Atmos. Chem. Phys. Discuss., 6, S3719–S3732, 2006
www.atmos-chem-phys-discuss.net/6/S3719/2006/

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.

F. M. San Martini et al.

Received and published: 12 October 2006

I thank the reviewer for the effort and thoughtfulness that was clearly put into the review. Both this and the review of Hellmuth were insightful, fair and contributed positively to a better paper.

- Comment: *Clearly state the goal of the study. (a) Describe the research questions being asked.*

- *Is this a model evaluation study to find out how well the MCMC-ISORROPIA model predicts ambient partition?*
- *Is MCMC-ISORROPIA a tool that can be used to discriminate between measurements from different instruments for NH_3?*
- *MCMC can be used to predict gas-phase concentrations where they are not available. To support this statement, the application to predict HCl, for which measurements are not available, should be highlighted. Results for NH_3 and HNO_3 should be discussed for measurement periods where they are missing, if any.*

We clarified the goals of the study by modifying line 22 on p. 5936 to:

Here we apply the method to observations taken at the La Merced site to discriminate between differing observations of gas-phase ammonia and to predict (unobserved) gas-phase concentrations of hydrochloric acid.

We highlighted the prediction of HCl by adding the following statement to line 9, p. 5935:

. . . and predict gas-phase concentrations of hydrochloric acid.

- Comment: *Specify what "prior knowledge" is incorporated - do you mean the equilibrium relationships described within ISORROPIA?*

The following sentence was added to line 21, p. 5936:

The prior knowledge incorporated here are previous observations of gas- and particle-phase concentrations to construct lognormal probability distributions.

- Comment: *What are the values added by using the MCMC-enhanced model vs. standard ISORROPIA?*

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– *How different are the "most likely concentrations" compared with the deterministic values predicted by ISORROPIA using nominal measured values (and assumed values in the case of Na and HCl)?*

See final comment in this response.

- Comment: *In Equation 2, are "Data" and "theta" scalars or vectors? It is not clear if the definition of theta is constant (e.g., Appendix A) throughout the paper. If so, please move the definition in Appendix A into the text.*

The definition of θ has been moved into the text (see response to second referee's comment). In addition, page 5947, lines 16-18 was modified to read:

To incorporate both observations into the likelihood function we now define an augmented model space where, in addition to temperature, relative humidity, and inorganic gas- and particle-phase concentrations, θ includes the variable M, where $M \equiv (M_{FTIR}, M_{TILDAS})$, i.e., θ is defined as $\theta \equiv$ (*T, RH,* NH_3*,* HNO_3*, HCl,* NH_4*, Na,* NO_4*,* SO_4*, Cl,* H_2O, M).

(For reference, Equation (2) is general in that *Data* and θ can be scalars or vectors. In this work, both are vectors. θ is a ten-dimensional vector comprising 9 continuous (*T, RH,* NH_3*,* HNO_3*, HCl,* NH_4*, Na,* NO_4*,* SO_4*, Cl,* H_2O)and one binary (M) variable. *Data* is the set of measurements T, RH, NH_3, HNO_3, NH_4^+, NO_3^-, SO_4^{2-}, Cl^-.)

- Comment: *State that the posterior in Equation 2 is the quantity of interest.*

The following sentence was added to the text:

Determining the posterior is the object of all Bayesian inference (Gilks et al., 1996).

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- Comment: *In this implementation of the Bayes' theorem, theta is assumed to be a Markov Chain. How good is that assumption? Here, theta is the set of concentrations corresponding to some simultaneous measurements, so there is no time element. How are the different random samples of theta related to a Markov Chain? Please explain any assumption used in the representation of theta and Markov Chains.*

In this implementation of Bayes' theorem, we use samples drawn from a Markov chain to characterize θu Thus the Markov Chain is simply a tool to generate the samples of θ used to describe the posterior distribution. There is no time dependence to the Markov Chain. A separate MCMC analysis is conducted independently on each set of observations (where the observations are, as indicated above, T, RH, NH_3, HNO_3, NH_4^+, NO_3^-, SO_4^{2-}, Cl^-). In order to clarify this, the following two sentences were added to p. 5958, line 11 (before the Results section and, in the current version, after the section describing the probing distribution):

In sum, the MCMC method was applied independently to each set of observations, which comprise temperature, relative humidity, both ammonia observations, nitric acid, and the particle concentrations of ammonium, nitrate, sulfate, and chloride. Each set of observations is a 4-min average, and a total of 612 sets of observations were analyzed.

- Comment: *How is the initial guess defined in this work? How is theta0 related to theta?*

The following sentences were added to Section 3.4 to clarify the use of the initial guess:

The initial guess used to determine the first Markov step are the observations themselves, where the FTIR rather than the TILDAS and NO_z observations were used for the ammonia and nitric acid concentrations. The initial guess for the unobserved concentrations, *HCl* and *Na*, were set to 0 ppbv and the concentration required to ensure

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electroneutrality based on the AMS measurements, respectively. The initial guess for $M$was zero.

- Comment: *Does the acceptance probability alpha have any physical meaning?*

See response to comment from the other reviewer.

- Comment: *Why is 20% an optimal value for this quantity?*

A full discussion of this issue is beyond the scope of this work. The interested reader is referred to the work of Gelman et al. (1996). In brief, this is a heuristic that Gelman et al. suggest is consistent with theoretical results based on Langevin diffusion.

- Comment: *Is MCMC-ISORROPIA applied for each measurement period (hourly)? How many samples are analyzed? What is the minimum set of available measurements needed for a sample to be analyzed? How many have missing HNO3, NH3, or AMS measurements?*

MCMC-ISORROPIA was applied to each 4-minute measurement period and a total of 612 measurement periods were analyzed. As indicated above, each measurement period comprises observations of T, RH, NH_3, HNO_3, NH_4^+, NO_3^-, SO_4^{2-}, Cl^-. Since one of the primary goals of this work was to illustrate how the method can be used to discriminate between differing observations, the MCMC analysis was not conducted unless both the FTIR and TILDAS ammonia observations are available for that measurement period. As described in the text (p. 5949, line 20-22), for HNO_3 only the FTIR observation was used except for in three measurement periods (where the FTIR HNO_3 observations are either missing or negative). For these three measurement

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periods only, the NO_z observation was used in lieu of the FTIR observation. MCMC-ISORROPIA was not applied to measurement period if the AMS measurements were missing.

Also, see the response to the second reviewer's comment, which was addressed by adding the following to p. 5958, line 11 (before the Results section and, in the current version, after the section describing the probing distribution):

In sum, the MCMC method was applied independently to each set of observations, which comprise temperature, relative humidity, both ammonia observations, nitric acid, and the particle concentrations of ammonium, nitrate, sulfate, and chloride. Each set of observations is a 4-min average, and a total of 612 sets of observations were analyzed.

- Comment: *Is the same prior distributions applied for all time periods? Should the prior be a function of meteorology, chemical regime (e.g., ammonium-rich vs. sulfate-rich)? Should the prior distribution of inorganic compounds be correlated?*

The same prior distributions were used for all time periods. The prior distribution contains all the information about the unknown variables before the experiment begins. Thus the prior reflects the state of knowledge of the system *before* the new data arrives. Concentrations of the inorganic species are correlated. However, the previous observations used to construct the priors were insufficient to capture this level of detail.

In order to understand the importance of ensuring that the uncertainty bands of the chosen prior distributions reflect the state of knowledge *before* the experiment begins, consider Bayes' theorem:

$$p\left(\theta|Data\right) = \frac{p\left(Data|\theta\right)p\left(\theta\right)}{p\left(Data\right)} \quad (1)$$

*p(Data)*is a normalizing constant. Therefore,

$$p(\theta|Data) \propto p(Data|\theta)p(\theta) \quad (2)$$

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Taking the logarithm of equation (2) (and again ignoring the normalizing constant) tells us that:

$$\log(\text{posterior}) = \log(\text{likelihood}) + \log(\text{prior}) \quad (3)$$

or:

$$\text{posterior information} \sim \text{data information} + \text{prior information} \quad (4)$$

In words, equation (4) says that when few observations are available it is possible for the prior to swamp the data.

Previous observations of the gas-phase species in the MCMA are limited as detailed in Section 3.3. Specifically, two sources are used to determine the prior distribution for ammonia: the 1997 IMADA-AVER campaign (Edgerton et al., 1999) and an exploratory campaign undertaken at La Merced during February 2002 .(Grutter, 2002). The IMADA-AVER campaign provides 6-hour averaged measurements at La Merced (only), and 24-hour averaged measurements at 25 different sites throughout the MCMA (Chow et al., 2002), while the 2002 exploratory campaign yields 6-minute NH_3 concentrations measured using the same FTIR system used here. The nitric acid prior is based on observations of nitric acid taken during the IMADA-AVER. These measurements were taken as 6-hour averages at the La Merced site only. No observations of nitric acid are available from the 2002 exploratory campaign. To the authors' knowledge, no gas-phase observations of HCl from the MCMA are available. This data is insufficient to allow the dependence of the prior on meteorology, chemical regime, other inorganic species concentrations, time of day, etc. to be incorporated. However, future work should use data from the MCMA-2003 to refine the prior distributions for these types of dependencies.

- Comment: *How sensitive are the posterior estimates to the prior distributions?*

Previous work using MCMC-ISORROPIA investigated the sensitivity of the posterior on the selection of the prior (San Martini, 2004). In brief, the estimated posterior dis-

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tributions are not sensitive to the prior distributions if they are well-chosen priors, i.e., a distribution that is well-centered near the actual value of the unknown variables and whose uncertainty bands correspond well to the realized discrepancies between actual and predicted values. A poorly chosen prior (e.g., a prior with a smaller variance than that of the posterior or centered far from the mode of the posterior) will affect the posterior distribution.

- Comment: *How are below-detection (or negative) observations treated?*

See page 5951, lines 8-18 for an explanation of how below-detection observations are treated for the aerosol species. For below-detection observations of HNO3, see p. 5949, lines 17-22. For ammonia, see response to the other referee's comments (specifically, since one of the primary goals of this work was to illustrate how the method can be used to discriminate between differing observations, the MCMC analysis was not conducted unless both the FTIR and TILDAS ammonia observations are available for that measurement period).

- Comment: *The notations of [] and = (three bars) need to be defined.*

[] is used to denote an interval (e.g., see page 5941, line 20). The square brackets used to define θ and M on page 5947, lines 17, and page 5948, line 3 have been changed to regular brackets. The symbol $\equiv$ is standard notation for 'is defined as.'

- Comment: *For NH_3, theta seems to be defined as a two-dimensional quantity consisting of the FTIR and TILDAS measurements. Is that correct? This definition is different from the definition in Appendix A, where theta is defined as a set of 9 continuous + 1 binary variables.*

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This is not correct. The text on page 5947, lines 16-18 was unclear and has been clarified by replacing it with:

To incorporate both observations into the likelihood function we now define an augmented model space where, in addition to temperature, relative humidity, and inorganic gas- and particle-phase concentrations, θ includes the variable M, where $M \equiv (M_{FTIR}, M_{TILDAS})$, i.e., θ is defined as $\theta \equiv$ (*T, RH,* NH_3*,* HNO_3*, HCl,* NH_4*, Na,* NO_4*,* SO_4*, Cl,* H_2O, M).

- Comment: *How should the reader interpret p(*M_{TILDAS}*) +* $p(M_{FTIR})$ *= 1 when* M_{TILDAS} *and* M_{FTIR} *are different? Is one of them right and the other wrong? Is one right some time and the other right some other time? What if they are both wrong?*

As stated in the text, $p(M_{TILDAS})$ and $p(M_{FTIR})$ are the probabilities that the TILDAS and FTIR instrument reflect the true state of nature. For each measurement period, since M is a binary variable, each Markov step tests either observation (but not both). The set of samples generated via the Markov chain for each measurement period, however, allows us to test both observations. Since MCMC-ISORROPIA is run independently for each measurement period, we allow for the possibility that one instrument better reflects the true state of nature during some measurement periods but not in others. By assuming that $p(M_{TILDAS}) + p(M_{FTIR})$ = 1 we assume that either the TILDAS or the FTIR instrument better reflects the true state of nature; we thus do not consider the possibility that another measurement better reflects the true state.

- Comment: *In equation 19, is "Data" a scalar or a vector? What data are you referring to here?*

In equation 19 Data is the FTIR and TILDAS ammonia observations for the measurement period. See page 5947, line 13.

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- Comment: *Remove NOz from Figure 11 if it is not used in the MCMC analysis.*

The NOz observations were used in three cases for the MCMC analysis. See page 5947, lines 19-22.

- Comment: *Please clarify the sentence "...the TILDAS observations are more consistent with the observations." by specifying which observations the TILDAS observations are consistent with.*

This sentence has been clarified (see response to other reviewer). Specifically, this sentence has been clarified by substituting the sentence with:

This means that during these periods, given our understanding of aerosol thermodynamics, the TILDAS observations are more consistent with the temperature, relative humidity, AMS, and gas-phase observations.

- Comment: *The TILDAS measurements are more likely correct than the FTIR observations, which are still within 95% confidence interval. Under what conditions would FTIR be more probable? Elaborate on the conditions on 26 April that correspond to FTIR being the more likely correct value than TILDAS.*

The largest discrepancy between the two time series occurs at night and in the early morning hours. During these periods, the FTIR observations are significantly higher than the TILDAS observations. Presumably, conditions that would favor the FTIR observations over the TILDAS observations, i.e., would make the FTIR observations more probable, are if either the nitric acid concentrations and/or the temperature were lower. The FTIR observations are more likely than the TILDAS observations only for the afternoon of April 26; during the morning, when differences between the two measurements

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are up to 15 ppbv and higher, the probability density is centered on the TILDAS observations. For the afternoon, the difference between the time series is on the order of ppbv. This difference is within the uncertainty of the two time series.

- Comment: *A plot of the posterior median value +/- 33 percentile (equivalent to mean +/- standard deviation for normal distribution) against the measurements +/- error will be a useful tool to discriminate between measurements of NH3.*

Note that the posterior distribution for ammonia is in general not a normal distribution. We have made figures comparing the posterior mode +/- error (95% confidence level) with both the FTIR and the TILDAS measurements +/- error (29% at the 95% confidence level). These figures are available upon request (we are unable to include figures in author comments). We have not included the figures in the manuscripts because we believe Figures 9 and 10 in the manuscript provide a more useful summary.

- Comment: *Present the results of MCMC-ISORROPIA vs. standard (deterministic) ISORROPIA to highlight the value added using the MCMC method. Quantify the improvements of MCMC method over standard deterministic applications*.

The value of the MCMC method is that it allows for the direct incorporation of measurement uncertainty, missing observations to be inferred, and provides for a formal framework to combine measurements of different quality. It is difficult to quantify this benefit.

In order to compare MCMC-ISORROPIA to the standard (deterministic) ISORROPIA one has to ask which measurements are used in the analysis: the TILDAS or the FTIR observations? Taking an average of the two time series does not make sense when they diverge (i.e., at night and in the morning), so both cannot be used. Similarly, what value should be used for the concentration of crustal species and gas-phase

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hydrochloric acid, since these were not measured? The benefit of the MCMC method is precisely that it allows for all the observations to be used in the analysis, as well as prior knowledge.

However, since reviews of both papers suggest quantifying MCMC-ISORROPIA versus the standard (deterministic) ISORROPIA, the comparison is presented here. In order to make the most favorable comparison, for the deterministic model runs we utilize the TILDAS observations of ammonia. When the chloride observation is above the detection limit we use the mode of the prior HCl distribution (see Figure 8 in the manuscript), and use the mode of the equivalent sodium distribution (see Figure 5 in the manuscript) for cases where the AMS measurements do not satisfy electroneutrality due to an excess of anions.

Table 1 compares the mean normalized bias and error for ISORROPIA run deterministically versus MCMC-ISORROPIA, where only the most likely value of the MCMC analysis is used for the comparison. Run deterministically, ISORROPIA over predicts nitrate significantly (mean normalized error of 323% versus 2% for MCMC-ISORROPIA). Similarly, ammonium is over predicted (mean normalized error of 112%) when ISORROPIA is run deterministically versus slightly under predicted for MCMC-ISORROPIA (mean normalized error of 17%). In general, ISORROPIA is not able to accurately predict aerosol chloride concentrations above the detection limit when run deterministically (see Table 1). Figures comparing the particle- and gas-phase observations versus those predicted with MCMC-ISORROPIA and ISORROPIA run deterministically are available upon request (we are unable to include figures in author comments).

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Table 1: Mean normalized bias and error for ISORROPIA run deterministically and MCMC-ISORROPIA.

	Mean Normalized Bias, %					
	Ammonium	Nitrate	Sulfate	Chloride	Nitric Acid	Ammonia
Deterministic	85	259	0	-96	-34	-2
MCMC-ISORROPIA	-14	-1	-5	-18	-40	34
	Mean Normalized Error %					
	Ammonium	Nitrate	Sulfate	Chloride	Nitric Acid	Ammonia
Deterministic	112	323	0	96	41	28
MCMC-ISORROPIA	17	2	7	19	64	37

Additional correction from the author:

- p. 5949, line 19-21 originally read:

Out of a total of 612 data points analyzed, there are three points except either the FTIR HNO_3 observation is missing or negative.

This has been corrected to:

Out of a total of 612 data points analyzed, there are three points where either the FTIR HNO_3 observation is missing or negative.

References

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Interactive comment on Atmos. Chem. Phys. Discuss., 6, 5933, 2006.