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Impact of the East Asian summer monsoon on long-term variations in the acidity of summer precipitation in Central China

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Abstract

The acidity of precipitation has been observed at stations of the Acid Rain Monitoring Network run by the China Meteorological Administration (CMA-ARMN) since 1992. Previous studies have shown that different long-term trends exist in different regions but detailed analysis of the causes of these is lacking. In this paper, we analyze summertime precipitation acidity data from the CMA-ARMN during 1992–2006 using EOFs and show that the summertime pH in China had different trends before and after 2000. The most significant decrease of pH is found in Central China. To investigate the causes of this decrease of pH in summer, we explore the relationship between changes in the pH value, the East Asian summer monsoon index, rainfall data, and pollutants emissions. We find that the East Asian summer monsoon can significantly affect the acidity of summer precipitation in Central China. In strong monsoon years, the pH in Central China is about 0.33 lower than that in weak monsoon years. Chemical transport model simulations using fixed emissions indicate that about 65% of the pH value difference (i.e., 0.22) is related to the summer monsoon, and constitutes 18–36% of the observed pH change (0.6–1.2) in Central China during 1992–2006. Further studies reveal a teleconnection between the pH in Central China and the rainfall in the middle and lower reaches of the Yangtze River (MLYR), which can explain about 24% of the variance of pH in Central China. Simulations using an annually varying emission inventory show that at least 60% of the variation in precipitation acidity in Central China can be attributed to changes in pollutant emissions. Therefore, the increase in emissions of acidic species is the most important cause for the observed decrease of pH in Central China, and changes in meteorological factors, such as rainfall and other parameters related to the East Asian summer monsoon, play a less important but still significant role.

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1 Introduction

Acid rain has been one of the most significant environmental problems in China since the late 1970s. Rapid economic development and population growth has lead to increases in the emission and subsequent deposition of sulfur, and widespread acid rain was observed in Southern and Southwestern China between the 1980s and the mid 1990s (Ding et al., 1997, 2004; Wang et al., 1995, 1996; Zhao et al., 1988; Huang et al., 1995). The rapid expansion of the acid rain zone exposes citizens and ecosystems to great risk in Southern and Southwestern China, and after the mid 1990s the region of acid rain extended into Central China (Zhang et al., 2007; Xie et al., 2009). In order to reduce the emission of SO_2 and mitigate acid rain in China, the Chinese government issued the "Atmospheric Pollution Prevention and Control Act of the Peoples Republic of China" in 1995. Following this act, a national control measure known as "Two Control Zones" (TCZ) was enacted in 1998 with the aim of strengthening control of SO_2 emissions (Liu et al., 1998). Meanwhile, municipal governments attempted to improve air quality in different ways to strengthen the control of the emissions of gaseous pollutants and particulate matter. Although these efforts had some positive effects in the first few years, rapid economic development and an increased demand for energy have caused further increases in the emissions of SO_2 and NO_2 over the last decade. A large number of reports (Zhang et al., 2008; Xie et al., 2009; Wang et al., 2009; SEPA, Gao et al., 2009) reveal that nationwide emissions of SO_2 and NO_2 have increased significantly since 2000, following the temporary decrease in emissions in the 1990s.

Most studies on acid rain link its variation to the emissions and transport of SO_2 and NO_2 (Khemani et al., 1994; Browning et al., 1991; Wang et al., 2007; Vogt et al., 2006; Quan et al., 2007; Liu et al., 2008), but few consider the impacts of climatic conditions (Xie et al., 2009; Dayana et al., 2008; Rai et al., 2009; Yeung et al., 2007; Tiwari et al., 2007; Ravichandran et al., 1994; Davies et al., 1991). Previous studies have shown that before the 1990s acid rain occurred mainly in Southern and Southwestern regions of China. More recently, however, acid rain has seriously affected the central parts

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of China, especially in eastern areas (Xie et al., 2009). Tang et al. (2010) used the Man-Kendall method to obtain a trend in precipitation acidity in China, and show that during 2000–2006 acid rain moved from Southwestern to Eastern and Central China. We analyzed the change in precipitation acidity in China between 1992 and 2006, and found that the most distinct increase occurred in Central China. What are the causes of this increase and are they related to changes in climatic conditions? In this paper, we report the potential contributions of the summer monsoon and rainfall in the middle and lower Yangtze River regions to precipitation acidity in Central China. We also evaluate the influence of variations in emissions on changes in the acidity of precipitation in Central China.

2 Data and methodologies

2.1 Data

It is well known that soil aerosol/dust originating from Northern China can affect precipitation acidity over almost all of the country in winter and springtime under conditions of continental outflow during the East Asian winter monsoon (Wang et al., 2002; Rodhe et al., 2002; Wai et al., 2005; Yeung et al., 2007). In order to exclude this factor we choose to focus on summertime and study the contributions from the East Asian summer monsoon and pollution to the variation in the acidity of precipitation in Central China.

Precipitation acidity, conductivity and rainfall are observed at stations of the Acid Rain Monitoring Network run by the China Meteorological Administration (CMA-ARMN). During the period 1992–2006 the network was composed of 88 stations. Strict quality assurance and quality control was applied to the dataset from the CMA-ARMN. Data for 14 of the 88 stations were found to be unsuitable for long-term trend analysis (Tang et al., 2007, 2010) and precipitation acidity data from the 74 remaining stations are used in this study. For meteorological data we use reanalysis data for 850 hPa wind

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fields from the National Centers for Environmental Prediction (NCEP) and rainfall at 753 stations selected by CMA. To define the monsoon intensity and to investigate the influence of the monsoon on precipitation acidity in China, we used a dynamical normalized seasonality Monsoon Index (MI), which was developed by Li and Zeng (2002) on the basis of grid-by-grid and season-by-season calculations of the climatological wind field.

2.2 Modeling

The modeling system used in this study is CMAQ version 4.4 (Byun and Ching, 1999) driven by meteorological fields calculated by the Regional Atmospheric Modeling System (RAMS) Version 4.3 (Cotton et al., 2003; Pielke et al., 1992), with initial and boundary conditions defined by NCEP reanalysis data. The horizontal resolution of the model is 80 km for the mother domain and 20 km for the nested domain, and there are 19 layers in the vertical following a sigma-z coordination system up to 23 km. The model uses the Regional Emission Inventory in Asia (Ohara et al., 2007), which is based on energy statistics, emission factors, and other socioeconomic information and covers the years 1980–2003 (He et al., 2007, 2008; Yamaji et al., 2006). For the purpose of comparison, we conducted three simulations to derive SO_2, NO_2, SO_4^{2-} and NO_3^- concentrations as monthly averages for 1980–2003, but do not continue beyond 2003 in the absence of a suitable emission inventory. In the first simulation annually varying meteorological conditions were used along with the 2000 emission inventory, that is, only meteorological conditions change (hereafter MC); in the second, meteorological conditions for 2000 were used along with annually-varying emissions (hereafter EC); and in the third both meteorological conditions and emissions varied from year to year (hereafter Normal).

The CMAQ model is widely used and is well validated with measurements from Chinese sites, e.g., Tieshanping in the Sichuan basin and Caijiatang in Hunan province (Quan et al., 2008), and it was found that simulated SO_2 and SO_4^{2-} agree well with observations. Ohara (2010) found that the model can reproduce the observed temporal

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variations in monthly wet deposition of SO_4^{2-} at long-term acid deposition monitoring sites in East Asia since 1988. In addition, many studies have validated O_3 and related species, which affect atmospheric oxidation, using measurements at EANET observation stations (Tanimoto et al., 2009; Ohara et al., 2008), at the mountain sites Taishan, Huashan and Huangshan in China (He et al., 2008) and observations during the TRACE-P measurement campaign (Zhang et al., 2006b). These studies all show that the model can reproduce the tempo-spatial distributions of these species reasonably well. Thus, the model reproduces many of the important features of SO_2 and SO_4^{2-} chemistry seen in the observations (Zhang et al., 2004; Zhang et al., 2006a). We have also compared the rainwater concentrations of SO_4^{2-} and NO_3^- from the CMAQ model with EANET observation stations in China, e.g., Hongwen in Xiamen city and Guanyinqiao in Chongqin, and the trends of our model results are similar to that observed (see Fig. 1). The correlations between model and observations were greater than 0.5 (significant at the 95% level) and the bias of the mean values were less than 30% (see Table 1).

2.3 Volume weighted average method

The volume weighted average (VWA) value (Huang et al., 2008; Yeung et al., 2007; Seqheira et al., 1998) of pH is used, as this eliminates the influence of different rainfall intensities on the pH. VWA pH at a station in a certain period is calculated by multiplying the volume of precipitation collected using the equation

$$\mathrm{pH_{VWA}} = -\log\left(\sum\left(10_i^{-\mathrm{pH}} \times V_i\right) / \sum V_i\right) \quad (1)$$

where $\mathrm{pH_{VWA}}$ represents the volume weighted average pH, and pH_i and V_i are the pH value and sample volume of the sample i, respectively.

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2.4 EOFs and the SVD method

Empirical Orthogonal Functions (EOFs) are a set of independent and orthonormal eigenvectors that most efficiently represent a given set of data. The objective of the method is to split the temporal variance of spatially distributed data into orthogonal spatial patterns called EOFs or empirical orthogonal models. The relative importance of any individual eigenvector to the total variance in the field is measured by its associated eigenvalue or variance contribution. Each eigenvector, which may represent the spatial patterns of its variance, is associated with a series of time coefficients that describe the time evolution of that particular eigenvector (Gianelli et al., 2007; Calbet et al., 2006).

Singular Value Decomposition (SVD) aims to find the linear combination or coupling mode of two sets of data. The objective is to separate the highly correlated areas of these two set of data (Jordi et al., 2009; Alter et al., 2000). The SVD was firstly used in diagnosing the relationship between monthly surface temperature in America and sea level pressure in North Pacific (Prokasha, 1976). After that, a lot of studies (Wang et al., 2004; Ding et al., 1996) have used SVD analysis to investigate the correlations among meteorological parameters, i.e., rainfall, u and v wind, SST, and even aerosol (Shi et al., 2007). It is one of the best tools to study the correlations of two factors with large number of spatial and temporal data. Using this method, we can obtain a series of left and right singular vectors, standing for two factors, respectively. The SVD defines the relations of left (right) variable or left (right) factor and time coefficients of right (left) singular vector (of the other factor) as the left (right) heterology correlation coefficients field. This one pair of heterology correlation coefficients field represent one kind of distribution of correlations between two factors, the area where corelated significantly is the key area of interaction between two factors. Thereafter, a pair of heterology correlation coefficients field stands for one type of teleconnection of two factors to some extent.

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3 Result and discussion

3.1 Description of the dataset

3.1.1 Spatial patterns of VWA pH

We divide mainland China into eight regions, shown in Fig. 2: the middle reaches of the Yangtze River (YRM, 109–117° E, 26–32° N); lower reaches of Yangtze River (YRL, 117–123° E, 26–33° N); Southern China (SC, 109–123° E, 20–26° N); Southwest China (SW, 95–109° E, 20–33° N); Center of China (CT, 109–117° E, 32–42° N); East China (EC, 117–123° E, 33–40° N); Northeast China (NE, 117–135° E, 40–55° N); and Northwest China (NW, 72–109° E, 33–49° N). Statistics are collected for the whole country and for these different regions. The results for pH_{VWA}, together with the arithmetic mean pH, rainfall, and the number of stations, are listed in Table 2. As can be seen in the table, the lowest pH value is in SW and YRM, while the highest is in NW and NE for both pH averaging methods. In this study, we focus on YRM and CT, and call them Central China.

In the following analysis, we use pH_{VWA} as it eliminates the influence of different rainfall intensities. Figure 3a shows the spatial patterns of pH_{VWA} in China during the summers of 1992–2006. It is clear that acid rain occurred mainly in the south of China in summer during this period, with the most severe acid rain in Sichuan and Guizhou provinces, in the southwestern part of China. The other severe acid rain areas are the Yangtze River Delta, Northwestern Guangxi and the Pearl River Delta, which are located in Southeastern and Southern China. This distribution is similar to that found by Xie et al. (2009).

The changes in pH_{VWA} during 1992–2006 are shown in Fig. 3b. In Southwestern China, the acidity of precipitation decreases significantly during 1992–2006, with pH increasing by 0.3–0.6 (at α=0.10), However, a substantial increase in the acidity of precipitation in summer was observed in Central China, as shown in Fig. 3b and in (Tang et al., 2010), with the pH value decreasing by 0.6–1.2 (at α=0.10).

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Using the EOF method, the summer pH dataset from the CMA-ARMN stations is separated into a set of spatial functions (or EOF eigenvectors) and a series of time weighting coefficients. Figure 4a and b shows the spatial distribution of the EOF eigenvectors and the variation of the time weighting coefficients, respectively. The variance contributions from the first EOFs eigenvectors of the original pH dataset is greater than 99%, and its spatial patterns are similar to those of pH_{VWA} (Shi et al., 2007; Gu et al., 2007) (see Fig. 3a). The variation in the time weighting coefficients in Fig. 4b symbolizes the overall variation in the acidity of summer precipitation in China. The variation in the time weighting coefficients follows a parabola, and can be divided into two different periods, i.e., 1992–1999 and 2000–2006, with pH increasing between 1992 and 1999 and decreasing between 2000 and 2006. This general trend based on summertime data is consistent with that obtained from the whole dataset by Tang et al. (2010).

To further investigate regional differences in the trends of acid rain in China, we calculated pH_{VWA} for the periods 1992–1999 and 2000–2006. The spatial distributions of the calculated pH_{VWA} values for the two periods are shown in Fig. 5a and b, and the differences between the distributions for both periods are shown in Fig. 5c. In Southeastern China, the area with pH_{VWA} lower than 4.8 is significantly larger during 2000–2006 than during 1992–1999, indicating a worsening trend of acid rain in this area. As shown in Fig. 5c, the trend of precipitation acidity is very different from region to region. The contrasting trends become clearer on drawing a southeast-northwest dividing line from 22° N, 112° E to 42° N, 105° E. Northeast of the line, the acidity of precipitation increased (pH decreased) from 1992–1999 to 2000–2006, while southwest of the line, the opposite trend occurred. The most distinct acidification trends are found in Central China. In the SW area, the precipitation acidity decreased significantly (significant at a 90% level) from 1992–1999 to 2000–2006.

3.1.2 Acidity of precipitation in different areas

Figure 6 shows the time series of monthly pH_{VWA} in summer during 1992–2006 for different regions. In SW, the pH_{VWA} of precipitation increased gradually during 1992–

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2006, consistent with Tang et al. (2010) and Xie et al. (2009); in SE, NW and CT, pH_{VWA} first showed an increase and then a decrease, similar to the general trend over the whole country; in NE, pH_{VWA} decreased consistently. In CT, pH_{VWA} showed a regular pattern, with the lowest pH_{VWA} almost always occurring in August. In summer, the mean rain pH values decreased from June to August over CT. The substantial increase in the acidity of precipitation in this area might be explained by the following mechanism: developed cities inland emit heavy air pollution, in particular SO_2 and NO_x, and this pollution is transported to Central China under summertime winds, leading to accumulation and to an increase in the acidity of precipitation, especially in years with a strong summer monsoon. The impacts of the East Asian Summer Monsoon and precipitation in the middle and lower reaches of the Yangtze River (MLYR) on the variation in acidity of precipitation in Central China are addressed in the following sections.

3.2 Effects of summer monsoon and rainfall in YRD

3.2.1 Relationship between summer monsoon and pH

The monsoon is an important component of the global circulation system. In monsoon regions, the local weather and climate, and especially precipitation, are strongly influenced by the monsoon circulation. In order to study the potential effects of the summer monsoon on acid rain in China, the East Asian Monsoon Index (EAMI) (Li and Zeng, 2002), which characterizes the summertime climate in China (Li and Zeng, 2005), has been adopted by National Oceanic and Atmospheric Administration (NOAA), and is used to denote the intensity of summer monsoon.

Figure 7a shows the time series of EAMI (http://www.lasg.ac.cn/staff/ljp/data-monsoon/EASMI.htm). Based on this figure, we define years above the solid line as strong summer monsoon years (high MI), and those below the dashed line as weak summer monsoon years (low MI). Figure 7b and c shows average spatial patterns of summer pH_{VWA} in low and high MI years, respectively. The difference in summer pH_{VWA}

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between low and high MI years is shown in Fig. 7d. In MLYR, the pH_{VWA} values in high MI years are about 0.1–0.2 lower than in low MI years. In CT, the difference in pH_{VWA} values is 0.2–0.4, and in some areas it even exceeds 0.4. These results indicate that the precipitation in YRL and Central China is more acidic in strong summer monsoon years than in weak years. It is known generally that in the strong monsoon years the climate in the Yangtze River Delta (YRD) is characterized by strong winds and little precipitation (Li and Zeng, 2005). Model simulations with different scenarios in the following sections are used to estimate how much these climate features contribute to the worsening of acid rain in Central China.

China relies heavily on coal combustion for energy and recently the volume of motor vehicles has increased sharply, leading to significant increases in emitted SO_2 and NO_x (Hao et al., 2001; Zhao et al., 2008). These air pollutants are the dominant precursors of acidic species, such as SO_4^{2-} and NO_3^- ions, which control almost 90% of the acidity of precipitation in Southern and Central China (Wang et al., 1995, 1996, 2009; Zhang et al., 1996; Lei et al., 1997). We simulate the distribution of these two key gaseous pollutants (SO_2 and NO_2) and ions (SO_4^{2-} and NO_3^-) in low and high MI years for different scenarios (see Sect. 2.2) using the CMAQ model. Note that the neutralization of rain by aerosols is not considered here as alkaline aerosol are not significant in this area (only about 11–25%) compared to Northern China (60–70%) (Wang et al., 1995; Qin et al., 2001; Terada et al., 2002). Figure 8 shows the differences in the simulated SO_4^{2-} and NO_3^- concentrations in rainwater between low and high MI years for the Normal and MC Scenarios. For the Normal Scenario, the simulated SO_4^{2-} and NO_3^- concentrations in Central China are clearly lower in low MI years than in high MI years, as shown in Fig. 8a and b. The differences in the simulated SO_2 and NO_2 concentrations (not shown) have similar patterns. These differences may be attributed to differences in meteorological conditions, or pollution emissions, or both, between weak and strong monsoon years. The simulations for MC (varying meteorological conditions and fixed emission inventory) show similar patterns to the differences in the simulated SO_4^{2-} and NO_3^- concentrations, but with reduced extent, as shown in Fig. 8c

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and d. This suggests that meteorological conditions related to the summer monsoon have caused higher concentrations of SO_4^{2-} and NO_3^- in rainwater (and hence higher precipitation acidity) in Central China in high MI years. The differences in the SO_4^{2-} and NO_3^- concentrations simulated for MC can be attributed solely to changes in the intensity of the summer monsoon, while those simulated for Normal can be attributed to intensity changes of the summer monsoon and to pollutant emissions. Assuming that the differences in the simulated SO_4^{2-} and NO_3^- concentrations result in corresponding changes in the precipitation acidity in Central China, we can estimate the contribution of the summer monsoon to the change of precipitation acidity by comparing the values in Fig. 8c and d with those in Fig. 8a and b. We obtain a summer monsoon contribution of almost 65% ($-1.17\,mg/m^3$ in Fig. 8c and $-1.79\,mg/m^3$ in Fig. 8a; $-0.076\,mg/m^3$ in Fig. 8d and $-0.123\,mg/m^3$ in Fig. 8b) to the change of precipitation acidity in Central China. Since the overall difference in pH_{VWA} between low and high MI years is 0.33, we deduce a summer monsoon contribution of 0.22 to the pH_{VWA} difference, about 18–36% of the observed pH_{VWA} change (0.6–1.2, see Fig. 1b) in Central China during 1992–2006.

3.2.2 Influence of MLYR rainfall on pH_{VWA} change in Central China

We used the SVD method (Sect. 2.4) to investigate the relationship between rainfall and pH_{VWA} in China. The first pair of heterology correlation coefficients field is shown in Fig. 9 and the variance contribution is greater than 30%. It is shown that the spatial patterns of left of first SVD eigenvectors (LFSE), which stands for the correlations of pH_{VWA} and time coefficient of rainfall in China, and right of first SVD eigenvectors (RFSE), which stands for the correlations of rainfall and time coefficient of pH_{VWA} in China. Obviously, the pH_{VWA} value in Central China is positively correlated to the rainfall in the MLYR (the correlation coefficients of two fields are both 0.4). This suggests that there is a teleconnection between the observed decrease of the pH_{VWA} value in Central China during 1992–2006 and the decrease of rainfall in the MLYR. Actually,

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a decreasing trend of the rainfall was observed in the MLYR, as shown in Fig. 10a. The rainfall decreased significantly in this area with the velocity of 1.2–1.8 mm per year during 1992–2006. As we discussed above, the pH value decreased significantly either in Central China. These two evidences prove the teleconnection mentioned above in detail.

To further support our hypothesis of a teleconnection, we calculated the total rainfall in the MLYR during 1980–2006 and standardized the time series by taking the difference between the total rainfall each year and the mean value over 1980–2006 and dividing by the standard deviation over this period. Figure 10b shows that the standardized rainfall varied within the range −1.5 to 1.5 before 1998, underwent a sudden increase in 1998–1999, and then dropped to normal levels. For years up to 1997, we separately identify low and high rainfall years in Fig. 10b. We simulated the concentrations of SO_4^{2-} and NO_3^- in rainwater for these low and high rainfall years using MC. Figure 11 shows the differences in the simulated rainwater SO_4^{2-} and NO_3^- concentrations between the low and high rainfall years (SO_4^{2-} and NO_3^- concentrations in low rainfall years minus that in high rainfall years). It shows that both SO_4^{2-} and NO_3^- concentrations have the greatest differences in Central China. Similar results are obtained by comparing the SO_2 and NO_2 concentrations simulated for low and high rainfall years. Moreover, we find that the pH_{VWA} in Central China is positively correlated with rainfall in the MLYR with R^2=0.24 (significant at a 90% level) and explains 24% of the variance in pH in Central China, as shown in Fig. 10c. Based on these results we conclude that less rainfall in the MLYR may enhance the concentrations of acidic gases and their products in Central China, and hence increase the acidity of precipitation in this region. Statistically, about 24% of the variance in pH in Central China can be explained by this fluctuation in rainfall in the MLYR.

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3.3 Characteristics of SO_4^{2-} and NO_3^- ion concentration during 1992–2003

In Sect. 3.2, the contributions of changes in the summer monsoon and rainfall in the MLYR to the increase in precipitation acidity in Central China are studied using fixed pollutant emission intensities. However, the emissions of acidic gases (SO_2 and NO_x) are not stable, and hence the impacts of changes in the emission intensities on precipitation acidity should also be addressed. For this purpose, we simulated rainwater SO_4^{2-} and NO_3^- concentrations during 1992–2003 using the EC scenario (i.e., changing the emission inventory and using fixed meteorological conditions for 2000). Figure 12 shows the simulated annual changes in rainwater SO_4^{2-} and NO_3^- concentrations during 1992–2003. The SO_4^{2-} and NO_3^- concentrations in Central China show distinct increases at a rate of 0.3–0.5 $mg\,m^{-3}\,yr^{-1}$ and 0.04–0.08 $mg\,m^{-3}\,yr^{-1}$ (significant at a 95% level) for SO_4^{2-} and NO_3^-, respectively.

To estimate the relative contribution of pollutants emissions to the changes in SO_4^{2-} and NO_3^- concentrations, we divided the rates of change of SO_4^{2-} and NO_3^- concentrations simulated for EC by those simulated for the Normal scenario. The results are shown as contours in Fig. 10 and suggest that about 60–80% of the changes in SO_4^{2-} concentration and 70–80% of the changes in NO_3^- concentration in Central China are attributable to the changes in emissions. This confirms that most of the changes in SO_4^{2-} and NO_3^- concentrations in Central China are caused by changes in emissions, at least during 1992–2003. Assuming that these changes in SO_4^{2-} and NO_3^- ion concentrations contributed to changes in the pH of precipitation, we can conclude that changes in pollutant emissions contributed at least 60% of the variance of precipitation acidity in Central China during 1992–2003.

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4 Conclusions

Summertime precipitation acidity data from CMA-ARMN stations between 1992 and 2006 have been analyzed using the EOFs method. We find that summertime pH in China experienced two different periods of variation, with pH increasing during 1992–1999 and decreasing during 2000–2006, which is similar to results obtained using the whole dataset (Tang et al., 2010). The most significant decrease of pH is found in Central China. To investigate the causes of the observed decrease of summertime pH in this region, the East Asian summer monsoon index and rainfall data are analyzed, together with the pH data, and simulations using CMAQ are performed for different scenarios.

We find that the East Asian summer monsoon can significantly affect the acidity of summer precipitation in Central China. For example, there is a difference of 0.33 in pH in Central China between years with weak and strong summer monsoons, and about 65% of this difference (i.e., 0.22) is related to the summer monsoon when using simulations with fixed emissions, accounting for 18–36% of the observed pH variation (0.6–1.2) in Central China during 1992–2006. Our SVD analysis and simulations reveal that there is a teleconnection between the pH in Central China and the rainfall in the MLYR. The pH value of precipitation in Central China is positively correlated with the rainfall in the MLYR, with R^2=0.24 (significant at a 90% level), suggesting that 24% of the variance in pH in Central China can be explained by the fluctuation in rainfall in the MLYR. However, the East Asian summer monsoon influences the rainfall in the Yangtze River regions, so the contribution of rainfall to the precipitation acidity in Central China may partially overlap with that of the summer monsoon.

The impacts of pollutant emissions on precipitation acidity in Central China are investigated using the CMAQ model with an annually varying emission inventory, and show that at least 60% of the variance of precipitation acidity in Central China can be attributed to changes in pollutant emissions. Therefore, increasing emissions of acidic species are the dominant factor contributing to the observed significant decrease of

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pH in Central China, and changes in meteorological factors, such as rainfall and other parameters related to the East Asian summer monsoon, play a less important but still significant role. Although this study estimates the impacts of the East Asian summer monsoon, rainfall in MLYR and pollutants emissions on the variation in pH in Central China, further studies are needed to confirm these effects and to investigate the type of acid rain in this area.

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References

Alter, O., Brown, P. O., and Botstein, D.: Singular value decomposition for genome-wide expression data processing and modeling, P. Natl. Acad. Sci. USA, 97, 10101–10106, 2000.

Browning, K. A., Allam, R. J., Ballard, S. P., Barnes, R. T. H., Bennetts, D. A., Maryon, R. H., Mason, P. J., Mckenna, D., Mitchell, J. F. B., Senior, C. A., Slingo, A., and Smith, F. B.: Environmental effects from burning oil-wells in Kuwait, Nature, 351, 363–367, 1991.

Byun, D. W. and Ching, J. K. S.: Science algorithms of the EPA Models-3 community multiscale air quality (CMAQ) modeling system, EPA/600/R-99/030. Natl. Exposure Res. Lab., Research Triangle Park, NC, 1999.

Calbet, X. and Schlüssel, P.: Technical note: analytical estimation of the optimal parameters for the EOF retrievals of the IASI Level 2 Product Processing Facility and its application using AIRS and ECMWF data, Atmos. Chem. Phys., 6, 831–846, doi:10.5194/acp-6-831-2006, 2006.

Cotton, W. R., Pielke, R. A., Walko, R. L., Liston, G. E., Tremback, C. J., Jiang, H., McAnelly, R. L., Harrington, J. Y., Nicholls, M. E., Carrio, G. G., and McFadden, J. P.: RAMS 2001: current status and future directions, Meteorol. Atmos. Phys., 82, 5–29, 2003.

Davies, T. D., Dorling, S. R., Pierce, C. E., Barthelmie, R. J., and Farmer, G.: The meteorological control on the anthropogenic ion content of precipitation at 3 sites in the Uk – the utility of lamb weather types, Int. J. Climatol., 11, 795–807, 1991.

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10, 19593–19630, 2010

Dayana, U. and Lamb, D.: Influences of atmospheric circulation on the variability of wet sulfate deposition, Int. J. Climatol., 28, 1315–1324, 2008.
Ding, G. A., Xu, X. B., and Fang, X. M.: The current status and trends of acid rain in China, Chinese Sci. Bull., 42, 169–173, 1997 (in Chinese).
Ding, G. A., Xu, X. B., and Wang, S. F.: Database from the acid rain network of China Meteorological Administration and its preliminary analysis, J. Appl. Meteorol. Sci., 15(suppl.), 85–94, 2004 (in Chinese).
Ding, Y. and Jiang, Z.: Generality of singular value decomposition in diagnostic analysis of meteorological field, Acta Meteorol. Sin., 54, 365–372, 1996 (in Chinese).
Gao, C. L., Yin, H. Q., Ai, N. S., and Huang, Z. W.: Historical analysis of SO_2 pollution control policies in China, Env. Manag., 43, 447–457, 2009.
Gianelli, S. M., Carlson, B. E., and Lacis, A. A.: Using EOF analysis to qualitatively analyze, and identify inhomogeneities in, data from ground-based aerosol monitoring instruments, J. Geophys. Res., 112, D20210, doi:10.1029/2006JD008300, 2007.
Gu, Z., Fen, G., Gu, J., and Shi, N.: EOF of 500 hPa wind fields and its relationship to large scale abnormal climate in midsummer of China, Sci. Meteorol. Sin., 27, 245–252, 2007 (in Chinese).
Hao, J. M., Wang, S. X., Liu, B. J., and He, K. B.: Designation of sulfur dioxide and Acid Rain Pollution Control Zones and its impacts on energy industry in China, J. Chem. Eng. Jpn., 34, 1108–1113, 2001.
He, Y., Uno, I., Wang, Z., Ohara, T., Sugirnoto, N., Shimizu, A., Richter, A., and Burrows, J. P.: Variations of the increasing trend of tropospheric NO_2 over Central East China during the past decade, Atmos. Environ., 41, 4865–4876, 2007.
He, Y. J., Uno, I., Wang, Z. F., Pochanart, P., Li, J., and Akimoto, H.: Significant impact of the East Asia monsoon on ozone seasonal behavior in the boundary layer of Eastern China and the west Pacific region, Atmos. Chem. Phys., 8, 7543–7555, doi:10.5194/acp-8-7543-2008, 2008.
Huang, K., Zhuang, G. S., Xu, C., Wang, Y., and Tang, A. H.: The chemistry of the severe acidic precipitation in Shanghai, China, Atmos. Res., 89, 149–160, 2008.
Huang, M., Shen, Z., and Liu, S.: A study on the formation processes of acid rain in some areas of Southwest China, Sci. Atmos. Sin., 19, 359–366, 1995 (in Chinese).
Jordi, A., Basterretxea, G., and Angles, S.: Influence of ocean circulation on phytoplankton biomass distribution in the Balearic Sea: study based on Sea-viewing Wide Field-

ACPD
10, 19593–19630, 2010

of-view sensor and altimetry satellite data, J. Geophys. Res.-Oceans, 114, C11005, doi:10.1029/2009JC005301, 2009.
Khemani, L. T., Momin, G. A., Rao, P. S. P., Pillai, A. G., Safai, P. D., Mohan, K., and Rao, M. G.: Atmospheric pollutants and their influence on acidification of rain water at an industrial-location on the west-coast of India, Atmos. Environ., 28, 3145–3154, 1994.
Lei, H. C., Tanner, P. A., Huang, M. Y., Shen, Z. L., and Wu, Y. X.: The acidification process under the cloud in Southwest China: observation results and simulation, Atmos. Environ., 31, 851–861, 1997.
Li, J. and Zeng, Q.: A unified monsoon index, Geophys. Res. Lett., 29, 1151–1154, 2002.
Li, J. and Zeng, Q.: A new monsoon index, its interannual variability and relation with monsoon precipitation, Clim. Environ. Res., 10, 42–46, 2005.
Liu, B. J., Hao, J. M., and He, K. B.: Study on designation of acid rain and SO_2 pollution control areas and policy implementation, Acta Sci. Circumst., 18, 1–7, 1998 (in Chinese).
Liu, C. Q., Lang, Y. C., Satake, H., Wu, J. H., and Li, S. L.: Identification of anthropogenic and natural inputs of sulfate and chloride into the karstic ground water of Guiyang, SW China: combined delta Cl-37 and delta S-34 approach, Environ. Sci. Technol., 42, 5421–5427, 2008.
Ohara, T., Akimoto, H., Kurokawa, J., Horii, N., Yamaji, K., Yan, X., and Hayasaka, T.: An Asian emission inventory of anthropogenic emission sources for the period 1980–2020, Atmos. Chem. Phys., 7, 4419–4444, doi:10.5194/acp-7-4419-2007, 2007.
Ohara, T., Yamaji, K., Uno, I., Tanimoto, H., Sugata, S., Nagashima, T., Kurokawa, J. I., Horii, N., and Alkimoto, H.: Long-term simulations of surface ozone in east Asia during 1980–2020 with CMAQ and REAS inventory, NATO Sci. Peace Secur., in: Air Pollution Modeling and Its Application XIX, edited by: Borrego, C. and Miranda, A. I., Springer Netherlands, Environment, 136–144, 2008.
Ohara, T.: Long-term trends for anthropogenic SO_2 emissions and sulfur depositions in East Asia, in: International Workshop on Atmospheric Modeling Research in East Asia, 18–19 Mar 2010, Express Holiday Inn City Center Dalian, China, 2010.
Pielke, R. A., Cotton, W. R., Walko, R. L., Tremback, C. J., Lyons, W. A., Grasso, L. D., Nicholls, M. E., Moran, M. D., Wesley, D. A., Lee, T. J., and Copeland, J. H.: A comprehensive meteorological modeling system – Rams, Meteorol. Atmos. Phys., 49, 69–91, 1992.
Prohaska, J.: A technique for analyzing the linear relationships between two meteorological fields, Mon. Weather Rev., 104, 1345–1353, 1976.

ACPD
10, 19593–19630, 2010

Qin, G. Y. and Huang, M. Y.: A study on rain acidification processes in ten cities of China, Water Air Soil Poll., 130, 163–174, 2001.
Quan, J., Zhang, X., and Duan, N.: Numerical modeling of sulfur deposition in South and Southwest China, Plateau Meteorol., 26, 326–332, 2007 (in Chinese).
Quan, J. N., Zhang, X. S., Zhang, Q., Guo, J. H., and Vogt, R. D.: Importance of sulfate emission to sulfur deposition at urban and rural sites in China, Atmos. Res., 89, 283–288, 2008.
Rai, H. C., Sharma, A., and Sharma, V. M.: Studies on temporal variation of acid precipitation in Delhi, Asian J. Chem., 21, 5391–5398, 2009.
Ravichandran, C. and Padmanabhamurty, B.: Acid precipitation in Delhi, India, Atmos. Environ., 28, 2291–2297, 1994.
Rodhe, H., Dentener, F., and Schulz, M.: The global distribution of acidifying wet deposition, Environ. Sci. Technol., 36, 4382–4388, 2002.
SEPA.: Report on the status quo of the environment in China from 1990 to 2006, available at: http://www.zhb.gov.cn/plan/zkgb/, 2006.
Seqheira, R. and Lai, C.: Small-scale spatial variability in the representative composition of rainwater within urban Hong Kong, Atmos. Environ., 32, 133–144, 1998.
Shi, X., Xu, X., and Xie, L. A.: Interdecadal Spatial-Temporal change trend of East Asian winter monsoon in the last 40 yr, Chinese J. Atmos. Sci., 31, 747–756, 2007 (in Chinese).
Tang, J., Chen, H. B., Yu, X. L., et al.: Evaluation of results of station inter-comparison with blind samples in acid rain monitoring network in China, Meteorol. Mon., 33, 75–83, 2007 (in Chinese).
Tang, J., Xu, X., Ba, J., and Wang, S.: Trends of the precipitation acidity over China during 1992–2006, Chinese Sci. Bull., 5, 1–9, 2010.
Tanimoto, H., Ohara, T., and Uno, I.: Asian anthropogenic emissions and decadal trends in springtime tropospheric ozone over Japan: 1998–2007, Geophys. Res. Lett., 36, L23802, doi:10.1029/2009GL041382, 2009.
Terada, H., Ueda, H., and Wang, Z. F.: Trend of acid rain and neutralization by yellow sand in East Asia – a numerical study, Atmos. Environ., 36, 503–509, 2002.
Tiwari, S., Kulshrestha, U. C., and Padmanabhamurty, B.: Monsoon rain chemistry and source apportionment using receptor modeling in and around National Capital Region (NCR) of Delhi, India, Atmos. Environ., 41, 5595–5604, 2007.
Vogt, R. D., Seip, H. M., Larssen, T., Zhao, D. W., Xiang, R. J., Xiao, J. S., Luo, J. H., and Zhao. Y.: Potential acidifying capacity of deposition – experiences from regions with high

ACPD
10, 19593–19630, 2010

NH_4^+ and dry deposition in China, Sci. Total Environ., 367, 394–404, 2006.
Wai, K. M. and Tanner, P. A.: Relationship between the ionic composition in PM_{10} and the synoptic-scale and mesoscale weather conditions in a South China coastal city: a 4-yr study, J. Geophys. Res., 110, D18210, doi:10.1029/2004JD005385, 2005.
Wang, Q. Q. and Chen, S.-D.: SVD analysis of the relationship between Jiangnan rainy season precipitation and sea surface temperature in the Tropical Oceans, Arid Meteorol., 22, 11–16, 2004 (in Chinese).
Wang, T. J., Jiang, F., Li, S., and Liu, Q.: Trends in air pollution during 1996–2003 and cross-border transport in city clusters over the Yangtze River Delta region of China, Terr. Atmos. Ocean. Sci., 18, 995–1009, 2007.
Wang, W. X. and Wang, T.: On the origin and the trend of acid precipitation in China, Water Air Soil Poll., 85, 2295–2300, 1995.
Wang, W. X. and Wang, T.: On acid rain formation in China, Atmos. Environ., 30, 4091–4093, 1996.
Wang, W. X. and Xu, P. J.: Research progress in precipitation chemistry in China, Prog. Chem., 21, 266–281, 2009 (in Chinese).
Wang, Z. F., Akimoto H., and Uno, I.: Neutralization of soil aerosol and its impact on the distribution of acid rain over East Asia: observations and model results, J. Geophys. Res., 107(D19), 4389, doi:10.1029/2001JD001040, 2002.
Xie, Z. Q., Du, Y., Zeng, Y., Li, Y. C., Yan, M. L., and Jiao, S. M.: Effects of precipitation variation on severe acid rain in Southern China, J. Geophys. Res., 19, 489–501, 2009.
Yamaji, K., Ohara, T., Uno, I., Tanimoto, H., Kurokawa, J., and Akimoto, H.: Analysis of the seasonal variation of ozone in the boundary layer in East Asia using the Community Multi-scale Air Quality model: what controls surface ozone levels over Japan?, Atmos. Environ., 40, 1856–1868, 2006.
Yeung, M. C., Lee, S. C., Lun, B. H., and Tanner, P. A.: Summer rain events in South-East Asia: spatial and temporal variations, Atmos. Res., 86, 241–248, 2007.
Zhang, C., Wang, S., and Xing, J.: Current status and future projections of NO_x emissions from energy related industries in China, Acta Sci. Circumst., 28, 2470–2479, 2008 (in Chinese).
Zhang, G., Zeng, G. M., Du, C. Y., Jiang, Y. M., Su, X. K., Xiang, R. J., Huang, L., Xu, M., and Zhang, C.: Deposition patterns in bulk precipitation and throughfall in a subtropical mixed forest in Central-South China, Forestry, 80, 211–221, 2007.
Zhang, M. G., Uno, I., Yoshida, Y., Xu, Y. F., Wang, Z. F., Akimoto, H., Bates, T., Quinn, T.,

ACPD
10, 19593–19630, 2010

Bandy, A., and Blomquist, B.: Transport and transformation of sulfur compounds over East Asia during the TRACE-P and ACE-Asia campaigns, Atmos. Environ., 38, 6947–6959, 2004.
Zhang, M. G., Pu, Y. F., Zhang, R. J., and Han, Z. W.: Simulation of sulfur transport and transformation in East Asia with a comprehensive chemical transport model, Environ. Modell. Softw., 21, 812–820, 2006a.
Zhang, M. G., Uno, I., Zhang, R. J., Han, Z. W., Wang, Z. F., and Pu, Y. F.: Evaluation of the Models-3 Community Multi-scale Air Quality (CMAQ) modeling system with observations obtained during the TRACE-P experiment: comparison of ozone and its related species, Atmos. Environ., 40, 4874–4882, 2006b.
Zhang, F. Z., Zhang, J. Y., Zhan, H. R., Ogura, N., and Ushikubo, A.: Chemical composition of precipitation in a forest area of Chongqing, Southwest China, Water Air Soil Poll., 90, 407–415, 1996.
Zhao, D. W., Xiong, J. L., Xu, Y., and Chan, W. H.: Acid-rain in Southwestern China, Atmos. Environ., 22, 349–358, 1988.
Zhao, Y., Wang, S. X., Duan, L., Lei, Y., Cao, P. F., and Hao, J. M.: Primary air pollutant emissions of coal-fired power plants in China: current status and future prediction, Atmos. Environ., 42, 8442–8452, 2008.

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Table 1. Statistics of model results and observations.

Guanyinqiao		*N*	Mean (μmol/L)	std	Error	*R*
SO_4^{2-}	Model	48	192.43	52.55	16.07%	0.60 (sig. 95%)
	Obs	37	161.51	69.03		
NO_3^-	Model	48	48.56	46.71	−29.27%	0.84 (sig. 95%)
	Obs	48	68.65	49.82		
Hongwen						
SO_4^{2-}	Model	48	78.51	34.99	10.91%	0.65 (sig. 95%)
	Obs	43	69.94	63.16		
NO_3^-	Model	48	32.99	29.81	−11.80%	0.50 (sig. 95%)
	Obs	44	37.40	32.81		

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Table 2. pH_{VWA} and mean pH in summer during 1992–2006.

Defined region	YRM	YRL	SW	SC	NW	NE	CT	EC
pH^{*}_{VWA}	4.75	4.85	4.73	4.81	5.43	5.49	5.13	5.05
mean-pH^{**}	4.79	4.89	4.75	4.86	5.74	5.55	5.34	5.41
Rainfall(mm)***	422.4	522.5	487.1	545.7	122.1	370.4	340.8	423.1
Number of stations	6	8	14	11	10	9	13	3

* VWA average pH, ** direct average pH, *** total rainfall in summer per year per station

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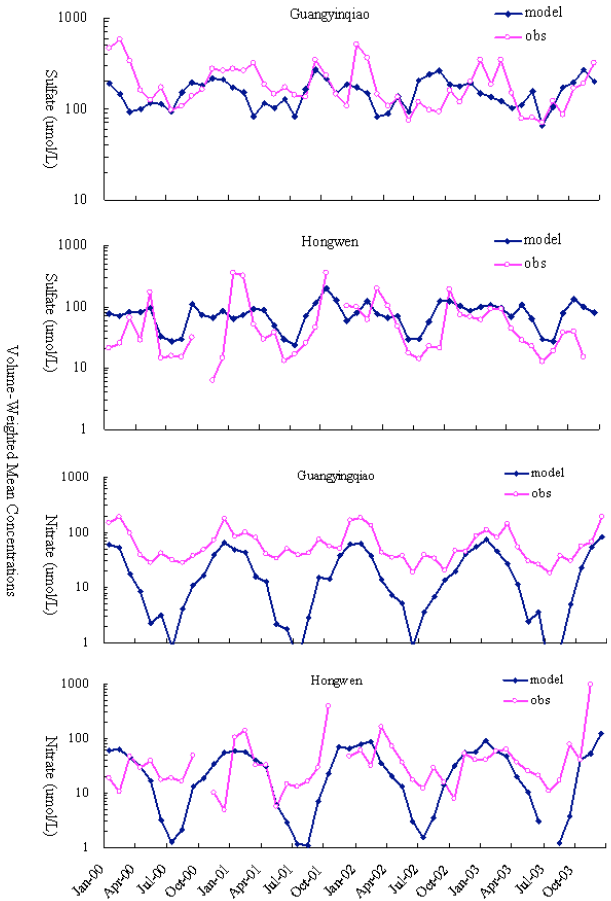

Fig. 1. Time series of monthly volume-weighted mean concentrations of sulfate and 2000–2003.

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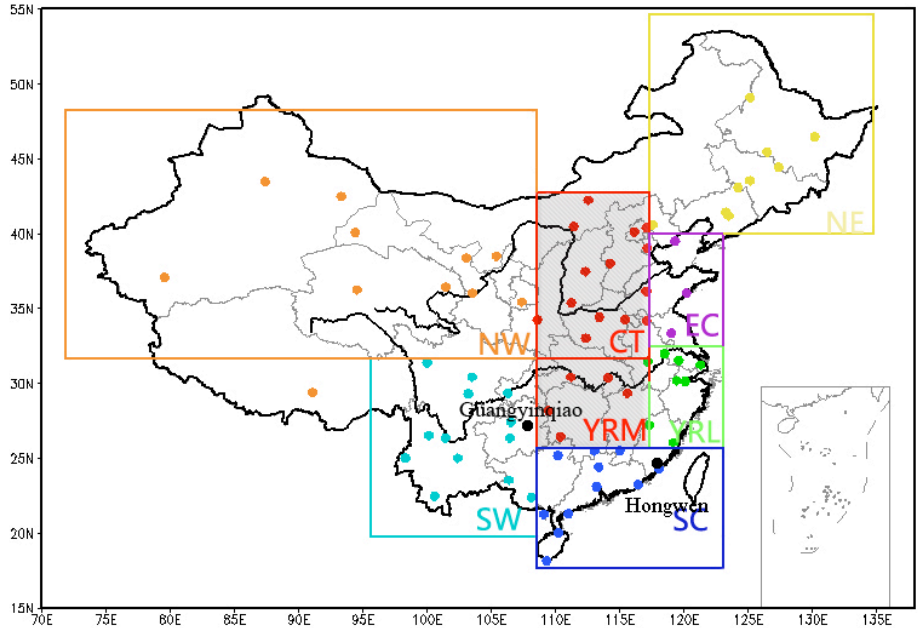

Fig. 2. Distribution of stations of CMA-ARMN and two EANET stations (Guangyinqiao and Hongwen) marked by black dot, the shadow area in CT and YRM means the key area of our study.

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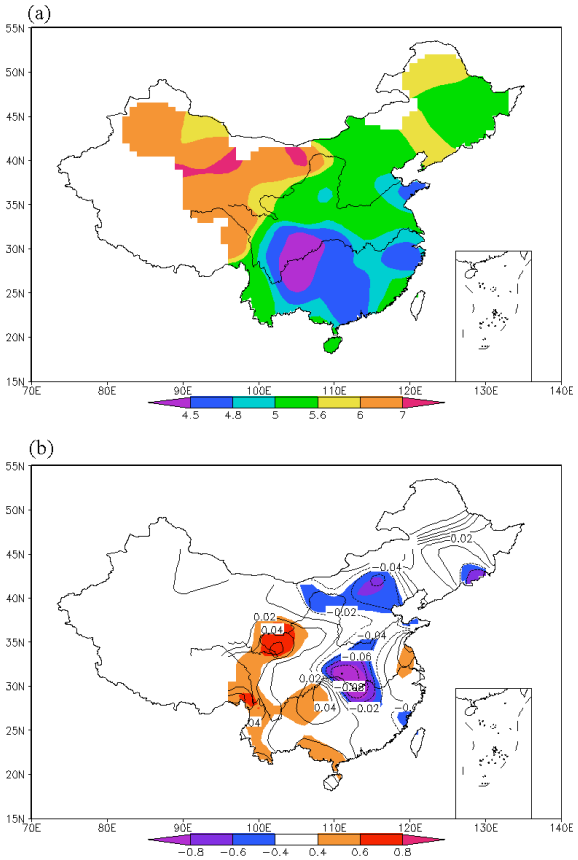

Fig. 3. Spatial patterns of the pH_{VWA} **(a)** and the changes in pH_{VWA} in China during the summer time of 1992–2006 **(b)**. The shadowed color areas in **(b)** indicate the areas with changes significant at 90% level (α=0.10) and the contour lines and colors represent the changes of pH per year and correlation coefficient.

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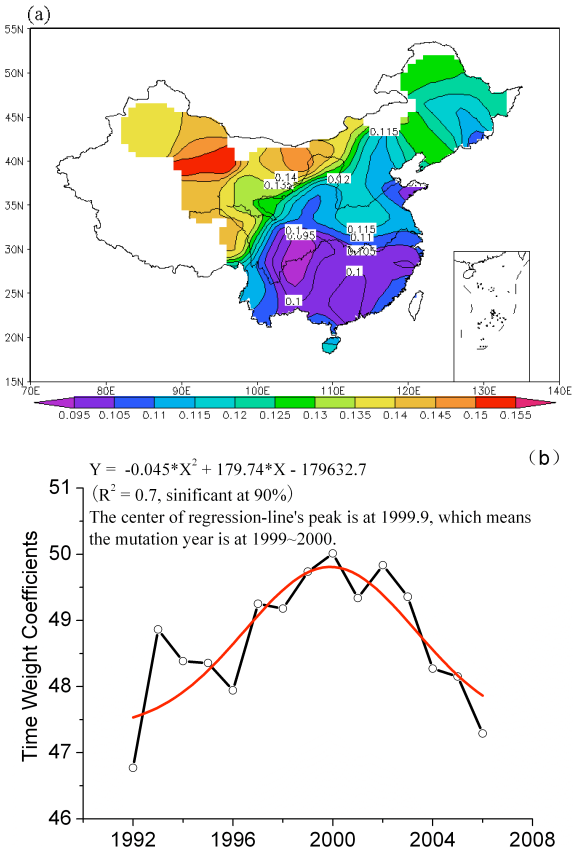

Fig. 4. Spatial distributions of the EOF eigenvectors of pH original dataset **(a)** and variation of time weighting coefficient **(b)**. The black line with circles represents the actual variation of the time weight coefficients and the red line shows the regression line with R^2=0.70 (significant at 90% level).

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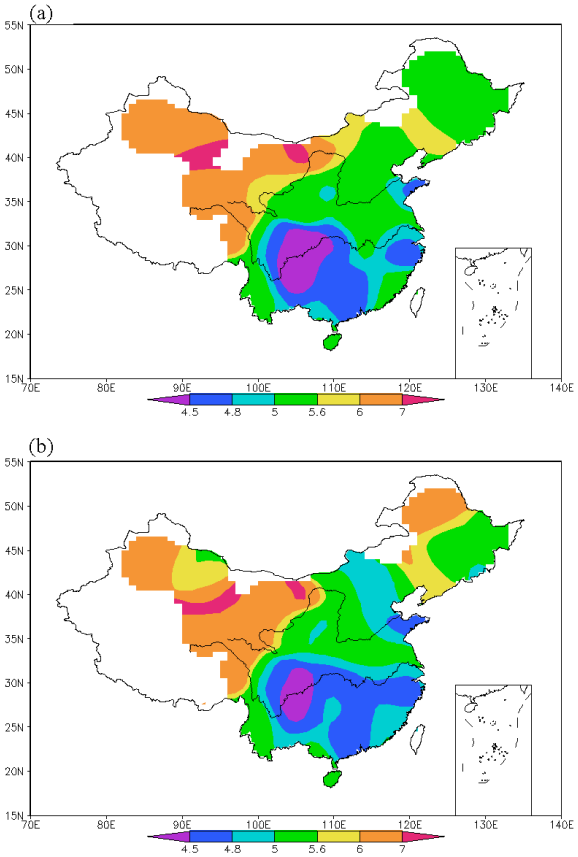

Fig. 5. Spatial distributions of the pH_{VWA} values for 1992–1999 **(a)** and for 2000–2006 **(b)**, and the differences between them **(c)**. The green and yellow shadowed areas in **(c)** indicate areas in which the differences are significant at 90 and 95% level, respectively, the real line is southeast-northwest line from 22° N, 112° E to 42° N, 105° E.

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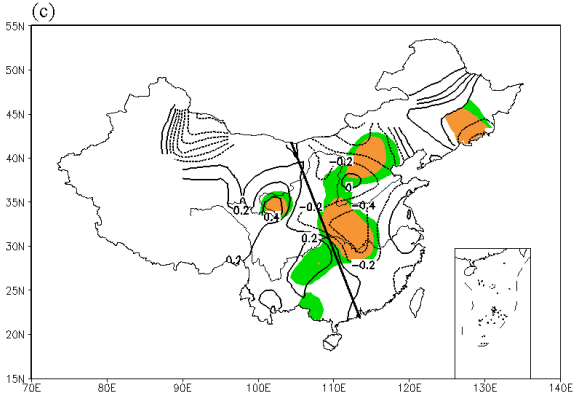

Fig. 5. Continued.

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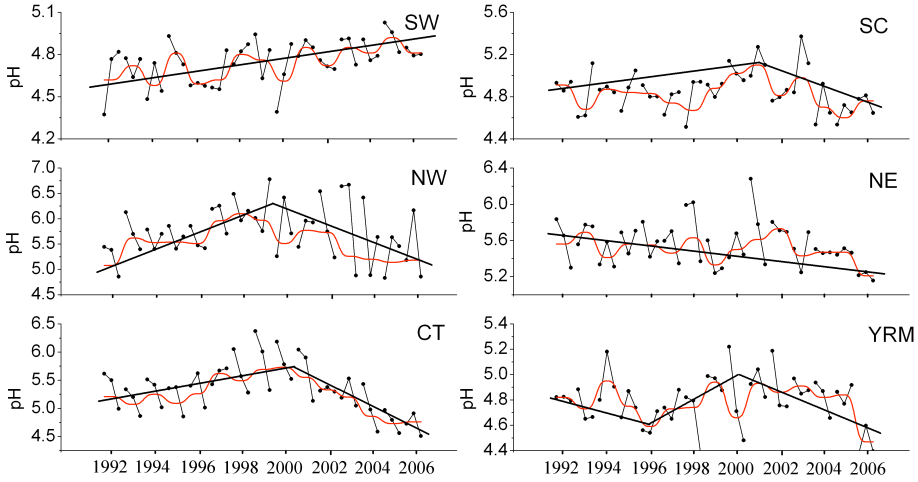

Fig. 6. Three point dash-dotted time series of pH_{VWA} in the selected regions in summer during 1992–2006.

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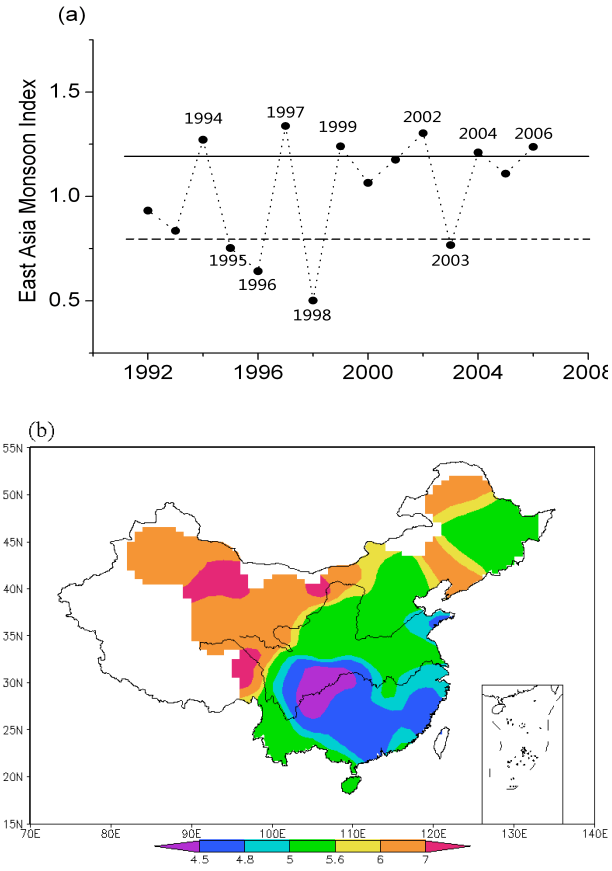

Fig. 7. Time series of EAMI **(a)**, average spatial patterns of summer pH_{VWA} in weak **(b)** and strong **(c)** summer monsoon years, and the difference between strong and weak monsoon years **(d)**.

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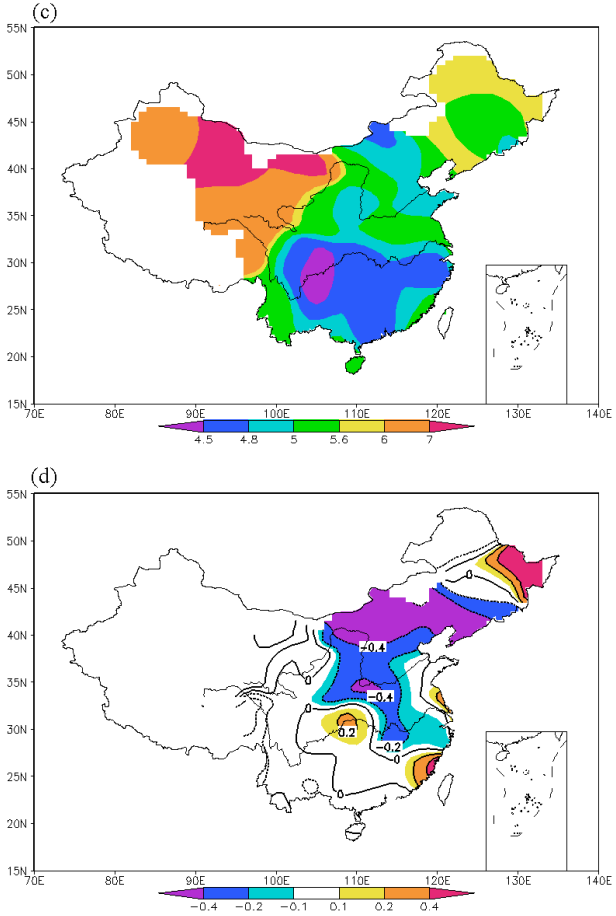

Fig. 7. Continued.

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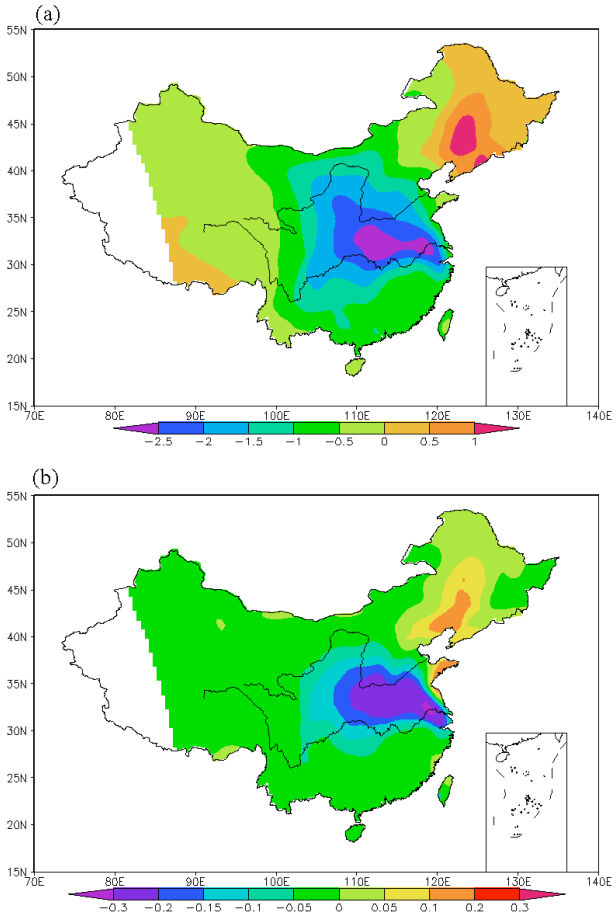

Fig. 8. Differences in the SO_4^{2-} and NO_3^- concentration (mg/m^3) between weak and strong summer monsoon years, simulated for the Normal Scenario **(a,b)** and the MC **(c,d)**.

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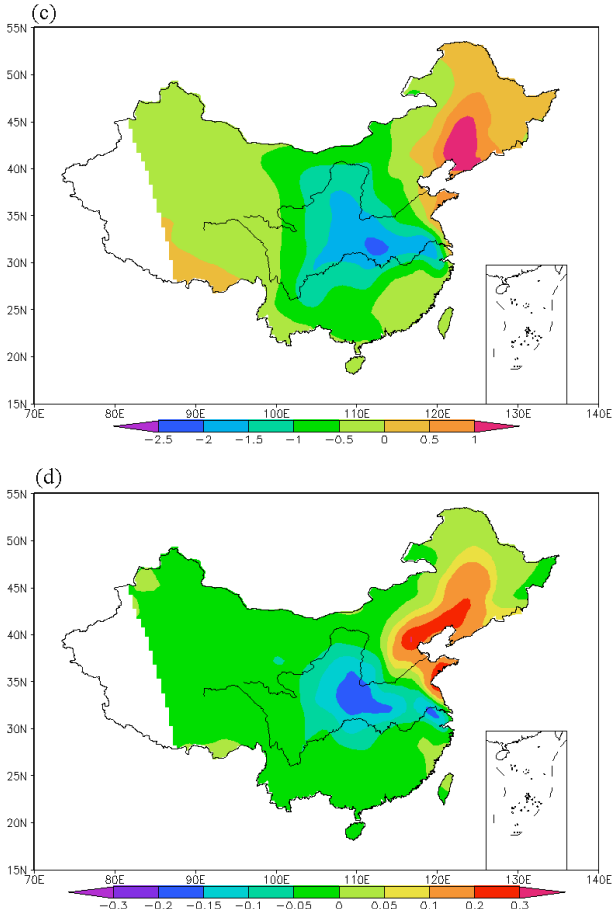

Fig. 8. Continued.

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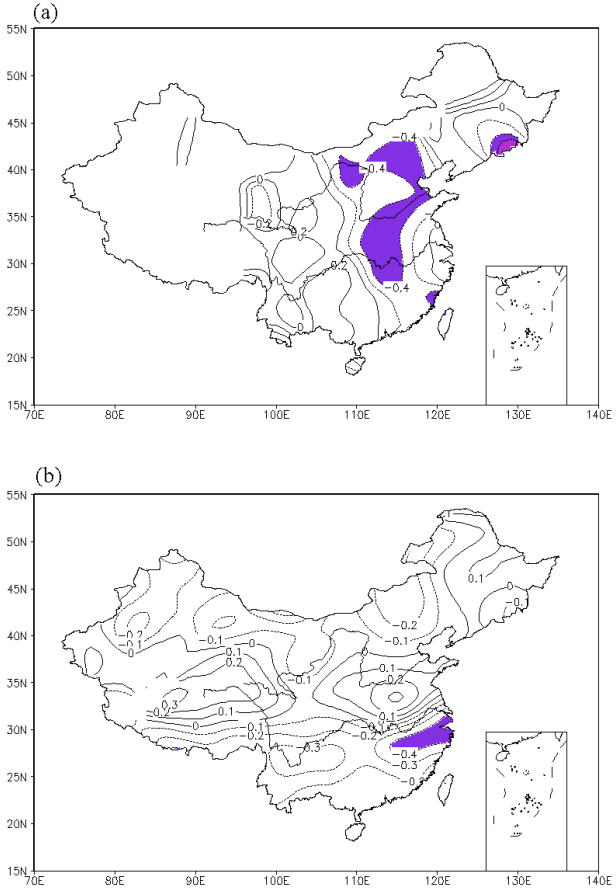

Fig. 9. The spatial patterns of left of first SVD eigenvectors (LFSE) **(a)** and right of first SVD eigenvectors (RFSE) **(b)** of summer rainfall and pH_{VWA} in China.

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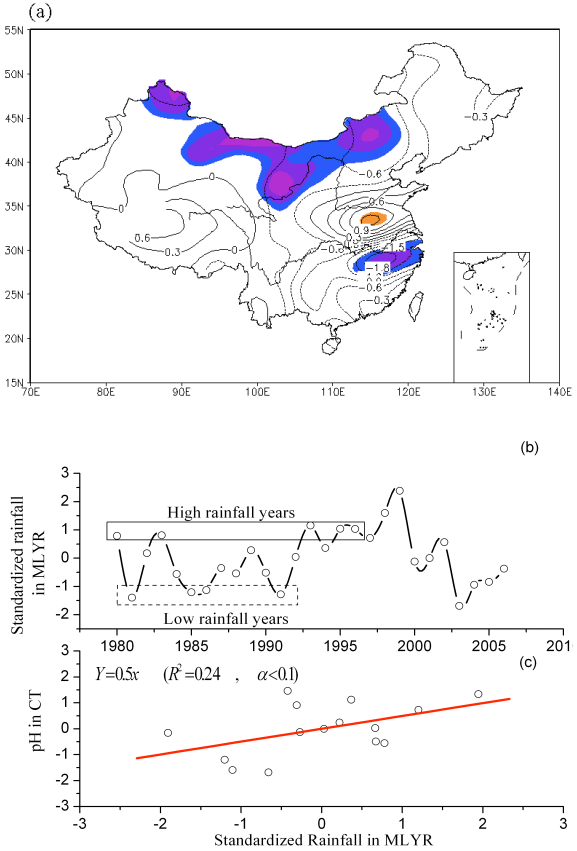

Fig. 10. (a) Changes in rainfall (mm yr^{-1}) during 1992–2006 with the shadowed areas indicating values significant at 90% level; **(b)** time series of the standardized rainfall in the MLYR during 1980–2006; **(c)** the correlation between rainfall in MLYR and pH_{VWA} in Central China during 1992–2006.

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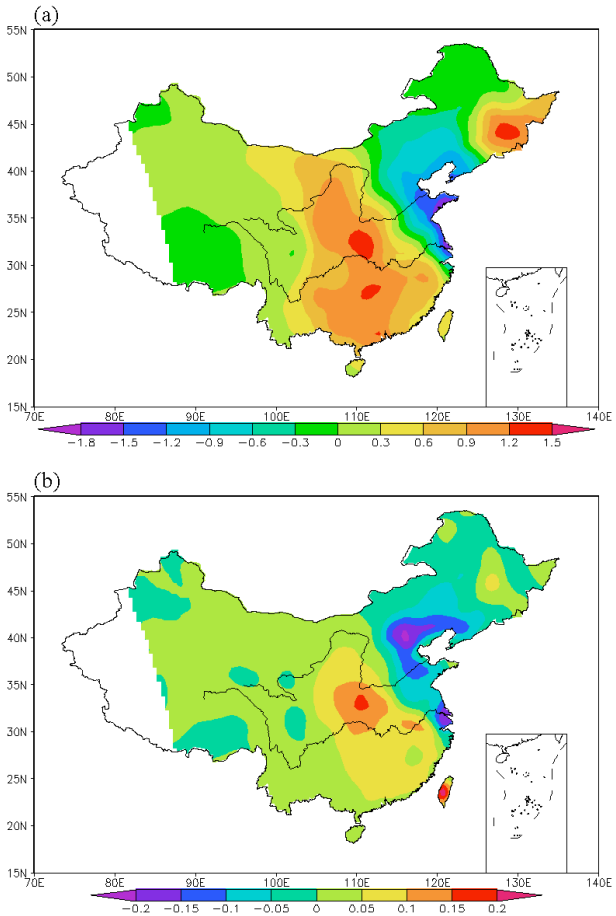

Fig. 11. Differences in the simulated rainwater SO_4^{2-} **(a)** and NO_3^- **(b)** concentrations (mg/m^3) between the low and high rainfall years.

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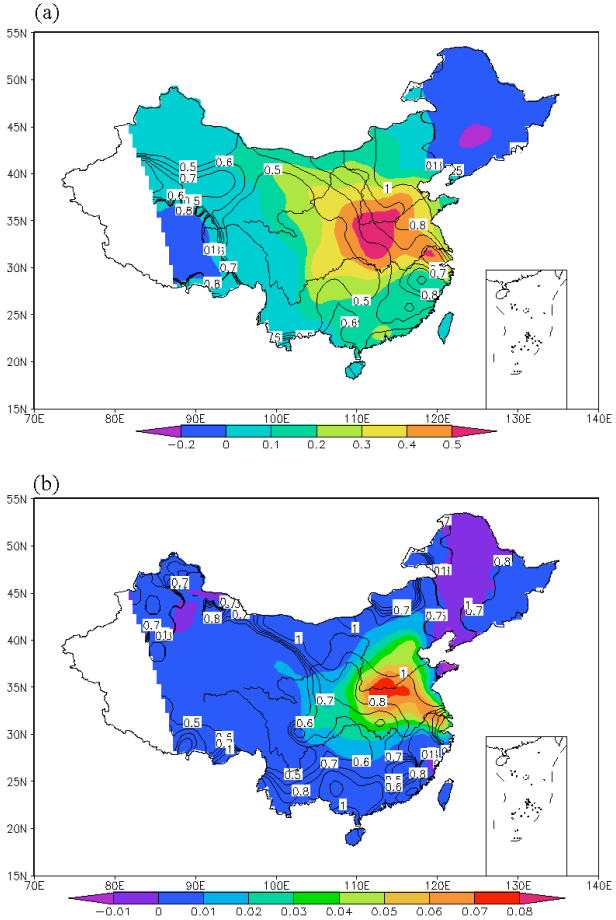

Fig. 12. Annual changes in rainwater SO_4^{2-} **(a)** and NO_3^- **(b)** concentrations during 1992–2003.

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