INFLUENCE OF GASEOUS NITRIC ACID ON SULFATE PRODUCTION AND ACIDITY IN RAIN

JACK L. DURHAM
Environmental Sciences Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711, U.S.A.

JOHN H. OVERTON, JR. and VINEY P. ANEJA
Environmental Sciences Group, Northrop Services, Inc., Research Triangle Park, NC 27709, U.S.A.

Abstract—A physico-chemical subcloud rain model is used to simulate the effect of gaseous HNO₃ and NO₂ on pH and SO₄²⁻ production in a 10 mm h⁻¹, 1000-m fall distance rain event. The ambient gases considered in the chemistry were SO₂, NO, NO₂, HNO₃, O₃, and CO₂. Raindrops initially at a pH of 5.5 absorbed these gases, and as they fell through a polluted zone, produced SO₄²⁻ and NO₃⁻ by the oxidation of dissolved SO₂ by O₃ and the dissociation of HNO₃, which reduced the pH. For the chemical mechanism and the below-cloud washout rain events considered, it was observed that: absorption of gaseous HNO₃ controlled the acidification in the initial stages of a rain event, and inhibited the production of SO₄²⁻; NO and NO₂ played no direct role in the acidification or formation of NO₃⁻ or SO₄²⁻; pre-acidified raindrops (pH of 4) were further acidified only by absorbing HNO₃.

NOTATION

D  Diffusion coefficient, cm² s⁻¹
H  Henry's law constant, dimensionless. Equilibrium ratio of gas phase concentration to liquid phase concentration of same species
R  Drop radius (mm)
η  Indicates gas phase
i  Rate constant subscript, reaction equation number
kᵢ  Rate constant for i-th reaction
s  Indicates a chemical species such as SO₂, HNO₃, H⁺, HSO₃⁻, etc
r  Time
u  Fall velocity (m s⁻¹)
z  Fall distance (m)
l  Indicates liquid phase
[ ]  Molar concentration
ν  Kinematic viscosity of air, 0.133 cm² s⁻¹
φ  Reaction rate
ψ  Mass transfer rate
μM  10⁻⁶ moles/cm³

INTRODUCTION

It was recognized over a decade ago that the acidity of precipitation was increasing and leading to environmental damage in Sweden (Oden, 1968). Trend analysis of content of precipitation samples indicate that the pH at stations in Sweden and Norway are declining at approximately the same rate (Oden, 1976), suggesting a regional behavior and long-range transport of pollutants from the United Kingdom, western Europe, and eastern Europe. There is no comparable long-term data base for precipitation acidity in the United States.

Using data from 1964-72, Likens and Bormann (1974) have reported for a station in New Hampshire an upward trend for nitrate and hydrogen ion and a downward trend for sulfate; similar trends for sulfate and nitrate were observed in Geneva and Ithaca, New York. Although the period of their acidity observations (9 years in New Hampshire) is not ideal for demonstrating a trend, they did succeed in directing attention to the potential seriousness of this problem which may become more important in the future. An increase in acid precipitation is to be expected because sulfur and nitrogen oxides emissions are projected to increase by 12 and 61%, respectively, over their 1975 values by the year 2000 (Glass, 1978).

The present state of knowledge of acid rain is insufficient to permit a quantitative cause-effect analysis. It is suspected that the increased acidification of precipitation in the northeastern U.S. is being brought about by at least several factors, which include: (a) the path of major storm tracks, which usually pass through the industrialized Tennessee River Valley, the Ohio River Valley, or the north Atlantic states, (b) use of tall stacks to control SO₂ concentrations by dispersion instead of suppression, (c) the use of electrostatic precipitators to selectively remove basic fly ash, but with no reduction of the acid gases SO₂ and NO, and (d) the absence of basic mineral dust in the natural environment of the northeastern U.S. The U.S. Environmental Protection Agency has recognized the need for developing regulatory programs to permit the control of acid precipitation (Berry and Bachmann, 1977). Among the research needs to support such an effort is an understanding of the pollutant chemistry leading to rain acidification.

The acidification of rain is principally due to the
oxidation of SO$_2$ or N-oxides in cloud droplets and raindrops, the absorption of free gaseous acids by droplets and raindrops, or scavenging of acid aerosol by the falling raindrops. Although the acid aerosol scavenging and in-cloud processes are important, we shall not consider them in our treatment presented here. Instead, we shall focus on the non-photochemistry of the N-oxides, S-oxides, and O$_3$ in both the gas and aqueous phases, which is an extension of our previous treatment on acid sulfate formation by O$_3$ and Fe-catalyzed reactions in falling raindrops (Overton et al., 1979).

The chemical composition of rainfall due to subcloud scavenging collected at ground level will be calculated by a physical-chemical model employing the gas-phase and aqueous-phase reactions for N-oxide and S-oxide species presented below. CO$_2$ is also included because of its action in buffering liquid water to a pH of 5.6 in the absence of strong acids. The principal oxidant considered is O$_3$. Due to a lack of information, N-oxide species were not considered to be significant oxidants nor were transition metal ions, but in reality, they may be. Also H$_2$O$_2$, which is known to be important (Penkett et al., 1979) is not yet part of our reaction scheme. Initially, before the raindrops begin to fall, we assume that only these reaction gases are important in the polluted atmosphere: SO$_2$, NO, NO$_2$, HNO$_3$, CO$_2$, and O$_3$.

The aqueous chemistry of N-oxide species is not well known, and the best current sources of rate constants refer to conditions appropriate for combustion emission control. In some cases the reaction rates for these species were measured at concentrations several orders of magnitude greater than of interest in the free atmosphere. Realizing that the kinetic mechanisms may be different at lower concentrations, we embrace these rate constants reluctantly.

The phenomenon of subcloud scavenging (rain falling through a polluted zone) is modeled, but in-cloud scavenging (formation of rain in the polluted zone) and the effect of in-cloud processes are ignored, although they may be significant.

**PHYSICAL MODEL**

Our physical model of a rain event, raindrops and mass transfer are described by Overton et al. (1979) and repeated here for completeness.

The atmosphere has been divided into two regions, shown in Fig. 1. Raindrops are formed in the upper region in the presence of CO$_2$ and other compounds which establish the initial pH. The drops enter and fall through a stable polluted region at a constant velocity. In the polluted region are the trace gas SO$_2$, O$_3$, HNO$_3$, NO, and NO$_2$. As the drop falls, gases are absorbed, react and produce SO$_2^-$ and NO$_3^-$. A raindrop is taken to be a uniform sphere composed of water and trace quantities of O$_3$, SO$_2$, CO$_2$, HNO$_3$, NO, NO$_2$ and their products. The concentrations are assumed to be uniformly distributed at all times throughout the drop, (i.e., no concentration gradients in the drop). The temperature of the raindrops is assumed to be in equilibrium with an isothermal atmosphere at 25°C (a choice dictated by the available chemical rate constant data).

![Fig. 1. Environmental model. The raindrops form above and fall through the polluted zone. In the polluted zone, they absorb reactive gases which produce SO$_2^-$ and NO$_3^-$.](image)

The rate, per unit fall distance, at which a gaseous species (e.g., O$_3$, HNO$_3$, NO, NO$_2$, SO$_2$, and CO$_2$) crosses the gas-water interface of a drop of radius $R$ is given by Equation (1):

$$\frac{d[s]}{dz}_{\text{transfer}} = \frac{0.3k_d}{R} ([s]_g - [s]_w)$$

(1)

The species, $s$, is assumed to be distributed uniformly throughout the drop. The mass transfer coefficient, $k_d$, is obtained from the Frossling correlation (Frossling, 1938).

$$k_d = \frac{10D}{R} \left[ 1 + 0.3 \left( \frac{20R}{v} \right)^{1/2} \left( \frac{v}{D} \right)^{1.3} \right]$$

(2)

where $u$ is the fall velocity and $v$ is the kinematic viscosity of air. Values of $u$ are obtained from a formula by Markowitz (1976):

$$u = 9.58 \left[ 1 - \exp \left( - (R/0.885)^{1.47} \right) \right].$$

(3)

Values of $H$, Henry's law constant, and $D$, gas-phase diffusion coefficient, for molecular species are given in Table 1.

**CHEMICAL REACTION WITHIN THE DROP**

In Table 2 are the chemical reactions selected for calculating the acidification of falling raindrops. Equations 1–11 are the reversible reactions for the CO$_2$–SO$_2$–NO–NO$_2$–N$_2$O$_5$–H$_2$O–HNO$_3$–HNO$_2$–water system. The reverse reaction for Equation 10 has not been reported, but due to the expected extremely low concentrations of molecular HNO$_2$ and HNO$_3$, we have assumed that it is unimportant. Equations 12–15 are the irreversible oxidation steps for forming NO$_3^-$ and SO$_2^-$. There is considerable uncertainty in the rate constants for reactions 6, 7, 10 and 11. For the constants used these reactions were found not to be important and large variations in the constants are not expected to change the importance of these reactions for the conditions chosen. The rate constants for reactions 8 and 9 were chosen to give the correct equilibrium constant since these reactions are, for practical purposes, in equilibrium.

**MATHEMATICAL MODEL FORMULATION**

The concentration of each chemical species within a drop of radius $R$ as a function of fall distance, $z$, was obtained by numerically integrating the coupled non-linear differential equations derived from the kinetic and mass transport
Table 1. Gas phase diffusion coefficients and Henry's law constants

<table>
<thead>
<tr>
<th>Species</th>
<th>$D^* \text{ cm}^2 \text{s}^{-1}$</th>
<th>$H$</th>
<th>Source of $H$ values</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>0.166</td>
<td>1.2</td>
<td>Perry &amp; Chilton (1973)</td>
</tr>
<tr>
<td>O$_3$</td>
<td>0.157</td>
<td>3.36</td>
<td>Perry &amp; Chilton (1973)</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>0.136†</td>
<td>0.0332</td>
<td>Hales &amp; Suter (1973)</td>
</tr>
<tr>
<td>HNO$_3$</td>
<td>0.136</td>
<td>0.46E-6</td>
<td>Abel &amp; Neusser (1929); McKay (1956)</td>
</tr>
<tr>
<td>HNO$_2$</td>
<td>0.159</td>
<td>0.11E-2</td>
<td>Komiyama &amp; Inoue (1978)</td>
</tr>
<tr>
<td>N$_2$O$_4$</td>
<td>0.113</td>
<td>0.25E-1</td>
<td>Komiyama &amp; Inoue (1978)</td>
</tr>
<tr>
<td>NO</td>
<td>0.199</td>
<td>2.1</td>
<td>Komiyama &amp; Inoue (1978)</td>
</tr>
<tr>
<td>N$_2$O$_3$</td>
<td>0.125</td>
<td>0.16E-2</td>
<td>Komiyama &amp; Inoue (1978)</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>0.160</td>
<td>1.0</td>
<td>Andrew &amp; Hanson (1961)</td>
</tr>
</tbody>
</table>

* $D^* = \left( \frac{\text{molecular weight of SO}_2}{\text{molecular weight of species } \times \text{mol wt of SO}} \right)^{1/2}$

† Fish and Durham (1971).

Table 2. Kinetic mechanism of CO$_2$-SO$_2$-HNO$_x$-O$_3$-Aqueous phase system used for raindrops$^*^*^*^$

<table>
<thead>
<tr>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. H$_2$O $\xrightarrow{1.3E+3 \over 1.9E+1} H^+ + OH^-$ Eigen et al. (1964).</td>
</tr>
<tr>
<td>2. CO$_2$ + H$_2$O $\xrightarrow{4.3E+2 \over 3.6E+4} HCO_3^- + H^+$ Eigen et al. (1964)</td>
</tr>
<tr>
<td>3. HCO$_3^-$ $\xrightarrow{1.0E-4 \over 1.4E+5} CO_3^- + OH^-$ Eigen et al. (1964)</td>
</tr>
<tr>
<td>4. SO$_2$ + H$_2$O $\xrightarrow{3.4E+6 \over 2.0E+8} H^+ + HSO_3^-$ (20°C) Eigen et al. (1964)</td>
</tr>
<tr>
<td>5. HSO$_3^-$ $\xrightarrow{1.0E+4 \over 1.0E+11} SO_3^{2-} + H^+$ Erickson &amp; Yates (1976), Erickson et al. (1977)</td>
</tr>
<tr>
<td>6. N$_2$O$_3$ + H$_2$O $\xrightarrow{5.3E+3 \over 1.2E+2} 2$HNO$_2$ Gratzel et al. (1970), Schmid &amp; Krenmayr (1967), Komiyama &amp; Inoue (1978)</td>
</tr>
<tr>
<td>7. N$_2$O$_3$ $\xrightarrow{1.6E+8 \over 1.0E+9} NO + NO$_2$ Komiyama &amp; Inoue (1978) Gratzel et al. (1970)</td>
</tr>
<tr>
<td>8. HNO$_3$ $\xrightarrow{2.2E+8 \over 1.0E+8} H^+ + NO$_3^-$ McKay (1956)</td>
</tr>
<tr>
<td>9. HNO$_2$ $\xrightarrow{5.1E+5 \over 1.0E+9} H^+ + NO$_2^-$ Schmid et al. (1937)</td>
</tr>
<tr>
<td>10. N$_2$O$_4$ + H$_2$O $\xrightarrow{2.0E+2 \over 1.0E+8} HNO_3 + HNO_2$ Komiyama &amp; Inoue (1978) Gratzel et al. (1969)</td>
</tr>
<tr>
<td>11. N$_2$O$_4$ $\xrightarrow{7.7E+3 \over 3.0E+8} 2$NO$_2$ Grützelt et al. (1969), Komiyama &amp; Inoue (1978)</td>
</tr>
<tr>
<td>12. O$_3$ + NO$_2$ $\xrightarrow{1.6E+5 \over 5.0E+8} NO_5^-$ (9°C) Penekett (1972)</td>
</tr>
<tr>
<td>13. O$_3$ + SO$_2$ $\xrightarrow{5.9E+2 \over 2.0E+8} 2$H$^+ + SO_4^{2-}$ Erickson et al. (1977)</td>
</tr>
<tr>
<td>14. O$_3$ + SO$_3^{2-}$ $\xrightarrow{2.2E+5 \over 2.0E+8} SO_4^{2-}$ Erickson et al. (1977)</td>
</tr>
</tbody>
</table>
Table 2 (contd.)

<table>
<thead>
<tr>
<th>Source</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O$_3$ + HSO$_3^-$ $\rightarrow$ H$^+$ + SO$_4^{2-}$</td>
</tr>
</tbody>
</table>

* Units are in liters, moles, seconds

† There is considerable uncertainty in the rate constants for the nitrogen species reactions. The values used are, in most cases, compromises between values reported in more than one reference. In some cases forward or backward rate constants are inferred from equilibrium data from one reference (reaction 8 and 9) and/or from a backward or forward constant reported in a second reference at a different temperature (reactions, 6, 7, 10 and 11).

equations. That is, a set of the following type of equations was integrated,

$$\frac{d}{dz} [x](Z, R) = \phi_x(Z, R) + \psi_x(Z, R).$$ (4)

φ, the chemical rate was obtained from the kinetics equations in Tables 1 and 2; the mass transfer rate, ψ, (if any) is given in Equation (1). A complete set of the differential equations is given in the Appendix.

In order to simulate the chemistry in a rain event after a given fall distance, we must take into consideration drops of every size that reach the ground. To do this we have used the raindrop size distribution in air developed by Best (1950). This distribution is presented in Fig. 2. It depends only on the precipitation rate. To obtain the size distribution at ground level, the air size distribution must be multiplied by the fall velocity (Best, 1950).

The average ground level concentration, $[x]$, of a species, s, after a fall distance z is computed as

$$[x](z) = \frac{w}{p} \int_0^w u(R)[x](R, z) f(R)dR;$$ (5)

$$w = \frac{p}{\int_0^w u(R)f(R)dR.}$$ (6)

w is the ratio of the volume of rain water in air to the volume of air containing the water; p is the precipitation rate; f(R)dR is the fraction of water in drops of radius between R and R+dR.

Time dependence of chemical species as well as vertical

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**Fig. 2.** Raindrop size density (fraction of water) function for various precipitation rates. Calculated curves are shown for precipitation rates $p = 1, 10,$ and 25 mm h$^{-1}$ (Source: Best, 1950; and Hill and Adamowicz, 1976).
Influence of gaseous nitric acid

1063

dependence of ambient gases is obtained in steps. The vertical
is divided into zones with ambient concentrations independ-
ent of height within each zone. After the calculation for rain
reactions the ambient values, held constant in each zone
during the calculation, are appropriately modified. They are
modified to account for the material gained or lost for the
time of the step due to the effect of the rain as well as any effect
due to gas phase reactions. Vertical gas phase mixing is not
considered. The process is repeated with the net result, as time
(number of steps) increases, of variations in height and time of
ambient as well as liquid species concentrations. Most of the
data presented in this paper, however, are for a few minutes of
a 1000 m fall distance, 10 mm h⁻¹ rain event in which the
ambient concentrations are assumed constant in height and
time. Further, the model assumes that the raindrop size
distribution is that of an ideal fully developed rain event; that
is, the distribution is independent of fall distance and time.
Thus the average concentration has the following meaning: if A
is the area of a container perpendicular to falling rain and t
is the time spent in collecting the rain, then the total amount
of species s collected is Ap[t]. In the collector, continued
oxidation by O₂ will not significantly change [SO₂⁻].
[NO₂⁻] or pH. This is due to the low concentration of O₂ in
the rainwater that is collected. However, other oxidation
pathways (e.g. catalysis by metal ions) may convert the HSO₃⁻
to SO₂⁻, which could significantly alter the measured
[SO₂⁻], and perhaps, the pH. The model values of [SO₂⁻],
[NO₂⁻] and pH that we present are integrated averages from
the beginning of the rain until time t without chemical
reactions occurring in the container.

The assumption of an ideal fully developed rain event is
partly justified by the fact that 92% (rain rate = 10 mm h⁻¹) of
the initial model drops will have fallen 1000 m in the first
3.7 mm of the rain event, and 97% will have fallen the 1000 m
in 6.3 mm after the first drops hit the ground. Thus the ideal
raindrop distribution for a 10 mm h⁻¹ rain rate is essentially
developed at 1000 m after the first four minutes of the
beginning of the rain event as the ground. Therefore we
interpret our results as obtained from rain samples collected
after the first few minutes of the beginning of the rain event.
This interpretation will be reasonable if the ambient concen-
trations do not change very much during the time of interest.
For example, at the end of a 5-min simulation of a 1000 m,
10 mm h⁻¹ rain event (initially [HNO₃] = 10 ppb, [SO₂⁻] =
20 ppb, [O₃] = 50 ppb), ambient HNO₃ was reduced by
97%, while other significant species, liquid or gas, decreased by
less than half this amount.

RESULTS AND DISCUSSIONS

In order to explore the effects of nitric acid and the
nitrogen oxides on sulfate formation and acidification
in a rain event, we have considered four cases. The first
cases are concerned with effects in the first few
minutes of a rain event; whereas the last cases present
the results of the simulation of an extended rain event.

Case I. Effect of HNO₃ on acidification and SO₂⁻
formation

For the first several minutes of a steady-state rain,
we have calculated the pH, [SO₂⁻], and
[NO₅⁻],[SO₂⁻] for the rainfall collected at ground level. The acidification due to SO₂(0-20 ppb) oxidation by O₃ in the droplet and the HNO₃(0-10 ppb) subcloud scavenging are displayed in Fig. 3. The concentration range for HNO₃ is in agreement with recent observations of Spicer (1979). The fall distance was taken to be 1000 m, and the O₃ concentration was
assumed to be 50 ppb. The initial pH II was set to 5.56 for the raindrops entering the polluted zone. For case I, the initial concentrations of NO and NO₂ in the polluted zone were set equal to zero in order to first
determine the acidification due solely to subcloud scavenging of HNO₃. That is, only reactions 1-5, 8,
and 13-15 in Table 2 were used.

The ability of absorbed HNO₃ to retard the forma-
tion of SO₂⁻ is shown in Fig. 3. In the absence of
HNO₃, the [SO₂⁻] in the collected rainfall is 7 μM if
the ambient [SO₂⁻] = 8 ppb. However, in the presence
of [HNO₃] = 4 ppb, the rainwater [SO₂⁻] = 5 μM,
which is a decrease of almost 30%. Note, however, that
the presence of the HNO₃ causes the pH to change
from 4.70 to 4.50. At [SO₂⁻] = 8 ppm, the variation of
[HNO₃] from 0 to 8 ppb results in a pH change from
4.70 to 4.30. Thus HNO₃ reduces pH more than SO₂
alone does and this further reduction of pH retards
SO₂⁻ formation relative to quantities formed in the
absence of HNO₃. Also, for the initial portion of the
model steady-state rain, the molar concentration of
NO₃ will dominate that of SO₂⁻ if [HNO₃] ≥ 2 ppb
and [SO₂⁻] ≤ 20 ppb.

For the constraints imposed here, it is expected that
for [SO₂⁻] ≤ 20 ppb and [HNO₃] = 0, the pH would
remain above 4.50; an increase of [SO₂⁻] to 40 ppb
would lower the pH only to about 4.40. However, the
subcloud scavenging of HNO₃ at concentrations from
21 to 210 ppb would yield pH's of 4 to 3, respectively,
regardless of the SO₂.

Case II. Effect of NO, NO₂, HNO₃ on acidification

The conditions for Case II are similar to those for
Case I, but the following additions were incorporated:
(a) the complete reaction mechanism shown in Tables
2 and 3 were used and (b) the pollution zone was
assumed to have initial [NO₂⁻] = 10 ppb; the initial
concentrations of NO, N₂O₃, N₂O₄, and HNO₂ were
assumed to be zero.

Thus reactions 11 and 17 were used to transform
NO₃ into N₂O₅, which produced HNO₃ and HNO₂
(reaction 10) in the droplets. The binary reaction of
HNO₂ (reaction 6) produced N₂O₅, which in turn
produced NO (reaction 7). Thus, the initial
NO₂ (10 ppb) was caused to re-distribute among all the N-
oxides and HNO₂, and to participate in the sink
reaction (number 12) leading to NO₃.

The influence of these N-oxides and HNO₂ result-
ing from the initial NO₂ (10 ppb) on the pH, NO₂⁻,
NO₃⁻, and SO₂⁻ content of the collected rainwater is
compared with Case I in Table 4. It can be seen in this
table that NO₂ (10 ppb) and its progeny have no
significant influence on the pH, NO₃⁻, or SO₂⁻
content.

That NO₂ has no significant influence can be
understood by considering (a) the liquid phase reac-
tions involved in its transformation to NO₃ and
(b) its Henry's law constant which is 1.0. In the water
drop, NO₂ quickly comes into equilibrium with the
ambient concentration of the gas phase. NO₂ must
Fig. 3. The effect of ambient SO$_2$ and HNO$_3$ on pH, sulfate and nitrate in rain. Plotted are isopleths of pH (...........), SO$_4^{2-}$ (--- micromoles/liter), and the ratio (NO$_3^-$/SO$_4^{2-}$) (-----) for ambient values of SO$_2$ and HNO$_3$. The data are from a model simulation of a subcloud scavenging rain event. Conditions: Fall distance = 1000 m, initial pH = 5.54, ambient [O$_3$] = 50 ppb, ambient [NO] = [NO$_3$] = 0 ppb. The absorption of HNO$_3$ by the falling droplets lowers the pH and retards the formation of SO$_4^{2-}$ due to liquid phase reaction between dissolved O$_3$ and SO$_2$ species.

Table 3. Gas phase reactions*

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reaction</th>
<th>Authors, Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>16. N$_2$O$_3$</td>
<td>NO + NO$_3$(30°C)</td>
<td>Vlastaras &amp; Winkler (1967)</td>
</tr>
<tr>
<td>17. N$_2$O$_4$</td>
<td>2NO$_2$</td>
<td>Gray &amp; Yoffe (1955)</td>
</tr>
<tr>
<td>18. NO + O$_3$</td>
<td>NO$_2$ + O$_2$</td>
<td>Demerjian et al. (1974)</td>
</tr>
</tbody>
</table>

* Units are in liters, moles, seconds.

Table 4. Effect of N-oxides on acidification

<table>
<thead>
<tr>
<th>NO$_2$(ppb)</th>
<th>HNO$_3$(ppb)</th>
<th>pH</th>
<th>NO$_3^-$ (µM)</th>
<th>NO$_2^+$ (µM)</th>
<th>SO$_4^{2-}$ (µM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>4.51</td>
<td>0</td>
<td>0</td>
<td>9.62</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>4.51</td>
<td>$&lt;10^{-4}$</td>
<td>$&lt;10^{-3}$</td>
<td>9.62</td>
</tr>
<tr>
<td>0</td>
<td>10</td>
<td>4.17</td>
<td>0</td>
<td>47.8</td>
<td>5.80</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>4.17</td>
<td>$&lt;10^{-4}$</td>
<td>47.8</td>
<td>5.80</td>
</tr>
</tbody>
</table>

* [SO$_2$] = 20 ppb, [O$_3$] = 100 ppb.
† Initial pH = 5.54.
‡ Initially, the sole N-oxide species.
then react with itself (reaction II) in order to produce products that can lead to NO$_3^-$. This reaction is an inefficient process compared to that of SO$_2$ and its chemical mechanistic analogue, HNO$_3$. In these cases the species rapidly dissociates into products that are immediately oxidized by O$_3$. HNO$_3$, of course, dissociates directly into H$^+$ and NO$_2$. Thus in view of the chemical kinetics of HNO$_2$ and HNO$_3$ and their Henry's law constants of much less than 1.0, we can understand why these species have a much greater effect on pH and on NO$_3^-$ production than does NO$_2$.

**Case III. Effect of acidification prior to entering polluted zone**

Raindrops may be acidified prior to entering the polluted zone, perhaps due to formation from strongly acidic cloud condensation nuclei. Here we assume that occurs, and that the raindrops have an initial pH = 4 and [SO$_2^-$] = 50 $\mu$M prior to entering the polluted zone. The calculated values for selected gas phase concentrations of HNO$_3$ and SO$_2$ are presented in Table 5.

<table>
<thead>
<tr>
<th>HNO$_3$(ppb)</th>
<th>SO$_2$(ppb)</th>
<th>pH</th>
<th>NO$_3^-$($\mu$M)</th>
<th>SO$_2^-$($\mu$M)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>20</td>
<td>3.83</td>
<td>47.8</td>
<td>50.7</td>
</tr>
</tbody>
</table>

* Raindrops entering polluted zone have pH = 4, [SO$_2^-$] = 50 $\mu$M

If the [SO$_2$] = 20 ppb in the polluted zone, the change in pH and [SO$_2^-$] for the collected rainwater is insignificant. The falling rain is already too acidic to support the reactions between dissolved O$_3$ and HSO$_3^-$ and SO$_2^-$, however, the presence of HNO$_3$ leads to further acidification independently of the [SO$_2^-$].

**Case IV. Effect of HNO$_3$ on SO$_2^-$ and NO$_3^-$ production and pH in an extended rain event**

Figure 4 presents the variation of SO$_2^-$, NO$_2^-$, pH and ambient HNO$_3$ as a function of time resulting from the simulation of a 1000-m, 10-mm h$^{-1}$ rain event over a period of one hour. The initial values of pH, ambient O$_3$, SO$_2$, and HNO$_3$ are 55, 50 ppb, 20 ppb, and 5 ppb respectively. Liquid phase values are for simulated cumulative quantities (which are essentially the same as the instantaneous quantities in this example) collected at the ground from the beginning of the rain event to the time of interest, whereas HNO$_3$ values are instantaneous. The most noticeable feature of the figure is the rapid decrease in NO$_2^-$ (41 % in 1 h) and HNO$_3$ (70 % in 1 h) as compared to a slight increase in pH and SO$_2^-$.

The results of the simulation, presented in Fig. 4 could have been inferred by considering Fig. 3: for approximately constant O$_3$ and SO$_2$ concentrations, a lowering of ambient HNO$_3$ increases pH, sulfate and reduces NO$_3^-$ in drops reaching the ground. More generally by tracing changes in HNO$_3$ and SO$_2$ in Fig. 3 an idea as to the sequential properties of the rain event can be obtained.

For the chemical mechanisms used in the model we can expect a more rapid decrease in time of ambient HNO$_3$ than SO$_2$. Thus the qualitative results of the simulated 60-min subcloud scavenging rain event are expected to be valid for model conditions other than the ones used. That is, in general, we can expect a rapid decrease in time of NO$_2^-$ relative to changes in SO$_2^-$ and pH. Of course if the rain continues long enough, SO$_2^-$ concentrations will decrease as a result of the loss of ambient SO$_2$.

**SUMMARY**

The results of model simulations have been presented that describe the effect of ambient gases on sulfate and nitrate production and acidity in rain. The model is limited in that it attempts only to describe the subcloud scavenging of select ambient gases (SO$_2$, HNO$_3$, O$_3$, NO$_2$, and CO$_2$) and includes only one path by which SO$_2$ is transformed to SO$_2^-$ (oxidation by O$_3$). Thus, important processes such as incloud scavenging, subcloud scavenging of aerosols and SO$_2$ oxidation by steps other than reaction with O$_3$ (e.g., H$_2$O$_2$ and catalysts) are ignored. In addition, NH$_3$ has been excluded from the ambient gases; its effect would be to raise the pH and to counter the effects of HNO$_3$. Other features not included in the model are in-cloud processes, atmospheric dynamics, temperature variations, and drop dynamics. For example, drops can be retained in polluted regions for longer than their ‘fall time’ (as calculated from the terminal velocity). As the ambient gases are absorbed by the drops at rates that depend on height, gas phase concentration gradients are formed; however, vertical mixing of gases was not considered. Temperature changes could play an important role as rate constants and solubility constants depend on temperature. What can be expected for rain events occurring at different temperatures is not clear due to the complicated nature of the equations describing the process as well as due to the lack of information.
Fig. 4. Variations of $\text{SO}_2^{2-}$, $\text{NO}_3^-$, $S_T$ (total sulfur), and pH of cumulative (≈ instantaneous values) collected rain water and ambient $\text{HNO}_3_{\text{eq}}$ as a function of time during a 1000-m, 10-mm h$^{-1}$, 60-minute simulated subcloud scavenging rain event. Reactions in the collector are assumed not to occur. Initial conditions: pH = 55 ambient gas phase value; $[\text{O}_3] = 50$ ppb, $[\text{SO}_2] = 20$ ppb, $[\text{HNO}_3] = 5$ ppb, $[\text{NO}] = [\text{NO}_2] = 0$ ppb (liquid phase values are for quantities collected from the beginning of the event. Time = 0, to the time of interest). Note the rapid decline in $[\text{NO}_3^-]$ compared to the slight rise in [$\text{SO}_2^{2-}$] and pH. If the rain should stop at 60 min. and all of the HSO$_3^-$ were oxidized in the collector then $[\text{SO}_2^{2-}] = 17$ $\mu$M, and pH = 4.3.

CONCLUSIONS

As a result of this investigation of the effect of $\text{HNO}_3$ on the production of acidity, $\text{NO}_3^-$ and $\text{SO}_2^{2-}$, with $\text{O}_3$ as the only oxidizing agent, we have concluded that:

1. The subcloud scavenging of $\text{HNO}_3$ may control acidification in the initial stages of a rain event and may have a greater control over final pH than gaseous $\text{SO}_2^-$.

2. Gaseous $\text{HNO}_3$ inhibits the production of sulfate in rain by lowering the pH.

3. The oxides of nitrogen, NO and NO$_2$, play no role in acidification, nitrate and sulfate production in a subcloud scavenging rain event.
Influence of gaseous nitric acid

Precipitation (cloud scavenging) can have a greater control over final acidity than the subcloud scavenging of HNO$_3$ or SO$_2$. In this case sulfate production is reduced, but nitrate production is independent of the initial pH.

Gaseous HNO$_3$ is more rapidly removed from the atmosphere as compared to SO$_2$ and O$_3$.

In a subcloud scavenging rain event, as the event progresses, nitrate concentrations decrease much more rapidly than sulfate values. In the present simulation cumulative NO$_3^-$ decreases by about 42% in one hour, whereas SO$_2^{2-}$, as well as pH slightly increased.

Comparison of the results of the simulations to experimental values (Raynor et al., 1979 and Robertson et al., 1980) indicate that the quantitative results presented fall within the range of measured values; however this does not prove the model to be useful in simulating the results of specific rain events. Before this can be done more information that is usually obtained about a rain event is necessary. For example, we need to know the fall distance, ambient concentrations, drop size distribution and rain rate as a function of time, temperature, type of rain event (subcloud, inclow scavenging, or combination of both) and raindrop initial conditions. This, of course, is not a complete list of the conditions of a rain event; nevertheless such information in addition to rain species concentrations would be very helpful in validating a rain model.

Simulations, not discussed in this paper, indicate that, qualitatively, the conclusions presented here hold for substantially decreased rain rates (which is equivalent to a reduction in average drop size). These simulations also show that the processes we have taken into account do not have the capacity to lower pH below ~ 3.5. Since there is evidence of pH's as low as ~ 2.2 (Likens and Bormann, 1974) we conclude that our present model has deficiencies. Our next step will be to include H$_2$O$_2$ in model calculations.

As a final word, we would like to reiterate that this exercise has been to theoretically investigate the effects of a limited set of possible processes that may occur in a rain event, namely the effect of gaseous nitric acid on sulfate and nitrate production and acidity in a rain event. With respect to this a better understanding of the chemistry of rain has been obtained.

REFERENCES


Presented here is the set of differential equations used for the chemical kinetics in the aqueous droplets. The equations are the mathematical formulation of the reactions in Table 2. All concentrations are for the liquid phase, unless denoted with a subscript g (gas phase). The value of the mass transfer coefficient, $k_\infty$, and Henry's law constant, $H$, depend on the species.

\[ \frac{d[H^+]}{dz} = -k_1[H^+][OH^-] + k_{-1} \]
\[ + k_{+1}[CO_2][HCO_3^-] \]
\[ + k_{+4}[SO_2][SO_3^{2-}] + \frac{3k_s}{R}[SO_2]_g - H[SO_2]_g \]
\[ \frac{d[H^+][SO_3^{2-}]}{dz} = k_{+4}[SO_2]_g - k_{-4}[H^+][HSO_3^-] \]
\[ - k_{-5}[HSO_3^-] + k_{+4}[SO_3^{2-}][H^+] \]
\[ - k_{+5}[O_3^-][HSO_3^-] \]
\[ \frac{d[SO_3^{2-}]}{dz} = k_{+5}[SO_3^{2-}][H^+] - k_{-5}[SO_3^{2-}][H^+] \]
\[ - k_{+4}[O_3^-][SO_3^{2-}] \]
\[ \frac{d[N_2O_5]}{dz} = -k_{+8}[N_2O_5] - k_{-11}[NO][NO_2] \]
\[ + k_{10}[N_2O_4] + \frac{3k_s}{R}[NO_2]_g - H[NO_2]_g \]
\[ \frac{d[NO]}{dz} = k_{+1}[N_2O_5] - k_{-1}[NO][NO_2] \]
\[ - k_{+10}[N_2O_4] + \frac{3k_s}{R}[NO_2]_g - H[NO_2]_g \]
\[ \frac{d[HNO_2]}{dz} = -k_{-8}[HNO_3] + k_{-8}[H^+][NO_3^-] \]
\[ + k_{10}[N_2O_4] + \frac{3k_s}{R}[NO_2]_g - H[NO_2]_g \]
\[ \frac{d[N_2O_4]}{dz} = k_{+1}[N_2O_5] - k_{-11}[NO_2]^2 \]
\[ - k_{+10}[N_2O_4] + \frac{3k_s}{R}[NO_2]_g - H[NO_2]_g \]
\[ \frac{d[NO_2]}{dz} = k_{+8}[HNO_2] - k_{-2}[H^+][NO_3^-] \]
\[ + k_{12}[O_3][SO_2] + k_{13}[SO_2][HO_3^-] \]
\[ + \frac{3k_s}{R}[O_3]_g - H[O_3] \]
\[ \frac{d[O_3]}{dz} = -k_{+1}[SO_2] + k_{-1}[SO_3^{2-}] \]
\[ + k_{14}[SO_2][SO_3^{2-}] \]