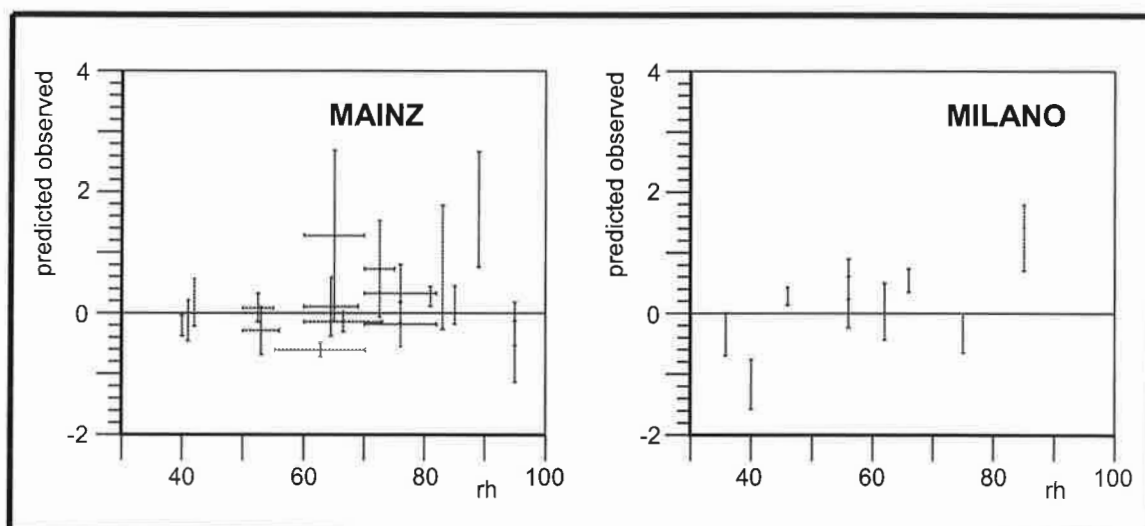




Max-Planck-Institut für Meteorologie

REPORT No. 286



FORMATION OF NITROUS ACID: PARAMETERISATION AND COMPARISON WITH OBSERVATIONS

by
Gerhard Lammel

HAMBURG, January 1999

AUTHOR:

Gerhard Lammel

Max-Planck-Institut
für Meteorologie
und Universität für Meteorologie Hamburg
Bundesstr. 55
20146 Hamburg
Germany

MAX-PLANCK-INSTITUT
FÜR METEOROLOGIE
BUNDESSTRASSE 55
D - 20146 HAMBURG
GERMANY

Tel.: +49-(0)40-4 11 73-0
Telefax: +49-(0)40-4 11 73-298
E-Mail: <name> @ dkrz.de

ISSN 0937-1060

FORMATION OF NITROUS ACID: PARAMETERISATION AND COMPARISON WITH OBSERVATIONS

Gerhard Lammel

*Max Planck Institute for Meteorology, Bundesstr. 55, 20146 Hamburg, Germany
and University of Hamburg, Meteorological Institute, lammel@dkrz.de*

Abstract

Nitrous acid formation in the troposphere is described in the light of the most recent advances of knowledge on NO_x chemistry on ground and aerosol surfaces. It is suggested to follow the stoichiometry of the reaction $2 \text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_2 + \text{HNO}_3$ on all ambient surfaces except those of carbonaceous particles. The influences of ambient humidity on aerosol (water uptake) and ground surface area (surface to area indices) and on water availability for surface reactions are considered. It is concluded that the state of the reacting H_2O molecule, chemisorbed to the surface or other, is determining: The kinetics of the process obeys first order in NO_2 concentration and either pseudo-zeroth order (for low surface coverage with H_2O , using $\gamma_{\text{NO}_2} = 0.1 - 1 * 10^{-6}$ for the various surface types) or first order in water vapour concentration (for water molecules available on the surface in multilayer adsorption; using $k^{\text{het}} = 1.36 * 10^{-20} \text{ cm}^4 \text{ molec}^{-1} \text{ s}^{-1}$ as determined in a laboratory experiment on a humid vessel wall). A reaction mechanism is proposed. The scheme differentiates between 4 ground surface and 4 aerosol surfaces types.

Predicted and observed nitrous acid formation rates from two urban sites are compared. For this purpose, observed rates and their error bars were derived with particular care. Despite large uncertainties for both predicted and observed values, the agreement is good for both low and high humidities (mean predicted/observed = 138 % for 18 nights in Mainz, 1986/87, and 132 % for 9 nights in Milano, 1994).

Keywords nitrous acid, nitrogen oxide chemistry, ground surfaces, aerosol surfaces, water vapour adsorption

1. Introduction

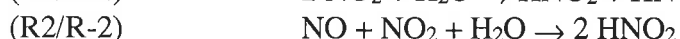
Nitrous acid, HNO_2 , formation has been observed in many nighttime atmospheric environments, urban, rural, and remote. Due to rapid photolysis, daytime levels are low. The formation process is of central interest, because of the large potential impact of HNO_2 as a hydroxyl radical precursor on tropospheric chemistry in NO_x loaded air masses (Harris et al., 1982; Jenkin et al., 1988) - during both the night and day. Additional interest arises from the fact that nitrous acid might be converted to substances harmful for the human health, an aspect which is underlined by observations of quite high HNO_2 levels indoors (Pitts et al., 1985; Febo and Perrino, 1991). The formation reaction is heterogeneous in nature and there is evidence from field observations that both the aerosol (Lammel and Perner, 1988) and the ground surfaces (Harrison and Kitto, 1994) can act as sources for HNO_2 . Despite two decades of awareness the chemistry of HNO_2 formation is still not clear. A compilation of atmospheric observations of HNO_2 (Lammel and

Cape, 1996) shows that despite higher HNO₂ concentrations in urban compared to rural areas (a factor of three, by average) the source strength when normalized to NO₂ levels is very similar in both environments. It spans exactly the same range, namely 1.7 - 13 % (determined for the time of the nighttime maximum of nitrous acid). Considerable efforts have been undertaken in the laboratory in recent years to clarify this important chemistry. An adequate description of the process for use in atmospheric modeling is urgently needed - not only for urban air chemistry studies but for the tropospheric chemistry as a whole. Recent progress justifies an assessment which is the scope of this article: A chemical parameterisation of NO_x reactivity which can be used for model applications is developed (in Section 3) based on the most recent advances of knowledge (outlined in Section 2). The parameterisation is then applied to predict the nitrous acid source term after sunset at urban sites and evaluated through comparison with observations and the results are discussed (Section 4). Conclusions are made in Section 5.

2. Compilation of the knowledge on nitrous acid formation on surfaces

2.1 The nitrogen oxide precursor

Nitrous acid is formed from nitrogen oxides. NO₂ is a reactive trace gas upon contact with many surfaces (cf. Table 1). The reactivity of nitric oxide, NO, under atmospheric conditions on the other hand, is low, which is reflected, besides other, in very low deposition velocities (van Aalst, 1982; Behlen, 1996). Even on soot surfaces NO is not activated. At present no evidence exists for the direct, abiotic conversion of NO into NO₂ or nitrous acid on whatever surface of relevance in the atmospheric environment. While the involvement of NO₂ in the occurrence of nitrous acid in the atmosphere was soon obvious (indicative for R1 stoichiometry), a possible involvement of NO (and, hence, R2) remained open (Sjödin and Ferm, 1985; Calvert et al., 1994).



However, observed correlations between NO and HNO₂ concentrations could be explained in the light of emission strength and mixing volume (Febo, 1994; Lammel, 1996) and thus do not provide any evidence for precursorship of NO. Once NO₂ is oxidized to the nitrate radical, NO₃, or is in the form of the adduct N₂O₅, its fate in heterogeneous reactions will be exclusively N(V), i.e. nitrate (Platt et al., 1980).

We resume that NO₂ is the only nitrogen oxide precursor of HNO₂ in the troposphere.

2.2 Influence of the surface area

A nitrous acid formation rate unambiguously proportional to the surface area was observed in laboratory experiments on vessel walls (Sakamaki et al., 1983; Svensson et al., 1987; besides others) and on stone surfaces (possibly less than linearly related to the pore area; Kirkitis and Sikiotis, 1996). In smog chambers, metal surfaces are always present in the form of end plates and mirrors of optical components. Thus, in these cases the apparent formation rate in smog chambers has to be regarded as a superposition of different surface activities and amplification of the surface area usually will not lead to a linear increase in the apparent reaction rate. It became nonetheless obvious from such experiments that the reaction rate is proportional to the surface area.

2.3 Influence of water availability

NO₂ is strongly adsorbed on many dry surfaces (Table 2) and is, albeit only little, soluble in water ($H = 1.2 \cdot 10^{-7} \cdot e^{2500 \cdot (1/T - 1/298)}$ M Pa⁻¹; Lee and Schwartz, 1981; Schwartz and White, 1981). NO₂ deposition on vegetation surfaces (fern, spruce and wheat) was found to increase linearly with humidity. This behaviour is apparently not directly linked to stomatal aperture but indicates dissolution in a forming water film (Weber and Rennenberg, 1996, and references therein). On seasalt particles, the reaction R1 proceeds in the liquid phase at relative humidity $rh > ca. 80 \%$ (Karlsson and Ljungström, 1995). Also, the combined reactivity of NO₂ and SO₂ on stone surfaces is only explicable when seen as involving an aqueous phase: NO₂ reacts with SO₂ on silica and silica-alumina unless the surfaces were dehydrated (in vacuo at 800 K; Davis and Lunsford, 1978). SO₂ deposition onto and oxidation on stone surfaces is largely enhanced if NO₂ is present under high humidity ($rh = 90 \%$), while the effect is negligible at $rh = 50 \%$ (Clifton et al., 1988; Johansson et al., 1988).

A particular high NO₂ reactivity was observed on glass which was freshly rinsed with water (according to R1, again; Svensson et al., 1987). Also, the formation of nitrous acid from NO₂ on the surface of material rich in carbon is more efficient at higher humidities (Gundel et al., 1989). On stone surfaces, different chemical mechanisms occur on the dry surface on one hand and in the presence of water films on the other: At relative humidity $rh \leq 50 \%$ considerable production of gas-phase NO and adsorbed nitrate is observed, which is indicative for the combined reaction $R3 = 2 \cdot R1 + R-2$, while dismutation of NO₂ according to R1 takes place with little yield independent of humidity (Johansson et al., 1988; Baumgärtner et al., 1992; Behlen, 1996; Kirkitos and Sikiotis, 1996).



R3 is favoured by acid conditions and suppressed by an aqueous phase on the surface.

In conclusion it is noteworthy to emphasize that dry deposition and heterogeneous chemistry of NO₂ is clearly influenced by humidity and surface wetness.

2.4 Kinetics of nitrous acid formation

Surfaces of vessels used in laboratory experiments: In many investigations and using a wide variety of surfaces (borosilicate glass, quartz, fluorinated polymers, sodium halogenides, oxalic acid) it was shown that gas-phase HNO₂ formation from NO_x in humid and dry air proceeds with R1 stoichiometry (Table 3). N(V) keeps strongly adsorbed to the surface. For $rh > 0$ it was found that the kinetics obeys a second order rate law, both first order with respect to NO₂ and H₂O concentrations (Sakamaki et al., 1983; Pitts et al., 1984; Svensson et al., 1987; Jenkin et al., 1988; Febo and Perrino, 1991). In most of these studies, NO_x was applied in the ppmv concentration range.

A heterogeneous rate constant, k_{R1}^{het} , is derived from these laboratory studies, defined as $d_{\text{CHNO}_2}/dt = k_{R1}^{het} S/V \cdot C_{\text{NO}_2} \cdot C_{\text{H}_2\text{O}}$ (Table 3). The results have been selected for Table 3 so as to suppress those experiments where the N mass balance was not closed. This is mostly due to HNO₂ kept adsorbed to the vessel wall (Pitts et al., 1984; Febo and Perrino, 1991; besides others). The superposition of different surface activities resulting from various surface types which are necessarily present in smog chambers are accounted for in some of the k_{R1}^{het} values.

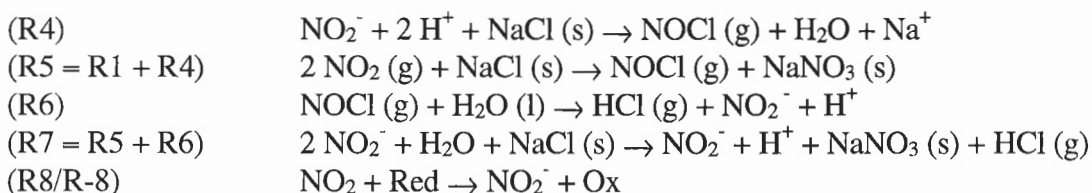
The reactivity is certainly influenced by temperature (negative dependence found on on borosilicate glass and on seasalt particles; Jenkin et al., 1988; Karlsson and Ljungström, 1995), surface wetness and surface chemical properties. A considerable range for k_{R1}^{het} is spanned even when similar surfaces were studied. The reaction is found to be particularly fast on carbonaceous surfaces, cleansed glass (after rinsing with water) and on metal surfaces. The rate constants on aged surfaces of different materials do agree pretty well with a range of $k_{R1}^{\text{het}} = (1.5 - 6) * 10^{-22} \text{ cm}^4 \text{ molec}^{-1} \text{ s}^{-1}$ or $(2 - 8) * 10^{-9} \text{ m ppmv}^{-1} \text{ min}^{-1}$ (298 K; Pitts et al., 1984; Svensson et al., 1987; Febo and Perrino, 1991; Pitts et al., 1985).

Aqueous surfaces: A surface and a bulk reaction is expected to occur simultaneously. On bulk aqueous surfaces, continuously renewed neutral or alkaline, a very high rate was observed (Mertes and Wahner, 1996). It should be mentioned here that despite numerous experimental studies the two-phase chemistry, air and aqueous phase, of NO_2 is still not fully understood (cf. Bambauer et al., 1994, besides others). No unambiguous observation from field measurements are available. We will come back to that point in Section 3.2.2.

Vegetation surfaces: Trace gas deposition to vegetation surfaces is a complicated facet of the biosphere-atmosphere interface. Stomata, when open, represent a perfect sink, whereas the cuticle, which is wax covered (however not homogeneously), represents a significant resistance for most trace gases. The influence of stomata aperture on NO_2 deposition is reflected in by far higher deposition velocities during the day (0.83 cm s^{-1} vs. 0.036 during the night; Wesely, 1989).

Whether nitrous acid is formed directly on vegetation surfaces is an open question. Vertical gradient measurements of nitrous acid over vegetated areas (low vegetation) showed the surface to be a sink (Slanina et al., 1994; Neftel et al., 1996) or a sink as well as a source depending on NO_x concentration (Harrison and Kitto, 1994; Harrison et al., 1996). No rates have been measured.

Seasalt: NaNO_3 is formed on seasalt particles in R5, which is the overall reaction of R1 and R4. HNO_2 and/or NO_2^- is recycled from the other product, NOCl , in the presence of water vapour through subsequent hydrolysis (R6; Finlayson-Pitts, 1983; Winkler et al., 1991; Junkermann und Ibusuki, 1992; Fenter et al., 1995; Karlsson and Ljungström, 1995).



As R6 is only suppressed under dry conditions, for atmospheric situations the balance R7 applies, which stoichiometry besides ion exchanges is identical to R1. The reaction is rapid. With respect to nitrous acid formation, no rates have been measured.

Soot particle surfaces: When NO_2 was bubbled through a slurry of activated carbon, much more nitrite than nitrate was produced in clear deviation from known stoichiometries (Gundel et al., 1989). A particularly high reactivity was observed on supposedly carbon rich particles from industrial and other burners (de Santis and Allegrini, 1992). NO_2 , under reduction to N(III), enhances largely the oxidation of SO_2 on freshly generated soot and combustion aerosols (Britton and Clarke, 1980; Cofer et al., 1981; de Santis and Allegrini, 1992).

There is evidence for the involvement of the reactions R1/R-1, R2/R-2 and R8 on neutral to acidic reacting coal and other carbonaceous surfaces with HNO₂ and - in some cases - NO being the major products (Kalberer et al., 1996; Gerecke et al., 1998; besides others).

Other surfaces: For indoor surfaces (wall paper, instrumented mobile laboratory) the findings are in full agreement with those made on surfaces of vessels used in laboratory experiments (above; Pitts et al., 1985; Brauer et al., 1990).

3. Parameterisation

3.1 Water uptake of surfaces

Water adsorbed to surfaces is either physisorbed (van der Waals type) or chemisorbed. Physisorption can be considered irrelevant for activation. The activity of chemisorbed H₂O molecules will be different depending on whether adsorbed to active surface sites (irreversible adsorption) or to other H₂O molecules (multilayer adsorption, which is a quasi-reversible adsorption i.e. the molecules are more mobile; e.g. Laidler, 1950). One can easily imagine that the type of adsorption gives rise to different mechanisms of reaction between H₂O and NO₂ and, in fact, water availability (henceforth expressed as wetness type) is relevant for NO₂ reactivity (Section 2.3).

Besides kinetics also the specific surface (henceforth expressed as surface-to-area index, SAI) of many surface types is humidity dependent: Outer surfaces might grow and - when pores are filled with condensing water - inner surfaces might shrink under the influence of water uptake.

In the following, the water uptake characteristics of surface types are outlined and wetness types and SAI are attributed to surfaces relevant to the atmospheric environment as a function of humidity (summarized in Table A2, Appendix):

Glass and other laboratory surfaces: Water adsorption occurs at very low humidities and is not necessarily uniform, as clusters of water molecules tend to stick to active sites. Ca. 2 monolayers are formed until $rh = 60\%$ and accelerated above (Carman and Pantano, 1990; Benner et al., 1992).

Unfortunately, the temperature range and range of surface wetness (denoted as estimated number of monolayers, Table 3) spanned by laboratory experiments is not wide. The influence of humidity has not been studied systematically in smog chamber studies into HNO₂ formation. Sakamaki et al., 1983, studied HNO₂ formation over $rh = 10 - 65\%$ on a wall coated with a perfluorinated polymer (PFA). These materials, however, absorb H₂O within their fibre structure for a wide range of humidities before a water film gets formed on the surface. (Fig. 1)

Vegetation surfaces: These are covered by a hydrophobic wax layer which is depleted with ageing or as wax particles are removed by off-rolling water drops. Despite the existence of wax layers, water films are formed on vegetation surfaces keeping them wet in the absence of rain, for long periods (Cape, 1996) and can be excellent sinks at least for water soluble gases. This was found for coniferous needles and leaves, besides other species (Burkhardt and Eigen, 1994; van Hove and Adema, 1996). As the film disappears with washing of the needles, its extent appeared to be mainly dependent on the amount of deposited hygroscopic material (and, hence, on ambient humidity, the elapsed time since the last precipitation event washing off the needles or leaves and of the frequency of wax layer recovery) and of stomata distribution (leading to a humidity gradient on the surface and herewith of the diurnal cycle). These influences do not necessarily result in uniform water films, but in surfaces partly covered and partly uncovered by

water films.

The water uptake of spruce needles was recently studied under different weather conditions and related to the amount of (partially water soluble) deposited material on the needles' surface (Burkhardt and Eigen, 1994; Klemm et al., 1998). For our purposes, we transform the result of numerous measurements of leaf wetness (as measurable as electrical conductivity by clip sensors) to a step function of the degree of wetness (dry for $rh < 55\%$, partially wet for $55\% < rh < 90\%$, and totally wet for $rh > 90\%$; cf. Appendix, Table A2). Obviously, vegetation surfaces add uncertainty to the parameterization of heterogeneous NO_x chemistry: Plant genera distribution, canopy roughness, seasonal variable leaf extent and degree of deposited material on the leaves or needles are usually unknown.

For the wetness of the vegetation surfaces, partially aqueous above 55% and completely aqueous above 90% (according to Klemm et al., 1998) is assumed. The season, vegetated or not, is taken into account for the surface-to-area index of ground surfaces. The reactivity is taken to be zero on hydrophobic surfaces. For the simulation of atmospheric situations, the hygroscopicity at $rh < 55\%$ could, in addition, be attributed dependent on the of most recent precipitation event. Without respective knowledge, it is assumed that half of the vegetation surface is hygroscopic while no water molecules are adsorbed on the other half.

Sand and bare soil: Under atmospheric conditions a water film develops on sand (SiO_2). At $70^\circ C$ the first monolayer is being completed at 26% , and 5 - 10 are completed at $rh = 100\%$ (Goss, 1992). Soils are porous materials and adsorb reactive gases and water vapour. Water monolayers for soils are formed below 40% rh , mostly between 12 and 20% rh , and two layer are completed at $64 - 77\%$ (52% for clays; Niskanen and Mäntylähti, 1988; Karathanasis and Hajek, 1982). Rapid capillary condensation occurs at $rh > 95\%$.

Urban surfaces: Building stones, concrete and mortar are porous materials. These surfaces are covered by the amount of water corresponding to one monolayer (thickness ca. 0.3 nm) at ca. 15% rh . A water film grows under the influence of increasing humidity until $rh = 50 - 90\%$, from where on capillary condensation enhances considerably the uptake establishing an aqueous phase. (Hagymassy et al., 1969; Koz_owski et al., 1992; Krus, 1995; Behlen, 1996) $rh = 50\%$ is considered as the onset of quasi-reversible water adsorption.

Seasalt and sulfuric acid aerosol: The wetness type of seasalt, as any other salt, is determined by the rh of deliquescence ($rh_{D_{NaCl}} = 76\%$ at 283 K; Tang and Munkelwitz, 1994). The acidic aerosol is assumed to consist of a mixture of ammonium sulfate, bisulfate and is considered to be dry below 40% rh , to be wet for $30\% \leq rh < 95\%$ and aqueous for $rh \geq 95\%$; Tang and Munkelwitz, 1977).

Carbonaceous aerosol: Even at low humidity, fresh combustion soots and commercially available black carbons do carry some irreversibly adsorbed (chemisorbed) water on the surface. The surface coverage is limited by the availability of polar functional groups on the surfaces, e.g. $16 - 18\%$ for diesel and aircraft fuel soots. Quasi-reversible (via hydrogen bonding between surface sites and adsorbate) and multilayer adsorptions start above $rh \approx 25\%$ and $rh = 50 - 60\%$, respectively (Chughtai et al., 1996 and 1998). It was also observed that wood smoke and diesel soot take up water linearly with relative humidity over the whole range (Jang and Kamens, 1998). These results suggest the onset of multilayer adsorption in the same humidity range.

Basing on the behaviour of several atmospheric relevant materials rich in carbon (n-hexane, diesel and aircraft fuel soots, pine needle and coal combustion soots; Chughtai et al., 1998), and

assuming the ageing of carbonaceous material in the atmosphere does not significantly enhance the density of functional groups on the surface, we assume that 85 % of the surface of carbonaceous particles are dry (no NO_x reactivity), while the remaining 15 % are wet and show NO_x reactivity.

Other particulate matter: The water uptake behaviour of mixed aerosols is steady and smooth, unlike those of pure salts. As the particulate matter contains hygroscopic salts, water vapour condensation is not expected to occur exclusively on the surface of particles, but a supersaturated aqueous solution droplet is formed gradually with increasing humidity. The water uptake of particulate matter is understood as the combined effects of water soluble and insoluble mass fractions. It has been found that aerosols in rural areas show similar growth curves as aerosols in urban areas with a tendency to faster uptake related to a larger fraction of soluble material, 60 %, in the so-called continental aerosol (Winkler and Junge, 1972; Winkler, 1973). Non-seasalt and non carbonaceous particles are differentiated between acidic aerosol particles and a chemically unspecified rest. The latter is assumed to have a water uptake behaviour similar to continental aerosol, while acid aerosol particles are assumed to behave like a equimolar mixture of sulfuric acid and ammonium sulfate. The growth is described by empiric relationships (which cover the dependancies on the tendency to dissociate into ions and on the fraction of soluble material; Winkler, 1973).

The water uptake characteristics as outlined above are shown qualitatively in Fig. 1. Due to the variability of the properties of surfaces of the same type the range of behaviour is quite large. Hence, a significant amount of uncertainty is introduced with such an attribution. A sensitivity test was performed to investigate the influence of the attribution of wetness types and of SAI to humidity classes on the nitrous acid formation rate. Sets of thresholds leading to lower and upper estimates of the reactivity have been applied (see Table A2, values in brackets, Appendix). The results are listed in Table 5.

3.2 Attribution of chemical kinetic regimes and selection of rate coefficients

3.2.1 Reaction order with respect to water vapour

Pseudo-zeroth as well as first order kinetics in water vapour concentration were observed in laboratory experiments. Pseudo-zeroth order kinetics indicates NO₂ but no H₂O limitation in the rate determining step, e.g. an excess of available H₂O over NO₂. Water molecules can be either gaseous or in an adsorbed state. If in the rate determining step water vapour reacted with an adsorbed NO₂ molecule, one would expect a change from first to pseudo-zeroth order above some threshold c_{H_2O} . This was never observed, however. In contrary, such a change in reaction order was observed on fluorinated polymers (Sakamaki et al., 1983; Pitts et al., 1984) and on borosilicate glass (Jenkin et al., 1988) when humidity was decreased or when the temperature was increased. This is plausible, because when moving to 'dry' conditions the amount of available water does not approach zero, but the chemisorbed fraction of water molecules, which even might be almost independent of humidity. That is, why at zero humidity, nitrous acid formation can be observed (Jenkin et al., 1988; Wiesen et al., 1995) - obviously from the reaction with strongly adsorbed H₂O molecules.

If chemisorbed H₂O molecules were consumed only slowly (relative to the total amount of adsorbed water molecules), the supply from the gas-phase which maintains the film of adsorbed molecules could not limitate the reaction. But it could in a regime which is characterized by fast

consumption of chemisorbed water molecules and their substitution by gaseous H₂O. A strong negative temperature dependence of the rate (observed in the ppmv NO₂ range; Svensson et al., 1987) can also be seen as resulting from limited availability of (condensed) surface water. It is therefore appropriate to expect pseudo-zeroth order behaviour below and first order behaviour above some threshold determined by the available reactants, NO₂ and H₂O, their adsorptivity and the surface chemical characteristics. Such thresholds were observed and are listed in Table 4 as $\mu_{\text{NO}_2}^2 / \mu_{\text{H}_2\text{O}}$, a ratio which is suggested by the stoichiometric ratio of the reactants in R1. We note that atmospheric water vapour concentrations would lead to $\mu_{\text{NO}_2}^2 / \mu_{\text{H}_2\text{O}} < 6 * 10^{-6}$ ppmv for the range of parameters covered by the laboratory studies (T = 20 - 30°C, rh ≥ 30 %, $\mu_{\text{NO}_2} < 0.2$ ppmv). This is below most of the observed threshold values of this ratio (Table 4) and no such observations from laboratory experiments have been reported for lower temperatures.

3.2.2 Rates for different surface types

'Dry' surfaces: R1 obeys first order kinetics in NO₂ for $\mu_{\text{NO}_2} = 0.001 - 20$ ppmv (Kleffmann et al., 1998) on 'dry' and on aqueous surfaces. Like a laboratory surface under 'dry' conditions, ambient surfaces (even 'hydrophobic' surfaces such as carbonaceous particles might provide under certain circumstances) are at least partially covered with chemisorbed water molecules and we hold that the high availability of H₂O in the atmosphere to replace reacted chemisorbed molecules constitutes pseudo-zeroth order kinetics in c_{H₂O}.

The kinetics of the individual steps contributing to the heterogeneous nitrous acid formation are not known. For aqueous and 'dry' quartz surfaces accommodation coefficients mass transfer control was observed with uptake coefficients of $\gamma = 0.1 - 1 * 10^{-6}$ and on dry NaCl $\gamma = 0.1 * 10^{-6}$ was determined (Table 1). Higher accommodation coefficients were found for surfaces (salts, besides other, cf. Table 1), supposedly covered with much more than 1 monolayer of water molecules. When the mass transfer is the rate determining step of the overall process, the uptake coefficient reflects the mass accommodation, $\alpha \approx \gamma$, and the formation rate can be described by the kinetic law of this step alone. We, therefore, take the phase transfer controlled rate as representative for ambient surfaces covered with chemisorbed water (wetness type 'dry'). This pseudo-zeroth order (in water vapour concentration) nitrous acid formation rate is calculated according to:

$$-dc_{i(g)} / dt = k^{\text{het}(1)} K_{i \text{ sat}} c_{i(g)}$$

$$k^{\text{het}(1)} = \alpha_i (S/V) \beta_i \langle v_i \rangle / 4$$

$$\beta_i = (1 + Kn_i) / (1 + 1.71 Kn_i + 1.33 Kn_i^2)$$

$$\langle v_i \rangle = (8 RT / \pi M_i)^{0.5}$$

with: $c_{i(g)}$ = concentration of i far from the interface, k^{het} = loss rate to condensed phase, α_i = mass accommodation coefficient, S/V = aerosol or ground surface concentration, $\langle v_i \rangle$ = mean velocity of gas molecules, R = molar gas constant, T = absolute temperature, M_i = molar mass, β_i = correction for non-continuum effects (Fuchs und Sutugin, 1971): $\beta_i \rightarrow 1$ for $Kn \rightarrow 0$ and $\beta_i \rightarrow 0.75 Kn$ for $Kn \rightarrow \infty$, with $Kn_i = \lambda_i / r = Knudson \text{ number}$, $\lambda_i = (\sqrt{2} \pi \sigma_i^2 N_i)^{-1}$ = mean free path of gas molecules, $\pi \sigma_i^2$ = collision cross-section of gas molecules in air, N_i = molecule number concentration, r = particle radius.

Wet surfaces: A second order rate ($k^{\text{het}} (2)$, first order both in NO_2 and water vapour concentration) has to be chosen for 'wet' surfaces, i.e. those with sufficient water adsorbed (cf. Sections 2.4.1 and 3.2.1). Unfortunately, from studying the water uptake on materials which have been used in laboratory experiments we learnt (Section 3.1) that laboratory findings made with suitable humid surfaces are scarce (cf. estimated number of water monolayers, Table 3). It is recommended to use a rate determined on a glass wall, which was freshly saturated with water after rinsing ($1.36 * 10^{-20} \text{ cm}^4 \text{ molec}^{-1} \text{ s}^{-1}$; Svensson et al., 1987).

Aqueous surfaces: Our knowledge of NO_x chemistry on these surfaces is incomplete. Experimental results using a freshly renewed water surface (water jet; Mertes and Wahner, 1996) suggested second order kinetics in NO_2 (cf. Table 3). We hesitate to recommend these for application for the atmospheric situation, however: The experimental results are difficult to interpret. More important, much higher NO_2 concentrations than in the ambient atmosphere ($\mu_{\text{NO}_2} > 40 \text{ ppmv}$) have been applied. The reaction order is influenced by concentration regimes and second order kinetics at such high concentrations is not necessarily applicable to the $\mu_{\text{NO}_2} < 1 \text{ ppmv}$ range. Furthermore, high concentrations of HNO_2 , $\mu_{\text{HNO}_2} > 2 \text{ ppmv}$, gave possibly rise to R-2 or other reactions. It is suggested to assume a mass-transport controlled process and subsequent bulk phase reaction R1. Such a process was observed on acid and water surfaces when low NO_2 concentrations were applied (mentioned above under 'dry' surfaces; Kleffmann et al., 1998). A study on NO_x chemistry in urban fogs supports a low accommodation coefficient, such as $1 * 10^{-6}$ (Lammel and Metzger, 1998).

Seasalt particle surfaces: R6, which occurs only under dry conditions, can be neglected for atmospheric situations. HNO_2 formation on seasalt particles is considered to obey the same kinetics as described for the other surfaces. This is in accordance with the findings on NO_x reactivity observed on denuder walls coated with NaCl (Febo and Perrino, 1991).

Soot particle surfaces: The reactivity of fresh soot surfaces is not relevant for the atmospheric situation else than, eventually, very close to the sources such as smoke stacks and vehicle pipes, but the reactivity of aged surfaces (hours to days) is. Furthermore, fast declining reactivities due to saturation effects are neither relevant for the atmospheric situation.¹ Only an upper limit for the uptake coefficient as low as $\gamma_{\text{NO}_2} < 2 * 10^{-8}$ could be derived from a 5-day experiment under dry conditions in a large aerosol chamber ($\text{rh} = 0$; Kamm et al., 1998; Table 1). We expect this reactivity to be higher under $\text{rh} \gg 0$ and thus recommend $\gamma_{\text{NO}_2} = 10^{-7}$ for carbonaceous surfaces.

The stoichiometry on carbonaceous surfaces deviates considerably from that of reaction R1. $a = 0.9$ is chosen for this surface type in agreement with studies on fresh soots (Kalberer et al., 1996). There is considerable uncertainty related to this choice, because $a > 0.5$ implies either the presence of a consumable reductant (e.g. reduced activity of aged compared to fresh soot surfaces) or of a renewable surface reactivity (e.g. through action of a catalyst). With the choice of $a = 0.9$, we try to account to a moderate extent for the possible effect of heavy metal

¹ Very high reactivities, $\gamma = 0.3 * 10^{-4}$ up to ca. $\gamma = 0.1$, have been determined during the initial uptake on various types of soots and other model carbonaceous materials (aerosol and bulk; Tabor et al., 1994; Kalberer et al., 1996 and 1997; Rogaski et al., 1996). These do not persist, however. Obviously, these surfaces when saturated with ca. one monolayer of NO_2 lost their particular reactivity within minutes.

impurities carried by at least some of the particulate materials rich in carbon which occur in the atmosphere (fly ash, besides others; see above).

3.2.3 Dark nitrous acid chemical sinks

The dark sink reaction according to R-2 stoichiometry was observed on pyrex glass and polyethylene to obey second order kinetics ($k_{R-2}^{(2)} = 1.5 * 10^{-19} \text{ molec cm}^{-3} \text{ s}^{-1}$ when applying 1 - 10 ppmv NO_2 ; ten Brink and Spoelstra, 1998). The reaction is obviously heterogeneous in nature, the S/V value of these experiments is not known, however. As S/V was certainly considerably higher than under atmospheric conditions, the rate is judged much too slow to be significant, though. There is experimental evidence for the case of NO_2 reacting with water chemisorbed to a quartz surface or on the surface of bulk sulfuric acid that reaction R2/R-2 becomes only significant for $\mu_{\text{NO}_2} > 20$ ppmv while R1 is the only relevant reaction for $\mu_{\text{NO}_2} < 20$ ppmv (Kleffmann et al., 1998). No unambiguous ascertainment are available from field measurements, although indications which suggest nitrous acid removal were reported (for two nights at an urban site; Lammel and Cape, 1996).

The homogeneous reaction R-2 is known to be insignificant ($k_{R-2 \text{ hom}} < 5.2 * 10^{-20} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$; Wahner and Mentel, 1995).

Dark reverse reactions are therefore not recommended for consideration in atmospheric modelling.

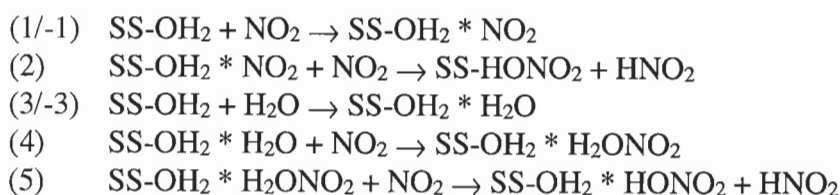
3.2.4 Heterogeneous source term: Synopsis

Resuming the above, we suggest to describe nitrous acid formation according to the rate law

$$d_{\text{CHNO}_2} / dt = a * c_{\text{NO}_2} * \{ [(S_{\text{dry}}/V) + (S_{\text{aqueous}}/V)] k^{\text{het}(1)} + (S_{\text{wet}}/V) k^{\text{het}(2)} c_{\text{H}_2\text{O}} \}$$

with $a = 0.9$ for soot particle surfaces and $a = 0.5$ for all other surfaces, S_{dry} and S_{wet} being the sum of the ground and aerosol surfaces carrying chemisorbed and multilayer, more mobile adsorbed water molecules, respectively, and $k^{\text{het}(1)}$ and $k^{\text{het}(2)}$ are mass-transfer limited, pseudo-first order (zeroth order in $c_{\text{H}_2\text{O}}$) and second order (first order in $c_{\text{H}_2\text{O}}$) rate coefficients, respectively.

A reaction mechanism for R1 can be proposed which starts from a water molecule chemisorbed to an active surface site, SS-OH₂:



This mechanism is in agreement with experimental findings. Chemisorbed water will either adsorb another water molecule reversibly (3) or a NO_2 molecule (1). (1) would presumably only occur below a threshold humidity. The sequence of the steps (3)+(4) would obey first order kinetics in $c_{\text{H}_2\text{O}}$. Such a mechanism would be in agreement with isotopic studies of the reaction on laboratory vessel surfaces (Sakamaki et al., 1983; Svensson et al., 1987). These showed, that below a humidity threshold, two reaction paths compete (hence, either (2) or (3)+(4)+(5)), while

above this threshold, there is only evidence for one reaction path, (3)+(4)+(5).

3.3 Parameterisation: Ranges of predicted source strength

Ranges of formation rates for HNO_2 (ppbv h^{-1}) as predicted by the parameterisation are given in Table 5 for typical situations of mixing height, humidity and aerosol and ground surface types. Formation rates $d_{\text{CHNO}_2}/c_{\text{NO}_2}/dt \leq 0.3 \% \text{ h}^{-1}$ are reached at $h_{\text{mix}} = 500 \text{ m}$ and $d_{\text{CHNO}_2}/c_{\text{NO}_2}/dt > 1 \% \text{ h}^{-1}$ in small mixing volumes with highest values at high humidity. Vegetation covered surfaces are expected to be less reactive, a factor of 2 in small mixing volumes. The large impact of the mixing height on the predicted rate stresses the importance of the ground surfaces. For moderate aerosol concentrations ($c_{\text{aer}} < 10 \mu\text{g m}^{-3}$), mixing heights below $h_{\text{mix}} < 1000 \text{ m}$ and $\text{rh} < 80 \%$, the ground surfaces are expected to dominate the source term by contributing 80 % and more.

The aerosol surface represented in the scheme consists of two particle sizes, corresponding to the large and giant particles. Although the Aitken mode can provide a significant fraction of the total aerosol surface, it is neglected as its presence is mostly coupled to photoinduced particle formation - not relevant for the nighttime. Mean radii and mass concentration and distribution over the modes were chosen as considered typical for urban and rural aerosols (following Jaenicke, 1988; cf. Footnotes 1 and 3 of Table 5 for values). A particulate matter density of 1.85 g cm^{-3} for large and 2.0 g cm^{-3} for giant particles was assumed. The composition of the particulate matter was chosen in such a way that it can be taken as representative for urban aerosols (cf. Footnote 1 of Table 5; following Warneck, 1988; Heintzenberg, 1989). Numerous test runs showed that the choice of the size distribution is in most relevant cases not significant for the predicted formation rate.

The influence of the uncertainty of ground surface areas on the formation rate - mediated through the attribution of surface-to-area indices and to water film growth - is considerable, while the aerosol surface is less critical. It becomes obvious from Table 5 that the uncertainty of predicted formation rates - at least at 50 and 80 % humidity - is usually within $\pm 50 \%$. The overall effect of the surface area and wettability uncertainties on the formation rate should be estimated to be as large as a factor of two.

4. Comparison of predicted and observed formation rates and discussion

Field measurements of nitrous acid were at single sites, while simultaneous or Lagrangian experiments at more than one site, which would allow to separate transport and chemical processes have not been reported so far. Only few field observations of nitrous acid with additional information on height of the mixing layer and on the particulate matter have been performed, at Mainz, Germany, 1986/87 (Lammel, 1988) and Milano, Italy, 1994 (Febo et al., 1996; Febo and Perrino, personal communication, 1996) and these are used in the following to test the parameterisation.

The concentration increase of nitrous acid after sunset, when observed at a single site, directly reflects the source strength of the formation process under study. Eventual dark decay processes are insignificant as long as HNO_2 levels are still low.

4.1 Procedure to derive the observed formation rate

The identification of the HNO_2 formation rate based on measurements at a single site is by far not trivial (Lammel, 1996). Every conclusion on a chemical transformation of trace substances which combines information gathered at different times, t' and t_0 , at the same site has to rely to some extent on the assumption of horizontal homogeneity of the advected air. In the evening, there is considerable variation of primary and secondary pollutants even under low winds on the time scale of one hour and less. This is the result of the combined effects of source strength variation (declining emission activity from traffic, for instance) and movement of the height of the mixing layer (cf. Febo et al., 1996, besides others). The observed nitrous acid evening formation rate was derived in the following manner:

The formation rate (ppbv h^{-1}) was calculated applying a correction for the variation of the precursor mixing ratio, μ_{NO_2} , according to:

$$\frac{d \mu_{\text{HNO}_2}}{dt} = \frac{(\mu_{\text{HNO}_2})_{t'} * \frac{(\mu_{\text{NO}_2})_{t_0}}{(\mu_{\text{NO}_2})_{t'}} - (\mu_{\text{HNO}_2})_{t_0}}{t' - t_0}$$

with t_0 being before sunset and t after sunset. This is to prevent a source of systematic error to the application of the assumption on horizontal homogeneity of the air for near-source sites: Advection tends to reduce the apparent formation rate as observable at one site, if emission strength upwind was less than close to the site. The concentration of the other precursor, CH_2O , can be considered unvariable during time intervals of hours. The trace gas measurement uncertainties (± 0.1 ppbv for HNO_2 and ± 1 ppbv for NO_2 in most cases) introduce some error to this values. For better comparison we refer to the relative formation rate ($\% \text{ h}^{-1}$):

$$\frac{d \mu_{\text{HNO}_2}}{\mu_{\text{NO}_2} * dt} = 100 * \frac{(\mu_{\text{HNO}_2})_{t'} * \frac{(\mu_{\text{NO}_2})_{t_0}}{(\mu_{\text{NO}_2})_{t'}} - (\mu_{\text{HNO}_2})_{t_0}}{(\mu_{\text{NO}_2})_{t_0} * (t' - t_0)}$$

Ideally t should be chosen such that $(t' - t_0)$ is short such that the error related to discrepancies from perfect horizontal homogeneity of the advected air is small and a simultaneous information of the height of the mixing layer is available. The mixing volume is in fact crucial for comparisons between observed and predicted values: The predicted value is strongly dependent (almost inversely proportional) on the mixing height. In the evening hours, the mixing height is highly variable and it is therefore substantial for the comparison to refer to the just mixing height.

The time variation of primary and secondary pollutants at the site provides insight whether or not a derived formation rate can be related to the height of the mixing layer if no simultaneous, but a later information of this parameter is available at time t_h . With respect to the time variation of the product-to-educt ratio, HNO_2/NO_2 , after sunset four cases can be identified (cf. Fig. 2). The time variation of Case 1 is obviously dominated by transport rather than chemistry. The same holds for Case 2 which results from insignificant transformation. An upper limit for the formation rate can nevertheless be derived from such a behaviour and will be dependent on the

choice of t' . $t' = t_h$ is chosen for those nights where the time variation of primary pollutants is dominated by continuous advection from sources upwind or by continuous dispersion (Case b). This situation is similar to the archetypal 'receptor site situation' with a well defined reaction time since pollutant emission, while Case a reflects more the archetypal situation of a smogchamber during filling (undefined reaction time; Lammel, 1996). In Case 3 and Case 4 the chemical conversion of NO_2 into HNO_2 strongly influences the time variation of these trace substances. Unlike in Case 4, in Case 3 the choice $t' = t_h$ would obviously cause an underestimate of the true formation rate. Its apparent decline may result from a reverse reaction (R-2, for instance) or - more likely - is transport controlled. Only in 'receptor site situations' the derived formation rates can be based on $t' < t_h$ (Case 3b).

This procedure implies the assumption that the precursors for HNO_2 were emitted before sunset. If NO_x emissions in the dark upwind had influenced the trace gas composition, the derived formation rate would reflect a lower bound for the true rate.

The so derived rates and their uncertainties are listed in Table 6 together with other relevant parameters and the predicted values and shown in Fig. 3. The observed relative evening formation rates are $0.47 \pm 0.38 \text{ \% h}^{-1}$ and $0.48 \pm 0.68 \text{ \% h}^{-1}$ for the Mainz and Milano data sets, respectively (mean \pm standard deviation).

4.2 Observational characteristics and scheme initialization

As the calculations of the predicted nitrous acid formation rate values were initialized with observed values determined with a significant amount of uncertainty (trace gas concentrations, aerosol concentration and size distribution, humidity, mixing height), upper and lower estimates are derived which are based on respective combinations of upper and lower boundaries of these parameters. Mean values of temperature and humidity between t_0 and t were taken. The aerosol surface represented in the scheme is given by the observed TSP concentration and the assumed size distribution for urban aerosols (described in Section 3.3). Upper and lower boundaries of the aerosol surface are based on mass distributions of 15 and 85 % and 8 and 92 % (instead of 11.3 and 88.7 %).

Mainz: Based on 28 min averages of the trace gas measurements (differential optical absorption, DOAS: space integrating optical absorption measurement at the outskirts of the city, 3.4 km light path running 3 - 42 m, by average 26 m above ground). Radio-soundings are available from 40 km off the site (DWD, Offenbach) at 07:00 h, and from some 70 km off the site (Idar-Oberstein) at ca. 02:00, 08:00 and 15:00 h. The mixing height observation at 02:00 h was used and the observed rate was based on observations before sunset (t_0 between 17:00 and 19:00 h) and after midnight (t' between 00:00 and 02:00 h; $t' - t_0 = 5 - 8$ h). An uncertainty of $\pm 10 \text{ \%}$ of the mixing height was then assumed. In some cases, only upper limits of the mixing height could be inferred from the temperature profiles (namely when higher temperatures were measured aloft than at the ground). In these cases 50 % of the 07:00 h value or 25 m was taken as a lower estimate and 110% of the height of the first measurement aloft as the upper estimate for the mixing height. HNO_2 mixing ratios before sunset were < 1 ppbv, mostly < 0.3 ppbv in Mainz. Out of 20 nights with sufficient trace gas and mixing height measurements, 2 were rejected from the analysis (Case 3a). SO_2 (measured by DOAS) was taken as the primary pollutant to discriminate between Cases a and b. As NO_x emissions in the dark upwind could well have significantly influenced the trace gas composition, the upper value for the observed formation

rate was multiplied by 1.5 for those nights with $t' - t_0 > 4$ h (17 out of the remaining 20 nights). This factor is reasonable regarding on the results which arise from deriving the formation rate based on different time periods each starting at sunset. Humidity was during some nights not continuously measured, but only morning values (07:00 h) are available. In these cases the morning values are taken as upper limits, and a reasonable estimate is made for the lower limit. Particulate matter mass concentration was $c_{\text{aer}} = 76 \pm 36 \mu\text{g m}^{-3}$ (total suspended particulates, TSP, mean of 3 - 4 day averages \pm standard deviation). This parameter is subject to variability on a shorter time scale, however. Based on the variation in the Milano TSP dataset, 70 and 130 % of these values were taken as lower and upper estimates, respectively.

Milano: Trace gas measurements are 6 min averages in the city (DOAS, 0.4 km light path). Average mixing heights for the time period 20:00 - 22:00 h or 22:00 - 24:00 h were obtained by the application of a simple box model to two-hourly R_n measurements (Febo, personal communication, 1996). The mixing height observation at 21:00 h was used and the observed rate was based on observations around sunset (t_0 between 18:00 and 19:00 h; t' between 20:00 and 21:30 h; $t' - t_0 = 2 - 3$ h). In Milano, HNO_2 mixing ratios before sunset were 2 - 3 ppbv. Particulate matter mass concentration was higher at Milano, $c_{\text{aer}} = 222 \pm 160 \mu\text{g m}^{-3}$ (TSP, 4 h mean, 18:00 - 22:00). Out of 11 nights with sufficient trace gas and mixing height measurements, 2 were rejected from the analysis (Case 2a). CO (infrared analyser) and NO (chemiluminescence analyser) were taken as the primary pollutants to discriminate between Cases a and b. The humidity at sunset was extrapolated from humidity and temperature measurements at midnight assuming constant water vapour concentration. 90 and 110 % of these values were taken as lower and upper estimates, respectively.

4.3 Discussion

Despite large error bars, agreement between observed and predicted nitrous acid formation rates is established (Fig. 3). Significant disagreements are found for 7 out of 20 evenings with significant nitrous acid formation (5 overestimates, 2 underestimates). The mean agreements are 138 % and 132 %, and the correlations between predicted and observed are $r = 0.23$ and $r = 0.56$ for the Mainz and Milano data sets, respectively. This agreement is totally satisfying regarding that NO_x emissions in the dark upwind might have influenced the trace gas composition, which causes underestimations of the observed rates (Section 4.1) and might part of the discrepancy.

Humidity dependency: The scatter is not related to humidity (Fig. 4). Significant positive discrepancies (predicted - observed > 0), however, are related to situations of high humidities (Mainz, 12.03.87, Milano, 10.03.94). This result, nevertheless, implies a significantly improved predictability for low humidities. Hence, the representation of water vapour in the kinetic law used in the parameterisation is suitable and the second-order rate coefficient applied was not chosen too high. Tests show that the assumption of a first-order dependency on water vapour concentration independent of water availability on the surface leads to considerable underestimates at low humidity.

Aerosol vs. ground surfaces: Significant overestimates (Mainz, 12.03.87, Milano, 10.03.94) do correspond with particularly high particulate matter concentrations. This suggests that aerosol surface reactivity is not underestimated in comparison to ground surface reactivity. On the other hand, despite some good agreements at both high and low h_{mix} , there is a tendency in the results of underestimation of HNO_2 formation at high h_{mix} and overestimation at low h_{mix} (Table 6).

Aerosol surfaces gain importance with increasing h_{mix} . This, in contrary to the above, suggests a too modest role allocated to the aerosol surfaces. Two sources of uncertainty are in particular important in this context: The ground surface area at different sites does vary in a wide range but was estimated based on insufficient site-specific knowledge and similar for the two sites (Table A2). The uncertain and potentially particularly high reactivity of the surfaces of carbonaceous particles was only moderately represented in the scheme: Carbonaceous particles in the atmosphere are no pure substances, but are partially oxygenated and mostly internally mixed with soluble material (when aged) and do contain heavy metal ions (as a result of the combustion process; cf. Gieray et al., 1993; Murphy and Thomson, 1997; besides others). Some metal ions were found to catalyse HNO_2 formation from NO_2 (ten Brink et al., 1978) and it is likely that metal impurities are of high influence on the catalytic properties of soots - rather than the partially oxygenated carbonaceous material itself. This was shown for the catalytic oxidation of SO_2 (Chughtai et al., 1993) and an extraordinarily strong NO_2 conversion was observed on particulate matter emitted by industrial and household burners (de Santis and Allegrini, 1992; cf. Table 3). As a sensitivity study, the possible effect of this high rate was investigated. The result is that this rate has a significant impact on nitrous acid formation in the urban environment. The effect is so large that it can compensate for an assumed reduced reactivity of all other surfaces: If one choses a medium value of the rate constants determined on aged surfaces of different materials (Table 3) which do agree pretty well, namely $k_{\text{R1}}^{\text{het}} = 3 * 10^{-22} \text{ cm}^4 \text{ molec}^{-1} \text{ s}^{-1}$ instead of $1.36 * 10^{-20} \text{ cm}^4 \text{ molec}^{-1} \text{ s}^{-1}$ and applies this second-order rate for all humidities one would be able to meet almost the observations (predicted/observed = $(80 \pm 82) \%$ for Mainz, and $(82 \pm 120) \%$ for Milano).

No final ascertainment is possible on whether ground vs. aerosol surfaces or vice versa have been allocated a too modest role in the parameterisation.

5. Conclusions

The conversion of NO_x into HNO_2 in the cloud-free troposphere occurs through NO_2 reactivity on ground and aerosol surfaces. NO_2 reactivity is influenced by humidity and water availability on the surface. The stoichiometry on most surfaces is according to R1. A parameterisation of nitrous acid formation assuming first order behaviour of HNO_2 formation in NO_2 concentration and either pseudo-zeroth order (for low water availability at the surfaces) or first order in water vapour concentration (for high availability) leads to fully satisfying agreement when applied to the evening nitrous acid formation as observed at two European urban sites under low, medium and high humidities. The parameterisation could not be validated sufficiently, however, because of the uncertainties (expressed by large error bars for observed and predicted values) and due to the small data sets.

There are still considerable sources of uncertainty in our understanding of this important chemistry: Most relevant surfaces are covered by 1 - 10 monolayers of water at $\text{rh} \ll 100 \%$. Because there are still insufficient data available to describe the kinetics on important surface types, any parameterisation still has to rely on the assumption that many surfaces behave like a humid vessel wall. Hence, the predicted values are still estimated to be uncertain by a factor of ca. 3: The overall effect of the uncertainties coming with the assumptions made with respect to surface area and wettability on the formation rate is estimated to be up to a factor of two. The uncertainties related to chemical kinetics, i.e. as related to the choice of chemical regimes and rate coefficients might be even higher than that.

Research needs: It is mostly the mix and state of internal (aerosol) and external (ground) surfaces which an air parcel contains or passes by during transport which steers the reactivity. An adequate field experiment to test our knowledge on nitrous acid formation has to control ground surface distribution and mixing height along the trajectory and particulate matter composition and size distribution besides the gaseous reactants.

Still, for only part of the atmospheric relevant surface types chemical kinetics data do exist, however: Vegetation surfaces, aged (in terms of hours to days) carbonaceous particles, particles containing heavy metals and urban surfaces (building materials) are prime candidates for studying temperature and humidity dependent NO_x reactivity. On this state of knowledge it is still not possible to decide on whether ground or aerosol surfaces are the more relevant.

From field measurements more parameters are necessary to be measured in order to allow for the validation of models comprising heterogeneous chemistry: The ground surface type distribution should be known (along the trajectory of the air mass) including the specific surface distribution (SAI). The characterization of the aerosol composition (mass fractions of soluble, insoluble and carbonaceous materials, size resolved for fine vs. coarse particles) and size distribution (at least 2 size fractions) are very important.

Another lack of knowledge identified in this research project are standard surface-to-area indices of relevant surfaces (vegetated and urban area), which would be helpful in many, mostly small scale model applications.

Application of the parameterisation: For use in higher dimensional models the scheme is available in an explicit or in a condensed form. The latter, besides meteorological and trace gas parameters, only requires information on TSP and is recommended for simulations with no particular information on ground surface type distribution and particulate matter composition and size distribution.

Acknowledgement:

I am indebted to Antonio Febo and colleagues, CNR-IIA, Montelibretti/Rome, and the German Weather Service, DWD, for datasets relevant for the Milano and Mainz case studies and to Marion Grunert for help with the drawings. This work was supported by the Commission of the European Union, contract No. ENV4-CT95-0055 (Formation and Occurrence of Nitrous Acid in the Atmosphere).

References

- Akimoto H., Takagi H., Sakamaki F.:
Photoenhancement of the nitrous acid formation in the surface reaction of nitrogen dioxide and water vapor: Extra radical source in smog chamber experiments,
Intl. J. Chem. Kin. **19** (1987) 529 - 551
- Bambauer A., Brantner B., Paige M., Novakov T.:
Laboratory study of NO₂ reaction with dispersed and bulk liquid water,
Atmospheric Environment **28** (1994) 3225 - 3232
- Baumgärtner M., Bock E., Conrad R.:
Processes involved in uptake and release of nitrogen dioxide from soil and building stones into the atmosphere, *Chemosphere* **24** (1992) 1943 - 1960
- Behlen A.:
Reaktive Stickstoffverbindungen in der Atmosphäre - Konzentrationsbestimmung und trockene Deposition auf Natursteine,
Ph.D. Thesis, University of Hamburg, Schriftenreihe Angewandte Analytik Vol. 29, Germany, 1996, 207 pp.
- Behnke W., Krüger H.-U., Scheer V., Zetzsch C.:
Formation of ClNO₂ and NOCl in the presence of NO₂, O₃ and wet NaCl aerosol, in:
Proceedings of the EUROTRAC Symposium 1992 (P.M.Borrell, P.Borrell, T.Cvitas, W.Seiler, eds.), Garmisch-Partenkirchen, 23.-27.3.1992,
SPB Academic Publishing, Den Haag, 1992, pp. 565 - 570
- Benner W.H., Ogorevc B., Novakov T.:
Oxidation of SO₂ in thin water films containing NH₃,
Atmospheric Environment **26** (1992) 1713 - 1723
- Britton L.G., Clarke A.G.:
Reactions of SO₂ and SO₂/NO₂ mixtures with a carbon soot aerosol,
Atmospheric Environment **14** (1980) 829 - 839
- Burkhardt J., Eiden R.:
Thin water films on coniferous needles,
Atmospheric Environment **28** (1994) 2001 - 2017
- Caloz F., Fenter F.F., Tabor K.D., Rossi M.J.:
Design and construction of Knudson cell reactor for the study of heterogeneous chemical reactions over the temperature range 130 - 750 K:
Performances and limitations, *Rev. Sci. Instrum.* **68** (1997) 3172 - 3179
- Calvert J.G., Yarwood G., Dunker A.M.:
An evaluation of the mechanism of nitrous acid formation in the urban atmosphere,
Res. Chem. Intermed. **20** (1994) 463 - 502
- Cape J.N.:
Surface wetness and pollutant deposition, in: *Plant cuticles* (G.Kerstiens, ed.),
BIOS Scientific Publ., Oxford, 1996, pp. 285 - 303
- Carman L.A., Pantano C.G.:
Water-vapor adsorption on calcium-boroaluminosilicate glass fibers,
J. Non-Cryst. Solids **120** (1990) 40 - 46
- Chughtai A.R., Brooks M.E., Smith D.M.:
Effect of metal oxides and black carbon (soot) on SO₂ / O₂ / H₂O reaction systems,
Aerosol Sci. Technol. **19** (1993) 121 - 132
- Chughtai A.R., Brooks M.E., Smith D.M.:
Hydration of black carbon, *J. Geophys. Res.* **101** (1996) 19505 - 19514
- Chughtai A.R., Williams G.R., Atteya M.M.O., Miller N.J., Smith D.M.:
Carbonaceous particle hydration, *Atmospheric Environment* **32** (1998) in the press
- Clifton C.L., Altstein N., Huie R.E.:
Rate constant for the reaction of NO₂ with sulfur(IV) over the pH range 5.3 - 13,
Envir. Sci. Technol. **22** (1988) 586 - 589

- Cofer W.R., Schryer D.R., Rogowski R.S.:
The oxidation of SO₂ on carbon particles in the presence of O₃, NO₂ and N₂O,
Atmospheric Environment **15** (1981) 1281 - 1286
- Davis S.M., Lunsford J.H.:
Surface reactions of SO₂ with NO₂ on hydrated silica and silica-alumina,
J. Colloid Interf. Sci. **65** (1978) 352 - 364
- de Santis F., Allegrini I.:
Heterogeneous reactions of SO₂ and NO₂ on carbonaceous surfaces,
Atmospheric Environment **26A** (1992) 3061 - 3064
- de Santis F., Febo A., Perrino C.:
Nitrite and nitrate formation on a sodium carbonate layer in the presence of nitrogen dioxide, *Ann. Chimica* (1987) 763 - 768
- Dubinin M.M.:
Water vapour adsorption and the microporous structures of carbonaceous adsorbents,
Carbon **18** (1980) 355 - 364
- Febo A.:
Nitrous acid in the oxidation processes in urban areas,
in: Physico-chemical behaviour of atmospheric pollutants (Angeletti G., Restelli G., eds.),
European Commission Report EUR 15609/1EN, Luxembourg, pp. 277 - 286
- Febo A., Perrino C.:
Prediction and experimental evidence for high air concentration of nitrous acid in indoor environments, *Atmospheric Environment* **25A** (1991) 1055 - 1061
- Febo A., Perrino C., Allegrini I.:
Measurement of nitrous acid in Milan, Italy, by DOAS and diffusion denuders,
Atmospheric Environment **30** (1996) 3599 - 3609
- Febo A., de Santis F., Perrino C., Liberti A.:
The study of the reaction between nitrogen oxides and water vapour by means of annular denuder tubes.
In: 'Tropospheric NO_x chemistry - gas phase and multiphase aspects' (Nielsen O.J., Cox R.A., eds.),
Commission of the European Communities, Report Nr. EUR 11440, pp. 61 - 67, 1988
- Fenter F.F., Caloz F., Tabor K.D., Gutzwiller L., Rossi M.J.:
Kinetics of heterogeneous reactions relevant to tropospheric chemistry.
In: *Tropospheric oxidation mechanisms* (K.H.Becker, ed.),
Commission of the European Communities Report Nr. EUR 16171EN, 1995, S. 39 - 44
- Finlayson-Pitts B.J.:
The reaction of NO₂ with NaCl and atmospheric implications of NOCl formation,
Nature **306** (1983) 676 - 677
- Fowler D., Duyzer J.H., Baldocchi D.D.:
Inputs of trace gases, particles and cloud droplets to terrestrial surfaces.
Proc. R. Soc. Edinburgh **97B** (1991) 35 - 59.
- Fuchs N.A., Sutugin A.G.:
High-dispersed aerosols, *Intl. Rev. Aerosol Phys. Chem.* **2**, (1971) 1 - 60.
- Gerecke A., Thielmann A., Gutzwiller L., Rossi M.J.:
The chemical kinetics of HONO formation resulting from heterogeneous interaction of NO₂ with flame soot, *Geophys. Res. Letters* (1998), in the press
- Gieray R., Lammel G., Metzger G., Wieser P.
Size dependent single particle and chemical bulk analysis of droplets and interstitial particles in an orographic cloud, *Atmos. Res.* **30** (1993) 263 - 293
- Goss K.-U.:
Effects of temperature and relative humidity on the sorption of organic vapors on quartz sand, *Environ. Sci. Technol.* **26** (1992) 2287 - 2294
- Gundel L.A., Guyot-Sionnest N.S., Novakov T.:
A study of the interaction of NO₂ with carbon particles,
Aerosol Sci. Technol. **10** (1989) 343 - 351

- Hagymassy J., Brunauer S., Mikhail S.:
Pore structure analysis by water vapor adsorption, I. t-curves for water vapor,
J. Colloid Interf. Sci. **29** (1969) 485 - 491
- Harris G.W., Carter W.P.L., Winer A.M., Pitts J.N., Platt U., Perner D.:
Observations of nitrous acid in Los Angeles atmosphere and implications for
predictions of ozone-precursor relationships,
Environ. Sci. Technol. **16**, (1982) 414 - 419
- Harrison R.M., Kitto A.-M.N.:
Evidence for a surface source of atmospheric nitrous acid,
Atmospheric Environment **28** (1994) 1089 - 1094
- Harrison R.M., Peak J.D., Collins G.M.:
Tropospheric cycle of nitrous acid, *J. Geophys. Res.* **101** (1996) 14429 - 14439
- Harrison R.M., Peak J.D., Collins G.M.:
Studies of nitrous acid (HONO) in the lower troposphere,
in: The oxidizing capacity of the troposphere (B.Larsen, B.Versino, G.Angeletti, eds.),
Report No. EUR17482EN, Brussels, 1997, pp. 182 - 186
- Hartkopf A., Karger B.L.:
Study of the interfacial properties of water by gas chromatography,
Acc. Chem. Res. **6** (1973) 209 - 216
- Heintzenberg, J.:
Fine particles in the global troposphere. A review, *Tellus* **41B** (1989) 149 - 160
- Jaenicke R.:
Aerosol physics and chemistry.
In: Landolt-Börnstein Neue Serie Vol. 4b (Fischer G., ed.),
Springer, Berlin, 1988, pp. 391 - 456
- Jang M., Kamens R.M.:
A thermodynamic approach for modelling partitioning of semivolatile organic com-
pounds of atmospheric particulate matter: Humidity effects,
Environ. Sci. Technol. **32** (1998) 1237 - 1243
- Jenkin M.E., Cox R.A., Williams D.J.:
Laboratory studies of the kinetics of formation of nitrous acid from the thermal reaction
of nitrogen dioxide and water vapor,
Atmospheric Environment **22** (1988) 487 - 498
- Johansson L.-G., Lindqvist O., Mangio R.E.:
Corrosion of calcareous stones in humid air containing SO₂ and NO₂,
Durab. Building Mater. **5** (1988) 439 - 449
- Judeikis H.S., Wren A.G.:
Laboratory measurements of NO and NO₂ depositions onto soil and cement surfaces,
Atmospheric Environment **12** (1978) 2315 - 2319
- Judeikis H.S., Siegel S., Stewart T.B., Hedgpeth H.R., Wren A.G.,
in: *Nitrogenous air pollutants. Chemical and biological implications* (D.Grosjean, ed.),
Ann Arbor Science, Ann Arbor, 1979, pp. 83 - 109
- Junkermann W., Ibusuki T.:
FTIR spectroscopic measurements of surface bond products of nitrogen oxides on
aerosol surfaces - implications for heterogeneous nitrous acid production,
Atmospheric Environment **26A** (1992) 3099 - 3103
- Kalberer M., Tabor K., Ammann M., Parrat Y., Weingartner E., Piguet D., Rössler E., Jost D.T.,
Türler A., Gäggeler H.W., Baltensperger U.:
Heterogeneous chemical processing of ¹³NO₂ by monodisperse carbon aerosols at very
low concentrations, *J. Phys. Chem.* **100** (1996) 15487 - 15493
- Kamm S., Möhler O., Naumann K.H., Saathoff H., Schurath U.:
Heterogeneous interaction of ozone, NO_x and N₂O₅ with soot aerosol,
Proc. EUROTRAC-2 Symposium, Garmisch-Partenkirchen, Germany, 23. - 27.3.1998

- Karathanasis A.D., Hajek B.F.:
Quantitative evaluation of water adsorption on soil clays,
Soil. Sci. Soc. Am. J. **46** (1982) 1321 - 1325
- Karlsson R., Ljungström E.:
Nitrogen dioxide and seasalt particles. A laboratory study.
J. Aerosol Sci. **26** (1995) 39 - 50
- Kirkitsos P., Sikiotis D.:
Deterioration of pentelic marble, Portland limestone and Baumberger sandstone in laboratory exposures to NO₂: A comparison with exposures to gaseous HNO₃,
Atmospheric Environment **30** (1996) 941 - 950
- Kleffmann J., Becker K.H., Wiesen P.:
Heterogeneous NO₂ conversion processes on acid surfaces: Possible atmospheric implications, *Atmospheric Environment* **32** (1998) 2721 - 2730
- Klemm O., Burkhardt J., Gerchau J.:
Leaf wetness - now a quantifiable parameter in deposition studies,
Proc. EUROTRAC Symposium, Garmisch-Partenkirchen 23.-27.3.1998
- Kozłowski R., Hejda A., Ceckiewicz S., Haber J.:
Influence of water contained in porous limestone on corrosion,
Atmospheric Environment **26A** (1992) 3241 - 3248
- Krus M.:
Feuchtetransport- und Speicherkoeffizienten poröser mineralischer Baustoffe.
Theoretische Grundlagen und neue Meßtechniken,
Ph.D. Thesis, University of Stuttgart, Germany, 1995, 106 pp.
- Laidler K.J.:
Chemical kinetics, McGraw-Hill, New York 1950
- Lammel G.:
Salpetrige Säure und Nitrit im Mehrphasensystem der belasteten Atmosphäre,
Ph.D. Thesis, University of Mainz, Germany, 1988, 222 pp.
- Lammel G.:
Comment on 'A DOAS study on the origin of nitrous acid at urban and non-urban sites', *Atmospheric Environment* **30** (1996) 4101 - 4103
- Lammel G., Cape J.N.:
Nitrous acid and nitrite in the atmosphere, *Chem. Soc. Rev.* **25** (1996) 361 - 369
- Lammel G., Metzger G.:
On the occurrence of nitrite in urban fogwater, *Chemosphere* **37** (1998) 1603 - 1614
- Lammel G., Perner D.:
The atmospheric aerosol as a source for nitrous acid in the polluted atmosphere,
J. Aerosol Sci. **19** (1988) 1199 - 1202
- Larcher W.:
Ökologie der Pflanzen, Ulmer, Stuttgart 1976
- Lee J.H., Tang I.N.:
Accommodation coefficient of gaseous NO₂ on water surfaces,
Atmospheric Environment **22** (1988) 1147 - 1151
- Lee Y.-N., Schwartz S.E.:
Reaction kinetics of nitrogen dioxide with liquid water at low partial pressure,
J. Phys. Chem. **85** (1981) 840 - 848
- Mamane Y., Gottlieb J.:
Heterogeneous reaction of nitrogen oxides on seasalt and mineral particles - a single particle approach, *J. Aerosol. Sci.* **21** (1990) S
- Mertes S., Wahner A.:
Uptake of nitrogen dioxide and nitrous acid on aqueous surfaces,
J. Phys. Chem. **99** (1995) 14000 - 14006
- Msibi I.M., Li Y., Shi J.P., Harrison R.M.:
Accommodation coefficient for trace gas uptake using deposition profile measurement in an annular reactor, *J. Atmos. Chem.* **17** (1993) 339 - 351

- Murphy D.M., Thomson D.S.:
Chemical composition of single aerosol particles at Idaho Hill: Positive ion measurements, *J. Geophys. Res.* **102** (1997) 6341 - 6352
- Neftel A., Blatter A., Hesterberg R., Staffelbach T.:
Measurements of concentration gradients of HNO₂ and HNO₃ over a semi-natural ecosystem, *Atmospheric Environment* **30** (1996) 3017 - 3025
- Niskanen R., Mäntylähti V.:
Determination of soil specific area by water vapor adsorption. III. Comparison of surface areas determined by water vapor and nitrogen gas adsorption, *J. Agricult. Sci Finland* **60** (1988) 73 - 79
- Pitts J.N., Sanhueza E., Atkinson R., Carter W.P.L., Winer A.M., Harris G.W., Plum C.N.:
An investigation of the dark formation of nitrous acid in environmental chambers, *Intl. J. Chem. Kin.* **16** (1984) 919 - 939
- Pitts J.N., Wallington T.J., Biermann H.W., Winer A.M.:
Identification and measurement of nitrous acid in an indoor environment, *Atmospheric Environment* **19** (1985) 763 - 767
- Platt U., Perner D., Winer A.M., Harris G.W., Pitts J.N.:
Detection of NO₃ in the polluted troposphere by differential optical absorption, *Geophys. Res. Lett.* **7** (1980) 89 - 92
- Ponche J.L., George C., Mirabel P.:
Mass transfer at the air/water interface: Mass accommodation coefficients of SO₂, HNO₃, NO₂, and NH₃, *J. Atmos. Chem.* **16** (1993) 1 - 21
- Rogaski C.A., Golden D.M., Williams L.R.:
Reactive uptake and hydration experiments on amorphous carbon treated with NO₂, SO₂, O₃, HNO₃, and H₂SO₄, *Geophys. Res. Lett.*, in the press
- Sakamaki F., Hatakeyama S., Akimoto H.:
Formation of nitrous acid and nitric oxide in the heterogeneous dark reaction of nitrogen dioxide and water vapor in a smog chamber, *Intl. J. Chem. Kin.* **15** (1983) 1013 - 1029
- Schwartz S.E., White W.H.:
Solubility equilibria of the nitrogen oxides and oxyacids in dilute aqueous solution, *Adv. Environ. Sci. Eng.* **4** (1981) 1 - 45
- Sjödén A., Ferm M.:
Measurement of nitrous acid in an urban area, *Atmospheric Environment* **19**(1985) 985 - 992
- Slanina J., Wyers G.P., Kieskamp W.M., ten Brink H.M.:
Analytical chemistry in the troposphere. In: Physico-chemical behaviour of atmospheric pollutants (G.Angeletti, G.Restelli, eds.), Report EUR15609, pp. 639 - 651, 1994
- Svensson R., Ljungström E., Lindqvist O.:
Kinetics of the reaction between nitrogen dioxide and water vapour, *Atmospheric Environment* **21** (1987) 1529 - 1539
- Tabor K., Gutzwiller L., Rossi M.J.:
Heterogeneous chemical kinetics of NO₂ on amorphous carbon at ambient temperature, *J. Phys. Chem.* **98** (1994) 6172 - 6186
- Tang I.N., Munkelwitz H.R.:
Aerosol growth studies: III. Ammonium bisulfate aerosols in a moist atmosphere, *J. Aerosol Sci.* **8** (1977) 321 - 330
- Tang I.N., Munkelwitz H.R.:
Aerosol phase transformation and growth in the atmosphere, *J. Appl. Meteor.* **33** (1994) 791 - 796
- ten Brink H.M., Spoelstra H.:
The dark decay of HONO in environmental (smog) chambers, *Atmospheric Environment* **32** (1998) 247 - 251

- ten Brink H.M., Bontje J.A., Spoelstra H., van de Vate J.F.:
The interaction between NO_x, O₃ and airborne particles,
Studies Environmental Sci. **1** (1978) 239 - 244 (in: Atmospheric Pollution 1978,
M.M.Bénarie, ed.)
- van Aalst R.M.:
Dry deposition of NO_x. In: *Air pollution by nitrogen oxides* (T.Schneider, L.Grant, eds.),
Elsevier, Amsterdam 1982, pp. 263 - 270
- van Hove L.W.A., Adema E.H.:
The effective thickness of water films on leaves,
Atmospheric Environment **30** (1996) 2933 - 2936
- Wahner A., Becker D.:
Heterogeneous processes of NO₂ and HNO₂ on aqueous surfaces,
in: *Proc. EUROTRAC Symposium 1996* (P.M.Borrell, P.Borrell, W.Seiler, eds.),
SPB Academic Publ., Den Haag 1996
- Wahner A., Mentel T.:
Experimental investigation of the nighttime chemistry,
in: *AERONOX The impact of NO_x emissions from aircraft upon the atmosphere at flight
altitudes 8 - 15 km* (U.Schumann, eds.),
Rep. European Commission No. EUR16209EN, 1995, pp.252 - 264
- Warneck, P.:
Chemistry of the natural atmosphere, Academic Press, San Diego 1988
- Weber P., Rennenberg H.:
Dependency of nitrogen dioxide (NO₂) fluxes to wheat (*triticum aestivum* L.) leaves from
NO₂ concentration, light intensity, temperature and relative humidity determined
from controlled dynamic chamber experiments,
Atmospheric Environment **30** (1996) 3001 - 3009
- Wesely M.L.:
Parameterization of surface resistances to gaseous dry deposition in regional-scale
numerical models, *Atmospheric Environment* **23** (1989) 1293 - 1304
- Wiesen P., Kleffmann J., Kurtenbach R., Becker K.H.:
Mechanistic study of the heterogeneous conversion of NO₂ into HONO and N₂O on acid
surfaces. *Faraday Disc.* **100** (1995) 121 - 127
- Winkler P.:
The growth of atmospheric aerosol particles as a function of humidity - II. An improved
concept of mixed nuclei, *Aerosol Sci.* **4** (1973) 373 - 387
- Winkler P., Junge C.:
The growth of atmospheric aerosol particles as a function of humidity - I. Method and
measurements at different locations, *J. Rech. Atmos.* (1972) 617 - 638
- Winkler T., Goschnick J., Ache H.J.:
Reactions of nitrogen oxides with NaCl as model of seasalt aerosol,
J. Aerosol Sci. **22** (1991) S605 - S608

Appendix: Attribution of parameters to the ground and aerosol surface types
A1. Attribution of values of the accommodation coefficient

Table A1. Values of the accommodation coefficient, α , for various dry and aqueous surface types used to derive $k^{\text{het}(1)}$, pseudo-zeroth order in water vapour concentration (Section 3.2.1).

	dry * 10^{-6}	aqueous * 10^{-6}
Vegetation	0.7 ⁽¹⁾	-
Soils	0.7	1.0
Urban surfaces	0.7	1.0
Water	-	1.0
Aerosol (continental)	0.7	0.7
Seasalt	0.1	0.7
Sulfuric acid aerosol	-	0.4
Carbonaceous aerosol	0 ⁽²⁾	-

⁽¹⁾ For the wettable fraction of the dry vegetation surfaces. $\alpha = 0$ for the non-wettable fraction.

⁽²⁾ For the unwettable fraction of carbonaceous particles surfaces, assumed to account for 85 %.

A2. Attribution of wetness types and surface area indices as a function of humidity

For the scheme 4 types of ground surfaces (vegetation, (bare) soils, urban surfaces (building stones, asphalt) and water) and 4 types of aerosol surfaces (continental aerosol, seasalt, acidic aerosol, carbonaceous aerosol (black carbon)) are considered. The uptake of water, expressed as water layer thickness, is qualitatively shown in Fig. 1. Wetness types and specific surface area are attributed to these 8 surfaces as a function of ambient humidity (Table A1).

Table A2. Summary: Attribution of **a.** wetness types and **b.** surface area indices (SAI = total surface / cross section) to the various ground and aerosol types under various conditions of humidity (values in %) as considered in the scheme. Values considered in a sensitivity study in brackets (for lower estimate / for upper estimate). rh = relative humidity (%)

a.	'dry'	'wet'	'aqueous'
Vegetation	< 55 (80 / 55)	$\leq 100^{(1)}$ ($100^{(1)} / 95^{(2)}$)-	
Soils	< 65 (80 / 50)	< 95	$\leq 100^{(3)}$
Urban surfaces	< 50 (80 / 50)	< 95	≤ 100
Water	-	-	≤ 100
Aerosol (continental)	< 30 (40 / 35)	< 80 (95 / 75)	≤ 100
Seasalt	< 77	-	≤ 100
Sulfuric acid aerosol	-	-	≤ 100
Carbonaceous aerosol	$\leq 100^{(4)}$ ($100^{(4)} / 100^{(5)}$)-	-	-
b.	'dry'	'wet'	'aqueous'
Vegetation	8 (5 / 10) ⁽⁶⁾	8 (5 / 10) ⁽⁶⁾	8 (5 / 10) ⁽⁶⁾
Soils	5 (3 / 10)	5 (3 / 10)	1.5 (1.5 / 5)
Urban surfaces	10 ⁽⁷⁾ (5 / 12)	10 ⁽⁷⁾ (5 / 12)	3 (3 / 10)
Water	-	-	1 (1 / 1.1) ⁽⁸⁾
Aerosol (continental)	1	droplet growth function ⁽⁹⁾	droplet growth function ⁽⁹⁾
Seasalt	1	-	droplet growth function ⁽⁹⁾
Sulfuric acid aerosol	-	-	droplet growth function ⁽⁹⁾
Carbonaceous aerosol	1 (1 / 2 + 0.1*rh) ⁽¹⁰⁾	-	-

⁽¹⁾ slope for 55 % < rh < 90 %: $SAI_{dry\ vegetation} = SAI_{vegetation}$ for rh < 0.55; $SAI_{dry\ vegetation} = SAI_{vegetation} * [1 - (rh - 55) / 35]$ for 55 % \leq rh < 90 %; $SAI_{dry\ vegetation} = 0$ for rh \geq 90

⁽²⁾ slope for 80 % < rh < 100 %: $SAI_{dry\ vegetation} = SAI_{vegetation}$ for rh < 0.55; $SAI_{dry\ vegetation} = SAI_{vegetation} * [1 - (rh - 80) / 20]$ for 80 % \leq rh < 100 %

⁽³⁾ aqueous phase attributed to parts, namely 10 %, of the surface (pores)

⁽⁴⁾ 85 % of the surface of carbonaceous particles is assumed to be dry, while the remaining 15 % are assumed to be wet and show NO_x reactivity independent of humidity

⁽⁵⁾ same as ⁽⁴⁾ but 75 % dry and 25 % wet

⁽⁶⁾ The most frequent SAI value for boreal and temperate forests is 12 (range of 5 - 14) and for agricultural vegetation 4 (range of 4 - 12; Larcher, 1976).

⁽⁷⁾ Based on values for inner surfaces (i.e. regarding the pore structure) of buildings, streets, roads and courts (building surfaces SAI = 4 for rh < 95 % and SAI = 1.05 for rh > 95 %) and the distribution of buildings, streets, roads and courts areas in a Hamburg innercity district which is believed to be representative for German cities.

⁽⁸⁾ The dependency on wind velocity and depth of water body is complex. In most cases it causes only negligible deviations from SAI = 1.0. A quadratic fit to observations made in the open Atlantic leads to $SAI = 0.997 + 0.00732 u - 0.000164 u^2$, i.e. SAI = 1.08 at $u = 20 \text{ m s}^{-1}$ (u = horizontal wind velocity).

⁽⁹⁾ droplet growth function as given by Winkler, 1973

⁽¹⁰⁾ modest growth, linear with humidity ($SAI = 1 + 10 * rh$), assumed for an upper estimate

Table 1. Uptake coefficients, γ , of NO_2 on various surfaces. Coefficients for initial uptake have been neglected.

Surface	Condensed phase	γ	Reference
H_2O , pH 7	bulk	$8.7 * 10^{-5}$	Msibi et al., 1993
H_2O , 273 K	bulk	$6.3 * 10^{-4}$	Lee and Tang, 1988
H_2O , 278 K	bulk	$1.5 * 10^{-3}$ ⁽¹⁾	Ponche et al., 1993
H_2O , 278 K	bulk	$\geq 2 * 10^{-4}$ ⁽²⁾	Mertes and Wahner, 1995
H_2O , 298 K	bulk	$9 * 10^{-7}$	Kleffmann et al., 1998
NaOH , pH 9.3	bulk	$4.2 * 10^{-4}$	Msibi et al., 1993
Seasalt	aerosol	$3 * 10^{-4}$	Karlsson and Ljungström, 1995
NaCl (dry)	bulk	$\approx 10^{-7}$	Caloz et al., 1997
NaCl (humid)	aerosol	$< 10^{-4}$	Behnke et al., 1992
NaCl (50 % sol.), 279 K	bulk	$1.1 * 10^{-3}$	Harrison et al., 1997
NaCl (80 - 90 % sol.), 279 K	bulk	$(3 - 3.2) * 10^{-4}$	Harrison et al., 1997
$(\text{NH}_4)_2\text{SO}_4$ (50 % sol.)	bulk	$5.1 * 10^{-4}$	Harrison et al., 1997
$(\text{NH}_4)_2\text{SO}_4$ (85 % sol.)	bulk	$7.2 * 10^{-4}$	Harrison et al., 1997
H_2SO_4 , 30 - 96 %	bulk	$(3 - 6) * 10^{-7}$	Kleffmann et al., 1998
Quartz wall		$7 * 10^{-7}$	Kleffmann et al., 1998
Soot (dry)	aerosol	$< 2 * 10^{-8}$	Kamm et al., 1998

⁽¹⁾ value possibly in doubt (Mirabel, personal communication, 1996)

⁽²⁾ results difficult to interpret

Table 2. Deposition velocities, v_{dep} , of NO_2 determined over various materials as influenced by relative humidity, rh. $\mu_{\text{NO}_2} = \text{NO}_2$ mixing ratio.

Laboratory surface	v_{dep} (cm s^{-1})			μ_{NO_2} applied (ppmv)	Reference
	rh < 15 %	rh=40 - 50 %	rh \geq 95 %		
Sand	< 0.015	0.47		26	Judeikis et al., 1979
Sandstone	0.05	0.02	0.02	0.17	Behlen, 1996
Sandstone	\geq 0.21	\geq 0.11	\geq 0.08	58	Kirkitsos and Sikiotis, 1996
Marble		low	high	0.35 - 3	Johansson et al., 1988
Marble	\geq 0.20	\geq 0.10	\geq 0.10	58	Kirkitsos and Sikiotis, 1996
Limestone	\geq 0.41	\geq 0.41	\geq 0.41	58	Kirkitsos and Sikiotis, 1996
Cement	0.32		0.32	13 - 52	Judeikis and Wren, 1978
Sandy loam	0.60		0.60	13 - 52	Judeikis and Wren, 1978
Clay soil	0.77		0.77	13 - 52	Judeikis and Wren, 1978
Seasalt		low	high	0.05 - 0.5	Karlsson and Ljungström, 1995
$(\text{NH}_4)_2\text{SO}_4$	< 0.015	0.05		26	Judeikis et al., 1979
H_2SO_4	< 0.015	0.05		26	Judeikis et al., 1979

Table 3. Heterogeneous nitrous acid formation rate constants, k^{het} , based on laboratory experiments. $k_{\text{RI}}^{\text{het}} = (d_{\text{CHNO}_2}/dt) / (c_{\text{NO}_2} * c_{\text{H}_2\text{O}} * S/V)$ for smog chamber experiments, and $k_{\text{RI}}^{\text{het}} = (dq_{\text{HNO}_2}/dt) / (c_{\text{NO}_2} * c_{\text{H}_2\text{O}} * S)$ for flow reactor experiments, with amount of nitrous acid formed, $d_{\text{CHNO}_2} = V * d_{\text{CHNO}_2}$, both under humid conditions and according to the rate law $d_{\text{CHNO}_2}/dt = k_{\text{RI}}^{\text{het}} S/V c_{\text{NO}_2} c_{\text{H}_2\text{O}}$. For dry conditions see footnote 1. Applied μ_{NO_2} are in the ppmv range.

Surface	$k_{\text{RI}}^{\text{het}}$ (10^{-9} m ppmv $^{-1}$ min $^{-1}$)	T ($^{\circ}\text{C}$)	rh (%)	no. of water monolayers	Reference
Fluorinated polymers	$1.1 * 10^{-5}$ ^(1,2)	30	0	0 (absorbed)	Sakamaki et al., 1983
	$1.0 * 10^{-4}$ ⁽¹⁾	23	0	0 (absorbed)	Jenkin et al., 1988
	0.6 - 2.5 ⁽³⁾	22	4 - 76	0 (absorbed)	Svensson et al., 1987
	1.5 - 4.0 ⁽²⁾	30	10 - 65	0 (absorbed)	Sakamaki et al., 1983
	4.2 ⁽²⁾	30	20 - 24	0 (absorbed)	Akimoto et al., 1987
	0.60	24	50	0 (absorbed)	Pitts et al., 1984
	1.5 - 3.0 ⁽⁴⁾	24	50	0 (absorbed)	Pitts et al., 1984
	1.8 - 3.2 ⁽⁴⁾	32	50	0 (absorbed)	Pitts et al., 1984
	1.4 ⁽²⁾	30	63 - 65	0 (absorbed)	Akimoto et al., 1987
	5.0 ⁽³⁾	7	ca. 99	?	Svensson et al., 1987
Stainless steel	33	22	4	< 1	Svensson et al., 1987
Quartz	0.8 - 1.8	30	11	1 - 2	Sakamaki et al., 1983
	5.3 - 8.3 ⁽⁵⁾	24	50	2 - 5	Pitts et al., 1984
	$5.7 * 10^{-3}$ ^(1,3)	25	0	1 - 2	Wiesen et al., 1995
	$5.6 * 10^{-3}$ ⁽¹⁾	25	0	1 - 2	Kleffmann et al., 1998
Borosilicate glass	3.0 ⁽³⁾	22	4	ca. 1	Svensson et al., 1987
	37 ⁽⁶⁾	23	8 - 25	1 - 4	Jenkin et al., 1988
	7.4 - 30	25	64	2 - 10	Febo et al., 1988
	1.3 - 42	25 ⁽⁷⁾	64	2 - 10	Febo and Perrino, 1991
Na ₂ CO ₃	0.13 ⁽⁸⁾	25	50	? (< rhD)	de Santis et al., 1987
NaCl, NaF, Na ₂ C ₂ O ₄	5 - 50 ⁽⁹⁾	25 ⁽⁷⁾	64	? (< rhD)	Febo and Perrino, 1991
Combustor samples	600 - 1200	25	60, 90	?	de Santis and Allegrini, 1992
NaOH, 0.01 M	0.026 ⁽¹⁰⁾	5	100	∞ (water jet)	Mertes and Wahner, 1995
H ₂ O	0.019 ⁽¹¹⁾	5	100	∞ (water jet)	Mertes and Wahner, 1995
(rinsed glass)	210	22	4	large	Svensson et al., 1987

⁽¹⁾ according to the rate law $dc_{\text{HNO}_2}/dt = k_{\text{RI}}^{\text{het}} S/V c_{\text{NO}_2}$ (m min $^{-1}$) as no water vapour introduced.

⁽²⁾ Reaction cell surface with 9 % quartz and borosilicate glass parts.

⁽³⁾ Corrected for the contribution of stainless steel present (7 % of the total surface) using k^{het} (stainless steel) = 33 m ppmv $^{-1}$ min $^{-1}$ (Svensson et al., 1987).

⁽⁴⁾ Reaction cell surface with 18 % quartz glass parts.

-
- ⁽⁵⁾ Inferred from measurements in Teflon chambers with and without partial quartz surface. Lower limit: assuming that the discrepancy between $(-dc_{\text{HNO}_2}/dc_{\text{NO}_2})_{\text{observed}}$ and $-dc_{\text{HNO}_2}/dc_{\text{NO}_2} = 0.50$ was due to HNO_2 adsorption to the walls, upper limit: assuming no HNO_2 adsorbed.
- ⁽⁶⁾ Reaction cell surface with ca. 13 % stainless steel and gold covered parts.
- ⁽⁷⁾ assumed (no temperature reported)
- ⁽⁸⁾ Main reaction path of NO_2 was reduction to NO_2^- .
- ⁽⁹⁾ The authors observed order of magnitude agreement with rate on borosilicate glass surface.
- ⁽¹⁰⁾ $k^{\text{het}} = (dq_{\text{HNO}_2}/dt) / (c_{\text{NO}_2}^2 * S)$ assuming that the reaction of 2 molecules NO_2 adsorbed was rate limiting (according to Wahner and Becker, 1996). In case that adsorption of the NO_2 molecules was the rate limiting step, then $k^{\text{het}} = 0.86 \text{ m min}^{-1}$ would result.
- ⁽¹¹⁾ same as ⁽¹⁰⁾, with $k^{\text{het}} = 0.62 \text{ m min}^{-1}$ in the latter case

Table 4. Conditions and reaction orders of R1 with respect to $\text{CH}_2\text{O}(\text{g})$ as observed in kinetic studies under various conditions of NO_2 and water vapour pressures applied (see text) and for comparison the range of respective conditions during HNO_2 measurements at Mainz and Milano (cf. Table 7).

Wall material	T (°C)	μ_{NO_2} (ppmv)	$\mu_{\text{NO}_2^2} / \mu_{\text{H}_2\text{O}}$ (ppmv)	order of kinetics in $\text{CH}_2\text{O}(\text{g})$	Reference
Fluor. polymer ⁽¹⁾	19	4 - 40	ca. 0.002 - 0.55 ⁽²⁾	1	Jenkin et al., 1988
Fluor. polymer	24	0.35 - 0.75	(4.5 - 32) * 10^{-5}	1	Pitts et al., 1984
Fluor. polymer	32	0.34 - 0.60	< / > $1.5 * 10^{-5}$	0 / 1	Pitts et al., 1984
Fluor. polymer	30	0.78 - 19	< / > $4.3 * 10^{-4}$	0 / 1	Sakamaki et al., 1983
Quartz	25	0.002 - 0.2	< / > ca. 10^{-6}	0 ⁽²⁾ / > 0 ⁽³⁾	Kleffmann et al., 1998
Borosilicate glass	22	5 - 80	0.029 - 6.4	1	Svensson et al., 1987
Borosilicate gl. ⁽¹⁾	23	4 - 40	< / > ca. 0.2	0 / 1	Jenkin et al., 1988
Mainz 1986/87	-4 - 16	0.017 - 0.125	0.01 - $3.4 * 10^{-6}$		
Milano 1994	7 - 20	0.030 - 0.085	0.1 - $0.88 * 10^{-6}$		

⁽¹⁾ according to the authors, reaction supposedly took place on metal parts

⁽²⁾ and under dry conditions, i.e. rh = 0 %

⁽³⁾ reaction order increases slowly for $\mu_{\text{NO}_2} > 0.05$ ppmv (Kleffmann, personal communication, 1998)

Table 5. Range of predicted relative formation rates $d\mu_{\text{HNO}_2}/\mu_{\text{NO}_2}/dt$ ($\% \text{ h}^{-1}$, values are independent of μ_{NO_2}) as predicted by the parameterisation. Given are best guess values and, in brackets, upper and lower bounds for $h_{\text{mix}} = 50 \text{ m}$ and 500 m , $rh = 50$ and 80% for urban aerosol ⁽¹⁾ over urban ground ⁽²⁾ (UU), rural aerosol ⁽³⁾ over urban ground (UR) and rural aerosol over vegetation canopies ⁽⁴⁾ (VR). The upper and lower bounds reflect the uncertainties related to the surface-to-area indices and to the water film growth as functions of humidity (cf. Table A2).

	h_{mix} (m)	$rh = 50 \%$ best guess	(lower - upper)	$rh = 80 \%$ best guess	(lower - upper)
UU	50	1.50	(1.10 - 1.80)	2.46	(1.24 - 2.94)
UR	50	1.49	(1.09 - 1.79)	2.41	(1.19 - 2.89)
VR	50	0.63	(0.40 - 0.83)	1.59	(0.63 - 2.09)
UU	500	0.16	(0.12 - 0.20)	0.30	(0.18 - 0.35)
UR	500	0.15	(0.11 - 0.18)	0.25	(0.13 - 0.30)
VR	500	0.07	(0.06 - 0.09)	0.18	(0.08 - 0.22)

⁽¹⁾ urban aerosol: $170 \mu\text{g m}^{-3}$ of mean density 1.96 g cm^{-3} , 35 % continental aerosol, 40 % acidic, ionic material, 25 % carbonaceous material ($m = 34 \%$, $r = 0.172 \mu\text{m}$) + 85 % continental aerosol, 10 % NaCl, 5 % acidic, ionic material ($m = 66 \%$, $r = 2.65 \mu\text{m}$)

⁽²⁾ urban ground: 75 % urban surfaces, 15 % vegetation canopies, 8 % bare soil, 2 % water

⁽³⁾ rural aerosol: $42 \mu\text{g m}^{-3}$ of mean density 1.95 g cm^{-3} , 85 % continental aerosol, 10 % acidic, ionic material, 5 % carbonaceous material ($m = 24 \%$, $r = 0.09 \mu\text{m}$) + 90 % continental aerosol, 10 % NaCl ($m = 76 \%$, $r = 2.26 \mu\text{m}$)

⁽⁴⁾ vegetated ground: 90 % vegetation canopies, 8 % bare soil, 2 % water

Table 6. Observed and predicted relative nitrous acid formation rates, $d\mu_{\text{HNO}_2}/\mu_{\text{NO}_2}/dt$, in urban areas (a.) Mainz, 1986/87 (Lammel, 1988), (b.) Milano, 1994 (Febo et al., 1996; Febo and Perrino, personal communication, 1996) together with other parameters ($\mu_{\text{NO}_2}(t_0)$ = NO_2 mixing ratio before sunset, rh = relative humidity, h_{mix} = height of the mixing layer).

date	$\mu_{\text{NO}_2}(t_0)$ (ppbv)	rh (%)	h_{mix} (m)	$d\mu_{\text{HNO}_2}/\mu_{\text{NO}_2}/dt$ observed (% h^{-1})	$d\mu_{\text{HNO}_2}/\mu_{\text{NO}_2}/dt$ predicted (% h^{-1})
a. Mainz					
23.04.86	43	65 ± 5	115 ± 90	0.25 ± 0.15	1.60 ± 1.29
12.10.86	19	83	120 ± 55	0.51 ± 0.43	1.17 ± 0.54
14.10.86	81	72 ± 2	115 ± 50	1.08 ± 0.38	1.51 ± 0.70
08.01.87	37	81	150 ± 10	0.07 ± 0.13	0.33 ± 0.02
14.01.87	53	40	725 ± 75	0.31 ± 0.14	0.15 ± 0.01
19.01.87	29	85	200 ± 20	0.18 ± 0.28	0.31 ± 0.03
02.02.87	87	42	170 ± 60	0.42 ± 0.17	0.73 ± 0.27
25.02.87	67	95	220 ± 50	0.44 ± 0.17	0.12 ± 0.03
04.03.87	54	53 ± 2	130 ± 10	0.21 ± 0.19	0.29 ± 0.03
05.03.87	60	64 ± 4	110 ± 50	0.52 ± 0.17	0.60 ± 0.31
08.03.87	35	53 ± 3	170 ± 20	0.49 ± 0.35	0.20 ± 0.03
09.03.87	32	95	250 ± 25	0.75 ± 0.46	0.10 ± 0.01
12.03.87	55	89	40 ± 15	0.39 ± 0.15	2.10 ± 0.80
13.03.87	47	41	265 ± 115	0.52 ± 0.16	0.49 ± 0.21
17.03.87	21	76 ± 6	1400 ± 150	0.24 ± 0.34	0.03 ± 0.01
19.03.87	22	66 ± 6	1050 ± 100	0.19 ± 0.15	0.04
26.03.87	17	76 ± 6	180 ± 100	0.22 ± 0.17	0.53 ± 0.29
30.03.87	36	62 ± 7	2650 ± 250	0.65 ± 0.10	0.01 ± 0.01
b. Milano					
04.03.94	64	40	170 ± 10	1.70 ± 0.37	0.64 ± 0.04
05.03.94	60	46	490	-0.07 ± 0.14	0.22
08.03.94	64	75	150 ± 10	1.42 ± 0.24	1.10 ± 0.08
09.03.94	63	66	230	0.11 ± 0.19	0.66 ± 0.01
10.03.94	53	85	95 ± 15	0.95 ± 0.21	2.19 ± 0.33
11.03.94	82	56	290 ± 150	0.36 ± 0.14	0.55 ± 0.28
12.03.94	40	62	3070	0.01 ± 0.46	0.05 ± 0.01
13.03.94	30	56	925	-0.44 ± 0.33	0.11
14.03.94	45	36	3360	0.38 ± 0.35	0.03

Fig. 1. Water uptake expressed as number of monolayers of H₂O as a function of humidity for ambient and laboratory surfaces.

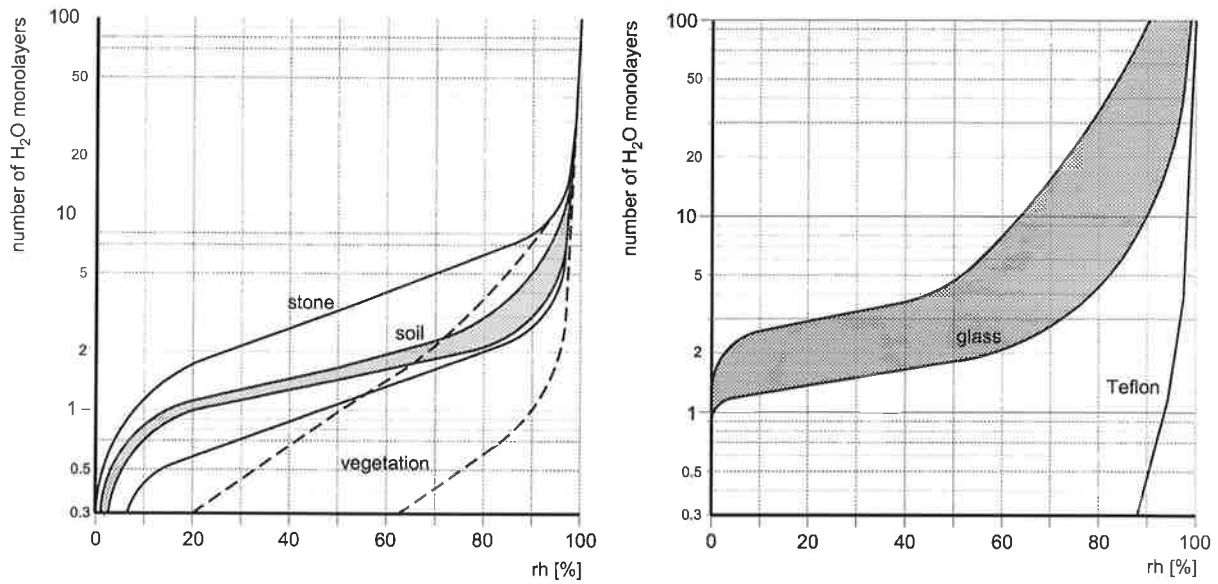


Fig. 2. Cases of the time variation of primary and secondary pollutants relevant for the derivation of evening formation rates from trace gas measurements. Cases 1, 2a and 3a are rejected from the analysis (see text).

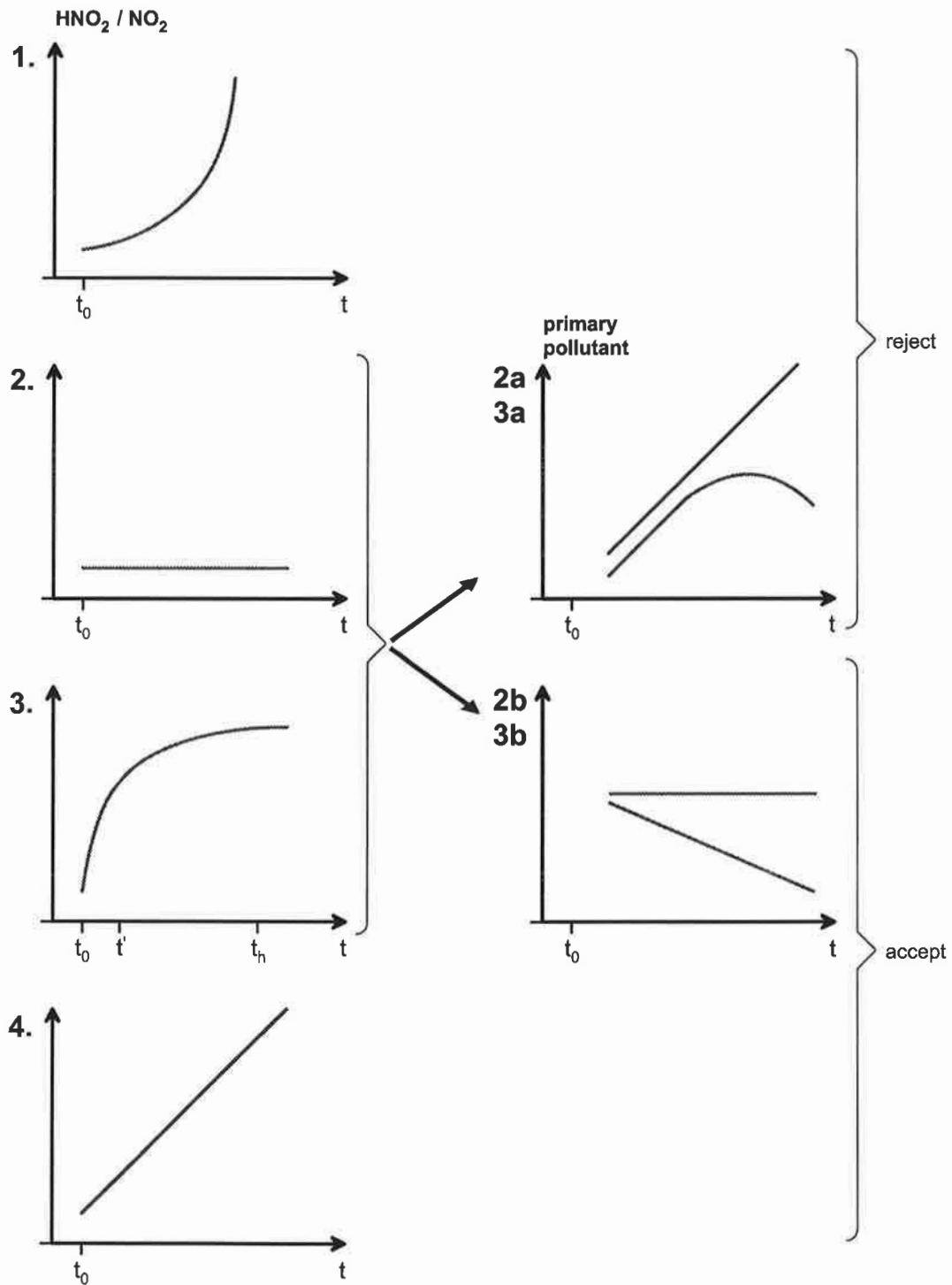


Fig. 3. Observed and predicted values of the relative nitrous acid formation rate, $d\mu_{\text{HNO}_2}/\mu_{\text{NO}_2}/dt$ ($\% \text{ h}^{-1}$), for Mainz and Milano (cf. Table 7)

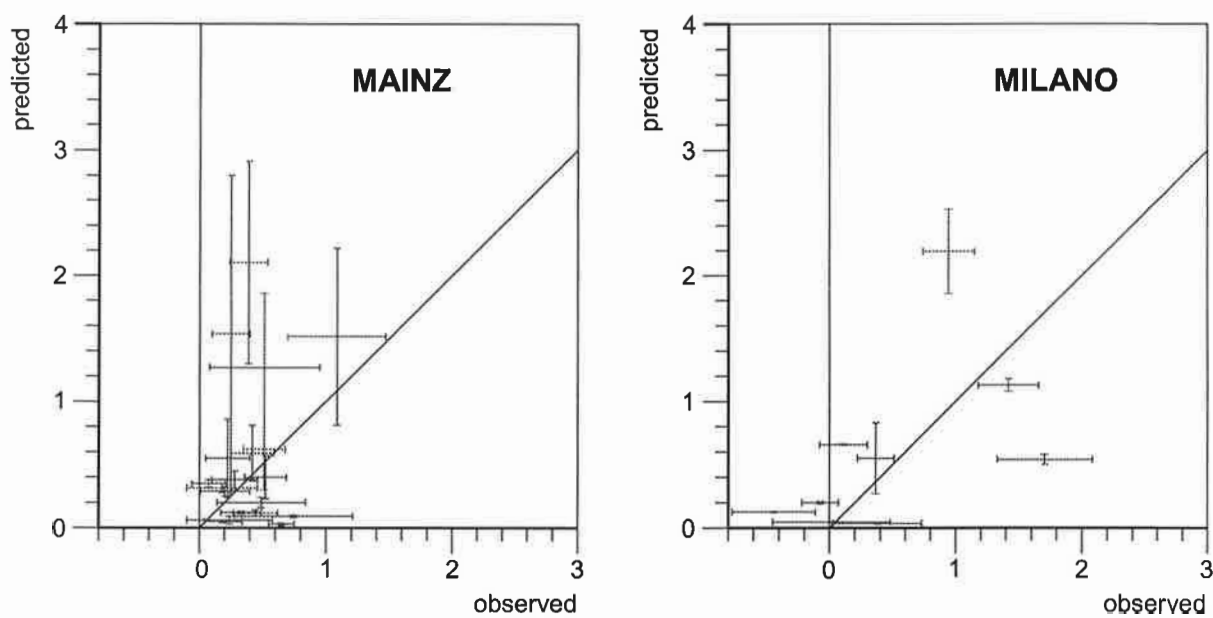


Fig. 4. Agreement between observed and predicted values of the relative nitrous acid formation rate, expressed as $(d\mu_{\text{HNO}_2}/\mu_{\text{NO}_2}/dt)_{\text{predicted}} - (d\mu_{\text{HNO}_2}/\mu_{\text{NO}_2}/dt)_{\text{observed}}$ ($\% \text{ h}^{-1}$), in relation to the relative humidity (%) for Mainz and Milano (cf. Table 7).

