Atmos. Chem. Phys. Discuss., 6, S3799–S3804, 2006
www.atmos-chem-phys-discuss.net/6/S3799/2006/

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 II: Model application to the CENICA, Pedregal and Santa Ana sites" *by* F. M. San Martini et al.

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Received and published: 15 October 2006

Does MCMC performs better than a traditional, deterministic application of ISORROPIA using the best guess of any missing measurements?

See response to reviewer 1 for Part I.

A comparison of the performance of the MCMC at different locations would be very interesting indeed, especially in light of the land use difference. The authors may also wish to review both Part I and II papers together to make sure that redundant discus-

sions are kept to a minimum.

We have kept redundant discussions at a minimum.

Detailed comments, abstract (1) The model accurately predicts aerosol phase observations with one exception. Can you comment on the reason why model performance is less satisfactory for that one time period?

The following sentence was added to the abstract: This period had a low planetary boundary layer, very high particle concentrations, and higher than expected nitrogen dioxide concentrations.

(2) Please comment on the range of HCl concentrations that would be obtained if MCMC is not used (i.e., from the application of ISORROPIA using nominal values).

See response to reviewer 1 for Part 1. In general, ISORROPIA is not able to accurately predict aerosol chloride concentrations above the detection limit when run deterministically when nominal HCl (g) values are used. Using the predictions discussed in the response to reviewer 1 for Part 1, the average, minimum and maximum HCl (g) concentration when the AMS Cl observation was above the detection limit is 0.6, 0, and 1.9 ppbv, respectively. For MCMC-ISORROPIA, the average, minimum and maximum of the most likely (i.e., the mode of the posterior distributions) of HCl (g) concentration when the AMS Cl observation was above the detection limit is 2.5, 0.36, and 27.6 ppbv, respectively.

(3) In the abstract, it is better to state what the indicators properties of HCl are.

Page 6007 gives the conditions under which HCl (g) is predicted.

Detailed comments, experimental. How are negative observations treated?

The MCMC analysis was not run for measurement periods with a missing or negative ammonia measurement. See page 6006, line 24 though page 6007, line 18 for a discussion of how particle phase measurements below the detection limit are treated.

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Detailed comments, results. (1) If 97 percent of the analysis with MCMC produce NH3 results within measurement uncertainty, what is the value added for this species? Why not just use the measurements?

Measurements are uncertain. Including this uncertainty in the analysis is more realistic than using a nominal value. In addition, ISORROPIA calculates equilibrium concentrations given total ammonia (i.e., gas + particle; see Eq. 5 in Part I). This facilitates treating both the particle and gas phase concentrations as random variables.

(2) Of the 31 points outside the measurement uncertainty, what are the potential reasons for the disagreement? Are the MCMC estimates more reliable in those cases? Are there any evidence of non-equilibrium conditions or larger-than-normal measurement errors that can support such an interpretation?

As indicated in the text, (page 6008, lines 7-13) of the 1140 points analyzed, the mode of 1,109 of the posterior ammonia distributions was within the measurement uncertainty (i.e., of the 1140 points analyzed, the predicted mode of 97 percent of these points was within the 29 percent measurement uncertainty, while the mode of the remaining 31 points was beyond 29 percent of the measurement). The remaining 31 points are not outside the measurement uncertainty; only for a single point did the uncertainty bands of the posterior distribution not overlap with the measurement uncertainty bands. Thus, of the 31 points where the mode of the distribution fell outside of the measurement uncertainty, the 95 percent confidence interval of the posterior distribution overlapped the measurement uncertainty in 30 cases. In other words, of the 1140 points analyzed, in 1139 cases the distribution of predicted ammonia concentration overlapped with the 95 percent confidence interval of the measurement. The single point where this was not the case was at 20:34 on 30 April, when the measured ammonia concentration was 1.6 ppbv. MCMC-ISORROPIA predicted (to 95 percent confidence) a concentration between 2.2 ppbv and 3.1 ppbv, with a most likely concentration of 2.6 ppbv.

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(3) In cases where the predictions are sensitive to assumptions of stable vs. metastable aerosols, it could be useful to point out what measurements in Rood et al. (1989) that would help evaluate the state of the aerosol.

The following sentence was added to page 6010, line 15: During this period the relative humidity varied between 49 and 68

(4) That the availability of NH3 data is helpful in reducing the uncertainties of estimated HCl concentrations is a useful conclusion that should be highlighted in the abstract.

The following sentence was added to the abstract: The availability of gas-phase ammonia observations helps constrain the predicted HCl (g) concentrations.

(5) Please provide an idea of what the prevalent pH range is in contrast to the 9-11 April period. The sentence on page 6013, line 13 was modified to: Finally, it is interesting to note that the predicted pH for the acidic period is comparable to the predicted pH at La Merced when the aerosols are assumed to be metastable; the most likely pH varies between 2.5 and 4.0 (see Part I).

(6) For Pedregal and Santa Ana, please list how many points are analyzed and how many of the NH3 predictions are within measurement error. The following sentences were added to page 6013, line 19: Of the 311 points that were analyzed, the mode of 301 of the posterior ammonia distributions was within the measurement uncertainty. Of the 10 points where the mode of the distribution was outside of the measurement uncertainty, the 95 percent confidence interval overlapped the measurement uncertainty in all but two cases.

The following sentences were added to page 6014, line 26: Of the 152 points that were analyzed, the mode of 140 of the posterior ammonia distributions was within the measurement uncertainty. Of the 12 points where the mode of the distribution was outside of the measurement uncertainty, the 95 percent confidence interval overlapped the measurement uncertainty in all but four cases.

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Discussion Can the AMS measurements be used to verify the discussions regarding SOA?

As discussed in the text, the effect of SOA on aerosol water content and nitrate predictions is the subject of considerable uncertainty. We examined whether the nitrate underprediction in this period was correlated to the organic particle concentration measured by the AMS. Unfortunately, the data is insufficient to support such a trend. Specifically, between 10:00 a.m. and 19:35 p.m. (CDT) on 9 April (when the nitrate is consistently underpredicted), a total of 71 points were analyzed. In this period, the concentration of organics in the particles varied between 17 and 41 micrograms per cubic meter. In this limited dataset, the nitrate underprediction does not appear to depend on the particle organic concentration. In order for the discussion regarding the effect of SOA to be verified, speciated concentrations would be required, as well as a model that accounted for the effect of the organic species on the inorganic aerosol.

The upper limit estimate of the importance of Cl reactions (2 percent) seems inconsistent with the conclusion that direct HCl observations are important. Is it because the upper end limit is “on the verge of being relevant”? Some elaboration of the discussion is needed.

As explained in the text, the effect of Cl radicals from HCl to alkane photochemistry is expected to be very minor (e.g., concentrations of HCl (g) approximately equal to 10 ppbv yield only a 2 percent contribution of Cl radicals to RH oxidation). Also pointed out in the text, the only source for Cl radicals we considered were the most likely concentrations of HCl (g). Other sources of Cl radicals were neglected (e.g., photolysis of Cl2, ClNO2, ClNO, etc.). Chlorine chemistry has been shown to be important in other urban areas (see, e.g., Tanaka et al., 2003). Recent work demonstrated the presence of chlorinated hydrocarbons in Mexico City (Velasco et al., 2006). Beyond this, however, very little is known about sources for HCl (g) and other chlorinated species in the MCMA. Measurements of Cl2 and HCl have to our knowledge never been reported in Mexico City. Given these uncertainties, we therefore feel that further investigation of

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the importance of chlorine on the photochemistry in the MCMA is warranted.

Editorial comments: p. 6002, line 29. “needed” Corrected.

p. 6003, line 12. missing period at the end of paragraph Corrected.

p 6006, line 13. missing comma between two Greek letters describing the normal distribution Corrected.

p 6011, line29. capitalize “C” in “HCl” Corrected.

Figure 1. What do the contours, pink line, and shaded area represent?

The following was added to the figure caption: The contours are elevation contours, the pink line represents the Federal District and Estado de México limits, and the shaded area is the urban area of 1995.

Figure 2. Are the predictions HNO3 or NOz?

Corrected (predictions are for HNO3).

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 5999, 2006.