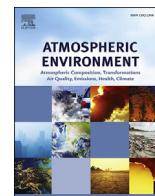




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# Atmospheric Environment

journal homepage: [www.elsevier.com/locate/atmosenv](http://www.elsevier.com/locate/atmosenv)

## Spatial and seasonal variations of atmospheric sulfur concentrations and dry deposition at 16 rural and suburban sites in China



Xiaosheng Luo<sup>a, b</sup>, Yuepeng Pan<sup>c</sup>, Keith Goulding<sup>d</sup>, Lin Zhang<sup>e</sup>, Xuejun Liu<sup>a, \*</sup>, Fusuo Zhang<sup>a</sup>

<sup>a</sup> College of Resources and Environmental Sciences, Center for Resources, Environment and Food Security, Key Lab of Plant-Soil Interaction, MOE, China Agricultural University, Beijing, 100193, China

<sup>b</sup> Institute of Plant Nutrition, Resources and Environmental Sciences, Henan Academy of Agricultural Sciences, Henan Key Laboratory of Agricultural Environment, Zhengzhou, 450002, China

<sup>c</sup> State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry (LAPC), Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, China

<sup>d</sup> The Sustainable Soils and Grassland Systems Department, Rothamsted Research, Harpenden, AL5 2JQ, UK

<sup>e</sup> Laboratory for Climate and Ocean-Atmosphere Studies, Department of Atmospheric and Oceanic Sciences, School of Physics, Peking University, Beijing, 100871, China

### HIGHLIGHTS

- Sulfur (S) dry deposition was quantified at eight southern and eight northern sites in China.
- Total SO<sub>2</sub> plus pSO<sub>4</sub><sup>2-</sup> deposition (3.1–27.1 kg S ha<sup>-1</sup> yr<sup>-1</sup>) showed large spatial variation across all sites.
- Concentration and dry deposition of S were remarkably higher at northern than southern sites.
- Low pSO<sub>4</sub><sup>2-</sup>/pNO<sub>3</sub> ratios at most sites reflected increasing NO<sub>x</sub> relative to SO<sub>2</sub> emissions.

### ARTICLE INFO

#### Article history:

Received 11 January 2016

Received in revised form

8 July 2016

Accepted 12 July 2016

Available online 14 July 2016

#### Keywords:

Acid rain

Particulate matter

SO<sub>2</sub>

Sulfate

Dry deposition

China

### ABSTRACT

The large emissions of sulfur dioxide (SO<sub>2</sub>) in China have raised worldwide concerns due to its contribution to acid rain and particulate pollution. Monitoring sulfur (S) concentrations and estimating its deposition are important for evaluating air quality and its effects on ecosystems and human health. To date atmospheric dry S deposition in China remains unclear due to the paucity of measurements, especially in rural regions where the ecosystems are sensitive to acid deposition. In this study, we monitored both SO<sub>2</sub> and particulate SO<sub>4</sub><sup>2-</sup> (pSO<sub>4</sub><sup>2-</sup>) concentrations at 8 sites south and 8 sites north of the Huai River in rural and suburban parts of China between 2010 and 2012. The measured concentration of SO<sub>2</sub> and pSO<sub>4</sub><sup>2-</sup> were combined with GEOS-Chem modeled dry deposition velocities to estimate dry S deposition inputs to the surfaces. SO<sub>2</sub> and pSO<sub>4</sub><sup>2-</sup> concentrations were high from October/November to next March/April and they (esp. SO<sub>2</sub>) decreased sharply since March/April at the northern sites, reflecting elevated SO<sub>2</sub> emissions by winter heating (which normally starts in October/November and ends in March/April in the north of the Huai River). However the southern sites did not show this trend. Annual dry deposition of SO<sub>2</sub> plus pSO<sub>4</sub><sup>2-</sup> in this study ranged from 3.1 to 27.1 kg S ha<sup>-1</sup> across all the sites in the year 2011 (except one site from May 2011 to April 2012) and showed large spatial variation. The sites in northern China had greater dry deposition due to the higher S concentrations compared with sites in southern China. We also found relatively low pSO<sub>4</sub><sup>2-</sup>/pNO<sub>3</sub> ratios at most sites, reflecting NO<sub>x</sub> emissions had a larger influence than SO<sub>2</sub> emissions on particle composition during the 2010–2012 period at the measurement sites. Our results suggest that dry S deposition is still important input to ecosystems in spite of slow reduction of Chinese national SO<sub>2</sub> emissions since 2005. More research on both wet and dry S deposition and their impacts on the environment and human health should be carried out following the introduction of policies to reduce SO<sub>2</sub> emissions.

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\* Corresponding author.

E-mail address: [liu310@cau.edu.cn](mailto:liu310@cau.edu.cn) (X. Liu).

## 1. Introduction

Global anthropogenic sulfur dioxide (SO<sub>2</sub>) emissions increased rapidly from the 1850s and peaked in the 1970s (Smith et al., 2011), mainly caused by an increasing use of coal for industrial activities. As the precursor of sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), gaseous SO<sub>2</sub> contributes to acid deposition, which affects the environment in a variety of ways (Su et al., 2011). H<sub>2</sub>SO<sub>4</sub> can react with NH<sub>3</sub> to form NH<sub>4</sub>HSO<sub>4</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> in air (Fagerli and Aas, 2008), which contribute significantly to secondary aerosols with significant health and climate concerns (Mensah et al., 2012; Zhang et al., 2012a). Besides, SO<sub>2</sub> has many detrimental effects on the global environment such as soil and water acidification and direct damage to crop plants. In addition, sulfur (S) deposition can increase the emissions of nitrous oxide (N<sub>2</sub>O) and nitric oxide (NO) from soil indirectly by acidifying the soil and increasing the proportions of these gases produced by denitrification, which has an adverse effect on global climate (Cai et al., 2012). In light of these concerns, control of SO<sub>2</sub> emission is crucial to improving air quality and decreasing damage to the environment and health worldwide. In fact, total global SO<sub>2</sub> emissions have decreased over the last 30 years, mainly due to substantial reductions in major developed economies such as North America and Europe as coal has been replaced by natural gas and other forms of energy (Sickles and Shadwick, 2015; Fowler et al., 2009).

Anthropogenic SO<sub>2</sub> emissions in China are an environmental concern because they have contributed approximately 25% of global emissions and more than 90% of those in East Asia since the 1990s (Lu et al., 2010). The very high SO<sub>2</sub> emissions in China are mainly due to both rapid economic development and the large consumption of coal. China's energy consumption structure lays particular stress on coal. The consumption of coal contributes to about 70% of total energy use - much more than the world average; 90% of national SO<sub>2</sub> emissions derive from coal burning (Kanada et al., 2013). The Chinese Government took measures to control SO<sub>2</sub> emissions following the 10th Five-Year Plan (2001–2005). However, the 10% reduction target from the 2000 level was not achieved by the end of 2005 (Lin et al., 2012). China therefore set new targets and effective measures to control SO<sub>2</sub> emissions, such as insisting that all new thermal power units as well as most existing units must have flue gas desulphurization (FGD) systems installed, and small units with low energy efficiency should be gradually shutdown. As a result, total national SO<sub>2</sub> emissions decreased by 14.3% from 2005 to 2010 (Zhao et al., 2008; Wang et al., 2012) and very significant decreases in SO<sub>2</sub> emissions and concentrations were reported in some Chinese megacities such as Beijing (SO<sub>2</sub> concentrations declined from 120 μg m<sup>-3</sup> in 1998 to 47 μg m<sup>-3</sup> in 2007) and Shanghai (SO<sub>2</sub> concentrations decreased by about 50% from 2005 to 2010) (Zhang et al., 2011; Wang et al., 2014). However, controlling SO<sub>2</sub> emissions still remains a big challenge for China because the economy and industry continue to develop, and some industrial facilities (such as iron, steel and cement works) continue to consume very large amounts of coal without installing desulfurization systems (Zhang et al., 2012b).

Sulfur deposited from emitted SO<sub>2</sub> has been regarded as the main contributor to acid deposition, which is an important environmental problem in China (Pan et al., 2013). Compared to developed countries, which conducted much research on S deposition, developing countries including China have conducted very little research (Fowler et al., 2009). Though China is the largest SO<sub>2</sub> emitter in the world, research into S deposition, especially dry deposition, is still lacking (Pan et al., 2013).

To determine the distribution of acid rain in China, many acid rain monitoring sites and programs have been introduced since the 1980s (Wang and Hao, 2012; Wang et al., 2012). However, the current national particulate sulfate (pSO<sub>4</sub><sup>2-</sup>) monitoring network is

poor, especially in rural regions, and cannot provide a complete analysis of SO<sub>2</sub> mitigation policy, in particular how it affects current particulate pollution and S deposition in China (Xin et al., 2015). China is a large agricultural country and the rural regions are very important for food production. As well as being a pollutant in natural ecosystems, S is one of the essential elements for plant growth and S deposition is an important input to croplands (Zhang et al., 2003). Therefore monitoring atmospheric S concentrations and calculating its dry deposition in typical Chinese rural regions will provide detailed information on the nutritional requirements of crops for S, the country's S pollution status, and the effectiveness of the SO<sub>2</sub> emission control measures.

In this study we selected 16 representative rural and suburban sampling sites, of which eight sites were located north of the Huai River (a border line dividing China into North and South in terms of its centralized home heating policy, with heating in the north but not the south), and eight sites were located south of the Huai river (shown in Fig. 1). We measured SO<sub>2</sub> and pSO<sub>4</sub><sup>2-</sup> concentrations and calculated their dry deposition at the sampling sites. The objective of this study was to provide an overall evaluation of atmospheric S pollution and dry deposition, as well as their potential environmental effects in typical rural and suburban regions of China.

## 2. Materials and methods

### 2.1. Monitoring approach on SO<sub>2</sub> and pSO<sub>4</sub><sup>2-</sup>

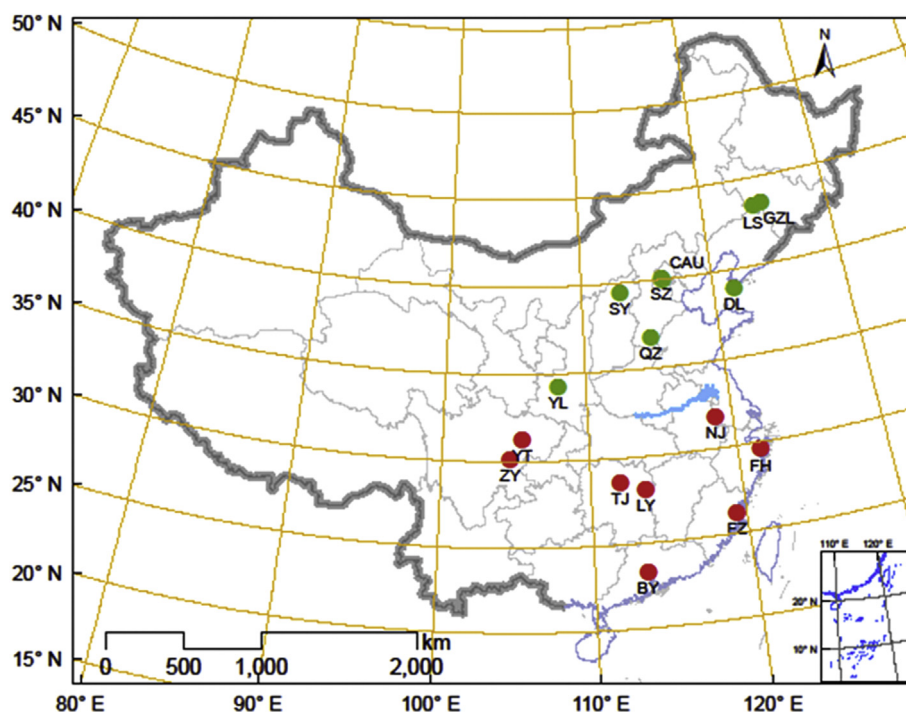
Atmospheric SO<sub>2</sub> and particulate sulfate (pSO<sub>4</sub><sup>2-</sup>) were collected using a DELTA (DENuder for Long-Term Atmospheric Sampling) system. The DELTA system contains denuders collecting reactive nitrogen (N) gases and SO<sub>2</sub> and filters to collect, in order, the particulate nitrate (pNO<sub>3</sub>), particulate ammonium (pNH<sub>4</sub><sup>+</sup>) and pSO<sub>4</sub><sup>2-</sup>. The system contains a mini pump (air flow rate was 0.3 L min<sup>-1</sup>) to maintain air flow through the denuders and filters (Tang et al., 2009). We used the system previously to monitor the atmospheric reactive N concentrations and estimate N deposition in different regions of China (Luo et al., 2013, 2014; Xu et al., 2015). The sampling frequency of the DELTA system was once per month at all the sampling sites. The first and second denuders were extracted with 10 ml 0.05% H<sub>2</sub>O<sub>2</sub> solution. Following analysis of NO<sub>3</sub><sup>-</sup>-N and NH<sub>4</sub><sup>+</sup>-N in the solution with a continuous-flow analyzer (Seal AA3, Germany), SO<sub>4</sub><sup>2-</sup> (transformed from SO<sub>2</sub>) in solution was measured by ion chromatography (761 Compact, Swiss); all analyses were made within one month of extraction. All the samples were refrigerated (at 4 °C) and the analyses made at China Agricultural University, Beijing. The sampling period was from the beginning to the end of each calendar month. After extraction and analysis, the concentration of S in air can be calculated from the measured concentrations and the volume of air passing through the Delta sampler. The formula for this is:

$$\chi_a = (C_e - C_b) \times v/V$$

where  $\chi_a$  represents S concentration (μg S m<sup>-3</sup>),  $C_e$  represents the concentration of S in the extract (μg S L<sup>-1</sup>),  $C_b$  represents the concentration of S in the blank (μg S L<sup>-1</sup>),  $v$  represents the volume of the extract (L), and  $V$  the volume of air passing through the sampler during the sampling period (m<sup>3</sup>). The sampling and S measurements were conducted at ambient temperature and air pressure and the final S concentrations and dry deposition fluxes at all sites were also expressed at ambient temperature and pressure.

### 2.2. Sampling sites and sampling period

A total of 16 sampling sites were established to monitor the SO<sub>2</sub>



**Fig. 1.** Distribution of the sixteen sampling sites. Eight sampling sites north of the Huai River (Green circles) and eight were south of the Huai River (Red circles). Blue line represents the Huai River, Red color circles all belong to south China and green color circles belong to North China. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

and  $\text{pSO}_4^{2-}$  concentrations. All the sites were located in rural regions or suburban areas. Considering the observed close relationship between winter heating (coal burning induced  $\text{SO}_2$  emissions) and  $\text{SO}_2$  concentrations in air, we divided the monitoring sites into two groups: 8 sampling sites to the north of the Huai River (where heating is used in winter) and 8 sampling sites to the south of the Huai River (where there is no heating in winter). The distribution of specific sampling sites is shown in Fig. 1. The northern sampling sites were Lishu (LS), Gongzhuling (GZL), Dalian (DL), China Agricultural University (CAU), Shangzhuang (SZ), Quzhou (QZ), Yangling (YL) and Shanyin (SY). LS and GZL are in Jilin province and DL is in Liaoning province. All these three sampling sites can be regarded as being in the Northeast region of China. LS and GZL are rural, near farmland, where the crop was spring maize. DL is in a suburb of Dalian city, and is therefore a suburban site. The North China region contained 3 sampling sites which were CAU, SZ, and QZ. CAU and SZ are located in a suburb of Beijing, with CAU being closest to downtown Beijing. CAU and SZ belong to the experimental station of China Agricultural University and the crops grown during sampling were mainly winter wheat and summer maize. QZ was a rural site in Quzhou county, Hebei province, and the cropping system was a rotation of winter wheat and summer maize. YL is a rural site in Shaanxi province and the crops grown were also winter wheat and summer maize. SY was a rural site in north Shanxi province and the crop grown was mainly spring maize. The Southern sampling sites were Ziyang (ZY), Yanting (YT), Liuyang (LY), Taojiang (TJ), Nanjing (NJ), Fenghua (FH), Fuzhou (FZ), and Baiyun (BY). ZY and YT are in a rural region of Sichuan province and crops grown were wheat, rice and oilseed rape. LY and TJ are in Hunan province. LY is in a suburb of Changsha city and TJ is a rural site of Taojiang county. Double rice is the main cropping system at the two sites. NJ is a suburban site in Jiangsu province, and it is located at an experiment station of Nanjing Agricultural University and the crops grown were rice and wheat. FH is a rural site in Zhejiang province where the crops are mainly rice and vegetables.

FZ is a mountainous rural site near Fuzhou city, Fujian province, where rice and tobacco are the main crops. BY is located at an Agricultural Experimental Station in a suburb of Guangzhou city, Guangdong province, and the cropping system is double rice. The monitoring started in 2010 and ended in 2012 at all sites except YT (monitoring started in 2011 and ended in 2012). Detailed sampling periods at all sites were as follows: QZ, SY (2010.4–2012.6), CAU, FZ, LS, SZ, YL (2010.4–2012.8), BY (2010.5–2012.8), ZY (2010.7–2012.2), GZL (2010.7–2012.8), FH (2010.8–2012.5), LY (2010.9–2012.2), NJ (2010.9–2012.6), DL (2010.9–2012.7), TJ (2010.10–2012.8), and YT (2011.5–2012.8).

### 2.3. Backward trajectories of $\text{SO}_2$ using TrajStat analysis

In order to identify the origin of air mass and the source of  $\text{SO}_2$  from northern China, three-day backward trajectories arriving at five selected sampling sites (NJ, YT, TJ, FH, BY) during January, April, July and October in the monitoring period were calculated using TrajStat (version 1.4.4R4). TrajStat is a GIS-based software, including a trajectory calculation module of HYSPLIT (Hybrid Single Particle Lagrangian Integrated Trajectory Model) (Wang et al., 2009). Meteorological data with a resolution of  $0.5^\circ \times 0.5^\circ$  were inputted from the Global Data Assimilation System (GDAS) meteorological data archives of the Air Resources Laboratory, National Oceanic and Atmospheric Administration (NOAA). All backward trajectories were calculated at 6 h intervals (00:00, 06:00, 12:00, 18:00 UTC) at each day, with an arrival height of 500 m above the ground.

### 2.4. Sulfur dry deposition

The inferential technique, which combines the measured concentration and a modeled dry deposition velocity ( $V_d$ ), was used to estimate the dry deposition flux of S species (Schwede et al., 2011; Pan et al., 2012). The concentrations of gaseous  $\text{SO}_2$  and  $\text{pSO}_4^{2-}$  were measured as described in Section 2.1. The  $V_d$  of  $\text{SO}_2$  and  $\text{pSO}_4^{2-}$  were

calculated based on a GEOS-Chem chemical transport model (CTM) for all the sampling sites. In brief, the GEOS-Chem 3-D global CTM (<http://geos-chem.org>) was driven by GEOS-5 (Goddard Earth Observing System) assimilated meteorological data from the NASA Global Modeling and Assimilation Office (GMAO), with a temporal resolution of 6 h (3 h for surface variables and mixing depths) and a horizontal resolution of  $1/2^\circ$  latitude  $\times$   $2/3^\circ$  longitude. We used a nested-grid version of GEOS-Chem for Asia that has the native  $1/2^\circ \times 2/3^\circ$  resolution over East Asia ( $70^\circ\text{E}$ – $150^\circ\text{E}$ ,  $11^\circ\text{S}$ – $55^\circ\text{N}$ ), and a  $2^\circ \times 2.5^\circ$  resolution over the rest of the world (Chen et al., 2009; Zhao et al., 2015). A similar nested model for North America has been previously applied to analyze N deposition over the United States (Zhang et al., 2012c; Ellis et al., 2013).

In GEOS-Chem parameterization of the dry deposition of gases and aerosols follows a standard big-leaf resistance-in-series model (Wesely, 1989). The  $V_d$  is calculated as the function  $v_d = (R_a + R_b + R_c)^{-1}$  determined by local meteorological conditions and surface type, as described in Zhang et al. (2012c). Here  $R_a$  is the aerodynamic resistance to turbulent transfer from the lowest model layer (70 m above the surface) to the roughness height,  $R_b$  is the boundary layer resistance to molecular diffusion, and  $R_c$  is the canopy or surface uptake resistance. In this study we have run the model calculation of dry deposition velocities for the whole of 2012 and archived the hourly values for both gases and aerosols over the model domain. Monthly  $V_d$  was then calculated based on the hourly outputs (Table 1) for further estimation of the dry deposition flux of each species during the observation period from 2010 to 2012.

Considerable uncertainties may exist due to the relatively coarse model  $1/2^\circ \times 2/3^\circ$  resolution for representing the local land characteristics at the monitoring sites. For the 16 sites, rural or cropland sites have relatively homogenous agricultural land uses within the

model grid cell, while the land uses for suburban sites can be a mixture of croplands and some urban constructions. Further increasing the grid resolution for the  $V_d$  calculation would require assimilated meteorological fields at a finer resolution or in-situ meteorological measurements, which are not available at present. We compare the GEOS-5 derived  $V_d$  values with those from GEOS-FP data (a newer version replacing GEOS-5 with a finer resolution of  $1/4^\circ \times 5/16^\circ$ , yet only available after 2013). The hourly  $V_d$  values for  $\text{SO}_2$  and  $\text{pSO}_4^{2-}$  can differ by 40%, but much smaller (15%) when averaged monthly.

We calculate the dry deposition fluxes for  $\text{SO}_2$  and  $\text{pSO}_4^{2-}$  using the measured monthly mean concentrations multiplied by the modeled monthly  $V_d$ . It shall be acknowledged that this approach would omit the deposition covariance term associated with higher temporal variations, such as hourly and daily. In a study at a northeastern US forest site, Horii et al. (2005) found that the diel concentration and inferred deposition velocity of  $\text{SO}_2$  had been shown to correlate strongly, with highest values in the daytime; thus, when average weekly  $\text{SO}_2$  concentration was used to calculate the flux,  $F(\text{SO}_2)$  can be systematically underestimated by as much as 40% (Matt and Meyers, 1993). Adon et al. (2013) suggested that this missing covariance term would induce an uncertainty of ~20% to dry deposition estimates of species with strong diurnal variations.

### 3. Results

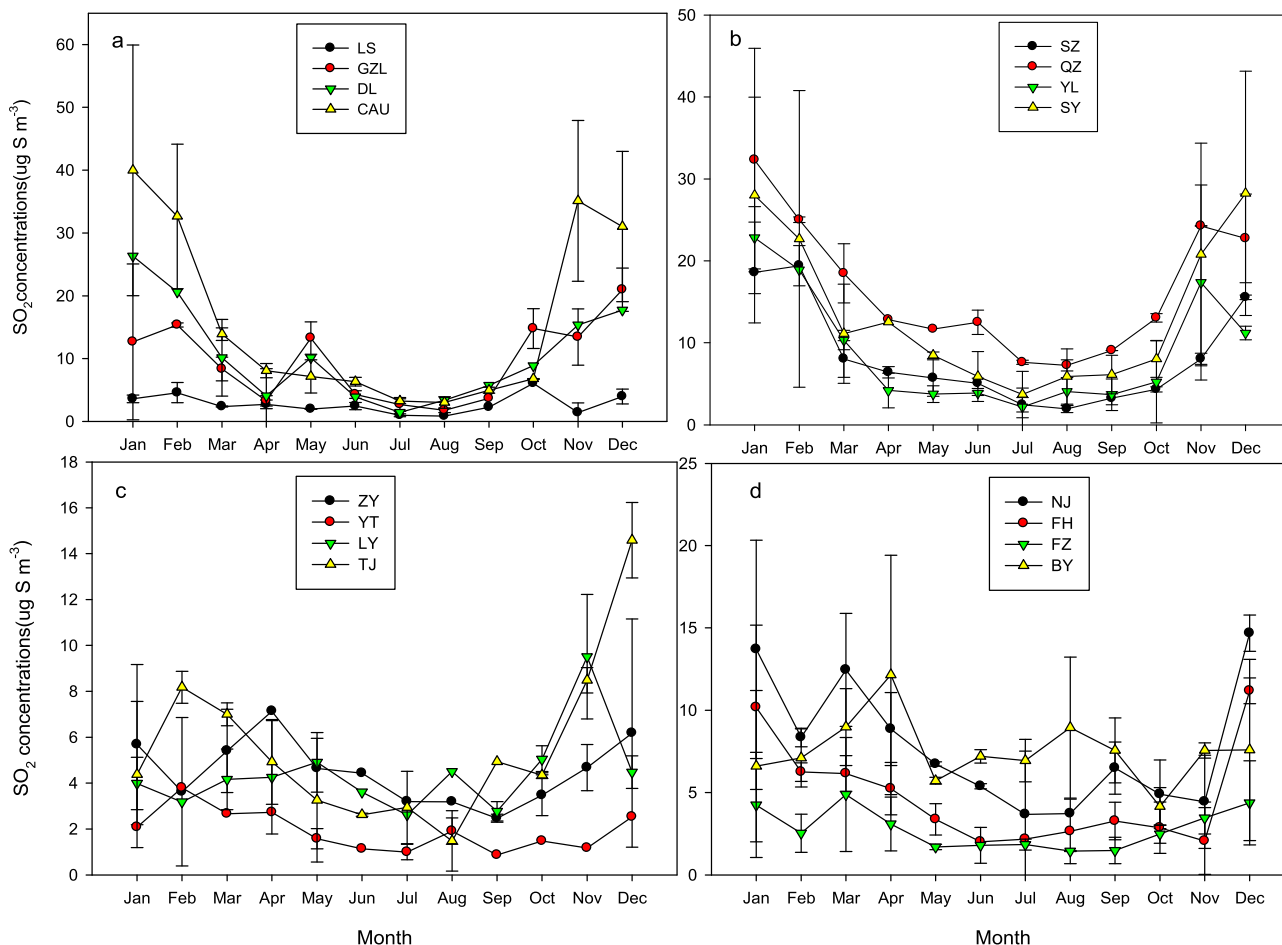
#### 3.1. Atmospheric $\text{SO}_2$ concentrations

Fig. 2 shows the monthly  $\text{SO}_2$  concentrations at all 16 sampling sites. To show the results clearly, each sub-figure contains results from 4 sampling sites: Fig. 2 a and b represent the Northern region

**Table 1**  
Monthly  $V_d$  ( $\text{cm s}^{-1}$ ) of  $\text{SO}_2$  and  $\text{pSO}_4^{2-}$  at the different sampling sites.

Site	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Ave.
$\text{SO}_2$													
LS	0.30	0.30	0.30	0.32	0.37	0.48	0.54	0.52	0.47	0.36	0.26	0.20	0.37
GZL	0.30	0.29	0.30	0.30	0.36	0.50	0.54	0.52	0.48	0.34	0.26	0.20	0.37
DL	0.49	0.56	0.87	1.18	0.96	1.22	1.16	0.92	1.11	1.21	1.33	0.68	0.97
CAU	0.30	0.30	0.32	0.38	0.54	0.59	0.57	0.58	0.56	0.49	0.32	0.30	0.44
SZ	0.30	0.30	0.32	0.38	0.54	0.59	0.57	0.58	0.56	0.49	0.32	0.30	0.44
QZ	0.30	0.31	0.35	0.40	0.38	0.34	0.42	0.46	0.44	0.36	0.31	0.30	0.36
YL	0.29	0.30	0.34	0.42	0.48	0.48	0.47	0.50	0.48	0.40	0.31	0.30	0.40
SY	0.30	0.30	0.30	0.31	0.37	0.41	0.42	0.42	0.40	0.36	0.30	0.30	0.35
ZY	0.30	0.30	0.34	0.32	0.31	0.36	0.43	0.39	0.36	0.32	0.30	0.31	0.34
YT	0.31	0.33	0.36	0.36	0.38	0.42	0.45	0.44	0.43	0.39	0.34	0.31	0.38
LY	0.32	0.30	0.34	0.37	0.44	0.43	0.43	0.44	0.46	0.46	0.39	0.31	0.39
TJ	0.31	0.30	0.32	0.36	0.39	0.39	0.41	0.43	0.45	0.41	0.35	0.31	0.37
NJ	0.31	0.32	0.35	0.41	0.40	0.39	0.42	0.42	0.43	0.36	0.31	0.31	0.37
FH	0.31	0.32	0.35	0.41	0.45	0.42	0.43	0.48	0.47	0.40	0.34	0.30	0.39
FZ	0.67	0.69	0.71	0.70	0.71	0.76	0.72	0.74	0.68	0.69	0.65	0.65	0.70
BY	0.35	0.35	0.35	0.36	0.36	0.37	0.37	0.37	0.38	0.41	0.42	0.36	0.37
$\text{pSO}_4^{2-}$													
LS	0.10	0.13	0.15	0.20	0.25	0.19	0.21	0.19	0.17	0.13	0.09	0.07	0.15
GZL	0.10	0.13	0.16	0.20	0.25	0.19	0.19	0.19	0.16	0.13	0.09	0.07	0.16
DL	0.11	0.09	0.08	0.08	0.08	0.09	0.09	0.08	0.09	0.09	0.11	0.12	0.09
CAU	0.14	0.18	0.21	0.24	0.30	0.28	0.24	0.18	0.22	0.18	0.14	0.12	0.20
SZ	0.14	0.18	0.21	0.24	0.30	0.28	0.24	0.18	0.22	0.18	0.14	0.12	0.20
QZ	0.11	0.16	0.21	0.24	0.31	0.31	0.25	0.24	0.25	0.22	0.14	0.12	0.21
YL	0.14	0.17	0.19	0.24	0.27	0.32	0.23	0.24	0.20	0.19	0.15	0.12	0.21
SY	0.13	0.16	0.19	0.22	0.29	0.30	0.23	0.19	0.21	0.17	0.13	0.13	0.20
ZY	0.18	0.21	0.26	0.29	0.26	0.25	0.15	0.19	0.19	0.19	0.18	0.16	0.21
YT	0.16	0.18	0.21	0.26	0.25	0.26	0.14	0.18	0.17	0.17	0.16	0.14	0.19
LY	0.17	0.17	0.17	0.17	0.19	0.14	0.10	0.12	0.15	0.18	0.12	0.13	0.15
TJ	0.17	0.18	0.18	0.18	0.18	0.16	0.10	0.12	0.15	0.18	0.13	0.13	0.16
NJ	0.14	0.16	0.16	0.17	0.20	0.22	0.11	0.11	0.12	0.15	0.13	0.12	0.15
FH	0.15	0.16	0.17	0.17	0.16	0.12	0.09	0.12	0.12	0.14	0.13	0.12	0.14
FZ	0.11	0.12	0.14	0.12	0.13	0.11	0.09	0.10	0.11	0.11	0.10	0.10	0.11
BY	0.16	0.17	0.17	0.15	0.10	0.10	0.08	0.09	0.09	0.14	0.12	0.13	0.13





**Fig. 2.** Monthly average  $\text{SO}_2$  concentrations at 16 sampling sites from varying monitoring period 2010 or 2011 to 2012 ( $\mu\text{g S m}^{-3}$ ). a, b represent Northern China; c, d represent Southern China. Error bars represent the variations each month across the 1–3 years of sampling at each site, with warm season (April to August) monthly averages based on 2–3 years of data and cold season (September to March) on 1–2 years of data. The meaning of the ends of the whiskers represent minimum and maximum values of the monitoring period at each site.

(north of the Huai River) and Fig. 2 c and d the Southern region (south of the Huai River). Airborne  $\text{SO}_2$  concentrations showed large seasonal variation in the North (Fig. 2a,b). Peak  $\text{SO}_2$  concentrations mainly occurred in winter. LS and GZL are in the Northeast of China and the  $\text{SO}_2$  concentrations there increased in October, consistent with the onset of winter heating provided by coal burning (usually starting in mid-October).  $\text{SO}_2$  concentrations at the other sites DL, CAU, SZ, QZ, YL, SY increased sharply in November and also matched the onset of heating in these areas. Average  $\text{SO}_2$  concentrations at LS, GZL, DL, CAU, SZ, QZ, YL, SY were 2.76 (27-month average), 9.54 (26-month average), 10.64 (23-month average), 16.01 (27-month average), 8.23 (27-month average), 16.40 (25-month average), 8.96 (27-month average), 13.46 (25-month average)  $\mu\text{g S m}^{-3}$ , respectively. The highest value was observed in QZ in Hebei province. The two sites in Beijing did not show very high  $\text{SO}_2$  concentrations compared with other sites in Northern China.

Atmospheric  $\text{SO}_2$  concentrations at Southern sites did not increase quite so obviously in the winter. Fig. 2c shows a peak  $\text{SO}_2$  concentration in December at TJ but not at the other sites YT, LY, ZY. Fig. 2d indicates higher  $\text{SO}_2$  concentrations ( $>10 \mu\text{g S m}^{-3}$ ) at NJ and FH in December, January and March (March only for NJ) compared with other months, but with no strong peaks. The two southern tropical sites FZ and BY did not show any distinct seasonal variations of  $\text{SO}_2$  concentrations (Fig. 2d). The average  $\text{SO}_2$  concentrations at ZY, YT, LY, TJ, NJ, FH, FZ, BY were 4.51 (20-month average),

1.91 (16-month average), 4.42 (18-month average), 5.59 (23-month average), 7.78 (22-month average), 4.78 (22-month average), 2.77 (27-month average), 7.54 (28-month average)  $\mu\text{g S m}^{-3}$ , respectively. The sites with the highest average  $\text{SO}_2$  concentrations were NJ and BY, two suburban sites. In general,  $\text{SO}_2$  concentrations at southern sampling sites were lower than those at northern sites. Compared to the 8 southern sites, all the northern sites showed sharply decreased  $\text{SO}_2$  concentrations after March, consistent with the time when heating stopped in northern China (Fig. 2).

In order to identify potential transport of  $\text{SO}_2$  from the northern China, we calculated three-day backward trajectories arriving at five southern sites NJ, TY, TJ, FH, BY during January, April, July and October using the TrajStat. The TrajStat analysis showed that the transport of  $\text{SO}_2$  from northern settlements would lead to an increase of  $\text{SO}_2$  concentrations in winter south of Huai river, especially at the NJ site (Fig. 3). The high frequency of flow from north to south in the wintertime suggests that long range transport of  $\text{SO}_2$  and perhaps  $\text{pSO}_4^{2-}$  from northern China could contribute to wintertime concentrations in the south.

### 3.2. Atmospheric $\text{pSO}_4^{2-}$ concentrations

Monthly atmospheric  $\text{pSO}_4^{2-}$  concentrations at the sixteen sites are shown in Fig. 4. In contrast to  $\text{SO}_2$  concentrations which peaked in winter at all northern sites,  $\text{pSO}_4^{2-}$  concentrations increased sharply in the winter only at CAU, QZ, and SY of the eight northern

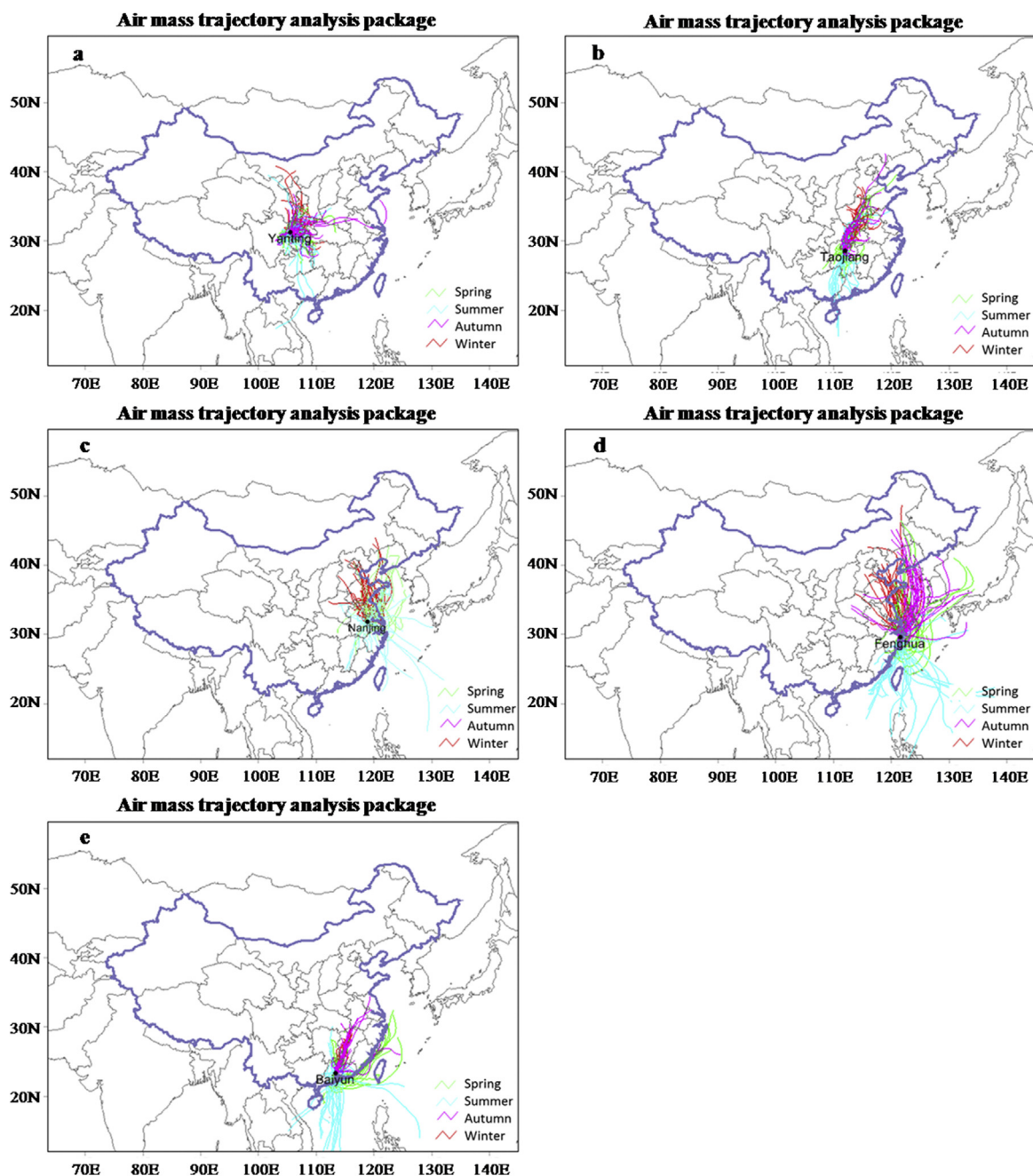


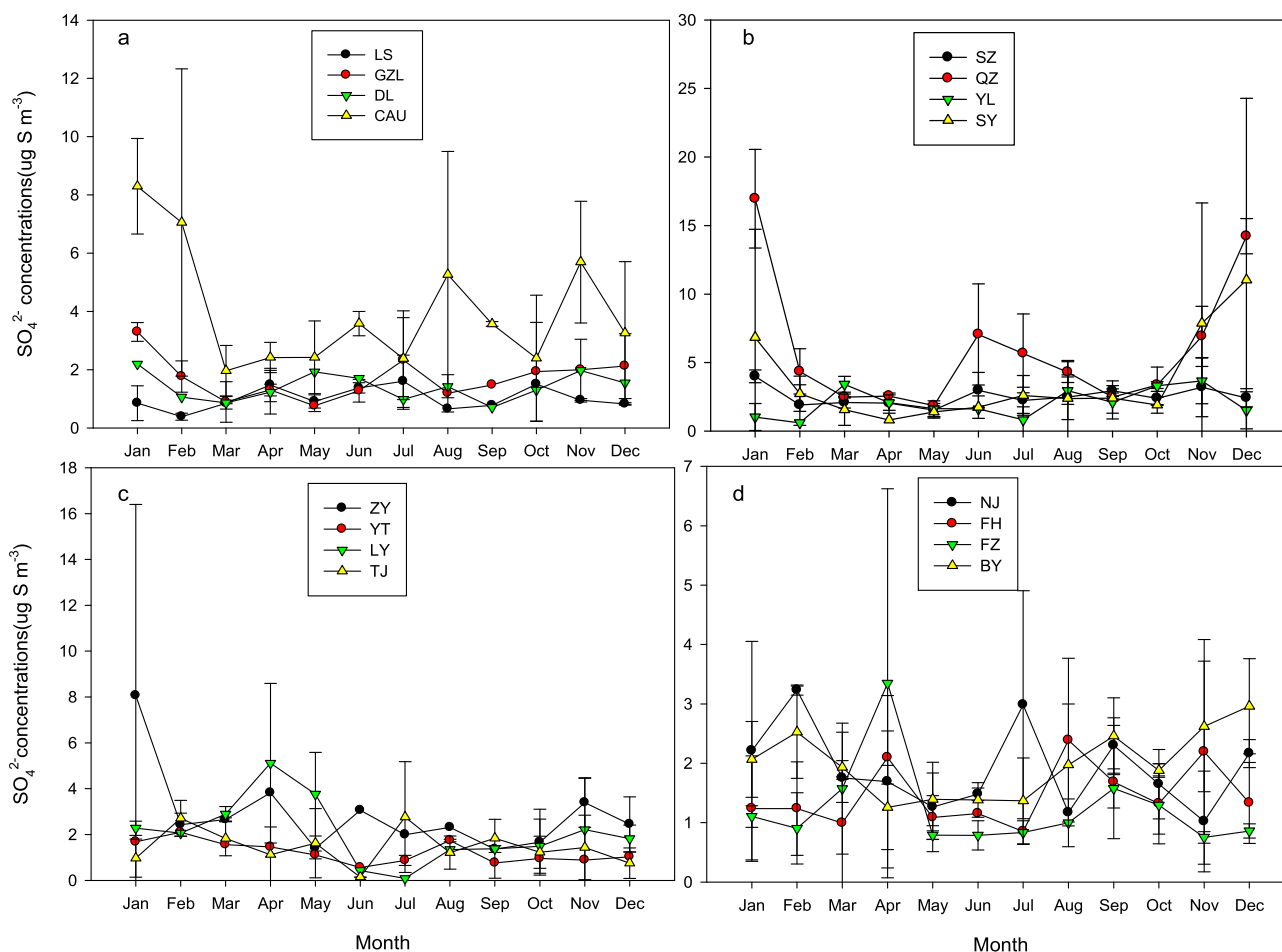
Fig. 3. HYSPLIT back-trajectories analysis on the path of air parcels ( $\text{SO}_2$ ) prior to arrival at five selected sites in south China during different seasons (January–Winter, April–Spring, July–Summer, October–Autumn). “a, b, c, d, and e” represent Yanting (YT), Taojiang (TJ), Nanjing (NJ), Fenghua (FH), and Baiyun (BY) sites, respectively.

sites. Although GZL, DL, SZ, YL had higher  $\text{SO}_2$  concentrations in winter, there were no obvious peak  $\text{pSO}_4^{2-}$  concentrations. The average  $\text{pSO}_4^{2-}$  concentrations were 1.00 (27-month average), 1.69 (26-month average), 1.40 (23-month average), 4.02 (27-month average), 2.51 (27-month average), 6.01 (25-month average), 2.05 (27-month average), 3.60 (25-month average)  $\mu\text{g S m}^{-3}$  at LS, GZL, DL, CA, SZ, QZ, YL, SY, respectively. The highest  $\text{pSO}_4^{2-}$  concentration was observed at QZ in Hebei province. This was consistent with the severe S (Pan et al., 2013) and reactive N pollution and deposition in the same area (Shen et al., 2009; Liu et al., 2013; Luo et al., 2013). The lowest  $\text{pSO}_4^{2-}$  concentrations were found at LS, a rural northeastern site. Seasonal  $\text{pSO}_4^{2-}$  concentrations did not show obvious variation at the southern sites. The average  $\text{pSO}_4^{2-}$  concentrations were 2.89

(20-month average), 1.23 (16-month average), 2.07 (18-month average), 1.47 (23-month average), 1.91 (22-month average), 1.47 (22-month average), 1.24 (27-month average), 1.99 (28-month average)  $\mu\text{g S m}^{-3}$  at ZY, YT, LY, TJ, NJ, FH, FZ, BY, respectively. The  $\text{pSO}_4^{2-}$  concentrations exhibited less spatial variation at the southern sites during the sampling period and high concentrations almost always occurred at the same time as high  $\text{SO}_2$  concentrations.

### 3.3. Particulate sulfate, nitrate and ammonium ions characteristics at the sampling sites

The concentrations of  $\text{SO}_2$ ,  $\text{pSO}_4^{2-}$ ,  $\text{pNO}_3$ ,  $\text{pNH}_4^+$ , the  $\text{pSO}_4^{2-}/\text{pNO}_3$  ratios (ratios of mass concentration) and the  $([\text{NH}_4^+]-[\text{NO}_3^-])/[\text{SO}_4^{2-}]$



**Fig. 4.** Monthly average  $pSO_4^{2-}$  concentrations at 16 sampling sites during sampling period ( $\mu\text{g S m}^{-3}$ ). a, b represent Northern China; c, d represent Southern China. Error bars represent the variations each month across the 1–3 years of sampling at each site, with warm season (April to August) monthly averages based on 2–3 years of data and cold season (September to March) on 1–2 years of data. The meaning of the ends of the whiskers represent minimum and maximum values of the monitoring period at each site.

ratios (ratios of micromolar concentrations), i.e.  $([\text{NH}_4^+] - [\text{NO}_3^-]) / [\text{SO}_4^{2-}]$  values (which were used to identify the  $\text{NH}_3$ -poor, -neutral, or -rich conditions) at all sampling sites are summarized in Table 2. The sum of major secondary aerosols  $pSO_4^{2-}$ ,  $pNO_3^-$  and  $pNH_4^+$  (SNA) concentrations ranged from 11.6 to 51.8  $\mu\text{g m}^{-3}$  compared with  $\text{SO}_2$  concentrations 3.65–33.2  $\mu\text{g m}^{-3}$  (Table 2). Higher SNA concentrations appeared at the northern sites where severe particulate pollution existed (Pan et al., 2012);  $pNO_3^-$  was highest compared with that of  $pSO_4^{2-}$  and  $pNH_4^+$  at the most sampling sites. The  $pSO_4^{2-}/pNO_3^-$  ratios were  $<1.0$  at most sampling sites and reflected the increasing or stabilized  $\text{NO}_x$  emissions relative to reduced  $\text{SO}_2$  emissions in many regions of China.  $\text{H}_2\text{SO}_4$  and nitric acid (formed directly from  $\text{SO}_2$  and  $\text{NO}_x$ , respectively) react with the  $\text{NH}_3$  to form ammonium sulfate and ammonium nitrate in air, and  $\text{H}_2\text{SO}_4$  react with  $\text{NH}_3$  firstly. DSN values  $<2$ ,  $=2$ , and  $>2$  indicate  $\text{NH}_3$ -poor (sulfate is insufficiently neutralized),  $\text{NH}_3$ -neutral (sulfate is exactly neutralized) and  $\text{NH}_3$ -rich (sulfate is sufficiently neutralized) condition (Wang et al., 2011; Dong et al., 2014), respectively. The average monthly DSN values were  $>2$  at most sites in our monitoring period, suggesting that there was enough  $\text{NH}_3$  to form nitrate particulates in the most months (Table 2). The average monthly DSN values of  $<2$  at FZ and BY reflected  $\text{NH}_3$  restricted conditions in the most months. Meanwhile, we found substantial variations for DSN for all sites, suggesting large seasonal and month-to-month variations of DSN in both north and south China.  $pNO_3^-$  and  $pNH_4^+$  had significantly positive relationship across all

sampling sites ( $R^2 = 0.59$ ,  $P < 0.01$ ).  $pSO_4^{2-}$  also correlated with  $pNH_4^+$ , although the correlation coefficient ( $R^2 = 0.36$ ,  $P < 0.05$ ) was lower than that between  $pNO_3^-$  and  $pNH_4^+$ .

### 3.4. Sulfur dry deposition

Deposition velocities of  $\text{SO}_2$  ranged from 0.20 to 1.33  $\text{cm s}^{-1}$ , being highest in the summer; while monthly deposition velocities of  $pSO_4^{2-}$  ranged from 0.07 to 0.32  $\text{cm s}^{-1}$  (Table 1). Table 3 shows the 2011 (except YT from May 2011 to April 2012) dry deposition fluxes of  $\text{SO}_2$ ,  $pSO_4^{2-}$  and total S species at the 16 sites. Dry  $\text{SO}_2$  deposition ranged from 2.3 to 26.5  $\text{kg S ha}^{-1} \text{yr}^{-1}$  and showed a large spatial variation across all the sites. Dry  $pSO_4^{2-}$  deposition (0.5–3.4  $\text{kg S ha}^{-1} \text{yr}^{-1}$ ) was much lower than that of  $\text{SO}_2$  and showed much less spatial variation between all sites. Total dry S deposition (sum of  $\text{SO}_2$  and  $pSO_4^{2-}$ ) ranged from 3.1 to 27.1  $\text{kg S ha}^{-1} \text{yr}^{-1}$  with average values at northern sites  $>$  southern sites (14.7 vs 7.6  $\text{kg S ha}^{-1} \text{yr}^{-1}$ ,  $P < 0.05$ ). The lowest dry S deposition was at YT in southwest Sichuan while the highest deposition was at DL in Liaoning, northeast China. Dry deposition depends on both concentrations and deposition velocities of  $\text{SO}_2$  and  $pSO_4^{2-}$ , so the highest dry S deposition did not occur at CAU (15.1  $\text{kg S ha}^{-1} \text{yr}^{-1}$ ) and QZ (10.6  $\text{kg S ha}^{-1} \text{yr}^{-1}$ ) where the highest S concentrations were observed but the deposition velocities here were smaller. Although dry deposition of both  $\text{SO}_2$  and  $pSO_4^{2-}$  was estimated in current study, we realize that uncertainties cannot

**Table 2**  
Sulfur dioxide, particulate sulfate ( $\text{pSO}_4^{2-}$ ), nitrate ( $\text{pNO}_3$ ) and ammonium ( $\text{pNH}_4^+$ ) concentrations ( $\mu\text{g m}^{-3}$ ),  $\text{pNO}_3/\text{pSO}_4^{2-}$  ratios (based on mass concentration) and DSN<sup>#</sup> values (ratios based on (micro)molar concentration, identifying the  $\text{NH}_3$ -poor (<2), -neutral (=2), or -rich (>2) conditions) at the sampling sites at ambient temperature and pressure.

Site	Gas or ions concentrations ( $\mu\text{g m}^{-3}$ )				Ratio $\text{pSO}_4^{2-}/\text{pNO}_3$	Value DSN <sup>#</sup>
	$\text{SO}_2$	$\text{pSO}_4^{2-}$	$\text{pNO}_3$	$\text{pNH}_4^+$		
LS	5.43 ± 3.00	3.07 ± 1.48	7.46 ± 3.06	9.45 ± 6.59	0.41 ± 0.14	14.9 ± 16.3
GZL	19.6 ± 13.9	5.05 ± 2.94	9.06 ± 3.54	6.69 ± 4.36	0.69 ± 0.77	4.12 ± 2.38
DL	20.3 ± 14.9	4.31 ± 1.61	8.98 ± 6.45	5.22 ± 2.45	0.60 ± 0.34	3.41 ± 1.55
CAU	31.0 ± 30.2	12.3 ± 8.24	21.8 ± 9.06	11.0 ± 6.79	0.69 ± 0.96	2.29 ± 3.60
SZ	16.0 ± 12.5	7.44 ± 3.31	13.7 ± 4.90	8.15 ± 5.35	0.63 ± 0.48	3.37 ± 4.92
QZ	33.2 ± 17.8	18.0 ± 4.83	20.0 ± 13.0	13.8 ± 7.22	1.06 ± 0.72	3.25 ± 2.68
YL	16.7 ± 14.6	6.45 ± 3.73	15.9 ± 12.3	14.3 ± 8.38	0.49 ± 0.27	10.0 ± 10.0
SY	26.4 ± 22.1	10.9 ± 14.7	11.9 ± 6.83	5.31 ± 2.77	0.72 ± 0.44	2.03 ± 2.56
ZY	9.05 ± 4.47	8.94 ± 8.40	9.77 ± 5.24	7.33 ± 4.79	1.19 ± 1.85	4.44 ± 4.90
YT	3.65 ± 1.70	3.62 ± 1.39	4.09 ± 1.50	4.97 ± 4.34	1.14 ± 0.89	4.56 ± 2.92
LY	9.06 ± 4.49	6.88 ± 5.21	9.19 ± 6.14	6.64 ± 4.09	1.22 ± 1.52	3.98 ± 3.22
TJ	11.24 ± 7.49	4.42 ± 3.35	3.98 ± 2.70	4.00 ± 2.49	1.34 ± 1.45	5.27 ± 5.02
NJ	16.55 ± 8.26	6.23 ± 2.90	13.8 ± 5.03	6.56 ± 2.80	0.45 ± 0.27	3.09 ± 3.46
FH	10.05 ± 6.82	4.62 ± 2.52	9.45 ± 3.29	5.23 ± 2.38	0.56 ± 0.47	4.44 ± 4.57
FZ	5.55 ± 3.45	3.69 ± 3.09	4.96 ± 1.37	2.93 ± 1.60	0.75 ± 0.51	1.95 ± 1.91
BY	15.19 (6.35)	5.93 (2.27)	12.1 ± 3.95	5.28 ± 2.89	0.51 ± 0.20	1.32 ± 2.12

<sup>#</sup> DSN =  $([\text{pNH}_4^+] - [\text{pNO}_3]) / ([\text{pSO}_4^{2-}])$ , where  $[\text{pNH}_4^+]$ ,  $[\text{pNO}_3]$  and  $[\text{pSO}_4^{2-}]$  denotes micromolar concentrations ( $\mu\text{mol m}^{-3}$ ) of particulate ammonium, nitrate and sulfate, respectively.

**Table 3**  
Annual dry deposition of  $\text{SO}_2$ ,  $\text{pSO}_4^{2-}$  and total S species at the 16 Chinese sampling sites in 2011 (except YT from May 2011 to April 2012, unit:  $\text{kg S ha}^{-1} \text{ yr}^{-1}$ ). Ave. and sd denote regional average deposition and standard deviation, respectively.

North- site	$\text{SO}_2$	$\text{pSO}_4^{2-}$	Total	South- site	$\text{SO}_2$	$\text{pSO}_4^{2-}$	Total
LS	3.37	1.16	4.53	YT	4.57	1.8	6.37
GZL	9.33	0.73	10.1	ZY	2.29	0.82	3.11
DL	26.5	0.65	27.1	LY	5.56	1.75	7.31
CAU	13.9	1.24	15.1	TJ	6.78	0.58	7.36
SZ	8.99	1.6	10.6	NJ	10.2	1	11.2
QZ	18.5	3.4	21.9	FH	6.18	0.5	6.68
YL	9.87	1.32	11.2	FZ	7.51	0.72	8.23
SY	14.3	2.49	16.8	BY	10.1	0.73	10.8
Ave. ± sd	13.1 ± 7.0	1.6 ± 0.9	14.7 ± 7.2	Ave. ± sd	6.6 ± 2.7	1.0 ± 0.5	7.6 ± 2.6

completely avoided because of (1) only a same whole one-year data used and (2) still some improvement space for calculating  $V_d$  of  $\text{SO}_2$  and  $\text{pSO}_4^{2-}$  using the GEOS-Chem 3-D global CTM in the future.

## 4. Discussion

### 4.1. Atmospheric S concentrations and other inorganic ions in particulate matter

Our results show that high  $\text{SO}_2$  concentrations occurred in the winter in northern China from 2010 to 2012 consistent with additional wintertime emissions in the north from home heating by coal burning (Fig. 2). That large emissions of  $\text{SO}_2$  and other pollutants in winter contributed significantly to air pollution in northern China was observed in previous studies (Duan et al., 2005; Chan and Yao, 2008; Huang et al., 2014; Song et al., 2015). Centralized heating with coal contributed only 6.93% of the national  $\text{SO}_2$  emissions in China in 2007 and was small compared to the emissions from power plants (Su et al., 2011). However, heating clearly made an important contribution to ground  $\text{SO}_2$  concentrations; previous research showed that it can reach 39% of the total (Hao et al., 2005). This is because the height of the emission source from home heating is relatively low while those of power and industry point sources are always high. China's North Huai River Policy, which states that large scale heating for homes is only provided to the north of the Huai River, has a close relationship with air quality and people's health. Chen et al. (2013a) reported that the North Huai River Policy greatly increased pollution from

total suspended particulates (TSPs) and led to negative health effects for the 500 million residents in Northern China, with more than 2.5 billion life years lost or a reduction of 5.5 years of life expectancy per person. Therefore taking more effective measures to reduce the  $\text{SO}_2$  emissions in the North Huai River region when home heating is used is very important for winter air quality and human health.

$\text{SO}_2$  is the important precursor of  $\text{pSO}_4^{2-}$ , and so it makes a significant contribution to current  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  pollution in China (Yang et al., 2011; Zhang et al., 2012a). As shown in Table 2,  $\text{pNO}_3$  was the dominant particulate component at most sites of SNA, which reflected higher  $\text{NO}_x$  emissions promoted more  $\text{pNO}_3$  formation in air at most sampling sites during the sampling periods. Another important factor is that most of our sampling sites, being in rural regions, have fewer local stationary  $\text{SO}_2$  emissions (i.e. power plants, industry, etc).  $\text{NH}_3$  plays a major role in the formation of  $\text{pSO}_4^{2-}$  and  $\text{pNO}_3$  in air because  $\text{NH}_3$  reacts with  $\text{H}_2\text{SO}_4$  firstly then with  $\text{HNO}_3$  (Zhang et al., 2012d). Therefore higher  $\text{NH}_3$  emissions will stimulate the transformation of  $\text{NO}_x$  to  $\text{pNO}_3$  (Wang et al., 2011). Of course, we believe there are indeed sources of  $\text{pSO}_4$  (e.g.,  $\text{CaSO}_4$ , transformed from  $\text{H}_2\text{SO}_4$  reacting with  $\text{CaCO}_3$ ) other than  $\text{p}(\text{NH}_4)_2\text{SO}_4$  at the monitoring sites especially at sites in northern China where calcareous arable soils are widely distributed.

The higher  $\text{pNO}_3/\text{pSO}_4^{2-}$  ratios at sites in or near in Beijing and Shanghai are consistent with other similar studies (e.g., Chen et al., 2013b; Huang et al., 2012). There was a significant positive correlation between the average  $\text{SO}_2$  concentrations and  $\text{pSO}_4^{2-}$



concentrations ( $r = 0.597$ ;  $p < 0.05$ ) (Fig. 5), indicating that high  $\text{SO}_2$  concentrations will promote the formation of  $\text{pSO}_4^{2-}$  in the air.

We calculated the monthly DSN values at all sampling sites during the sampling periods. We noticed the uncertainties of the DSN values due to the sea-salt and soil dust containing  $\text{NaNO}_3$  and/or  $\text{CaSO}_4$ . Sea salt is one of the sources of aerosol which may affect the constitution of aerosols especially in coastal area. Sea salt contribution to PM was up to  $5 \mu\text{g m}^{-3}$  at an urban area of Germany (Beuck et al., 2011). Sea salt source  $\text{SO}_4^{2-}$  and/or  $\text{NO}_3^-$  will potentially decrease the real DSN values of our study and the further research about how sea salt affect the ion concentrations and DSN values should be carried out in the future study. Lee et al. (1999) confirmed that soil-derived calcium from arid regions is an important contributor to base cation deposition, but also suggested that agricultural activities are a major regional source of airborne calcium. Authors of both studies pointed to large uncertainties in quantifying the sources and deposition rates of base cations. Zhang et al. (2012c) reported poor correlations between  $\text{pSO}_4^{2-}$  and  $\text{pCa}^{2+}$  in urban areas, but relationship between  $\text{pSO}_4^{2-}$  and  $\text{pCa}^{2+}$  is significantly different from rural sites, especially at remote sites exhibiting relative stronger neutralization of acidic sulfate by  $\text{Ca}^{2+}$ . Most of our sampling sites were in rural or near the farmland, so parts of  $\text{pSO}_4^{2-}$  (e.g., in the form of  $\text{CaSO}_4$ , transformed from  $\text{H}_2\text{SO}_4$  reacting with  $\text{CaCO}_3$ ) may be derived from soil dust, due to widely distributed calcareous soils in north and northwest China. The dust source  $\text{pSO}_4^{2-}$  in the air will underestimate the DSN values as well, which should be considered carefully in the future study.

As for concerns on why  $\text{pSO}_4^{2-}$  concentrations did not show similar seasonal variations to  $\text{SO}_2$  concentration at the northern monitoring sites, our hypothesis is that there may be a 'buffering' system to form  $\text{pSO}_4^{2-}$  in different seasons. In winter or cold season, reduced  $\text{NH}_3$  emission will limit the formation of ammonium sulfate and/or ammonium bisulfate (the majority of  $\text{pSO}_4^{2-}$ ) when  $\text{SO}_2$  emissions are high; in summer or warm season, coexistence of reactive N ( $\text{NH}_3$  and  $\text{NO}_x$ ) may enhance the transformation of  $\text{pSO}_4^{2-}$  from  $\text{SO}_2$  when its emissions are low. Shen et al. (2009) reported high concentrations and deposition of reactive N species in North China Plain. The interactions and/or co-deposition of S and N species could partly explain the different seasonal variations of  $\text{SO}_2$  and  $\text{pSO}_4^{2-}$  (Shen et al., 2011; Wang et al., 2013).

China has achieved the  $\text{SO}_2$  emission reduction targets in both the 11th Five-Year Plan (FYP) (2006–2010), and the 12th FYP (2011–2015). However, there was no target for  $\text{NO}_x$  emission

reduction in the 11th FYP (2006–2010), and only a small reduction target in the 12th FYP (2011–2015). If the  $\text{NO}_x$  emissions increased in 12th FYP (2011–2015), nitrate will be the most important part of the three inorganic components (sulfate, nitrate and ammonium) in the secondary particulates in South and North China (Wang et al., 2013). Controlling  $\text{SO}_2$  emissions will change the composition of secondary aerosols and/or particles. In the United States, modeling results showed that particulate matter would contain more  $\text{pNO}_3^-$  if  $\text{SO}_2$  emissions decreased (Pye et al., 2009). However, China began to control  $\text{SO}_2$  emissions only recently. How  $\text{SO}_2$  emission control policy will affect China's air quality (e.g.  $\text{SO}_2$  and  $\text{PM}_{2.5}$ ) requires further research and long-term observation.

#### 4.2. Sulfur dry deposition and its implications

Acid rain is closely related to S deposition, but research into S deposition has mainly focused on wet deposition in China (Pan et al., 2013). Compared with north China, the south of China has a higher rainfall and more acidic soils (Guo et al., 2010) and its precipitation is more acidic. So the wet deposition of S has been studied much more intensively in southern China. Aas et al. (2007) surveyed  $\text{SO}_2$  weekly concentrations at five sites in southern China in 2001–2003, where the annual average concentrations ranged from lower values of  $0.55\text{--}2.59 \mu\text{g S m}^{-3}$  to the highest values of  $37.2\text{--}42.7 \mu\text{g S m}^{-3}$ , showing large spatial variation. The precipitation-weighted mean concentration of  $\text{SO}_4^{2-}$  in rainwater ranged from  $41.8$  to  $1227.6 \mu\text{eq L}^{-1}$  (every rain event) in Chengdu in 2008 (Wang and Han, 2011). Annual average wet deposition of  $\text{SO}_4^{2-}\text{-S}$  at two sites in southeastern China were  $31.0$  and  $87.2 \text{ kg S ha}^{-1}$  respectively during 2010 and 2011 (Cui et al., 2014). Pan et al. (2013) reported dry deposition of S at ten sites in northern China between December 2007 and November 2010, which ranged from  $20.4$  to  $80.0 \text{ kg S ha}^{-1} \text{ yr}^{-1}$  with an average value of  $45.2 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ ; the lowest value was at a rural site. In our study, dry deposition at the northern Chinese sites was  $3.1\text{--}27.1 \text{ kg S ha}^{-1} \text{ yr}^{-1}$  in 2011 (Table 3), i.e. much smaller than values at urban sites but closer to the lowest rural site ( $20.4 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ ) recorded by Pan et al. (2013). The monthly  $V_d$  of  $\text{SO}_2$  were  $0.30\text{--}0.59 \text{ cm s}^{-1}$  in northern China of our study (5 sampling sites: CAU, SZ, QZ, YL, SY). Pan et al. (2013) had similar  $V_d$  values ( $0.15\text{--}0.77 \text{ cm s}^{-1}$ ) to estimate S dry deposition in northern China. So the lower concentrations of  $\text{SO}_2$  and  $\text{pSO}_4^{2-}$  at our monitoring sites than the sites in Pan et al. (2013) should explain the relatively low atmospheric dry S deposition in northern China. This may reflect the decreased  $\text{SO}_2$  emissions with the Chinese emission control policy for  $\text{SO}_2$ .

#### 5. Conclusion

Acid deposition is formed from a range of anthropogenic and natural emissions, including  $\text{SO}_2$  and  $\text{NO}_x$ . These gases can be transformed to  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  in the atmosphere and which can form condensation nuclei for aerosols and clouds, acidifying precipitation. Since S deposition has declined dramatically across Europe, N is now making a greater contribution to acid rain than S on a mass basis at current deposition levels. China has taken effective measures to control  $\text{SO}_2$  emission since the 10th FYP (2001–2005) and, if this trend continues, S deposition will further decrease. As in Europe, this will have interesting and potentially important effects on ecosystems and human health in China that should be researched. The higher  $\text{pNO}_3^-/\text{pSO}_4^{2-}$  (mass basis) at most sampling sites reflected relative importance of mobile sources for the particulates formation in our study. We evaluated only the dry deposition of S, and only at 16 representative rural and suburban sampling sites. Monitoring the deposition of both dry and wet

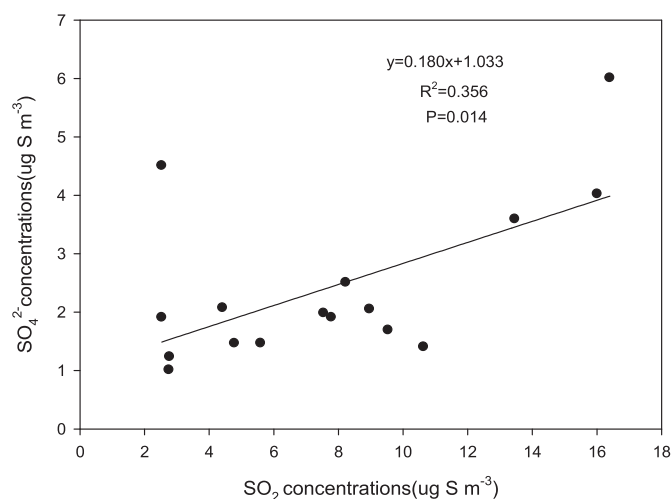


Fig. 5. Correlation between average  $\text{SO}_2$  concentrations and  $\text{pSO}_4^{2-}$  concentrations across 16 monitoring sites.

forms is necessary for a more complete evaluation of S deposition and its effects. Also the present research was conducted before 2012. More work is needed under current conditions to keep pace with the SO<sub>2</sub> emission control policy of China. Taking more effective measures to reduce the SO<sub>2</sub> emissions here will be very important for winter air quality and human health.

## Acknowledgements

This work was financially supported by Chinese National Basic Research Programme (2014CB954202, 2016YFD0800101 and 2012CB417100), China National Funds for Distinguished Young Scientists (40425007), and the National Natural Science Foundation of China (31421092, 41405144 and 41321064).

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