CAN THE THERMODYNAMIC MODEL AND 3-D AIR QUALITY MODEL PREDICT THE AEROSOL NO$_3^-$ REASONABLY?

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1. INTRODUCTION

Studying the behaviors of nitrate is one of most intriguing aspects of atmospheric aerosols because particulate nitrate concentrations depend not only on the amount of nitric acid, but also on availability of ammonia, sulfate concentrations, temperature and relative humidity. It is still one of the most challenging tasks to partition the semi-volatile inorganic aerosol components between the gas and aerosol phases correctly, especially when the thermodynamic models are incorporated in a 3-D air quality model.

2.0 MODELING AEROSOL NITRATE THERMODYNAMICS AND OBSERVATIONAL DATASETS

Given total (gas + particulate phase) concentrations of H$_2$SO$_4$, HNO$_3$, and NH$_3$, and temperature and RH as inputs, ISORROPIA (Nenes et al., 1999) and AIM2-Model II (Clegg et al., 1998) can predict the partitioning of these inorganic species between the gas and aerosol phases on the basis of thermodynamic equilibrium. In this study, TNH$_4$ and TNO$_3$ are referred to as aerosol NH$_4^+$+gas NH$_3$ and aerosol NO$_3^-$+gas HNO$_3$, respectively. In order to render the thermodynamic model as fast and computationally efficient as possible, ISORROPIA utilizes the optimal solution of the thermodynamic equations and precalculated tables, whenever possible (Nenes et al., 1999). On the contrary,

AIM2 is a theoretically complete and accurate phase equilibrium model that does not apply any simplifying assumptions for the inorganic aerosol systems.

For the observational datasets, the concentrations of PM$_{2.5}$ SO$_4^{2-}$, NO$_3^-$, and NH$_4^+$ were measured with a 5-minute sampling at the Atlanta site during the SOS/Atlanta '99 Supersite Experiment from August 18 to September 1, 1999, (Weber et al., 2003). NH$_3$ (g) and HNO$_3$ (g) concentrations were measured with a time resolution of 15 and 9 minutes, respectively. These gas (HNO$_3$ and NH$_3$) concentrations were parsed into 5-minute averages so as to overlap with 5-minute mean concentrations of PM$_{2.5}$ SO$_4^{2-}$, NO$_3^-$, and NH$_4^+$. Temperature and RH with 1-minute time resolution were averaged to 5 minutes. A total of 325 data points at the Atlanta site was obtained in this way. At the Clinton Horticultural Crop Research Station (35^{0}01' latitude, 78^{0}16' longitude), North Carolina, 12-hour (0600-1800 h day cycle; 18-0600 h night cycle) mean concentrations of PM$_{2.5}$ NH$_4^+$, NO$_3^-$ and SO$_4^{2-}$, and gas NH$_3$ and HNO$_3$ were measured from January 20 to November 2, 1999. The hourly temperature and RH data at the site were provided by State Climate Office of North Carolina at North Carolina State University.

3.0 RESULTS AND DISCUSSIONS

3.1 Test of thermodynamic models with observational data

ISORROPIA and AIM2 were used to partition TNH$_4$ and TNO$_3$ between aerosol and gas phases.

Figure 1 shows comparisons of observed aerosol NO_3^- and NH_4^+, and gaseous HNO_3 and NH_3 concentrations with those calculated by the models at the Atlanta site. As given in Table 1, 94% and 96% of the NH_4^+ predictions are within a factor of 1.5 for ISORROPIA and AIM2, respectively. (In shorthand, NH_4^+: 94% (ISORROPIA) and 96% (AIM2) within a factor of 1.5). Predictions for gas HNO_3 are also good (HNO_3: 86% (ISORROPIA) and 87% (AIM2) within a factor of 1.5, see Table 1). This is partially because most of TNH_4 and TNO_3 are located in the aerosol and gas phases, respectively. However, both models cannot reproduce most of observed aerosol NO_3^- and gas NH_3 (NO_3^-: 32%% (ISORROPIA) and 48% (AIM2) within a factor of 2, and NH_3: 25% (ISORROPIA) and 51% (AIM2) within a factor of 2, see Table 1). A further analysis, not shown, indicates that the periods of overprediction are associated with low temperature, high RH and sulfate-poor conditions ($TNH_4/SO_4^{2-}>2.0$), while those of underpredictions are associated with the conditions of high temperature, low RH and sulfate-rich ($TNH_4/SO_4^{2-}<2.0$).

For the Clinton site, Figure 2 shows that both models reproduced observed NH_3 concentrations very well (95% (ISORROPIA) and 97% (AIM2) within a factor of 1.5) due to the fact that most of TNH_4 is in the gas phase. Both models performed a little better on aerosol NO_3^- at the Clinton site than at the Atlanta site. Most of the cases at the Clinton site are representative of very sulfate-poor conditions. However, there are many cases in which the observations show the existence of low aerosol NO_3^- (such as 0.1 to 0.8 $\mu g\ m^{-3}$) but the thermodynamic models predicted either zero or negligible amounts of aerosol NO_3^- like those at the Atlanta site (see Figures 1 and 2). The possible reasons for this are as follows: (1) a dynamic instead of an equilibrium model may be more suitable for these cases, i.e., they are not in complete thermodynamic equilibrium; (2) thermodynamic models are not able to accurately simulate such cases for the conditions encountered; (3) other ions (such as Na^+, Cl^-, Ca^{2+} and Mg^{2+}) made significant contributions to aerosol components and the thermodynamic models do not consider their effects; (4) other mechanisms such as absorption by carbonaceous aerosol instead of thermodynamic equilibrium produce aerosol NO_3^-; (5) There are significant errors in observations of other important aerosol components (such as SO_4^{2-}) and TNH_4.

3.2. Effects of errors in SO_4^{2-}, total ammonia ($NH_3+NH_4^+$), temperature and relative humidity on predicting aerosol NO_3^-

Since the 3-D air quality model such as the CMAQ can only reproduce 46-79% of SO_4^{2-} and 39-72% of aerosol NH_4^+ within a factor of 1.5 (Eder et al., 2003), the 3-D air quality models can make ±50% errors in simulations of SO_4^{2-} and NH_4^+ very frequently. In order to test how much these errors will affect the predictions of aerosol NO_3^-, a test dataset of total 163 data points, in which both ISRROPIA and AIM predict the existence of aerosol NO_3^-, was obtained on the basis of observational data (total 325 data points, see Figure 1) at the Atlanta site. Then the different combinations of errors in SO_4^{2-} and TNH_4 are applied to this test dataset as shown in Table 2. The prediction results of each thermodynamic model for the test dataset before introduced errors are considered as the base-case results. As shown in Figure 3, both ISORROPIA and AIM2 have similar responses in the predicted aerosol NO_3^- to the possible errors in SO_4^{2-} and TNH_4 although the aerosol NO_3^- predictions by ISORROPIA are modestly more sensitive to the errors in SO_4^{2-} and TNH_4 than those by AIM2. Under the conditions with -50% errors in TNH_4 including cases 5, 6 and 7, both ISORROPIA and AIM will underpredict almost all aerosol NO_3^- concentrations by more than a factor of 2 (Table 2 and Figure 3). Under the conditions with +50% error in SO_4^{2-} (case 1), or +50% error in TNH_4 (case 2), or –50% error in SO_4^{2-} and +50% error in TNH_4 (case 8), both model cannot reproduce most of aerosol NO_3^- concentrations within a factor of 2 (percentage<40% within a factor of 2). The conditions with the case 3 (+50% errors in both SO_4^{2-} and TNH_4) and case 4 (-50% errors in SO_4^{2-}) show relative less effects on the prediction of aerosol NO_3^-. This is due to the fact that there is compensation error from both SO_4^{2-} and TNH_4 in the case 3.

As shown in Figure 4, in contrast to big effects from the errors in SO_4^{2-} and TNH_4, the responses of the aerosol NO3 predictions are less sensitive to the errors in temperature and somewhat less sensitive to errors in RH. However, ±20% errors in both temperature and RH still result in both models not being able to reproduce most of aerosol NO_3^- within a factor of 1.5 (percentage<42%, see Table 2) although both models can capture 53-69% of aerosol NO_3^- within a factor of 2. This analysis indicates that errors in

TNH_4 are more critical than errors in SO_4^{2-} to prediction of NO_3^-. Regardless, the 3-D model performance on SO_4^{2-} and TNH_4 needs to be quit good and better than current daily performance, before the 3-D air quality model can predict aerosol NO_3^- reasonably although it can predict TNO_3 reasonably.

4. REFERENCES

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Table 1. Statistical summaries of the comparison of the modeled partitioning of total nitrate (gas + aerosol) and total ammonia (gas + aerosol) between gas and aerosol phases with that of observations at the Atlanta SuperSite, GA, and Clinton site, NC.

Parameters	<C>			Within a factor of 1.5, (%)		Within a factor of 2, (%)	
	OBS	ISORROPIA	AIM2	ISORROPIA	AIM2	ISORROPIA	AIM2
At Atlanta site (N=325)							
Aerosol NO_3^-	0.53	0.54	0.61	21.8	33.2	31.7	48.3
Gas HNO_3	7.15	7.13	7.06	86.2	87.1	91.7	92.9
Aerosol NH_4^+	3.60	4.06	3.85	94.8	96.0	98.5	98.8
Gas NH_3	0.74	0.31	0.50	16.6	31.4	25.2	51.4
At Clinton site (N=479)							
Aerosol NO_3^-	0.30	0.28	0.24	58.0	47.2	71.8	62.0
Gas HNO_3	0.27	0.29	0.33	52.4	49.3	78.7	69.5
Aerosol NH_4^+	1.15	1.44	1.42	74.5	76.2	92.5	92.5
Gas NH_3	5.13	4.86	4.88	95.4	96.5	97.5	97.9

* <C> is the mean concentration ($\mu g\ m^{-3}$), percentages (%): are the percentages of the comparison points whose model results are within a factor of 2 (or 1.5) of the observations (See Figures 1 and 4). N is number of samples.

Table 2. Statistical summaries of the comparison of the modeled aerosol NO_3^- for different sensitivity cases vs. those of base cases on the basis of observational data at the Atlanta SuperSite, GA

Cases	Conditions	<C>			Within a factor of 1.5, %	
		Base-case	ISORROPIA	AIM	ISORROPIA	AIM
1	+50% error in SO_4^{2-}	1.00	0.43	0.53	0.14	0.24
2	+50% error in TNH_4	1.00	2.13	2.00	0.14	0.16
3	+50% error in SO_4^{2-} and TNH_4	1.00	1.43	1.51	0.27	0.33
4	-50% error in SO_4^{2-}	1.00	1.64	1.53	0.40	0.61
5	-50% error in TNH_4	1.00	0.11	0.16	0.00	0.00
6	-50% error in SO_4 and TNH_4	1.00	0.46	0.49	0.03	0.04
7	+50% error in SO_4^{2-}, -50% error in TNH_4	1.00	0.07	0.09	0.00	0.00
8	-50% error in SO_4^{2-}, +50% error in TNH_4	1.00	2.31	2.18	0.15	0.20
9	+20% error in Temp (^0C)	1.00	0.69	0.72	0.26	0.25
10	-20% error in Temp (^0C)	1.00	1.32	1.44	0.42	0.42
11	+20% error in RH (%)	1.00	2.69	2.76	0.29	0.37
12	-20% error in RH (%)	1.00	0.44	0.41	0.19	0.37

* <C> is the mean NO_3^- concentration ($\mu g\ m^{-3}$), percentages (%): are the percentages of the comparison points whose model results are within a factor of 2 (or 1.5) of the observations. The number of samples is 163.
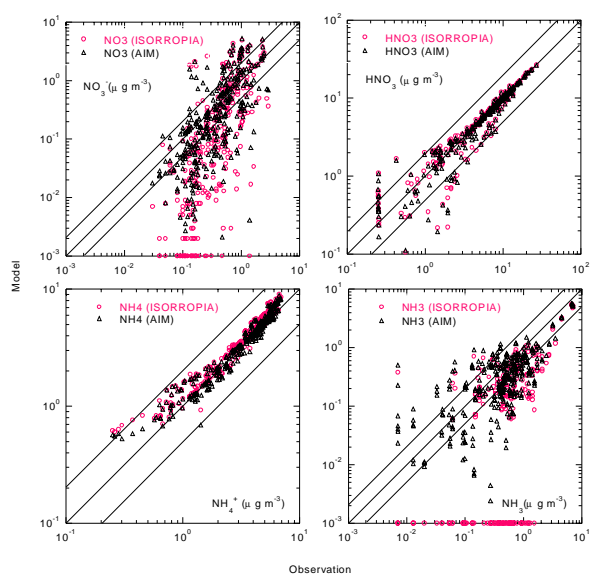

Figure 1. Comparison of the modeled partitioning of total nitrate and total ammonia between gas and aerosol phases with that of observations at the Atlanta supersite in summer of 1999.
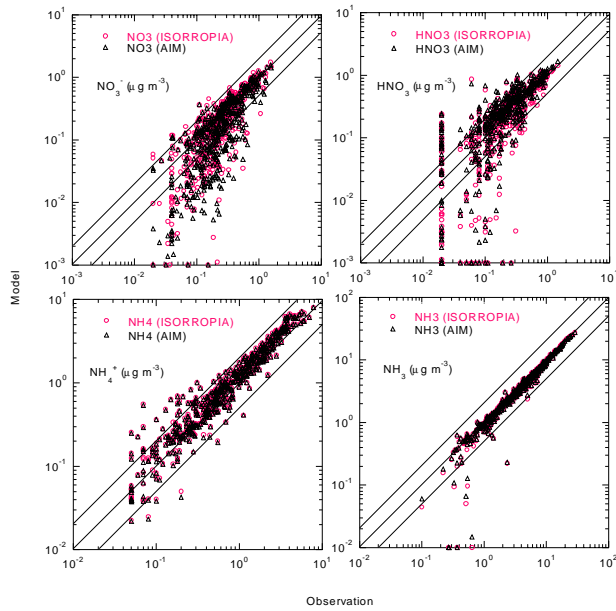
Figure 2. Same as Figure 1 but at the Clinton site, NC, during the period of January 20 to November 2, 1999.
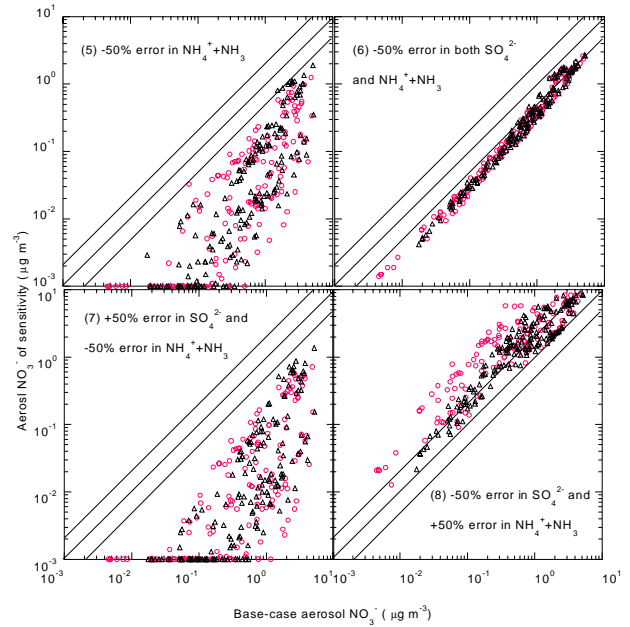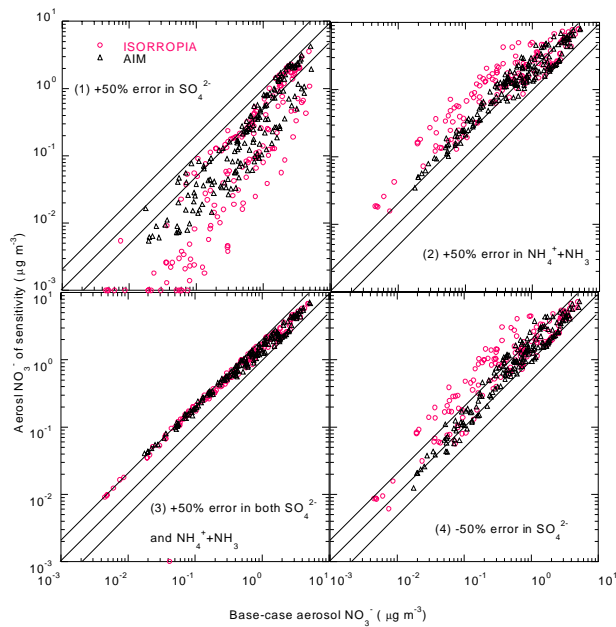
Figure 3 (Continued)

Figure 3. Aerosol NO$_3^-$ of sensitivity cases with different assumed errors vs. base-case NO$_3^-$ for different thermodynamic models on the basis of observational data at the Atlanta site.
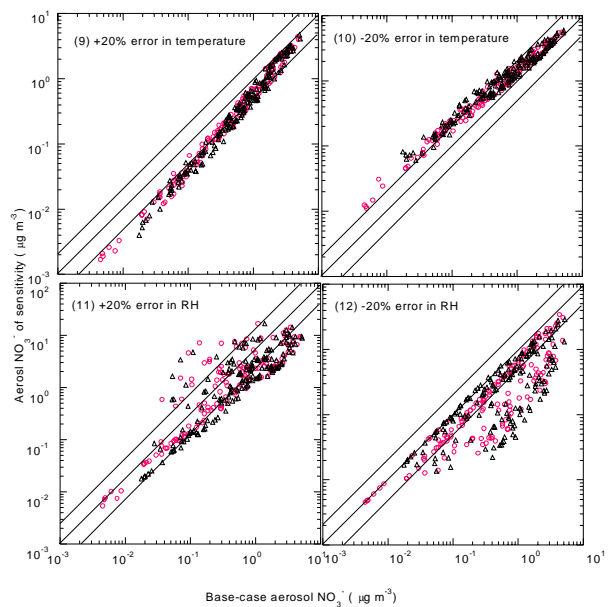
Figure 4. Same as Figure 3 but for the assumed errors in temperature and relative humidty.