



A Modeling Study of the Influence of Ice Scavenging on the Chemical Composition of Liquid-Phase Precipitation of a Cumulonimbus Cloud

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trainment and/or washout. The balance of these two last processes will determine the possible enhancement of sulfates and hydrogen peroxide in the gaseous phase. One can expect that the result of this balance may differ from one cloud involving ice to another. Moreover, if ice-phase processes are taken into account in the exchanges of species between different classes of hydrometeors, previous results could be strongly modified with changes in scavenging rates, as experimentally observed by Topol (1986). The fraction of species retained in ice would not participate in the aqueous-phase chemistry but rather would be released into atmospheric layers that are undersaturated relative to ice. Such detrainment events would alter the chemical composition of the low layers even though the ice-phase processes took place in upper levels.

Direct freezing of droplets and their hydrodynamical collection by sedimenting ice particles constitute alternative ways for the removal of species, disturbing the usual interphase transfer. During field experiments Murakami et al. (1983) observed that below-cloud sulfate particles were removed by snow twice as efficiently as by rain.

Direct uptake of aerosol particles by snow or hail seems to be particularly efficient. Laboratory studies (Mitra et al. 1990) show that substantial amounts of SO_2 can be adsorbed onto ice surface during growth of snow crystals by vapor deposition, while the entrapped fraction of SO_2 becomes negligible once the crystals have ceased their growth. However, Diehl et al. (1996) have emphasized that the uptake of gaseous chemicals by snow via adsorption is less rapid than the uptake by drops. Much larger quantities are thus accommodated by a drop than by an ice crystal of the same water mass. Hence, it is expected that in the lower troposphere the microphysical processes linked to the ice-phase and relevant for the scavenging of chemicals are those involving exchanges with the liquid phase rather than with the gas phase directly. Among them, riming and the freezing of drops are likely to be the dominant processes. Their relative importance will depend on the stage of development of the cloud. Riming covers the highest spatial extent in the cloud compared to interactions between rain and graupel.

Direct uptake of chemical species (adsorption) by ice becomes important when larger exposure times of snow particles are involved, as is the case for fresh ground-deposited snow. Until the next snowfall event adsorption/desorption of the chemical species will probably affect the composition of the snow at the surface (Sigg et al. 1992). The knowledge of this process (as well as possible diffusion into the ice lattice) is important for chemical retrieval of past atmospheres from ice core analyses. Nevertheless, to assess the relative contribution of this process compared to the others, one needs to know the exchange of species in the cold-precipitating cloud that yielded the snowfall.

Two-dimensional kinetic models including ice phase

chemistry have been formulated by Hegg et al. (1984, 1986), Barth et al. (1992), Leighton et al. (1990), and Rutledge et al. (1986) to study scavenging in warm- and cold-frontal rainbands. Whereas Leighton et al. (1990) found no impact of ice on rain sulfate concentrations because the 0°C isotherm was well above the scale height of the sulfur dioxide profile, Barth et al. (1992) showed significant amounts of sulfate and hydrogen peroxide to exist in ice particles of cold-frontal rainbands. Hence, the impact of ice-phase chemistry has not clearly been assessed, particularly for gas-phase concentrations.

Besides the evaluation of the amount of acid precipitation in regional models in order to drive some parameterizations (e.g., Song and Leighton 1996) for global chemistry models, it is of interest to assess the extent to which an isolated cloud alters gas-phase concentrations and how long these remain disturbed after the cloud event. This last point is particularly relevant for organized cloud systems, in which clouds succeed rapidly one after another. Strong convective clouds are very efficient at transporting ground-emitted chemical products to higher altitudes where mixed-phase conditions exist. These conditions can be found at the rear of the warm sector just ahead of the cold front where significant updrafts advect substantial amounts of pollutants to ice levels through a zone of liquid water. From a chemical point of view, it is important to discriminate the processes involving the ice-phase during the cloud lifetime in order to spare computational costs for irrelevant processes and to help find suitable parameterizations for larger-scale models.

In this paper, we investigate the role of ice-phase processes on the chemistry in the case of an isolated strong convective cloud system. Exchanges of species with the ice particles will be limited to interactions with cloud water and rainwater. This study employs a two-dimensional model and aims to evaluate the relative importance of various microphysical processes on the cloud chemistry using the latest laboratory findings relative to uptake of chemical species by ice.

2. Description of the model

The cloud model is a two-dimensional (x, z) time-dependent Eulerian scheme (Cautenet and Lefeuvre 1994). It is nonhydrostatic and anelastic. Both horizontal and vertical grid resolutions are of 200 m and the overall dimension of the domain is $11 \text{ km} \times 11 \text{ km}$. The microphysical code uses four classes of hydrometeors: cloud water, rain, cloud ice and snow, and graupel (or hail). The scheme of Kessler (1969) is used for the cloud droplet coalescence with a threshold put at 1 g kg^{-1} and rain distribution follows the scheme of Marshall and Palmer (1948). Cloud ice and snow are regrouped into the same category. The reader is referred to these publications for further details. Hereafter, some features that are most relevant for chemistry are summarized. The cloud droplet population is monodisperse

TABLE 1. List of the reactions and equilibrium in the gas phase with corresponding rate and equilibrium constants [from Lelieveld and Crutzen (1991), G27 from De More et al. (1994), G4 modified by Stockwell (1994)].

Gas-phase reaction scheme		Rate constants
G1 ^c	$\text{O}_3 + \text{H}_2\text{O} + h\nu \rightarrow 2\text{OH}\cdot + \text{O}_2$	J_{eff}
G2	$\text{O}_3 + \text{OH}\cdot \rightarrow \text{HO}_2 + \text{O}_2$	$1.6 \times 10^{-12} \exp(-940/T)$
G3	$\text{O}_3 + \text{HO}_2\cdot \rightarrow \text{OH}\cdot + 2\text{O}_2$	$1.1 \times 10^{-14} \exp(-500/T)$
G4	$2\text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	$[2.3 \times 10^{-13} \exp(600/T) + 1.7 \times 10^{-33} [\text{M}] \exp(1000/T)] \times [1 + 1.4 \times 10^{-21} [\text{H}_2\text{O}] \exp(2200/T)]$
G5	$\text{H}_2\text{O}_2 + h\nu \rightarrow 2\text{OH}\cdot$	4.6×10^{-6}
G6	$\text{H}_2\text{O}_2 + \text{OH}\cdot \rightarrow \text{HO}_2 + \text{H}_2\text{O}$	$3.3 \times 10^{-12} \exp(-200/T)$
G7	$\text{CH}_4 + \text{OH}\cdot + \text{O}_2 + \text{M} \rightarrow \text{CH}_3\text{O}_2 + \text{H}_2\text{O} + \text{M}$	$2.3 \times 10^{-12} \exp(-1700/T)$
G8	$\text{CH}_3\text{O}_2\cdot + \text{HO}_2\cdot \rightarrow \text{CH}_3\text{O}_2\text{H} + \text{O}_2$	4.0×10^{-12}
G9	$\text{CH}_3\text{O}_2\text{H} + \text{O}_2 + h\nu \rightarrow \text{CH}_2\text{O} + \text{HO}_2 + \text{OH}\cdot$	4.6×10^{-6}
G10	$\text{CH}_3\text{O}_2\text{H} + \text{OH} \rightarrow \text{CH}_3\text{O}_2 + \text{H}_2\text{O}$	5.6×10^{-12}
G11	$\text{CH}_3\text{O}_2\text{H} + \text{OH} \rightarrow \text{CH}_2\text{O} + \text{OH}\cdot + \text{H}_2\text{O}$	4.4×10^{-12}
G12	$\text{CH}_2\text{O} + 2\text{O}_2 + h\nu \rightarrow \text{CO} + 2\text{HO}_2$	1.7×10^{-5}
G13	$\text{CH}_2\text{O} + h\nu \rightarrow \text{CO} + \text{H}_2$	3.3×10^{-5}
G14	$\text{CH}_2\text{O} + \text{OH}\cdot + \text{O}_2 \rightarrow \text{CO} + \text{HO}_2 + \text{H}_2\text{O}$	1.1×10^{-11}
G15	$\text{CO} + \text{OH}\cdot + \text{O}_2 + \text{M} \rightarrow \text{CO}_2 + \text{HO}_2 + \text{M}$	2.4×10^{-13}
G16	$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$	$2.0 \times 10^{-12} \exp(-1400/T)$
G17	$\text{NO}_2 + \text{O}_2 + h\nu \rightarrow \text{NO} + \text{O}_3$	5.6×10^{-3}
G18	$\text{NO} + \text{HO}_2\cdot \rightarrow \text{NO}_2 + \text{OH}\cdot$	$3.7 \times 10^{-12} \exp(240/T)$
G19	$\text{NO} + \text{CH}_3\text{O}_2\cdot + \text{O}_2 \rightarrow \text{NO}_2 + \text{CH}_2\text{O} + \text{HO}_2\cdot$	$4.2 \times 10^{-12} \exp(180/T)$
G20	$\text{NO}_2 + \text{OH} (+ \text{M}) \rightarrow \text{HNO}_3 (+ \text{M})$	1.2×10^{-11}
G21	$\text{HNO}_3 + h\nu \rightarrow \text{NO}_2 + \text{OH}$	3.2×10^{-7}
E22	$\text{CH}_2\text{O} + \text{HO}_2\cdot \rightleftharpoons \text{O}_2\text{CH}_2\text{OH}$	6.7×10^{-15}
G23	$\text{O}_2\text{CH}_2\text{OH} + \text{HO}_2\cdot \rightarrow \text{HCO}_2\text{H} + \text{HO}_2 + \text{O}_2$	2.0×10^{-12}
G24	$\text{O}_2\text{CH}_2\text{OH} + \text{NO} + \text{O}_2 \rightarrow \text{HCO}_2\text{H} + \text{HO}_2 + \text{NO}_2$	7.0×10^{-12}
G25	$\text{O}_2\text{CH}_2\text{OH} + \text{O}_2\text{CH}_2\text{OH} \rightarrow 2\text{HCO}_2\text{H} + \text{HO}_2 + \text{H}_2\text{O}$	1.2×10^{-13}
G26	$\text{HCO}_2\text{H} + \text{OH} + \text{O}_2 \rightarrow \text{CO}_2 + \text{HO}_2 + \text{H}_2\text{O}$	3.2×10^{-13}
G27	$\text{SO}_2 + \text{OH} (+ \text{M}) \rightarrow \text{H}_2\text{SO}_4 + \text{HO}_2$	$k_\infty = 1.5 \times 10^{-12}; \text{Fc} = 0.6; k_0 = 3. \times 10^{-31} (T/300)^{-3.3}$

* Reaction rate constants of first-order reactions are in s^{-1} , of second-order reactions in $\text{molecule}^{-1} \text{cm}^3 \text{s}^{-1}$.

${}^1\text{O}_3 + \text{h}\nu \rightarrow \text{O}_2 + \text{O}({}^1\text{D})$	$J_0 = 1.6 \times 10^{-5}$
$\text{O}({}^1\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH}$	$k_1 = 2.2 \times 10^{-10}$
$\text{O}({}^1\text{D}) + \text{N}_2 \rightarrow \text{O}({}^3\text{P}) + \text{N}_2$	$k_2 = 4. \times 10^{-11} \exp[67(1/T - 1/298.)]$
$\text{O}({}^1\text{D}) + \text{O}_2 \rightarrow \text{O}({}^3\text{P}) + \text{O}_2$	$k_3 = 2.6 \times 10^{-11} \exp[110(1/T - 1/298)]$
$J_{\text{eff}} = J_0 k_1 [[\text{H}_2\text{O}]/(k_1 [\text{H}_2\text{O}] + k_2 [\text{O}_2] + k_3 [\text{N}_2])]$	

TABLE 2. List of the gas-aqueous phase equilibria with corresponding Henry's law constants and of aqueous equilibria with corresponding dissociation constants (from Lelieveld and Crutzen 1991).

Gas-aqueous and aqueous phase equilibria		Henry's law and dissociation constants K_{298}^*
E1	$\text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{OH}^-$	$1.0 \times 10^{-14} \exp[-6716(1/T - 1/298)]$
H1	$\text{O}_3 \text{ (gas)} \leftrightarrow \text{O}_3 \text{ (aq)}$	$1.1 \times 10^{-2} \exp[2300(1/T - 1/298)]$
H2	$\text{H}_2\text{O}_2 \text{ (gas)} \leftrightarrow \text{H}_2\text{O}_2 \text{ (aq)}$	$7.4 \times 10^4 \exp[6615(1/T - 1/298)]$
E2	$\text{H}_2\text{O}_2 \text{ (aq)} \leftrightarrow \text{HO}_2^- + \text{H}^+$	$2.2 \times 10^{-12} \exp[-3730(1/T - 1/298)]$
H3	$\text{CH}_3\text{O}_2\text{H (gas)} \leftrightarrow \text{CH}_3\text{O}_2\text{H (aq)}$	$2.2 \times 10^2 \exp[5653(1/T - 1/298)]$
H4	$\text{CH}_2\text{O (gas)} \leftrightarrow \text{CH}_2\text{(OH)}_2 \text{ (aq)}$	$6.3 \times 10^3 \exp[6425(1/T - 1/298)]$
H5	$\text{HNO}_3 \text{ (gas)} \leftrightarrow \text{HNO}_3 \text{ (aq)}$	$2.1 \times 10^5 \exp[8700(1/T - 1/298)]$
E3	$\text{HNO}_3 \text{ (aq)} \leftrightarrow \text{H}^+ + \text{NO}_3^-$	15.4
H6	$\text{HO}_2 \text{ (gas)} \leftrightarrow \text{HO}_2 \text{ (aq)}$	$2.0 \times 10^3 \exp[6600(1/T - 1/298)]$
E4	$\text{HO}_2 \text{ (aq)} \leftrightarrow \text{H}^+ + \text{O}_2^- \text{ (aq)}$	3.5×10^{-5}
H7	$\text{OH}^* \text{ (gas)} \leftrightarrow \text{OH}^* \text{ (aq)}$	$25 \exp[5025(1/T - 1/298)]$
H8	$\text{NO}_2 \text{ (gas)} \leftrightarrow \text{NO}_2 \text{ (aq)}$	$6.4 \times 10^{-3} \exp[2500(1/T - 1/298)]$
H9	$\text{NO (gas)} \leftrightarrow \text{NO (aq)}$	$1.9 \times 10^{-3} \exp[1480(1/T - 1/298)]$
H10	$\text{CH}_3\text{O}_2 \text{ (gas)} \leftrightarrow \text{CH}_3\text{O}_2 \text{ (aq)}$	$2.0 \times 10^3 \exp[6600(1/T - 1/298)]$
H11	$\text{HCO}_2\text{H (gas)} \leftrightarrow \text{HCO}_2\text{H (aq)}$	$3.7 \times 10^3 \exp[5700(1/T - 1/298)]$
E5	$\text{HCO}_2\text{H (aq)} \leftrightarrow \text{H}^+ + \text{HCO}_2^-$	$1.8 \times 10^{-4} \exp[-1510(1/T - 1/298)]$
H12	$\text{SO}_2 \text{ (gas)} \leftrightarrow \text{SO}_2 \text{ (aq)}$	$1.2 \exp[3120(1/T - 1/298)]$
E6	$\text{SO}_2 \text{ (aq)} \leftrightarrow \text{H}^+ + \text{HSO}_3^-$	$1.7 \times 10^{-2} \exp[-2090(1/T - 1/298)]$
E7	$\text{HSO}_3^- \leftrightarrow \text{H}^+ + \text{SO}_3^{2-}$	$6. \times 10^{-8} \exp[-1120(1/T - 1/298)]$

* Henry's law constants in mol L⁻¹ atm⁻¹ and dissociation constants in mol L⁻¹ at 298 K.

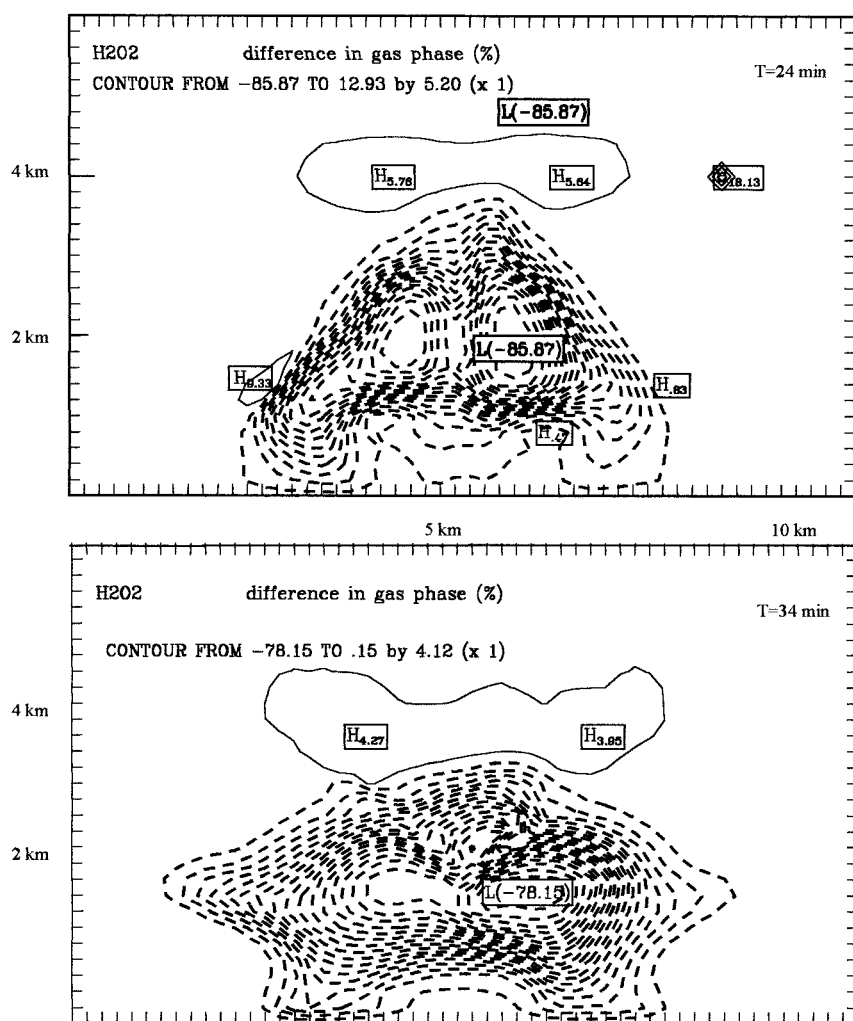


FIG. 16. Difference in gas phase concentrations of hydrogen peroxide expressed relative to the case where ice is accounted for in the chemistry module (given in percent).

storm. The partitioning of the species between the different phases depends strongly on how many processes are dominant and which they are. The nature of these processes and their number (one or more process to be dominant) evolves following the stage of development of the cloud and can differ from one species to another. The reason for this last point comes from the fact that each species has its own solubility and retention coefficient. The scenario developed by this cumulonimbus cloud allows us to distinguish the following features.

- First, when freezing of drops and graupel riming are the dominant processes for the transfer of species from liquid phases to graupel, a change in sulfate production is observed. This change is made through a feedback effect of the riming process, that is, enhancement of the oxidation of SO₂ in sulfates in cloud droplets, reducing both SO₂ and H₂O₂ available for transfer to rain.
- Second, when only one process dominates the ex-

change of species with graupel, the result depends on whether it is the riming of graupel or freezing of drops. When riming is the main process both for SO₂ and H₂O₂, the production of sulfate in rainwater is more efficient, whereas when freezing of drops is dominant for S(IV) a reduction of sulfate production in rain is observed.

- Finally, the decaying stage of the cloud allows a competition between riming and sedimentation processes. S(IV) is more sensitive than hydrogen peroxide to sedimentation effects, which induces a net decrease in its content in rainwater (subsequently over all condensed phases).

The chemical role of ice can be summarized as follows: there is an enrichment in precipitation in the oxidant H₂O₂, while slightly more sulfates and less S(IV) are found in this precipitation (solid and liquid). Ice-phase processes also induce higher contents of sulfates in the gas phase as a consequence of the riming process.

