A TEST OF THERMODYNAMIC EQUILIBRIUM MODELS AND 3-D AIR QUALITY MODELS FOR PREDICTIONS OF AEROSOL NO_3^-

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1. INTRODUCTION

The inorganic species of sulfate, nitrate and ammonium constitute a major fraction of atmospheric aerosols. The behavior of nitrate is one of the most intriguing aspects of inorganic atmospheric aerosols because particulate nitrate concentrations depend not only on the amount of gas-phase nitric acid, but also on the availability of ammonia and sulfate, together with temperature and relative humidity. Particulate nitrate is produced mainly from the equilibrium reaction between two gas-phase species, HNO_3 and NH_3.

It is a very challenging task to partition the semi-volatile inorganic aerosol components between the gas and aerosol phases correctly. The normalized mean error (NME) for predictions of nitrate is typically three times that for predictions of sulfate for a variety of 3-D air quality models applied to sections of the U.S. (Odman, et al., 2002; Pun, et al, 2004) For an annual average across the entire U.S. the NMEs of the predictions of nitrate from the U.S. EPA Models-3/Community Multiscale Air Quality Model (CMAQ) are two to three times larger than the NMEs for sulfate.

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2. THERMODYNAMIC MODELS AND OBSERVATIONAL DATASETS

Given total (gas + fine particulate phase) concentrations of H_2SO_4, HNO_3, and NH_3, and temperature and RH as inputs, ISORROPIA and AIM (AIM model II is used in this study) predict the partitioning of these inorganic species between the gas and fine particle ($PM_{2.5}$) phases on the basis of thermodynamic equilibrium. More detailed descriptions of the equilibrium reactions and the solution procedures for AIM and ISORROPIA are given by Wexler and Clegg (2002) and Nenes et al. (1999), respectively.

Three sites were chosen that had high time resolution data to test the equilibrium models. At the Atlanta site (33.78 ^{0}N, 84.41 ^{0}W), a total of 325 observational data points were obtained during the SOS/Atlanta '99 Supersite Experiment from August 18 to September 1, 1999, by parsing the 9-minute HNO_3 and 15-minute NH_3 concentrations 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^+ (Weber et al., 2003) (summer case). At the Pittsburgh Supersite (40.44 ^{0}N, 79.94 ^{0}W), Pennsylvania, a total of 313 data points for two-hourly mean concentrations of $PM_{2.5}$ NH_4^+, NO_3^- and SO_4^{2-}, and gas-phase HNO_3 were obtained during the period of January 2 to January 31, 2002 (Wittig et al., 2004) (winter case). At the Clinton Horticultural Crop Research Station (35^{0}01' N, 78^{0}16' W), North Carolina, a total of 479 data points for 12-hour (0600-1800 h (EST) day cycle; 1800-0600 h night cycle) mean concentrations of $PM_{2.5}$ NH_4^+, NO_3^- and SO_4^{2-}, and gas-phase NH_3 and HNO_3 were obtained by an annular denuder system from January 20 to November 2, 1999 (Robarge et al., 2002).

3. RESULTS AND DISCUSSION

3.1. TEST OF THERMODYNAMIC MODEL WITH OBSERVATIONAL DATA

Comparisons of observed aerosol NO_3^- and NH_4^+, and gaseous HNO_3 and NH_3 concentrations with those calculated by ISORROPIA and AIM at the three sites are listed in Table 1. At the Atlanta site, 94.8% and 96.0% of the ISORROPIA and AIM predictions of NH_4^+ are within a factor of 1.5 of the observations. ISORROPIA and AIM also predict HNO_3 well, with 86% and 87% of the predictions within a factor of 1.5 of the observations. However, both equilibrium models are unable to replicate a majority of the observed NO_3^- and NH_3 concentrations, see Figure 1 and Table 1. For NO_3^-, only 32% and 48% of the ISORROPIA and AIM predictions are within a factor of 2 of the observations, respectively. For NH_3, ISORROPIA and AIM replicate 25.2% and 51.4% of the observations within a factor of 2, respectively. At the Pittsburgh site, both AIM and ISORROPIA can correctly predict the NO_3^- concentrations to within a factor 2 of the observations for a majority of the data points (>76%) because the TNO_3 concentration is constrained and the aerosol fraction is dominant. On the other hand, both models perform much more poorly on HNO_3, the gas fraction, as compared to the Atlanta situation. At the Clinton site, both models reproduce observed NH_3 concentrations very well (>95% within a factor of 1.5) and reproduce a majority of NH_4^+ concentration data points within a factor of 2 (>92%). Performance of both models for aerosol NO_3^- at the Clinton site is better than at the Atlanta site but worse than at the Pittsburgh site.

Table 1. Statistical summaries of the comparison of the modeled (ISORROPIA and AIM) 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, Pittsburgh Supersite, PA, and Clinton site, NC. The mean concentrations (± standard deviation) of SO_4^{2-}, TNO_3 and TNH_4 ($\mu g\ m^{-3}$), and relative humidity (RH) (%) and temperature (T) (^0C) at each site are also listed.

	<C>*			% within a factor of 1.5 **		% within a factor of 2**	
Parameters	OBS	ISORROPIA	AIM	ISORROPIA	AIM	ISORROPIA	AIM
Atlanta site (N=325)							
(SO_4^{2-}=12.17±6.71, TNH_4=4.38±2.39, TNO_3=7.57±5.27, RH=68.9±19.9, T=25.0±3.3)							
Aerosol NO_3^-	0.53±0.51	0.54±0.92	0.61±0.92	21.8	33.2	31.7	48.3
Gas HNO_3	7.15±4.84	7.13±4.94	7.06±4.92	86.2	87.1	91.7	92.9
Aerosol NH_4^+	3.60±1.77	4.06±2.05	3.85±1.99	94.8	96.0	98.5	98.8
Gas NH_3	0.74±1.06	0.31±0.79	0.50±0.81	16.6	31.4	25.2	51.4
Pittsburgh site (N=313)							
(SO_4^{2-}=2.46±1.14, TNH_4=1.74±0.77, TNO_3=3.08±2.18, RH=67.1±17.6, T=3.9±5.9)							
Aerosol NO_3^-	2.09±1.51	2.04±1.74	1.98±1.79	60.8	57.4	77.0	75.7
Gas HNO_3	1.01±0.68	0.96±0.78	1.02±0.74	37.7	39.6	56.5	62.0
Clinton site (N=479)							
(SO_4^{2-}=3.64±4.05, TNH_4=6.29±5.51, TNO_3=0.57±0.51, RH=79.9±14.2, T=19.1±7.7)							
Aerosol NO_3^-	0.30±0.26	0.28±0.28	0.24±0.27	58.0	47.2	71.8	62.0
Gas HNO_3	0.27±0.25	0.29±0.28	0.33±0.30	52.4	49.3	78.7	69.5
Aerosol NH_4^+	1.15±1.27	1.44±1.57	1.42±1.54	74.5	76.2	92.5	92.5
Gas NH_3	5.13±4.73	4.86±4.62	4.88±4.63	95.4	96.5	97.5	97.9

* <C> is mean ± standard deviation ($\mu g\ m^{-3}$)

** Percentages (%): are the percentages of the comparison points whose model results are within a factor of 1.5 and 2.0 of the observations. N is number of samples.

There are many possible reasons for the discrepancies between the model predictions and observations in partitioning of TNO_3 for aerosol NO_3^-. To show how the measurement errors in SO_4^{2-} and TNH_4 can contribute to uncertainties in model predictions of aerosol NO_3^-, Gaussian (normally distributed) random errors are added to the input SO_4^{2-} and TNH_4 (base-case concentrations, C_b) to create the sensitivity-case concentrations (C_s) as follows

$$C_s = C_b + \varepsilon_p^{'} \qquad (1)$$

where $\varepsilon_p^{'}$ represents truncated Gaussian random errors with zero mean and standard deviation equal to 15%×C_b. An error of ±15% is used to correspond with the measurement uncertainty for both SO_4^{2-} and TNH_4 that was estimated as part of the U.S.

EPA supersite program (Solomon et al., 2003). The errors are truncated so that only values within 2 standard deviations ($2\times15\%\times C_b$) are allowed. As shown in Figure 2, the model with the measurement errors in both SO_4^{2-} and TNH_4 can only reproduce 61.3 % of the base-case aerosol NO_3^- within a factor of 2. This indicates that random errors in SO_4^{2-} and TNH_4 measurements can account for most of the discrepancies between the model predictions and observations of aerosol NO_3^- in Figure 1 at the Atlanta site. Similar conclusions can be obtained for the results at the Pittsburgh and Clinton sites and for the AIM model.

3.2. EFFECTS OF 3-D MODEL PREDICTION ERRORS IN SO_4^{2-}, TNH_4, TEMPERATURE AND RELATIVE HUMIDITY ON PREDICTING AEROSOL NO_3^-

The 3-D CMAQ model can only reproduce 46-79% of SO_4^{2-} and 39-72% of aerosol NH_4^+ within a factor of 1.5 (Yu et al., 2004). This means that the 3-D air quality models are frequently making errors on the order of ±50% in the simulations of SO_4^{2-} and NH_4^+. To test how much the errors in SO_4^{2-} and TNH_4 associated with predictions from a 3-D air quality model such as CMAQ will affect the predictions of aerosol NO_3^- in the thermodynamic model, sensitivity-case concentrations (C_s) of SO_4^{2-} and TNH_4 are generated by adding independent Gaussian (normally distributed) random errors to their base-case concentrations (C_b) as follows:

$$\ln(C_s) = \ln(C_b) + \varepsilon\ ,\ \varepsilon \sim G(0, \sigma = RMSE) \tag{2}$$

where ε represents Gaussian random errors with zero mean and standard deviation equal to the *RMSE*, the root mean square error. The *RMSE* used in this study is obtained from comparisons of the paired 3-D model predictions and observations for each species (Yu et al., 2004). The comparison of predictions of aerosol NO_3^- between the sensitivity-case and the base-case is shown in Figure 3 and summarized in Table 2. The equilibrium models with the 3-D air quality model-derived random errors in SO_4^{2-} and TNH_4 can only predict <50% and <62% of aerosol NO_3^- within a factor of 1.5 and 2, respectively, as shown in Table 2, although the modeled means are close to the observations. For ISORROPIA in Table 2, 47% and 60% of the NO_3^- predictions from the sensitivity cases are within a factor of 2 of the base case for Atlanta and Pittsburgh, respectively. This study suggests that a large source of error in predicting aerosol NO_3^- stems from the errors in 3-D model predictions of SO_4^{2-} and TNH_4 for the Eastern U.S. Table 2 and Figure 3 also indicate that errors in TNH_4 are more critical than errors in SO_4^{2-} to prediction of NO_3^- and that the higher the NO_3^- concentration, the less sensitive the predicted NO_3^- concentrations are to the errors in SO_4^{2-} and TNH_4. These results indicate that the ability of 3-D models to simulate aerosol NO_3^- concentrations is limited by uncertainties in predicted SO_4^{2-} and TNH_4.

Additional studies were carried out for the comparison of sensitivity-case NO_3^- for single relative fixed errors of ±10% individually in temperature and RH with those of the base-case in the summer and winter times. In contrast to large effects from the errors in SO_4^{2-} and TNH_4, the responses of the aerosol NO_3^- predictions are less sensitive to errors in temperature and RH. Generally, both models can reproduce a majority of the aerosol NO_3^- data points within a factor of 1.5 if there are only ±10% errors in temperature and RH, especially for the winter times, with somewhat more sensitivity to errors in RH.

However, ±20% errors in both temperature and RH can result in neither model being able to reproduce a majority of aerosol NO_3^- data points within a factor of 1.5 (percentage<42%) (not shown) although both models can still capture 53-69% of aerosol NO_3^- within a factor of 2 in the summer case. For the winter case, the predicted aerosol NO_3^- is much less sensitive to errors in temperature and RH. This may be due to the fact that temperatures in the winter times are very low (3.9±5.9 ^{0}C), and most of TNO_3 concentration is in the aerosol phase. This is generally in agreement with Takahama et al. (2004), who found that errors in temperature measurements do not contribute significantly to model errors when temperatures are low and most of the nitrate concentration is in the aerosol phase.

Table 2. Statistical summaries of the comparisons of the modeled (ISORROPIA and AIM) aerosol NO_3^- for the different sensitivity cases created by the Gaussian random errors (see text explanation) vs. those of the base cases on the basis of observational data at the Atlanta Supersite (summer case) and Pittsburgh Supersite (winter case).

	<C>*			% within a factor of 1.5*		% within a factor of 2*	
Condition	Base-case	ISORROPIA	AIM	ISORROPIA	AIM	ISORROPIA	AIM
Atlanta data (N=163)							
Errors in SO_4^{2-} and TNH_4	0.99±1.12	1.11±1.38	1.11±1.34	30.1	40.5	47.2	62.6
Errors in SO_4^{2-}	0.99±1.12	1.03±1.26	1.05±1.22	43.6	58.9	59.5	71.2
Errors in TNH_4	0.99±1.12	1.10±1.35	1.12±1.30	34.4	42.3	54.6	68.1
Pittsburgh Data (N=312)							
Errors in SO_4^{2-} and TNH_4	2.00±1.72	1.80±1.84	1.80±1.85	48.4	48.1	60.3	60.3
Errors in SO_4^{2-}	2.00±1.72	1.93±1.78	1.91±1.82	70.2	75.6	77.6	84.3
Errors in TNH_4	2.00±1.72	1.81±1.84	1.82±1.86	48.1	46.8	61.2	61.9

* Same as Table 1

4. SUMMARY

The capability of thermodynamic models to reproduce the observed partitioning of TNO_3 and TNH_4 between gas and aerosol phases differed from site to site depending on chemical and meteorological conditions at the site. For example, at the Atlanta site, for NH_4^+ 94% and 96% of ISORROPIA and AIM predictions are within a factor of 1.5 of observations, respectively. For HNO_3, 86 and 87% of ISORROPIA and AIM predictions are within a factor of 1.5 of observations. However, neither model reproduced a majority of observed aerosol NO_3^- and gas NH_3 within a factor of 2 (NO_3^-: <48% and NH_3: <51%) at the Atlanta site. At the Pittsburgh site, both models can predict a majority of NO_3^- data points within a factor of 2 (>76%), especially when NO_3^- concentrations are higher than 1.0 μg m^{-3} (>89%), whereas both models perform more poorly on HNO_3 than at the Atlanta site. At the Clinton site, both models reproduce observed NH_3 concentrations very well (>95% within a factor of 1.5), and performe a little better on aerosol NO_3^- (47-58% within a factor of 1.5) than at the Atlanta site but worse than at the Pittsburgh site.

The different chemical and meteorological conditions at the three sites can explain why both models perform differently in partitioning of TNO_3 and TNH_4. There are many different possible reasons for the discrepancies between the models and observations in partitioning of TNO_3. The sensitivity test indicates that in many cases measurement uncertainties in SO_4^{2-} and TNH_4 can explain a major fraction of the discrepancies between the model predictions and observations in partitioning of TNO_3. Sensitivity tests show that random errors associated with SO_4^{2-} and TNH_4 predictions of the 3-D model can result in the thermodynamic model calculation replicating only 47% and 60% of the base case NO_3^- within a factor of 2 for summer and winter cases, respectively. This suggests that a large source of error in predicting aerosol NO_3^- stems from the errors in 3-D model predictions of SO_4^{2-} and TNH_4 for the Eastern U.S. It was found that errors in TNH_4 are more critical than errors in SO_4^{2-} to prediction of NO_3^- and that the responses of the aerosol NO_3^- predictions are not very sensitive to the errors in temperature and RH under the tested conditions. The ability of 3-D models to simulate aerosol NO_3^- concentrations is limited by uncertainties in predicted SO_4^{2-} and TNH_4. While there is feedback between partitioning and the levels of predicted TNO_3, errors in TNO_3 are much less sensitive to these uncertainties and 3-D models are capable of predicting TNO_3 with accuracy comparable to that of SO_4^{2-} or TNH_4.

5. REFERENCES

Byun, D.W. and J.K.S. Ching, Eds.,: Science algorithms of the EPA Models-3 Community Multi-scale Air Quality (CMAQ) modeling system, EPA/600/R-99/030, Office of Research and Development, U.S. Environmental Protection Agency, 1999.

Clegg, S.L., P. Brimblecombe, and A.S. Wexler, A thermodynamic model of the system H^+-NH_4^+-SO_4^{2-}-NO_3^--H_2O at tropospheric temperatures. *J. Phys. Chem*., A, 102, 2155-2171, 1998.

Nenes, A., C. Pilinis, and S.N. Pandis, Continued development and testing of a new thermodynamic aerosol module for urban and regional air quality models. *Atmos. Environ*., 33, 1553-1560, 1999.

Odman, M.T., J.W. Boylan, J.G. Wilkinson, A.G. Russell, S.F. Mueller, R.E. Imhoff, K.G. Doty, W.B. Norris, and R.T. McNider, SAMI Air Quality Modeling, Final Report, Southern Appalachian Mountains Initiative, Asheville, NC, 2002.

Pun, B., C. Seigneur, S-.Y. Wu, E. Knipping, and N. Kumar, Modeling Analysis of the Big Bend Regional Aerosol Visibility Observational (BRAVO) Study, Final Report 1009283, EPRI, Palo Alto, CA, 2004.

Robarge, W.P., J.T. Walker, R.B. McCulloch, and G. Murray, Atmospheric concentrations of ammonia and ammonium at an agricultural site in the southeast United Sates. *Atmos. Environ*., 36, 1661-1674, 2002.

Solomon, P.A., K. Baumann, E. Edgerton, R. Tanner, D. Eatough, W. Modey, H. Marin, D. Savoie, S. Natarajan, M.B. Meyer, and G. Norris. Comparison of Integrated Samplers for Mass and Composition During the 1999 Atlanta Supersites Project. *J. Geophys. Res*., 108(D7), 8423, doi:10.1029/2001JD001218, 2003.

Takahama, S., B. Wittig, D.V. Vayenas, C.I. Davidson, and S.N. Pandis, Modeling the diurnal variation of nitrate during the Pittsburgh Air Quality Study, *J. Geophys. Res*., 109, D16S06, doi:10.1029/2003JD004149, 2004

Wittig, B., S. Takahama, A. Khlystov, S.N. Pandis, S. Hering, B. Kirby, and C. Davidson, Semi-continuous PM2.5 inorganic composition measurements during the Pittsburgh Air Quality Study. *Atmos. Environ*., 38, 3201-3213, 2004.

Weber, R.J., et al., Intercomparison of near real-time monitors of $PM_{2.5}$ nitrate and sulfate at the Environmental Protection Agency Atlanta Supersite. *J. Geophys. Res*., 108, 8421, doi:10.1029/2001JD001220, 2003.

Wexler, A.S., and S.L. Clegg, Atmospheric aerosol models for systems including the ions H^+, NH_4^+, Na^+, SO_4^{2-}, NO_3^-, Cl^-, Br^-, and H_2O, *J. Geophys. Res*., 107 (D14), doi:10.1029/2001JD000451, 2002.

Yu, S.C., R. Dennis, S. Roselle, A. Nenes, J. Walker, B. Eder, K. Schere, J. Swall, W. Robarge, An assessment of the ability of 3-D air quality models with current thermodynamic equilibrium models to predict aerosol NO_3^-. *J. Geophys. Res*., 2004 (in press).

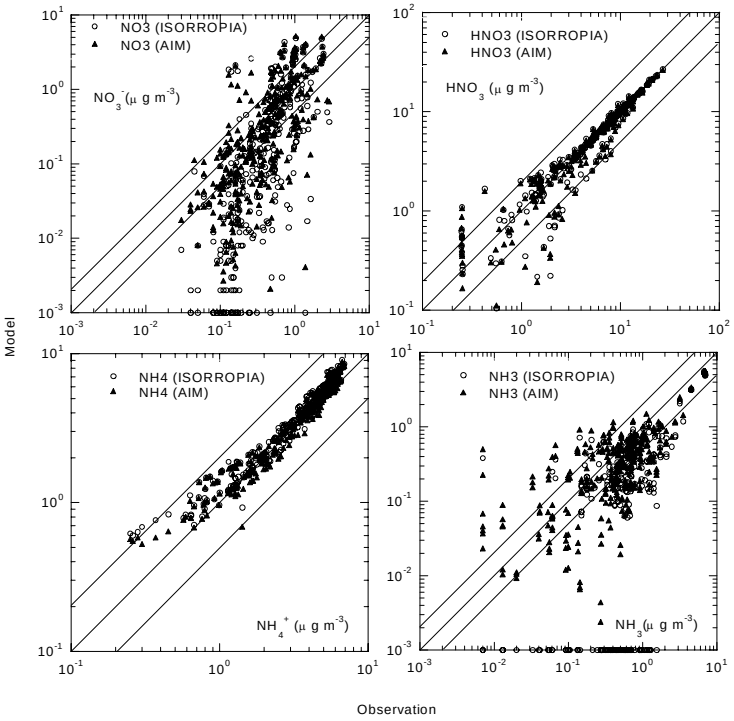

Fig 1. Comparison of the modeled (ISORROPIA and AIM) partitioning of total nitrate (gas + aerosol) and total ammonia (gas + aerosol) between gas and aerosol phases with that of observations for aerosol NO_3^-, HNO_3, aerosol NH_4^+ and NH_3 at the Atlanta supersite in summer of 1999. The 1:1, 2:1, and 1:2 lines are shown for reference.

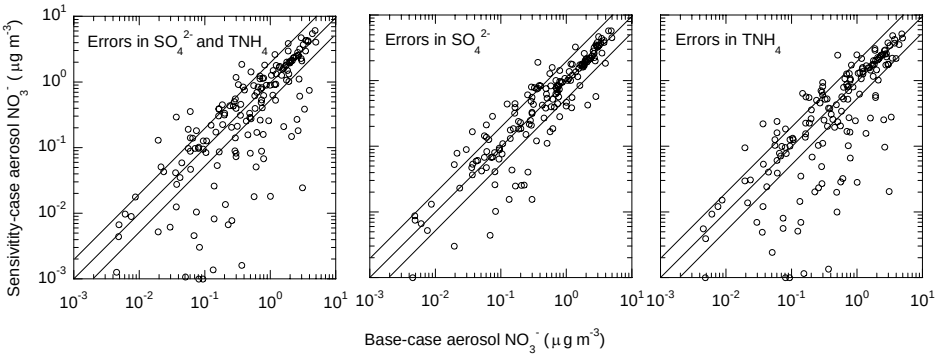

Figure 2. Sensitivity-case NO_3^- with assumed Gaussian random errors in observed SO_4^{2-}, TNH_4 vs. the base-case NO_3^- for the ISORROPIA model at the Atlanta site

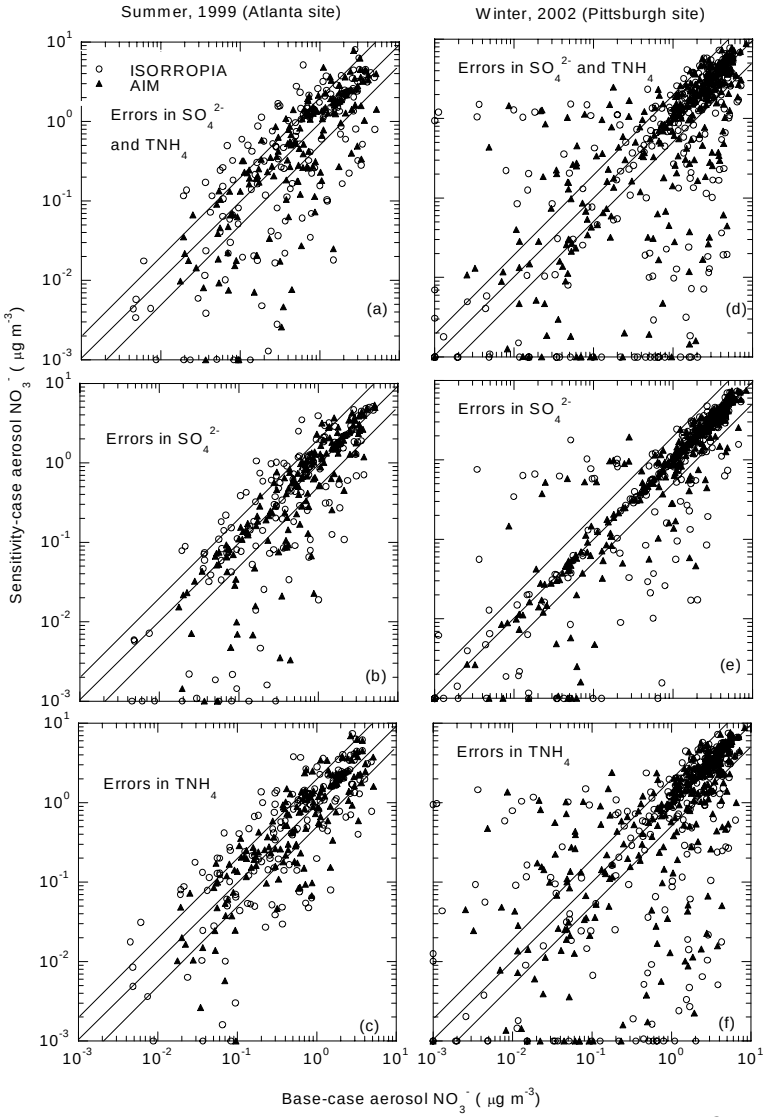

Fig. 3. Sensitivity-case NO_3^- with assumed Gaussian random errors in SO_4^{2-}, and/or TNH_4 vs. the base-case NO_3^- for AIM and ISORROPIA for summer case ((a), (b), (c)) and winter case ((d), (e), (f)).

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