Assessing the role of ammonia in sulfur transformation and deposition in China

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Received 3 May 2007; received in revised form 2 October 2007; accepted 2 October 2007

Abstract

Inorganic thermodynamic equilibrium model (ISORROPIA) coupled with the Models-3 Community Multi-scale Air Quality modeling system (CMAQ) was used to understand the role of ammonia (NH_3) in sulfur dioxide (SO_2) transformation and sulfur (S) deposition in China.

The simulated S and nitrogen (N) compounds in gas (SO_2 , NH_3) and aerosol (sulfate (SO_4^{2-}), ammonium (NH_4^+)) phases and wet deposition were compared against observations at two non-urban sites: Tie Shan Ping (TSP) and Cai Jia Tang (CJT). Observations showed that SO_4^{2-} was the predominant anion in aerosol and precipitation at the sites, and there were not enough NH_3 and alkaline dusts (i.e. mineral oxides and carbonates) to neutralize all acidity. Most of the NH_4^+ was therefore probably bound to SO_4^{2-} .

The presence of NH_3 significantly altered the regional distributions of S compounds in gas and aerosol phases. Model simulations showed SO_4^{2-} concentration increased by 10–15% while SO_2 concentration decreased by 10–60% over polluted regions due to NH_3 . Furthermore, the presence of NH_3 enhanced long-range S transportation for the longer lifetime of sulfate than of SO_2 in the atmosphere. S deposition thereby decreased by 10–30% over polluted regions.

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Keywords: Aerosol thermodynamics; CMAQ; Sulfur deposition; Ammonia

1. Introduction

In China, coal accounts for about 70% of the energy production (CESY, 2005), which leads to large emissions of SO_2 (SEPA, 2004). Part of SO_2 can be converted to SO_4^{2-} through gas phase or multiphase reactions in the atmosphere, and results in SO_4^{2-} as the predominant anion in aerosol and precipitation in China (Aas et al., 2007). The amounts of NH_3 , mineral oxides and carbonates dusts are not sufficient to neutralize all acidity over

large regions of China, allowing for acid rain to prevail especially in the southern parts of the country (i.e. south of Yangtze River).

SO_2 and NH_3 are primary pollutants playing important roles in aerosol processes and influencing the acidity of precipitation (Dentener and Crutzen, 1994). Sulfate is mainly produced from the oxidation of SO_2 , and NH_3 plays an important role in this process (Coffman and Hegg, 1995; Ally et al., 2001; Colberg et al., 2000). NH_3 reacts with H_2SO_4 to form stable ammonium sulfate that is mainly confined to the fine aerosol fraction (Lestaria et al., 2003; Yao et al., 2003; Metzger et al., 2006). Although the mechanism for the formation of ammonium sulfate is still unclear, the prevailing

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hypothesis is that this aerosol fraction may be the result of cloud formation and evaporation cycles (Pandis et al., 1995). Cloud formation allows the heterogeneous oxidation of SO_2 to form H_2SO_4 in the cloud droplets, which then reacts with NH_3 that might exist in the cloud droplets. The lifetime of sulfate in the atmosphere is about a week, which is much longer than that of SO_2 (Rodhe et al., 1981; Roelofs et al., 1998). Both the distribution and deposition of SO_2 and sulfate are probably influenced by the presence of NH_3 .

In the past two decades, numerous inorganic thermodynamic equilibrium models have been developed to calculate aerosol composition (e.g., ADDEM (Topping et al., 2005a,b), AIM (Clegg and Pitzer, 1992; Clegg et al., 1998a,b), AIM2 (Wexler and Clegg, 2002), EQSAM (Metzger, 2000; Metzger et al., 2002a,b), EQSAM2 (Trebs et al., 2005; Metzger et al., 2006), EQSAM3 (Metzger and Lelieveld, 2007), EQUISOLV (Jacobson et al., 1996), EQUISOLVII (Jacobson, 1999), GFEMN (Ansari and Pandis, 1999), HETV (Makar et al., 2003), ISORROPIA (Nenes et al., 1998; Pilinis et al., 2000), ISORROPIA2 (Fountoukis and Nenes, 2007), MARS-A (Binkowski and Shankar, 1995), MESA (Zaveri et al., 2005a,b), SCAPE (Kim et al., 1993a,b; Kim and Seinfeld, 1995), SCAPE2 (Meng et al., 1995), UHAERO (Amundson et al., 2006)). Some of them were implemented in global models for simulating aerosol distributions (Metzger, 2000; Jacobson, 2001; Metzger et al., 2002b; Liao et al., 2003; Martin et al., 2004; Rodriguez and Dabdub, 2004; Feng and Penner, 2005; Liao and Seinfeld, 2005; Liao et al., 2006; Tsigaridis et al., 2006; Bauer et al., 2007a,b; Luo et al., 2007). In China, both emissions of SO_2 and NH_3 are very large (Streets et al., 2003), SO_4^{2-} and NH_4^+ have been found to be the main components in airborne particles (Aas et al., 2007). The interaction of SO_2 and NH_3 may be especially important to secondary aerosol formation and acid rain in China.

To understand the role of NH_3 in SO_2 transformation and S deposition in China, we simulated the distribution and deposition of SO_2 , SO_4^{2-} with and without NH_3 interactions in this study by an inorganic thermodynamic equilibrium model (ISORROPIA; Nenes et al., 1998) coupled with a three-dimensional chemical transport model (CMAQ; Byun and Ching, 1999).

2. Model description

The Models-3 Community Multi-scale Air Quality modeling system (CMAQ; Byun and Ching, 1999) with an embedded inorganic thermodynamic equilibrium model ISORROPIA (Nenes et al., 1998) was used in

this study. CMAQ is an Eulerian-type model developed by the U.S. Environmental Protection Agency to address tropospheric ozone, acid deposition, visibility, particulate matter and other pollutants issues in the context of a “one atmosphere” perspective. The applied current version of CMAQ is configured with fourth of the carbon-bond mechanisms (CB-IV; Gery et al., 1989), including 36 species and 96 reactions of which 11 are photolytic. The current cloud scheme in CMAQ is derived from the diagnostic cloud model in RADM Version 2.6 (Walcek and Taylor, 1986; Chang et al., 1990; Dennis et al., 1993). Pollutant scavenging is calculated by two methods depending upon whether the pollutant participates in the cloud water chemistry or on the liquid water content. For those pollutants that participate in the cloud chemistry (and provided that the liquid water content is $>0.01 \text{ g m}^{-3}$), the amount of scavenging depends on Henry’s law constants, dissociation constants, and cloud water pH. For pollutants that do not participate in the aqueous chemistry (or for all pollutants when the liquid water content is below 0.01 g m^{-3}), the model uses the Henry’s Law equilibrium equation to calculate ending concentration and deposition amounts (Roselle and Binkowski, 1999). Dry deposition of gases and aerosols is calculated with a resistance-in-series scheme (Wesely and Hicks, 1977). The three-dimensional meteorological fields used in this study are provided by the Fifth-Generation NCAR/Penn State Mesoscale Model (MM5; Dudhia et al., 1998). The three-dimensional meteorological fields for MM5 were obtained from the European Center for Medium-Range Weather Forecasts (ECMWF) analyzed datasets, and were available every 6 h with $1^\circ \times 1^\circ$ resolution.

The aerosol systems of ammonium and sulfate are calculated by the ISORROPIA model (Nenes et al., 1998) which estimates gas–aerosol partitioning based on thermodynamic equilibrium. Aerosol particles are assumed to be internally mixed, meaning that all particles of same size have the same composition. Since the significant portion of aerosol mass is in diameter size much larger than $0.1 \mu\text{m}$, the Kelvin effect is neglected (Bassett and Seinfeld, 1984).

Anthropogenic emissions of SO_2 used in the CMAQ model are obtained from the Chinese Research Academy of Environmental Sciences (CRAES). These data are provided as $1^\circ \times 1^\circ$ grid area sources in addition to 1800 coal-fired power plants point sources. Natural and anthropogenic emissions of NH_3 and other pollutants (including nitrogen oxides (NO_x), carbon monoxide, VOCs etc.) come from the emission inventory on a $1^\circ \times 1^\circ$ grid specially prepared by the Center for Global and Regional Environmental Research at the University of Iowa

(Streets et al., 2003) for the TRACE-P (Transport and Chemical Evolution over the Pacific) and ACE-Asia (Aerosol Characterization Experiment in Asia) projects. VOCs emissions were apportioned appropriately among lumped-carbon categories used in CB-IV.

The model domain for CMAQ is $5427 \times 4455 \text{ km}^2$, with 81 km mesh, centered at (36°N , 105°E). MM5 has 23 vertical layers in the σ_z coordinates system unequally spaced from the ground to $\sim 23 \text{ km}$. About 9 of these layers are concentrated in the lowest 2 km of the atmosphere in order to resolve the planetary boundary layer. The CMAQ has 12 levels, with the lowest 7 layers being the same as those used in MM5.

3. Results and discussion

Air qualities along with precipitation chemistry are monitored at two field sites established by the Integrated Monitoring Program on Acidification of Chinese Terrestrial Systems (IMPACTS, 2004). Monitoring data for 2003 (Aas et al., 2007) are used in this study. Tie Shan Ping (TSP) ($106^\circ 41'\text{E}$, $29^\circ 38'\text{N}$, 450 m a.s.l.) is located about 25 km from the centre of Chongqing city, in the southeast of the Sichuan basin; Cai Jia Tang (CJT) ($112^\circ 26'\text{E}$, $27^\circ 55'\text{N}$, 450 m a.s.l.) is located in an agricultural region 130 km southwest of the Hunan province capital, Changsha. Data on air concentrations of SO_2 , NH_3 , nitric acid (HNO_3) and the water-soluble species (SO_4^{2-} , NH_4^+ , nitrate (NO_3^-), chloride (Cl^-), and sodium (Na^+), potassium (K^+), calcium (Ca^{2+}) and magnesium (Mg^{2+})) in aerosol and precipitation were used in this study to assess the model results. The sampling and analyzing methods of the fields and laboratories at CJT and TSP are described in detail in IMPACTS (2004). The model simulation period covered the whole year of 2003. Simulation results were averaged to be consistent with the monitoring data.

3.1. Monitoring data and correlation analysis

Annual average concentrations of main inorganic components in the air and aerosol observed at two sites

are shown in Table 1. Annual mean SO_2 concentration in 2003 at TSP is higher than at CJT, while NH_3 concentration at TSP is lower than at CJT. SO_2 concentration is higher than NH_3 concentration at both TSP and CJT. The spatial differences of SO_2 and NH_3 concentrations between the two sites might be due to their different emission sources. SO_2 comes primarily from fossil fuel burning activities (e.g., coal consumption), while NH_3 comes generally from agricultural activities (Schlesinger and Hartley, 1992; Zhao and Wang, 1994; ECETOC, 1994; Bouwman et al., 1997). No evident correlation between SO_2 and NH_3 concentrations in the air at the two sampling sites (Fig. 1) also indicated that the two pollutants were from different emission sources.

SO_4^{2-} is the predominant ion in aerosol and precipitation while the content of sea salt is as expected very low (Tables 1 and 2) at these continental sites. The low pH in precipitation (Table 2) indicates that the overall deposition is acidic, and that NH_3 and alkaline dusts are not sufficient to neutralize all acidity of the deposition at TSP and CJT (see also Vogt et al., 2006 and 2007). Observed SO_4^{2-} and NH_4^+ in aerosol and precipitation at CJT and TSP are very strongly correlated. The correlation coefficients between SO_4^{2-} and NH_4^+ are over 0.8 in aerosol and close to 0.9 in precipitation at both sites (Fig. 1). Most of NH_4^+ is probably associated with SO_4^{2-} since NO_3^- concentration is relatively low, amounting to only 20% of the SO_4^{2-} concentration.

3.2. Comparison between simulations and observations

Model simulated S and N compounds in gas and aerosol phases and wet deposition generally agree well with the observations at TSP and CJT (Figs. 2 and 3). Correlation coefficients between simulated and observed values are given in Table 3. It should be mentioned that ISORROPIA is limited to the ammonium-sulfate–nitrate–sodium-chloride–water system. Alkaline dusts (i.e. base cation oxides and carbonates) and organic acids are therefore not included. Trebs et al. (2005) and Metzger et al. (2006) found that mineral cations and organic acids are important for the gas–aerosol

Table 1
Annual average air and aerosol concentrations at TSP and CJT in 2003

Site	Air			Aerosol							
	SO_2 ($\mu\text{g S m}^{-3}$)	HNO_3 ($\mu\text{g N m}^{-3}$)	NH_3 ($\mu\text{g N m}^{-3}$)	SO_4^{2-} ($\mu\text{g S m}^{-3}$)	NO_3^- ($\mu\text{g N m}^{-3}$)	NH_4^+ ($\mu\text{g N m}^{-3}$)	Na^+ ($\mu\text{g m}^{-3}$)	K^+ ($\mu\text{g m}^{-3}$)	Ca^{2+} ($\mu\text{g m}^{-3}$)	Mg^{2+} ($\mu\text{g m}^{-3}$)	Cl^- ($\mu\text{g m}^{-3}$)
TSP	20.2	0.8	2.4	7.92	1.46	4.58	0.95	3.08	3.63	0.33	0.93
CJT	10.8	0.9	3.0	5.46	0.91	3.19	0.31	1.67	1.67	0.15	0.29

Data except HNO_3 and NH_3 are from Aas et al. (2007).

Fig. 1. Correlations of observed S versus N (NH₄⁺ and NH₃) wet deposition, SO₄²⁻ versus NH₄⁺ concentration, and SO₂ versus NH₃ concentration at TSP and CJT. Linear correlation coefficient r , and best-fit parameters to $y=a+bx$.

partitioning of reactive nitrogen compounds, particularly for the semi-volatile NH₃. Therefore, simulated results by using the model of ISORROPIA might pose a potential problem. However, SO₄²⁻ is the dominant anion at TSP and CJT, while the amounts of NH₃ and alkaline cations are not sufficient to neutralize all the acidity. Therefore, the contribution of mineral cations and organic acids to the gas–aerosol partitioning of ammonium and NH₃ might be not important at TSP and CJT.

Simulated SO₄²⁻ levels in air and S wet deposition are lower by about 24 and 31%, and 39 and 45% compared to the observed data at TSP and CJT, respectively (see Table 3). Anthropogenic SO₄²⁻ emissions may be the main reason for the differences between simulations and observations, since all SO₄²⁻ in the model is assumed to be from transformation of SO₂. Particles concentrations in the ambient air are still at relatively high level in China due to insufficient controlling measures, in more

than half of the cities, for example, annual average concentration of particles (PM₁₀) exceeded Grade II (0.1 mg m⁻³) (SEPA, 2004). The atmospheric particles from the direct anthropogenic emissions (e.g. construction activities and coal consumption) account for large fraction of the total atmospheric particles (Yang et al., 2001), and SO₄²⁻ has been found in these particles from the anthropogenic emissions (Xie et al., 2005).

Correlation coefficients between the simulated and monitored data at TSP are somewhat poorer than at CJT.

Table 2

Annual volume weighted concentrations of main ions in precipitation in 2003 (Aas et al., 2007)

Site	pH	Ca ²⁺ μEq L ⁻¹	Mg ²⁺ μEq L ⁻¹	Na ⁺ μEq L ⁻¹	K ⁺ μEq L ⁻¹	NH ₄ ⁺ μEq L ⁻¹	SO ₄ ²⁻ μEq L ⁻¹	NO ₃ ⁻ μEq L ⁻¹	Cl ⁻ μEq L ⁻¹
TSP	4.1	58	9	3	8	76	184	35	11
CJT	4.3	60	10	7	10	112	155	60	11

Fig. 2. Model-observation comparisons of SO_2 , NH_3 , SO_4^{2-} and NH_4^+ at TSP and CJT, statistics parameters are same as in Fig. 1.

Fig. 3. Model-observation comparisons of S and N wet deposition at TSP and CJT, statistics parameters are same as in Fig. 1.

For example, the correlation coefficient for ammonia is only 0.33 at TSP while at CJT it is 0.56. As mentioned above, TSP is located in the vicinity of a major city. Pollution loading at this site is therefore caused by a large number of emission sources that are difficult to estimate, especially for NH_3 . This uncertainty in estimation of NH_3 at TSP is also reflected in a poor simulation of ammonium and its deposition.

3.3. Distribution of S and N species

Simulated monthly mean concentrations and depositions of S species (SO_2 and SO_4^{2-}) and N species (NH_3 and NH_4^+) in July 2003 are depicted in Fig. 4. Regions with high SO_2 concentration (up to $20 \mu\text{g S m}^{-3}$) are located in and around major cities in northern (Beijing), eastern (Shanghai) and southwestern China (Chongqing).

Table 3
Correlations between simulated and observed values

	SO_2 ($\mu\text{g S m}^{-3}$)		SO_4^{2-} ($\mu\text{g S m}^{-3}$)		S wet deposition ($\text{mg S m}^{-2} \text{yr}^{-1}$)		NH_3 $\mu\text{g N m}^{-3}$		NH_4^+ ($\mu\text{g N m}^{-3}$)		N wet deposition ($\text{mg N m}^{-2} \text{yr}^{-1}$)	
	TSP	CJT	TSP	CJT	TSP	CJT	TSP	CJT	TSP	CJT	TSP	CJT
Observation	20.16	10.77	7.92	5.46	3087	2485	2.45	3.02	4.57	3.19	1106	1513
Simulation	23.14	9.32	6.13	3.62	1884	1377	2.83	3.14	3.68	3.37	1536	1395
R	0.74	0.76	0.44	0.56	0.56	0.63	0.33	0.56	0.36	0.53	0.48	0.67
SD	6.05	3.13	2.12	1.23	28.9	22.8	0.77	1.67	0.89	1.22	17.6	22.8
P	<0.0001	<0.0001	0.00136	<0.0001	<0.0001	<0.0001	0.12168	0.00092	0.01637	<0.0001	0.00705	<0.0001

R is correlation coefficient; SD is standard deviations; P is confidence interval.

Fig. 4. Distribution of SO_2 , NH_3 , SO_4^{2-} and NH_4^+ and their deposition in July 2003.

SO_4^{2-} is more widely distributed compared with SO_2 , due to its longer residual lifetime in the atmosphere. According to the simulations, two regions with high levels of SO_4^{2-} are found: one is in northern China (including Beijing, Hebei and Shanxi) and the other one around Shanghai. Distribution of S deposition is the combined effects of SO_2 and SO_4^{2-} pollution levels along with meteorological factors. Regions with high S deposition are located in northern and eastern China (Fig. 4).

Due to different type of sources, the distribution of NH_3 is rather different from that of SO_2 . Regions with high NH_3 concentration are mainly located in eastern China,

especially in Jiangsu province, where NH_3 concentration is up to $7 \mu\text{g N m}^{-3}$. The distribution of NH_4^+ is very similar to that of SO_4^{2-} , suggesting the important role of NH_3 in governing sulfate levels. The correlation coefficients between simulated NH_4^+ and SO_4^{2-} values are all greater than 0.95 at TSP and CJT, which are consistent with their strong correlations of the observed data (Fig. 1).

3.4. The role of NH_3

In order to study the effect of NH_3 in SO_2 transformation and S deposition, we omitted the NH_3 emissions

in sensitivity experiment. Simulation period is in July 2003. The simulated SO_2 and SO_4^{2-} levels and S deposition with and without NH_3 are shown in Fig. 5. Without NH_3 emissions, the monthly average SO_4^{2-} concentration decreases by 10–15%, while monthly average SO_2 concentration increases by 10–60% over polluted regions. Likewise, S deposition increases by 10–30% over polluted areas due to decreased long-range S transportation.

The effect of NH_3 is likely overestimated since all NH_4^+ is assumed to be bound to SO_4^{2-} , while association

to NO_3^- will surely consume part of the NH_4^+ . Additional uncertainties lie in the role of alkaline dusts in north-western China, where owns several extensive deserts (e.g. Tengger, Taklimakan and Gobi desert etc.). The concentration of mineral dusts in the atmosphere is high in these regions, especially during the dry spring season when wind is strong and sandstorms occur frequently. High mineral dusts in northwestern China will affect the phase partitioning and ion balance of ammonium, so the roles of NH_3 in sulfur transformation and deposition could thereby be overestimated in northwestern China.

Fig. 5. Differences of SO_2 , SO_4^{2-} concentration and S deposition with and without NH_3 interaction in July 2003 (A, C, E represent the difference of SO_2 , SO_4^{2-} and S deposition with and without NH_3 emission; B, D, F represent their rate of change).

4. Conclusions

SO_4^{2-} is the predominant anion in aerosol and precipitation at TSP and CJT due to large SO_2 emission. The amounts of NH_3 and alkaline dusts (i.e. mineral oxides and carbonates) were not sufficient to neutralize all the acidity. Observed SO_4^{2-} and NH_4^+ in aerosol and precipitation at TSP and CJT were strongly correlated. In addition, the concentration of SO_4^{2-} in the atmosphere is much higher than NO_3^- . Most of the NH_4^+ was therefore probably bound to SO_4^{2-} at TSP and CJT.

Model simulations show that SO_4^{2-} concentration increased by 10–15% while SO_2 concentration decreased by 10–60% over the most polluted regions due to the role of NH_3 . S deposition thereby decreased by 10–30% over polluted areas due to enhanced long-range S transportation. Therefore the role of NH_3 in SO_2 transformation and S deposition could not be neglected in China.

Acknowledgements

This work was financially supported by Major Project of Chinese National Programs for Fundamental Research and Development (973 Program) (Project number: 2005CB422206). We thank Prof. Yujing Mu for helpful suggestions during preparation of the manuscript. We also thank Prof. Rolf D. Vogt at University of Oslo for his insightful discussions.

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