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PAPER

Chemical composition, sources, and deposition fluxes of water-soluble inorganic ions obtained from precipitation chemistry measurements collected at an urban site in northwest China

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Precipitation samples were collected at an urban site in Xi'an, northwest China during March to November in 2009 and were then analyzed to determine the pH and concentrations of water-soluble inorganic ions (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, SO_4^{2-}, NO_3^-, Cl^-, and F^-) in precipitation. The pH of precipitation ranged from 4.1 to 7.6 for all of the samples with an annual volume-weighted mean of 6.4. While a large portion of the precipitation events were weakly acidic or alkaline, around 30% of the precipitation events in the autumn were strongly acidic. Precipitation events with air masses from the northeast and the southeast were weakly acidic while those with air masses from the northwest and the southwest were alkaline. SO_4^{2-}, Ca^{2+}, NH_4^+, and NO_3^- were dominant ions in the precipitation, accounting for 37%, 25%, 18%, and 9%, respectively, of the total analyzed ions. Ca^{2+} and NH_4^+ were found to be the major neutralizers of precipitation acidity; however, the contribution of Mg^{2+}, although much lower than those of Ca^{2+} and NH_4^+, was important, in many cases, in changing the precipitation from weakly acidic to weakly alkaline. Enrichment factor analysis confirmed that SO_4^{2-} and NO_3^- were produced from anthropogenic sources, Ca^{2+}, K^+, and 80% Mg^{2+} were from crustal sources, and Na^+, Cl^-, and ~20% of Mg^{2+} were from marine sources. The annual wet depositions were estimated to be 3.5 t km^{-2} per year for sulfur; 2.3 t km^{-2} per year for nitrogen, of which 0.8 t km^{-2} per year was oxidized nitrogen and 1.5 t km^{-2} per year was reduced nitrogen; and 3.0 t km^{-2} per year for Ca^{2+}.

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1. Introduction

Atmospheric precipitation, one important part of the natural water cycle, plays a significant role in carrying chemical pollutants from the atmosphere to the earth's surface.[1,2] Water-soluble inorganic ions constitute a significant portion of total particulate matter and precipitation samples and thus have direct and indirect impacts on air quality, climate and ecosystems.[2–5] To address various issues related to these ions, their concentrations in air

Environmental impact

In this manuscript we investigated the chemical composition, sources, and deposition fluxes of water-soluble inorganic ions in precipitation observed in Xi'an, Northwest China. The pH in precipitation ranged from 4.1 to 7.6 for all the samples with an annual volume-weighted mean of 6.4. SO_4^{2-}, Ca^{2+}, NH_4^+ and NO_3^- were dominant ions in precipitation. SO_4^{2-} and NO_3^- were produced from anthropogenic sources, Ca^{2+}, K^+, and 80% Mg^{2+} were from crustal sources, and Na^+, Cl^-, and ~20% of Mg^{2+} were from marine sources. The annual wet deposition of sulfur at Xi'an was in the medium range among the major Chinese cities where data were available. The annual nitrogen deposition was in the lower range among the Chinese cities but much higher than a few rural locations. It is likely that the benefit of nitrogen deposition in this region is more than its damage to the ecosystem considering the much higher deposition of ammonium than that of nitrate.

and in precipitation and the sources and chemical mechanisms producing those ions need to be understood at local, regional, and global scales. To date, many studies around the world have revealed the source types, formation mechanisms, chemical and physical characteristics, and dry and wet deposition of the major water-soluble inorganic ions.[2,6–10]

The rapid economic growth in China during the past three decades has caused many environmental pollution problems. For example, one third of the Chinese territory has been affected by acid rain, with some megacities in southern China experiencing rain with an annual mean pH as low as 3.[11] A significant number of studies on precipitation have been focused on water-soluble inorganic ions, especially in the heavily polluted regions of China, e.g., Pearl River Delta region, Yangtze Delta region, and Beijing–Tianjin region.[12–14] Earlier studies have mostly focused on acid rain[12,14,15] while recent studies have also included other ambient data, especially on size-segregated ions.[16,17]

However, studies in the northwest region of China are still limited. Xi'an is the largest city in northwest China, with an urban area of 1066 km^2 and a population of 5.1 million. Increased aerosol concentrations due to rapid increase in the number of motor vehicles and energy consumption has a strong impact on air quality.[16,18–22] To fill the knowledge gaps on precipitation chemistry in this city, precipitation samples were collected during March to November in 2009. This study presents the analysis results of the collected precipitation samples focusing on precipitation acidity, the ions' concentrations in the precipitation, and their sources, transportation, and annual wet deposition. The results generated from this study are expected to be useful in making emission-control policies.

2. Methodology

2.1 Data collection

2.1.1 Site description. The rainfall samples were collected on the roof of a 15 m high building in Xi'an Jiaotong University, which is located in the southeast area of downtown Xi'an (Fig. 1). To the north and east of the sampling site are residential areas and the campus of Xi'an Jiaotong University. There is heavy traffic most of the time to the south and to the west of the site, where the South Second Ring and the Xingqin Road pass through. Xi'an is the capital of Shaanxi Province, China. The climate in Xi'an is cold and dry in the winter and hot and wet in the summer. Summer monsoons from the southeast carry an abundance of rainfall to Xi'an; in contrast, winter monsoons from the northwest bring cold air masses accompanied by high wind speeds, leading to low temperatures and snow. The annual average temperature is 13.3 °C and the recorded highest and lowest temperatures are 45.2 °C and −20.6 °C, respectively. The annual average precipitation is about 604.2 millimeters.

2.1.2 Sample collection and chemical analysis. The precipitation samples were collected by a SYC-2 automatic rainfall monitor (made at the Qingdao Laoshan Instrument Factory, China) from March to November 2009. The funnel lid opened and closed automatically when rainfall occurred and ceased, preventing wet samples from mixing with dry deposits. After sampling, the collection system was systematically cleaned with ultra-pure water (a resistivity of 18.2 MΩ). Rainfall samples were stored in a 500 ml plastic bottle (before use, it was cleaned with ultra-pure water three times until the Electric Conductivity (EC) was lower than 2 µS cm^{-1}). The pH and EC were measured immediately after collection of the samples using a DELTA320 pH meter (Mettle Corp.) and a conductivity meter of DDB - 303A type (Leici Corp.). The rainfall samples were filtered with a 0.45 µm pore size microporous membrane and were then stored in a refrigerator at 3–5 °C prior to chemical analysis. A total of 42 event-based precipitation samples were collected in this study. Snow samples were not collected in this study. In fact, winter snow in the year of 2009 (equivalent to 29.7 mm of precipitation) was only 4% of the total annual precipitation (660.3 mm).

The concentrations of four anions (SO_4^{2-}, NO_3^-, Cl^-, and F^-) and five cations (Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}) in all

Fig. 1 Location of sampling site.

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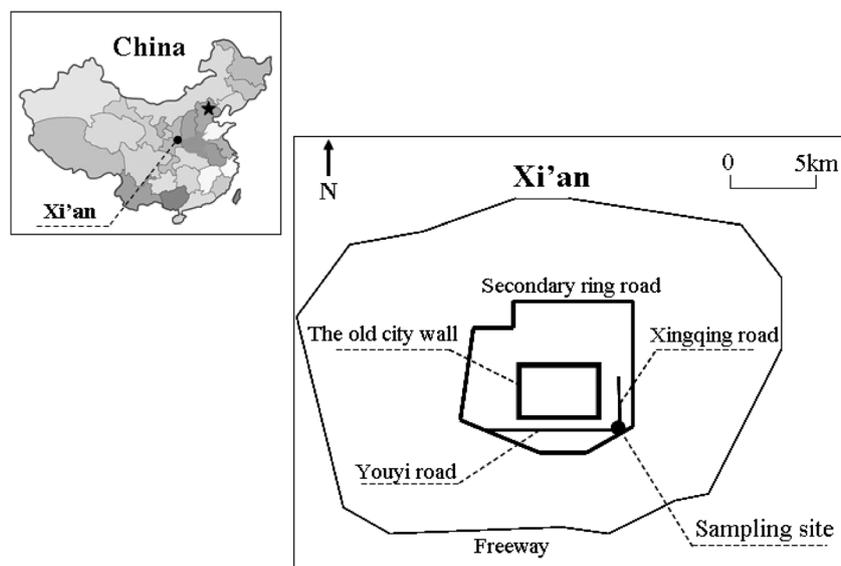
precipitation samples were determined by a DX 500 ion chromatograph (IC, Dionex Corp, Sunnyvale, CA). Cation concentrations were determined using a CS12A column (Dionex Corp.) with 20 mM methanesulfonate as an eluent. Anions were separated by an AS11-HC column (Dionex Corp.) using 20 mM KOH as the eluent. Standard reference materials produced by the National Research Center for Certified Reference Materials, China, were analyzed for quality assurance purposes. The maximum relative precisions were 1.8% for Na^+, 0.9% for NH_4^+, 0.6% for K^+, 4.0% for Ca^{2+}, 1.0% for Mg^{2+}, 1.2% for SO_4^{2-}, 2.6% for NO_3^-, 0.3% for Cl^-, and 1.4% for F^-. Strong linear correlations existed between the EC and total ion concentration ($R = 0.95$), suggesting reliable sampling and determination methods. H^+ concentrations were obtained from the pH values. Accordingly, the average pH in any period can be calculated from the volume-weighted average concentration of H^+, *i.e.* pH $= -\log H^+$.

2.2 Data analysis

2.2.1 Ion balance. Ion balance provides a useful tool to evaluate the reliability of the ionic determination method and to explain the acid–base balance of rainfall samples. The cation and anion microequivalents were calculated as follows:

$$C \text{ (cation microequivalents)} = Na^+/23 + NH_4^+/18 + K^+/39 + Mg^{2+}/12 + Ca^{2+}/20 + H^+/1 \quad (1)$$

$$A \text{ (anion microequivalents)} = F^-/19 + Cl^-/35.5 + NO_3^-/62 + SO_4^{2-}/48 \quad (2)$$

2.2.2 Neutralization factor. The neutralization factor (NF) can be used to describe the interaction between cations and anions.[23] The NF of Ca^{2+}, NH_4^+, and Mg^{2+} were calculated using their equivalent concentrations:

$$NF_{Ca^{2+}} = \frac{Ca^{2+}}{SO_4^{2-} + NO_3^-} \quad (3)$$

$$NF_{NH_4^+} = \frac{NH_4^+}{SO_4^{2-} + NO_3^-} \quad (4)$$

$$NF_{Mg^{2+}} = \frac{Mg^{2+}}{SO_4^{2-} + NO_3^-} \quad (5)$$

2.2.3 Enrichment factor. Enrichment Factor (EF) analysis is commonly used to distinguish the relative contributions of crustal or marine sources from other sources for aerosol samples or precipitation samples.[24–26] In this study, Ca^{2+} and Na^+ were selected as the references for the crustal and marine sources, respectively.[27,28] The EF was calculated according to:

$$E_{marine} = [x/C_{Na^+}]_{rainwater}/[x/C_{Na^+}]_{marine} \quad (6)$$

$$E_{crust} = [x/C_{Ca^{2+}}]_{rainwater}/[x/C_{Ca^{2+}}]_{crust} \quad (7)$$

In these equations, x/C_{Na^+} was taken from Keene *et al.*[28] and $x/C_{Ca^{2+}}$ was taken from Safai *et al.*[27] An EF value smaller than 10

suggests that the chemical species was mainly from crustal or marine sources; otherwise, it had been heavily influenced by anthropogenic sources.

The contribution of sea salt (SS) and non-sea salt (NSS) sources to an ionic species can also be separated according to:

$$X_{marine} = [C_{Na^+}]_{rainwater} \times [x/C_{Na^+}]_{seawater} \quad (8)$$

$$SS = (X_{marine}/X_{rain}) \times 100\% \quad (9)$$

$$NSS = 1 - SS \quad (10)$$

where X_{marine} is the sea salt origin concentration of the ionic component of X, and X_{rain} is the concentration of the ionic component of X in rainwater.

2.2.4 Air mass back-trajectory analysis. Air mass back-trajectory is another useful tool to identify the possible sources and transport pathways of air pollution and precipitation.[2,9] In this study, a 48 h air mass back-trajectory was generated using the NOAA HYSPLIT 4 trajectory model to help analyze the sources of ionic species in the collected precipitation samples. Precipitation events from the air masses of the same directions will be defined as the same trajectory cluster.

2.2.5 Estimation of wet deposition of ionic species. The wet deposition flux of an ionic species can be estimated as the product of the precipitation amount (P) and ionic concentration in precipitation (C). The annual wet deposition is then calculated as:

$$Fw = \sum_{i=1}^{n} C_i P_i \quad (11)$$

3. Results and discussion

3.1 Precipitation acidity

The frequency distribution of the pH values is shown in Fig. 2. The pH values ranged from 4.1 to 7.9 for all of the samples collected. A large portion of the precipitation events were weakly acidic or alkaline with a pH higher than 5.6. This is in agreement with earlier studies in other arid or semi-arid regions where alkaline precipitation was frequently reported.[29–32] However, the present study also suggested that acidic precipitation was possible even in semi-arid regions. For example, 22% of all of the samples collected in this study were acidic based on their pH values, which were smaller than 5.6. Therefore, the influence of anthropogenic pollution on acid deposition can be a serious issue even in semi-arid regions.

The annual volume-weighted mean (VWM) pH was 5.27 while the seasonal VWM pH was 5.85 in the summer, 5.93 in the spring, and 4.76 in the autumn (Table 1). High levels of dust-originated ionic species (*e.g.*, Ca^{2+} and Mg^{2+}) increased the pH in the spring and summer.[19] In contrast, 30% of the samples in the autumn belonged to the strong acid rain category (pH < 5, as defined in Seinfeld and Pandis[33]) (Fig. 3b).

3.2 Precipitation concentration of ionic components

Table 1 summarizes the volume-weighted mean (VWM) concentrations of the ionic species in the rainfall samples
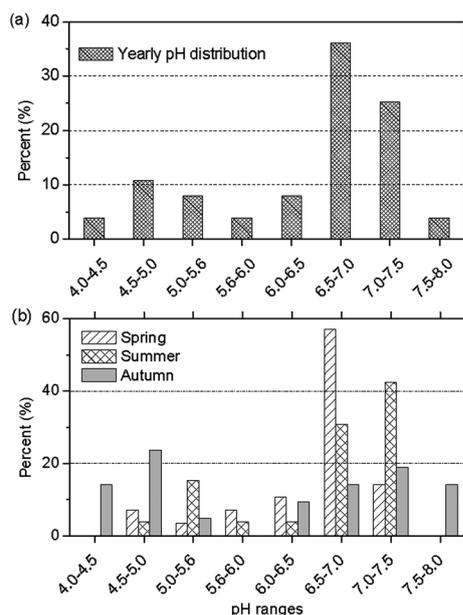
Fig. 2 pH frequency distribution from all precipitation events in 2009 (a) and in different seasons (b).

Fig. 3 Plots of total anions *versus* total cations.

collected in Xi'an. The total anion (or cation) concentration was on the order of 500 μeq. L^{-1}. SO_4^{2-} and NO_3^- were the dominant contributors to the total anion mass, accounting for 74.3% and 17.4% respectively, followed by Cl^- (6.4%) and F^- (1.8%). Ca^{2+} and NH_4^+ were the dominant cations, accounting for 50.1% and 35.4%, respectively, of the total cation mass, followed by Mg^{2+} (6.3%), Na^+ (5.5%), and K^+ (2.7%). The phenomenon that Ca^{2+} prevailed over NH_4^+ in the precipitation was also observed in Shanghai, Guangzhou, Chongqing, Kunming, and Lhasa;[34–38] however, the NH_4^+ concentration exceeded Ca^{2+} in rainfall samples in Beijing.[39]

Evident seasonal variations in mass concentrations were found for all major ionic species. For example, a 30% difference was found for SO_4^{2-} with the highest concentration in the spring and the lowest in the summer. A 30% difference was also found for NO_3^- but with the highest concentration in autumn and the lowest in the summer. The two major cations of Ca^{2+} and NH_4^+ were both highest in the spring and lowest in autumn. Different seasonal patterns between major anions and cations (*e.g.*, NO_3^- *versus* Ca^{2+} and NH_4^+) caused different precipitation acidities, as shown in Section 3.1. The relative contributions of the above four major ions to the total ionic mass followed the same order in every season, that is, SO_4^{2-} > Ca^{2+} > NH_4^+ > NO_3^-. The total contribution of SO_4^{2-} and NO_3^- in autumn reached 52%,

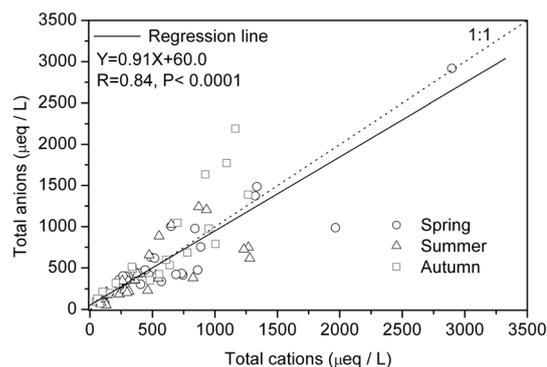resulting in more acidic precipitation in this season as compared to the other seasons. Total concentrations of the detected ions showed the highest concentrations in the spring and the lowest in the summer. The highest spring concentrations of total ions should be caused by a combination of heating (heating season is normally from 15 November to 15 March), which releases anthropogenic pollution such as SO_2, NO_x, and PM, and frequent dust events from both the long-range transport and local fugitive dusts, noting that Xi'an is located on the Loess Plateau.[19,20]

3.3 Ion balance and neutralization factors

The reasonable agreement between total cations and anions suggests that the five cations and four anions analyzed in this study were the major ions in the precipitation (Fig. 3). It can be seen that most of the samples in the spring had a good anion–cation balance (close to the 1 : 1 line), the samples in the summer showed a scatter distribution (on both sides of the 1 : 1 line), and a large portion of the samples in autumn had excess anions (above the 1 : 1 line). The anion–cation balance shown in Fig. 3 is in good agreement with the precipitation pH shown in Fig. 2. For example, the majority of the spring samples had a pH value of 6.0–7.5, a small portion of the summer samples had a pH of <5.6 and a larger portion of the summer samples had a pH > 6.5, and about 30% of the samples in the spring had a pH smaller than 5. The deficiency in anions in some of the precipitation samples should be attributed to other anions, such as HCO_3^-, CO_3^{2-}, CH_3COO^-, $HCOO^-$, $C_2O_4^{2-}$, and PO_4^{3-}, which were not investigated in this study.

The contribution of NO_3^- to the acidification was estimated to be 19% (from the ratio NO_3^-/(NSS SO_4^{2-} + NO_3^-) in their equivalent concentrations),[27] and the rest was from SO_4^{2-}. The

Table 1 Volume-weighted mean concentrations of inorganic ions and pH values

	Ion concentrations (μeq. L^{-1})										
	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	F^-	Cl^-	NO_3^-	SO_4^{2-}	NO_2^-	pH
Spring	29.1	191.5	10.4	29.6	323.5	11.0	27.0	93.4	420.5	0.0	5.93
Summer	30.3	171.4	13.7	38.1	226.1	6.9	39.2	67.5	303.8	0.1	5.85
Autumn	23.0	164.3	17.5	25.2	178.6	9.3	26.9	103.0	380.5	0.6	4.76
Yearly	27.9	180.9	13.7	32.4	255.9	9.2	32.3	87.9	374.3	0.2	5.27

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contribution of SO_4^{2-} to the precipitation acidification was much higher than the global average (60–70%).[40,41] This is mainly because China consumes 25% of the world's total coal consumption, and coal produces 70% of its national energy budget.[42]

The annual volume-weighted mean values of NF for Ca^{2+}, NH_4^+, and Mg^{2+} were 0.55, 0.39 and 0.07, respectively, indicating that Ca^{2+} and NH_4^+ were the major neutralizers in precipitation in Xi'an. Note that NF was calculated using eqn (3)–(5) which only included two major acidifying ions; thus, the sum of NF for the three cation species could slightly exceed 1.0. To clearly show the neutralization contribution of these three cations in each and all of the samples, a triangular diagram was created (Fig. 4). It can be seen that Ca^{2+} and NH_4^+ were the two major neutralizers in the precipitation samples, and the contribution of Mg^{2+} was always lower than 12.5% except in three of the samples. However, the small contribution of Mg^{2+} changed the precipitation from weakly acidic to weakly alkaline in many precipitation samples. The NH_4^+/Ca^{2+} ratio was 0.6, 1.0, and 0.8 in the spring, summer, and autumn, respectively, suggesting that Ca^{2+} played a dominant role in the spring acid neutralization while NH_4^+ had a stronger buffering ability in the summer.

3.4 Comparison with other Chinese cities

The composition of rainwater is determined by the scavenging of both gases and particles in the air. The magnitude of the concentrations of ionic species in precipitation samples may thus reflect air pollution levels. To gain an insight into the air pollution levels in mainland China and regional variations in rain acidity, the ionic composition and pH of precipitation obtained for major cities in China were compared (Table 2). The pH of rainwater in China showed a distinct geographical variation. The acidities of rainwater in southern Chinese cities, e.g., Kunming,[37] Chongqin,[36] and Guangzhou,[38] were stronger than those in central-eastern and northern cities, e.g., Shanghai,[34] Beijing,[39] and Lhasa.[35] Cities with the highest anthropogenic emissions were not among those with the strongest acidity; instead, the cities that were affected the most by soil dusts experienced less acidic conditions (e.g., a few cities in eastern and northern China). Lhasa is the capital of Tibet and had the highest pH,
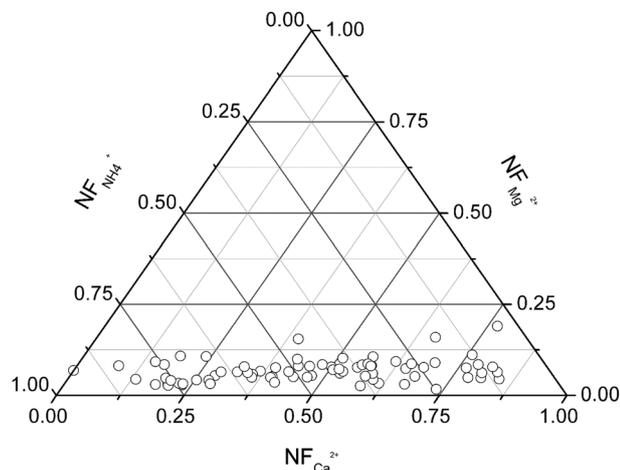
apparently caused by a combination of low anthropogenic emissions and high soil dust influences. Therefore, the north-to-south decreasing trend in rainwater pH (or increasing trend in acidity) was mostly a result of soil dust geographical distributions. It is noted that a large area of northern China belongs to arid or semi-arid regions and is subject to high dust loading.[20,43]

There is no clear geographical pattern in the total ion concentrations since anthropogenic emissions and dust influences (both local and those transported from deserts) both contributed to the total ions. The total major ions in precipitation followed a decreasing order of Xi'an > Beijing > Chongqin > Guangzhou > Shanghai > Lhasa. The highest total ions in Xi'an was mostly due to the high dust concentration; the also very high total ion concentration in Beijing was due to high anthropogenic emissions and the frequent dust influence; and the lowest concentration in Lhasa was mainly due to the very low anthropogenic emissions. SO_4^{2-} was the most abundant ion in rainwater in all of the cities except Lhasa. Thus, reducing the use of coal, a major source for SO_2 emission, should reduce the precipitation acidity and improve the air quality level in many Chinese cities.

The acidity of precipitation is mainly determined by strong acids, e.g., H_2SO_4 and HNO_3. While SO_4^{2-} and NO_3^- were the main acidifying components of rainwater (AP), Ca^{2+} and NH_4^+ served as the main neutralization components (NP) in many cities. The ratio of NP/AP could be used as an index to assess the balance between the acidity and the alkalinity. Here the NP/AP ratios were defined as $(Ca^{2+} + NH_4^+)/(SO_4^{2-} + NO_3^-)$, with ions in their equivalent concentrations. As shown in Table 2, the NP/AP ratio in Xi'an was around 1.0, a little higher than those in Beijing,[39] Guangzhou,[38] and Kunming[37] but lower than those in Shanghai,[34] Chongqin[36] and Lhasa.[35] It is noticed that the NP/AP ratio in some northern cities (e.g., Xi'an and Beijing) were lower than in some southern cities (e.g., Shanghai and Chongqin), while the pH exhibited an opposite variation. This was caused by the non-negligible concentrations of other cations (e.g., Mg^{2+}) that were not included in the NP/AP ratio. For example, the concentrations of Mg^{2+} in precipitation in Beijing and Xi'an were nearly four times higher than those in Shanghai and Chongqin.[36,38,39] Thus, the role of Mg^{2+} in acid neutralization in many northern cities cannot be ignored.

3.5 Enrichment factor (EF) and air mass back-trajectory analysis – sources of water-soluble ions

To obtain a better idea of the sources of all major ions, enrichment factor and air mass back-trajectory analysis were conducted. As shown in Table 3, the EF_{soil} and EF_{marine} for SO_4^{2-} and NO_3^- were all much higher than 10; this suggests that these two species were not from soil or marine sources. Anthropogenic sources such as coal burning and vehicle emission should be the main sources producing SO_4^{2-} and NO_3^-. EF_{soil} for K^+ and Mg^{2+} were lower than 1, implying that they were mainly from crustal origins. However, an EF_{marine} value of 5.1 for Mg^{2+} also suggests the possibility that additional marine sources, besides the crustal sources, contributed to Mg^{2+}. The EF_{soil} and EF_{marine} for Cl^- were 40.7 and 1.0, respectively, indicating that Cl^- was mainly from marine sources. The marine contribution to Ca^{2+} should be also negligible based on the high EF of Ca^{2+}.

Fig. 4 Triangular diagrams of NF for three major cations.

Table 2 Summary of ionic concentrations and pH in precipitation at major Chinese cities

	NH_4^+ (μeq. L^{-1})	Ca^{2+} (μeq. L^{-1})	NO_3^- (μeq. L^{-1})	SO_4^{2-} (μeq. L^{-1})	$(Ca^{2+}+NH_4^+)/$ $(SO_4^{2-} + NO_3^-)$	pH	Ref.
Xi'an	180.9	255.9	87.9	374.3	0.9	6.4	This study
Beijing	210.7	159.0	117.9	380.1	0.7	6.5	Tang et al.[39]
Shanghai	85.6	95.0	40.4	95.0	1.3	5.9	Xu et al.[34]
Chongqing	138.3	285.5	41.8	338.0	1.1	4.9	Zhou et al.[36]
Guangzhou	66.2	130.6	51.8	202.2	0.8	4.5	Huang et al.[38]
Kunming	51.6	111.9	13.2	199.2	0.8	4.9	Zhu[37]
Lhasa	8.7	198.8	7.3	6.1	15.5	7–8	Zhang et al.[35]

Table 3 Enrichment factors for ionic components relative to soil and seawater

	K^+	Mg^{2+}	Cl^-	SO_4^{2-}	NO_3^-
Soil ratio	0.5040	0.5610	0.0031	0.0188	0.0021
Rainwater ratio (element/Ca)	0.0536	0.1266	0.1263	1.4628	0.3433
EF_{soil}	0.11	0.23	40.73	77.81	163.50
Seawater ratio (element/Na)	0.022	0.227	1.16	0.125	0.00002
Rainwater ratio	0.491	1.161	1.158	13.414	3.148
EF_{marine}	22.3	5.1	1.0	107.3	157424.5

Table 4 shows the estimated percentage contributions from different sources to the ion species. 99.4% of NO_3^- and 97.8% of SO_4^{2-} were from anthropogenic sources; 99.5% of Ca^{2+}, 95.5% of K^+ and 80.4% of Mg^{2+} were from crustal sources; and 97.5% of Cl^- and 19.6% of Mg^{2+} were from marine sources. Note that the percentage contributions shown in Table 4 should only be treated as a rough estimation since various chemical and physical processes, besides measurement uncertainties, can cause errors in the estimation. One example is Cl^- depletion (aging of sea salt aerosols) which might cause an underestimation of marine sources for Cl^-. However, the underestimation might also be compensated by the precipitation collection of gaseous HCl.

Air mass back-trajectory analysis was conducted for the time periods with precipitation. 48 h air mass back-trajectories arriving at the site at the 500 m level were calculated using the NOAA HYSPLIT 4 trajectory model. The 500 m level was selected considering that cloud formation and wet deposition frequently occurred around this height.[44] Four typical clusters of transport pathways (NW, NE, SE and SW) were identified for the three seasons' precipitation periods (Fig. 5). The mean pH and chemical composition of the rainfall samples in each group are summarized in Table 5.

Table 4 Source contributions (%) for different ionic constituents in precipitation

	Sea salt	Crustal source	Anthropogenic source
Na^+	100.0		
K^+	4.5	95.5	
Mg^{2+}	19.6	80.4	
Ca^{2+}		100	
Cl^-	97.5	2.5	
SO_4^{2-}	0.9	1.3	97.8
NO_3^-	0.0	0.6	99.4

Air masses in the NW cluster were mainly from the northwest (Fig. 5a), passing over arid and semi-arid regions in northwest China. Thirteen precipitation events (31% of the total), including six in the spring, five in the summer and two in autumn, belong to this cluster. The precipitation samples in this group had high levels of crustal-originated ion species, leading to the highest pH among the four clusters.

Air masses in the NE cluster generally passed over big cities like Beijing, Shijiazhuang, and Zhengzhou before arriving in Xi'an (Fig. 5b). Nine precipitation events (21% of the total), including three in the spring, two in the summer and four in autumn, belong to this cluster. High anthropogenic emissions were expected from these big cities. Besides, the coal chemical industry region, centered in Weinan city, is also located northeast of Xi'an. Furthermore, the lowest Ca^{2+} concentration was also observed in this pathway. Thus, the precipitation samples in this cluster had the strongest acidity among the four clusters with an average pH of 5.2.

Air masses in the SE cluster normally passed over the developed regions of southeast China, such as the Pearl River Delta region and Yangtze River Delta region, where the air pollution levels were relatively high. Ten precipitation events (24% of the total), including one in the spring, four in the summer, and five in autumn belong to this cluster. It was not surprising that the concentrations of SO_4^{2-} and NO_3^- were the highest in the four groups, although the pH of this cluster was the second lowest.

Air masses in the SW cluster passed over Sichuan province, Guizhou province, or Tibet Plateau. Ten precipitation events (24% of the total), including one in the spring, six in the summer and three in autumn, belong to this cluster. Total ionic concentrations were the lowest among the four clusters. The mean pH of this cluster was 5.9.

It is evident that the precipitation events with air masses from the eastern directions (NE and SE clusters) had stronger acidity than those from the western directions (NW and SW clusters). This phenomenon is also supported by the geographical
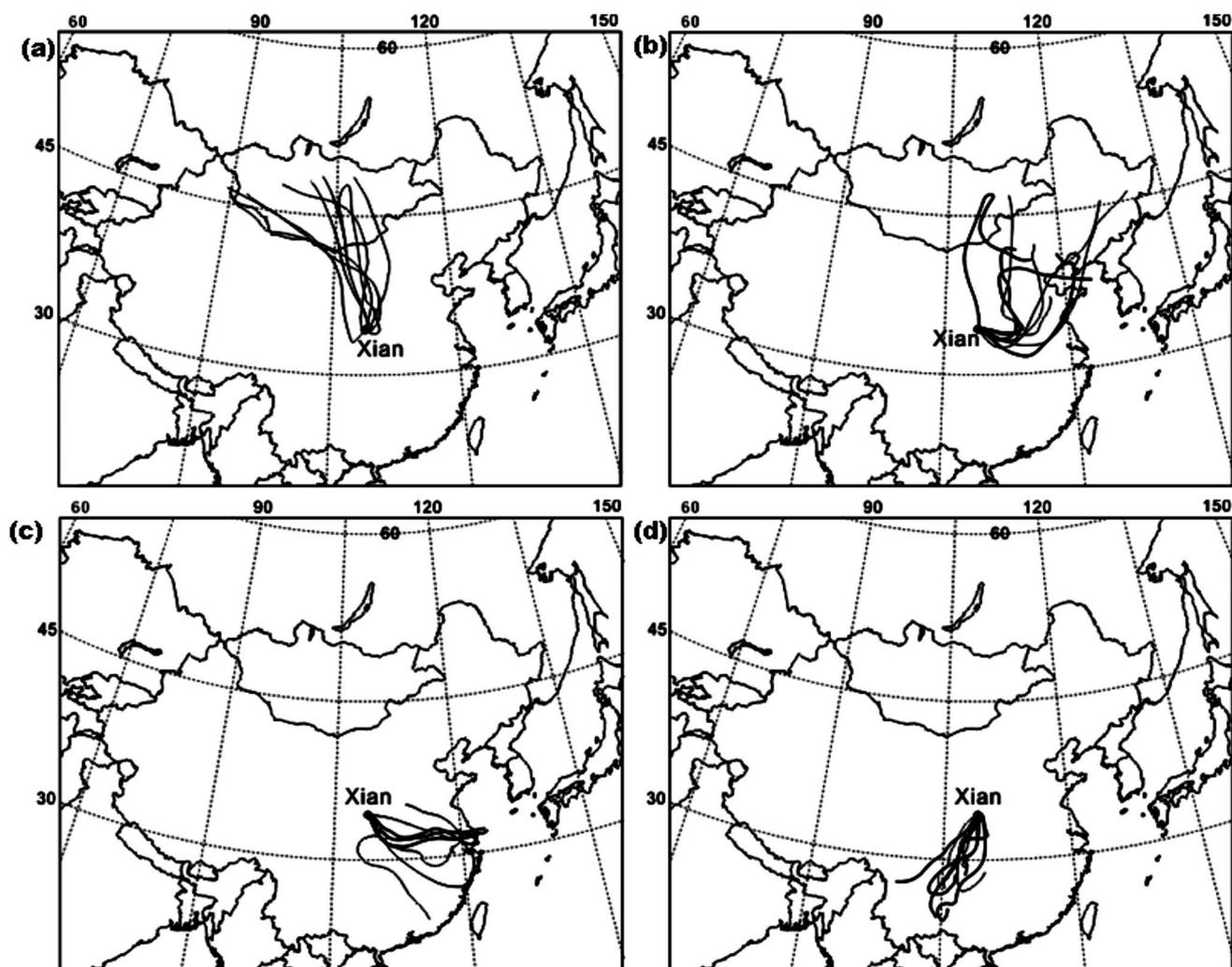
Fig. 5 48 h air mass back-trajectory of precipitation events from four typical directions at a height of 500 m, (a) NW, (b) NE, (c) SE, and (d) SW.

distributions of the observed surface layer SO_4^{2-}, NO_3^- and crustal materials in $PM_{2.5}$.[5] For example, the fractions of crustal matter in $PM_{2.5}$ mass in northwest Chinese cities (7.1–43%) were mostly higher than those in eastern Chinese cities (<20%) while the acidifying components showed a reverse pattern. The eastern region of China has been experiencing rapid industrialization and urbanization during the past three decades. The sulfur dioxide and nitrogen oxide emissions in this region were 3.3 and 4.4 times, respectively, the national averages. Secondary aerosol formation of fine particles has thus been increased dramatically.[45] Apparently, high fractions of acidic components in $PM_{2.5}$ in the eastern regions of China have contributed to acid rain, both locally and at regional to national scales.

3.6 Estimation of wet deposition of major ionic species

Wet deposition by snow in the winter was not included in the numbers presented in Table 6. Thus, the annual wet deposition listed in Table 6 might need to be adjusted up by 5–10% based on the amount of snow in 2009 (as mentioned above).

The annual sulfur wet deposition in Xi'an was 3.5 t km^{-2} per year. This amount is in the medium range compared to other major cities in China, *e.g.*, Beijing[46] (1.8 t km^{-2} per year), Shanghai[47] (3.4 t km^{-2} per year), Guangzhou[48] (6.5 t km^{-2} per year), and Chongqin[36] (6.7 t km^{-2} per year). Wet deposition of NO_3^--N and NH_4^+-N were 0.8 and 1.5 t km^{-2} per year, respectively, with a total nitrogen deposition of 2.3 t km^{-2} per year. It is noticed that the deposition of NH_4^+-N was two times

Table 5 pH value and ionic concentrations of precipitation samples with air masses from four typical transport pathways in Xi'an

Trajectory cluster	Sample number	pH	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	F^-	Cl^-	NO_3^-	SO_4^{2-}
NE	12	5.2	24.0	152.7	11.5	25.9	219.8	9.3	22.6	73.6	309.7
SE	10	5.5	50.7	432.5	31.0	63.0	474.5	25.5	76.8	187.0	979.6
NW	14	6.4	44.9	187.9	22.8	49.0	502.9	12.7	44.8	117.3	448.6
SW	14	5.9	24.2	148.3	11.9	32.3	254.7	8.8	28.2	58.0	290.7

Table 6 Wet depositions of major ions in Xi'an

	NH_4^+ (t km^{-2})	Ca^{2+} (t km^{-2})	NO_3^- (t km^{-2})	SO_4^{2-} (t km^{-2})
Spring	0.66	1.15	1.14	3.50
Summer	0.94	1.35	1.35	4.82
Autumn	0.39	0.50	0.93	2.28
Yearly	2.00	3.01	3.42	10.60

that of the NO_3^--N deposition in Xi'an. This implies that the benefit of the nitrogen deposition, *e.g.*, providing nutrients and enhancing the biological activities by NH_4^+, might be larger than by NO_3^-, in this region. The nitrogen deposition should provide significant nutrients to algae, rice, and wheat crops.[49] The total nitrogen deposition in Xi'an was in the low range compared to other major Chinese cities, *e.g.*, 2.0 t km^{-2} per year in Beijing[46] and Shanghai,[47] 3.1 t km^{-2} per year in Chongqin,[36] and 4.1 t km^{-2} per year in Guangzhou[48] but was substantially higher than at rural locations, *e.g.*, 0.24 t km^{-2} per year in Linzhi in Tibet and 1.45 t km^{-2} per year in the Liaohe River Plain.[50,51] Wet deposition of all of the major ions was highest in the summer and lowest in autumn, corresponding to the seasonal patterns of precipitation amounts.

4. Conclusions

Precipitation samples during a one year period (except winter snow) were collected and analyzed for pH and major inorganic ions at an urban site located in a semi-arid area of northwest China. As expected, many precipitation events were alkaline, similar to what was observed in other semi-arid and arid areas around the world. Yet a significant portion of weakly acidic precipitation events were observed in all seasons and ~30% of the precipitation events in autumn were found to be strongly acidic with a pH smaller than 5. Precipitation events with air masses from the east were more acidic than those from the west.

Both anthropogenic and crustal emissions affect precipitation acidity and ionic concentrations in precipitation. SO_4^{2-} and NO_3^- were major acidifying pollutants, accounting for 81% and 19%, respectively, of the total acidity. Ca^{2+} and NH_4^+ were major alkaline cations, accounting for 55% and 39%, respectively, of the neutralization. Ca^{2+} played a dominant role in spring acid neutralization, while NH_4^+ had a stronger buffering ability in summer. Although the contribution of Mg^{2+} in acid neutralization was mostly less than 10%, it was important in many precipitation events, *e.g.*, changing the precipitation from weakly acidic to weakly alkaline. Almost all of SO_4^{2-} and NO_3^- (>98%) were from anthropogenic origins; most Ca^{2+} and K^+ (>95%) were from the crustal sources; and most Cl^- and Na^+ (>97%) were from marine sources. The only exception was for Mg^{2+} for which 80% was from crustal sources and 20% from marine sources.

The annual wet deposition of sulfur in Xi'an was in the medium range among the major Chinese cities where data were available. The annual nitrogen deposition was in the lower range among the Chinese cities but was much higher than at a few rural locations. It is likely that the benefit of nitrogen deposition in this region is higher than its damage to the ecosystem, considering the significantly higher deposition of ammonium than that of nitrate. However, the high concentration of SO_4^{2-} in precipitation and its associated wet deposition, which also implies high ambient concentrations of sulfur species and associated dry deposition, all have harmful effects to humans as well as to ecosystems.

Although the city politically belongs to the northwest of China, geographically it is in the central area of the Chinese mainland. To reduce the acidity in the precipitation, sulfur emissions from eastern China need to be reduced. However, to improve the air quality in this city and to reduce the aerosol effects on climate, both anthropogenic emissions from eastern China and soil dust from western semi-arid and arid areas need to be controlled. The results from the present study provide useful scientific evidence for making emission-control policies on regional scales in China.

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