**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on **"Estimating the impact of natural and anthropogenic emissions on cloud chemistry: the influence of organic compounds"** *by* **L. Alfonso and G. B. Raga**
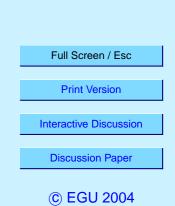
L. Alfonso and G. B. Raga

Reply to Reviewers

First, we would like to thank the anonymous reviewers for their comments that will improve the quality of our final paper. Our revised version will several of their suggestions.

Reviewer 1

Major comments:

a) Aerosol number concentration: We agree with the referee that the results are specific, but the aim of the paper is to simulate the influence of Petroleum Industry emissions in the Campeche Area in Mexico. That is why we choose a maritime aerosol distribution with low aerosol number concentrations (100 1/cm3). This value of the

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concentration is in agreement with the values reported by Hoppel et al. (1990) and their measurements of aerosol size distributions in the marine boundary layer over the Atlantic Ocean. The shape of the distribution is discussed carefully in a previous paper (Alfonso and Raga, 2002), and also follows the results of Hoppel et al. (1990). We could consider higher aerosol concentrations, but by using the dynamic framework developed by Asai and Kasahara (1967) we always obtained, for concentrations higher than 200 1/cm3, an unrealistically long cloud lifetime for maritime conditions. This is not an error of the microphysical component of the model, but a limitation of the 1.5 dimensional dynamic eulerian framework. In general, it represents in a correct way the life cycle of a convective cloud, as was demonstrated by Ogura and Takahashi (1971), but a cloud of an infinite cloud lifetime was obtained when a small autoconversion coefficient was set in the parameterization for the autoconversion (Ogura and Takahashi, 1971). This finding was corroborated by Takahashi (1976) when he modelled continental clouds with the same dynamics, but coupled with a detailed microphysical framework. In this case, a continental cloud is equivalent to a small autoconversion coefficient in the parameterized case. A posible solution to this problem is to improve the parameterization for the horizontal turbulent transport, as was pointed out by Cotton (1975), but this is beyond the scope of our investigation. Nevertheless, to fully clarify this point in the revised version of the paper, we now introduce the following changes in the original title of the paper, as suggested by the reviewer. ("Te influence of organic compunds on the development of precipitation acidity in maritime clouds")

b) Organic and Inorganic fraction: Putaud et al. (2000) measured organic, inorganic, mineral content and mass concentration of the submicron aerosol for maritime conditions. In the unperturbed marine boundary layer the aerosol average composition was 37% for non-sea-salt SO42-, 21% for sea salt, and 20% for organic compounds. On the other hand, Penner and Novakov (1997) reported that, in urban areas, in comparison to organic carbon, average sulfate concentrations were low, about 4.7% of total suspended particles (TSP). Following these results in our study we considered an intermediate fraction (10%) of non-sea-salt (NH4)2SO4, taking into account the

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large component of non soluble hydrocarbons from Petroleum Industry emissions in the Campeche area. Also, we took into account the effect of anthropogenic emissions from Petroleum Industry by considering large SO2 concentrations up to 20 ppb and an ammonium sulfate + organic soluble matter aerosol composition (Ramos, 1997).

c) Parameterizing the chemical composition of the organic part: Since this is a modelling study and the composition of WSOC in the aerosol phase is such a complex problem, a parameterization is needed in order to model properly the activation of droplets. Mircea et al. (2002) parameterized the low molecular weight organic in the Koehler equation, as a non-specified dycarboxylic acid having molecular mass M=100, and number of dissociated ions = 3. For the rest of the water soluble organic fraction they choose fulvic acid, with M=732 and number od dissociated ions=5. Feingold and Chuang (2002), in their study consider that the particles are partially soluble and the composition to be 50% ammonium sulfate and 50% of an unspecified nonhygroscopic material. The aerosol composition is, of course, much more complex, and a simplification is needed in order to effectively address the problem of the composition in cloud models. In our study, we parameterized the WSOC as oxalic acid, with molecular mass M=90 and number of dissociated ions =3. We choose oxalic acid since it is one of the most abundant dicarboxylic acids in aerosols. As pointed out by Kawamura et al. (1996), dicarboxylic acids are mostly present in particulate phase in the ambient atmosphere. Kawamura and Kaplan (1987) measured the aerosol concentrations of dicarboxylic acids in the urban atmosphere of Los Angeles. They found that oxalic acid was the dominant dicarboxylic acid followed by succinic, malonic, maleic, adipic and phtalic acidis. Yao et al. (2002) studied the PM2.5 concentrations and the size distributions of dicarboxylic acids in Hong Kong. On average, they found that the oxalate concentration was larger than the malonate and succinate concentrations. Low molecular weight dicarboxylic acids and their salts are highly water soluble. Among these, oxalic acid is generally the most abundant (Kawamura et al., 1996), and they are hygroscopic (Peng et al., 2001) and act as condensation nuclei. The above mentioned reasons justify our parameterization of the WSOC as oxalic acid.

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Minor comments:

1) p. 593 The reference to the paper by Mary Barth et al. (2000) was removed in the revised version of the paper, as suggested by the referee.

2) p. 595 In our model we have 64 bins for the entire CCN spectrum (from 0.0041 to 5.93 μm), 48 bins for the small droplets (from 0.0041 to 1μm) and 73 bins for the rest of the droplet spectrum (from 1 to 4096 μm). Therefore, we could have droplets smaller that 1μm after the activation of CCN. Within our formalism, these small droplets are immediately transferred to the small droplets grid. Without this additional grid, there would be a need to extrapolate these droplets onto the grid for the rest of the spectrum (from 1 to 4096 μm), and, as a result, there would be an artifficial peak in the smaller bin (for 1μm). By doing this, we avoided an artifficial accumulation of activated droplets in the smaller bin, droplets that are actually smaller than 1μm. On the other hand, interpolation methods are very diffusive and result in an artifficial broadening of the aerosol and droplet spectra. By using our additional grid, we reduce the numerical diffusion during activation.

3) In the revised version, symbols are explained after they are first used, as suggested by the referee.

4) p. 598: the corresponding modification was made, as suggested.

5) p. 602: That is correct, the results are qualitatively the same as found by Mircea et al. 2000. The corresponding reference to them has been added to Table 1 in the final revised version.

6) p. 610: Text has been changed, actually, collision and coalescence explain the behaviour of gas concentrations in drops between 500-4000μm.

Reviewer 2

Major comments:

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As was pointed out in the reply to the first reviewer, we now introduce changes in the original title of the paper, in order to avoid misunderstandings. Also a discussion about the emissions from Petroleum Industries (that are mentioned in the abstract) is now included in the text. This is very important since the composition of the aerosols in our model, and the gas phase concentrations chosen for the simulations are influenced by these anthropogenic sources. This was addressed in the answer to the first reviewer (point b of the discussion, "organic and inorganic fraction"). We carefully discussed why we modelled the organic fraction as oxalic acid in the answer to the fisrt reviewer (point c) of the discussion ("Parameterizing the chemical composition of the organic part"). The form of the Koehler equation we used in our study was developed by Mircea et al. (2002), to take into account the influence of the WSOC. As you pointed out, the dicarboxylic acid is treated as if it is fully dissociated. We did not do any other calculation based on the dissociation constants, since any improvement of the mentioned equation is beyond the scope of our modelling study. The influence of soluble gases during activation is not considered. In the revised version of the paper, the figure captions clearly indicate now high and low sulfuric acid concentrations, as suggested.

Detailed comments:

p. 593 lines 7-8. That is correct. In our simulations, aqueous-phase refers to cloud droplets. The revised version now refers to cloud droplets.

p. 593 lines 20-23. Thanks. Some modifications have been made in the revised version.

p. 596 line 1. The reference is now added to the reference list.

p. 601 line 4-5. This sentence has now been re-written. Actually there is a 10% ammonium sulfate fraction, but most of the remaining 90% are non soluble hydrocarbons.

p. 601 line 28. The corresponding modification was made.

p. 605 line l8-p. 606 line 1-2. Yes, the model is able to reproduce the precipitation. It was demonstrated in a previous study with the same dynamic, but with parameterized microphysics (Alfonso et al., 1998). We discussed very carefully this issue in the answer to the first reviewer (Point a) ŞAerosol number concentration).

p. 606 line 25. The corresponding change was made.

p. 607 line 19-21. Yes, concentration refers to initial drop number concentration, after activation, that depends on the chemical composition of the initial (non-activated) CCN distribution. But the precipitation development is very sensitive, for example, to the mean radius of the initial CCN distribution, and its dispersion. In our study we didn`t do a sensitivity study of these parameters. In the revised version we give a more detailed explanation of this issue.

p. 615 line 14. Thanks, the corresponding correction was made.

The 3 papers were eliminated from the reference list.

Table 5: Yes, the maximum concentration of droplets is higher than the initial aerosol particle concentration. This is a result of the sedimentation of droplets in an eulerian framework. In this case we have droplets that were activated at a different altitude within the cloud and have reached the 2000 m level because of their terminal velocity. Another point is the presence of CCN that enter the cloud from the side (our cloud is cylindrical, and there is an incloud radial velocity in the lower part), and are activated as soon they enter the cloud. A short discussion of this point is made in the revised version.

Figure 6 and 7: Actually, as an initial condition, there is an exponential decrease with altitude in the gas phase concentrations of all species. As a result of cloud development, the concentrations of all the species increased, because they are advected by the cloud, but the original concentrations at that level are very low. The 4000 m level in Fig 6 and 7 corresponds to the top of the cloud. Above that level, the gas phase concen-

trations are very low because they correspond to the initial conditions, that decreased exponentially with height. The original manuscript was carefully checked before re-submission . The suggestions made by the referees have improved the discussion of our results.

Additional References:

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Kawamura, K., Kaplan, I.R.: Motor exhaust emissions as primary sources for dicar-boxylic acids in Los Angeles ambient air, Envir. Sci. Technol., 21, 105-110, 1987.

Penner, J., Novakov, T.: Carbonaceous particles in the atmosphere: A historical per-spective to the Fifth International Conference on Carbonaceous Particles in the Atmo-sphere, J. Geophys. Res., Vol. 101, NO. D14, 19,373-19378, 1996.

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