ON THE OCCURRENCE OF NITRITE IN URBAN FOGWATER

G. Lammel and G. Metzig

Max-Planck-Institut für Meteorologie, Bundesstr. 55, 20146 Hamburg, Germany
Forschungszentrum Karlsruhe, FTU, Karlsruhe, Germany

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ABSTRACT

Nitrite was observed in fogwater samples 3 - 52 µmol L⁻¹, in a polluted source region in Germany. The fogwater contained high concentrations of various pollutants but only little or no acidity. The concentrations of oxidizable S(IV) were in the range 6 - 290 µmol L⁻¹.

A two-phase chemical box model is used to interpret the chemistry. Fogwater N(III) is found to be sensitive to gas-phase HNO₂ and also to HCHO (which were both not measured). From the distribution of S(IV) between oxidizable and non-oxidizable species (the latter is suspected to be dominated by the complex formed from S(IV) and dissolved HCHO), it is inferred that HCHO most likely was low. The reaction between dissolved NO₂ and S(IV) was an important N(III) source and could even explain the observed fogwater nitrite concentrations, if no gas-phase HNO₂ was fed into the fog. The comparison between observed and model predicted suggests that interphase mass transfer of NO₂ is characterized by a low mass accommodation coefficient.

1. INTRODUCTION

The occurrence of nitrite in the atmosphere is of interest, as it is an intermediate in NO₂ (= NO + NO₃) chemistry and is related to gas-phase nitrous acid, HNO₂. HNO₂ is a source of the hydroxyl radical (cf. Harris et al., 1982, besides others) and HNO₂ as well as nitrite in condensed phases are suspected to be precursors for carcinogens (nitrosamines).

Few observations of nitrite in fog- and cloudwater (Okita, 1968; Ruprecht and Sigg, 1990; Cape et al., 1992; Fuzzi et al., 1992) and in ambient particulate matter (Lammel and Perner, 1988; Allegrini et al., 1994) of anthropogenically influenced air masses have been reported.

In this contribution, the observation of fogwater nitrite is reported and interpreted in the light of heterogeneous chemistry.
2. METHODOLOGY

2.1. Measurements

Fog chemistry was studied in an episode of three subsequent fog events in Stuttgart, Germany, distanced 10 km from the city center in an agricultural surroundings and in the vicinity of major traffic sources (roads and freeway 0.3 - 1 km, airport 2 km). Traffic on the major roads prevails throughout the night. The site itself is located in fields, ca. 100 m away from farm buildings. During the measurements, temperatures were between -3.5 and +1.5 °C and winds were low, ca. 1 m s\(^{-1}\).

The experimental methodology has been introduced elsewhere (Lammel and Metzig, 1991; Lammel, 1995). The main characteristics are as follows: Fogwater was sampled with round nozzle jet impactors, with lower cutoffs at 2 and 5 µm. The collection efficiency of these collectors is a function of windspeed and shape of droplet spectra, besides other. An intercomparison and performance study suggests a collection efficiency of ca. 45 ± 15% for the prevailing conditions in the here reported measurements (Schell et al., 1992). Trace gases were measured using standard equipment (O\(_2\), SO\(_2\), NO\(_x\)) in a distance of 1 km (SO\(_2\)) and 3 km (O\(_2\), NO\(_x\)), both outside the fogs, and a denuder method (NH\(_3\); Lammel, 1991) at the site. Fogwater pH was measured at the field site with an electrode. As sample volumes were limited (to achieve a high time resolution), samples have been diluted prior to pH determination (with deionized water, by a factor of 3 - 10). Free acid concentrations measured are thus a function of the buffering capacity of the electrolyte and do not reflect the free acid concentration of the untreated sample. The pH of the diluted samples was in most cases higher than the pH of deionized water (pH 6.0), which obviously requires pH > 6 for the undiluted sample. Upper (or lower limits, respectively) for pH values (Table I) were derived through application of the simple mixing rule, i.e. under the assumption that dissociation equilibria were not affected by the mixing step (zero acid buffering capacity). However, the more weak acid anions were protonated (or weak acids dissociated) the more the sample pH would deviate from this upper (or lower) limit.

Nitrite was determined using a modified Lunge type reaction (Rider and Mellon, 1946). One out of four drainage bottles of the fogwater collectors was prepared for nitrite preservation prior to sampling by containing 2 ml of a sulfanilic acid solution (0.6 % in ca. 7.2 % HCl). The mixture of sample and sulfanilic acid (3 - 8 ml) was put into deep freeze for storage without any other manipulation (-18°C). Nitrite present in fogwater was thus preserved as the respective diazonium cation. Photometric determination (at 521 nm) was performed 10 - 30 min after addition of 1-naphthylamine (1 ml 0.6 % in ca. 0.36 % HCl) and buffering solution (sodium acetate, 1 ml of saturated solution). The signal was linear in the range 0.01 - 30 µmol L\(^{-1}\) nitrite. In parallel, realistic blanks have been produced by similar manipulations of the reagents without fogwater collection.

All other anions and cations were determined using ion chromatographic techniques (IC). A chemical differentiation method in combination with IC allowed for separate determination of oxidizable and non-oxidizable S(IV) species (Lammel, 1996). In the following the oxidizable fraction (the difference
between total and non-oxidizable fraction) is denoted as 'free S(IV)' and, though without direct analytical evidence, the non-oxidizable fraction of S(IV) species is denoted as 'HMS' (hydroxy methanesulphonate), as this species most likely dominated.

The total carbon content was determined by coulometric titration following combustion to CO₂ (Ströhlein Coulomat; 0.2 µg C absolute detection limit). This method was adapted to liquid samples in the following manner: 0.2 mL of aqueous sample were given without prior filtration in a pre-heated (at 1300°C) combustion boat and were then heated in a tubar furnace from room temperature to 1300°C in nitrogen and combusted in pure oxygen. The precision of blanks (deionized water, determined each day) and standards was very good (> 95%), the precision of sample values, however, was lower (> 70%), most likely due to the heterogeneity of the samples containing also insoluble carbon. The precision of the values derived is therefore estimated to be ± 30%.

2.2. Model

A zero-dimensional numerical model is used which comprises 63 reactions between 28 gas-phase species (including 9 photolysis rates) and 39 reactions of 39 aqueous phase species (including 7 photolysis rates). It puts the emphasis on the heterogeneous N and S chemistry. The variation of aqueous-phase and gas-phase concentrations with time is computed through integration of a stiff system of ordinary first-order differential equations (variable time step, backward differentiation formulae). Mass transfer between phases is either described as being in permanent phase equilibrium or controlled by mass transfer kinetics. In either case of mass transfer simulation, the time integration process is periodically adjusted to re-establish 'fast' equilibria. The adjustment frequency is chosen high enough such that it does not affect the results. In the phase equilibrium mode, Henry's law is applied and pH is calculated in an iteration scheme. The phase partitioning of species affected by pH (chemically modified Henry coefficients) and the respective dissociation equilibria are adjusted. In the mass transfer kinetics mode, mass transfer rate coefficients of 13 species (NO, NO₂, HNO₃, HNO₄, SO₂ besides others) are determined based on molecular diffusion in the gas-phase and through the droplet surface (Fuchs and Sutugin, 1971; Pandis and Seinfeld, 1989). The probability that a collision of a trace gas molecule with the droplet surface leads to an accommodation by the aqueous phase is quantified by the species' mass accommodation coefficient. Interphase transport of species is described as a set of pseudo-first order reactions. The description of the aqueous phase assumes well mixed droplets and instantaneously established dissociation equilibria. Electroneutrality is continuously maintained. Deviation from an ideal solution's behaviour are accounted for through representation of the activities rather than concentrations (Debye-Hückel). Kinetic data (including the temperature dependence) for homogeneous gas-phase reactions and aqueous phase equilibria were mostly taken as compiled by DeMore et al., 1987, and Pandis and Seinfeld, 1989, respectively. Data were updated according to publication in the more recent literature where possible. Metal ion catalysed autoxidation of sulfur(IV) nor other reactions of metal ions are not represented in the model so far. Aqueous phase
Table 1: 'Slow' aqueous phase reactions. $k^{\text{ref}}$ refers to the rate constant of n-th order at 298 K (mol, L, s units). More than one datum refers to individual rate constants corresponding to the S(IV) species, SO$_2^-$, HSO$_3^-$, and SO$_3^{2-}$, respectively. Deviations from mass balance and electroneutrality may occur in these lumped reactions. In the model the rate constants are represented in the van't Hoff form, $k(T) = k_{298} \exp \left[ E/R (1/T - 1/298) \right]$, if available.

| $A_1$ | NO + NO$_2$ + H$_2$O $\rightarrow$ 2 NO$_2^-$ + 2 H$^+$ | $k(2) = 3.0 \times 10^8$ | Hoffmann and Calvert, 1985 |
| $A_2$ | 2 NO$_2$ + H$_2$O $\rightarrow$ NO$_2^- + NO_3^- + 2 H^+$ | $k(2) = 6.5 \times 10^7$ | Lee and Schwartz, 1981 |
| $A_3$ | 2 NO$_2$ + O$_2$ $\rightarrow$ 2 NO$_3^-$ | $k(3) = 7.2 \times 10^3$ | Damschen and Martin, 1983 |
| $A_4$ | NO$_3^- + O_3$ $\rightarrow$ NO$_3^- + O_3$ | $k(2) = 5.0 \times 10^5$ | Damschen and Martin, 1981 |
| $A_5$ | NO$_2^-$ + H$_2$O$_2$ $\rightarrow$ NO$_3^-$ + H$_2$O | $k(3) = 6.3 \times 10^3$ | Lee and Lind, 1986 |
| $A_6$ | SO$_3^{2-} + H_2O \rightarrow SO_4^{2-} + H_2O$ | $k(2) = 8.4 \times 10^3 \left( 1 + [H^+] \right)$ | Martin, 1984 |
| $A_7$ | S(IV) + O$_3$ $\rightarrow$ SO$_4^{2-} + O_3$ | $k(2) = 2.4 \times 10^5, 3.7 \times 10^7, 1.5 \times 10^9$ | cf. Hoffmann, 1986 |
| $A_8$ | S(IV) + CH$_3$(OH)$_2$ $\rightarrow$ CH$_3$(OH)SO$_3^-$ + H$_2$O | $k(2) = 0.42, 2.1 \times 10^4$ | Deister et al., 1986 |
| $A_9$ | CH$_3$(OH)SO$_3^-$ + H$_2$O $\rightarrow$ S(IV) + CH$_3$(OH)$_2$ | $k(1) = 0.1, 1.1 \times 10^{-3}$, $k(2) = 3.7 \times 10^5$ | Deister et al., 1986 |
| $A_{10}$ | 2 NO + S(IV) $\rightarrow$ HON(NO)SO$_3^-$ | $k(2) = 0.32, 620$ | Litticjohn et al., 1986 |
| $A_{11}$ | 2 NO$_2$ + S(IV) + H$_2$O $\rightarrow$ 2 NO$_2^- + S(VI) + 3H^+$ | $k(2) = 0.3 \times 10^5, 1.0 \times 10^5$, cf. Wameck, 1988 |
| $A_{12}$ | NO$_2^- + 2$ HSO$_3^- \rightarrow$ HON(SO$_3^-$)$_2^-$ + H$_2$O | $k(2) = 3.8 \times 10^5 \left[ H^+ \right]$, $k(3) = 9.0 \times 10^{-4}$ | Oblath et al., 1981 |

Reactions of the nitrogen and sulfur species, other than the reactions of the nitrate radical, NO$_3^-$, and pernitric acid, HNO$_4^-$, are listed in Table 2. NO$_3^-$ and HNO$_4^-$ were insignificant: NO$_3^-$ could not be formed, because ozone was very low in the here reported measurements and NO (from nearby traffic sources) would have limited the lifetime of the nitrate radical effectively. The chemistry of HNO$_4^-$ might constitute a source for aqueous phase N(III) and a relevant sink for S(IV) species under certain conditions, low acidity besides others (Lammel et al., 1990; Götz, 1996). However, as the lifetime of HNO$_4^-$ was on the order of minutes and as we have no evidence for a night-time radical source, its chemistry was neglected.

To fully account for mass transfer kinetic constraints on the multiphase system, the model was run in the mass transfer kinetics mode. Despite numerous experimental studies the heterogeneous chemistry of NO$_2$ in droplet systems is still not fully understood (cf. Bambauer et al., 1994, besides others). We study the significance of a recently determined, low value of the NO$_2$ mass accommodation coefficient for the multiphase chemistry ($\alpha_{\text{NO2}} = 10^{-6}$, based on bulk aqueous phase experiments; Kleffmann et al., 1998) and compare with the previous recommended value, $\alpha_{\text{SO2}} = 6.3 \times 10^{-4}$ (Lee and Tang, 1988) (section 3.2). Mass accommodation coefficients of other relevant trace gases used in the model are high: $\alpha_{\text{HNO2}} = 0.05$ (Bongartz et al., 1994), $\alpha_{\text{SO2}} = 0.13$ (Ponche et al., 1993), $\alpha_{\text{HCHO}} = 0.1$ (estimate).
3. RESULTS AND DISCUSSION

3.1. Measurements

The fogs' onset was during night-time and dissipation of fogs on 28. and 29.11.91 was before sunrise, whereas on 30.11.91 the fog lasted until 21:00. As nitrite was only measured from 00:20 until 02:15 on this day, only results from night-time measurements are presented here.

Fogwater nitrite concentrations were 3 - 52 µmol L\(^{-1}\) (0.46 - 3.7 nmol m\(^{-3}\)) and S(IV) (= dissolved SO\(_2\) + HSO\(_3\)\(^{-}\) + SO\(_4^{2-}\)) concentrations were 6 - 290 µmol L\(^{-1}\) (0 - 17 nmol m\(^{-3}\)). Fogwater constituents are listed in Table 1. The fluctuations of the atmospheric loadings (i.e. concentrations refering to volume of air, mmol m\(^{-3}\)) of individual fogwater constituents were mostly within a factor of 2 during fog events No. 1 and 3 and up to a factor of 10 during fog event No. 2. The atmospheric loading of nitrite decreased during fog No. 2 and increased during fog No. 3. The analyses of parallel samples addressing different droplet size collectives (fog No. 2) delivered no clear tendency to enrichment of constituents in smaller or larger droplets.

N(III) (= dissolved HNO\(_2\) + NO\(_2\)) as well as S(IV) enrichment in the aqueous phase can be of twofold origin, namely phase partitioning of HNO\(_2\) and SO\(_2\), respectively, or effective aqueous phase source reactions. Due to the high pH of the fogwater, phase partitioning was capable to maintain considerable concentrations of free S(IV) even at low to moderate SO\(_2\) levels: Equilibrium concentrations were in the range 0.25 - 1.5 mmol L\(^{-1}\) (based on the chemically modified Henry's coefficient). S(IV) species were dominated by HMS (Table 1), which is stable up to pH 6 - 7 (Deister et al., 1986).

HNO\(_2\) was not determined. Partial pressures in phase equilibrium with the observed fogwater nitrite concentrations would have been 0.060 ± 0.034, 0.42 ± 0.39, and 0.13 ± 0.12 parts per billion of HNO\(_2\) per volume of air (ppbv) for fog events No. 1, 2 and 3, respectively (\(H_{\text{HNO}} = 49 \times \exp[4780*(1/T - 1/298)]\) mol L\(^{-1}\) atm\(^{-1}\); Schwartz and White, 1981). These ranges do cover HNO\(_2\) concentrations which are consistent with the NO\(_2\) levels (5 - 6, 11 - 16 and 17 - 21 ppbv, respectively): HNO\(_2\), is formed from NO\(_2\) in the night-time atmosphere and measurements at various rural and urban sites in Europe showed that HNO\(_2\)-to-NO\(_2\)-ratios in most cases reach up to 5 % (Kessler and Platt, 1984; Sjödin and Ferm, 1985; Lammel and Perner, 1988; Allegrini et al., 1994; Harrison et al., 1996).

The aqueous phase contained millimolar concentrations of ammonium, nitrate, sulfate, formiate and acetate. The concentrations of carbonaceous material was very high, which, obviously, included soot, as fog samples were opaque. The gas-phase was only moderately polluted. Ammonia was not measured continuously. Its concentration corresponded to 1.1 ppbv after the dissipation of fog No. 2 and 3.0 ppbv before the onset of fog No. 3. Ammonia will be readily dissolved in fogwater (H = 74 mol L\(^{-1}\) atm\(^{-1}\) at 298
Table 2: Atmospheric conditions and pollutant concentrations during three subsequent fog events, 28., 29., and 30.11.91. Aqueous phase concentrations are given for 2, 7, and 3 fogwater samples, respectively. Data separated by a \textsuperscript{3} refer to two fogwater droplets size collectives, > 2 and > 5 pm, respectively. n.d. = not determined, fr. S(IV) = oxidizable S(IV) species, HMS = non-oxidizable S(IV) species.

<table>
<thead>
<tr>
<th>Fog event No.</th>
<th>1</th>
<th>1</th>
<th>2</th>
<th>2</th>
<th>2</th>
<th>2</th>
<th>3</th>
<th>3 \textsuperscript{(1)}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Start time (CET)</td>
<td>03:20</td>
<td>04:35</td>
<td>04:05</td>
<td>04:55</td>
<td>06:05</td>
<td>08:10</td>
<td>00:20</td>
<td>01:05</td>
</tr>
<tr>
<td>Stop time (CET)</td>
<td>04:20</td>
<td>05:20</td>
<td>04:45</td>
<td>06:00</td>
<td>07:55</td>
<td>08:45</td>
<td>00:50</td>
<td>01:40</td>
</tr>
<tr>
<td>( \text{O}_3 ) (ppbv)</td>
<td>0.5</td>
<td>0.5</td>
<td>2</td>
<td>3</td>
<td>1.5</td>
<td>1</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>( \text{NH}_3 ) (ppbv)</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>1.1 \textsuperscript{(2)}</td>
<td>3.0 \textsuperscript{(3)}</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>( \text{NO}_2 ) (ppbv)</td>
<td>5</td>
<td>6</td>
<td>11</td>
<td>10</td>
<td>16</td>
<td>15</td>
<td>17</td>
<td>19</td>
</tr>
<tr>
<td>( \text{SO}_2 ) (ppbv)</td>
<td>9</td>
<td>10</td>
<td>10</td>
<td>11</td>
<td>15</td>
<td>19</td>
<td>3</td>
<td>3</td>
</tr>
</tbody>
</table>

Droplet size, lower cutoff

| (μm) | 5 | 5 | 2 / 5 | 2 / 5 | 2 / 5 | 5 | 2 | 2 | 2 |

LWC\textsuperscript{(4)} (mg m\textsuperscript{-3})

| 29 | 62 | 82 / 71 | 56 / 60 | 27 / 31 | 40 | 39 | 18 | 20 |

\( \text{pH} \)\textsuperscript{(5)}

| \( \leq 6.2 \) | \( \leq 6.2 \) | \( \leq 6.8 \) | \( \leq 6.8 \) | \( \leq 7.0 \) | n.d. | \( \leq 6.5 \) | \( \geq 5.7 \) | \( \leq 6.8 \) | \( \leq 6.5 \) | \( \leq 6.2 \) |

\( \text{NO}_2^- \) (μmol L\textsuperscript{-1})

| 7 | 3 | 26 / 32 | 26 / 24 | 17 / 30 | 11 | 3 | 13 | 19 |

\( \text{NO}_3^- \) (mmol L\textsuperscript{-1})

| 1.5 | 0.9 | 1.4 / 1.7 | 0.7 / 0.2 | 0.65 / 0.24 | 0.62 | 0.21 | 1.4 | 0.97 |

fr. S(IV) (μmol L\textsuperscript{-1})

| 290 | 240 | 90 / 29 | 39 / 8 / 25 | 80 / 66 | 6 | 100 | 100 | 45 |

HMS (μmol L\textsuperscript{-1})

| 720 | 1020 | 230 / 140 | 310 / 260 | 290 / 150 | 210 / 160 | 140 | 140 |

\( \text{SO}_4^{2-} \) (mmol L\textsuperscript{-1})

| 2.3 | 1.9 | 1.2 / 2.6 | 0.77 / 0.46 | 0.81 / 0.22 | 1.0 | 0.13 | 0.47 | 0.46 |

Cl\textsuperscript{-} (mmol L\textsuperscript{-1})

| 0.17 | 0.18 | 0.39 / 0.25 | 0.52 / 0.78 | 0.64 / 0.096 | 0.25 | 0.059 | 0.27 | 0.25 |

HCOO\textsuperscript{-} (mmol L\textsuperscript{-1})

| n.d. | 0.53 | 0.63 / 0.80 | 1.1 / 1.3 | 1.2 / 0.86 | 1.9 | 0.98 | 0.76 | 0.81 |

CH\textsubscript{3}COO\textsuperscript{-} (mmol L\textsuperscript{-1})

| n.d. | 0.78 | 0.41 / 0.30 | 0.42 / 0.70 | 0.33 / 0.49 | 1.0 | 0.48 | 0.59 | 0.39 |

NH\textsubscript{4}\textsuperscript{+} (mmol L\textsuperscript{-1})

| 1.5 | 1.8 | 2.6 / 6.0 | 3.6 / 1.0 | 2.7 / 2.3 | 1.6 | 1.4 | 1.4 | 1.2 |

Na\textsuperscript{+} (mmol L\textsuperscript{-1})

| 0.22 | 0.21 | 0.40 / 0.60 | 0.39 / 1.04 | 0.63 / 0.85 | 1.47 | 0.86 | 0.26 | 0.24 |

K\textsuperscript{+} (μmol L\textsuperscript{-1})

| 43 | 69 | 54 / 37 | 48 / 83 | 73 / 21 | 40 | 64 | 36 | 27 |

Total C (mg L\textsuperscript{-1})

| 98 | 112 | 22 / 42 | 48 / n.d. | 58 / 38 | 50 | 40 | 44 | 44 |

\( ^{(1)} \) Time interval covered here; the fog lasted until 21:00 h.

\( ^{(2)} \) Measured after dissipation of the fog.

\( ^{(3)} \) Measured before the onset of fog.

\( ^{(4)} \) Inferred from the sampled fogwater volumes and corrected for the collection efficiency (Schell et al., 1992).

\( ^{(5)} \) Ranges of true values are between pH 6 and the limits given.
K). Available NH₃ most likely was the reason for high fogwater pH.

Observations of cloud- and fogwater N(III) are scarce. Unfortunately, so far none of the studies which addressed cloud or fog water N(III) included co-located gas-phase HNO₃ measurements to test Henry's law equilibria in the field. Up to 50 and 25 μmol L⁻¹ were observed in orographic and stratiform clouds in Japan (Okita, 1968, pH = 5.7 - 6.5) and up to 1.6 μmol L⁻¹ in orographic clouds in England (Cape et al., 1992, NOₓ = 6 - 38 ppbv). However, up to 500 μmol L⁻¹ were observed in neutral or weak acidic urban fogwater samples (Ruprecht and Sigg, 1990, pH = 6.3 - 7.5; Fuzzi et al., 1992, pH = 2.5 - 6.8).

3.2. Model

In the following an effort is undertaken to interpret the findings on fogwater nitrite through simulation of the two-phase system:

A potentially important oxidant was not measured, hydrogen peroxide. While photochemical sources in the gas and aqueous phases certainly predominate, H₂O₂ can be preserved until after sunset in cloudwater (Richards, 1995). However, as SO₃ will be in excess of the oxidant and SO₂ relaxation to phase equilibrium is fast, S(IV) availability is not expected to be affected by the (unknown) gas-phase H₂O₂ concentration.

The heterogeneous chemistry during the first hour of fog No. 1 as simulated by the model is shown in Fig. 1: A bimodal droplet collective, sizes 5 and 10 μm, is assumed. N(III) and HMS accumulate in the fogwater under SO₂ and HCHO depletion from the gas-phase. For initialization, temperature, LWC and trace substance concentrations were set as determined, except of N(III) and S(IV) species which were set to zero and HNO₃ was

**Fig. 1:** Simulation of gas-phase and aqueous phase constituents for the conditions of fog No. 1, first fogwater sample. Δt ≤ 1 h. Initial concentrations (Δt = 0) were: HCHO = 1.5 ppbv, S(IV) = 0, HMS = 0, either HNO₃ = 0 (left) or HNO₃ / NO₂ = 0.05 (right)
Fig. 2: N(III) (dissolved HNO₂ + NO₂⁻) concentrations in aqueous solutions as representative for fog- and cloudwater as a function of both NO₃⁻ and pH. Reaction time Δt = 1 h, temperature T = 273 K. Only cases with equal concentrations of NO and NO₂ are considered. a_{NO₂} = 10^6. Initial concentrations (Δt = 0) were:
(a.) HNO₂ = 0, SO₂ = NO₂, HCHO = 0.5 ppbv. (b.) HNO₂ = 0, SO₂ = NO₂, HCHO = 10 ppbv.
(c.) HNO₂ = 0, SO₂ = 0 (d.) HNO₂ / NO₂ = 0.05, SO₂ = 0.
Fig. 3: Same as Fig. 2a, 2b, but using a higher NO$_2$ mass accommodation coefficient to describe interphase mass transfer of NO$_2$, namely $\alpha_{\text{NO}_2} = 6.3 \times 10^{-4}$ (Lee and Tang, 1988) instead of $\alpha_{\text{NO}_2} = 10^{-6}$ (Kleffmann et al., 1998).

set to either zero or to 0.05 $\times$ $c^0_{\text{NO}_2}$. pH was kept constant during the simulation and HCHO was chosen so as to produce rough agreement between measured and modeled S(IV) species concentrations. A low value, 1.5 ppbv HCHO in this case, is suggested. The model results have been found to be insensitive to $H_2O_2$ concentrations between 0 and 1 ppbv and insensitive to NO. Within 1 h of model time, N(III) is formed from aqueous reactions and concentrations in the micromolar range are achieved for $c^0_{\text{HNO}_2} = 0$, while in the presence of high initial levels of HNO$_2$ ($c^0_{\text{HNO}_2} / c^0_{\text{NO}_2} = 5 \%$, 0.27 ppbv in this case) the nitrite formed in aqueous phase reactions just adds to phase partitioned N(III) in the 100 µmol/L range (Fig. 1). $\alpha_{\text{NO}_2} = 10^{-6}$ was used for these simulations. When using $\alpha_{\text{NO}_2} = 6.3 \times 10^{-4}$, nitrite is predicted to form one order of magnitude faster leading to 250 µmol L$^{-1}$ within one hour. Such high values are not supported by the measurements, but obviously overpredict those. Test runs show that without the advection of gas-phase HNO$_2$ into the fog the predicted N(III) is mostly due to reaction A11. Obviously, because the solubility of both NO$_2$ and SO$_3$ is strongly favoured by high pH, the reduction of dissolved NO$_2$ by dissolved SO$_2$, A11, gains importance despite the little solubility of NO$_2$ ($H_{\text{NO}_2} = 7 \times 10^{-3}$ mol L$^{-1}$ atm$^{-1}$ at 295 K; Lee and Schwartz, 1981). S(IV), however, would be prevented from oxidation in the presence of formaldehyde as it forms the adduct hydroxymethane sulfonate, which is particularly stable in the pH range 3 - 6 (Boyce and Hoffmann, 1984; Deister et al., 1986).
The reaction time in the droplet system is given by the transient time of the air mass, which is a function of extension of the fog and wind speed. From observation at the site it is concluded that reaction times were between 20 min and 2 h. For reaction time $\Delta t = 1\ h$, the ratio of free $S(IV) / HMS$ achieves values between 0.01 and 0.1 for $HCHO = 5\ -\ 30\ ppbv$ and values between 0.3 and 1 for $HCHO = 0.3\ ppbv$. Therefore, we suggest that HCHO most likely was low during the campaign.

Fogwater nitrite concentrations were calculated for wider ranges of fogwater pH and initial trace gas ($HNO_3$, $SO_3$, $NO_3$, and $HCHO$) concentrations. In Fig. 2 results are shown based on $\alpha_{n02} = 10^{-6}$ for one hour reaction time, $LWC = 75\ mg\ m^{-3}$. If gas-phase $HNO_2$ is advected into the fog, distinctly higher levels of $N(III)$ can be expected from $NO_3$ reactions in the presence of $SO_3$ (Fig. 2a and 2b) than without $SO_2$ present (Fig. 2c). Highest $N(III)$ concentrations are predicted for $HNO_2$ originating in the gas-phase ($c_{HNO_2}^0 / c_{NO_2}^0 = 5\ %$; Fig. 2d). Nitrite production is slightly weaker under high compared to low HCHO (cf. Figures 2b and 2a). When we describe interphase mass transfer of $NO_3$ using $\alpha_{n03} = 6.3\ *\ 10^{-4}$ instead of $10^{-6}$, significantly stronger nitrite production occurs and the effect of HCHO is more pronounced (cf. Figures 3a, 3b and 2a, 2b).

4. CONCLUSION

In the night-time in neutral or almost neutral fogwater, nitrite can be expected in the micromolar range under either situations of effective $NO_3$ to $HNO_2$ conversion (advection of gas-phase $HNO_2$ into the fog) or due to the reaction between dissolved $NO_3$ and $S(IV)$ (without nitrous acid originating in the gas-phase). Oxidizable $S(IV)$ can be expected in particular under conditions of high $SO_2$, low $HCHO$, high pH, and low oxidant concentrations. These preconditions are not uncommon in urban air, because sufficient ammonia to neutralize atmospheric acids is often available and ozone is usually titrated out from the night-time near-ground atmosphere by fresh NO emissions and under the influence of little mixing. During daytime, N(III) lifetime would be additionally limited by photolysis.

Our knowledge on $NO_2$ multiphase chemistry in droplet systems is still uncertain. The here presented model based interpretation of observations suggests that interphase mass transfer of $NO_3$ can be described by a low mass accommodation coefficient, $\alpha_{n02} = 10^{-6}$ rather than $\alpha_{n02} = 6.3\ *\ 10^{-4}$. For field experiments based investigations into fog chemistry, the extension of the fog (at least in the upwind direction) should be known to properly address the reaction time. The potential toxicological significance of fogwater nitrite should be clarified.

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