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The potential for elucidating sulfate and acidity production in clouds using a mesoscale model with quasi-spectral microphysics

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ABSTRACT

A three-dimensional mesoscale numerical model with detailed parameterized microphysics of clouds and precipitation has been applied to the study of gas and aerosol wet removal. Two-dimensional sensitivity tests combining meteorological predictions with pollutant scavenging and aqueous chemistry parameterizations have been carried out for continental and maritime clouds over an idealized topography. Model results indicate that nucleation scavenging is the most efficient in-cloud removal mechanism. Furthermore, differences in cloud droplet spectra in continental versus maritime cases, lead to different contributions of nucleation scavenging, in-solution oxidation of SO_2 by ozone and hydrogen peroxide, to wet sulfate deposition and acidity production. This results emphasizes the need for coupled treatment of dynamical, microphysical and chemical processes.

1. Introduction

It is now well-established that meteorological factors interact in a complex non-linear way with physicochemical factors to generate acid wet deposition. Several recent numerical studies have been performed with varying degrees of complexity of chemical processes and cloud dynamics (Tremblay and Leighton, 1986; Rutledge et al., 1986; Walcek and Taylor, 1986). Previously, we have presented such a study for the case of sulfur scavenging in a mesoscale meteorological model with semi-spectral microphysics (Chaumerliac et al., 1987). Here, we describe how this model has been extended to include both sulfate and acidity productions and to handle more detailed chemistry.

A typical meteorological scenario is illustrated with results of two-dimensional simulations performed for continental and maritime clouds forming over an idealized bell-shaped mountain. First, we recall that contributions of nucleation scavenging and dynamical capture of sulfate particles to wet sulfate deposition differ in continental versus maritime cases because of their contrasting droplet spectra. Then, we show that acidity is also distributed in a contrasting way in these two types of cloud depending on the efficiency of microphysical processes such as accretion or sedimentation.

2. Model presentation

We shall focus on the microphysical and physicochemical aspects of the model pertinent to the understanding of this paper. Further details can be found elsewhere (Chaumerliac et al., 1987; Nickerson et al., 1986; Chaumerliac et al., 1986). The model includes the following warm rain microphysical processes: nucleation, condensation, evaporation, accretion, autoconversion, self-collection and sedimentation. We make use of the following activation spectrum to form cloud droplets:

$$N = CS^k, \tag{1}$$

where S is the supersaturation, C and k empirical

constants related to the origin of the air mass (continental or maritime), and adopted by many authors (Pruppacher and Klett, 1978).

Liquid (both cloud and rain) water is assumed to be distributed log-normally with diameter. Thus,

$$dN = \frac{N}{\sqrt{2\pi}\sigma D} \exp\left(-\frac{1}{2\sigma^2} \ln^2 \frac{D}{D_0}\right) dD \qquad (2)$$

is the number of droplets in the size range D to $D + dD$. Here, σ and D_0 are distribution parameters. Only one of these two can be diagnosed, given q and N. The microphysical system of equations is closed by assuming a constant value of σ and by computing D_0. Assumed values for the cloud are $\sigma_c = 0.1575$ (continental case) or $\sigma_c = 0.2775$ (maritime case), whereas for the rain $\sigma_r = 0.547$. The conversion rates of cloud droplets to raindrops are computed according to Berry and Reinhardt's parameterizations (Berry and Reinhardt, 1973), appropriate to the log-normal distribution. Autoconversion and self-collection are parameterized in a stochastic mode, whereas accretion is treated as a continuous process.

The predictive variables for microphysics as well as the microphysical processes are summarized in Fig. 1. Sulfate particles are also assumed to be distributed according to a log-normal function, setting the dispersion parameter σ_p to 0.69.

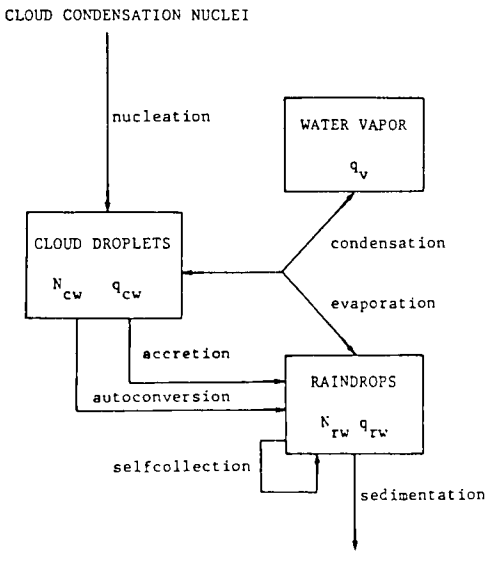

Fig. 1. Schematic diagram of microphysical processes.

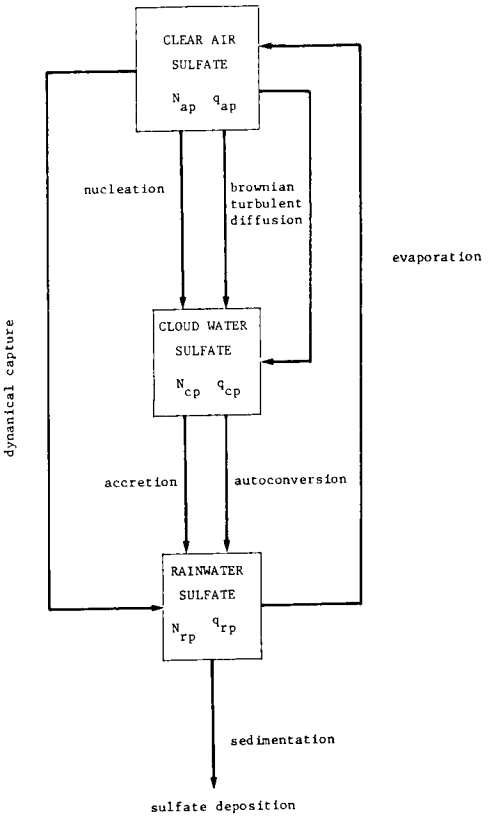

Fig. 2. Schematic diagram of aerosol physicochemical processes.

Number concentration N and volume concentration q are the predictive variables for aerosol particles. We distinguish between 3 categories of particle: some are free in the air, others are attached to cloud droplets and the 3rd category consists of aerosols removed by precipitation. A schematic diagram is provided in Fig. 2 for the description of the various processes at work between the three aerosol classes. Parameterizations developed for Brownian and turbulent diffusion rates are taken from Dingle and Lee (1973). The dynamical capture rate is calculated after Dana and Hales (1976).

In addition to aerosol physicochemical processes, chemical production of sulfate is introduced through SO_2 in solution oxidation by ozone and hydrogen peroxide in the presence of ammonia.

Gaseous concentrations are initialized with exponential profiles (Rutledge et al., 1986) as follows:

$$P_{SO_2} = 2.5 \exp\left(-\frac{z}{2000}\right) \text{ppb},$$

$$P_{NH_3} = P_{H_2O_2} = \exp\left(-\frac{z}{2000}\right) \text{ppb},$$

$$P_{O_3} = 30 \text{ ppb}, \quad (3)$$

where z is the altitude (m).

In this paper, we are not attempting a comprehensive study, but rather wish to illustrate what the model can do.

Equilibrium relations defining the various ionic concentrations in liquid water as related to the gas partial pressures are listed in Table 1. All equilibrium constants are adjusted for temperature according to Van't Hoff's relation:

$$K = K_{298} \exp(E/R(1/T - 1/298)), \quad (4)$$

where E is the activation energy, K_{298} the equilibrium constant at 298°K and R the universal gas constant.

SO_2 oxidation rates by H_2O_2 and O_3 are also reported in Table 1.

Both in cloud and rainwater, the following electroneutrality equation must be satisfied:

$$[H^+] + [NH_4^+] = [OH^-] + [HSO_3^-] + [2SO_4^{2-}]. \quad (5)$$

All the concentrations above can be expressed as a function of both the equilibrium constants in Table 1 and the hydrogen ion concentrations.

To adequately describe the processes involved in the gas removal by clouds and rain, we should have considered 3 forms for a soluble species: its gaseous phase, its dissolved form in the cloud water and its dissolved form in the rainwater. To limit the number of predictive equations of our model, we have merged the first 2 forms and we shall express the total double-phase concentration of a species X_{ac} in the air and cloud environments as:

$$X_{ac} = \frac{p_x}{RT} + \frac{\rho_a}{\rho_w} q_{cw} X_c, \quad (6)$$

where p_x (atm) is the partial pressure of the species in the air, X_c the concentration of this species in the cloud aqueous phase (mole/l_{water}). Then q_{cw} designates the cloud water mixing ratio (kg/kg) and the concentration X_{ac} is obtained in mole/l_{air}.

Finally, we define X_r as the species concentration in rainwater. We thus obtain the time rate of change of each concentration for a given soluble species X by the two following equations:

$$\frac{dX_{ac}}{dt} = -S_{acc} - S_{auto} - S_{scav} - S_{oxid} - S_{eva}, \quad (7)$$

$$\frac{dX_r}{dt} = S_{acc} + S_{auto} + S_{scav} - S_{oxid} - S_{eva} + S_{sed}, \quad (8)$$

where S stands for the various sources and sinks for concentrations. The subscript "acc" refers to accretion of cloud droplets by raindrops and "auto" to autoconversion of cloud droplets into raindrops. The subscripts "eva" and "sed" are related to rain evaporation and sedimentation,

Table 1. *Equilibrium and reaction rates*

Equilibrium	Equilibrium constant (M/atm)	$\Delta E/R$ (K)
$(SO_2)_g \rightleftarrows (SO_2)_{aq}$	$K_1 = 1.23$	3120
$(NH_3)_g \rightleftarrows (NH_3)_{aq}$	$K_3 = 58$	4085
$(H_2O_2)_g \rightleftarrows (H_2O_2)_{aq}$	$K_5 = 9.7.10^4$	6600
$(O_3)_g \rightleftarrows (O_3)_{aq}$	$K_6 = 1.15.10^{-2}$	2560
$(SO_2)_g \rightleftarrows HSO_3^- + H^+$	$K_2 = 1.7.10^{-2}$	2090
$(NH_3)_{aq} \rightleftarrows NH_4^+ + OH^-$	$K_4 = 1.7.10^{-5}$	−4325
Oxidation reactions	**Reaction rate (M s^{-1})**	
$(SO_2)_{aq} + H_2O_2 \rightarrow SO_4^{2-} + 2H^+$	$8.10^4 \exp(-3650(1/T - 1/298)/(0.1 + [H^+])$*	
$S_{IV} + O_3 \rightarrow SO_4^{2-} + 2H^+ + \text{products}$	$4.39.10^{11} \exp(-4131/T) + 2.56.10^3 \exp(-966/T)/[H^+]$†	

* Martin (1983). † Maahs (1983).

respectively. The subscripts "oxid" and "scav" designate oxidation in the aqueous phase (for SO_2 and H_2O_2) and scavenging from the gas phase to rainwater through mass transfer, respectively.

Accretion, autoconversion and evaporation rates are deduced from their corresponding microphysical rates with proportionality relationships.

The sedimentation term is formulated as follows:

$$S_{sed} = \frac{\partial}{\partial z}\left(\frac{X_r}{q_{rw}} S_q\right), \tag{9}$$

where q_{rw} is the rainwater mixing ratio and S_q is the sedimentation flux of raindrops.

Thus, the scavenging rate S_{scav} is given by:

$$S_{scav} = \int_0^\infty \left(k_g\left(\frac{p_x}{RT} - \frac{X_r}{H_{eff}\, RT}\right)\pi D^2\right) dN, \tag{10}$$

with

$$k_g = \frac{D_g}{D} 2\bar{f}, \tag{11}$$

where H_{eff} is the effective solubility constant for X in rainwater, D the mean raindrop diameter,

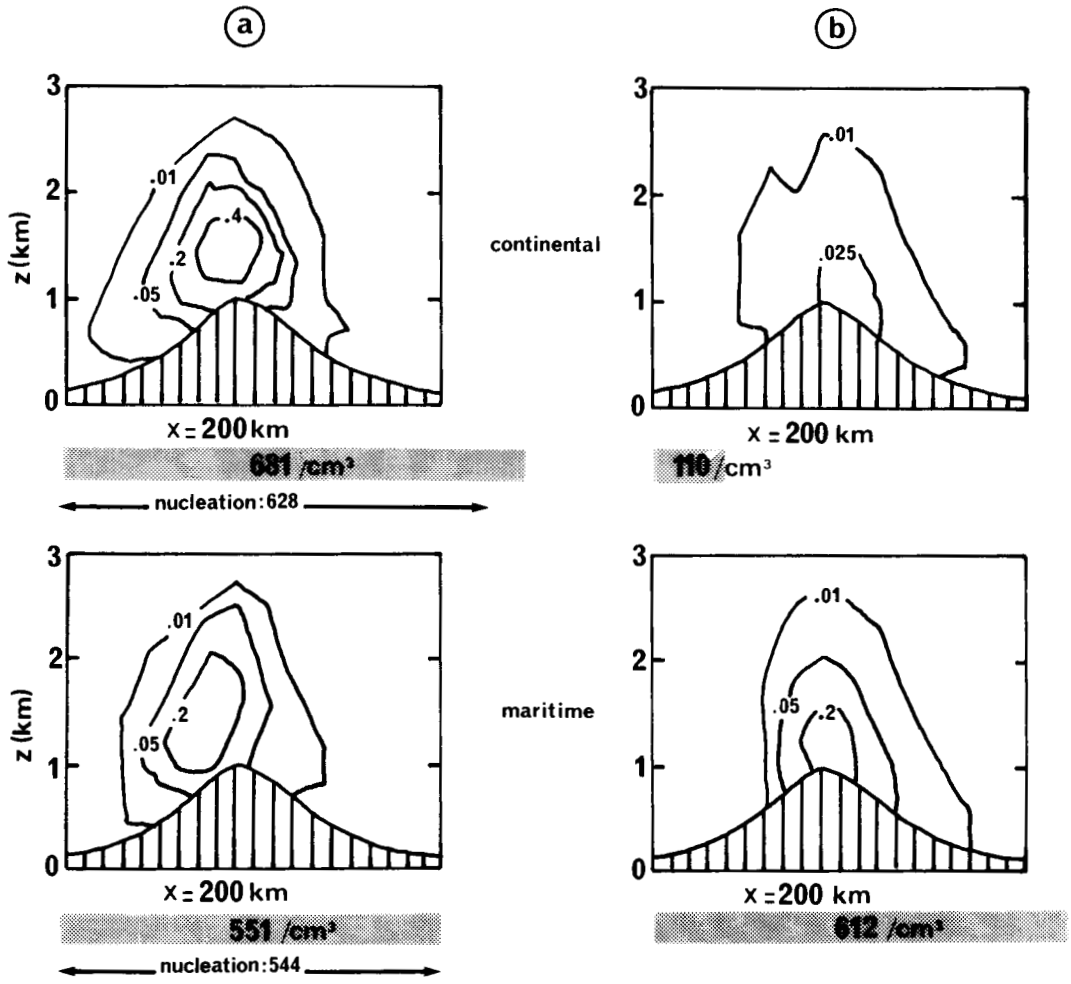

Fig. 3. Vertical cross-sections of: (a) cloud-water mixing ratio (g kg^{-1}) and (b) rainwater mixing ratio (g kg^{-1}) after a 1-h model time for continental and maritime cases. Below each figure, the maximum number concentration of aerosols captured by cloud-water and rainwater is reported (dashed areas) with indications of the relative contribution of nucleation scavenging effects.

D_g the molecular diffusion coefficient of X. The scavenging rate is integrated over the entire raindrop spectrum, dN being given by eq. (2). The ventilation factor $\bar{f}$, already used in the expression for the condensation of water vapor to rainwater is written (Pruppacher and Klett, 1978) as:

$$\bar{f} = 0.78 + 0.308\,\mathrm{Re}^{1/2}\mathrm{Sc}^{1/3}, \quad (12)$$

where Re is the Reynolds number and Sc the Schmidt number. We have fitted the expression $\mathrm{Re}^{1/2}\mathrm{Sc}^{1/3}$ as a function of diameter D by:

$$\mathrm{Re}^{1/2}\mathrm{Sc}^{1/3} = -1.406\,10^6\,D^2 + 1.725\,10^4\,D - 0.675. \quad (13)$$

The set of equations (7) and (8) is specified for SO_2, H_2O_2 and NH_3. Ozone is also considered in the model but is not advected because of its large excess with respect to the amount consumed in oxidizing SO_2.

3. Sulfate particle scavenging by maritime and continental clouds: nucleation effects

In order to simultaneously test the microphysical and physicochemical parameterizations, a series of two-dimensional sensitivity tests have been carried out. The model is run over an idealized bell-shaped mountain, 1 km high and 25 km in half-width. A two-layer atmosphere is considered, with a lower layer of constant lapse rate up to 8 km and an isothermal layer aloft. The surface temperature is set to 280°K. The initial

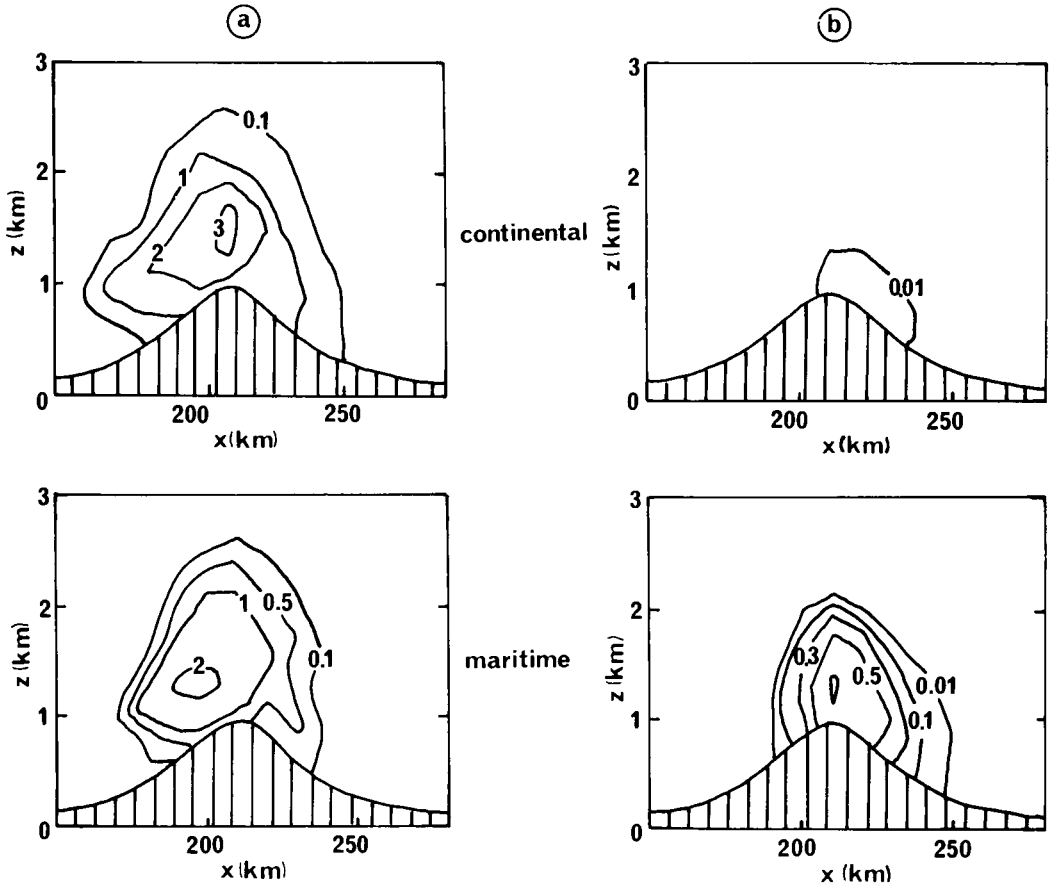

Fig. 4. Vertical cross-sections of mixing ratios of: (a) sulfates produced in cloud ($\mu g\ m^{-3}$), (b) sulfates produced in rain ($\mu g\ m^{-3}$) after a 1-h run for continental and maritime cases.

horizontal wind speed is uniformly 20 m s^{-1} and the relative humidity is 80% below 3 km.

Sulfate variables are initialized with exponential profiles, for number concentration c_{ap} and volume concentration q_{ap} as follows:

$$N_{ap} = 10^9 \exp(-z/3500), \quad (14)$$

$$q_{ap} = 4 \cdot 10^{-12} \exp(-z/3500), \quad (15)$$

where z is the altitude, all units being SI-units.

Our selected case is typical of background pollution in Western Europe (Georgii, 1978). Tests to evaluate the interactions between microphysical and physicochemical processes, together with comparisons between continental and maritime clouds are performed over a 1-h simulation period.

Clouds are generated by model dynamics which allow for the description of typical orographic waves. Due to a contrasting behaviour in latent heat release effects, continental and maritime cases have different dynamical features. In addition, cloud condensation nuclei spectra imply other typical differences between continental and martime clouds reflected in Fig. 3, which displays vertical cross sections of cloud water and rainwater mixing ratios. Cloud water contents are about twice as large in the continental case, while rainwater contents are considerably larger in the maritime case.

The maximum number of aerosols captured by cloud droplets and raindrops during a 1-h run is indicated under each figure. Nucleation effects give the main contribution to total in-cloud

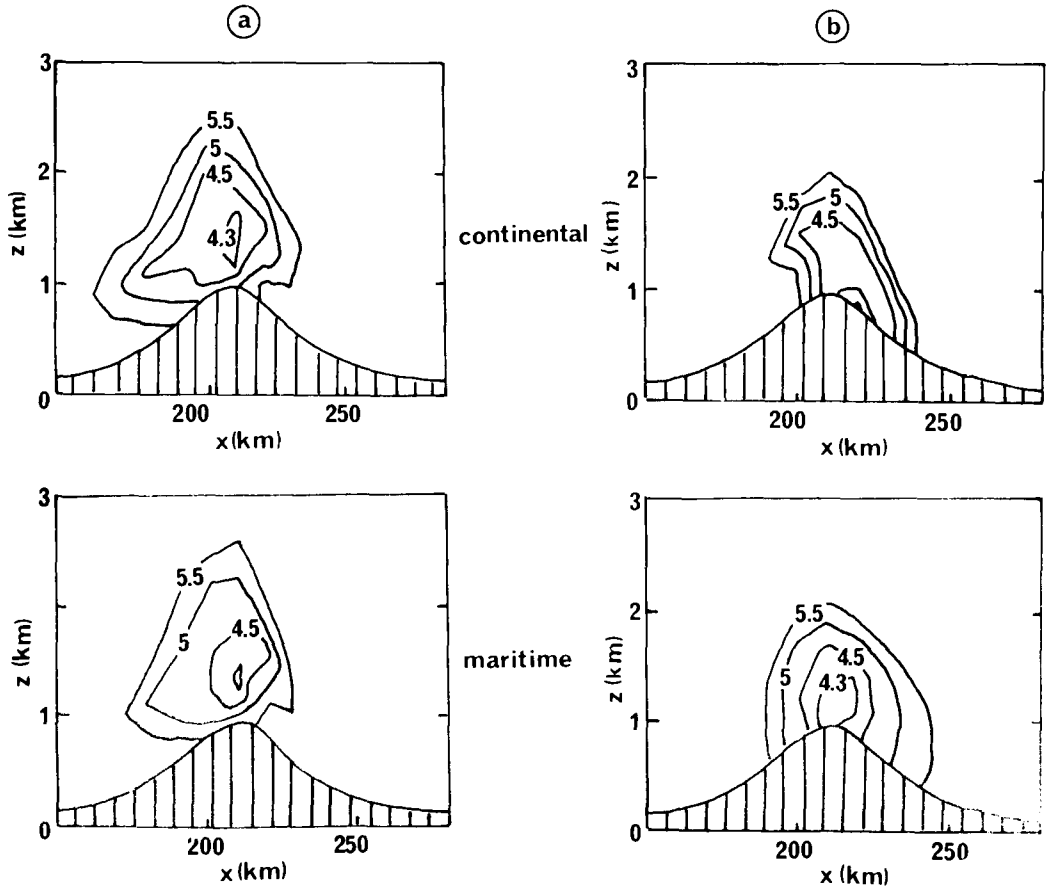

Fig. 5. Vertical cross-sections of cloud-water and rainwater pH's after a 1-h run under continental and maritime conditions.

scavenging. Maritime rainwater scavenges in these cases about 5 times more sulfate particles than continental rainwater, due to the much more vigorous rainfall in the maritime case and greater efficiency of microphysical processes such as accretion and autoconversion.

4. Acidity production in maritime and continental clouds

In the first version of our model (Chaumerliac et al., 1987), only very simple chemistry was incorporated. In particular, an ionic balance equation was missing and oxidant concentrations in the aqueous phase were just prespecified. Furthermore, an equilibrium assumption was made between gas and aqueous phase concentrations, resulting in over-prediction of SO_2 oxidation in raindrops. We have attempted to remedy such omissions by including a more complete chemical scheme with 3 predictive equations for airborne and cloud-borne species and 3 others for rain-borne SO_2, NH_3 and H_2O_2. Some preliminary results will be presented here. We have neglected initial sulfate particle loading and have just considered sulfates produced by SO_2 oxidation in solution. In Fig. 4, we have displayed vertical cross-sections of sulfate fields produced in clouds and in rain. We can see that sulfates are essentially produced in the cloud in the continental case. For the maritime case, sulfate is produced in both cloud and rain. In Fig. 5, cloudwater and rainwater pH's are shown with striking differences between these particular continental and maritime cases.

Acidity is particularly strong within the cloud droplets, but more of the cloud acidity is transferred to rain in the maritime case. This is consistent with the fact that smaller cloud

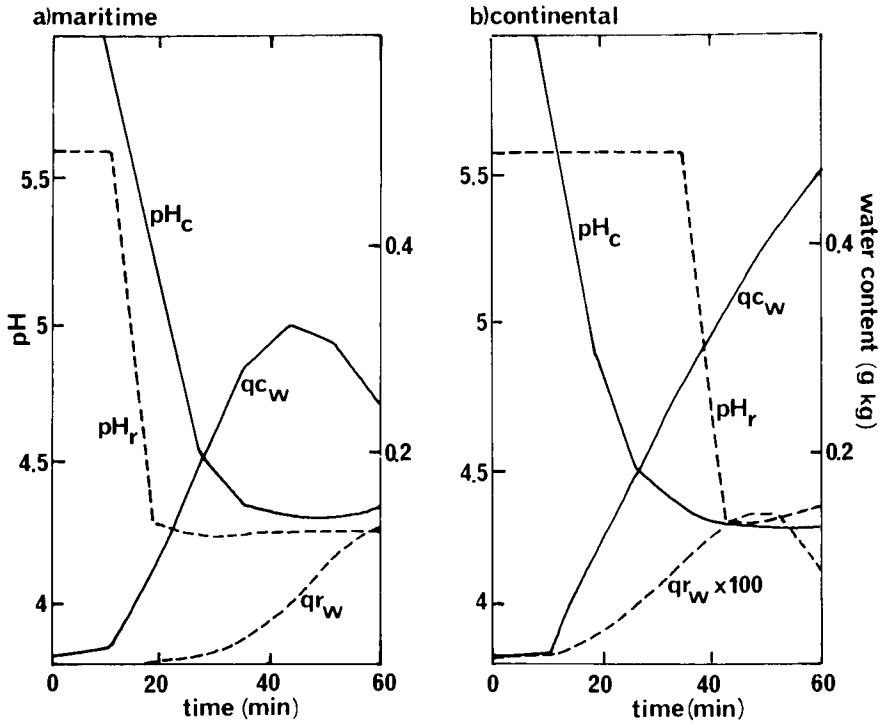

Fig. 6. Time evolution of cloud-water pH (dashed lines) and rainwater pH (solid lines) for (a) continental and (b) maritime clouds up to 1-h. Evolutions of rainwater mixing ratio q_{rw} and cloud-water mixing ratio q_{cw} are also reported. Time evolutions are drawn one grid point downwind from the mountian top. At this grid-point, coalescence occurs to convert cloud into rain, and precipitation drains off rain through sedimentation.

droplets are more acidic than larger raindrops and that autoconversion and accretion are more efficient processes under maritime conditions. Rainwater acidity in the continental case is not distributed as in the maritime case, since more of the acidity is transferred from the cloud and then advected downwind with a maximum near the ground, where small continental raindrops evaporate. Pursuing this comparison between continental and maritime clouds, we examine the behaviour in the time evolution of cloudwater pH and rainwater pH. In Fig. 6b, we can observe the cloud acidification followed by rain acidification in the almost non-precipitating continental case. In contrast, Fig. 6a shows a larger rain acidification due to the efficiency of coalescence processes under maritime conditions (q_{rw} regularly increases). The maritime rain pH is stabilized around a value of 4.3 even if the rainwater content increases, because acidity is removed through deposition.

In order to give a better illustration of the influence of these microphysical processes on rain-borne species concentrations, we present in Fig. 7 vertical cross-sections of rain-borne SO_2, NH_3 and H_2O_2 in continental and maritime cases. Rain-borne species' concentrations are 100 times larger in the maritime case than in the continental case. This reflects the difference between the autoconversion coefficients. The maritime autoconversion coefficient is 1.4 whereas the continental is 4.10^{-3}, so that they differ by 2 orders of magnitude. Another striking difference between Figs. 7a, b is the location of the maxima of the rain-borne concentrations. In the continental case, the maxima are shifted downwind from the mountain top, because small continental droplets are more sensitive to wind

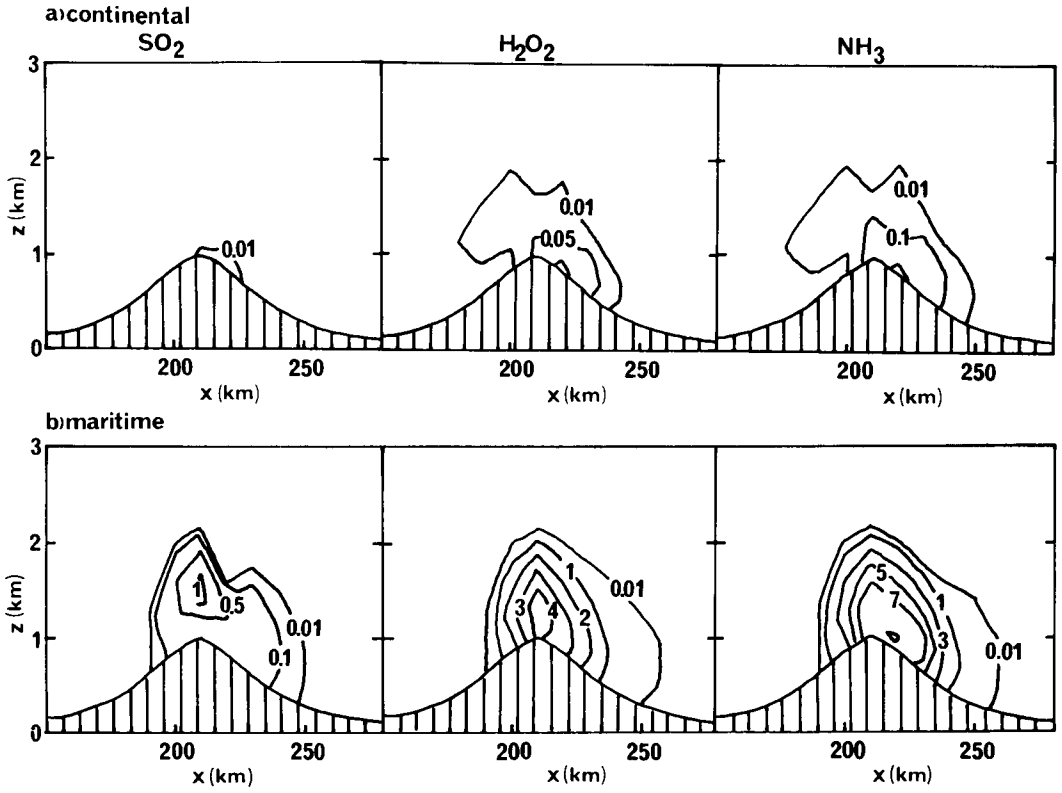

Fig. 7. Vertical cross-sections of rain-borne SO_2, NH_3 and H_2O_2 concentrations (mole l^{-1} air.10^{-12}) under (a) continental and (b) maritime conditions.

drift. Looking at the rain-borne SO_2 concentrations, their special distributions have to be related to those for sulfates in Fig. 4.

5. Conclusion

A semi-spectral parameterization for liquid water (both cloud-water and rainwater) has been included in a mesoscale model to quantify the interactive processes at work in pollutant wet removal. First, sensitivity tests have been performed to establish the following hierarchy among physicochemical processes (Chaumerliac et al., 1987). Nucleation scavenging has been found to be the most efficient in-cloud scavenging process: its computation requires knowledge of an explicit nucleation rate and is a function of supersaturation and the cloud droplet spectrum. During cloud formation, a part of total wet deposition is due to SO_2 scavenging which leads to acidity and sulfate production. Cloud water pH levels are determined by both meteorological factors, such as temperature and liquid water content variations, and chemical factors, such as the presence of neutralizing agents like ammonia. Dissolved sulfate condensation aerosols should influence cloud water acidity as well, but this was not considered here.

The results of this study suggest that a comprehensive numerical model can be effective in isolating the underlying interactions between meteorology, microphysics and chemistry and should be able to distinguish between their relative effects upon sulfate and acidity production.

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