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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 I: Model description and application to the La Merced Site" *by* F. M. San Martini et al.

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1 General comments

First of all, I have to apologise to the authors for not having been able to come up with my referee comment a little bit earlier to push the discussion. But the evaluation of a tricky subject presented in two comprehensive manuscripts with altogether 108 pages

takes its time.
The authors presented an interesting paper on an important subject. The approach is innovative, instructive, relevant for the ACP community, and of practical importance for air quality monitoring in megacities, but - of course - not only there. The Markov Chain Monte Carlo (MCMC) method is proposed to be a suitable tool to handle a general and well-known problem in air pollution monitoring/ modelling: the inference of missing and uncertain measurements. Thus, the approach presented here is of general interest. The application of the MCMC method to aerosol measurement data is reasonable. Its restriction to inorganic aerosols does not constrain the general value of the approach presented here.

However, a susceptible point concerns the presentation of the method. This refers to a lesser extent to what has been outlined in the manuscript, but to a greater extent, to what has been omitted there. ACP offers a good opportunity for scientists coming from different branches of atmospheric science (atmospheric chemistry and physics) and for potential users to benefit from synergetic effects. Thus, it is always a challenge to present an approach not only to specialists, but also to a relatively wide circle of readers. Owing to their importance for the appreciation of the results, some methodological aspects of the Markov Chain approach should be presented in more detail. My recommendations should be considered as an request to support readers, who are faced with a problem similar to that investigated here, and who are interested to apply this method for their own applications. I think, it should be possible to find a proper compromise to supply this need.
I recommend the editor to accept the paper after minor revisions.

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2 Evaluation according to the guidelines for ACP referee comments

1. Does the paper address relevant scientific questions within the scope of ACP?
   Yes, the subject of the paper fits into the ACP profile.

2. Does the paper present novel concepts, ideas, tools, or data?
   Yes, based on the classical MCMC concept, a new tool to infer missing and uncertain measurements of inorganic aerosol parameters is presented. The new tool is applied to recently obtained field measurements from the Mexico City Metropolitan Area (MCMA) 2003 Field Campaign. Thus, the approach is original.

3. Are substantial conclusions reached?
   Yes.

4. Are the scientific methods and assumptions valid and clearly outlined?
   In general, yes. Some questions regarding the presentation of the MCMC method are listed below.

5. Are the results sufficient to support the interpretations and conclusions?
   Yes. But the presentation of the method is needed to be clarified to support the results.

6. Is the description of experiments and calculations sufficiently complete and precise to allow their reproduction by fellow scientists (traceability of results)?
   To support the portability of the method to other applications, the calculation method presented in Section 3 should be outlined in more detail.

7. Do the authors give proper credit to related work and clearly indicate their own new/ original contribution?

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Yes, they did. The reference list is appropriate with respect to the question of interest.

8. Does the title clearly reflect the contents of the paper?
   Yes.

9. Does the abstract provide a concise and complete summary?
   Yes.

10. Is the overall presentation well structured and clear?
    Yes, the overall presentation is well structured. To enhance clarity, some specific comments are given below.

11. Is the language fluent and precise?
    As a non-native speaker I can neither evaluate the language nor give recommendations with respect to grammar etc.. However, I think, here and there the readibility can be improved by splitting some long sentences and/ or comma placement (see technical corrections).

12. Are the mathematical formulae, symbols, abbreviations, and units correctly defined and used?
    Yes.

13. Should any parts of the paper (text, formulae, figures, tables) be clarified, reduced, combined, or eliminated?
    See above. The introducing part of Section 3 should be clarified/ extended.

14. Are the number and quality of references appropriate?
    Yes. The pioneering paper of Hastings (1970), Biometrika, Vol. 57, No. 1, pp. 97-109 should be explicitly included in the reference list.

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15. Is the amount and quality of supplementary material appropriate?
Yes, it is. Some technical corrections are advisable to enhance the readibility of some figures.

3 Specific comments

The description of the method in the non-numbered introducing paragraph of Section 3 should be outlined in more detail[1]. To promote further applications of the Markov approach in aerosol science, it might be instrumental to outline the method in a self-explaining manner within the *present* manuscript.
Apart from the key paper of Metropolis et al. (1953)[2] it is sound to refer to a modern monograph, such as that of Draper (2006). It serves as a reference for the method and has been cited several times here (on pp. 5941, 5964, 5965). Unfortunately, it is still in preparation and, consequently, not freely accessible. Hence, in the present stage of the discussion it is actually difficult to accept it as the reference for the description of the MCMC approach. As the authors obviously have access to that monograph, they will hopefully find a way, to explicitly cite the corresponding paragraphs from there.

1. pp. 5940–5941: You refer to the "solution of Eq.(2)" (Bayes' Theorem).

$$p(\theta|\ \mathrm{Data}) = \frac{p(\mathrm{Data}|\ \theta)\ p(\theta)}{p(\mathrm{Data})}$$

To determine the *a posteriori* probability, denoted as $p(\theta|\ \mathrm{Data})$, one needs to know the *a priori* probability, denoted as $p(\theta)$, the probability of observations, denoted as $p(\mathrm{Data})$, and the conditional probability of the observation (realisation)

[1]For comparison, the experiment setup, equipment parameters, and the discussion of the inorganic aerosol model is described comparatively detailed.

[2]The Metropolis method was introduced in connection with work related to the hydrogen bomb project.

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"Data" of the variable θ, the intrinsic value of which is unknown. The latter is the so-called likelihood function, denoted by $p(\mathrm{Data}|\ \theta)$. Its determination is a key element in the present approach. The MCMC method is used to approximate $p(\theta|\ \mathrm{Data})$ by generating random samples, from which the parameters for the probing distribution $PD(\theta|\ \mathrm{Data})$ can be estimated.

- I recommend to move Appendix A1 "Probing distribution" (p. 5964) to the non-numbered introducing paragraph of Section 3. Perhaps, it is useful, to subsume the whole methodology in an own subsection. Can you regive the related parts of San Martini (2004) in more detail here?
- Please itemise the principal premises of the Markovian Chain approach.
- Is it possible to exemplarily illustrate, how the proposed new $\theta^\star$ and the probing distribution $PD(\theta^\star|\theta)$ are generated[3]? This is related to the question, how you arrive at a "**prediction value**" of, e. g., $\mathrm{NH_3}$ (Figs. 9, 10), $\mathrm{HNO_3}$ (Fig. 11), etc. I suspect, what you call "prediction" (denoted as "Mode", e.g., in Fig. 9), is nothing else but the **modal value** of the *a posteriori* PDF according to the l.h.s. of Eq. (2)[4]. Is this interpretation correct? This way, your "predictive values" are intrinsically diagnostic values. With respect to deterministic models, the word "prediction" colloquially refers to a **future state** along a trajectory in the phase space. This way, the evolution of an intrinsically **predictive** variable is fully determined by any conservation law with corresponding initial and boundary conditions. Measurements enter the prediction only via the determination of the initial and boundary conditions. I think, the situation here is different. You have observations, which are used the estimate the most likely "true" state.

[3] This can be done verbally.

[4] On p. 5961(!), line 25, you explicitly wrote: "[. . .] Fig. 21 compares the **mode of the** $\mathrm{NH_3}$**,** $\mathrm{HNO_3}$**, and** HCl **distribution**, respectively, **predicted** using [. . .]"

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- Can you give a physical interpretation of the "acceptance rule" for the probing distribution given by Eq. (3)?

2. Section 3.1 contains a comprehensive description of the inorganic aerosol model. The approach and description are sound.

3. Section 3.2 contains the determination of the likelihood functions $p(\mathrm{Data}|\ \theta) = p(X_{\mathrm{obs}}|\ X)$ of the observations, i.e.,

   - $p([\mathrm{NH_3}]_{\mathrm{obs}}|\ [\mathrm{NH_3}])$,
   - $p([\mathrm{HNO_3}]_{\mathrm{obs}}|\ [\mathrm{HNO_3}])$,
   - $p([\mathrm{ammonium}]_{\mathrm{obs}}|\ [\mathrm{ammonium}])$,
   - $p([\mathrm{nitrate}]_{\mathrm{obs}}|\ [\mathrm{nitrate}])$,
   - $p([\mathrm{sulfate}]_{\mathrm{obs}}|\ [\mathrm{sulfate}])$,
   - $p([\mathrm{chloride}]_{\mathrm{obs}}|\ [\mathrm{chloride}])$,
   - $p(T_{\mathrm{obs}}|\ T)$,
   - $p(RH_{\mathrm{obs}}|\ RH)$.

   The arguments for the setup of the likelihood functions are plausible. The observations X_{obs} entering into the likelihood functions $p(X_{\mathrm{obs}}|\ X)$ are formally "mean values". Do you use **time averaged values** derived from high-resolved time series for these "mean values", and do you presume thereby already the validity of the ergodic hypothesis?

4. Section 3.3 contains the determination of the *a priori* PDF's $p(\theta) = p(X)$. The approach is sound.

5. Section 4 "Results":

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- Do you use the same data set, already employed for the determination of the likelihood functions, also for the "model–observation" intercomparison (presented in Figs. 9–21)? Or did you use an independent control sample?
- Do you compare the modal values of the *a posteriori* PDF, i. e., $X_{\mathrm{post}}^{\mathrm{mode}}$, with X_{obs}? Are the latter time-averaged values? In the case of a "perfect prediction", the modal value of $p(\theta|\ \mathrm{Data})$ from the l.h.s of Eq. (2) should be identical with X_{obs} entering $p(\mathrm{Data}|\ \theta)$ at the r.h.s of Eq. (2). The aim of any solver is to ensure validity of the equal sign in Eq. (2) by searching for the solution $X_{\mathrm{post}}^{\mathrm{mode}}$. Is this correct?
- p. 5958, line 19-20: "This means that during these periods [. . .] the TILDAS **observations** are more consistent with the **observations.**"
  Actually, we have at least three different values of any variable: the **(unknown) true value**, an **observation**, and a **model estimation/prediction**. Hence, the predicted data can only be compared with observations, but not with the "truth". With respect to $\mathrm{NH_3}$ you have two measurement devices: open/long-path FTIR, closed-path TILDAS (=point measurements). The consistency with which observations do you mean? Apart from that, the $\mathrm{NH_3}$ posterior PDF given in Fig. 9b is difficult to read.
- Section 4.1: The message is, that the prediction of gas phase $\mathrm{HNO_3}$ and HCl is sensitive against deliquescence/ efflorescence, but the prediction of particle phase concentrations and $\mathrm{NH_3}$ is not. Is this correct?
  On p. 5961, line 14: The wet aerosol is predicted to be acidic even at high ammonia concentrations. Can you physicochemically explain this effect or it is a side effect of the uncertainty of the activity model, when the concentration of the solution becomes large (at comparatively low relative humidities considered here)?
- Section 4.2: On p. 5962, line 4–6: Please insert, which figure you are referring to (Figs. 11, 20). According to Subsection 3.1, Mozurkewich's revised

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constant has been used in Fig. 11. Even if it overpredicts the afternoon HNO_3 concentration on April 27, the revised equilibrium constant enhances the HNO_3 prediction compared to the original parameterisation.

- Conclusions: Assessments like **"extremely well"** (5962/19), **"excellent"** (5962/19), **"excellent job"** (5962/21, 5963/24) insinuate, that the method has already reached its final state. What comes beyond "excellent"? Hopefully, there is something left to improve with respect to the method etc.. I think, even a "good agreement" is always a very good result. Anyway, the conclusions are found to be sound and conclusive.

4 Technical corrections

4.1 Text

1. Overall: A list of all abbreviations used in the text would be useful.
2. p. 5935, line 3: "... to **develop (?)** a powerful tool"
3. p. 5935, line 5: "... provides **a basis (?)** for a formal framework"
4. p. 5935, line 7: "... to **particle-** and gas-phase observations of ammonia" (use here and elsewhere "particle phase" instead of aerosol phase; have in mind the definition of aerosol: an aerosol is at least a two-phase system; dispersion of gas and particles) (see also p. 5944, line 22, 24, 25; p. 5953, line 18)
5. p. 5935, line 15: "... **varying** between 0.4 and 5 ppbv"
6. p. 5937, line 3: explain the abbreviation of CENICA, when it appears the first time (see part II, p. 6003)

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7. p. 5937, line 17: “A full description of the experiment and location is presented **in Grutter et al. (2003)**.” (one can avoid “elsewhere”, when it is already known, where “else” is; see also p. 5939, line 9; p. 5954, line 22.)

8. p. 5938, line 5: “The AML contains a suite **of** fast-response instruments ...”

9. p. 5938, line 15: What does the abbreviation “hwhm” mean?

10. p. 5938, line 25: Please check parenthesises in quotations **(many times)!** Example: “The operation of the NO_2 TILDAS is described in **Li et al. (2004)**.” (see also: p. 5942, line 25; p. 5957, line 19 etc.)

11. p. 5939, line 7: NO_3^-

12. p. 5939, line 22: “Thus, although CENICA was considered **to be (OR as) (?)** the supersite ...”;
Constructions, in which I would intuitively add “to be” or “as” appear several times.

13. p. 5939, line 24: . . . where **both** co-located NH_3 and HNO_3 observations were available

14. P. 5943, line 26: “For the four models they examined, **Ansari and Pandis (1999a)** found minor differences in predicted chloride concentrations.”
This way, one can avoid quasi-double citation in one quotation (several times).

15. p. 5944, line 5: The sentence “Using the same dataset, San Martini . . .” is an example for a long sentence, which could be splitted.

16. p. 5950, Eq.(25) (several times): leave out brackets for the prefactor 0.3

17. p. 5952, line 14-15: **Laplace’s Principle of Insufficient Reason**
I would like to see this statement explicitly commented in a footnote or appropriately referenced.

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18. p. 5952, line 24: Please resolve the abbreviation pdf for “probability density function” in the text.

19. p. 5954, line 13: “Previous observations **have** found . . .”

20. p. 5955, line 12-14: Please examine this sentence. Make clear, to what part the half sentence “found using the method of moments” is referring to. Please add the page numbers in the citation of the textbook of Seinfeld and Pandis (1998).

21. p. 5957, line 3: Structurise the sentence by a comma.

22. p. 5959, line 26: $\sim$ O(? ppbv)

23. p. 5962, line 7–11: Please completely reformulate this sentence. I suspect the message is, it does not matter, which equilibrium constant is used.

24. p. 5963, line 9: “did not **reveal (?)** a comparable difference”

25. p. 5963, line 10: “versus **those (?)** in the AML”

26. p. 5963, line 29: “Finally, ...” (check comma placement, several times)

27. p. 5964, line 17: Please define, what an “**overdispersed** version of the posterior distribution” is.

28. p. 5964, line 19: Please reformulate the second half sentence of the second item “[. . .] is to remain at θ_t [. . .]”

29. p. 5964, line 21: “... The second suggestion ensures that there will be an approximate **left-right balance, which encourages rapid exploration of the entire solution space** ...”
In cases, this sentence is important to understand the approach, please make

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clear, what is meant[5]. In cases it is not, please try to generalise the message and add a reference, which is freely accessible.

4.2 References

1. p. 5943, line 27: Add year to Zhang et al.
2. p. 5957, line 20: Add year to Moya et al..
3. . . . see also p. 5958, line 4/5 etc.
4. Reference list:
   - Allen et al. (2002): Add page numbers or doi
   - Beier (1999): Check syntax of the German title
   - Li et al. (2004): The JGR appendix “Atmos.” can be omitted.
   - Zhang et al. (2003): Check reference. Please add doi-number.

4.3 Figures

1. Figs. 3, 7, 8: Check the range of the probability ($\leq$1).
2. Fig. 4: Graph colours are difficult to separate.
3. Figs. 9b, 11b: The probability density surface is difficult to read. The correspondings figures should be rescaled (e.g., there is only 1 cm ordinate length scale for 0-60 ppbv NH_3 range), Fig 11b: Check the range of the probability ($\leq$1).

[5] I have at least a suggestion.

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4. Fig. 5: Please add the units for the ordinate axises.

5. Fig. 10, Caption: Delete one “are shaded”

6. Fig. 21b: Correct ordinate: “Mode $\mathrm{HNO_3}$ (ppbv), **Modified** $K_p(\mathrm{NH_4NO_3})$”

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