

Interactive comment on “The impact of a deep convection on sulfate transport and redistribution” by V. Spiridonov and M. Curic

V. Spiridonov and M. Curic

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Authors response to anonymous referee #1

We are appreciated the detailed interactive comments of the anonymous referee #1, deep insight into the manuscript and his patience. We are almost agree with the part explaining the more detail comments, especially in regard to sections which would have to be rewritten. Of course we shall do that in the revised paper. But we are not at all convincing with Specific Comments and we shall try to clarify them in the following text and to answer some questions given in More Detailed Comments.

Specific Comments:

1. A three-dimensional Summer Case simulation is performed using the continental polluted distribution of the chemical species, taken from Taylor (1989b). The results of Section 4.5 are obtained using both continental non-polluted and continental polluted

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profiles, taken from the same study. For the initialization of the Spring Case experiment we have used vertical profiles of chemical species from Macedonia. The only exception is the initial concentration of hydrogen peroxide which has the same value as for the Summer Case.

2. The second specific comment arises from the fact that we have not clarified in the manuscript, which data are representative for the initialization of the Spring Case. In regard to comment about agreement between the calculated and observed parameters we would like to note that we have found relatively good agreement in regard to precipitation amount, the values of the sulfate volume concentration and sulfate wet deposition. One of the reasons for the higher measured pH value, is due to the fact that dust is alkali component which increases the pH value. But, we found similar values comparing calculated pH with the annual average data taken from EMEP data, for period (1985-1995).

3. That is correct that only oxidation of S(IV) by H₂O₂ and O₃ was included in the liquid phase chemical reactions. The results of cloud water pH and rainwater pH have shown increase of the acidity. As support to that statement are the smoothed averaged pH values in parentheses shown in Table 6.

Table 6. Parameters of numerical experiment on 3 April 2000. Values of parameters delineate in borders represent smoothed values

Values shown above those given in parentheses, delineate the maximum calculated values in the entire integration model domain. There are not smoothed or filtered values and we have to remove them in order to eliminate eventual misunderstanding. As has been seen from above table, the maximum calculated cloud water and rainwater pH are 6.5 and 7.0 respectively, and gradually decrease towards identical pH =5.5 in 60 min of the simulation time. However authors suggest to referee to reconsider the statement on page 402 line 8 (Lower calculated value of pH).

4. The presence of the ice phase is very important in liquid phase chemistry. This is not

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only phrase but authors supported that statement through the complex mixed-phased three-dimensional simulation of sulfate transport and redistribution in ice processes . In addition in Section 4.5 we have analyzed the relative contribution of various terms included in sulfate chemistry. It is demonstrated that ignoring ice-phase processes leads to underestimation of the total sulfur mass removed by wet deposition by a factor of 1 for continental non-polluted to factor 1.2 for continental polluted background. The lack of separate section devoted to the importance of ice phase processes is probably the main shortcoming of this issue. But how dissolved tracers react with frozen hydrometeors, the retention in the ice during conversion of cloud water and rainwater to ice, graupel or hail and snow are issues explained in Section 2.3. There, we have presented the schematics of sulfate and gases reactions which are participated in sulfate production, and various microphysical mass transfers between cloud hydrometeors (autoconversion, accretion, deposition etc.). Also, the numerical simulation of sulfate transport and redistribution shows the total mixing ratio (sum of mixing ratio in the gas phase, cloud water, rain and ice phase).

5. We have run our cloud-chemistry model in both 3-D and 2-D mode. The results by two-dimensional simulations are shown in Table 7. It is well evidenced in the front of Tab. 7 that number of sensitivity tests have been done by 2-D model run.

For the better comparison of the results, by oxidation off run and oxidation on run and to show the difference between reduction terms included in sulfate parameterization scheme, we have also performed a two-dimensional simulations. In addition, we show the new Fig. 8a obtained by 2-D version of the model, that more clearly illustrated the impact of oxidation processes in sulfate production.

Fig. 8a Evolution of the sulfate concentration (mg/m^3) in 20, 30 and 40 min. Panels on the l.h.s. represent sulfate distribution by oxidation off run, those on the r.h.s. represent distributions of oxidation on run.

Also we have performed simulation of sulfate transport and redistribution by 2-D version

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of the model (Fig6b).

Fig.6b. Time evolution of sulfate transport and redistribution in 10,20,30,40 and 60 min.

Fig. 8b. Time evolution of O3 and H2O2 in 30 min of the simulation. Panels on the l.h.s. represent distributions of reduction on run, those on the r.h.s. of reduction off run.

More Detailed Comments:

Abstract:

1. Line 4-5: As can be seen from the formulation of the continuity equations listed on page 391, the equations (1-5) represent the flux-conserving form of the continuity equations as mixing ratios of pollutant \dot{S}_i associated with air, cloud water, rainwater, graupel or hail and snow. But, gas-phase chemistry and photochemical and gaseous reactions are not included in the present study. 2. Line 6-7: Authors here wanted to emphasize the importance of all terms presented in the continuity : local change +advection =transport (l.h.s.) and subgrid contribution term, term represents micro-physical transfers, chemical transformation and deposition on redistribution of chemical species.. But we agree with the referee statement that we have to reformulate this sentence. 3. Line 7-8: The correct statement should be: The model includes the absorption of a chemical species by mass transfer limitation calculation (or a fully kinetic calculation of gas uptake by cloud water and rainwater). 4. Line 8-10: The schematic of the high solubility gas hydrogen peroxide is shown in Fig.2. H2O2 is destroyed in aqueous reaction:

$\text{HSO}_3^- + \text{H}_2\text{O}_2 \text{ (disociation) } \text{O}_2\text{SOOH} + | \text{H}_2\text{O} \text{ (1)}$

The source terms for H2O2 involve this reaction, mass transfer limitation calculation, and a set of transitions which represent the mass transfer of hydrogen peroxide through microphysical processes. There are also two terms representing reduction of H2O2 in cloud water and rainwater by SO2 in aqueous solution, given by equation (1). 5. Line 12-13: In Taylor (1989b) SO2, H2O2, and O3 concentrations in cloud water and rain-

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water are assumed to be in equilibrium with the local gas phase concentration and are carried as implicit fields, i.e., when required in the source terms, they are computed as function of the gas-phase concentrations. The treatment of gases in our chemistry parameterization scheme is explicit in regard to SO_4^{2-} reactions. S(IV) in solution in cloud water and rainwater is computed in the each time step of the model and depends also by microphysical transfers of the current time step. Also for computation of the oxidation terms we use the current calculated concentrations of SO_2 , O_3 and H_2O_2 . Also the difference is that O_3 is not constant in each time step as in Taylor (50 ppb). The absorption of highly soluble gases such as H_2O_2 into the cloud water and rainwater is computed using a fully kinetic calculation of gas uptake. For O_3 and SO_2 taking into account the effective Henry's law coefficients (Table 2), we assumed local chemical equilibrium i.e. these liquid phase concentrations are computed using Henry's law. In any case we have performed simulations with using Henry's law assumption and applying kinetic gas uptake methods for the gas species. Fig. 13 clearly illustrated the difference between both assumptions. As can be seen from the same figure, the difference is more evident for the highly soluble hydrogen peroxide gas . 6. Line 13-15: Yes. That is correct, it should be objective of this study. 7. Ok. Would be rewritten. 8. Ok. 9. Line 20: Even areas far away from Sahara (Africa) as far as Macedonia, under favorable atmospheric conditions are affected by Intercontinental (transboundary) dust transport and activity. That is usually case during Spring. For that purpose in order to examine the sulfate transport and redistribution, we have selected such case with representative conditions (unstable atmosphere + chemical composition of the atmosphere typical after dust transport. 10. Line 20-22: That is clarified in Specific Comments (1). 11. Line 25-27: Authors claimed that deep convection has impact of scavenging processes (nucleation + impact), mass transfers between pollutant associated with water categories, pollutant redistribution in the cloud environment and subsequently wet deposition with falling precipitation. 12. Ok.

1. Introduction:

Ok. Authors will rewrite all unclear sentences following referee comments.

2. Model formulation and description

1. Line 23, p389-Line 3, p390: We use monodisperse size distribution for cloud water and cloud ice. Exponential Marshal-Palmer type size distributions with fixed intercept parameters are hypothesized for the precipitation particles (rain, graupel or hail and snow). 2. Line 3-6, p 390. Ok. 3. Line 10-18: Ok. 4. Line 19-24: Ok. 5. Page 392: Formula (8) is used to compute the absorption of chemical species in the gas phase into the cloud water and rain. For the gases with lower solubility we apply the Henry's law equilibrium, where the aqueous phase concentration of a chemical species [A] to the gas phase concentration is given by the relation $[A] = KH pA$ or expanded term (9). Yes we have noticed two different symbols for the effective Henry's law coefficient and we shall checked all other parameters. 6. Line 12, p393. Here we have the following explanation:

PS4 $\hat{=}$ Scavenging of SO_4^{12} aerosol by Brownian diffusion in cloud drops

Stationary drops capture aerosol particles by simple Brownian diffusion. Supposing that the drops follow the monodisperse droplet spectrum the scavenging coefficient and collection kernel for convective Brownian diffusion could be expressed as $\hat{=}$ (see Pruppacher and Klett 1997, table 11.1).

7. Line 13-19: Ok. 8. Line 22-23: Ok. 9. Line 26-27, p393: It means that gaseous phase production on sulfuric acid is of importance in long-range transport studies (Eliassen et al., 1982) but for convective scale may be neglected. 10. Line 1, p394: Ok. 11. Line 5-6: Ok 12. Line 6-7: For the authors is not clear why to rewrite this paragraph. These are horizontal boundary conditions in order to maintain stability of numerical integration. Lateral boundary conditions are opened and time dependant so the disturbances can pass through with minimal reflection. Here we have to added this explanation: two different cases with regard to the wind velocity are considered, after Duran (1981). When the component of velocity normal to the boundary is directed

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toward the domain (inflow boundary), normal derivatives are set to be zero. At outflow boundaries, for all variables except pressure normal derivatives are computed by the upstream difference, with time lag of a large time step in order to ensure stability. 13. Line 15-17: The reduction terms are explained in More Detailed Comments, Line 8-10 in Abstract. The aqueous phase reactions terms include: absorption: either by Henry's law equilibrium or mass transfer limitation calculations, dissociation, oxidation, reduction and retention in the solid-or mixed-phase hydrometeor through the microphysical processes.

3. Numerical Experiments

1. Line 22-23, p395: Would be rewritten. 2. Line 26, p395. Yes. It should be weak not week.

4. Model results

1. Line 26, p397: When the cloud gradually enters the dissipating stage, when only fragmented structure of the cloud remains in the cloud model domain at the upper cloud level with cloud base above 7-8 km are broking cirrus cloud. The cloud structure at right corner of the integration domain, with cloud top lower than 5 km are Cu and Scum cloud elements, although sometimes the secondary cloud formation could be generated from the heat at the ground and evaporation of precipitation elements.

2. Line 9-14, p400: It is obvious that the referee suspicion is based on the assumed inconsistencies of the chemical field initialization. But we have previously clarified this point. The initial distributions for the second analyzed case (Spring Case) are taken from measurements in Macedonia at meteorological station ŠLazaropoleŠ that is included in EMEP programme. The missing data for the same station are extract from the EMEP data for the period (1985-1995). The comparative analysis between modeled data and those observed and measured at Lazaropole, and those averaged over entire period in frame of project JICA, has shown relatively good agreement. 3. Line 15-16, p400: The reason why we have added the subtitles in both Summer and Spring

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Case simulation is to clarify the atmospheric and chemical conditions in the selected cases. The first one is characterized by intensive convective cloud activity and a moderate air mass thunderstorm development. The atmosphere in the second case was also unstable as well as the change of the chemical composition under influence of dust long-range dust transport. That is the response why we have added the subtitle.

4. Line 7. p401: ($\text{SO}_4\text{q}^2 - \text{S}$) means sulfate aerosol concentration in precipitation. 5. Line 2, p402: Ok. 6. Line 3, p402: The ionic conductivity term would be eliminated in the revised manuscript. 7. p402: This is the similar comment as in (2). Ok. It is obvious that more comments and critical review are in regard to the second simulated Spring Case: We shall try to reconsider this section and to reformulate some unclear terms.

8. Line 17-18: p403: We claimed that Henry's law assumption for continental polluted distributions leads to 130% higher computed value of the total sulfur mass removed by wet deposition in comparison to that obtained by method of kinetic gas uptake. 9. Line 24-26, p403: The amounts of the $\text{H}^+ = 1000$, 10000, and 100000 tracers remaining relative to the insoluble tracer in the global model runs Crutzen and Lawrence (2000) were found to be about 80-90, 40-60% and 10-20%. 10. Line 8-11, p404: This paragraph emphasizes the relative importance of the ice processes in total sulfate mass removed by wet deposition. It is stated that neglect of the ice phase when considering chemistry in these clouds may lead to overestimation of about 100% for continental non-polluted distributions and of about 120 % for continental polluted distributions, in sulfate deposition. 11. The results of the 2-D runs are shown in Table 7. In the revised paper as we have explained before we shall add new figures with simulations by two-dimensional model runs.

5. Summary and conclusion

1. Line 17-19, p405: As can be seen from Fig. 4 and Fig. 6, in the early cloud development stage there is the strong vertical transport of pollutants. The dominant processes are the nucleation scavenging of aerosol, scavenging by Brownian diffusion and oxidation by O_3 and H_2O_2 , and absorption of a chemical species in gas phase into the

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cloud water. 2. Line 21-22,p405: This came from the subscale processes (sub-scale transport, buoyancy effects, shearing, diffusion and viscous dissipation) which are represented by the prognostic turbulent kinetic energy equation. These are the dynamical effects which have large impact on convection and redistribution of pollutants. 3. Line 24-25: The dominant process in the convective cloud mature stage are the formation of the frozen hydrometeors (cloud ice, hail and snow). The complex microphysical transformation mechanisms are responsible for the mass transfers of between cloud hydrometeors. 4. In the convective cloud mature stage , the frozen hydrometeors (cloud ice, hail and snow) wen the dissolved 5. Line 14: Ok. This paragraph could be completely eliminated, since these results are not related to Table 7, which presents the list of parameters and relative contribution in sulfate mass removed by wet deposition. In addition, we have performed a number of 2-d sensitivity test in order to examine the difference between terms computed by Henry's law equilibrium or a fully kinetic method of gas uptake by cloud water or rain. These values are very small although the difference is obvious. 6. Line 19-22: Authors claimed that the ice phase is important of dynamical and microphysical development of convective clouds. Tests of the aqueous-ice phase chemical reactions (not as in the text: liquid phase chemical reactions) upon in-cloud chemistry and deposition indicated that the total sulfur mass deposited is increased by about a factor 1,0 for continental non-polluted and 1,2 for continental polluted clouds, relative to the base run.

Tables and Figures

Not only captions, but as well as some unclear figures (oxidation, reduction, sulfate transport and redistributing) would be improved in the revised paper.

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