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*Manuscript*

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## **Abstract**

The Model of Multiphase Cloud Chemistry M2C2 has recently been extended to account for nucleation scavenging of aerosol particles in the cloud water chemical composition. This extended version has been applied to multiphase measurements available at the Puy de Dôme station for typical wintertime anthropogenic air masses. The simulated ion concentrations in cloud water are in reasonable agreement with the experimental data. The analysis of the sources of the chemical species in cloud water shows an important contribution from nucleation scavenging of particles which prevails for nitrate, sulphate and ammonium. Moreover, the simulation shows that iron, which comes only from the dissolution of aerosol particles in cloud water, has a significant contribution in the hydroxyl radical production. Finally, the simulated phase partitioning of chemical species in cloud are compared with measurements. Numerical results show an underestimation of interstitial particulate phase fraction with respect to the measurements, which could be due to an overestimation of activated mass by the model. However, the simulated number scavenging efficiency of particles agrees well with the measured value of 40% of total number of aerosol particles activated in cloud droplets. Concerning the origin of chemical species in cloud water, the model reproduces quite well the contribution of gas and aerosol scavenging estimated from measurements. In addition, the simulation provides the contribution of in-cloud chemical reactivity to cloud water concentrations.

Keywords: aerosol particles, cloud chemistry, droplets nucleation, Puy de Dôme station

## 1. Introduction

For several years, significant efforts were made by the scientific community to understand tropospheric chemistry. However, these investigations have been mainly focused on homogeneous gas phase chemistry, which is currently well documented (Atkinson et al., 2004; 2006). At a global scale, cloud chemistry has a potential impact on the atmospheric oxidizing capacity and on climate change via the indirect effect of aerosols on the radiative budget of the earth's system, which is still poorly understood and is a major source of uncertainties in climate forecasting (Ramaswamy et al., 2001). Some modeling studies have attempted to assess the overall impact of cloud chemistry on global atmospheric composition and climate with a particular focus on the ozone chemistry (Lelieveld and Crutzen, 1991; Liang and Jacob, 1997; Barth et al., 2002) and on the sulfur cycle (Dentener et al., 2002; Kreidenweis et al., 2003). However, the details of in-cloud processes are still poorly understood and some new aspects of cloud chemistry have recently been put forward concerning for instance its potential contribution to the formation of secondary organic aerosol particles (Blando and Turpin, 2000; Gelencsér and Varga, 2005; Carlton et al., 2006). More efforts are needed to improve our understanding of the cloud impact at local scale critical for radiative and health effects, in particular via integrated modeling and in-situ studies.

A cloud is a multiphase system comprising a gaseous phase, a particulate phase, and an aqueous phase. To assess the role of cloud chemistry at a local scale, interactions between gases, cloud droplets and aerosol particles have to be taken into account in numerical cloud chemistry models. The interactions between aerosol particles and cloud droplets are usually not considered in cloud chemistry models (Ervens et al., 2003; Williams et al., 2002). Aerosol particles contribute to the chemical composition of cloud droplets by nucleation and impaction scavenging followed by dissolution of soluble

compounds. During the cloud lifetime, the cloud chemistry leads to the formation of new chemical species with relatively low volatility such as inorganic and organic acids, which can modify the physico-chemical properties of aerosol particles after the cloud dissipates (Feingold and Kreidenweis, 2002; Yin et al., 2005) and lead to secondary organic aerosols formation (Gelencsér and Varga, 2005). For some chemical species, aerosol particles dissolution is the only source in cloud droplets; an example is transition metal ions, and in particular iron, which is well known to play a major role in the oxidizing capacity of clouds (Deguillaume et al., 2004; 2005). Study of such complex interactions needs laboratory experiments for kinetics and thermodynamics database development and modelling efforts integrating in-situ measurements.

In this framework, the Model of Multiphase Cloud Chemistry model (M2C2) (Leriche et al., 2003; Deguillaume et al., 2004) has recently been developed to simulate aerosol particles temporal evolution and their activation in cloud droplets. This cloud chemistry model includes aerosol particles, cloud microphysics and chemistry in both aqueous and gas phases. While measurements do not allow the determination of the origin of the different sources of chemical species in the cloud water and to identify these sources, the model provides this information as well as the main chemical production pathways and the impact of cloud microphysical processes on chemistry. In this study, the M2C2 model is used to simulate typical wintertime anthropogenic air masses at the Puy de Dôme station. At this station, continuous measurements (<http://www.obs.univ-bpclermont.fr/observ/en/index.htm>) as well as intensive field campaigns are performed leading to an interesting and explicit multiphase dataset including physico-chemical characterisation of air mass, aerosol particles and clouds encountered at the high altitude site. The present study aims at evaluating the role of the chemistry versus both the gas scavenging and the aerosol particles nucleation scavenging in the cloud water chemical

composition. Then, the role of the chemistry in the phase partitioning can be determined and the various sources of chemical species inside the cloud, either from gas phase or from particulate phase are quantified.

Firstly, the model, its new developments and the initial conditions of the simulation are presented. Secondly, numerical concentrations in cloud water are compared to experimental values to assess the quality of the simulation. Then, the analysis of the different sources of chemical species in cloud water is performed. Finally, the partitioning of chemical species obtained from measurements and from simulation are compared and discussed.

## **2. Model description**

### *2-1 Model formulation*

The Model of Multiphase Cloud Chemistry (M2C2) results from the coupling (Leriche et al., 2001) between a multiphase chemistry model described in Leriche et al. (2000) and a two-moment warm microphysical scheme module predicting the number concentration of cloud droplets and raindrops and the mixing ratio of cloud water and rainwater categories using log-normal distributions (Caro et al., 2004). The dynamical framework of the model is an air parcel (Gérémy et al., 2000). The chemistry included in the chemical module is explicit. The exchange of chemical species between the gas phase and the aqueous phase is parameterized following the mass transfer kinetic formulation developed by Schwartz (1986). The aqueous phase chemistry includes the detailed chemistry of HO<sub>x</sub>, chlorine, carbonates, NO<sub>y</sub>, sulphur, the oxidation of organic volatile compounds (VOCs) with one carbon atom (Leriche et al., 2003), the chemistry of transition metal ions for iron, manganese and copper (Deguillaume et al., 2004) and the oxalate oxidation and interaction with iron chemistry (Table 1). Oxalate represents a strong organic iron complexing agent and the highest fraction of dicarboxylic acids in

Table 1
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aerosol particles (Legrand et al., 2005). The value of the accommodation coefficient for oxalic acid is estimated to be 0.05 (Leriche et al., 2000) because no measurement is available. The model considers calculations of photolysis frequencies both in the gas phase and in cloud droplets. The pH is calculated at each time step by solving the electroneutrality equation.

The activation of aerosol particles into cloud droplets is parameterized according to Abdul-Razzak et al. (1998) and Abdul-Razzak and Ghan (2000). Aerosol particles are represented by the sum of four log-normal distributions as follows:

$$\frac{dN_{ap}}{d \ln a_{ap}} = \sum_{i=1}^4 \frac{N_{api}}{\ln \sigma_i \sqrt{2\pi}} \exp \left[ -\frac{\ln^2(a_{ap} / a_{mi})}{2 \ln^2 \sigma_i} \right] \quad (1)$$

Where  $N_{ap}$  is the total number concentrations of aerosol particles,  $N_{api}$  is the number concentrations of aerosol particles for each mode;  $a_{mi}$  is the median radius of the log-normal distribution for each mode;  $\sigma_i$  is the geometric standard deviation of the log-normal distribution of each mode and  $a_{ap}$  is the radius of aerosol particles.

The parameterization used to allow for nucleation of cloud droplets comes down to find an expression for the maximum of the supersaturation on each model time step (Abdul-Razzak et al., 1998; Abdul-Razzak and Ghan, 2000) considering the physico-chemical properties of aerosol particles and based upon the Köhler theory (Köhler, 1936; Pruppacher and Klett, 1997). For each mode, the activated fraction is calculated and leads to the number of droplets newly formed by nucleation and to the associated cloud water mixing ratio.

The introduction of the cloud droplets nucleation process in the model allows for the monitoring of the evolution of aerosol particle size distribution with time. The microphysical scheme for aerosol particles is a two-moment scheme in which the prognostic variables are the number concentration of aerosol particles and the

corresponding volumetric concentration (Caro et al., 2004). At each time step, the evolution of aerosol particles size distribution is computed from the number of nucleated droplets and the associated activated aerosol mass. Until now, the impaction scavenging is neglected in the model, which is not very restrictive as nucleation scavenging in non precipitating clouds represents more than 90% of the total aerosol particles scavenged by the cloud droplets (Flossmann, 1991).

The impact of aerosol particles on cloud chemistry is considered in the model via the activated mass of aerosol particles. The fraction of soluble chemical species in aerosol particles is used to compute the chemical concentrations in cloud droplets of species coming from the activated particles. The mass fraction of soluble chemical species in each aerosol mode is prescribed from measurements.

## *2.2 Initialization of the model: Anthropogenic air mass at the Puy de Dôme station*

The Puy de Dôme station is located in the centre of France at the summit of the Puy de Dôme Mountain (1465 m above sea level) and is well recognized in the scientific community (Van Dingenen et al., 2004; Putaud et al., 2004). The station is equipped with continuous measurements since June 1995 for meteorological variables and ozone; since February 1998 for radiation fluxes (UV, visible, diffusive fluxes and  $J(\text{NO}_2)$ ); since May 2000 for number concentration of aerosol particles; since September 2000 for black carbon content; since November 2000 for  $\text{CO}_2$ ; since April 2002 for CO; since January 2003 for  $\text{SO}_2$  and  $\text{NO}_x$ ; since April 2003 for  $\text{NO}_y$ ; and since June 2003 for drop surface area, liquid water content and effective radius when a cloud is present on the site (free access to data from <http://www.obs.univ-bpclermont.fr/observ/en/index.htm>). In addition, detailed measurements of the cloud liquid phase are made since February 2001 for selected cloud events mainly during winter and spring in the framework of the ORE-BEAM (Observatoire de Recherche en Environnement Biophysicochimie de l'Eau



Atmosphérique et Modifications anthropiques) project database (<http://www.obs.univ-bpclermont.fr/atmos/orebeam/orebeampage1.htm>) including measurements of iron (total content and oxidation state), ionic chromatography, dissolved organic carbon; conductivity, redox potential, pH and some biological parameters (see Amato et al., 2005). Intensive field campaigns are regularly organized at the station like the European CIME experiment (Wobrock et al., 2001) as well as various national campaigns as the 2001 Puy de Dôme campaign during winter 2001.

In order to perform a simulation of a typical wintertime anthropogenic air mass at the Puy de Dôme station with the M2C2 model, a scenario based upon the air mass classification of Sellegri et al. (2003a), which defines a typical anthropogenic influenced free tropospheric air mass encountered at the station, was elaborated using the available measurements.

The air trajectory used to initialize the parcel comes from a three dimensional simulation of a typical dynamical situation corresponding to wintertime polluted air masses at the Puy de Dôme station coming from the North-North-East. This three dimensional simulation was performed with the meso-scale non-hydrostatic Clark model (Clark and Hall, 1991) using three nested grids. The trajectory used in M2C2 corresponds to the back-trajectory computed by the three dimensional model arriving at noon local time at the summit of the Puy de Dôme. The trajectory is shown in Figure 1 together with the corresponding vertical wind speed. This trajectory at noon corresponds to the maximum of the photolysis leading to the highest intensive photochemistry. The beginning of the lifting of the air parcel is also indicated in Figure 1. At this moment, the M2C2 simulation run was started for a duration of twelve minutes.

Figure 1

The gas phase chemical species are initialized using measurements from Voisin et al. (2000), performed during the CIME experiment in winter 1997-1998. During this campaign, a large amount of chemical species was measured in addition to continuous measurements of, e.g., ammonia and nitric acid. An event corresponding to an anthropogenic air mass arriving at the Puy de Dôme station as defined in Sellegri et al. (2003a) was selected in this database. Initial concentrations taken from this event for gas phase chemical species are shown in Table 2.

Table 2

The initialization of the physico-chemical properties of aerosol particles are derived from Sellegri et al. (2003a) and Sellegri (2002) for anthropogenic influenced free tropospheric aerosols without marine input sampled at the Puy de Dôme station. The

Figure 2

chemical composition for these aerosol particles is shown in Figure 2 for each four identified modes: Aitken, accumulation 1, accumulation 2 and coarse mode. Usually, at the Puy de Dôme station, the accumulation particles are spread in two distinct modes with different chemical signature as shown in Figure 2. As expected, the dust contribution is significant for the coarse mode whereas the organic contribution decreases with the particle size. The coarse mode appears to be acidic with a low contribution of ammonium. The initial number distribution of aerosol particles

Figure 3

corresponding to this chemical composition are represented in Figure 3 together with the four log-normal distributions used to fit it. Starting from the left-hand side, the first fitted distribution represents the Aitken mode, the second and the third ones the two accumulation modes and the fourth one the coarse mode. Table 3 presents the physico-chemical properties of aerosol particles and the fitting parameters of the number distribution used in the simulation. The density, the number of dissociated ions, the mass fraction of soluble materials, the mass fraction related to soluble mass of nitrate, sulphate, ammonium, formate, oxalate and soluble iron, and the molar mass of aerosol

particles in each mode was derived from the aerosol particle measurements database following Sellegri (2002). The mass fraction of iron is estimated from Particle Induced X-Ray Emissions (PIXE) data (Sellegri et al., 2003a) and assuming an iron solubility of 15% (Deguillaume et al., 2005). The oxalic acid is assumed to represent 60% of total measured organic acids and formic acid, 40%. This partitioning followed the ratio observed between dicarboxylic and mono-carboxylic acids (Sellegri et al., 2003a) if we assume that mono-carboxylic acids are mainly represented by formic acid and dicarboxylic acids by oxalic acid.

### 3. Results and discussion

#### *3.1 Comparisons between simulated and observed cloud concentrations for main chemical species*

Table 4

The simulated concentrations and pH in cloud water are compared with observed values as shown in Table 4. Numerical results are averaged values on the whole simulation. Observed values are taken from previous studies using the database of chemical measurements available in cloud water at the Puy de Dôme station coming from the ORE-BEAM project mentioned above (Marinoni et al., 2004; Parazols et al., 2006), which used air mass classification similar to Sellegri et al. (2003a). The maximum value of the simulated cloud liquid water content is  $0.4 \text{ g m}^{-3}$  at the top of the mountain and the mean value is  $0.16 \text{ g m}^{-3}$ . For anthropogenic influenced free tropospheric air masses, the measured cloud liquid water content is around  $0.3 \text{ g m}^{-3}$  and hence there is a reasonable agreement between model and measurements. Simulation and in-situ measurement indicate both acidic pH values for the wintertime anthropogenic air masses at the Puy de Dôme station. In general, results from the model compare favorably with the measured concentrations. However, formate and oxalate are overestimated by the model and iron is underestimated.

For both carboxylic acids (formate and oxalate), the overestimation is about a factor 2. However, the amplitude of this factor is quite uncertain because of the low accuracy for carboxylic acids concentrations determined by ion chromatography due to their low concentrations close to the detection limit. Overestimation of formic acid has also been obtained by the SPACCIM model applied on a continental event of the FEBUKO field campaign, which took place at the Schmücke Mountain (937m above sea level) located in central Germany in October 2001 (Wolke et al., 2005). However, the SPACCIM chemical mechanism takes into account organic acids with up to four carbon atoms and the modelled acetic acid concentrations compared well with those obtained from the FEBUKO measurements. This suggests that the observed overestimation of formic acid is not solely due to weighing formic acid as the source of mono-carboxylic acid. Measurements show that oxalic acid is the main dicarboxylic acid in aerosol particles. Moreover, recent studies have shown that, in addition to aerosol particles, chemical reactivity is an important source of oxalic acid in cloud droplets, especially in rural areas influenced by biogenic emissions (Ervens et al., 2004; Sorooshian et al., 2006). Thus, no satisfactory reason is available to explain the simulated overestimation of oxalic acid by the model.

The only source of iron in cloud droplets is from aerosol particles, hence, its underestimation is explained by: the uncertainty on measured iron concentration in aerosol particles which are often close to the detection limit; the fact that measurements of elemental species in aerosol particles were not available for all anthropogenic events used to estimate physico-chemical properties of initial aerosol particles; and the two assumptions made to estimate the iron soluble part in the particulate phase (Table 3). Measurements of iron in particles have been made using PIXE analysis which gives the elemental species concentration, the two assumptions made to estimate soluble iron

mass fraction are: all iron in the particulate phase is iron oxide (FeO) and the solubility of iron is 15%. The first assumption could lead to an underestimation of iron mass fraction in the particulate phase depending on the real chemical species of iron which occur in various forms: iron oxides, iron hydroxides, adsorbed iron, etc...(Deguillaume et al., 2005). For the second assumption, available values of iron solubility are in the range of 0.01 to 35% depending on the occurrence of iron in a crystalline or in a carbaceous matrix (Desboeufs et al., 2005) and the dissolution is instantaneous in the model although it is well known that the dissolution is a kinetic process (Deguillaume et al., 2005). Thus, the underestimation of iron by the model is still an open question.

In the model, the cloud water chemical composition is initialized by chemical species coming from the activation of aerosol particles. In this study, the whole coarse mode and accumulation mode 2 are activated, as well as a large fraction of the accumulation mode 1, and only a small part of the Aitken mode. Cloud water concentrations do not only reflect the chemical composition of activated aerosol particles which would lead to similar concentrations for nitrate and sulphate as shown by the chemical composition of aerosol particles (Figure 2). Indeed, the nitrate concentration in cloud droplets is higher than the concentration of sulphate due to the impact of chemical reactivity on cloud water concentrations as will be demonstrated later. To quantify the contribution of reactivity, the sources of chemical species in cloud water have to be determined.

### *3.2 Quantifications of chemical species sources in cloud water*

While measurements do not allow determining the origin of the different chemical species in cloud water without artefacts, the model can provide this information. Analysis of the sources of chemical species (particulate, gaseous, or chemical reactivity in cloud water) is shown in Table 5 as relative contributions to their final concentration in the liquid phase. These results show that, for inorganic compounds, the scavenging of

Table 5

aerosol particles predominates due to the complete activation of the accumulation mode 2 and the coarse mode with the largest contribution for sulphate and ammonium.

In the cloud droplets, 72.5% of the ammonium concentration comes from the dissolution of activated aerosol particles. The 27.5% remaining comes from the gas phase, as ammonia is a very soluble gas, and it is nearly completely scavenged by the cloud water. Similar ratios are observed for sulphate, with 73% of its cloud droplets concentration coming from the dissolution of activated aerosol particles whereas the remaining 27% are chemically produced in the aqueous phase. This aqueous phase production is due to the scavenging of gaseous sulphur dioxide in cloud droplets where it is oxidized into sulphate by pernitric acid and hydrogen peroxide. Despite the high iron concentrations in cloud droplets, as Deguillaume et al. (2004) showed, the catalysis of sulphur autoxidation by iron is negligible in the formation of sulphate.

For nitrate, the situation is quite complex: 56% of the nitrate-containing cloud droplets come from activated aerosol particles, 15.5% come from the gas phase initial concentration, 23% come from a gas phase in cloud production and the remaining 5.5% come from an aqueous phase in cloud production. As nitric acid is a very soluble gas, its initial gas phase concentration and its gas phase production are completely and rapidly scavenged in cloud droplets in a similar way to ammonia. The simulated air mass has anthropogenic characteristics, hence the nitrogen oxides concentration levels are high (Table 2) and lead to a significant production of nitric acid in the gas phase and of nitrate in the aqueous phase. The main chemical pathway producing nitrate in the aqueous phase is the oxidation of sulphur dioxide by pernitric acid, which also contributes to the sulphate production (Leriche et al., 2003). This analysis of nitrate sources in cloud droplets explains the higher concentration of nitrate than sulphate in cloud droplets mentioned above (Table 4). Indeed, as the nitrate mass fraction in

activated particles is as high as those of sulphate (Table 3) and its main aqueous phase chemical production pathway is the same as for sulphate, its higher concentration in cloud droplets may be explained by its efficient gas phase chemical production followed by its scavenging. High  $\text{NO}_x$  levels lead to this efficient nitrate production, which confirms the hypothesis of Sellegri et al. (2003b) of a favoured nitrate production in cloud over sulphate under the atmospheric conditions typical of the Puy de Dôme site.

In cloud droplets, iron, which is a major OH precursor (Deguillaume et al., 2005), come only from the dissolution of activated particles as seen before, as well as the oxalic acid which can inhibit the role of iron in the OH production due to its complexing ability. Introducing aerosol particles in the M2C2 model allows for correctly representing the in-cloud source of these two chemical species, and thus, the in-cloud OH production. Analysis of the relative contribution of the main OH production pathways in cloud

Table 6

droplets shows that iron reactivity contributes 30% to the OH production in droplets via the photolysis of iron(III) and the Fenton reaction (Table 6) while its scavenging is the main pathway contributing 57%. In order to study the impact of oxalate on OH production in cloud droplets, an additional simulation was performed neglecting oxalate in aerosol particles. Results show that, when oxalate chemistry is not considered, the contribution of iron in OH aqueous phase production is higher, 57%, and the scavenging is less important (Table 6). Oxalate chemistry leads to a decrease in the contribution of iron in OH production as expected by its inhibiting role due to its high complexing power on iron. However, these results show that, even if oxalate chemistry is considered and despite a relatively low photochemical activity due to the hibernal situation, iron contributes significantly to the OH radical production inside the cloud.

All these results show the interest of such an approach, which allows for quantifying the relative importance of gas and aqueous phase chemistry against aerosol particles as

source of soluble chemical species in cloud droplets by considering explicitly the chemical source coming from activated particles.

### *3.3 Partitioning of chemical species among cloud phases: droplets, interstitial aerosol particles and gas*

To get a global view of chemical species in cloud, the phase partitioning between the gas phase, the particulate phase and the liquid phases is calculated for nitric acid,

Figure 4

sulphuric acid, ammonium and formic acid. Results of this analysis are shown in Figure 4, which can be directly compared to the estimated phase partitioning from

Figure 5

measurements shown on Figure 5 (adapted from Sellegri et al., 2003b) for anthropogenic influenced free tropospheric air masses sampled during the 2001 Puy de Dôme campaign in winter 2001. The experimental procedure is explained in detail in Sellegri et al. (2003b), but we will briefly summarize its principle. During a cloud event, interstitial and residual phases are separately sampled with specific inlets: Round Jet Impactor (RJI) and Counterflow Virtual Impactor (CVI, Noone et al., 1988). The gas phase is sampled using mist chambers, while the particulate phase is sampled using cascade impactors, both in the residual and interstitial phases. Moreover, the bulk liquid concentrations were measured with a CDI device (Cloud Droplet Impactor, Kruisz et al., 1993). While the contributions of gaseous, particulate and liquid concentrations to the total atmospheric concentration of a given species can be experimentally evaluated within the experimental uncertainties, it is difficult to evaluate the particulate and gaseous origin of the liquid concentration by an experimental procedure. Sellegri et al. (2003b) attempted to do this by neglecting the in-cloud chemical liquid production. The experimental gas and particulate originating liquid concentrations were deduced by combining the results from the CVI device and the results from the CDI device. The strong hypothesis in this calculation was that the fraction of gaseous species which were



evaporating from cloud droplets was equivalent to the one which had absorbed from the original gas phase and dissolved in the liquid phase during the formation of the cloud. In the present study, it is possible to evaluate this hypothesis by modelling the fractions of gas-originating and particle-originating compounds present in the liquid phase as well as the contribution of chemical reactivity in liquid phase concentrations.

First, the model can be compared to measurements regarding the three phase apportionment (interstitial gas, interstitial particles and liquid phase). The main difference between measurements and simulation lies in the fraction of the interstitial particulate phase. This fraction is close to zero for numerical results (in black in Figure 4) whatever the chemical species considered whereas it ranges from 1% to 12.4% of the total concentration for in-situ data. Measurements showed bulk mass scavenging efficiencies for anthropogenic air mass of 0.91 for sulphate, 0.96 for nitrate and 0.88 for ammonium, no data were available for formic acid (Sellegri et al., 2003c) whereas numerical results show bulk mass scavenging efficiencies close to 1 for all species as almost all aerosol mass is activated. However, the in-situ number scavenging efficiency is between 0.4 and 0.48 which is similar to the simulated value (0.41) highlighting the ability of the model to simulate the cloud droplets nucleation process. The discrepancy in the mass scavenging efficiencies indicates an overestimation of the activated mass by the model. This drawback could be improved in the future by the implementation of the effect of organic compounds on the surface tension and on the bulk hygroscopicity of the particles following Abdul-Razzak and Ghan (2004).

With respect to measurements, in addition to gas and aerosol particles scavenging, the simulation allows to identify the chemical production sources in the liquid phase as detailed above. For an improved comparison with the partitioning obtained from measurements, the contribution of the chemical gas phase production in the liquid phase

concentrations has been included in gas-originating liquid. For nitric acid, the fraction present in the gas phase agrees between simulation and measurements. For the liquid phase, the simulation shows a small but appreciable amount of nitrate originating from chemical production. The amount of gas and particulate originating nitrate in the liquid phase as determined from the model simulation and the measurements are within experimental uncertainties. For sulphuric acid, a direct comparison between measured and simulated results is not possible because the phase partitioning obtained from measurements is for the system  $\text{SO}_2/\text{SO}_4^{2-}$ . The experimental findings that a large amount of sulphate in cloud droplets originates from particles are confirmed by the simulation. For ammonium, measured and simulated partitioning show completely different patterns: while the measured interstitial gas fraction is about 56 %, the simulated fraction is 1% of the total atmospheric ammonium concentration. Moreover, for measurements, the amount of gas-originating ammonium in the liquid phase is close to the particles-originating concentration, while it is three times more for the simulation. These two discrepancies could be related to high ammonium emission around the Puy de Dôme Mountain not considered in the simulation and leading to observed subsaturation of the liquid phase as underlined by Sellegri et al. (2003b). For formic acid, the simulated and measured partitioning compare well with the major contribution coming from the gas phase. Moreover, the simulation shows a negligible production in the liquid phase, which is consistent with the observations.

Finally, such a modelling approach leads to a global view of the partitioning of chemical species in clouds including the identification of their various sources. This approach is globally in quite good agreement with the measured partitioning, which makes it a valuable tool for evaluating liquid concentrations in clouds, without developing a heavy instrumental set-up.

#### **4. Conclusion**

Partitioning of chemical species between the liquid, gaseous and particulate phases was simulated for typical wintertime anthropogenic air masses at the Puy de Dôme research station using the M2C2 model. The M2C2 model has been extended to include the aerosol particles evolution due to nucleation scavenging which is parameterized using the Abdul-Razzak and Ghan (2000) formulation. The model simulates the chemical and the microphysical evolution of clouds including the interactions between aerosol particles and chemical reactivity in both liquid and gaseous phases. Modelled chemical concentrations could be compared to measurements performed at the station during extensive field campaigns.

The comparison of the simulated and measured concentrations in cloud water shows a good agreement for major species found in droplets, i.e. for sulphate, nitrate and ammonium ions. The model and measurements agree to a smaller extent for organic acids which are overestimated and iron which is underestimated by the model. The reasons for the overestimation of organic acids are not clear and the discrepancy could be partly due to larger uncertainties in the experimental determination of organic concentrations in cloud water, compared to major ions. The underestimation of iron can be explained by the uncertainties on its measured concentration in the particulate phase and by the assumptions made for estimating its soluble fraction in aerosol particles depending on its chemical form into the particle matrix and on its solubility.

The simulated concentrations in cloud water correctly reflect the chemical composition of the activated aerosol particles. Indeed, the analysis of the sources of the chemical species in cloud water shows an important contribution from nucleation scavenging of particles which prevails for nitrate, sulphate and ammonium. However, the gas scavenging is the main source for formic acid in cloud water. The chemical reactivity is

a significant source for nitrate and for sulphate. In addition, the calculation of OH production in cloud droplets shows the significant contribution from iron even if the oxalate inhibiting role is considered.

Finally, the model could further estimate which fraction of the liquid droplets was due to particulate scavenging, gas dissolution, or chemical reaction in the liquid phase. Again, results could be compared to experimental measurements performed by Sellegri et al. (2003b). Numerical results show an underestimation of the interstitial particulate phase which could be due to an overestimation of the activated mass by the model. However, the numerical number scavenging efficiency of particles is in agreement with measured value. Another important discrepancy is found for ammonium partitioning: while measurements show a predominant fraction of the species present in the interstitial gas, the simulation prevails almost all of ammonium in the liquid phase. An explanation for this discrepancy may be the large emissions of ammonium around the Puy de Dôme as suggested by measurements. In general, other results show good agreement with the partitioning obtained from measurements. Moreover, the simulation provides the quantification of chemical in-cloud production which can not be obtained directly from measurements.

In conclusion, this study shows the ability of the M2C2 model to study the complex interactions between cloud microphysics, aerosol particles and photo-chemical reactivity. In future work, such an approach will be extended to the study of organic compounds chemistry in cloud including photochemistry and biologic pathways using the ORE-BEAM (Observatoire de Recherche en Environnement Biophysicochimie de l'Eau Atmosphérique et Modifications anthropiques) project database (<http://wwwobs.univ-bpclermont.fr/atmos/orebeam/orebeampage1.htm>) with special

focus on dicarboxylic acids chemistry representing a crucial scientific issue in organic aerosol particles chemistry (Fuzzi et al., 2006).

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## Figure captions

Figure 1. Back-trajectory arriving at noon at the top of the Puy de Dôme and the corresponding vertical wind speed, the topography is indicated in grey and the summit of the Puy de Dôme by the black arrow. The simulation starts when the air parcel begins its lifting as indicated with the black dashed arrow.

Figure 2. Chemical composition of the four modes of aerosol particles for anthropogenic air mass sampled at the top of Puy de Dôme mountain, adapted from Sellegri et al. (2003a).

Figure 3. Fit of the observed aerosol mass distributions with four lognormal distributions for anthropogenic air mass sampled at the top of Puy de Dôme mountain, adapted from Sellegri et al. (2003a). The solid grey line is the distribution obtained from measurements (obtained by weighting), the dotted grey line is the fitted distribution, the solid black line is the first lognormal distribution for the Aitken mode, the dot-dashed black line is the second lognormal distribution for the accumulation mode 1, the dotted black line is the third lognormal distribution for the accumulation mode 2, and the dashed black line is the fourth lognormal distribution for the coarse mode.

Figure 4. Simulated phase partitioning between the gas, particulate and liquid phases in cloud. The contributions of activated particles, gas scavenging and chemical production are reported for the liquid phase.

Figure 5. Estimated phase partitioning from measurements for anthropogenic influence free tropospheric air masses between the gas, particulate and liquid phases in cloud

calculated from concentrations from the RJI+Cascade Impactor (particulate), RJI+Mist chambers (interstitial gas phase) and CDI (liquid phase). Further partitioning within the liquid phase between the gas-originating fraction and the particle-originating fraction are calculated from the CVI/CDI comparison. Gas concentrations are below detection limits for HCl, HNO<sub>3</sub>, SO<sub>2</sub> and H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, and thus their concentration are assimilated to detection limits. Adapted from Sellegri et al. (2003b).

Table 1. Henry's law constant and equilibrium constants for oxalic acid, and oxalate oxidation and iron-oxalate chemistry in M2C2 model. No temperature dependence (i.e. activation energy) is available for these equilibriums and reactions.

Henry's law constant		H (M atm <sup>-1</sup> )	References
COOHCOOH(g) $\leftrightarrow$ COOHCOOH(w)		5.0 10 <sup>8</sup>	Saxena and Hilderman, 1996
Equilibrium constant		K (M)	Reference
H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> $\leftrightarrow$ H <sup>+</sup> + HC <sub>2</sub> O <sub>4</sub> <sup>-</sup>		5.6 10 <sup>-2</sup>	Smith and Martell, 1976
HC <sub>2</sub> O <sub>4</sub> <sup>-</sup> $\leftrightarrow$ H <sup>+</sup> + C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>		5.42 10 <sup>-5</sup>	Smith and Martell, 1976
Reactions		k <sub>298</sub> (M <sup>-n+1</sup> s <sup>-1</sup> )	References
HC <sub>2</sub> O <sub>4</sub> <sup>-</sup> + OH <sup>-</sup> $\rightarrow$ C <sub>2</sub> O <sub>4</sub> <sup>-</sup> + H <sub>2</sub> O	(A1)	4.7 10 <sup>7</sup>	Getoff et al., 1971
C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> + OH <sup>-</sup> $\rightarrow$ C <sub>2</sub> O <sub>4</sub> <sup>-</sup> + OH <sup>-</sup>	(A2)	7.7 10 <sup>6</sup>	Getoff et al., 1971
HC <sub>2</sub> O <sub>4</sub> <sup>-</sup> + NO <sub>3</sub> <sup>-</sup> $\rightarrow$ NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> + C <sub>2</sub> O <sub>4</sub> <sup>-</sup>	(A3)	6.8 10 <sup>7</sup>	Raabe, 1996
C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> + NO <sub>3</sub> <sup>-</sup> $\rightarrow$ NO <sub>3</sub> <sup>-</sup> + C <sub>2</sub> O <sub>4</sub> <sup>-</sup>	(A4)	2.2 10 <sup>8</sup>	Raabe, 1996
HC <sub>2</sub> O <sub>4</sub> <sup>-</sup> + Cl <sub>2</sub> <sup>-</sup> $\rightarrow$ C <sub>2</sub> O <sub>4</sub> <sup>-</sup> + 2Cl <sup>-</sup> + H <sup>+</sup>	(A5)	1.3 10 <sup>6</sup>	Estimated as in Ervens et al., 2003
C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> + Cl <sub>2</sub> <sup>-</sup> $\rightarrow$ C <sub>2</sub> O <sub>4</sub> <sup>-</sup> + 2Cl <sup>-</sup>	(A6)	4.0 10 <sup>6</sup>	Estimated as in Ervens et al., 2003
HC <sub>2</sub> O <sub>4</sub> <sup>-</sup> + SO <sub>4</sub> <sup>-</sup> $\rightarrow$ SO <sub>4</sub> <sup>2-</sup> + H <sup>+</sup> + C <sub>2</sub> O <sub>4</sub> <sup>-</sup>	(A7)	3.4 10 <sup>5</sup>	Buxton et al., 1999
C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> + SO <sub>4</sub> <sup>-</sup> $\rightarrow$ SO <sub>4</sub> <sup>2-</sup> + C <sub>2</sub> O <sub>4</sub> <sup>-</sup>	(A8)	1.0 10 <sup>6</sup>	Buxton et al., 1999
C <sub>2</sub> O <sub>4</sub> <sup>-</sup> + O <sub>2</sub> $\rightarrow$ 2CO <sub>2</sub> + O <sub>2</sub> <sup>-</sup>	(A9)	2.0 10 <sup>9</sup>	Estimated as in Ervens et al., 2003
[Fe(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> ] <sup>-</sup> + hv $\rightarrow$ Fe <sup>2+</sup> + C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> + C <sub>2</sub> O <sub>4</sub> <sup>-</sup>	(A10)	calculated	Faust and Zepp, 1993
[Fe(C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ] <sup>3-</sup> + hv $\rightarrow$ Fe <sup>2+</sup> + 2C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> + C <sub>2</sub> O <sub>4</sub> <sup>-</sup>	(A11)	calculated	Faust and Zepp, 1993
C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> + Fe <sup>3+</sup> $\rightarrow$ [Fe(C <sub>2</sub> O <sub>4</sub> )] <sup>+</sup>	(A12)	7.5 10 <sup>6</sup>	Estimated using stability constant: Martell and Smith, 1977
[Fe(C <sub>2</sub> O <sub>4</sub> )] <sup>+</sup> $\rightarrow$ C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> + Fe <sup>3+</sup>	(A13)	3.0 10 <sup>-3</sup> =k <sub>15</sub>	Estimated
C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> + [Fe(C <sub>2</sub> O <sub>4</sub> )] <sup>+</sup> $\rightarrow$ [Fe(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> ] <sup>-</sup>	(A14)	1.89 10 <sup>4</sup>	Martell and Smith, 1977
[Fe(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> ] <sup>-</sup> $\rightarrow$ C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> + [Fe(C <sub>2</sub> O <sub>4</sub> )] <sup>+</sup>	(A15)	3.0 10 <sup>-3</sup>	Moorhead and Sutin, 1966
C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> + [Fe(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> ] <sup>-</sup> $\rightarrow$ [Fe(C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ] <sup>3-</sup>	(A16)	4.8 10 <sup>1</sup>	Estimated using stability constant: Martell and Smith, 1977
[Fe(C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ] <sup>3-</sup> $\rightarrow$ C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> + [Fe(C <sub>2</sub> O <sub>4</sub> ) <sub>2</sub> ] <sup>-</sup>	(A17)	3.0 10 <sup>-3</sup> =k <sub>15</sub>	Estimated



Table 2. Initial gas phase concentrations from Voisin et al., 2000.

Species	Gaseous concentration (ppbv)
N <sub>2</sub>	7,8.10 <sup>8</sup>
O <sub>2</sub>	2,1.10 <sup>8</sup>
H <sub>2</sub> O	5,7.10 <sup>7</sup>
O <sub>3</sub>	37
NO	0.9
NO <sub>2</sub>	6.2
CH <sub>4</sub>	1600
CO	100
HNO <sub>3</sub>	0.15
HNO <sub>2</sub>	0.054
H <sub>2</sub> O <sub>2</sub>	0.07
HCHO	6
CH <sub>3</sub> OH	2.25
SO <sub>2</sub>	0.45
HCOOH	0.28
NH <sub>3</sub>	0.13
HCl	0.07

Table 3. Initial physico-chemical properties of aerosol particles; the first three parameters are defined in equation (1),  $\rho_{api}$  is the density of aerosols for mode i,  $z_i$  is the number of dissociated ion for mode i,  $\phi_i$  is the mass fraction of soluble materials in mode i,  $M_{api}$  is the molar mass of mode i. The mass fraction of chemical species is related to soluble mass.

Mode	$N_{api}$ (# cm <sup>-3</sup> )	$a_{mi}$ (μm)	logσi	$\rho_{api}$ (g cm <sup>-3</sup> )	$z_i$	$\phi_i$ (%)	$M_{api}$ (g mole <sup>-1</sup> )
1	111.9	0.038	0.255	1.75	2	31	175
2	4.2	0.205	0.278	1.74	2	40	274
3	1.5	0.330	0.041	1.74	2	61.5	248
4	0.026	1.300	0.301	1.75	2	65	272
Mode	Nitrate (%)	Ammonium (%)	Sulphate (%)	Formate (%)	Oxalate (%)	Iron (%)	
1	30	30.8	26.4	2.2	3.3	0	
2	29.6	18.2	35	1.2	1.8	0.1	
3	30	14.8	39.5	0.8	1.2	0.2	
4	43	2.7	19	2.5	3.7	0.8	

Table 4. Comparison of observed and simulated averaged pH value and concentrations in cloud water in  $\mu\text{g L}^{-1}$ , except for iron in  $\mu\text{M}$ . Observed values are adapted from Marinoni et al., 2004 and from Parazols et al. (2006) for anthropogenic air mass sampled at the Puy de Dôme station.

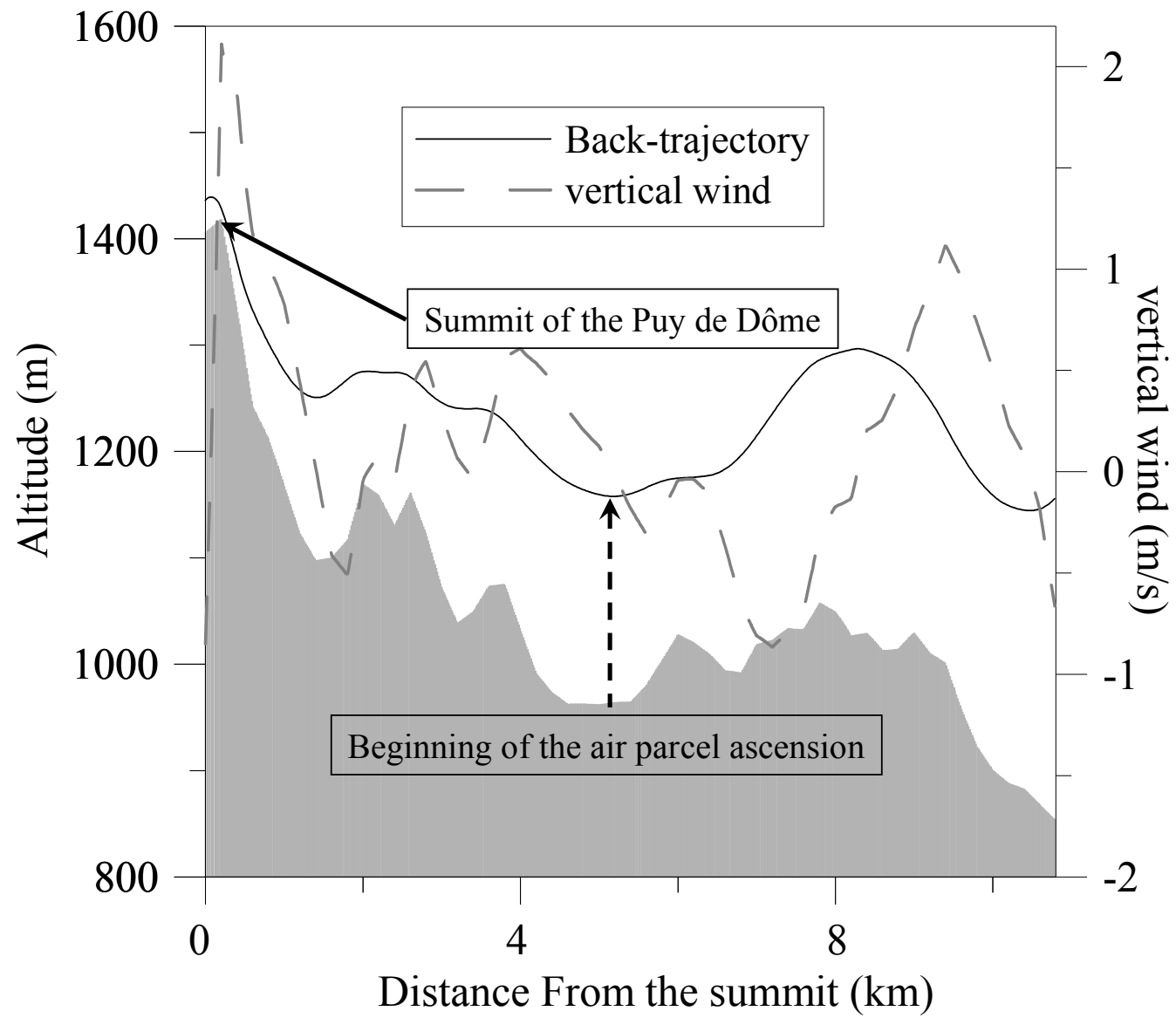
	pH	Nitrate	Ammonium	Sulphate	Formate	Oxalate	Iron ( $\mu\text{M}$ )
Observed	$3.7 \pm 0.4$	$10702 \pm 6631$	$3074 \pm 934$	$5460 \pm 1584$	$412 \pm 304$	$155 \pm 114$	$5.3 \pm 3.2$
Simulated	3.6	14880	2520	6940	920	360	1.9

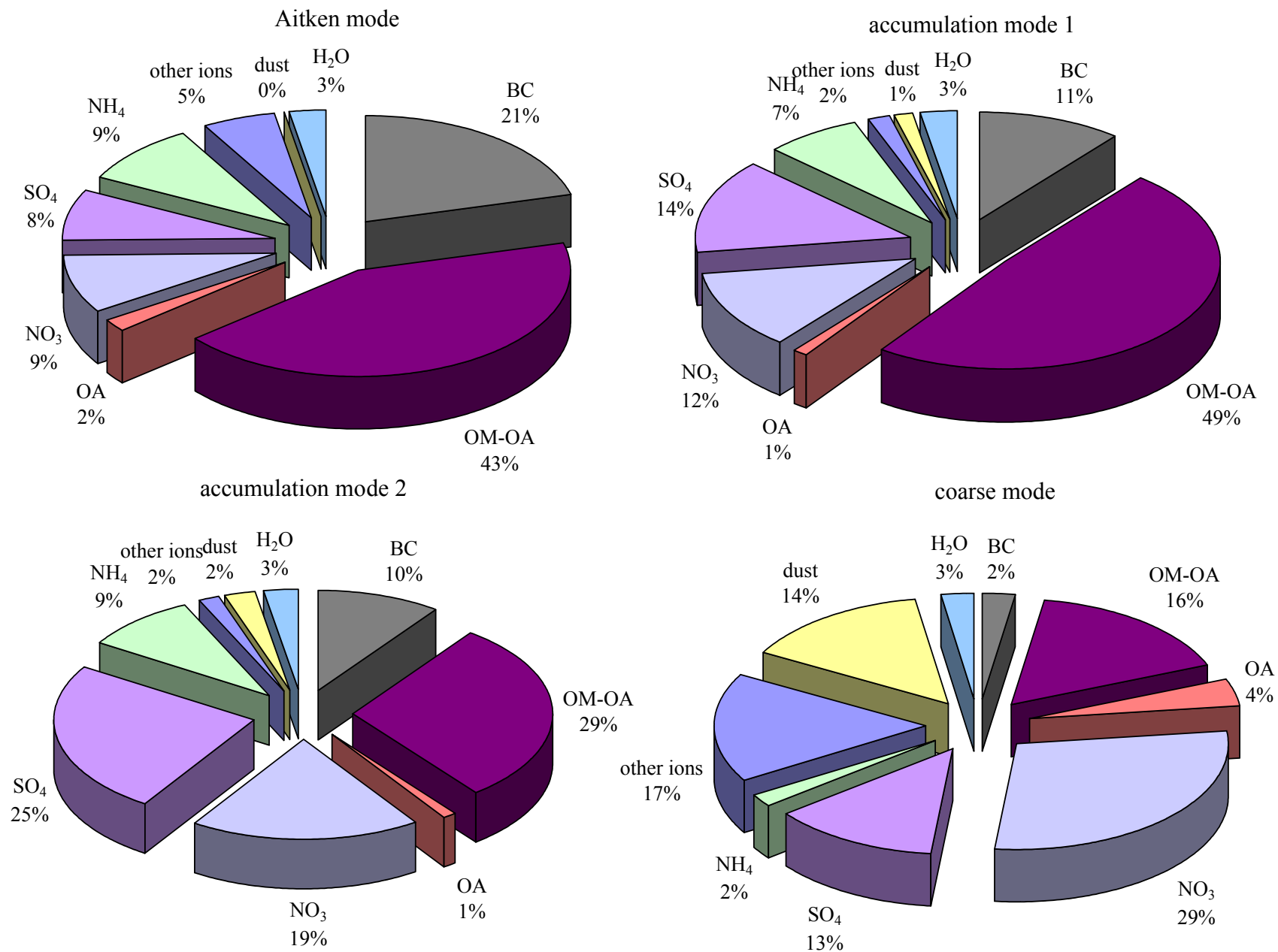
Table 5. Contribution to the concentrations of nitrate, sulphate, ammonium and formic acid in the liquid cloud droplet at the end of the simulation from activation of aerosol particles, from scavenging of gases and from chemical reactivity .

	<b>Aerosols scavenging</b>	<b>Gas scavenging</b>	<b>Chemistry</b>	
			Gas phase production	Aqueous phase production
Nitrate	56	15.5	23	5.5
Ammonium	72.5	27.5	0	0
Sulphate	73	0	0	27
Formate	20	75	0	5

Table 6. Contribution of gas scavenging, iron reactivity and other pathways in OH cloud droplets production for the reference simulation including iron-oxalate chemistry and a simulation neglecting oxalate chemistry.

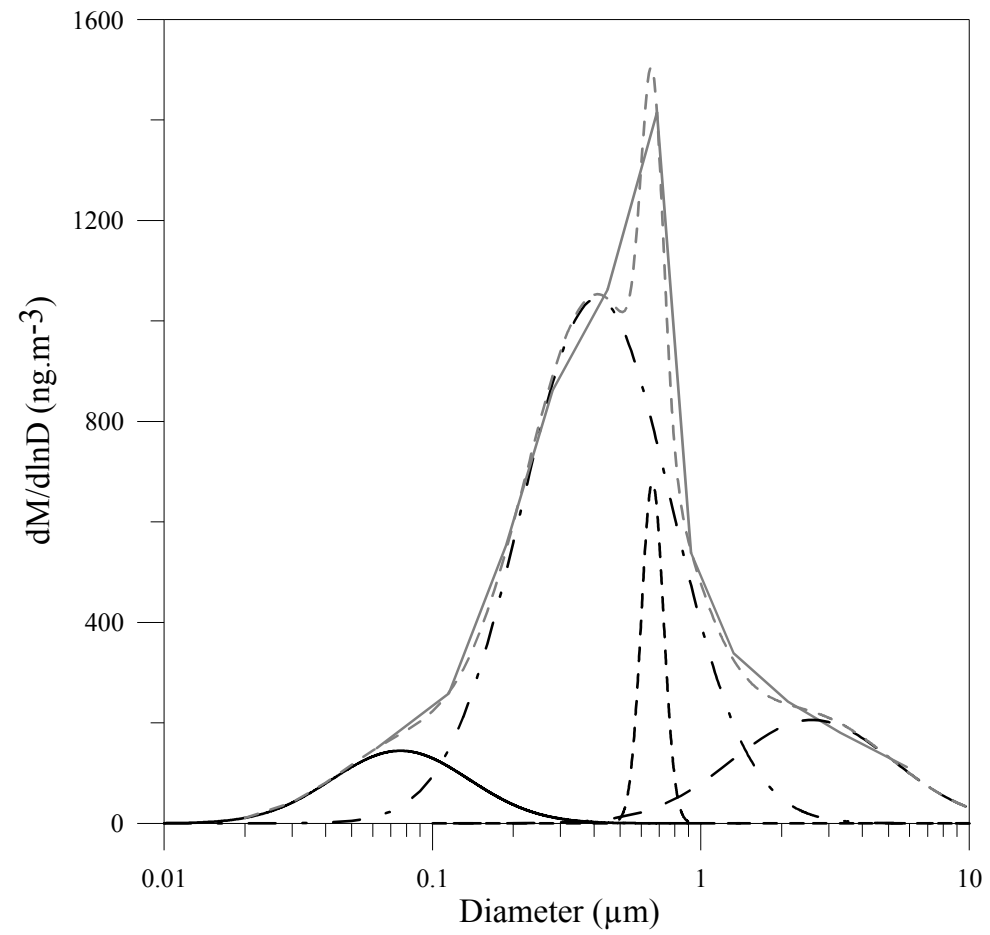
	<b>OH scavenging</b>	<b>Iron reactivity</b>		<b>Other pathways</b>
		Iron(III) + hv	Fenton	
Iron and oxalate	57%	26%	4%	13%
Iron	36%	55%	2%	7%



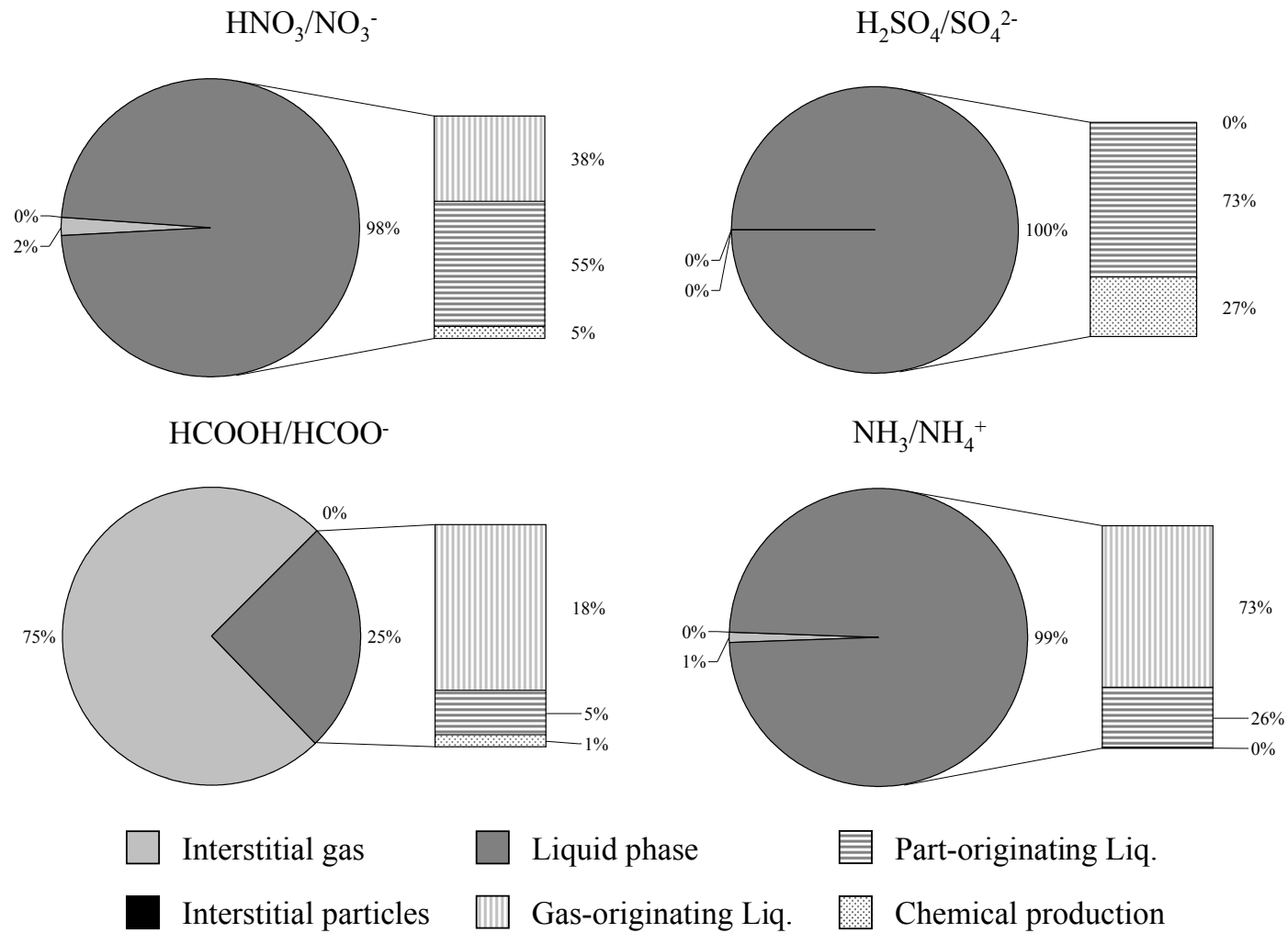


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