban surfaces<sup>39</sup>

Nitrite can also be formed on the surface of particles and water droplets by the same reactions (R1 and R2) which give gaseous HNO<sub>2</sub> It is here that the greatest interest and uncertainty lies, because this heterogeneous route may yet prove to be one of the most important in reconciling laboratory and field measurements The reaction of NO<sub>2</sub> with bulk liquid water is very slow at ambient concentrations, because it is a second-order reaction<sup>40</sup> Recent measurements suggest, however, that this reaction may not be so simple on finely divided water droplets, and the possibility of first-order behaviour has been raised Experimental determinations of the reaction rate in simulated clouds are not easy, and some controversy still



**Figure 4** Modelled  $\text{N}^{\text{III}}$  concentrations in aqueous solutions representative of fog and cloud water as a function of both  $\text{NO}_x$  and pH. Calculations were made with a two-phase box model of chemistry and interphase transport<sup>35</sup>. For the system under study, mass transport limitations are negligible (assumed droplet size 5–10  $\mu\text{m}$ ). Total solute concentration is ca. 2.5  $\text{mmol dm}^{-3}$ , reaction time is 1 h. Aqueous phase chemical kinetics include the reaction of  $\text{S}^{\text{IV}}$  species with dissolved  $\text{NO}_2$  ( $k^{(2)} = 1.3 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for weak acid and neutral media) which is the main source of  $\text{N}^{\text{III}}$  in the absence of gas-phase  $\text{HNO}_2$ . Only cases with equal concentrations of the gas phase pollutants  $\text{NO}$  and  $\text{NO}_2$  are considered. Initial concentrations (at  $t = 0$ ) are (a)  $\text{HNO}_2 = 0$ ,  $\text{SO}_2 = 0$ , (b)  $\text{HNO}_2 = 0$ ,  $\text{SO}_2 = \text{NO}_2$ ,  $\text{HCHO} = 0.5 \text{ ppbV}$ , (c)  $\text{HNO}_2 = 0$ ,  $\text{SO}_2 = \text{NO}_2$ ,  $\text{HCHO} = 10 \text{ ppbV}$ , (d)  $\text{HNO}_2/\text{NO}_2 = 0.05$ ,  $\text{SO}_2 = 0$ .





**Figure 5** Measurement of cloud water  $\text{N}^{\text{III}}$  concentrations in real time on 7 November 1991, on the summit of Great Dun Fell, Cumbria, England<sup>9,36</sup>. Direct measurements of  $\text{N}^{\text{III}}$  and pH are used to infer gas phase concentrations of  $\text{HNO}_2$ , on the assumption of Henry's Law equilibrium. The temporal pattern of gas phase  $\text{HNO}_2$  concentrations correlates with concentrations of  $\text{NO}_x$ , reflecting the influence of different air masses, either as sources of gas phase  $\text{HNO}_2$  before entering the cloud, or as precursors to  $\text{HNO}_2$  formation on droplet surfaces. The dashed lines show interpolations between measurements. GMT = Greenwich mean time.

exists on their interpretation<sup>41</sup>. Other indications of possible heterogeneous reactions at water surfaces have come from measurements of the accommodation coefficient of gaseous  $\text{NO}_2$  on a liquid water jet, with measured uptake of  $\text{NO}_2$  being much larger than calculated<sup>42</sup>. Until the mechanisms of these heterogeneous reactions are understood, the modelling of urban photochemistry, which is dependent on the correct formulation of  $\text{HNO}_2$  chemistry, may have to resort to empirical expressions. As an example of this approach, the co-variation of  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{HNO}_2$  in the Los Angeles area has been used to derive a pseudo-homogeneous reaction rate for R2, and apply it in a model of  $\text{HNO}_2$  production<sup>22</sup>. Whether this empirical expression will be useful in other regions, with very different mixes of precursor gases, remains to be seen.

## 6 Conclusions

Nitrous acid is an important trace gas for understanding tropospheric chemistry, largely because of its role as a source of the OH radical early in the day. Techniques are only now becoming

available to make routine measurements possible, although they are labour intensive, and as such data become available, a better picture of the overall importance of  $\text{HNO}_2$  will be gained. Despite a long-standing awareness of the heterogeneous reactions which link  $\text{NO}_x$  and  $\text{HNO}_2$ , there are still few experimental data from laboratory studies which are directly applicable to ambient conditions of concentration, temperature, pressure, humidity and active surfaces. Moreover, there appear to be large gaps in our understanding of the underlying mechanisms of the reaction of  $\text{NO}_2$  and liquid water. Until these gaps are filled, we have to accept that laboratory data cannot provide the numbers necessary for use in chemical modelling of  $\text{HNO}_2$  production and loss in the troposphere. We will have to rely on parametrisations based on field measurements, or take up the challenge, and characterise these heterogeneous reactions in the laboratory under realistic atmospheric conditions.

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