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Neutralization of soil aerosol and its impact on the distribution of acid rain over east Asia: Observations and model results

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[1] A comprehensive Air Quality Prediction Modeling System is applied to simulate the pH values in precipitation and to investigate neutralization by soil aerosols and their influence on the distribution of acid rain over east Asia. A modified deflation module is designed to provide explicit information on the soil aerosol loading. Numerical simulation was performed for 1 year, from 15 December 1998 to 31 December 1999. Wet deposition monitoring data at 17 sites of the Acid Deposition Monitoring Network in east Asia in addition to State Environmental Protection Agency data were used to evaluate the model, and a reasonable agreement was obtained. Observed evidence clearly shows that in northern China acid deposition is heavily influenced and buffered by natural soil dust from desert and semiarid areas. The observed mean rainwater pH value in northern China is the highest, between 6.0 and 7.2, while in southern China, where many areas severely impacted by acid precipitation are located, the pH value is much lower, between 3.5 and 5. In Japan the mean pH value is 4.7, significantly higher than that in southern China, while in South Korea the pH value is intermediate between those in northern China and Japan. The model is capable of reproducing this geographical distribution of rainwater pH over east Asia. The simulation results for 1999 demonstrated strong neutralization of precipitation by soil aerosols over northeast Asia, and the distribution pattern of acid rain was also altered. The annual mean pH values in northern China and Korea show a remarkable increase of 0.8–2.5, while the increase in mean pH values over southern China and Japan are less than 0.1. The neutralization effects vary by season, with the greatest influence in spring, when pH values increased by 0.1–0.4 in Japan, 0.5–1.5 in Korea, and more than 2 in northern China. *INDEX TERMS:* 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0320 Atmospheric Composition and Structure: Cloud physics and chemistry; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0330 Atmospheric Composition and Structure: Geochemical cycles; 5704 Planetology: Fluid Planets: Atmospheres—composition and chemistry; *KEYWORDS:* Asian dust, acid deposition, ph value, numerical simulation, neutralization

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1. Introduction

[2] Acid deposition is of serious environmental concern in east Asia. High-sulfur fuels widely used in China result in high sulfur levels in rainwater. Many long range transport models have been used during the last decade to assess air pollution and acid deposition and to develop effective emission control strategies for east Asia [*Arndt et al.*, 1998; *Chang et al.*, 2000; *Huang et al.*, 1995; *Ichikawa and Fujita*, 1995; *Kitada et al.*, 1992; *Kotamarthi and Carmichael*, 1990; *Maeda et al.*, 2001; *T. J. Wang et al.*, 2000; *Wang et al.*, 1996; *Xiao et al.*, 1997]. These models are used to provide information on the transport and fate of emissions from various locations in east Asia in support of science and policy applications. However, these studies all focused on deposition and transport of sulfur, and not on calculating the pH value of precipitation in spite of the environmental importance of rainwater acidity.

[3] Field observations indicate that acid precipitation often occurs in the southern part of China, even though emissions of the precursors are stronger in the north [*Wang and Wang*, 1995]. In northern China such high levels of strong acids in precipitation have not been widely detected and the pH value of precipitation still remains high. *Wang and Wang* [1995] explained the geographical distribution of acid precipitation in China and pointed out the importance of the alkaline ion content in soil and its buffering capacity

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in northern China. Thus, in northern China the acidity of rainwater is heavily influenced and modified by natural soil dust from desert and semiarid areas [*Larssen and Carmichael*, 2000]. As a high concentration of alkaline dust is an important feature of the atmosphere in large parts of China, base ion deposition such as that of Ca^{2+} must be taken into account when simulating the pH value of precipitation.

[4] In order to provide useful inputs for decision-making at national and regional levels, the Acid Deposition Monitoring Network in east Asia (EANET) was set up in 1998 by ten countries, namely, China, Indonesia, Japan, Malaysia, Mongolia, the Philippines, the Republic of Korea, Russia, Thailand, and Vietnam. The first observational data from EANET have been released showing the regional distribution of rainwater pH and ion composition in 1998–1999 [*Suzuki*, 2000]. In addition, relevant emission data sets are available for these years through the activity of the Aerosol Characterization Experiment in the Asian Pacific region (ACE-Asia) (Center for Global and Regional Environmental Research (CGRER), Emission data for ACE-Asia and TRACE-P experiments in 2001, available at http://www.cgrer.uiowa.edu, 2001)(hereinafter referred to as CGRER, 2001).

[5] The purpose of this research is to perform the first yearlong, quantitative simulation of rainwater pH in east Asia and to discuss the influence of alkaline soil aerosol on the distribution of rainwater acidity over east Asia. This soil aerosol, or ''Kosa'', is lifted from Asian deserts and the Loess plateau, and then carried by the prevailing wind over northern China. To deal with the complexity of the formation of acid rain, we employ a comprehensive Air Quality Prediction Modeling System (AQPMS) coupled with a modified dust deflation module to determine the principal factors that control the chemical composition of precipitation.

2. Model Description

[6] The AQPMS has been developed at the Institute of Atmospheric Physics, Chinese Academy of Science, and used for scientific studies and policy evaluation in east Asia since 1995 [*Huang et al.*, 1995; *Huang and Wang*, 1998; *Wang et al.*, 1996, 1997; *Maeda et al.*, 2001; *Zheng et al.*, 2000]. As a three-dimensional Eulerian numerical model, it simulates the time-varying three-dimensional distributions of trace gases and yellow-sand particles, as well as the temporal and spatial distribution of the dry and wet deposition of atmospheric trace species. A new deflation module for yellow sand is included in the model to provide dust emissions [*Z. Wang et al.*, 2000]. The current version of AQPMS includes 34 gas-phase species, 11 ions in rainwater and cloud water, and is capable of calculating pH values by dealing with all the major processes such as emission, advection, diffusion, deposition, gas-phase and aqueous-phase chemistry in detail. The model has previously been used to simulate the rainwater pH for the month of April 1995 and the results were found to be in reasonable agreement with observations in Japan [*Terada et al.*, 2001].

2.1. Physical and Chemical Processes

2.1.1. Emissions

[7] The model uses emissions of SO_2, NO_X, CO, and VOC, derived from emission inventories developed in support of ACE-Asia and Transport and Chemical Evolution over the Pacific experiment for 2000 with $1^\circ \times 1^\circ$ resolution (CGRER, 2001). Since the dataset does not include NH_3 emissions, we use the relevant data from The Global Emissions Inventory Activity [*Bouwman et al.*, 1997]. The total annual emissions within the model domain for each species are listed in Table 1.

[8] In order to simulate the spatial and temporal distribution of soil aerosol in the atmosphere, the loading intensity is calculated as a deflation flux with the deflation module [*Z. Wang et al.*, 2000]. The module has been designed after detailed analysis of the meteorological conditions, landform, and climatology from daily weather reports at about 300 local weather stations in northern China. The deflation module is separated into two parts: first, it predicts whether mobilization occurs, and then it calculates the dust loading if the mobilization condition is satisfied. The three predictors used for determining the mobilization condition are the friction velocity threshold, the surface humidity threshold and the predominant weather conditions. *Z. Wang et al.* [2000] demonstrated that the best criterion for predicting the occurrence of dust deflation and the emission intensity is to use all three predictors together in the deflation module, which leads to a minimum in the error ratio of falsely predicted events and missed events. In the northern part of China, widely distributed loess lands and deserts release millions of tons of dust into the atmosphere every year. Most dust storms emanate not only from natural deserts, but also from territory that has more recently turned to desert as a result of over-use and destruction of vegetation cover. Thus the potential source areas are divided into several distinctive types including desert, the Loess Plateau, grassland, cultivated land and deciduous forest. The particles of soil aerosol are divided into nine size bins from 0.5 μm to 90 μm [*Z. Wang et al.*, 2000]. The size distribution and weight factor of the dust load are assumed to change with season and location for each land type.

2.1.2. Advection and Diffusion

[9] The model solves a set of conservation equations for chemical species in spherical and terrain-following coordinates [*Wang et al.*, 1996; *Z. Wang et al.*, 2000]. A simplified, mass conservative advection algorithm is used to deal with the advection and diffusion processes [*Walcek and Aleksic*, 1998].

2.1.3. Dry Deposition

[10] To handle the dry deposition of gaseous species, the scheme by *Padro et al.* [1991] is adopted for AQPMS. The size-segregated particle dry deposition scheme designed by *Zhang et al.* [2001] is adopted here to estimate the dry deposition of soil particles. Gravitational setting is also included.

2.1.4. Gas-Phase Chemistry

[11] The gas-phase chemical reaction scheme used in the present work is a slightly modified version of the carbon-bond mechanism IV (CBM-IV) [*Gery et al.*, 1989; *Wang et al.*, 1996]. The modified mechanism includes 34 species and 86 photochemical, inorganic and organic reactions. 11 active species are predicted from the full equation of mass conservation including advection and diffusion, while reactive agents like radicals are calculated by the pseudo steady state assumption.

Table 1. Emission Data Sets Used in the Model

Species	Source	Base year	Total, Tg/yr
SO_2	CGRER (2001)	2000	22.4
NO_X	CGRER (2001)	2000	13.5
CO	CGRER (2001)	2000	94.0
NMVOC[a]	CGRER (2001)	2000	19.6
NH_3	*Bouwman et al.* [1997]	1990	11.6
Soil dust	*Z. Wang et al.* [2000]	1999	~100

[a] NMVOC stands for nonmethane volatile organic compounds.

2.1.5. Aqueous-Phase Chemistry and Scavenging

[12] Cloud and rainwater composition is computed with a 1-D cloud physical and chemical model modified from *Chang et al.* [1987]. The following balance is assumed to be maintained at all times:

$$[H^+] + [NH_4^+] + 2([Ca^{2+}] + [Mg^{2+}] + [Mn^{2+}]) + 3[Fe^{3+}] = [HCOO^-] + [HSO_3^-] + [OH^-] + [HCO_3^-] + [NO_3^-] + 2([SO_4^{2-}] + [CO_3^{2-}] + [SO_3^{2-}]) + [HSO_4^{2-}]$$

[13] The concentration of each ion is determined from Henry's law, the dissociation equilibrium and liquid phase reactions. Since these processes are strongly dependent on the H^+ ion concentration, $[H^+]$, concentrations of these ions must be calculated by an iterative method. SO_2 is oxidized by H_2O_2, O_3, and hydroperoxides. The neutralization capacity of soil aerosol is largely related to the calcite ($CaCO_3$) content of the soil. Here soil aerosol is assumed to contain 10 wt% of Ca^{2+}, 3 wt% of Mg^{2+}, 0.5 wt% of Mn^{2+} and Fe^{3+}. When dissolved in water droplets, soil aerosol neutralizes acid rain by reactions such as

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + CO_2 + H_2O$$
$$CaCO_3 + HNO_3 \rightarrow Ca^{2+} + NO_3^- + CO_2 + H_2O$$

[14] Below-cloud scavenging is considered in the 1-D cloud model to treat aerosol removal from the atmosphere between cloud-base and the ground by precipitation. The efficiency of this kind of wet removal is described by the scavenging ratio [*Z. Wang et al.*, 2000].

2.2. Model Setup and Meteorological Input

[15] The model domain covers east Asia from 16°N to 60°N, and from 72°E to 146°E with horizontal grids at 1° × 1° resolution (Figure 1). Vertically, the model uses an 18-layer terrain-following coordinate system, with the top of the model at 15 km above sea level. The vertical-grid spacing is increased gradually from 50 m at the surface to 2000 m at the top. The boundary conditions are very important and have been carefully considered in the model. In winter and spring, Asian dust can frequently travel with a speed of 100 km/h or more in the middle and upper troposphere. If heavy dust emissions occurred outside the model domain, they would be expected to have a significant impact on the central part of the domain in about one and half days. The boundaries have therefore been selected to minimize this problem. According to observations, most dust episodes in east Asia occur within the selected domain [*Z. Wang et al.*, 2000] and we expect the inflow of dust and acid aerosols from outside this domain to be small. The boundary conditions are set such that tracer species may be transported out of but not into the model domain. The bottom surface is assumed to be an absorbing boundary while the top boundary is closed. Even so in some special weather conditions, the boundary conditions may still cause some errors in the model results. The best way to solve this problem would be to use a global transport model to provide the boundary conditions for our model.

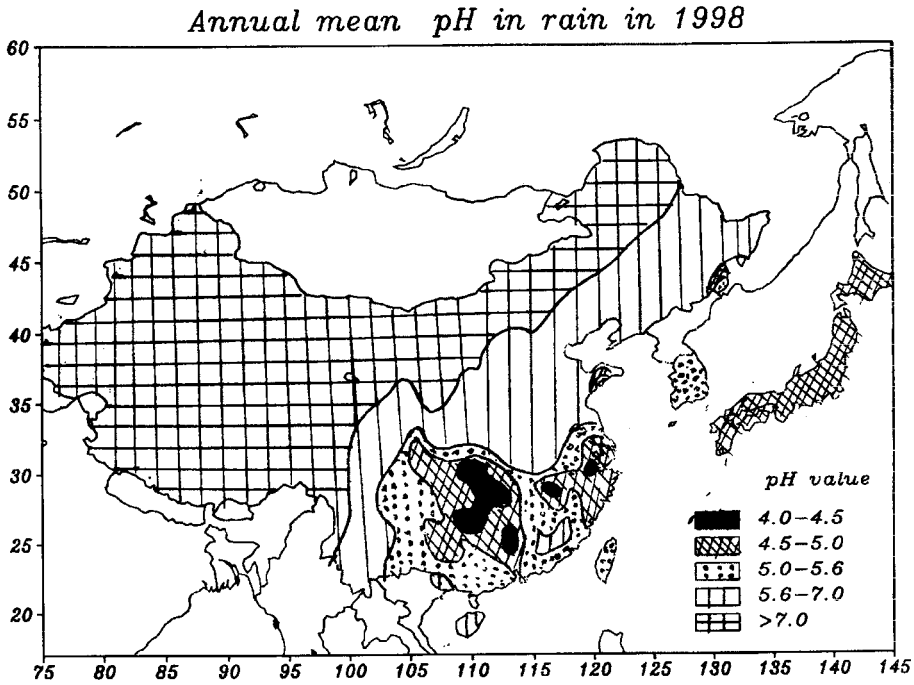

Figure 1. Annual mean pH value of precipitation over east Asia [*SEPA*, 1999].

Table 2. Locations of 17 Observation Sites of the Acid Deposition Monitoring Network in East Asia

Site	Group	Latitude	Longitude
1, Nanshan	S. China	29.55 °N	106.63 °E
2, Weishuiyuan	N. China	34.35 °N	108.85 °E
3, Dabaogou	N. China	33.90 °N	108.85 °E
4, Xiaoping	S. China	24.70 °N	118.03 °E
5, Zhuhai	S. China	22.20 °N	113.50 °E
6, Rishiri	Japan	45.10 °N	141.25 °E
7, Tappi	Japan	41.25 °N	141.35 °E
8, Sado	Japan	38.20 °N	138.40 °E
9, Happo	Japan	36.70 °N	137.80 °E
10, Oki	Japan	36.30 °N	133.23 °E
11, Ashizuri	Japan	32.72 °N	132.96 °E
12, Ogasawara	Ocean	27.09 °N	142.21 °E
13, Kunigami	Ocean	26.80 °N	128.22 °E
14, Lake Ijira	Japan	35.58 °N	136.70 °E
15, Lake Banryu	Japan	34.68 °N	131.70 °E
16, Kanghwa	Korea	37.61 °N	126.35 °E
17, Kosan	Korea	33.30 °N	126.18 °E

[16] Numerical simulation was performed for the year of 1999, from 15 December 1998 to 31 December 1999, with a 10-min time step. A 15-day "spin-up" beginning on 15 December 1998 was used to minimize the influence of the initial conditions. Meteorological fields for 1999 were obtained from the National Centers for Environmental Prediction (NCEP)- Aviation (AVN) with a spatial resolution of $1^\circ \times 1^\circ$ at 6-hour intervals. The relevant meteorological information includes surface winds, temperature and relative humidity, potential height, vertical velocity, cloud base, top, and water content and precipitation amount. Interpolation from pressure coordinates to terrain-following coordinates is performed using a simple spline interpolation method. Since the topography is very complex in northwest China, an objective analysis was made again after the spline interpolation.

[17] The precipitation distribution has significant influence on the simulation of acid rain. Here we obtain the precipitation amount every 6 hours from the NCEP-AVN forecast products at $1^\circ \times 1^\circ$, correcting them by comparing with the NCEP reanalysis datasets at $1.875^\circ \times 1.875^\circ$ and with observed precipitation data from China Meteorological Bureau and World Meteorological Organization stations. Comparing precipitation amounts used in the model with observed data from EANET, the correlation coefficients of monthly and annual precipitation amount are 0.89 and 0.93 (figure not shown), respectively, clearly showing that this kind of objective method can lead to good model reproduction of the observed precipitation amounts.

3. Observational Evidence

[18] East Asia has a varied climate. Northwest China has an arid desert climate with cold winters, and precipitation is distributed evenly throughout the year. Southwest China is mountainous with summer temperatures moderated by altitude, while winters are mild with little rain. Summers in southern China are hot and humid with heavy precipitation between April and September. Northern China and Korea have a continental climate with dry cold winters and hot humid summers. There is a rapid transition from winter to summer conditions between April and early May with an similar reversal in late October. Due to the Asian monsoon, the cold winter winds come from Manchuria and Siberia while in summer warm moist air comes from the Pacific Ocean. The most humid months are between June and September with at least one typhoon per year. The climate of Japan is of marine or oceanic type influenced by the Asian monsoon. Two periods of heavy rain occur, the Baiu rain in June and the other in September. Between these two periods it is hot and humid with less precipitation except for occasional typhoons from the end of summer until October.

[19] Acid rain in China is a typical sulfate kind characterized by higher concentrations of SO_4^{2-}, Ca^{2+} and NH_4^+, and with lower concentrations of NO_3^- [*Wang and Wang*, 1995]. On a national basis, the percentage of SO_4^{2-} and Ca^{2+} in precipitation is 32% and 21% of total ions equivalence [*T. J. Wang et al.*, 2000], suggesting that soil aerosol plays an important role as a major source of Ca^{2+}. Owing to the differences in soil acidity, the regions with and without acid rain are quite distinct. In the mid 1980s, the annual pH = 5.6 isopleth ran roughly between the Yangtze River and Huanghe River in the east and parallel to the Yangtze River in central China (30°N). In 1993–1995, the isopleth moved northward, reaching northern China (40°N) in the east [*Wang and Wang*, 1995]. Figure 1 shows the regional distribution of annual rainwater pH in 1998, compiled from data by the *State Environmental Protection Agency (SEPA)* [1999] for mainland China, EANET for Japan and South Korea from *Suzuki* [2000], and the Central Weather Bureau of Taiwan (CWB) (Data sets of annual average rain pH at various stations in Taiwan, available at http://www.cwb.gov.tw, 2000) for Taiwan. From this data, the mean rainwater pH in northern China is higher than 5.6, and in many areas more than 7. Southern China is still facing serious acid rain problems, with annual mean pH between 4.0 and 5.0. The pH in South Korea is between 5 and 5.6, higher than that in Japan, where it is between 4.5 and 5.0. It is interesting to note that the pH = 5.6 isopleth in China moved back toward the south in 1998, parallel to the Yangtze River in eastern China. In addition, regions with an annual mean pH $\leq$ 4.5 include eastern Sichuan province, Hunan province, Jiangxi province, northern Guangxi and also parts of the Hangzhou-Shanghai region in eastern China. In contrast, the area severely affected by acid precipitation covered much of Sichuan in 1993. The Chinese government has issued many countermeasures against acid rain since 1995 and SO_2 emissions have begun to decrease in China since then. It looks as though these countermeasures have contributed to the increase in the pH of rainwater. On the other hand, an increasing number of dust storms have been reported in northern China since 1998 [*Wilkening et al.*, 2000], which may also play an important role in the increasing pH value.

[20] During the preparatory phase for EANET from April 1998 to December 1999, wet deposition monitoring started at 38 sites, including 16 remote, 8 rural and 14 urban sites [*Suzuki*, 2000]. In order to briefly characterize acid deposition on a regional scale, 17 rural and remote sites in east Asia are selected covering five typical areas, i.e., southern China, northern China, Korea, Japan, and the Pacific Ocean/East China Sea (Table 2). The observed monthly mean pH value, and Ca^{2+}, SO_4^{2-}, NO_3^- and NH_4^+ concentrations in rainwater in these five areas are shown in Figure 2. The differences of pH values in northern and southern China are

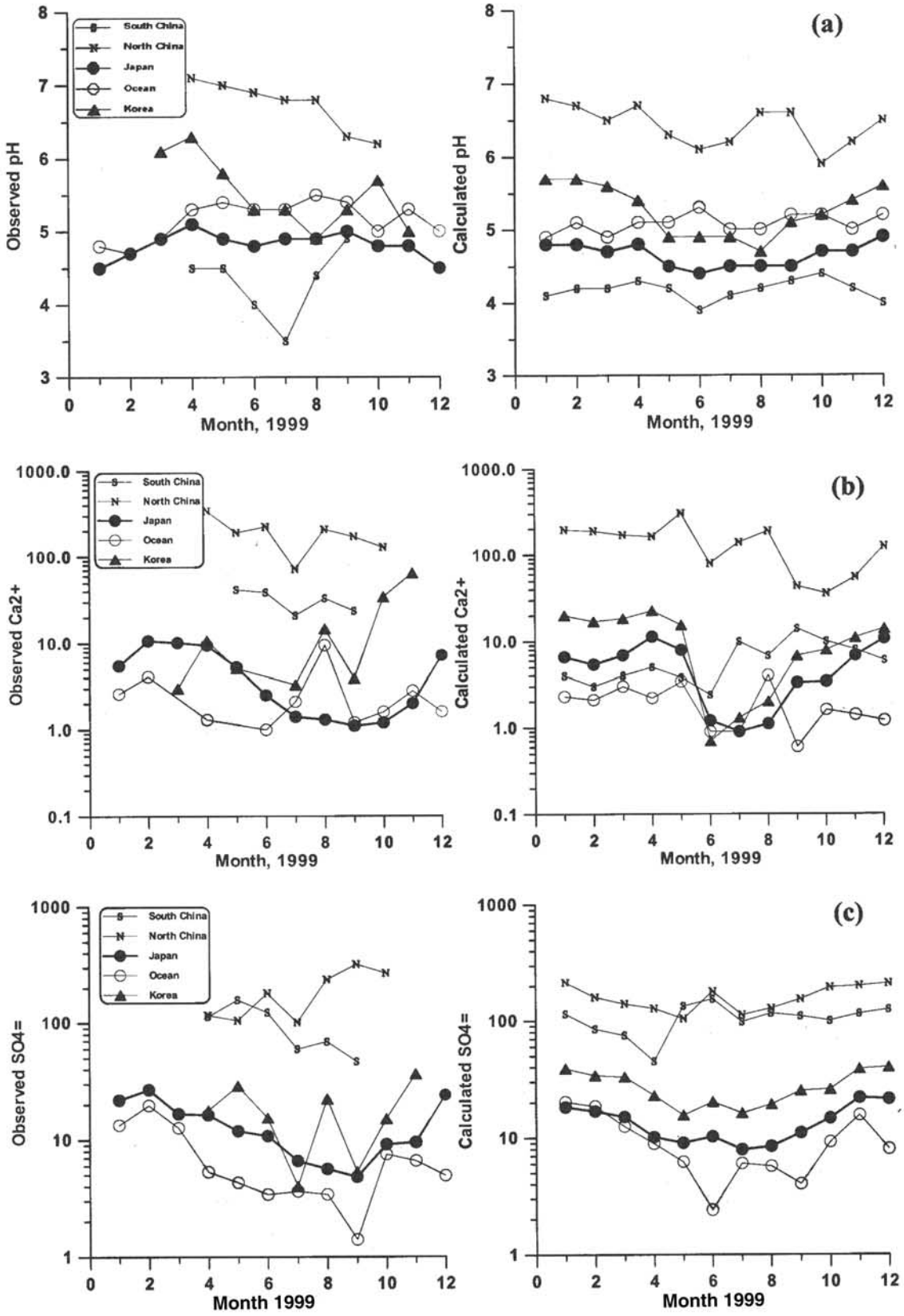

Figure 2. Observed and calculated monthly mean (a) pH value, (b) nss-Ca^{2+}, (c) nss-SO_4^{2-}, (d) NO_3^-, and (e) NH_4^+ in rainwater at various areas.

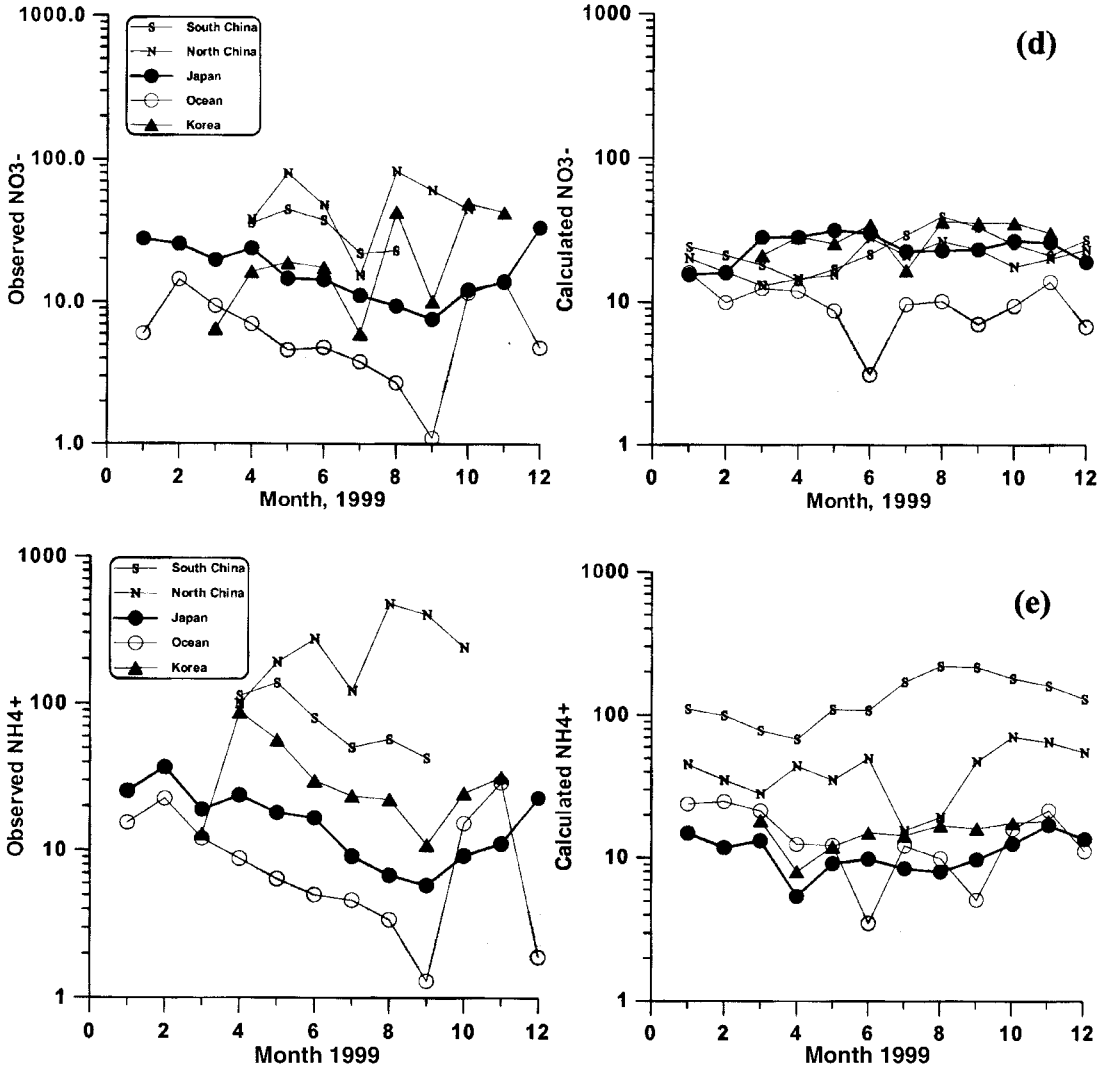

Figure 2. (continued)

quite distinct (Figure 2a). The monthly mean pH value in northern China is the highest, between 6 and 7.2, while in southern China, the pH value is the lowest, between 3.5 and 5. In Japan the mean pH value is 4.7 with the lowest being 4.4, significantly higher than the area severely affected by acid rain in China but much less than in northern China. The pH in South Korea is higher than in Japan but lower than in northern China, and shows a peak in April with pH value of 6.3. This coincides with the peak in transport of Kosa, and indicates the importance of the transport of soil aerosol from the continent in spring. Over the Pacific Ocean, the pH shows a similar seasonal tendency as seen in Japan, but with slightly higher values. Other than pH, the ion concentrations in rainwater in China are in general much higher than those in other countries in east Asia. The concentration of nss-Ca^{2+} in rainwater in Japan shows a seasonal cycle, with large values in winter and spring and low values in summer (Figure 2b). SO_4^{2-} and NO_3^- also show the same seasonal variation. In China, the concentration of nss-Ca^{2+} in rain is always high, about 5–10 times higher than other countries, especially for northern China with values more than 100 μeql^{-1}. The high concentration of SO_4^{2-} in northern China (Figure 2c) is caused by the high SO_2 emissions. This suggests that if there were no calcite ($CaCO_3$) supplied from the soil aerosol, acid rain would be widely distributed in northern China.

4. Results and Discussion

4.1. Model Validation

[21] There are significant differences in rainwater pH and ion concentrations among the five groups selected. For example, the concentration of ions in rainwater in China are much higher than in other regions. The seasonal changes in the calculated monthly mean pH, Ca^{2+}, SO_4^{2-}, NO_3^- and NH_4^+ in the five areas are compared with observed values (Figure 2). The simulated distribution patterns generally agree well with the observations. In each area, despite the difficulty of predicting absolute values of rain pH and ion concentrations because of the

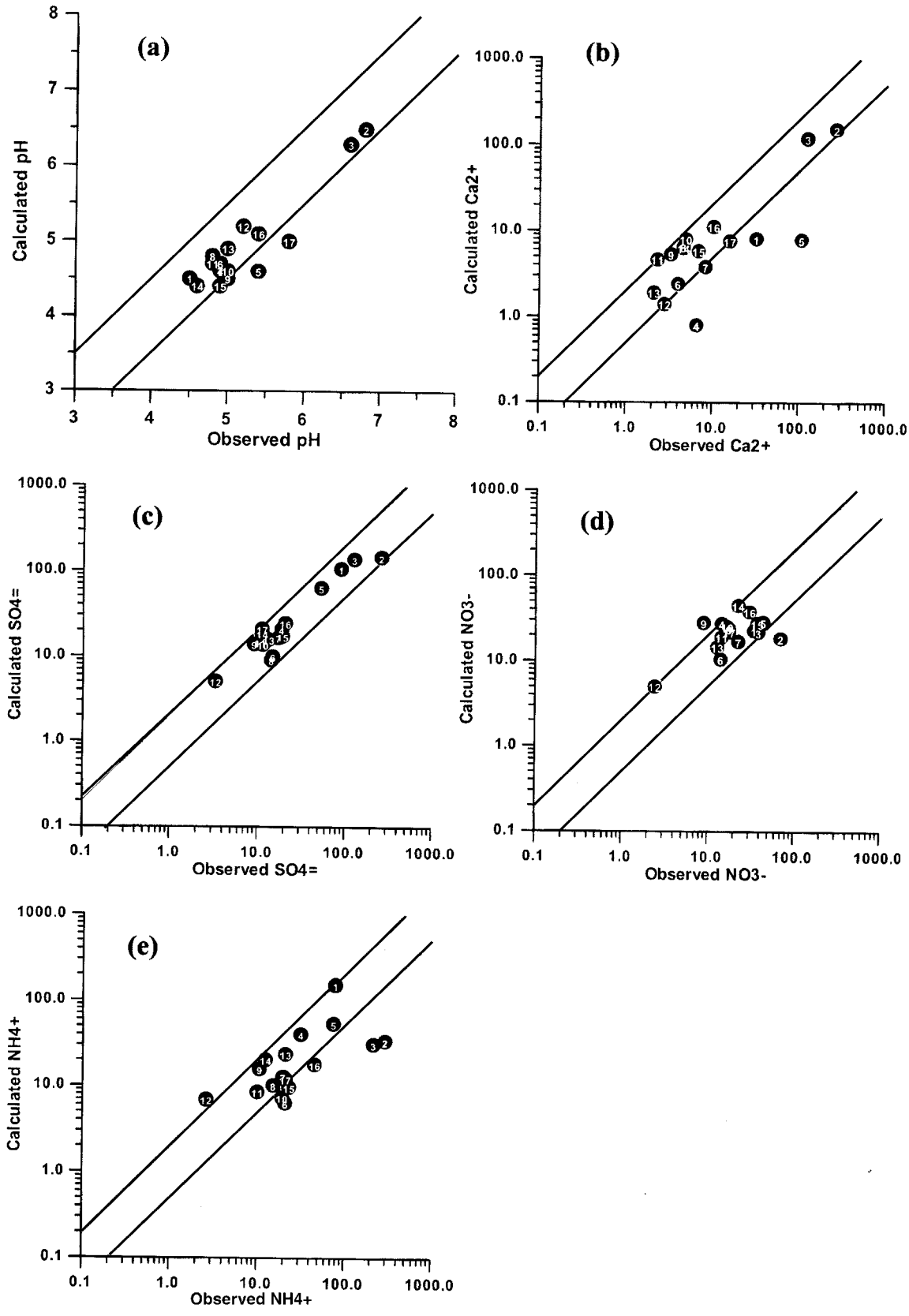

Figure 3. Comparison of calculated annual mean (a) pH value, (b) Ca^{2+}, (c) SO_4^{2-}, (d) NO_3^-, and (e) NH_4^+ concentration (μeq L^{-1}) in precipitation with observed data. Numbers in circles represent the observation sites shown in Table 2.

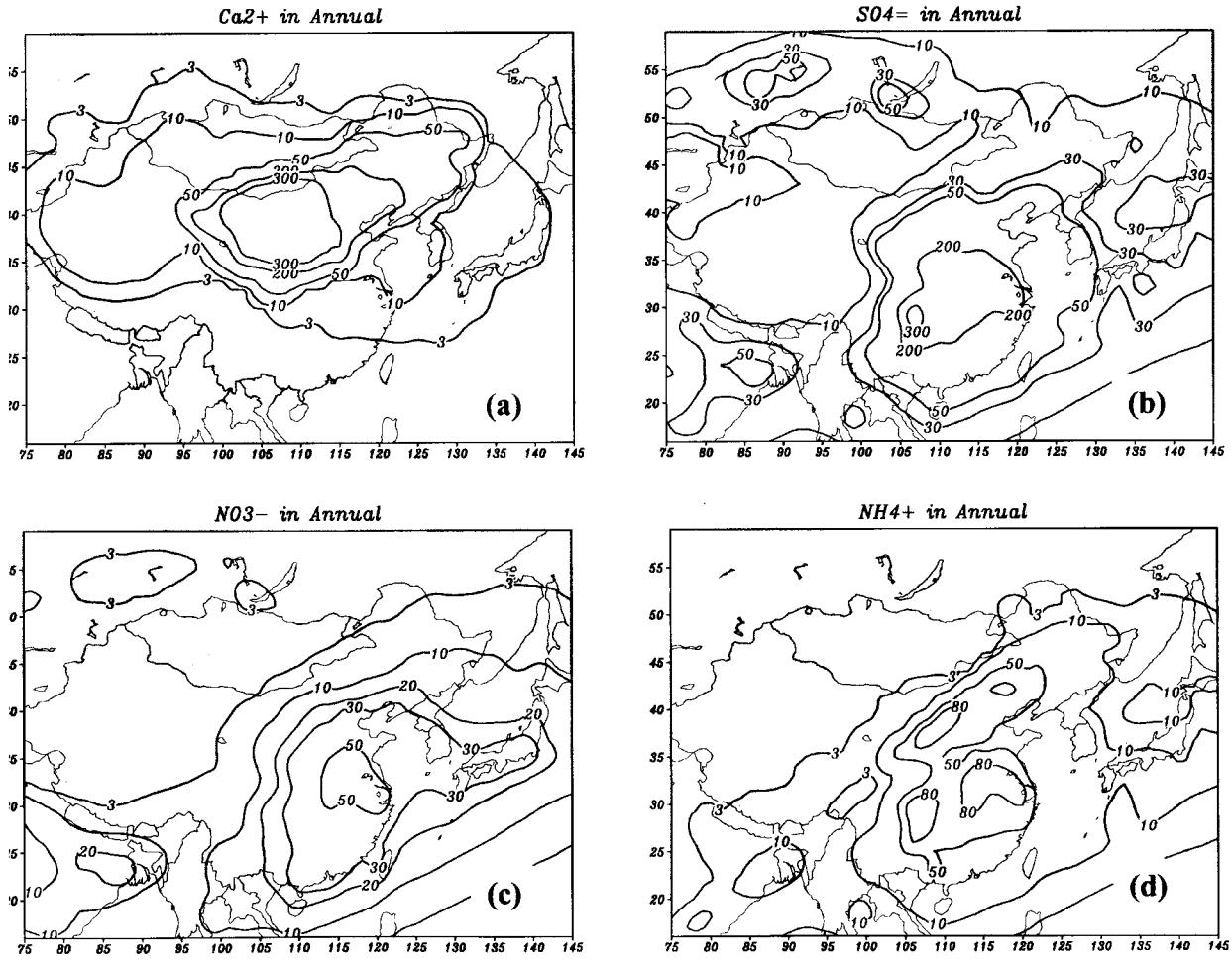

Figure 4. Annual mean (a) Ca^{2+}, (b) SO_4^{2-}, (c) NO_3^-, and (d) NH_4^+ levels (μeq L^{-1}) in precipitation in 1999 from the model. Lines indicate a factor of two.

influence of the amount of precipitation, the seasonal variation of pH in rainwater is predicted reasonably well (Figure 2a). The simulated pH is highest in northern China, then in Korea and Japan, and lowest in southern China, agreeing very well with observations. The simulated concentrations of Ca^{2+}, SO_4^{2-} and NO_3^- in rainwater, show similar good agreement, although it should be emphasized that the y axis in the figure has a log scale. For NH_4^+, the error is larger than that for other ions, suggesting that the NH_3 emission inventory has a greater degree of uncertainty than that of other sources. Particularly, a large underestimate of NH_3 emissions in northern China is noted. There is a clear seasonal cycle in ion concentrations in Japan, with the lowest values in summer and the highest in winter and spring, and the model reproduces this cycle well. In northern China, Ca^{2+} concentrations are greater than 100 μeq L^{-1} (Figure 2b) and agree well with observations. Ca^{2+} is underestimated in southern China, suggesting that there are other contributions to Ca^{2+} concentrations in rainwater.

[22] Scatterplots of the calculated and observed annual pH, Ca^{2+}, SO_4^{2-}, NO_3^- and NH_4^+ concentration in rainwater at 17 selected sites are shown in Figure 3. They show that there is a reasonably good correlation between the observed and simulated values, with most points within a factor of two. There are some exceptions for the underestimated Ca^{2+} in southern China (station 1,4,5) as discussed above (Figure 3b). This is partly because we only consider soil aerosols, but in southern China industrial aerosols are the dominant source of Ca^{2+}. Including industrial aerosol in the model would improve the prediction. It can be concluded, however, that the present model reproduces well the chemical composition of precipitation in east Asia.

4.2. Spatial Distributions of Rainwater pH and Ions

[23] The predicted spatial distribution of annual mean Ca^{2+}, SO_4^{2-}, NO_3^- and NH_4^+ levels in precipitation in 1999 are shown in Figure 4. High concentrations of Ca^{2+} over 200 μeql^{-1} in rainwater are distributed in northern China, and especially in the Loess Plateau and desert regions (Figure 4a), where the concentration exceeds 300 μeql^{-1}. This feature is emphasized as we consider only soil aerosols. Concentrations of SO_4^{2-} in rainwater greater than 50 μeql^{-1} are found over most of China and South Korea (Figure 4b). Concentrations greater than 200 μeq L^{-1} are predicted in the Yangtze River valley, including the Sichuan, Hubei, and Anhui provinces. Large values of this kind are

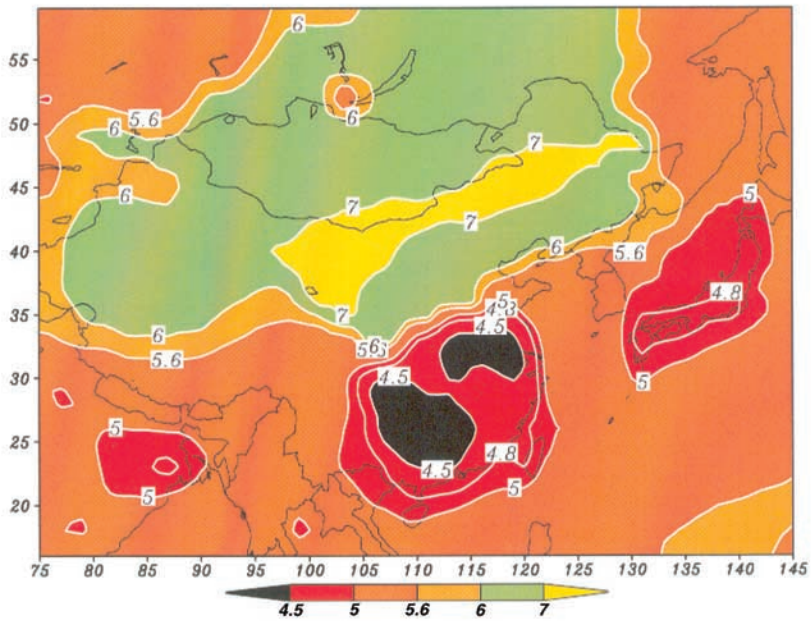

Figure 5. Simulated annual pH value in rainwater in 1999.

often reported in this region [*Wang and Wang*, 1995; *T. J. Wang et al.*, 2000]. The distribution of nitrate in rainwater is shown in Figure 4c. Its concentration is not high over the model domain compared with Ca^{2+} and SO_4^{2-}, with a maximum value of about 50 μeq L^{-1}. The relative contribution of nitrate to acidity in rainwater is much higher in Japan and Korea than in China. The predicted regional distribution of NH_4^+ in rainwater is shown in Figure 4d. Although there are many uncertainties associated with NH_3 emissions, the important role in neutralization of rainwater is demonstrated in the figure. In particular, relatively high concentrations of NH_4^+, over 50 μeq L^{-1}, are predicted in China.

[24] Figure 5 illustrates the annual mean pH value of precipitation in 1999 from the model. The pH = 7 isopleth covers Inner Mongolia, while the pH = 5.6 isopleth is in a roughly similar location in the north as that seen in the observations in Figure 1. Similar to the observations, the predicted annual pH value in rainwater is highest in northern China, above 6.0. The pH value in southern China is the

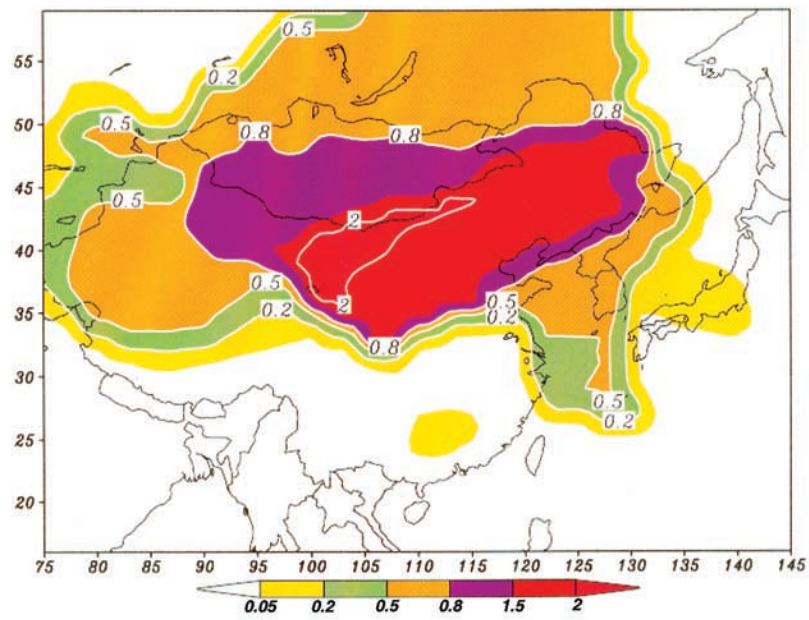

Figure 6. Difference of annual mean pH value in rainwater with and without neutralization reactions by Kosa in 1999.

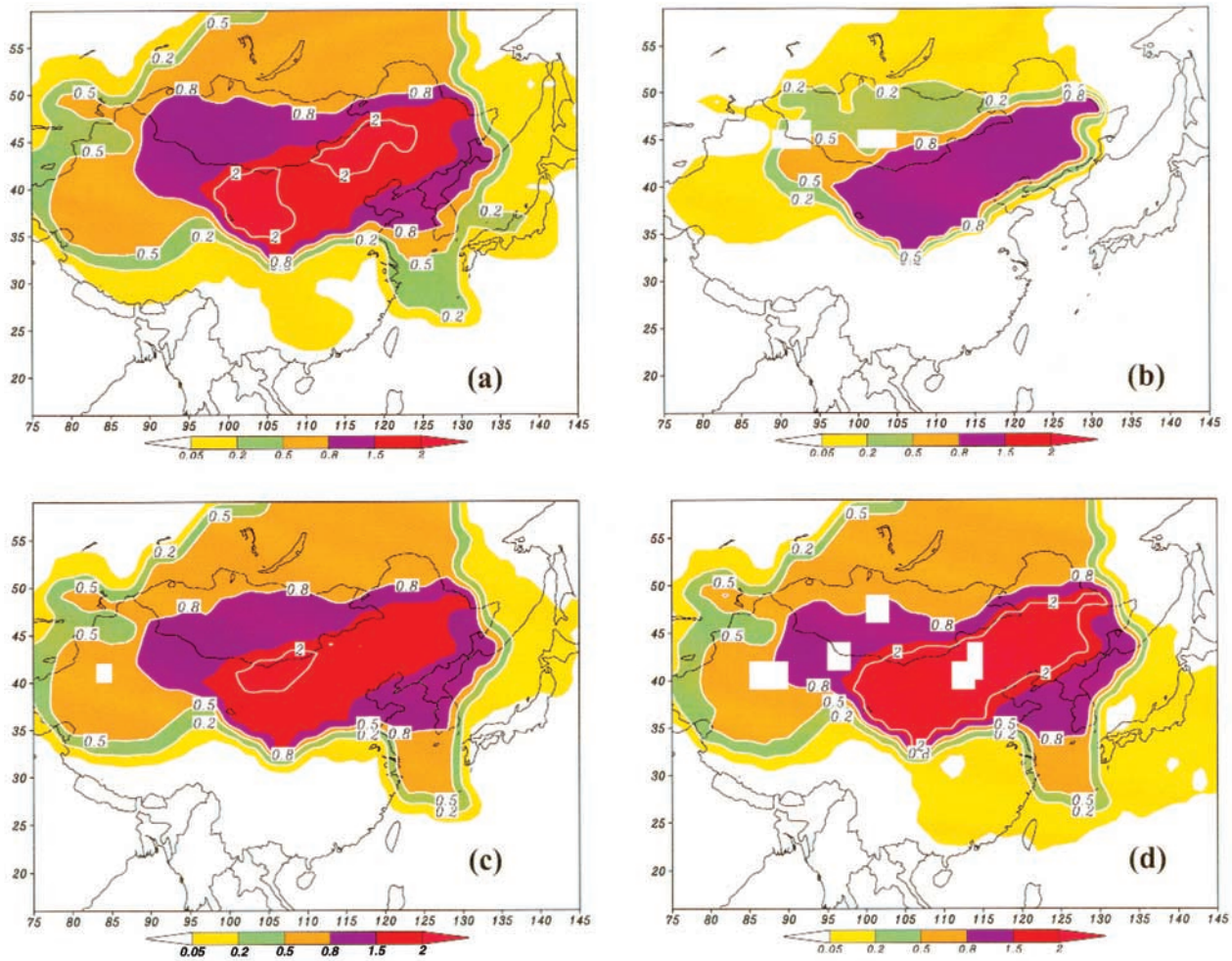

Figure 7. Difference of seasonal mean pH value in rainwater with and without neutralization reactions by Kosa in (a) spring, (b) summer, (c) autumn, and (d) winter in 1999.

lowest, between 4.0 and 5.0. There are also two areas severely affected by acid precipitation, one located in eastern Sichuan, Hunan, and Guangxi province, the other in southern Jiangsu province and Shanghai. In Japan the predicted pH value of rainwater is less than 5, significantly higher than that in southern China but lower than that in Korea. Rainwater pH values less than 4.8 are found in southern Japan. The simulated annual rainwater pH on the Korean peninsula is between 5 and 5.6, higher than that in Japan and lower than that in northern China. In general, the predicted geographical distribution of rain acidity agrees well with observations reported in east Asia (Figure 1).

4.3. Effects of Soil Aerosol Neutralization

[25] In order to evaluate the effect of soil aerosol neutralization, a numerical simulation was performed neglecting the neutralization reactions but with other conditions remaining the same. Figure 6 shows the difference in annual mean pH values in rainwater with and without the neutralization reactions. Around the Gobi desert, the Loess plateau and Inner Mongolia, the difference in monthly mean pH values is more than 2.0. The neutralization effect of soil aerosol is significant on the acidity of rainwater. The pH values increase more than 0.8 in the northernmost part of the Korean peninsula, where yellow sand is often reported from the weather charts. In contrast, the increase in pH in southern China and Japan is less than 0.2. The neutralization of the acidity of rainwater in Japan due to soil aerosol from China is rather small on an annual scale. Figure 7 shows the seasonal variation in pH value with and without neutralization reactions. When the precipitation rate is less than 1 mm/6 hours during the season, the difference of neutralization is not shown, resulting in a few white rectangular areas in the figure. It can be seen that the neutralization effect of soil aerosol is the most significant in winter and spring followed by in autumn but weak in summertime. In spring the pH values increase 0.1–0.4 in Japan, 0.5–0.8 in South Korea, 0.8–1.5 in North Korea, and more than 1.5 in northern China (Figure 7a). In summer, the neutralization is weak, even in northern China, and the pH values increase by between 0.5 and 1.5. There is nearly no influence on southern China, Korea and Japan. In summer and autumn, the influence of soil aerosol particles in Japan is not significant, but there is some influence in spring and winter. The greater the distance from the source region for soil dust, the smaller the influence. From these discussions, we can conclude that if there

Table 3. Overview of Sensitivity Runs[a]

Run	Parameter	Multiplied by
1	Ca^{2+} content in soil aerosol	1.5
2	dust emission rate	2
3	cloud liquid water content	2
4	precipitation rate	2
5	to add flux in boundary conditions	-

[a] Default values for control run are not available here but are shown in text.

were no soil aerosol in northern China, acid rain would widely affect northern China and Korea, with an decreased pH value of 0.8–2.5.

4.4. Uncertainty in the Model Results

[26] Each major process and assumption of the model affects the simulated results and this may lead to large uncertainties. Therefore the sensitivity of the model to different parameters is investigated for April 1999, when dust storms and soil aerosol neutralization effects are dominant. An overview of the sensitivity runs is shown in Table 3. The reference run is the one used in the model comparison with EANET, presented previously. Special attention is given to the Ca^{2+} content of soil aerosol, dust emission rate, cloud liquid water content, precipitation rate and boundary conditions and how they affect mean pH values and Ca^{2+} in rainwater in the model.

[27] Calculated monthly mean pH values and Ca^{2+} contents in rainwater for selected areas during the simulations are shown in Table 4. The locations of the stations in each area are listed in Table 2. In the first run (run 1) the Ca^{2+} content in soil dust was increased 50%. As one of the most important assumptions in the model, the content of Ca^{2+} in soil aerosols has a large impact on the model results; a 50% increase results in an increase in mean pH value of between 0.2 and 0.6. In contrast, mean Ca^{2+} content in rainwater increases between 16% and 82%. Accurately estimating the emissions of soil aerosols is still difficult due to the limitations in our understanding of deflation processes. The emission rate will affect the dust concentration and the aqueous phase chemistry with neutralization. In the second run (run 2) the emission rate of soil aerosols is doubled. This causes the mean pH value to increase 0.1–0.8 and the content of Ca^{2+} in rainwater to increase 20%–136%. From these two runs we can see that for April 1999 the calculated rainwater pH values and Ca^{2+} in rainwater are underestimated, suggesting that we need a better estimate of Ca^{2+} content of soil aerosols and of emission intensity in the model. Another interesting point is that for sites in Japan and the ocean area, the percentage increase of Ca^{2+} in rainwater is larger than in northern China, increasing 82% and 136% for run 1 and 2, respectively. The neutralization process by nitrate results in a greater increase of Ca^{2+} in rainwater than that of sulfate. In Japan and its surrounding ocean areas, nitrate and sulfate are distributed in similar quantities and this will cause the Ca^{2+} in rainwater to increase more than in northern China, where sulfate is dominant. Changes in cloud liquid water content (LWC) have implications for the scavenging efficiency of cloud droplets and may affect the formation of sulfate and the balance beween gas and aqueous concentrations. In the third run (run 3) LWC of the cloud is doubled. In general, this causes the mean pH value to decrease 0.1–0.5 and the content of Ca^{2+} to decrease 9%–36%. Increasing the precipitation rate makes the below-cloud washout of soil aerosols more efficient and affects the balance of ions in precipitation. The precipitation rate is doubled in the fourth run (run 4). This results in the content of Ca^{2+} in rainwater increasing 4%–17%, but mean pH values increase slightly in northern China, Korea and Japan and decrease 0.1 in southern China. It should be noted here that in April the precipitation amount and rainwater in northern China is very small, and that this may cause a greater change in pH value and Ca^{2+} in rainwater for run 3 and 4 than in other regions. For the boundary conditions used in the fifth run (run 5), we provide a continuous 3-day flux of soil aerosols across the northwest boundary (35°N–60°N, 75°E–100°E) on April 10. The intensity of the flux and its vertical profile is obtained from the mean value of dust storms occurring in this month in source regions. It appears that this kind of transport from the boundary only slightly increases the monthly mean pH value by 0.1–0.2

Table 4. Calculated Monthly Mean pH Value and Ca^{2+} Content in Rainwater in Sensitivity Runs for April 1999 as Compared With Observations

	Southern China	Northern China	Korea	Japan	Ocean
		Mean pH Value[a]			
Observed	4.5	7.1	6.3	5.1	5.3
Reference	4.3	6.7	5.4	4.8	5.1
Run 1	4.4(+0.1)	7.3(+0.6)	5.8(+0.4)	5.0(+0.2)	5.4(+0.3)
Run 2	4.4(+0.1)	7.5(+0.8)	5.9(+0.5)	5.1(+0.3)	5.5(+0.4)
Run 3	4.1(−0.2)	6.2(−0.5)	5.2(−0.2)	4.6(−0.2)	5.0(−0.1)
Run 4	4.2(−0.1)	7.3(+0.3)	5.5(+0.1)	4.9(+0.1)	5.1(−0.0)
Run 5	4.4(+0.1)	6.9(+0.2)	5.5(+0.1)	4.9(+0.1)	5.2(+0.1)
		Mean Ca^{2+} Content ($\mu eq\ L^{-1}$)[b]			
Observed	no data	343.	10.8	9.3	1.3
Reference	5.0	163.3	22.6	11.3	2.2
Run 1	5.8(+16%)	247.6(+51%)	30.7(+36%)	15.8(+40%)	4.0(+82%)
Run 2	6.0(+20%)	278.7(+71%)	32.9(+46%)	17.9(+58%)	6.2(+136%)
Run 3	3.8(−24%)	104.5(−36%)	17.2(−24%)	8.8(−22%)	2.0(−9%)
Run 4	5.2(+4%)	190.2(+17%)	24.2(+12%)	12.2(+8%)	2.3(+5%)
Run 5	5.1(+2%)	174.3(+7%)	23.8(+5%)	11.8(+4%)	2.4(+9%)

[a] The change in pH value is shown in parentheses.
[b] The percentage change in Ca^{2+} is shown in parentheses.

and Ca^{2+} by 2%–9%. From these studies, we conclude that while it is difficult to clearly quantify the uncertainties in the prediction of pH value in rainwater due to the number of processes involved, the greatest uncertainties lie in the emission rate of soil dust and its Ca^{2+} content.

5. Conclusions

[28] In this study, wet deposition data from 17 monitoring sites of EANET are analyzed and it is found that in northern China acid deposition is heavily influenced and buffered by natural soil dust from desert and semiarid areas. As high concentrations of alkaline dust are an important feature of the atmosphere over large parts of China, the deposition of ions such as Ca^{2+} must be taken into account when studying acid rain in east Asia.

[29] The AQPMS is applied to investigate neutralization by soil aerosols and its influence on the distribution of acid rain over east Asia. Comparison with observations shows that the present model reproduces reasonably well the key features of the chemical composition of precipitation in east Asia. Annual distributions of chemical composition in rain are discussed in the paper. The calculated annual pH = 5.6 isopleth lies in a close location to that observed. Numerical simulation results without soil aerosol clearly show the neutralization effects of soil aerosol. Soil aerosol can change the distribution pattern of acid rain in east Asia, especially over northern China. If no soil aerosol were lifted from the arid regions of China, the pH value in northern China and Korea would decrease by between 0.5 and 2. The neutralization effect is most significant in spring and winter, followed by autumn.

[30] Finally, the geographical distribution of rainwater pH in east Asia has been simulated successfully for the first time by taking into account the soil aerosol neutralization effect. However, there are many uncertainties in predicting pH in rainwater, such as the physical and chemical interactions between aerosols and cloud and rain droplets, the emission of NH_3, the amount of deflation of soil aerosols and the content of Ca^{2+}. Clearly, more work and analysis is needed to improve the model system and to reduce the uncertainties involved.

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