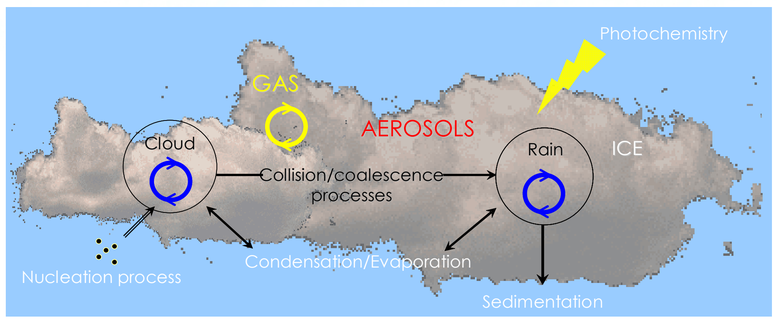
Effect of mixed-phase cloud on the chemical budget of trace gases: A modeling approach

Y. Long[1], N. Chaumerliac[1], L. Deguillaume[1], M. Leriche[2]
[1]LaMP/CNRS, Blaise Pascal University, 24 Av. des Landais, 63177, Aubière, France
[2]LA/CNRS, Paul Sabatier University, 14 Av. E. Belin, 31400, Toulouse, France

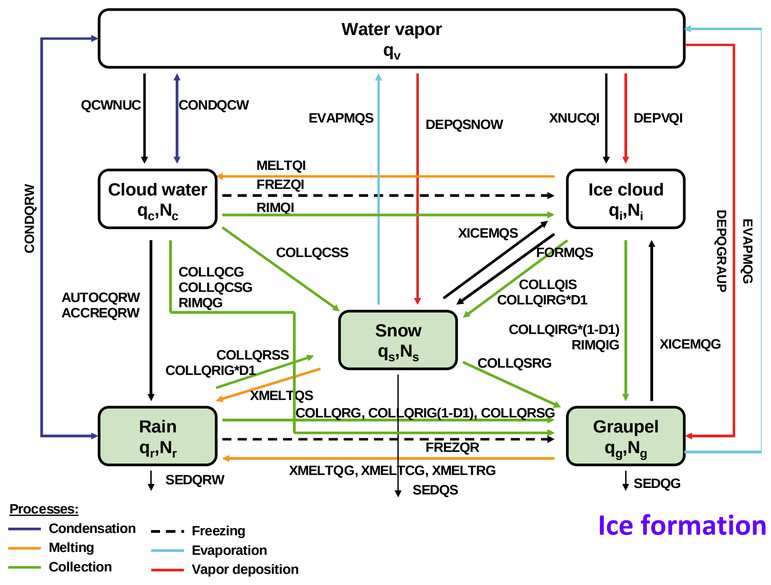
Scientific context

Since several years scientific studies have been performed to evaluate the role of clouds on chemistry and microphysics implied in tropospheric layer. Clouds which cover 50% of terrestrial surface, influence the redistribution of traces gas and modify the Earth radiative budget. Among those, mixed-phase clouds constitute 60 % of all clouds (Hegg, 2001).

However, in contrast to warm clouds, the presence of ice favors tracer vertical transport due to intensified latent heat effects, complicates the exchanges of matter among the various water phases, perturbs photochemistry through retroaction between ice and radiation and reactivity pathways.



The Model of Multiphase Cloud Chemistry (M2C2, Leriche et al., 2007), coupling a multiphase chemistry model and a two-moment microphysical scheme and allowing the simulation of cloud events has been extended to include ice phase processes.



Ice formation

Approach

First the dynamical framework now includes entrainment effects. Then, a mixed-phase cloud microphysical scheme is used to describe three ice categories distributed with a gamma function (Thompson et al., 2008). Finally, cloud scavenging of trace gases is parameterized, including gas redistribution by crystal growth, collection, aggregation, freezing, riming, melting… In addition to microphysical transfer, the probable two main processes incorporating soluble chemical species in iced hydrometeors are the retention in ice phase as riming and freezing occurs and the burial in the ice crystal as the crystal grows by diffusion.

Simulation Protocol

The mixed-phase cloud simulation with M2C2 required dynamics in favor of ice formation as previously described by Audiffren et al. (1998) with temperature and dew point profiles from Reisin et al. (1996). The 0°C isotherm is located around 2600 m.

The CCN spectrum at 1% supersaturation is representative of a moderate continental case as described in Reisin et al. (1996).

The convective air parcel starts at 600 m above ground level with temperature equal to 15°C. Cloud base and top are, respectively at the altitudes of 600m and 5100m where the temperature reaches -18°C.

General features of the cloud are given in Table 1, the chemical species initialization comes from Voisin et al. (2000). The main results from moderate continental cloud are presented in Table 2 and Figure 1.

Chemical species in gaseous phase	Concentration in molecules / cm^3
N_2	$1.840.10^{19}$
O_2	$4.960.10^{18}$
H_2O	$4.160.10^{17}$
O_3	$8.733.10^{11}$
NO	$2.214.10^{10}$
NO_2	$1.463.10^{11}$
CH_4	$4.012.10^{13}$
CO	$3.304.10^{12}$
CO_2	$7.789.10^{15}$
HNO_3	$3.540.10^{09}$
H_2O_2	$1.652.10^{09}$
CH_2O	$1.062.10^{10}$
CHO(OH)	$6.609.10^{09}$
$CH_3(OOH)$	$2.360.10^{10}$
CH_3OH	$5.311.10^{10}$
NH_3	$3.068.10^{09}$
HCl	$1.652.10^{09}$

Table 1: Chemical initialisation in gas phase

Parameter		Value
CCN spectrum : $N = C.S^k$	C (cm^{-3})	600
	k	0.7
Maximum updraft (m/s)		13
Location (m)		2500
Cloud duration (min)		14
Maximum mixing ratio (g/kg)	Cloud	5.59
	Ice	$7.6.10^{-3}$
	Snow	$4.3.10^{-2}$
	Graupel	4.3
Maximum number concentration (cm^{-3})	Cloud	$6.00.10^{9}$
	Ice	$7.77.10^{4}$
	Snow	$4.05.10^{4}$
	Graupel	$4.12.10^{4}$
Maximum mean diameter (m)	Cloud	$2.28.10^{-5}$
	Ice	$4.10.10^{-5}$
	Snow	$5.7.10^{-5}$
	Graupel	$3.77.10^{-4}$

Table 2: Main results for moderate continental case simulation

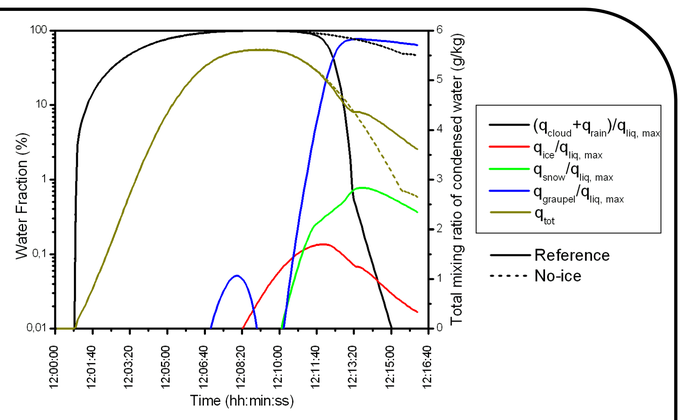


Figure 1: Relative water fractions (through maximum cloud water content) versus time for various phases

Figure 1 presents the relative water fractions normalized by the maximum liquid water content. The cloud formation starts readily around noon and does not produce much rain. Mixed-phase processes occur at -5°C and are mainly driven by graupel formation.

Sensitivity tests

To get insights in the relative effects of ice processes, retention, burial, crystal shapes on gas scavenging, it is interesting to proceed to sensitivity tests. Four simulations have been performed in addition to the reference case which considers complex crystal geometry, a burial efficiency of 1, a variable retention coefficient (Figure 2), together with mixed-phase processes:

1) a warm simulation where **ice processes are switched off**;
2) a case where the **burial efficiency** is set to 0;
3) a case where the **retention efficiency** is set equal to 1 for all chemical species;
4) a case where **ice crystals are considered as spheres**.

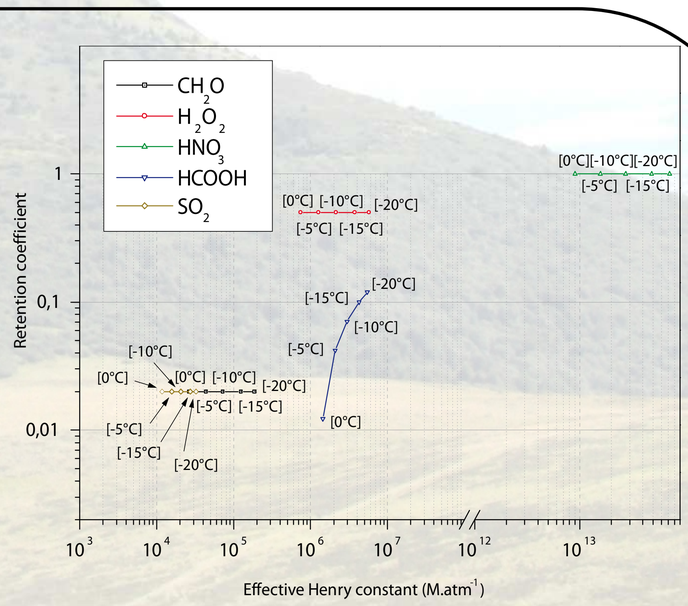
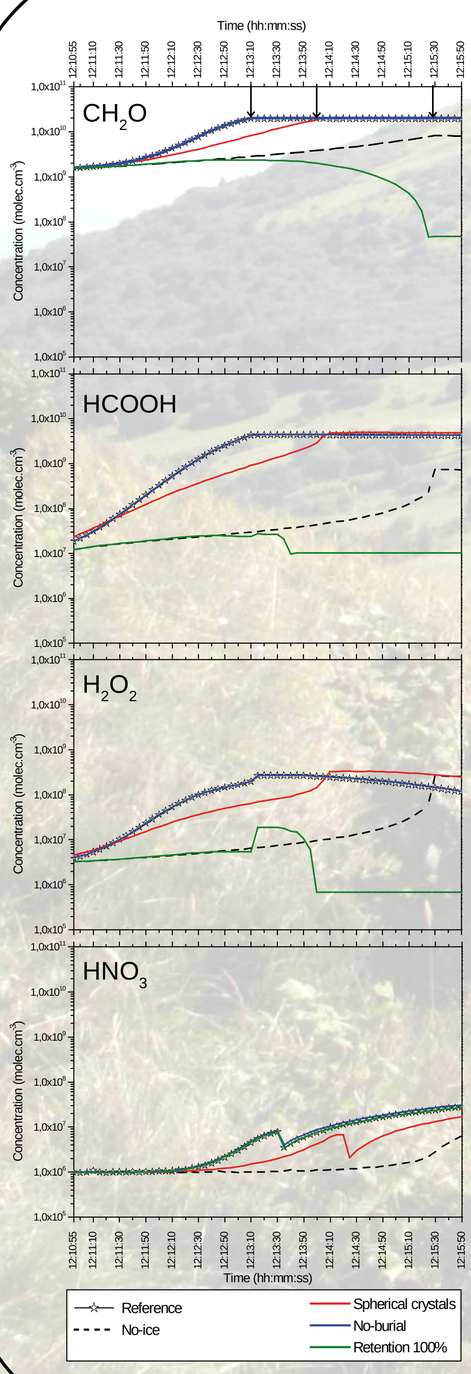


Figure 2: Values of retention coefficients and effective Henry's law constants (pH is varying around a value of 5) for different temperatures (0, -5, -10, -15 and -20°C) and for several chemical species (SO_2, CH_2O, H_2O_2, HNO_3, HCOOH)

Figure 3 shows the time evolution of gas concentrations for (a) CH_2O, (b) H_2O_2, (c) HNO_3 and (d) HCOOH zooming on the end of the simulation when ice processes can occur. One point that has to be raised is the abrupt changes in gas concentration that are observed at times denoted by the arrows on Figure 3, and that corresponds to cloud water decrease observed in every run (reference case, case without ice and case with spherical crystals).



The first main result is that burial is ineffective to scavenge all gases considered in our study by comparing case 2 with the reference case. Considering a full retention in ice for all species, obviously does not affect nitric acid but leads to large discrepancies for HCHO, H_2O_2 and HCOOH compared to their original retention coefficients respectively equal to 0.02, 0.5 and to $0.012+0.0058(T-T_0)$. Their evolution with time before the decrease of cloud water amount just reflects that, when graupels form, they are fully retained in ice phase. Then, the time evolution is different for these three species due to the competition between gas phase reactivity, exchanges between gas and liquid phases and aqueous phase reactivity.

Large deviations are observed between the run with and without ice for all compounds. For chemical species with a small retention coefficient (HCHO, H_2O_2 and HCOOH), their gaseous concentrations are smaller when no ice is considered because, in this case, soluble species are scavenged by cloud water whereas in the reference case, no more cloud water is available and species are released back to the gas phase when liquid water freezes. H_2O_2 has a contrasted behavior than the other compounds, at the end of the reference simulation. Its concentration increases as the total condensed water is depleted and then decreases when ice stabilizes in the form of graupels. The only possibility for H_2O_2 concentration to decrease is its reactivity with OH and its direct photolysis. In the meantime, nitric acid is produced from the gas phase reaction between NO_2 with OH radical. This continuous production explains the difference between the runs with and without ice for nitric acid: neglecting ice, nitric acid produced in gas phase is scavenged at once by cloud droplets whereas when ice is considered, burial is inefficient to scavenge nitric acid from the ice phase.

The influence of crystal shape is similar for all gases with a shift in time for the gas content evolution, due to different riming intensity of the regular vs complex crystals.

Figure 3: Time evolution of gas concentrations for CH_2O, HCOOH, H_2O_2, HNO_3
the reference case (solid line), a case without ice, a case considering spherical crystals, a case neglecting burial, a case assuming full retention

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