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Research Article

Variation characteristics of acid rain in Zhuzhou, Central China over the period 2011-2020

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ABSTRACT

Zhuzhou was one of the most polluted cities in China with the serious acid rain. Due to the implementation of air pollution control measures from 2016 to 2018, the acid rain pollution in this city has reduced. In order to understand the recent situation, a comprehensive study on the acid rain was carried out from January 2011 to December 2020. The pH values during the study period varied from 3.3 to 7.5, with a volume-weighted mean value of 4.7. The predominant acidic components of the precipitation were SO_4^{2-} and NO_3^-, accounting for 89.3% of the total anions. The ratio of non-sea-salt SO_4^{2-} to NO_3^- showed a decreasing trend, revealing that the pollution type of acid rain changed from sulfuric acid type to sulfuric acid and nitric acid compound type. The correlation analysis ($p < 0.05$) showed that SO_4^{2-} was positively correlated with NH_4^+, Ca^{2+}, and Mg^{2+}; hence, it predominated in precipitation as $(NH_4)_2SO_4$, NH_4HSO_4, $CaSO_4$, and $MgSO_4$. Significant positive correlation of Ca^{2+} with Mg^{2+} shows that they may originated mainly from crust. Significant positive correlation between SO_4^{2-} and F^- and Cl^- indicate that their source may be related to the non-ferrous metal smelting industry in Zhuzhou. Further correlation analysis shows that emissions from the non-ferrous metal smelting industry in the area have a large significant on SO_4^{2-} and F^- in precipitation, while Cl^- may still be emitted from other anthropogenic sources.

Introduction

Acid rain refers to atmospheric deposition with pH less than 5.6, such as acidic rainwater, snow, hail,dew, frost (Galloway et al., 1984). The acid rain acidifies the soil, corrodes cultural relics, destroys the ecosystem, and seriously threatens the living environment of human health, known as the grim reaper in the air, which is one of the environmental problems widely concerned by the world (Zhang et al., 2007, 2010; Liu et al., 2021). In the 1990s, the acid rain area in China accounted for 40% of the territory (Hao et al., 2000),

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and it was the third largest acid rain area in the world after Northeast America (Keresztesi et al., 2020) and Central Europe (Chang et al., 2022) at that time. However, the acid rain area has been decreased in recently years, the severe acid rain still restricts China's economic and social development (Dai et al., 2013; Shu et al., 2019; Chen et al., 2021).

In the 1980s, the Environment Protection Department and the Meteorological Department of China established a series of acid rain monitoring stations in China (Wang and Wang, 1996), revealing that the areas where suffering from acid rain were mainly concentrated in south area of the Yangtze River to the whole East China. Since the 1990s, the severe acid depositions appeared in four core zones of China, including Chongqing-Guiyang area in Southwest China, Changsha-Nanchong area in Central and South China, the Southeast coastal area, and the area near Qingdao city (Hao et al., 2000). The Central China was seriously polluted and became the area with the strongest acidity in precipitation at that time, the average annual pH values of precipitation in Changsha City and Zhuzhou City were lower than 4.0, and the acid rain frequency has reached 90% (Tian et al., 2001). At the beginning of the 21st century, the acid rain area in China generally showed a trend of expanding in area and slightly weakened in intensity and was characterized by high SO_4^{2-}, NH_4^+, Ca^{2+} concentrations and low NO_3^- concentration, which was identified as sulfuric acid type (Hao et al., 2000). At this time, the acid rain area in the South of China basically had no change, and Central China was still the most serious area of acid rain. Hunan Province was in a severe acid rain situation, and the average annual precipitation pH value was even less than 3.5 (Zhao and Hou, 2008).

In order to control the deterioration of acid rain, China has conducted extensive research on the formation and propagation mechanism, numerical simulation, control methods, and ecological effects. During the period of Ninth Five-year Plan, the well-known "Two Control Areas" plan was formulated, setting up SO_2 pollution control areas in the north and acid rain control areas in the south. During the Eleventh Five-year Plan, the Ministry of Science and Technology also set up a series of projects to comprehensively study the formation mechanism and control measures of acid rain (Hao et al., 2001). Hence, the concentration of SO_4^{2-}, frequency and area of acid rain decreased, the pH of acid rain increased, and the concentration ratio of SO_4^{2-}/NO_3^- decreased by more than 80%, but the type of acid rain was still dominated by sulfuric acid (Ministry of Ecology and Environment of the People's Republic of China, 2000-2005).

Zhuzhou City, located in the east of Hunan Province, was rated as one of the "Top Ten Polluted Cities in China" for two consecutive years in 2003 and 2004 because of its serious pollution. Its acid rain situation was the most serious among the cities in Hunan Province for several years (Ecology and Environment Department of Hunan, 2010-2020). This study focused on the precipitation characteristics and variation trend in Zhuzhou for a decade from January 2011 to December 2020, providing the reference for develop strategies of acid rain control in Hunan province or even Central China.

1. Experiment

1.1. Sampling sites

Zhuzhou City is one of the typical industrial cities in China, covering an area of 11,200 km^2, and with a population of 3.88 million. The chemical industry, non-ferrous metal smelting industry, and building materials industry are three main types of industries in this city. Zhuzhou has a humid subtropical monsoon climate, with an average annual temperature of 16°C to 18°C, and an average annual rainfall of 1500 mm. The predominant wind direction is south wind in summer and northwest wind in winter. Four sampling sites were established in this city by Zhuzhou Municipal Environmental Protection Bureau. As shown in Fig. 1, there had three sites in the urban area, which were located on the rooftops of Zhuye Hospital (S1), Municipal Monitoring Station (S2) and Tiantai Mountain Villa (S3). There are commercial areas near the sites, with busy traffic and developed industry. The background site was set up in Dajing Reservoir (S4), which is located in the scenic area and has no pollutant emissions sources around it.

1.2. Sampling and quality control

This study covered all rainfall events from January 2011 to December 2020. The polyethylene bottles were deployed to collect rain water in all sampling sites, and were cleaned three times by deionized water and other detergents. The bottles would be retrieved immediately after the rain stopped. A total of 1289 samples were collected in this study, and these samples were used to measure pH, electrical conductivity (EC), and the concentrations of anions and cations. Specifically, the pH of the precipitation was measured by a digital pH meter (PHGJ-3F, Rex, China) with a resolution of 0.01 pH unit and a range of -2.00 to 20.00. The EC was measured by a digital EC meter (DDS-307A, Rex, China) with a range of 0.00 µS/cm to 100 mS/cm. The cations (Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}) were detected using a Dionex ICS900 (Thermo Scientific, USA), while the anions (F^-, Cl^-, SO_4^{2-}, and NO_3^-) were detected by a Z2000 (Hitachi, Japan).

1.3. Method and data quality

1.3.1. Spearman's Correlation Coefficient

The Spearman's Correlation Coefficient is useful for exploratory data analysis in environmental investigations (Gautheir, 2001). In this idea, r_s is positive for positive correlation, negative for negative correlation, and significant for the trend when it is larger than the critical value in the Spearman Correlation Coefficients statistical table. The correlation coefficient can be calculated using the following equation:

$$r_s = \frac{6\sum d_i^2}{n(n^2-1)} \tag{1}$$

where, r_s is the correlation coefficient, d_i is the difference in rank between each pair of the two variables, which is the difference in permutation bits, n is the size of samples.

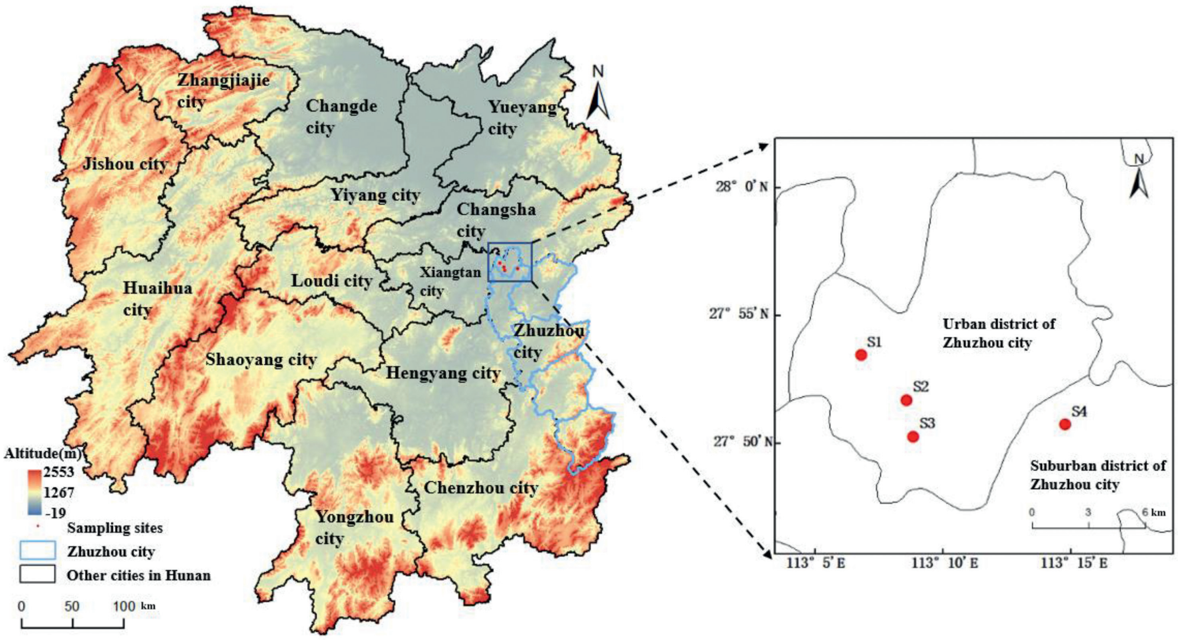

Fig. 1 – Location of sampling sites.

1.3.2. Fractional acidity (FA)

The relationship between acidic and neutralizing species was assessed by the following equation:

$$FA = [H^+]/([SO_4^{2-}] + [NO_3^-]) \quad (2)$$

1.3.3. Neutralization factor (NF)

NF was used to evaluate the relative neutralization of rainwater by following equation (Kulshrestha et al., 2003):

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

$$NF_{NH4}{}^{+} = [NH_4^+]/([NO_3^-]+[SO_4^{2-}]) \quad (4)$$

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

1.3.4. Cnss-SO_4^{2-}/CNO_3^-

Acid rain types were usually defined based on the ratio of the equivalent concentrations of SO_4^{2-} and NO_3^- in precipitation (Chen et al., 2021; Feng et al., 2021). For seasalt sulfate may also contribute to rainfall chemistry (Itahashi et al., 2018), we use the ratio of non-sea-salt SO_4^{2-} (nss-SO_4^{2-} = SO_4^{2-}-0.06028Na^+)/NO_3^- instead of SO_4^{2-}/NO_3^- in this study (Rodhe et al., 2002; Itahashi et al., 2018): (1) The equivalent concentration ratio of nss-SO_4^{2-} to NO_3^- (referred to as nss-SO_4^{2-}/NO_3^-) >3.0, for sulfuric acid type or coal-fired type; (2) 0.5 < nss-SO_4^{2-}/NO_3^- ≤ 3.0, for sulfuric acid and nitric acid type; (3) nss-SO_4^{2-}/NO_3^- ≤ 0.5, for the nitric acid type or fuel oil type.

1.4. Data quality

The US Environmental Protection Agency (EPA) range of ion difference in rainwater samples is 15%-30% for samples with an ion sum over 100 μeq/L and 30%-60% for samples with an ion sum of 50-100 μeq/L (Rastogi and Sarin, 2005; Lu et al., 2011), all the samples in this study met these criteria. Ion balance can be used to assess the data quality of each sample, as it reflects the possibility of missing ions (Kulshrestha et al., 2003; Obaidy and Joshi, 2006; Lu et al., 2011), the anions and cations by regression analysis in this study with R^2 of 0.825, which is shown in Appendix A Fig. S1 in the supplemental materials.

2. Results and discussion

2.1. Variation of pH value and acid rain frequency

The pH values of individual precipitation ranged from 3.3 to 7.5 during the study periods, with a volume-weighted mean (VWM) pH of 4.7. The VWM pH of samples collected in Dajing Reservoir (S4) was 5.1. The EC values varied from 21.7 to 119.8 μS/cm, with a VWM of 51.9 μS/cm, which is much higher than the background value in China in Waliguan mountain (14.8 μS/cm) (Tang et al., 2000), revealing that the air in Zhuzhou City was significantly polluted. The VWM pH exhibited a "high-low-high" upward trend (Fig. 2) with the VWM pH of 5.2 in 2020 being significantly higher than that of 4.5 in 2011. During the period of 2011 to 2020, the annual acid rain frequency ranged from 53.8% to 100%, the frequency of acid rain in 2011, 2012, 2013, and 2015 reached 100%. Due to the improvement in air quality, the VWM pH increased from 4.3 during 2016 to 5.3 during 2018, and the annual acid frequency decreased from 93.3% 2016 to 53.8% during 2018. The reason for the improvement may be attributed to the implementation of a number of effective air pollution control measures in this city. From 2016 to 2018, more than 200 enterprises including non-ferrous metal smelting, coal-fired power plants, and chemical industries, were relocated or shut down in the old

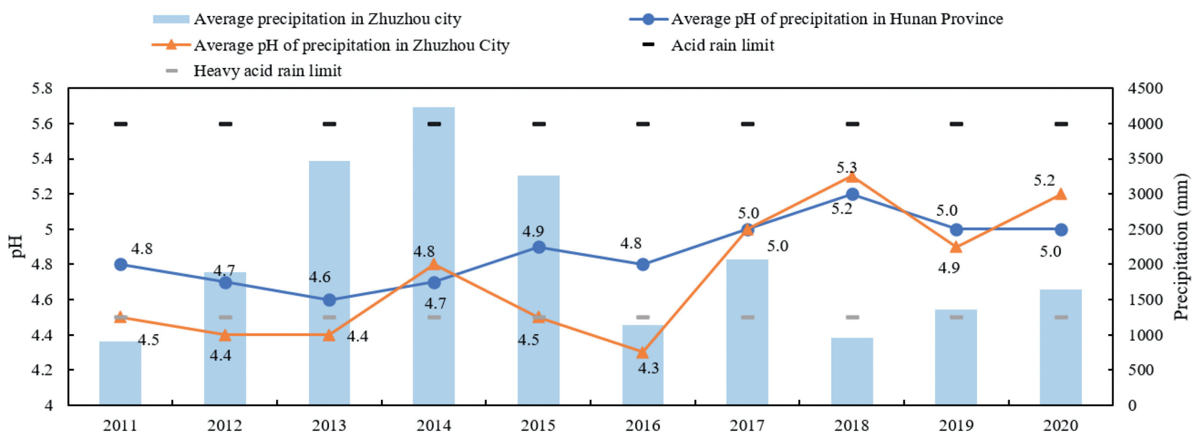

Fig. 2 – The annual VWM pH of precipitation in Zhuzhou and Hunan Province from 2011 to 2020.

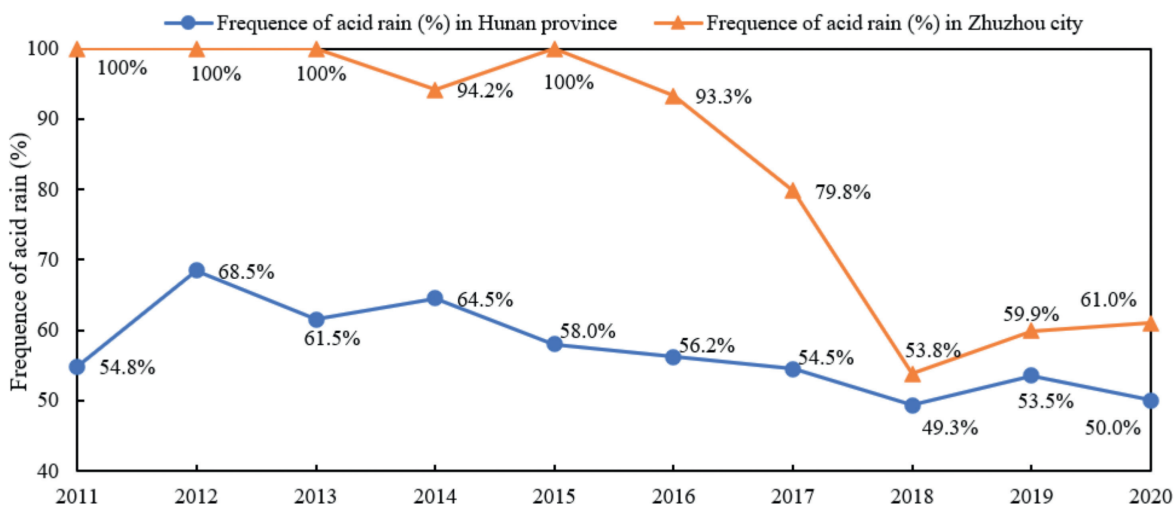

Fig. 3 – The annual acid rain frequency in Zhuzhou and Hunan Province from 2011 to 2020.

industrial zone of Qingshuitang. Moreover, severe restrictions on inefficient coal-fired boilers and motor vehicles with high-emission were imposed, resulting in a significant improvement in air quality.

In comparison with average level of Hunan Province (Ecology and Environment Department of Hunan, 2011-2020), the VWM pH of 2011-2016 in Zhuzhou (4.5) was lower than that in Hunan Province (4.7). After 2016, the annual VWM pH of precipitation in Zhuzhou has improved significantly, which has increased by 0.9 during 2016-2020. With the improvement of air quality, the VWM pH of 2019-2020 in Zhuzhou was 5.1, which was matched that in Hunan Province. The frequency of acid rain in Zhuzhou changed similarly to the VWM pH. From 2011 to 2016, the acid rain frequency in Zhuzhou City was 97.3%, which was much higher than that in Hunan Povince in the same period. After the improvement, in 2020, the acid rain frequency in Zhuzhou was 61.0% (Fig. 3), which was comparable to that of 50.0% in Hunan Province.

In this study, the pH of precipitation below 5.6 was used as the acid rain criterion. The rain with pH between 4.5 and 5.6 was classified as light acid rain, and the rain with pH below 4.5 was classified as heavy acid rain. The lowest annual VWM pH of precipitation in Zhuzhou City was 4.3 in 2016, which belonged to the type of heavy acid rain. The reason for the lowest annual VWM pH of precipitation may be that the precipitation in that year was less (1137.9 mm), which was much lower than the average precipitation of 2094.7 mm during study period. Precipitation has a weak scouring effect on atmospheric in this year, resulting in a low annual VWM pH of precipitation. The annual VWM pH of precipitation was also lower than heavy acid rain limit in 2012 and 2013 which indicated the serious acid rain situation of Zhuzhou during 2012-2013. The annual VWM pH of precipitation was 4.8 during 2014, the reason for the VWM pH being above 4.5 was likely due to the highest precipitation in this year (4233.7 mm), which was much higher than the average precipitation of 2094.7 mm during study period, and the scouring effect from large amounts of precipitation increased the pH value. Contrary to this phenomenon, the VWM pH of precipitation in Zhuzhou remained high in the case of low precipitation in 2017-2020, and the possible reason for this phenomenon was the implementation of strict atmospheric control measures in 2016-2018, which allowed the pH of precipitation in the city no longer depend on the scouring effect of precipitation to remain high.

Table 1 – Status quo of precipitation weighted average pH in some cities in China.

City	Region	Periods	VWM pH of precipitation	Refs.
Zhuzhou	China	2011-2020	4.7	This study
Beijing	China	2017-2018	6.7	Xu et al. (2020)
Shanghai	China	2016	5.3	Meng et al. (2019)
Lanzhou	China	2011-2014	6.7	Zhang (2019)
Lijiang	China	2014	6.1	Niu et al. (2014)
Guilin	China	2015-2017	5.5	Feng et al. (2021)
Zhuhai	China	2008-2018	5.2	Wang et al. (2021)
Xi'an	China	2016-2019	6.8	Li et al. (2022)
Taiyuan	China	2011-2018	6.1	Zhang et al. (2020)
Skukuza	South Africa	2009-2014	4.7	Conradie et al. (2016)
Princeton	America	1978-2017	4.3	Keresztesi et al. (2020)
Logan	America	1978-2017	6.4	Keresztesi et al. (2020)

The Spearman's correlation coefficient was used to analyze the trend of annual VWM pH of precipitation. To determine whether the correlation coefficient (0.648, $n = 10$) is significant, we can compare it to the critical value for $n = 10$ from the Spearman Correlation Coefficients statistical table. According to the table, the critical value is 0.564 ($\alpha = 0.05$). Since the calculated value of 0.648 exceeded the critical value when $\alpha = 0.05$, we can deduce the significantly upward trend of annual VWM pH of precipitation during 2011-2020 in Zhuzhou at the 95% probability level, which reveals that the acidity of precipitation in Zhuzhou during study period has improved.

As shown in Table 1, the VWM pH of the precipitation in Zhuzhou City was compared with those in other Chinese cities and in urban areas of other countries, such as skukuza in South Africa and Princeton, Logan in America. The VWM pH of precipitation in the study area was lower than that of all the cities in Northern China such as Beijing during 2017-2018 (6.7) (Xu et al., 2020), Lanzhou during 2011-2014 (6.7) (Zhang, 2019), Xi'an during 2016-2019 (6.8) (Li et al., 2022) and Taiyuan during 2011-2018 (6.1) (Zhang et al., 2020) and most of the cities in the southern region such as Shanghai during 2016 (5.3) (Meng et al., 2019), Lijiang during 2014 (6.1) (Niu et al., 2014), Guilin during 2015-2017 (5.5) (Feng et al., 2021) and Zhuhai during 2008-2018 (5.2) (Wang et al., 2021). The VWM pH of precipitation in the study area was also lower than that of Logan in America during 1978-2017 (6.4) (Keresztesi et al., 2020). The VWM pH of precipitation in Skukuza in South Africa during 2009-2014 (4.7) (Conradie et al., 2016) and Princeton in America during 1978-2017 (4.3) (Keresztesi et al., 2020) was almost matched that in Zhuzhou. In addition, according to the Chinese Ecological Environment Bulletin of 2020, among the 465 cities (districts and counties) monitoring precipitation, the frequency of acid rain was 10.3%, and the annual average pH was 5.6 in China, while the acid rain frequency of Zhuzhou in 2020 was 61.0%, and the annual VWM pH of precipitation was 5.2. Although it was a significant improvement compared with the acid rain situation of Zhuzhou in 2011, there was still a certain gap compared with other cities in China. In summary, the annual VWM pH of precipitation in Zhuzhou from 2011 to 2020 has increased, and the frequency of acid rain has decreased significantly. The annual VWM pH of precipitation and acid rain in 2018-2020 have been close to or better than that of Hunan Province, but is still behind of other Chinese cities.

2.2. *Origin of acidity*

In Zhuzhou, the predominant cations in the precipitation were SO_4^{2-} and NO_3^- which indicates the main precipitation acidity is due to H_2SO_4 and HNO_3 and it was consistent with previous studies in China (Pu et al., 2017; Chen et al., 2021). Meanwhile HCl, HF, and other organic acids are considered as negligible acidity contributors compared to H_2SO_4 and HNO_3 (Khwaja and Husain, 1990; Wang et al., 2012). The potential acidity could be estimated by the sum of non-sea-salt sulfate and nitrate in precipitation (Rodhe et al., 2002; Itahashi et al., 2018). In this study, the sum of annual concentration of nss-SO_4^{2-} and NO_3^- varied from 122.1 to 645.6 μeq/L with 10-year period VWM value of 332.1 μeq/L. These values correspond to the pH of precipitation in the range of 3.2-3.9, with a 10-year period VWM value of 3.5. The measured and estimated pH is given in Fig. 4, the measured pH value is on average 1.1 higher than estimated pH which indicated that without the neutralization of acidity, the pH of precipitation would be lower (around 3.5) than what it showed. The contribution of nss-SO_4^{2-} and NO_3^- to acidity can be calculated by the ratio of the respective equivalent concentration to their total (Wang et al., 2012). During the study period, nss-SO_4^{2-} and NO_3^- contributed 81.9% and 18.1% of the acidity in the precipitation.

In most areas of the Northern hemisphere, the acidity of rain is controlled by strong acids, such as H_2SO_4 and HNO_3 (Overrein et al., 1982). Considering that SO_4^{2-} and NO_3^- were the main acidogenic components, the relationship between acidic and neutralizing species was evaluated using the Fractional Acidity (FA). A value of 1 indicates that the acidity produced by the strong acid is not neutralized, whereas a value of 6.0% in precipitation in Zhuzhou from 2011 to 2020 indicated that approximately 94.0% of the acidity produced by the strong acid was neutralized. The reason why the precipitation in Zhuzhou was still acidic may be due to the joint effect of a small proportion of unnaturalized SO_4^{2-}, NO_3^-, and some organic acids such as formic acid and acetic acid.

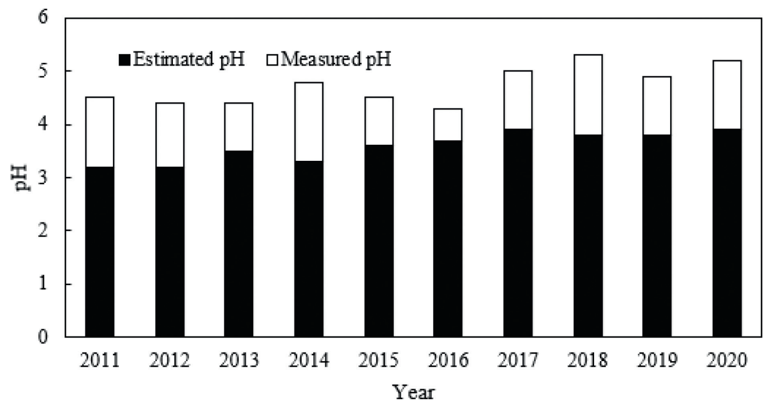

Fig. 4 – Variations of measured pH and estimated pH in Zhuzhou from 2011 to 2020.

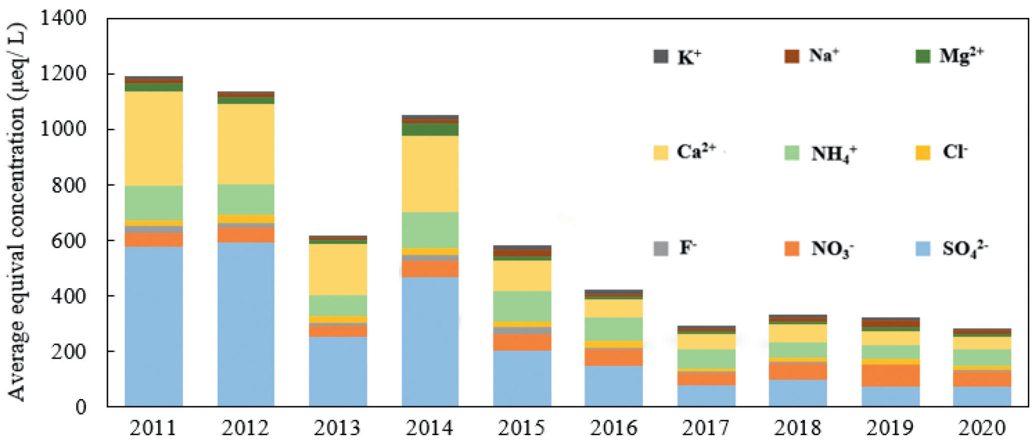

Fig. 5 – Changes of equivalent concentration of main ions in Zhuzhou from 2011 to 2020.

2.3. *Acid neutralization*

In Zhuzhou, the predominant cations in the precipitation were Ca^{2+} and NH_4^+, and the sum equivalent concentration of these two species account for about 53.5% of the total cations. The main anions were SO_4^{2-} and NO_3^-, with the sum equivalent concentration accounting for 89.3% of the total anions. Considering the entire study period, the annual weighted average concentrations of total amount of ions in precipitation exhibited a declining trend (Fig. 5). The annual average equivalent concentrations of SO_4^{2-} and Ca^{2+} decreased from 579.2 to 72.9 μeq/L, and 338.5 to 46.5 μeq/L, respectively, which was the primary reason for the significant decrease in the total number of ions. The equivalent concentrations of NH_4^+ and NO_3^- showed slight variation. The Na^+ and K^+ remained stable at a low level, and the sum equivalent concentration account for 11.8% of the total cations.

The high correlation between (SO_4^{2-}+NO_3^-) and (Ca^{2+}+NH_4^++Mg^{2+}) was 0.953 (Appendix A Fig. S2), demonstrating that the concentration of H^+ was not determined by a particular ion, but rather by the interaction of all acidogenic ions with neutralizing ions. In order to thoroughly examine the neutralizing capacity of alkaline species in precipitation, the neutralization factor was applied to Ca^{2+}, NH_4^+, and Mg^{2+}. The neutralization factor of Ca^{2+} in the precipitation was 0.49, indicating that Ca^{2+} could effectively neutralize acidity, and the neutralization factor of NH_4^+ was 0.28, which was the ion with the second highest contribution to neutralize acidity. Together with the neutralizing contribution of Mg^{2+}, the sum of them was 0.83, indicating that Ca^{2+}, NH_4^+, and Mg^{2+} were able to neutralize most of the SO_4^{2-} and NO_3^-.

From the annual variation analysis of neutralization contribution (Fig. 6), Ca^{2+} decreased from 0.54 during 2010 to 0.36 during 2020, whereas NH_4^+ increased from 0.20 during 2010 to 0.44 during 2020, indicating that NH_3 was the dominant factor in neutralizing precipitation acidity, and the increase of NH_4^+ neutralization contribution was mainly due to the reduction of other alkaline particles in the precipitation (Fig. 5). The average equivalent concentration of NH_4^+ in precipitation in Zhuzhou during 2010-2020 was 93.4 μeq/L, which was obviously higher than that in Jeju Island, South Korea during 1997-2015 (22.6 μeq/L) and in Tokyo, Japan during 1990-2002 (40.4 μeq/L) (Okuda et al., 2005; Bu et al., 2020). This phenomenon revealed that NH_3 could promote the occurrence of $PM_{2.5}$ pollution events, and there was an urgent need to control NH_3 emissions in China recent years. Considering that the reduction of NH_3 concentration may aggravate acid rain pollution, it is recommended that NH_3 emission reduction measures should be implemented prudently in Zhuzhou.

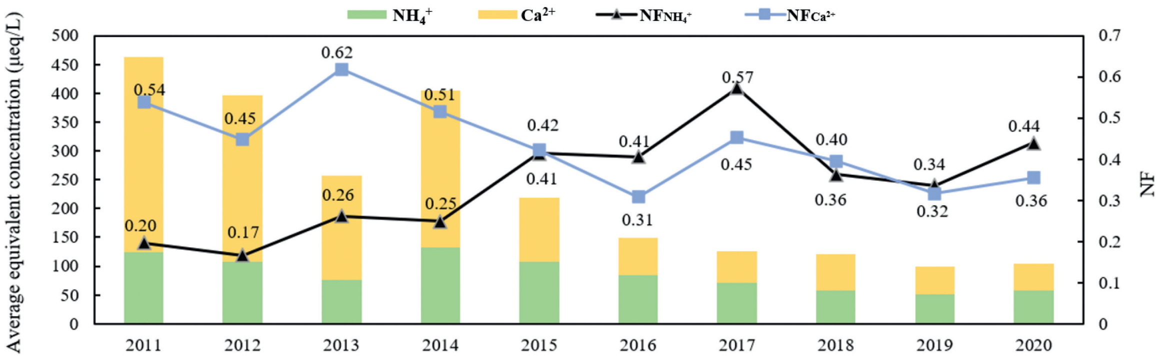

Fig. 6 – Annual variations of NH_4^+, Ca^{2+} concentrations and their neutralization factors during 2011-2020.

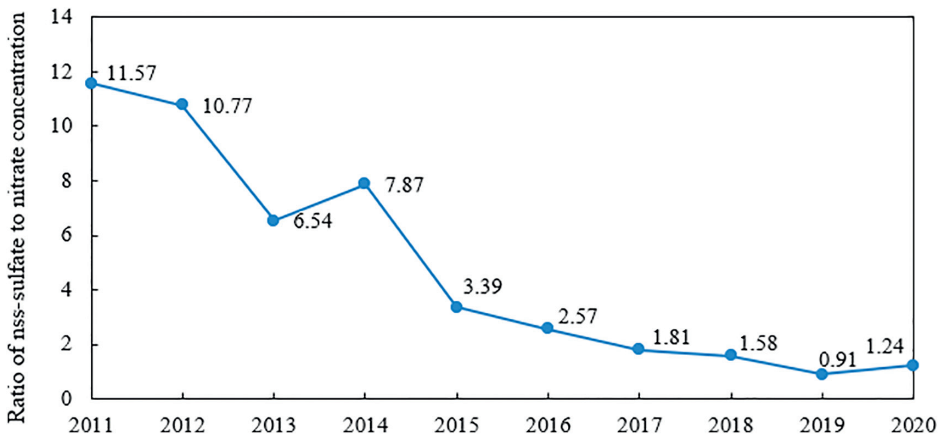

Fig. 7 – Changes in the ratio of nss-SO_4^{2-} to NO_3^- equivalent concentrations from 2011 to 2020.

2.4. *Changes of Cnss-SO_4^{2-}/CNO_3^- in precipitation*

In China, atmospheric SO_2 mainly comes from the combustion of fossil fuels, while NO_x mainly comes from sources such as vehicle exhaust (Chen et al., 2021). In previous studies, acid rain types were usually defined based on the ratio of their concentrations in precipitation (Chen et al., 2021; Feng et al., 2021). The ratio of nss-SO_4^{2-}/NO_3^- exhibited a downward trend over the 10-year study period (Fig. 7), and the contribution of NO_3^- in precipitation increased, indicating that the type of precipitation in Zhuzhou is gradually changing from "sulfuric acid type" to "sulfuric acid and nitric acid compound type". Changes in acid rain types was closely related to Chinese government's control policies and economic development, including the national acid rain and SO_2 pollution prevention and control during Eleventh Five-Year Plan, Action Plan for the Prevention and Control of Air pollution and a series of other policies. Additionally, Zhuzhou started the reconstruction of the Qingshuitang Industrial Zone. With the relocation or shutdown of a large number of chemical and smelting industries, both SO_2 and NO_x emissions in Zhuzhou showed significant decreasing trend. The SO_4^{2-} concentrations in precipitation decreased continuously from 2015 to 2020, and NO_3^- concentrations showed a slowdown in decline in 2017 and an increase in 2019 (Fig. 5), the reason that NO_3^- concentrations did not decrease to the same level as SO_4^{2-} concentrations could be the reduction in NOx emissions led to enhanced atmospheric oxidation which contributes to particulate nitrate pollution (Huang et al., 2020). The nss-SO_4^{2-}/NO_3^- value in precipitation in Zhuzhou was 1.24 during 2020, while it was 1.62 in New York (Ito et al., 2002), reflecting the serious local NO_x pollution, which was typical of photochemical pollution. Since the 1990s, China's energy structure has changed, and the proportion of clean energy has gradually increased, while the annual NO_x emissions have been increasing due to the increase in China's car ownership. Consequently, more and more nitrate aerosols are dissolving during precipitation, increasing the concentration of nitrate in precipitation (Liu et al., 2016; Chen et al., 2021). In this context, many cities in China have undergone similar changes in the type of pollution as Zhuzhou, such as Guangzhou where the value was 11.7 during 1998 and decreased to 2.1 during 2018 (Chen et al., 2021), and Beijing where the value was 3.1 (Hu et al., 2005) during 2003 and decreased to 0.5 during 2018 (Xu et al., 2020).

2.5. *Correlation analysis*

The correlation coefficients of ions in precipitation could reveal the origin of the ions or the characteristics of the chemical reaction processes undergone (Basak and Alagha, 2004). Hence, the ion correlation analysis can assist in determining the source of ions in precipitation. Previous researches

Table 2 – Correlation coefficients among the ionic constituents of precipitation.

	SO_4^{2-}	NO_3^-	F^-	Cl^-	NH_4^+	Ca^{2+}	Mg^{2+}	Na^+	K^+
SO_4^{2-}	1.000								
NO_3^-	-0.247	1.000							
F^-	0.744*	-0.202	1.000						
Cl^-	0.659*	-0.097	0.549	1.000					
NH_4^+	0.850*	-0.229	0.870*	0.626	1.000				
Ca^{2+}	0.983*	-0.313	0.742*	0.605	0.840*	1.000			
Mg^{2+}	0.797*	0.088	0.579	0.505	0.810*	0.816*	1.000		
Na^+	-0.127	0.666*	0.296	0.029	-0.017	-0.131	0.089	1.000	
K^+	-0.207	0.600	0.002	-0.203	0.090	-0.288	0.086	0.309	1.000

* Correlation is significant at $P < 0.05$ (two-tailed).

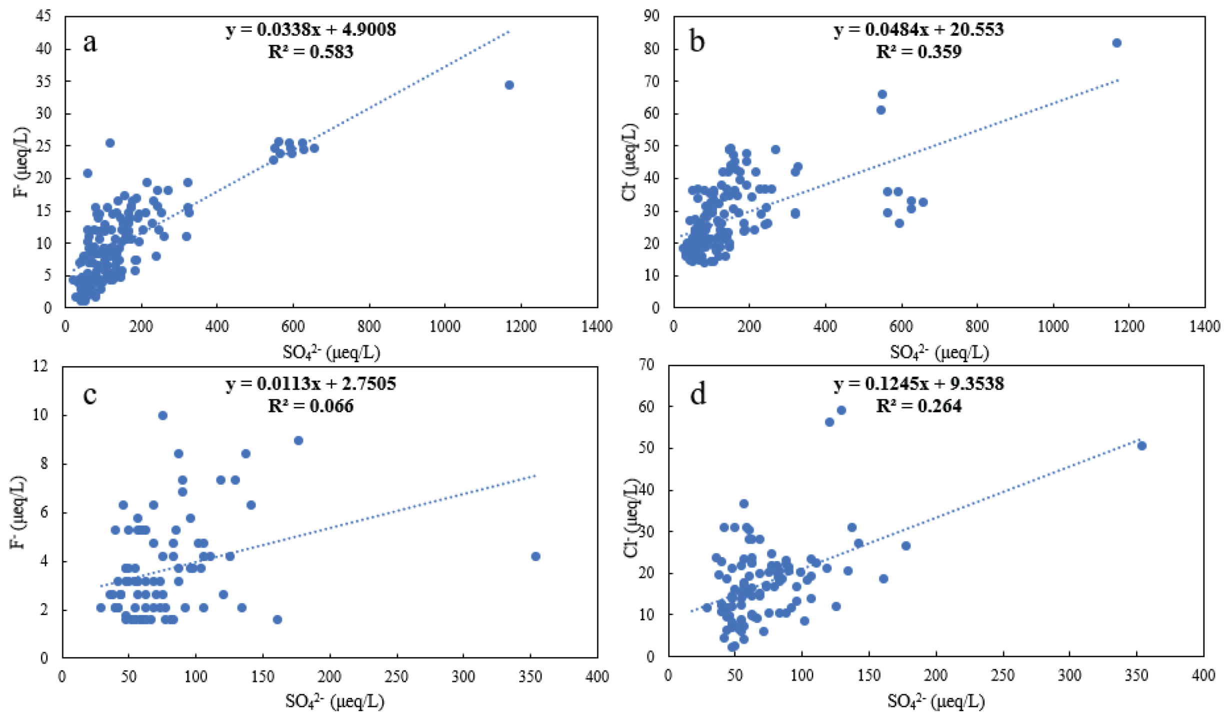

Fig. 8 – The correlation between SO_4^{2-} with F^- and Cl^- in precipitation in Zhuzhou in 2015 (a, b) and 2020 (c, d).

showed that SO_4^{2-} was significantly correlated with NO_3^- in precipitation in other cities in China (Hu et al., 2005; Lu et al., 2011; Rao et al., 2017). As shown in Table 2, in Zhuzhou City, Ca^{2+} showed the most significant positive correlation with SO_4^{2-} in precipitation, as well as NH_4^+ and Mg^{2+}, indicating that sulfate was mainly present in precipitation as $(NH_4)_2SO_4$, NH_4HSO_4, $CaSO_4$, and $MgSO_4$, and the most significant correlation with Ca^{2+} may be due to the higher stability of $CaSO_4$ (Cao et al., 2009). At the same time, NH_4^+, Mg^{2+}, and Ca^{2+} exhibited a significant correlation, which was also found in the precipitation of Xi'an (Lu et al., 2011). The significant correlation between Mg^{2+} and Ca^{2+} in precipitation indicated that soil and land dust were the main sources of both. The sources of NH_3 in the atmosphere included vehicle exhaust, chemical emissions, agricultural or biological processes (Grosjean, 1983), and biomass combustion in smoky condition can also produce high NH_3 (Keene et al., 1986). The significant correlation between Mg^{2+}, Ca^{2+} with NH_4^+ indicated that NH_4^+ mainly came from nitrogen fertilizers used in agricultural fields. Meanwhile, SO_4^{2-} showed a significant correlation with F^- and Cl^-, suggesting that they were from the same source and related to local industries.

In Zhuzhou City, SO_4^{2-} was an important acid-causing ion in precipitation, and the statistics of industrial energy consumption showed that non-ferrous metal smelting is the most consumed industry in the city for coke and electricity energy (People's Government of Zhuzhou city, 2010). While the electricity generation in Zhuzhou mainly depends on coal consumption, and the non-ferrous metal smelting industry is considered to be closely related to local SO_2 emissions, however, the non-ferrous metal smelting industry moved out of the city in 2016-2018, and took pollution control measures. SO_4^{2-} showed a high correlation with F^- and Cl^- in the analysis of precipitation ion correlation; Shenyang, as a city with developed nonferrous metal smelting industry, had same characteristic (Zhang et al., 2013). To investigate the reasons for the high correlation of SO_4^{2-} with F^- and Cl^- in the precipitation of the city, the precipitation data of 2015 and 2020 were selected. The correlation between SO_4^{2-} and F^- in precipitation in Zhuzhou decreased substantially from 2015 to 2020 (0.583→0.066), and the correlation between SO_4^{2-} and Cl^- decreased slightly (0.359→0.264) (Fig. 8). Combined with the changes in SO_2 emissions from 2016 to 2018, it suggested that emissions from the smelting industry at the site had a large impact on SO_4^{2-} and F^- in precipitation, while Cl^- may still be emitted in other artificial emission sources.

3. Conclusions

An investigation of precipitation in four sites of Zhuzhou was performed from January 2011 to December 2020. The major conclusions are summarized as follows:

During the study period, the pH values in Zhuzhou varied from 3.3 to 7.5 with a VWM of 4.7, and the frequency of acid rain ranged from 53.8% to 100%. Due to the implementation of air pollution control measures in Zhuzhou from 2016 to 2018, the acid rain situation has improved.

In terms of concentrations of ionic species during the study periods, the predominant cations in the precipitation of Zhuzhou were Ca^{2+} and NH_4^+, while the predominant anions were SO_4^{2-} and NO_3^-. The annual average concentration of total ions in precipitation showed a downward trend. NH_3 has become the dominant factor in neutralizing precipitation acidity, and the reduction of ammonia emissions may aggravate acid rain in Zhuzhou.

The concentration ratio of nss-SO_4^{2-}/NO_3^- exhibited a downward trend, and the type of precipitation in Zhuzhou is gradually changing from sulfuric acid type to the compound type of both sulfuric acid and nitric acid.

The correlation analysis revealed that sulfate in precipitation of Zhuzhou was mainly present in precipitation as $(NH_4)_2SO_4$, NH_4HSO_4, $CaSO_4$, and $MgSO_4$. The NH_4^+, Mg^{2+}, and Ca^{2+} in precipitation of Zhuzhou were mainly affected by land dust and nitrogen fertilizers used in agricultural fields. Moreover, the emissions from the non-ferrous metal smelting industry in the area had a large impact on SO_4^{2-} and F^- in precipitation, while Cl^- may still be emitted from other anthropogenic sources.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A Supplementary data

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jes.2023.03.035.

References

Basak, B., Alagha, O., 2004. The chemical composition of rainwater over Büyükekmece Lake, Istanbul. Atmos. Res. 71, 275–288.

Bu, J.O., Ko, H.J., Kang, C.H., Kim, W.H., Song, J.M., 2020. Composition and Pollution Characteristics of Precipitation in Jeju Island, Korea for 1997–2015. Atmosphere 12, 25.

Cao, Y.Z., Wang, S.Y., Zhang, G., Luo, J.Y., Lu, S.Y., 2009. Chemical characteristics of wet precipitation at an urban site of Guangzhou, South China. Atmos. Res. 94, 462–469.

Chang, C.T., Yang, C.J., Huang, K.H., Huang, J.C., Lin, T.C., 2022. Changes of precipitation acidity related to sulfur and nitrogen deposition in forests across three continents in north hemisphere over last two decades. Sci. Total Environ. 806, 150552.

Chen, X., Shan, X.R., Shi, Z.J., Zhang, J.E., Qin, Z., Xiang, H.M., et al., 2021. Analysis of the spatio-temporal changes in acid rain and their causes in China (1998–2018). Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences. 5, 593-599.

Conradie, E.H., Zyl, P.V., Pienaar, J.J., Beukes, J.P., Galy-Lacaux, C., Venter, A.D., et al., 2016. The chemical composition and fluxes of atmospheric wet deposition at four sites in South Africa. Atmos. Environ. 146, 113–131.

Dai, Z.M., Liu, X.M., Wu, J.J., Xu, J.M., 2013. Impacts of simulated acid rain on recalcitrance of two different soils. Environ. Sci. Pollut. Res. Int. 20, 4216–4224.

Ecology and Environment Department of Hunan, 2010-2020. Bulletin on the ecological environment of Hunan Province, Changsha.(In Chinese)

Feng, Q., Li, Y.L., Wen, J.H., Wang, H.Q., Liao, L., 2021. Analysis of wet deposition characteristics in the city of Guilin, China. Environ. Monit. Assess. 193, 597.

Galloway, J.N., Likens, G.E., Hawley, M.E., 1984. Acid precipitation: natural versus anthropogenic components. Science 226, 829–831.

Gautheir, T.D., 2001. Detecting trends using Spearman's rank correlation coefficient. Environ. Forensics 2, 359–362.

Grosjean, D., 1983. Atmospheric reactions of pyruvic acid. Atmos. Environ. 17, 2379–2382.

Hao, J.M., Duan, L., Zhou, X.L., Fu, L.X., 2001. Application of a LRT model to acid rain control in China. Environ. Sci. Technol. 35, 3407–3415.

Hao, J.M., Wang, S.X., Liu, B.J., He, K.B., 2000. Control strategy for sulfur dioxide and acid rain pollution in China. J. Environ. Sci. 12, 385–393.

Huang, X., Ding, A.J., Gao, J., Zheng, B., Zhou, D.R., Qi, X.M., et al., 2020. Enhanced secondary pollution offset reduction of primary emissions during COVID-19 lockdown in China. Natl. Sci. Rev. 8 (2), nwaa137.

Hu, M., Zhang, J., Wu, Z.J., 2005. Chemical composition characteristics of precipitation in Beijing and its removal effect on atmospheric particulate matter. Sci. Sin. 35, 169–176 (In Chinese).

Itahashi, S., Yumimoto, K., Uno, I., Hayami, H., Fujita, S., Wang, Y.S., et al., 2018. A 15-year record (2001-2015) of the ratio of nitrate to non-sea-salt sulfate in precipitation over East Asia. Atmos. Chem. Phys. 18 (4), 2835–2852.

Ito, M., Mitchell, M.J., Driscoll, C.T., 2002. Spatial patterns of precipitation quantity and chemistry and air temperature in the Adirondack region of New York. Atmos. Environ. 36, 1051–1062.

Keene, W.C., Pszenny, A.A.P., Galloway, J.N., Hawley, M.E., 1986. Sea-alt corrections and interpretation of constituent ratios in marine precipitation. J. Geophys. Res. 91, 6647–6658.

Keresztesi, G., Nita, I.A., Boga, R., Birsan, M.V., Bodor, Z., Szep, R., 2020. Spatial and long-term analysis of rainwater chemistry over the conterminous United States. Environ. Res. 188, 109872.

Khwaja, H.A., Husain, L., 1990. Chemical characterization of acid precipitation in Albany, New York. Atmos. Environ. 24, 1869–1882.

Kulshrestha, U.C., Kulshrestha, M.J., Sekar, R., Sastry, G.S.R., Vairamani, M., 2003. Chemical characteristics of rainwater at an urban site of south-central India. Atmos. Environ. 37, 3019–3026.

Li, R.F., Dong, X.Y., Xie, C., Zhao, L.J., 2022. Long-term observations of the chemical composition, fluxes and sources of atmospheric wet deposition at an urban site in Xi'an, Northwest China. Environ. Monit. Assess. 194, 68.

Liu, L., Zhang, X.Y., Lu, X.H., 2016. The composition, seasonal variation, and potential sources of the atmospheric wet sulfur (S) and nitrogen (N) deposition in the southwest of China. Environ. Sci. Pollut. Res. 23, 6363–6375.

Liu, Z.Q., Wei, H., Zhang, J., Saleem, M., He, Y.N., Zhong, J., et al., 2021. Seasonality regulates the effects of acid rain on microbial community in a subtropical agricultural soil of Southern China. Ecotoxicol. Environ. Saf. 224, 112681.

Lu, X.W., Li, L.Y., Li, N., Yang, G., Luo, D.C., Chen, J.H., 2011. Chemical characteristics of spring rainwater of Xi'an city, NW China. Atmos. Environ. 45, 5058–5063.

Meng, Y., Zhao, Y.L., Li, R., Li, J.L., Cui, L.L., Kong, L.D., et al., 2019. Characterization of inorganic ions in rainwater in the megacity of Shanghai: spatiotemporal variations and source apportionment. Atmos. Res. 222, 12–24.

Tang, J., Xue, H.S., Yu, X.L., Cheng, H.B., Xu, X.B., Zhang, X.C., et al., 2000. The preliminary study on chemical characteristics of precipitation at Mt. Waliguan. Acta Scientiae Circumstantiae 20, 420–425.

Ministry of Ecology and Environment of the People's Republic of China, 2005-2000. Chinese ecological environment bulletin, Beijing. (In Chinese)

Niu, H.W., He, Y.Q., Lu, X.X., Shen, J., Du, J.K., Zhang, T., et al., 2014. Chemical composition of rainwater in the Yulong Snow Mountain region, Southwestern China. Atmos. Res. 144, 195–206.

Obaidy, A., Joshi, H., 2006. Chemical composition of rainwater in a tropical urban area of northern India. Atmos. Environ. 40, 6886–6891.

Okuda, T., Iwase, T., Ueada, H., Suda, Y., Tanaka, S., Dokiya, Y., et al., 2005. Long-term trend of chemical constituents in precipitation in Tokyo metropolitan area, Japan, from 1990 to 2002. Sci. Total Environ. 339, 127–141.

Overrein, L.N., Seip, H.M., Tollan, A., 1982. Acid precipitation-Effects onforest and fish. Environ. Policy Law 8, 101–103.

People's Government of Zhuzhou city, 2010. Analysis of industrial energy consumption structure in Zhuzhou City, Zhuzhou.

Pu, W.W., Quan, W.J., Ma, Z.L., Shi, X.F., Zhao, X.J., Zhang, L.N., et al., 2017. Long-term trend of chemical composition of atmospheric precipitation at a regional background station in Northern China. Sci. Total Environ. 580, 1340–1350.

Rao, W.B., Han, G.L., Tan, H.B., Jin, K., Wang, S., Chen, T.Q., 2017. Chemical and Sr isotopic characteristics of rainwater on the Alxa Desert Plateau, North China: Implication for air quality and ion sources. Atmos. Res. 193, 163–172.

Rastogi, N., Sarin, M.M., 2005. Chemical characteristics of individual rain events from a semi-arid region in India: three-year study. Atmos. Environ. 39, 3313–3323.

Rodhe, H., Dentener, F., Schulz, M., 2002. The global distribution of acidifying wet deposition. Environ. Sci. Technol. 36, 4382–4388.

Shu, X., Zhang, K.R., Zhang, Q.F., Wang, W.B., 2019. Ecophysiological responses of Jatropha curcas L. seedlings to simulated acid rain under different soil types. Ecotoxicol. Environ. Saf. 185, 109705.

Tian, H.Z., Lu, Y.Q., Hao, J.M., Wang, S.X., Xue, Z.G., 2001. Control courses and progress of acid rain and SO_2 pollution in China. Electr. Power 34, 51–56 (In Chinese).

Wang, G.Z., Liu, S.J., Yu, X.N., 2021. Characteristics of precipitation chemistry and wet deposition in Zhuhai,China. Res. Environ. Sci. 34, 1612–1620 (In Chinese).

Wang, W.X., Wang, T., 1996. On acid rain formation in China. Atmos. Environ. 30, 4091–4093.

Wang, Y.S., Yu, W.P., Pan, Y.P., Wu, D., 2012. Acid neutralization of precipitation in Northern China. J. Air Waste Manag. Assoc. 62 (2), 204–211.

Xu, W., Wen, Z., Shang, B., Dore, A.J., Tang, A.H., Xia, X.P., et al., 2020. Precipitation chemistry and atmospheric nitrogen deposition at a rural site in Beijing, China. Atmos. Environ. 223, 117253.

Zhang, F.X., 2019. Spatial pattern and seasonal variation of alkaline precipitation observed in the Gansu Province, NW China. Environ. Earth Sci. 78, 185–193.

Zhang, L.J., Zhang, X.Y., Jiang, H., Zhang, Q.X., 2013. Chemical characteristics and source assessment of rainwater at Shenyang. Environ. Sci. 34, 2081–2088 (In Chinese).

Zhang, J.E., Ouyang, Y., Ling, D.J., 2007. Impacts of simulated acid rain on cation leaching from the Latosol in south China. Chemosphere 67, 2131–2137.

Zhang, X.M., Chai, F.H., Wang, S.L., Sun, X.Z., Han, M., 2010. Research progress of acid precipitation in China. Res. Environ. Sci. 23, 527–532 (In Chinese).

Zhang, Z.Q., Yang, C., He, Q.S., Guo, L.L., Tian, X., Zhang, K., et al., 2020. Predominant effects of emission reduction by recording 8-year water-soluble ions in precipitation in Taiyuan, North China. Atmos. Pollut. Res. 11, 1922–1932.

Zhao, Y.X., Hou, Q., 2008. An analysis on spatial/temporal evolution of acid rain in China (1993-2006) and its causes. Acta Meteorol. Sin. 1032–1042 (In Chinese).