Analysis of Spatial-temporal and Ion Characteristics Change of Precipitation in the Southwest of China, from Policy Perspective

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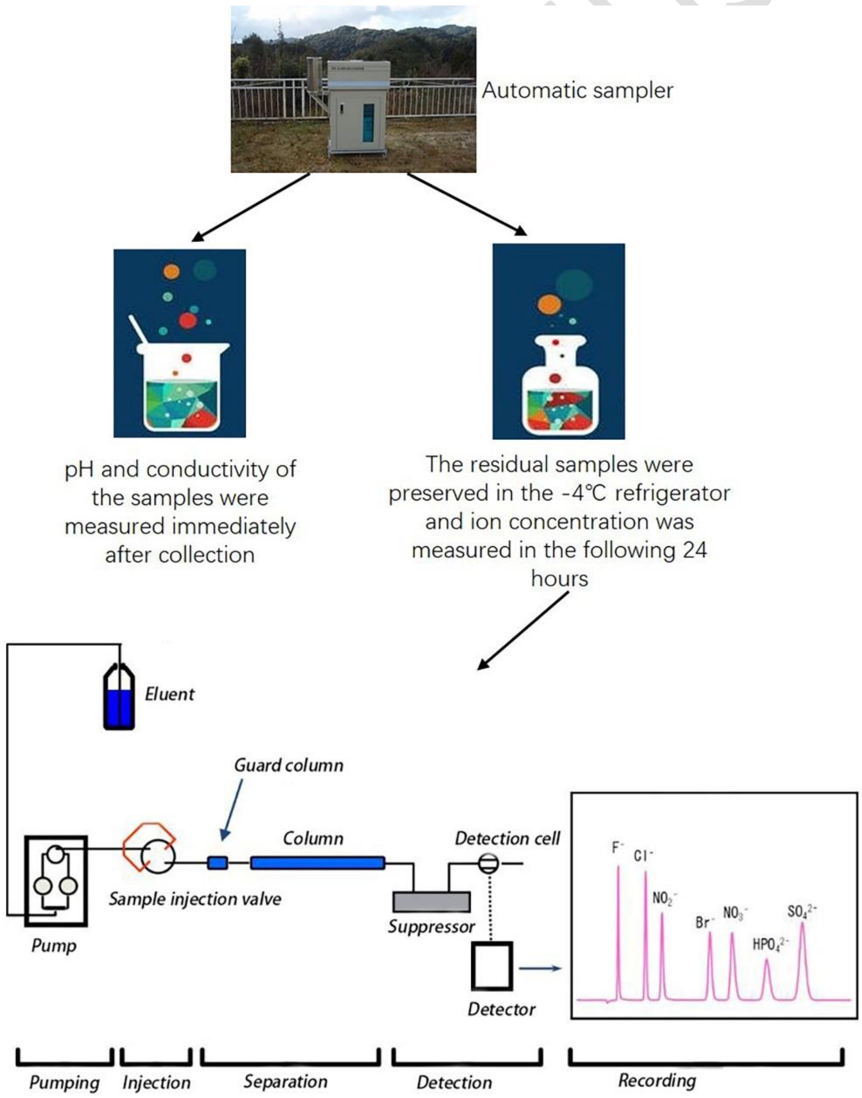
GRAPHICAL ABSTRACT



Abstract: According to the data from Luzhou environmental monitoring center from 2015 to 2018, the tendency of spatial-temporal and ion characteristics in precipitation have been analyzed in order to demonstrate the precipitation pollution status. Traditionally, the environment may become worse as the development of the economy, especially in the developing countries. However, the results show that the quality of precipitation has been improved during these four years. The annual average pH value of precipitation in Luzhou City increased, and the frequency and conductivity of acid rain declined, which indicates that the quality of precipitation improved annually. This may due to a strictly political strategy enacting. The decrease of the equivalent concentration ratio of SO_4^{2-} and NO_3^- demonstrated the transformation of pollution type, evolving from a typical sulfuric acid to a mixed type of sulfuric and nitric acid, indicating the economic transformation. The correlation coefficient between SO_4^{2-} and NO_3^- was high. This may be because SO_2 and NO_2 emitted from industrial enterprises entered the atmosphere together in the same way. The strong correlation between F^- and SO_4^{2-}, NO_3^- may relate the pollution sources such as cement and glass enterprises. It is necessarily to strengthen the management of relative enterprises.

Keywords: pH, precipitation, ion characteristics

1. Introduction

Air pollution has been a universal concern in many countries because of its harmful impacts on public health, ecosystem, and economy. The substances of air pollution contain sulfur dioxide (SO_2), nitrogen oxides (NO_X), excessive carbon dioxide (CO_2), Volatile Organic Compounds (VOCs), particulates (PM2.5, PM10), etc.(Siddiqi and Farsi 2019). These emissions are released to the atmosphere either by natural processes or human activities (US EPA, 2017a). Air pollutants lead numerous of environmental problems such as acid rain, climate changes, crop and forest damage and adverse impacts on wildlife. The effect of this pollution costs approximately $5 trillion per year to cure people and repair the environmental damage (World Bank, 2016). Therefore, more works along with governments and environmental agencies to decrease air pollution and damage it causes are needed.

One the environmental consequences of air pollution is atmospheric acid deposition including dry deposition and wet deposition. Precipitation is often recognized as wet deposition(Grimm and Lynch 2004). Its acidity can be expressed as the magnitude of solution acidity (H^+ concentration or pH). When the pH of precipitation is lower than 5.6, the precipitation is often renamed acid rain/precipitation which is one of the global environmental problems (Galloway et al. 1976). The performance of pH and other chemical parameters of precipitation has been monitored for many years to ensure the quality of precipitation. From such monitoring activities, data are evident for determining temporal and spatial deposition trend, predicting ecological effects, modeling atmospheric processes, or planning future emission control strategies (Wisniewski and Kinsman 1988).

The significant chemical factors in acid rain are nitrate and sulfate because NO_X and SO_2 exhausted from mobile and stationary sources mainly lead to a decrease of the rain acidity by chemical reactions (Wakida et al. 2001). Lightning and volcanic eruptions react with water molecules or get mixed with dust are typical natural processes to form these two chemical compounds. These molecules terminally fall as dry or wet deposition(Mutahharah et al. 2014). NO_X and SO_2 as precursors of acid rain may cause secondary pollutants like particles and nitrogen species(Menz and Seip 2004).

Acid rain predominates many countries such as the Canada, United States, China, and Europe(Bowman 1992). Although many researchers analyzed the characteristics of acid rain all over the world, there is limited literature addressing acid rain in China, especially in these highly developmental economic periods. This essay analyzed the data of the spatial-temporal and ion characteristics of precipitation in the recent four years in Luzhou city. The acidity of precipitation in this city was extremely serious. We hope this article would help to provide useful information about the quantity variation of ion characteristics and evaluate the quality of the atmosphere in Luzhou city.

2. Sampling site

Luzhou, N28°52′28.94″, E105°26′20.32″, is situated in the southwest of China. Geomorphologically, it is dominated by medium mountains (1000-1902m above the sea level) and low mountains (500-1000m above sea level). There are four distinct seasons in Luzhou because of its typical continental monsoon climate. According to Luzhou people's government data, the temperature and rainfall are relatively higher in Luzhou compared with surrounding cities. Rainfall mainly focused from July to August and the least concentrated from December to March next year.

By the end of 2017, Luzhou Economic and Social Development Statistic Bulletin presented that the population of the city has exceeded 5 million, and Gross Domestic Product was 159.6 billion RMB, and the contribution of the three industries to the growth of the economy was 5.0%, 59.7%, and 35.3% respectively. The second and third industries are still pillar industries.

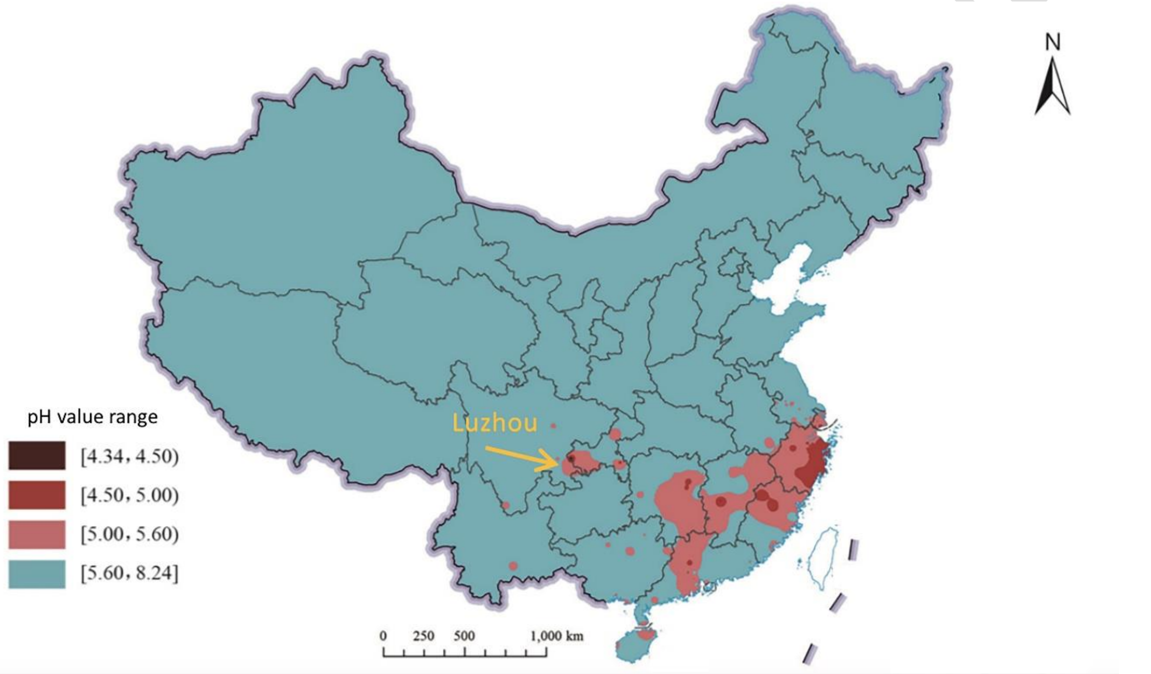


Fig 1 The location of Luzhou City and the distribution of acid rain in 2018 in China (according to Environmental Protection Administration of China)

3. Methods

The samples were collected with 500ml polyethylene bottles. They had been cleaned with hydrogen chloride (2-3 mol/L) and rinsed with Milli-Q water (18.25MΩ) before use (Hua and Han 2011). The bottles were located in the automatic sampler that immediately collected the sample when it was rain. The samplers were situated on the roofs 1.5m high above the ground, gathering 24 hours wet precipitation from 8 a.m. to 8 a.m. the next day as one sample to analyze, and 247 samples were collected.

We analyzed pH and conductivity of the samples immediately after collection. Then the residual samples were preserved in the -4°C refrigerator and ion concentration was measured in the following 24 hours after sampling. 0.45μm organic Millipore membrane was used to filtrate samples and then immersed by deionized water for 24 hours (Shi et al. 2013). This membrane is an inert material with features of Uniform aperture, fast rate passing and avoiding from the absorption with other chemical factors in the sample. Therefore, the samples were able to prevent loss and contamination of components to be tested.

Major anions (Cl^-, F^-, SO_4^{2-}, NO_3^-) were demonstrated by an ionic chromatography (ICS-1500, 09090451). The detection limits of F^-, Cl^-, NO_3^-, SO_4^{2-} were 0.03, 0.03, 0.1 and 0.1 mg/L. Major cations (K^+, Na^+, Mg^{2+}, Ca^{2+}, NH_4^+) were measured by ionic chromatography (ICS-90, 7100483). The detection limits of K^+, Na^+, Mg^{2+}, Ca^{2+}, NH_4^+ were 0.01, 0.01, 0.01, 0.03 and 0.01 mg/L. Reagent and procedural blanks were measured in parallel to the sample treatment and the blanks were below the detection limit of the measured species. The relative standard deviations (RSD%) of the method were below 5%. Quantitative recoveries of spiked samples ranged from 85% to 120%.

4. Results and discussion

4.1 pH value, frequency of acid rain and conductivity

From the previous studies, CO_2, NO_x, and SO_2 existing in the nature can dissolve into the clouds and droplets, causing pH values of the rain in the clean atmosphere to be between 5.0-5.6 (Charlson and Rodhe 1982), (Galloway et al. 1993). Precipitation with pH below 5.0 results from the presence of natural or anthropogenic emission of H_2SO_4 and/or HNO_3, while that of above 6.0 might consider certain inputs of alkaline species into the precipitation. It is shown in Table 1. 247 rain samples were collected from 2015 to 2018. The average pH value observed in Luzhou city increased from 4.28 in 2015 to 5.00 in 2018. Total rainfall is above 1000mm. The acid rainfall did not show significant difference from 2015 to 2017, however, it was observed obvious decrease in 2108 ($P<0.05$). Both maximum and minimum pH values of precipitation were observed in 2016.

Frequency of acid rain represents the intensity of acidity of precipitation. It equals the ratio of the number of acid rains to the total number of rains, It is an important indicator to ensure whether the certain area is an acid rain area besides pH value (Siddiqi and Farsi 2019). The frequency of acid rain observed a distinct decrease from 86% to 46% during the four years with consistency to the trend of pH value.

The conductivity of precipitation is considered to be a significant parameter in acid rain chemistry monitoring. The conductivity of ions in precipitation is generally used in the quality assessment on the analysis data of ionic components. Table.1 shows that the conductivity increased slightly in the first two years (5.78 to 6.20 mS/m), then decreased obviously from 2016 to 2018 (6.20 to 3.67).

pH value calculating equation is as follows. *n* indicates the number of rains. *Vi* indicates the *i*-th volume of rain.

$$pH = -log\frac{\sum_{i=1}^{n} 10^{-pH} \times Vi}{\sum_{i=1}^{n} Vi}$$

Table 1. The statistical results of precipitation in Luzhou, 2015-2018

Years	Number of samples	pH mean (in unit)	Total Rainfall (mm)	Acid rainfall (mm)	Frequency of acid rain	Max (in unit)	Min (in unit)	Conductivity (ms/m)
2015	51	4.28	1091.70	853.50	86%	6.64	3.25	5.78
2016	59	4.43	1022.80	917.20	85%	7.74	3.20	6.20
2017	79	4.41	1084.40	877.00	69%	6.74	3.55	4.67
2018	58	5.00	1005.30	390.10	46%	6.69	3.52	3.67

Therefore, pH value, frequency of acid rain and conductivity all present that the quality of atmospheric precipitation is improving annually. SO_2 and NO_2 are the main acid-producing precursors of precipitation (gao et al. 2001), (LIN et al. 1999). The main reason would be some relative policies enacted in this area. The government urged the enterprises with large pollutant emissions to enact strategy of "Total pollutant emission reduction" five years ago. According to the statistical data from Luzhou Environmental Protection of Agency, SO_2 emissions decreased from 68,900 tons in 2014 to 36,900 tons in 2018. Meanwhile, NO_2 emissions declined from 38,200 tons in 2014 to 24,400 tons in 2018.

4.2 ionic composition

The equivalence ratio of the sum of anions to that of cations (Σanions/Σcations) is usually regarded as an indicator of the completeness of the measured major constituents (Al-Khashman 2005). In this study, the mean equivalent sum of anions of that cations were between 0.92 and 0.96, which suggested that all major ions were measured.

Table 2 shows that, in these four years, the concentration of each cation was all in the order of $NH_4^+ > Ca^{2+} > Mg^{2+} > Na^+ > K^+$. The proportion of NH_4^+ and Ca^{2+} mass concentration ranged from 78.6% to 90.8% of the total amount of cations, indicating that the main cations of precipitation was NH_4^+ and Ca^{2+}. The order of mass concentration of each anion from high to low was: $SO_4^{2-} > NO_3^- > Cl^- > F^-$, wherein the percentage of SO_4^{2-} and NO_3^- mass concentration ranged from 92.1% to 95.4% of the total anion, showing that SO_4^{2-} and NO_3^- was the main anions of precipitation in Luzhou city.

Table 2. The ion concentration of precipitation in each year in Luzhou, mg/L

Years	**SO_4^{2-}**	**NO_3^-**	**NH_4^+**	**Ca^{2+}**	**Mg^{2+}**	**Cl^-**	**F^-**	**K^+**	**Na^+**
2015	9.86	4.52	1.29	1.61	0.18	0.48	0.21	0.32	0.29
2016	9.32	4.38	2.12	2.77	0.18	0.83	0.34	0.42	0.46
2017	8.24	4.57	2.42	1.29	0.10	0.39	0.23	0.19	0.09
2018	5.64	3.39	2.36	1.24	0.13	0.49	0.19	0.22	0.13

4.3 Ions proportion change in precipitation

According to previous literature, precipitation is mainly dominated by sulfuric acid-type precipitation in economically underdeveloped areas. With the rapid economic development in the region, precipitation acidification will change from the previous sulfuric acid type to the mixed type of sulfuric acid and nitric acid (Mai et al. 2010). It is shown in Fig.2 that the SO_4^{2-}/NO_3^- equivalent concentration ratio witnessed a decrease from the highest value of 4.4 in 2015 to 3.3 in 2018. It represents that the pollution type of acid precipitation in Luzhou city has gradually evolved from a typical sulfuric acid type to complex pollution of sulfuric acid plus nitric acid.

NH_4^+ and Ca^{2+} are the predominant neutralization substances in rainwater, however, the neutralization by Mg^{2+} and K^+ is negligible (Hua and Han 2011). Fig.1 shows that the equivalent concentration ratio of main cation Ca^{2+}/NH_4^+, which had a neutral effect in precipitation, increased in the first two years, then declined from a peak of 2.5 in 2015 to 1.0 in 2018. The concentration of NH_4^+ increased year by year shows that the content of NH_3 in the atmosphere of Luzhou has an increasing influence on the quality of precipitation. Moreover, the only large-scale power plant around the main city completed the ammonia desulfurization technical reform project in 2015. The chemical Plant installed a selective catalytic reduction unit for denitrification treatment.

Generally, agricultural sources are regarded as the main source of NH_3 emissions in the atmosphere (Kanakidou et al. 1995), (Hoek 1998), (Aneja and P. 2003). Besides, related research has found that in recent years, motor vehicle exhaust and industrial emissions have become the main non-agricultural sources of NH_3 in the atmosphere of urban areas (Whitehead et al. 2007), (Vollenweider 2010). The number of cars in Luzhou city increased from 373,400 in 2015 to 568,200 in 2018, increasing by 52.2%. Also, the Chuan Nan Power Plant, a famous coal-fired power plant around the main city, completed the ammonia desulfurization technical reform project in 2015. Some Chemical Nitrification Plant in the city installed a selective catalytic reduction unit for denitrification treatment. Chuan Tian Hua, a famous large-scale chemical enterprise producing nitrocellulose, installed ammonia desulfurization in 2015 to treat SO_2 emissions from the enterprise.

These treatment facilities will inevitably have an “ammonia escape” situation during use. This may be one of the reasons why the percentage of NH_4^+ equivalent in precipitation in Luzhou City has increased year by year. However, the NH_4^+ equivalent concentration ratio decreased slightly from 2017 to 2018. It may be because from 2015, Luzhou City has increased the management of poultry breeding, delineated strictly banned areas and limited areas in the urban area and shut down some livestock and poultry farms that do not meet the management requirements, resulting in a decrease in NH_3 emissions from agricultural sources and a decrease in the percentage of NH_4^+ equivalents in precipitation.

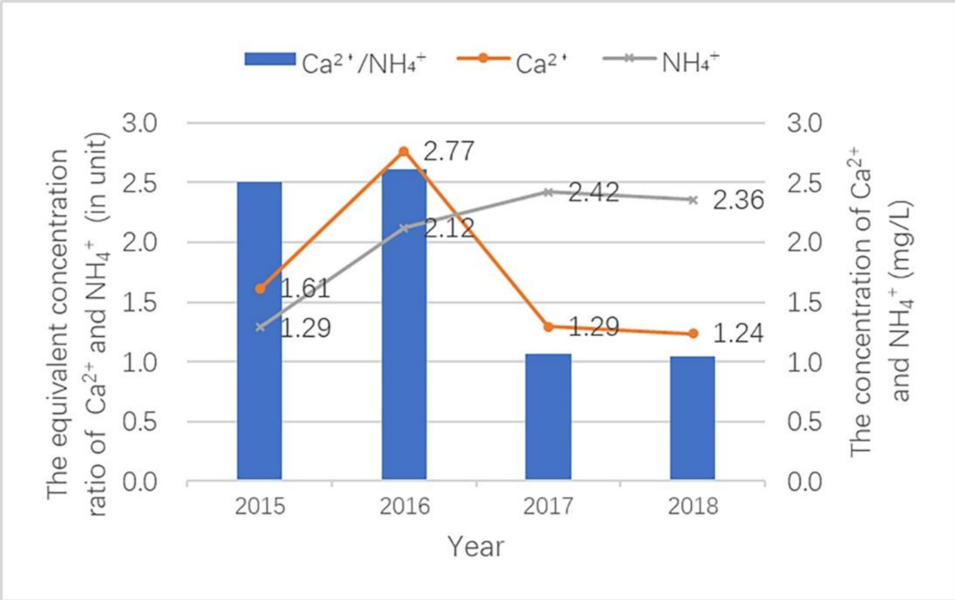


Fig 1. the equivalent concentration of Ca^{2+}/NH_4^+ and trend of Ca^{2+} and NH_4^+ concentration during 2015-2018

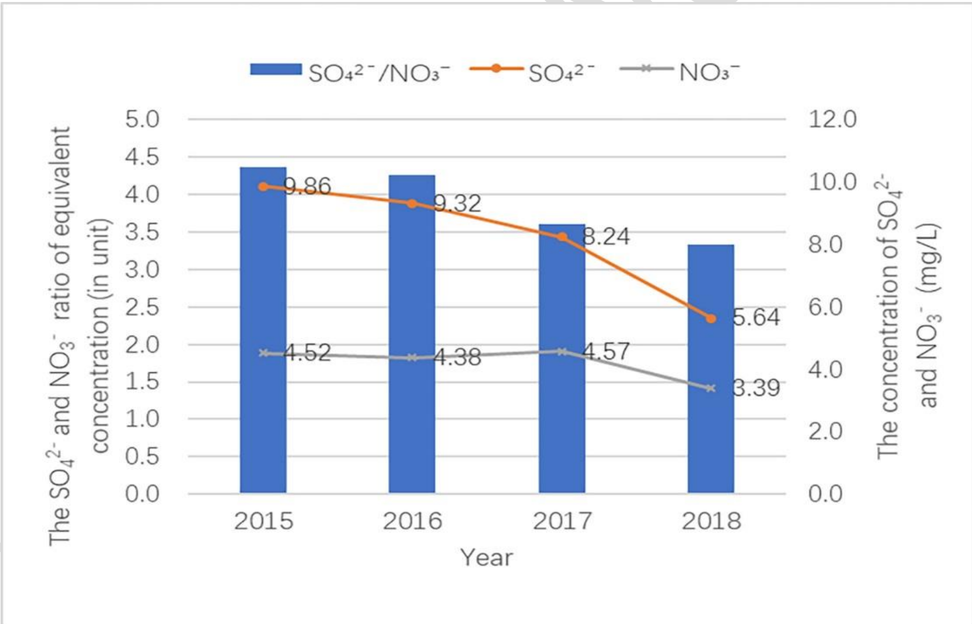


Fig 2. the equivalent concentration of SO_4^{2-}/NO_3^- and trend of SO_4^{2-} and NO_3^- concentration during 2015-2018

4.4 Trend analysis of characteristic ions in precipitation

An in-depth analysis of the correlation between the various ion components in the precipitation can show the relationship between the ions, and it is of great benefit to determine the source of the pollutants, to understand and master the influencing factors of acid rain formation and to effectively control them (Nam et al. 2001). Pearson analysis was carried out on the correlation of ions in precipitation in Luzhou City in 2018 via SPSS software. T-test was used to ensure the significance test. The results are shown in the following table 3.

Table 3 The correlation analysis of ions in Luzhou precipitation in 2018

		SO_4^{2-}	NO_3^-	F^-	Cl^-	NH_4^+	Ca^{2+}	Mg^{2+}	Na^+	K^+
SO_4^{2-}	Pearson	1.000								
NO_3^-	Pearson	0.933	1.000							
F^-	Pearson	0.958	0.902	1.000						
Cl^-	Pearson	0.474	0.420	0.462	1.000					
NH_4^+	Pearson	0.971	0.911	0.913	0.568	1.000				
Ca^{2+}	Pearson	0.890	0.818	0.860	0.407	0.867	1.000			
Mg^{2+}	Pearson	0.772	0.712	0.758	0.425	0.809	0.853	1.000		
Na^+	Pearson	0.176	0.128	0.158	0.914	0.304	0.160	0.283	1.000	
K^+	Pearson	0.670	0.512	0.663	0.841	0.748	0.595	0.684	0.700	1.000

Note: the correlation analysis significance level is 0.01.

It can be seen from the data in the Table 3 that the correlation coefficient of NH_4^+ with SO_4^{2-}, NO_3^- , and F^- is higher in 2018, 0.971, 0.911, and 0.913, respectively. The correlation coefficient between SO_4^{2-} and NO_3^- is as high as 0.933, which is a strong correlation between them. This may be because, during the year 2018, SO_2 and NO_2 emitted by industrial enterprises entered the atmosphere together in the same way. There is also a strong correlation between F^- and SO_4^{2-}, NO_3^-, which is 0.958 and 0.902, respectively. This may be related the pollution sources such as cement and glass enterprises.

5. Conclusion

Based on the analysis of acid precipitation in recent four years, we can note that the Luzhou government emphasis the control of pollutant emission even though Luzhou City is in the process of high economic development. This is beneficial to society and public health. The quality improvement of acid precipitation also presented that the economic transformation of Luzhou City.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgments

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