A modeling tool for studying interactions between aerosol particles and chemistry in cloud

M. Leriche, L. Deguillaume, F. Champeau, N. Chaumerliac

Laboratoire de Météorologie Physique (LaMP), Observatoire de Physique du Globe de Clermont-Ferrand (OPGC), UMR 6016 CNRS, France

SCIENTIFIC CONTEXT

For several years, significant efforts were made by the scientific community to understand tropospheric chemistry. However, these efforts have been mainly focused on homogeneous gas phase chemistry, which is currently well documented [1,2]. The role of clouds in the chemical composition of the atmosphere is significant in two aspects of the planetary evolution: the atmospheric oxidizing capacity and the greenhouse effect linked to the role of aerosols (direct and indirect) in radiative forcing. Even if some modeling studies have attempted to understand the overall role of cloud chemistry in global climate studies [3], our knowledge is still at a rudimentary stage when looking at the details of cloud processes. An integrated approach using modeling tools including laboratory data and field observations could help to improve our understanding of these processes.

MODEL DESCRIPTION

The M2C2 (Model of Multiphase Cloud Chemistry) model [4,5] is an air parcel model coupling aerosol and cloud microphysics with chemistry. For aerosol particles, a two-moment microphysical scheme is used and aerosols are represented by the sum of n ($n \in [1,6]$) lognormal distributions evolving due to nucleation and impaction scavenging. The cloud parameterization also considers a two-moment scheme with warm processes for cloud water and rainwater and with ice processes, which are under development, for three hydrometeors: pristine ice, snow and graupel. The multiphase chemistry module is explicit and is valid for any environment; the aqueous phase chemistry mechanism describes the chemistry of HO_x, sulfur, chlorine, carbonates, NO_y, transition metals and organic compounds [5,6]. Liquid drops pH is calculated at each time step by solving the electroneutrality equation. The dynamical trajectory used to initialize the air parcel comes from 3D meso-scale simulations using nested grids.

EXAMPLES of M2C2 APPLICATIONS

Study of wintertime polluted air mass at the Puy de Dôme mountain station

The M2C2 model has been applied to typical wintertime continental air mass under anthropogenic influence encountered at the Puy de Dôme station, an ACCENT super-site in the middle of France. The air parcel model has been initialized using a back-trajectory computed from a three dimensional simulation of the studies situation performed with a meso-scale meteorological model using three nested grids. The concentrations of trace gases are initialized with data from the CIME campaign. For aerosol particles, four modes are used and their physical and chemical properties are taken from the classification of aerosol particles depending on the air masses encountered at the Puy de Dôme [7]. Fine aerosol particles (Aitken mode) exhibit a high contribution of organic compounds while coarse aerosol particles show a high contribution of inorganic compounds, nitrate, sulfate and ammonium (Figure 1). Measurements show the presence of two accumulation modes, one with predominance of organic compounds and another one with predominance of inorganic compounds (Figure 1). Comparison of results with measurements show a good capability of the model to reproduce observed chemical concentrations in gas phase and in cloud water. While measurements do not allow determining the origin of the different sources of chemical species in cloud water and to identify these sources, the model provides this information. Results show that, for inorganic compounds, aerosol particles scavenging predominates (Table 1) with the highest contribution for sulphate due to activation of accumulation mode 2 and coarse mode. For nitrate, the contribution from aerosols scavenging is less important due to high NO_x levels leading to efficient nitrate production both in gas and aqueous phases (Table 1).

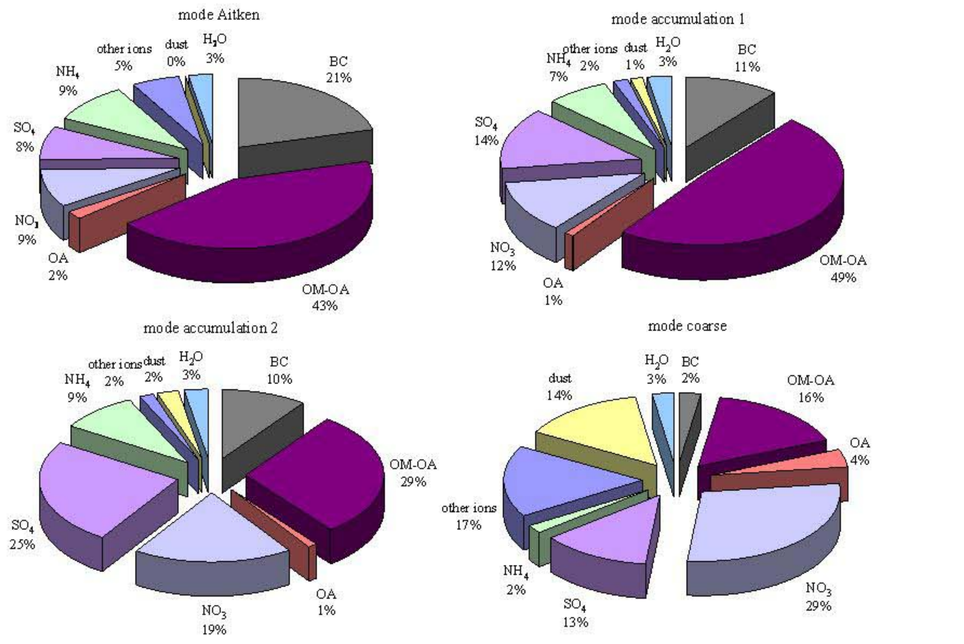

Figure 1. Chemical composition of the four modes of aerosol particles for continental air mass with anthropogenic influence sampled at the top of Puy de Dôme mountain [7].

Table 1. Contribution of the source from activation of aerosols and of sources from chemistry including scavenging of gases and chemical reactivity to the concentrations of nitrate, sulphate and ammonium at the end of the simulation.

	Aerosols scavenging	chemistry		
		Initialization in gas phase	Gas phase production	Aqueous phase production
Ammonium	65	35	0	0
Sulfate	90	0	0	10
Nitrate	50	27	10	13

Impact of radical versus non-radical pathway in the Fenton chemistry on the iron redox cycle in clouds

M2C2 model allows performing easily sensitivity tests either on chemistry or on microphysics processes. Such test has been performed for example on an important chemical production pathway of OH radical in cloud; the Fenton chemistry initiated by the oxidation of Fe(II) by hydrogen peroxide [8]. The first step of Fenton chemistry is actually under controversy [9], either it produces an OH radical (A1-radical pathway) or a ferryl ion (A2-non-radical pathway). These two pathways have been studied using M2C2 in order to assess their impact on HO_x chemistry in cloud through the redox cycle of iron. Results show that, considering the non-radical pathway, the production of OH radical in cloud decreases (Figure 2). However, for the non-radical case, the ferryl ion concentration is up to four orders of magnitude higher than the OH concentration highlighting its potential role in oxidative capacity of cloud droplets.

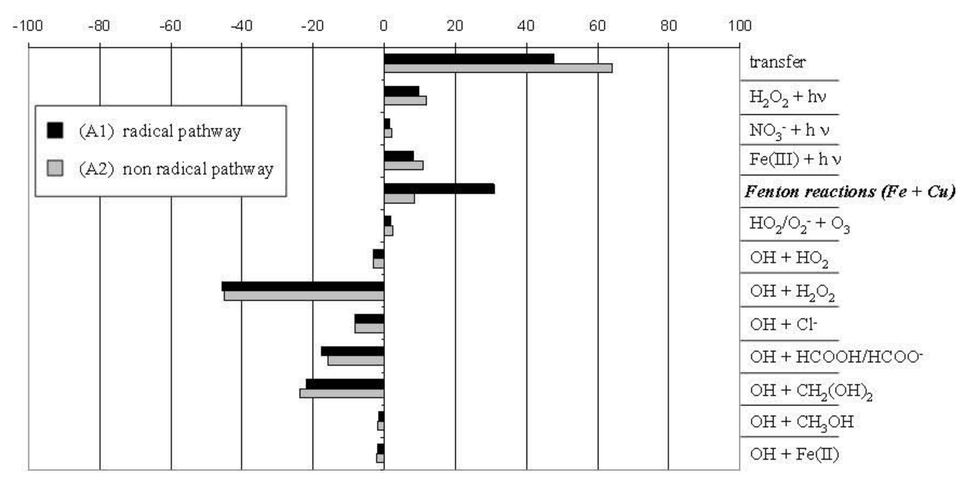

Figure 2. Sinks and sources of OH(aq) at noon considering, for the Fenton reaction, the radical pathway and the non-radical pathway.

Conclusion and perspectives

In conclusion, the M2C2 model is a powerful numerical tool to study interactions between aerosol particles, microphysical processes and chemistry in cloud. It could be used just as easily for interpretation of in-situ measurements and for theoretical studies to highlight the main reaction pathway in a given chemical mechanism. Moreover, the framework of the model allows performing sensitivity tests before setting up parameterizations to be included in chemical transport models. Following the implementation of the ice phase microphysics in the model, the interactions between chemistry and iced hydrometeors will be included in the model allowing the study of mixed phase clouds chemistry.

REFERENCES

[1] R. Atkinson and J. Arey, *Chemical Reviews*, 103 (2003) 4605-4638.
[2] R. Atkinson *et al.*, *Atmospheric Chemistry and Physics*, 4 (2004) 1461-1738.
[3] J. Lelieveld and P.J. Crutzen, *Journal of Atmospheric Chemistry*, 12 (1991) 229-267.
[4] M. Leriche *et al.*, *Journal of Geophysical Research*, 108 (2003) doi:10.1029/2002JD002950.
[5] L. Deguillaume *et al.*, *Atmospheric Chemistry and Physics*, 4 (2004) 96-110.
[6] M. Leriche *et al.*, *Atmospheric Environment*, 34 (2000) 5015-5036.
[7] K. Sellegri *et al.*, *Journal of Geophysical Research*, 108 (2003) doi:10.1029/2002JD002747.
[8] L. Deguillaume *et al.*, *Chemosphere*, 60 (2005) 718-724.
[9] L. Deguillaume *et al.*, *Chemical Reviews*, in press (2005).

ACKNOWLEDGEMENTS

This work was supported by the PNCA *Programme National de Chimie Atmospheric* National French program.
Computer resources were provided by I.D.R.I.S. *Institut du Développement et des Ressources en Informatique Scientifique*, project n°000187.