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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Implementation of a Markov Chain Monte Carlo Method to inorganic aerosol modeling of observations from the MCMA-2003 Campaign. Part II: Model application to the CENICA, Pedregal and Santa Ana sites" *by* F. M. San Martini et al.

F. M. San Martini et al.

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1. Section 3: A brief synoptical characterisation of all measurement periods might be instructive (synoptic situation, air mass influence, fronts, advection/ turbulence etc.). For April 9-11, this has been partially done.

The following sentence was added to page 6004, line 20: A synoptic characterization of the MCMA-2003 field campaign can be found in (de Foy et al., 2005)

2. Section 6: With respect to organic aerosols I recommend to consider also the

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comprehensive assessment study of Fuzzi et al. (2006, ACP, 6, 2017-2038).

The study of Fuzzi et al. was added to the text. Specifically, page 6015, the following sentence was added to line 14: In spite of impressive advances in recent years, present understanding of organic aerosol composition, physical and chemical properties, sources and transformation characteristics is still limited (Fuzzi et al., 2006).

In addition, page 6015, lines 17-19 were modified to read: The water absorption of atmospheric aerosols has conventionally been associated with their inorganic fraction; theoretically and experimentally, little information exists about the hygroscopic behavior of particles containing organic compounds (Fuzzi et al., 2006). The aerosol model used in this work, ISORROPIA, only treats the inorganic aerosol species.

3. Nitrate underprediction: With reference to Ansari and Pandis (2000) the NO-3 underprediction of ISORROPIA is supposed to be related to the impact of SOA's on the aerosol water content. This effect decreases with increasing relative humidity. Hence, the nitrate prediction capability of ISORROPIA should depend on the relative humidity. Is it possible, to classify your nitrate prediction error according to the observed relative humidity? This would give at least an empirical hint to verify/falsify your hypothesis on the SOA influence. Apart from the call for experimental data on water uptake on SOA and corresponding models, as stated in lines 5-8 on p. 6017 and which is absolutely right, one might also consider to perform dedicated model evaluation studies using pre-classified field measurements including SOA characteristics. Perhaps, the model prediction capability in dependence on pre-classified scenarios contains further information on the contribution of SOA.

The reviewer asks a very good question. If the predictions of Ansari and Pandis (2000) are correct, the underprediction of nitrate should decrease with increasing relative humidity. Unfortunately, the data is insufficient to support such a trend. Specifically, between 10:00 a.m. and 19:35 p.m. (CDT) on April 9 (when the nitrate is consistently underpredicted), a total of 71 points were analyzed. In this period, the relative humidity

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started at 69

4. p. 6021, lines 2-6: As already stated in Part I, ISORROPIA predicts pH values comparable to observed ones during an "acidic" period (9-11 April). The authors added, that the predicted pH, especially of the aqueous aerosol in the MCMA was 3-4, despite the high concentrations of gas phase ammonia observed. Can you physicochemically explain this finding?

(See also the authors' response in paper 1.) I know of no physiochemical explanation for this prediction. The explanation that the acidity may be an artifact of the activity coefficient model is reasonable to me (see response to Part I). The partial dissociation of the bisulfate ion is notoriously difficult to predict, especially at high ionic strengths.

4 Technical corrections

The corrections are addressed as follows: "6001/6" = "see p. 6001, line 6"

4.1 Text

1. 6001/6: "to predict"

Corrected

2. 6001/6: "In general, ..."

Corrected

3. 6001/14: I recommend to generally use "particle phase", when the liquid/ solid component of an aerosol is meant.

This has been corrected

4. 6001/15: Central Daylight Time (CDT)

Corrected

5. 6001/17-18: "... is able to both accurately predict the aerosol chloride mass concen-

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trations ..."

Corrected

6. 6002/4: "emission control strategies" (several times)

Corrected

7. 6002/16: "hydrochlorid acid concentrations."

Corrected

8. 6002/22:"modelling the aerosol behavior"

English vs. British spelling; left as is.

9. 6002/24-27: comma placement to disburden readability

Sentence was modified to: In particular, the finding that reductions in ammonia concentrations are likely to be less effective than expected at reducing particle concentrations in Mexico City is constrained by observations at a single site, La Merced (San Martini et al., 2005).

10. 6002/27: "Therefore, ..." (several times), also: "Note, that ..."

The former was corrected, the latter left unchanged.

11. 6002/29: "is required/ is needed"

Corrected

12. 6003/1-4: comma placement: "...model, introduced in Part I, to three ..." Sentence was modified to:

In this paper we use data from the MCMA-2003 campaign to expand the application of the model introduced in Part I to three very different measurement sites.

13. 6003/3: Check the brackets of all of your citations (several times).

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Corrected

14. 6003/12: Add full stop.

Corrected

15. Please add in Section 2 or 3 the measurement periods (!) for the different sites. Your figures refer sometimes to different measurement periods.

Added – specifically, the following sentences were added to Section 2: The AML was deployed in stationary mode at the CENICA site at various times throughout the campaign. The AML was deployed in stationary mode at the Pedregal site from 5:32 p.m. (CDT) on 21 April to 11:14 p.m. (CDT) on 23 April 2003. The AML was deployed in stationary mode at the Santa Ana site from 9:25 p.m. (CDT) on 14 April to 9:42 p.m. (CDT) on 16 April 2003.

16. 6003/14-18: Split this sentence: "... Cerro de la Estrella. It is in ..."

Corrected

17. 6003/24: "It is considered as a 'boundary' site ..."

Corrected

18. 6005/6: Remove comma: "The speciation and mass concentration ..."

Corrected

19. Subsection 5.1: Please explicitly add the measurement period.

The following was added: The agreement between the predicted and observed ammonia concentrations for the periods when the AML was deployed in stationary mode at the CENICA site, shown in Fig. 2a...

20. Eqs. (5),(6): Remove brackets for prefactor "0.3"

Corrected

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21. 6007/5: "and due to observed negative values." I think the value of the variable is negative, but not its observation.

Corrected

22. 6008/6: "excellent agreement" (several times). See my comment to Part I.

See author response to comment to Part I. 23. 6011/29: "HCl(g)"

Corrected

24. Subsection 5.2: Please explicitly add the measurement period.

The following was added: Figures 10 and 11 compare the predicted and observed particle and gas phase species at the Pedregal site for the 21-23 April measurement period.

25. Subsection 5.3: Please explicitly add the measurement period. The following was added: Figures 13 and 14 compare the predicted and observed particle and gas phase species at the Santa Ana site for the 14-16 April measurement period.

26. Comments on Eqs. (11)-(20) Eq. (16): Please explain explicitly the symbols RH and R. Make the difference between RH and radical (Rů) clear.

This was clarified by adding the following on page 6018, line 14: RH and Rů are e.g. an alkane and alkane radical

Introduce the rate constant k17 immediately after Eq. (17). Corrected.

Perhaps, it might be more consistent, to denote radicals also in the equations by a dot (such as in Eqs. (18), (19)).

Corrected.

6019/6-7: What the values 3E12 cm3/molecules x s and 2 x 10E10 cm3/molecules x s are standing for?

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Corrected (100 ppbv is approximately equal to 3E12 molecules/cm3 and 1 ppbv is approximately equal to 1E10 molecules/cm3).

6019/17: In the sentence just before you were talking about the ratio k20/k16 approx. equal 1/90 - 1/14. In the just following sentence, you derive a ratio of approx. 400. Which ratio you are talking about here?

As stated on line 9-12, the importance of HCl as a source of Cl radicals to the alkane photochemistry in the MCMA is determined by the relative importance of Reaction (16) and Reaction (20), i.e., (k20*RH*OH)/(k16*RH*Cl) = (k20/k16)*(OH/Cl) = (1/40)*(1/6E-5) = 417 is approx. equal to 400)

27. 6021/14-15: "... to a better understanding of the aerosol behavior"

Corrected to "These observations will lead to a better understanding of aerosol behavior in the MCMA..."

References The name of the author is: Hämeri.

Corrected

Figures 1. Figs. 4, 5, 6: Hopefully, these figures will be sufficiently enlarged in the final version. Excuse me, but they are a challenge for eyes, having been getting a bit long in the tooth ...

We have asked ACP to enlarge the figures.

2. Fig. 15: "15-16 April"

Corrected

References: de Foy, B., Caetano, E., Magaña, V., Zitácuaro, A., Cárdenas, B., Retama, A., Ramos, R., Molina, L.T. and Molina, M.J., 2005. Mexico City basin wind circulation during the MCMA-2003 field campaign. Atmospheric Chemistry and Physics, 5: 2267-2288.

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