P2.17 ESTIMATING THE IMPACT OF NATURAL AND ANTHROPOGENIC EMISSIONS ON CLOUD CHEMISTRY : THE INFLUENCE OF ORGANIC COMPOUNDS.

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1. INTRODUCTION

It has been known for many years that radically different cloud condensation nuclei (CCN) size distributions and compositions, play a clear role in precipitation development. A change in these characteristics is expected to produce changes in rain development. Even though a large number of efforts have been conducted in this direction, the role of organic compounds in the microphysical and dynamic structure of clouds remains unclear.

The potential role of organic compounds in the chemistry of wet aerosols was investigated many years ago, but over the last few years, the contribution of organic aerosols to the mass of cloud condensation nuclei (CCN) has been investigated by several authors (Novakov and Penner, 1993). They reported that pure organic smoke aerosols from cellulose combustion are efficient CCN without being associated to inorganic salts. The ability of organic compounds to act as CCN have been investigated in laboratory and field experiments (Saxena et al., 1995) and will be tested in future versions of this model.

In this study we present preliminary results from a theoretical 1-D cloud model that includes detailed microphysics and organic and inorganic chemistry. The goal is to incorporate chemical reactions both inorganic and simple organics to attempt to estimate the impact of emissions on precipitation development.

2. THE CLOUD MODEL

A 1-D Eulerian model with detailed microphysics is used in this study. The dynamical framework **is described** in Alfonso and Raga (2002**)**. The microphysical modules simulate the evolution of the raindrop, aerosol and gas concentration spectra by activation, condensation, coalescence. Three distribution functions were defined in the model, one for cloud condensation nuclei (CCN), with a maximum of 64 categories from 0.0041 to 5.93 µm; one for small drops up to 1µm, and another for drops up to 4096 µm with 73 categories. Aerosol, droplet and gas concentration evolution by condensation coalescence and breakup are computed.

3. CHEMISTRY

The microphysical model in the 1D dynamical framework has been coupled to an aqueous phase chemistry model, for calculating pH temporal evolution as a function of droplet size. The uptake and desorption of gas-phase species (SO_2, H_2O_2 ,OH, HCHO, HCOOH) was implemented by means of a quasi analytical solution of the diffusion equation. The aqueous phase chemistry follows Chameides (1984) and Seinfeld and Pandis (1998), in order to calculate the generation of sulfuric acid (S(IV) to S(VI) conversion) and the production of formic acid from hydrated formaldehyde, that is oxidized by the hydroxyl radical in the aqueous phase $(OH)_{aq}$. HSO_3^- and SO_3^{2-} react with disolved formaldehyde to produce hydroximethanesulfonate ion (HMSA), that is a member of the S(VI) family.

The gas-phase species included in the model, and the initial concentrations at the surface are listed in Table 1. The aqueous-phase species are listed in Table 2. The final $[H^+]$ is calculated from an equation that is derived from the electroneutrality condition. Finally the pH is calculated for each drop category.

4. INITIAL CONDITIONS.

Table 1 presents the initial concentrations at the surface for all the gases. Chameides (1984) have estimated the production of formic acid, he set very low initial concentrations of $HCOOH_{(g)}$.

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Table 1. Gas-phase chemical species and initial concentrations at the surface.

Gas-Phase Species	Initial concentrations at the surface. (ppb)
SO_2	20
H_2O_2	1
OH	5×10^{-4}
HCHO	1
HCOOH	1

Table 2. Aqueous-phase species.

Aqueous-phase species
$S(IV)=SO_2+HSO_3^-+SO_3^{2-}$
$S(VI)=SO_4^{2-}+HSO_4^-+H_2SO_{4(aq)}$
$HCOOH+HCOO^-$
$H_2C(OH)_2$
HCHO
$HOCH_2SO_3^{2-}$
H_2O_2
OH

For realistic atmospheric conditions initial $HCOOH_{(g)}$ concentrations are often higher (between 0.03-1.7 ppb), (Chebbi et al., 1996) and are close to $HCHO_{(g)}$. Finally a 1ppb initial concentration for both formic acid and formaldehyde was choosen. OH concentration has a high variability during the day. The concentration was set equal to $5*10^{-4}$ ppb following Ridley et al. (1990). A high background concentration of SO_2 (20 ppb) is assumed, and is associated with anthropogenic emissions from the petroleum platforms. Gas concentrations are assumed to decrease exponentially with height in our calculations.

For the initial CCN distributions we choose a two mode log-normal. The water soluble fraction is 10 % and consists of $(NH_4)_2SO_4$. The parameters of the distribution are listed in Table 3. The presence of dicarboxylic acids in the aerosol composition is not considered in these preliminar simulations.

Table 3. Parameters of the maritime CCN distribution; n_i is the number of CCN per cm^3 , R_i is the geometric mean aerosol particle radius in µm and σ_i is the standard deviation in mode i.

Mode	$n_I(cm^{-3})$	R_I(µm)	$\log\sigma_i$
1	50	0.01	0.3
2	50	0.1	0.1

The initial sounding corresponds to the city of Veracruz, located on the coast of the Gulf of Mexico. A small updraft is imposed to start convection in the layer below 2 km, with a maximun value of $1ms^{-1}$ at a height of 1 km. All the gases concentration are assumed to decrease exponentially with height in our calculations.

5. RESULTS

Four simulations were performed, with and with no aqueous phase reactions, and with different concentrations of formic acid at the surface.

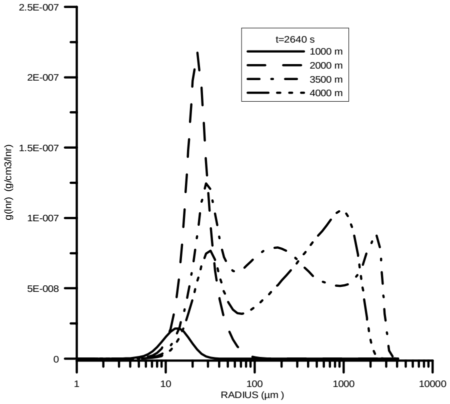

Fig. 1. The drop mass distribution function g(lnr) (g/cm^3 /lnr) versus radius at three different incloud levels at t=2640 s.

The drop size spectra obtained for four different cloud levels at t=2640 s (the same for the three experiments) are presented in Fig.1, displayed in terms of the liquid water content per unit lnr interval g(lnr). In our simulations, at the early stage of the cell development the drop size distributions are formed mainly by nucleation and condensation (1000 and 2000 m curves in Fig. 1), and these distributions are unimodal. In the upper levels, where cloud droplets have had a longer residence time (4000 m curve in Fig. 1) and therefore are large enough to initiate the coalescence process, bimodal drop size distributions are obtained. A trimodal distribution at 3500 m is observed as a result of the combined effect of condensation, coalescence and sedimentation (first, second and third mode respectively)

5.1. CASE WITH NO AQUEOUS-PHASE REACTIONS

In this case, the process that causes the increase of the acidity in the drops is the direct transfer of acidic aerosols and gases to droplets (the diffusion of SO_2 to form S(IV), and the diffusion and dissociation of HCOOH). The variation of the gas concentration in air with height at 2400 s for the HCHO, HCOOH and H_2O_2 that have an initial 1ppb concentration at the surface, is displayed in Fig. 2. Due to the high solubility constant for the H_2O_2, the gas concentrations in the air are lower for the H_2O_2 case, that diffusses more than the HCHO and the HCOOH. The HCOOH diffuses very efectively because of the relatively high solubility constant (see table 4.) and the effect of the dissociation that enhances the uptake.

Table 4. Solubility constants

Reaction	Solubility constant M atm^{-1}
$(SO_2)_g \leftrightarrow (SO_2)_{aq}$	1.23
$(H_2O_2)_g \leftrightarrow (H_2O_2)_{aq}$	9.7×10^4
$(OH)_g \leftrightarrow (OH)_{aq}$	10^5
$(HCHO)_g \leftrightarrow (CH_2(OH)_2)_{aq}$	7×10^3
$(HCOOH)_g \leftrightarrow (HCOOH)_{aq}$	3.7×10^3

The pH spectra obtained at three different incloud levels are displayed in Fig. 3. As height increases, drops became less acidic because they tend to be in equilibrium with the environmental gas concentrations, and the concentration decreases with height. As a result, aqueous S(IV) and HCOOH concentrations decrease with height and the pH increases. Larger than 200 µm drops at 2000 and 3000 m are mainly produced by collisions of numerous small drops that have scavenged SO_2 and HCOOH according to Henry's law at lower lewels. They are more acidic, because they desorb less efficiently than smaller ones. As a result, they have larger concentrations than equilibrium S(IV) and $HCOOH_{aq}$ concentrations at that height. At cloud base (1000 m) smaller drops are in equilibrium with gas concentrations and are more acidic than larger drops.

5.1.1. CONTRIBUTION OF FORMIC ACID TO RAIN ACIDITY

The contribution of monocarboxylic and dicarboxylic acids to bulk rain acidity was estimated by Kawamura et al. (1996) by using experimental data. They reported that, although nitric and sulfuric acid are the principal contributors to H^+ ion concentration in acid rain, organic acids do lower the pH of the rainwater from 0.1 to 1.9 pH units.

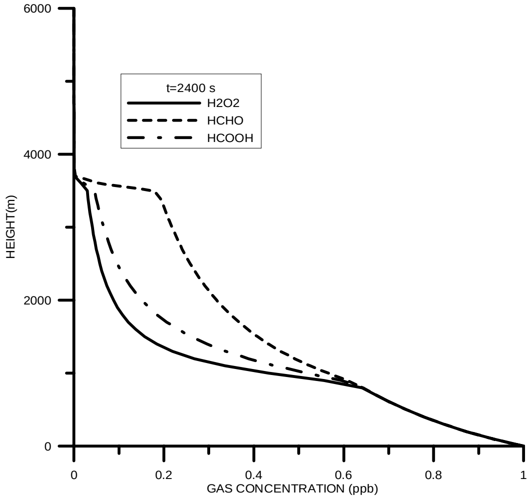

Fig. 2. Concentration (ppb) as a function of height for H_2O_2, HCHO and HCOOH at t=2400 s.

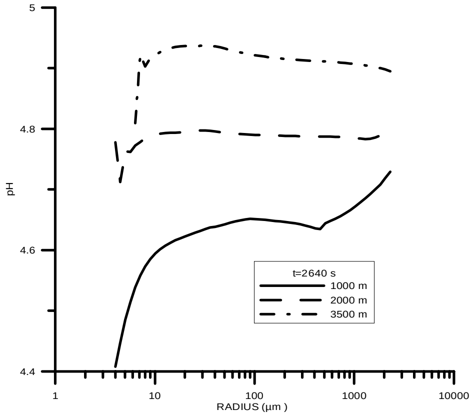

Fig. 3. pH at three different incloud levels at t=2640 s for the case with no aqueous-phase chemistry.

In this report a lowering of the pH in 0.1 pH (about 2 % reduction) units is observed for every drop category, because only one monocarboxylic acid (formic acid with dissociation constant $K_1=1.77*10^{-4}$) is included in our simulations.

Reductions down to 1.9 units are obtained when dicarboxylic acids with larger dissociation constants are included in the analysis (Kawamura et al. (1996)).

5.1 CASE WITH AQUEOUS-PHASE REACTIONS

Chemical reactions consume dissolved SO_2, H_2O_2, HCHO, OH to produce S(VI), HCOOH, HMSA and enhance cloud water acidity. This chemical reactions perturb the equilibrium aqueous phase levels of the species and a gas phase adjustment takes place.

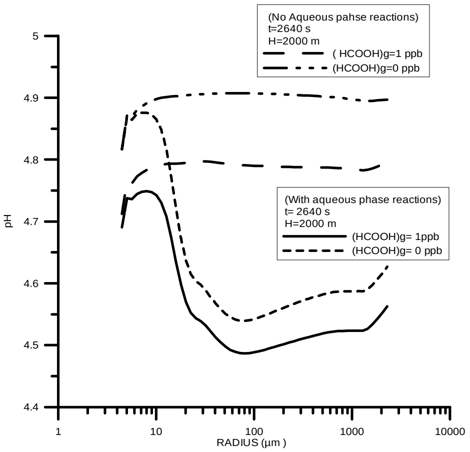

Fig. 4. pH at H=2000 m at t=2640 s for the cases with aqueous and no aqueous-phase reactions and different initial concentrations of HCOOH at the surface.

There is an enhance in the uptake for species that are depleted in the aqueous phase. As a consequence, a more drastical reduction of the gas-phase concentrations is observed (see Fig. 4).

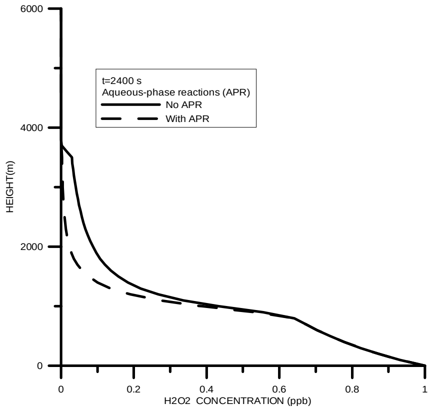

Fig. 5. H_2O_2 (ppb) as a function of height for H_2O_2 for the cases with aqueous and no aqueous-phase reactions.

The importance of the aqueous phase reactions for increasing the drops' acidity can be inferred from the results ilustrated in Fig. 4., where an important increase in the acidity is observed.

5.2.1. CONTRIBUTION OF FORMIC ACID TO RAIN ACIDITY

Although the generation of sulfuric acid is the most important factor in generating acidity in drops, there is a contribution due to the diffusion and generation of formic acid in drops. In this case, the more important reduction (due to diffusion) of the pH is observed at the small end of the spectra, resulting from the uptake of HCOOH that is confined mainly to small drops (from 0.1 to 0.15 pH units). At the large end the reduction is smaller, because the acidity generated by aqueous reactions (the production of formic acid from formaldehyde) tend to reduce the gap (less than 0.1 pH units).

6. CONCLUSIONS

A microphysical-chemical cloud model for calculating the uptake of both aerosols and gases was used to test the influence of aerosol composition, solubility, and background gas concentrations in the development of cloud and precipitation, and in the pH spectral evolution was studied. The reduction of the pH due to diffusion and aqueous phase production of HCOOH was tested (from 0.05 to 0.15 pH units). A more detailed follow up study will test the relative contribution of dicarboxylic acids in CCN on the drop concentration and the pH of precipitation.

7. ACKNOWLEDGEMENTS

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