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Article

Economic and Industrial Development SignificantlyContribute to Acidity and Ionic Compositions of Rainwaterin China

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Abstract: To achieve a holistic understanding of the intricate interactions among human activities, atmospheric chemistry, and acid rain in China, a rigorous analysis of rainwater chemistry was made using a dataset comprising 2656 data points from 24 sites. The main cation and anion in the chemical composition of precipitation were Ca^{2+} and $SO_4{}^{2-}$ in China, with an average concentration of 169.9 μeq/L and 135.4 μeq/L, respectively. Acid rain generally occurs in southern cities such as Shenzhen, Guangzhou, Zhuhai, Xiamen, and Chongqing. There were evident regional disparities in acidity and ion concentrations in rainwater, with an increase in acidity and a decrease in ion concentrations from north to south across China. Utilizing positive matrix factorization, the study found that $NH_4{}^+$, $SO_4{}^{2-}$, and $NO_3{}^-$ mainly originated from anthropogenic sources such as fossil fuel combustion, vehicle exhaust emissions, agricultural fertilization, and industrial emissions (as reflected by F3 and F4). Ca^{2+} mainly stems from crustal factors, including industrial dust and natural crust (as represented by F1 and F4). Na^+ and Cl^- were traceable from marine sources (as reflected by F5), while Mg^{2+} originated from crust origin (as presented by F1). K^+ was mainly derived from a mixed source of crust, marine, and biomass burning (as indicated by F2 and F3). The correlation analyses showed that $SO_4{}^{2-}$ and $NO_3{}^-$ showed significant correlations with GDP and population. F^- was associated with wastewater, which may be linked to the production of brick and tiles from clay with high fluoride contents. The pH was negatively related to industrial wastewater. Long-term analysis of precipitation chemistry in four cities suggested a clear decrease in the proportion of $SO_4{}^{2-}$ but a considerable increase in the proportion of $NO_3{}^-$ in anions in metropolitans of Shanghai and Chongqing due to the environmental measures that targeted reducing sulfur dioxide (SO_2) emissions and increase of vehicles. This showed that pollution control strategies had an impact on precipitation ion concentrations. These results can conclude that economic and industrial growth, which will increase energy consumption, utilization of coal combustion, and a subsequent rise in pollutant emissions, can contribute to the change in the chemical compositions of rainwater and the exacerbation of acid rain.

Keywords: precipitation; chemical composition; origin; economic activities; industrialization; China

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1. Introduction

Acid rain, recognized as one of the top 10 environmental issues, has significant effects on human health, ecosystems, and infrastructure [1]. With the development of industry and increasing energy demands, China has become the second-largest energy consumer in the world, according to the China Ministry of Environmental Protection [2]. However, this results in the fact that China has become the third-largest acid deposition region in the world after North America and Central Europe [3–7], with widespread occurrences of acid rain. According to the China Environmental Bulletin of 2021, approximately 140 out of 465 Chinese cities suffered from acid rain. The regions affected by acid rainfall are primarily located in the southern and central parts of China, which have witnessed remarkable progress in industrial development [8].

The dissolution of soluble aerosols in precipitation leads to the inclusion of water-soluble chemical components in rainwater. For example, NO_x and SO_2 could be easily transformed into HNO_3 and H_2SO_4 by dissolving into the water in the atmosphere. Chemical compositions of precipitation usually include Ca^{2+}, Mg^{2+}, NH_4^+, K^+, Na^+, SO_4^{2-}, NO_3^-, Cl^-, and F^-. An understanding of the chemical components of rainwater provides valuable evidence for the identification of the sources of these ions, anthropogenic effects, and relevant meteoric contaminants [9–11], which helps navigate effective pollution control strategies on the basis of specific sources of ions. Previous research indicates these ions mainly come from the ocean, soil, industrial emissions, vehicle exhaust emissions, and fertilizer [12–15]. The SO_4^{2-} and NO_3^- in the rainwater in Guiyang were mainly from anthropogenic sources, which contributed 98.1% and 94.7%, respectively [16]. The chemical composition characteristics of precipitation in different cities are highly variable due to differences in meteorological conditions, sources of water vapor, topographical structure, and underlying surface conditions [17]. Most studies concerning acid rain have focused on the chemical composition and their sources in a specific location within a short period of time [18–21]. However, there have been limited research efforts that investigate the multi-regional, multi-site, and long-term chemical characteristics of rainfall and the impacts of economic and industrial development on acidity and chemical composition in rainwater across China [22]. What's more, chemical species often come from multiple sources; it is thus not straightforward to uniquely identify and quantify a specific source contribution [23]. Models are constructed and utilized for source identification and source quantification.

Over the past four decades, China has experienced unprecedented economic and industrial growth. China is currently the world's second-largest economy and the largest industrial country. The GDP (gross domestic product) of China has surged from 910 billion RMB in 1985 to 121 trillion RMB in 2022. The population reached 1.4 billion in 2020. This rapid development and huge population are also accompanied by increasing energy consumption, the utilization of coal combustion, and a subsequent rise in pollutant emissions. The increasing emissions of SO_2 and NO_X from fossil fuel combustion have resulted in the intensification of acid rain and aerosol pollution. For example, the proportion of monitored cities in China that experienced acid rain during 2006–2010 was above 50% [24]. The paper aims to gain an initial understanding of the spatial and temporal variations of rainwater acidity and chemistry characteristics in China, with a focus on verifying conceivable sources that contribute to its chemical characteristics using the positive matrix factorization (PMF) model. By examining the chemical composition of rainwater and its potential sources, this study seeks to shed light on the intricate relationship between acid rain and economic and industrial development in China. Through a comprehensive analysis of available data and relevant literature, this research advances our understanding of the complex relationship between economic activities, industrialization, and the occurrence of acid rain in China.

2. Materials and Methods

2.1. Data Collection

The target literature was collected using the Web of Science (http://apps.webofknowledge.com, accessed on 29 September 2022), EANET (https://monitoring.eanet.asia/document/public/index, accessed on 4 October 2022), CNKI (https://www.cnki.net/, accessed on 29 September 2022) and the Ecological and Environmental Center of each municipality. The information was retrieved on 18 October 2022. The search terms are: "precipitation chemical composition", "rainwater chemical ions", "city name", etc. The target data of rainwater chemistry include major cations (Ca^{2+}, Mg^{2+}, NH_4^+, K^+, Na^+), anions (SO_4^{2-}, NO_3^-, Cl^-, F^-), and pH. The sampling sites include cities (provincial capital or typical city) and several remote mountain regions within 40 years (1980–2020) of available data. Only cities with at least two years of complete target chemical precipitation data have been retained. Ultimately, a total of 294 sets of data points and, thus, a total number of 2656 data points that met the established criteria were carefully scrutinized for analyses. The chemical composition and pH of rainwater were determined at each of the selected sites in China. Samples were collected using standardized rainwater collectors and analyzed using established methods. Generally, major cations are measured using an inductively coupled plasma atomic emission spectrometer (ICP-AES) or ion chromatography; major anions are measured by ion chromatography, with an uncertainty of <10%. pH is measured using pH-calibrated probes.

The socioeconomic data were collected from the National Bureau of Statistics (http://www.stats.gov.cn/, accessed on 29 September 2022) and the statistical yearbook from the Bureau of Statistics of each Municipality or city. The socioeconomic indicators in this research include population, GDP, GDP per capita, wastewater discharge, industrial wastewater discharge, SO_2, and industrial SO_2 discharge. It should be noted that the socioeconomic data are only involved for the corresponding year in which the precipitation chemistry data were available. A total of 277 sets of data, and thus a total number of 1289 data points, were collected.

2.2. Location and Sampling

China (3°51′ N–53°33′ N, 73°33′E–135°05′ E), located in eastern Asia along the west coast of the Pacific Ocean, spans an area of 9.6 million km^2 (Figure 1). China's terrain is characterized by high elevation in the west and low elevation in the east, forming a stepped pattern that contributes to a variety of climate types. According to the China Environmental Bulletin (2021), the country has a mean annual temperature of 10.53 °C and a mean annual rainfall of 672.1 mm. The acid rain area is prevalent in approximately 3.8% of the country's land area, mainly located in the south of the Yangtze River and east of the Yunnan-Guizhou Platea. The national average range of rainwater pH falls within 4.79~8.52. The main cations of the rainwater are Ca^{2+} and $NH_4{}^+$ and the main anions are $SO_4{}^{2-}$. Notably, sulfuric acid remains the prevailing type of acid rain throughout the country.

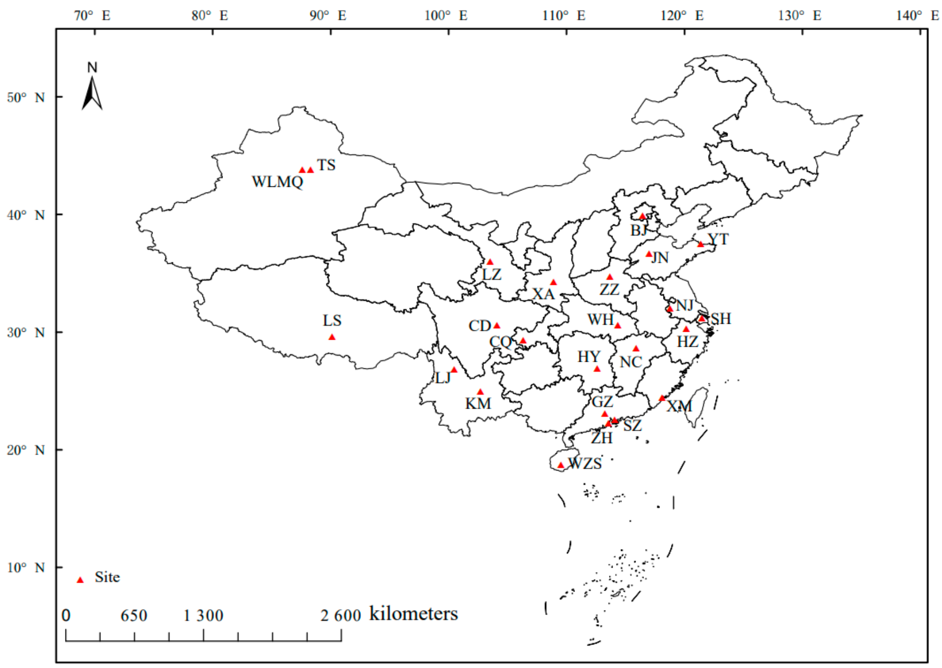

Figure 1. Locations of the rainwater data sites in China. Each site is indicated by its phonetic initials (BJ-Beijing, SH-Shanghai, HZ-Hangzhou, NJ-Nanjing, JN-Jinan, YT-Yantai, SZ-Shenzhen, GZ-Guangzhou, ZH-Zhuhai, XM-Xiamen, WH-Wuhan, ZZ-Zhengzhou, NC-Nanchang, HY-Hengyang, CQ-Chongqing, CD-Chengdu, KM-Kunming, LS-Lasa, LJ-Lijiang, XA-Xi'an, WLMQ-Wulumuqi, LZ-Lanzhou, TS-Tianshan, WZS-Wuzhishan).

The sites Involved in the research can be divided into north China, south China, and remote mountains. The north of China includes BJ-Beijing, XA-Xi'an, WLMQ-Wulumuqi, LZ-Lanzhou, JN-Jinan, YT-Yantai, and ZZ-Zhengzhou. The south of China contains SH-Shanghai, HZ-Hangzhou, NJ-Nanjing, WH-Wuhan, NC-Nanchang, HY-Hengyang, SZ-Shenzhen, GZ-Guangzhou, ZH-Zhuhai, XM-Xiamen, CQ-Chongqing, CD-Chengdu, KM-Kunming, LS-Lasa, and LJ-Lijiang. The remote mountains include Tianshan and Wuzhishan. Tianshan is located in Xinjiang Province at an altitude of 2119 m. Wuzhishan is located in Hainan Province and has an altitude of 958 m.

2.3. Data Processing and Statistical Analyses

The pH value and the mean of major ion concentrations at each site are presented in Table S1. The Spearman correlation analyses were carried out using IBM SPSS statistics. Several good models, i.e., the PCA-APCS-MLR model, the PMF model, and the HYSPLIT Trajectory Model, have widely been used in the source identification of rainwater. PMF is an internationally widely used and effective source allocation model for air pollutants that applies mathematical approaches to the chemical composition of samples with the aim of quantifying the relative contributions of variable sources [25]. In the study, the US EPA's PMF 5.0 (positive matrix factorization) was utilized to increase the rationality of source identification and consequently quantify the relative contributions of different sources. Prior to proceeding with the PMF model, a series of four preliminary experiments were conducted, each using a distinct number of factors: 3, 4, 5, and 6, respectively. The comparison and analysis of residual matrix values, interpretability of factors, and the fit of the simulation results were meticulously examined. Based on this evaluation, the model that opted for five factors yielded the most reliable and fitting results.

Shanghai, Xi'an, Xiamen, and Chongqing, where continuous time series precipitation chemical characteristic data lasting for 20 years were available, were selected to unravel the temporal variations of rainwater chemical ions. Shanghai is a city located in the southern coastal region, renowned for its developed industry, thriving economy, convenient transportation, and high population density [26]. Xi'an is a provincial capital city in western China with a developed economy and culture. The pollution caused by human activities such as industrial production, transportation, coal burning for daily life, and infrastructure construction, as well as the significant impact of dust deposition, has led to severe pollution in Xi'an [27]. Chongqing is located in southwest China, showing a subtropical monsoon humid climate with abundant rainfall and a high degree of agricultural land development. Due to its topography, pollutants are not easily dispersed [28]. Xiamen, located in Southeast China, belongs to a subtropical monsoon climate with moderate temperatures and humid air. In summer, it is greatly affected by oceanic monsoons [29].

3. Results

3.1. Spatial Variations Chemical Composition and pH of Rainwater

The concentrations of major ions and pH of rainwater are presented in Figure 2. The results revealed that the chemical composition of rainwater varied among different sites across China. The dominant cation observed in the rainwater samples was Ca^{2+}, except in Zhuhai, where the cation of Na^+ dominated while the main anion was $SO4^{2-}$ in all sites. Among the 24 sites studied, Lanzhou exhibited the highest average concentration of Ca^{2+} (775.72 μeq/L), NH_4^+ (224.20 μeq/L), K^+ (61.63 μeq/L), Na^+ (108.90 μeq/L), SO_4^{2-} (481.80 μeq/L), and NO_3^- (77.58 μeq/L), while Zhengzhou had the highest average concentration of Mg^{2+} (95.29 μeq/L) and Cl^- (355.02 μeq/L). In contrast, Wuzhishan had the lowest mean concentration of Ca^{2+} (14.05 μeq/L), Mg^{2+} (3.64 μeq/L), and Cl^- (7.93 μeq/L), while Wulumuqi had the lowest mean concentration of NH_4^+ (8.49 μeq/L) and K^+ (2.72 μeq/L) among all sites. Furthermore, the concentrations of ions were generally higher in the northern sites than those in the southern cities.

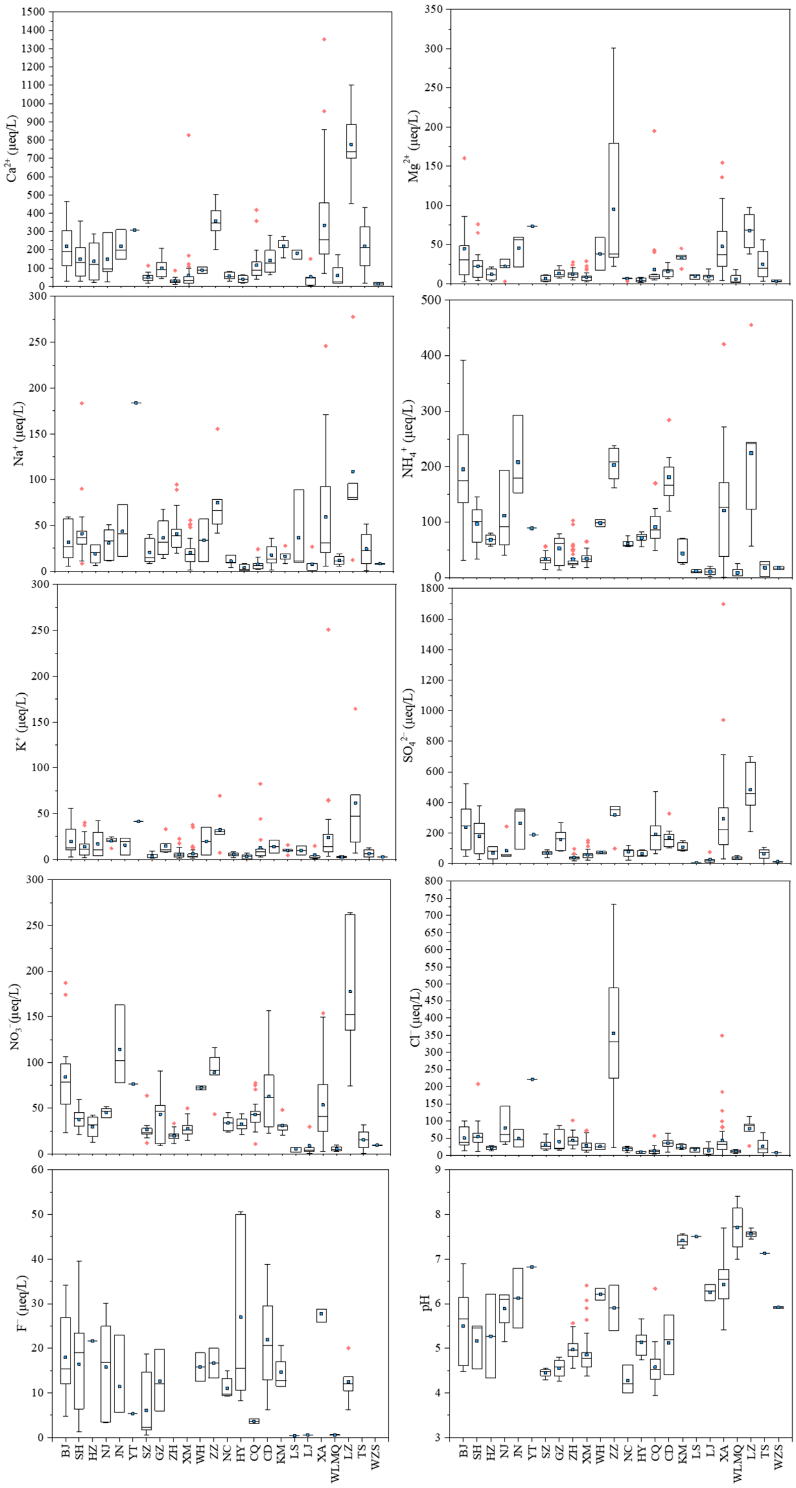

Figure 2. Rainwater ion concentrations at each site in China. The blue points represent the mean values and the red points represent the outliers.

The pH of natural rainwater is above 5.6. Precipitation with a pH lower than 5.6 is defined as acid rain [30]. The currently collected data suggested that the pH values of Shanghai (5.16), Shenzhen (4.45), Guangzhou (4.56), Zhuhai (4.97), and Nanchang (4.28) were all found to be below 5.6. More than 75% of the samples collected from Xiamen (4.85), Hengyang (5.14), Chongqing (4.58), and Chengdu (5.12) were identified to be acid rain. Conversely, Wuhan (6.21), Kunming (7.41), Lasa (7.50), Lijiang (6.26), Lanzhou (7.57), and

Tianshan (7.13) were identified as non-acid rain areas, as the pH values of rainwater in these regions were all over 6. The pH values in the Wuzhishan were lower when compared to the Tianshan. The pH of precipitation exhibits remarkable regionality, with strong acidity in south China, and acidity gradually decreases from south to north. The value of NP (neutralizing potential) was higher in the north than in the south (Table S4).

The elemental ratio corrected by Cl^- can effectively eliminate the influence of rainfall (Figure 3). Among the elemental ratios studied, K^+/Cl^- (0.12–0.84) and F^-/Cl^- (0.07–0.82) were found to be lower compared to the other elemental ratios. Among all the sites studied, Tianshan showed the highest mean values of Ca^{2+}/Cl^- (18.05) and Mg^{2+}/Cl^- (2.89), while Chongqing had the highest mean values of NH_4^+/Cl^- (9.08), SO_4^{2-}/Cl^- (16.34), and NO_3^-/Cl^- (4.71). The mean values of Na^+/Cl^- in Hengyang are the lowest.

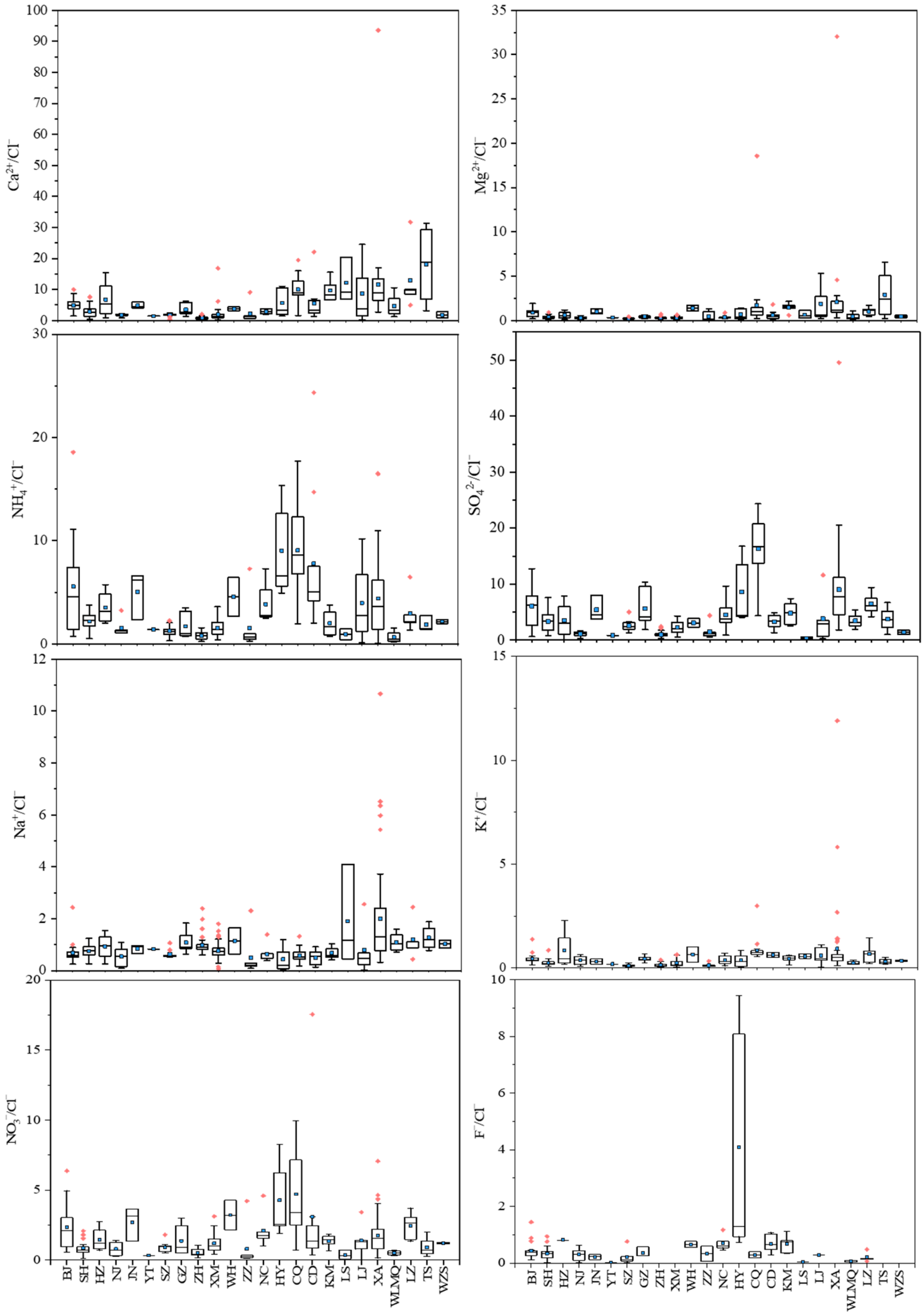

Figure 3. Cl-normalized equivalent unit ratios in rainwater. The blue points represent the mean values and the red points represent the outliers.

3.2. Temporal Variation of Rainwater Chemistry

Rainwater major ion data from four selected sites spanning over 20 years were analyzed to explore changes in rainwater chemistry over time, as deciphered in Figures 4 and 5. In Shanghai, Ca^{2+}, NH_4^+, and SO_4^{2-} appeared to show a declining trend of fluctuations during 1990–2010, with other ions showing undulations at low levels (Figure 4a). SO_4^{2-}/Cl^- exhibited a downward trend from 5.03 in 1990 to 2.96 in 2010, while NO_3^-/Cl^- showed an upward trend from 0.49 in 1990 to 1.54 in 2010 (Figure 5a). The proportion of NH_4^+ in cations increased from 22.42% to 37.63% during 1990–2009 (Figure 5c). In anions, the proportion of SO_4^{2-} decreased from 78.11% to 44.48%, while the proportion of NO_3^- rapidly increased from 7.22% to 33.67% during 1990–2009 (Figure 5d). In Xi'an, the pH of rainwater was consistently higher than 5.6 from 2000 to 2020 (Figure 4b). The Ca^{2+}, and SO_4^{2-} concentrations were extremely high in 2000–2003 but decreased in the subsequent period. K^+, Na^+, and Cl^- remained at a relatively low concentration. Over the past 20 years, Xiamen has experienced acid rain for the majority of the time (Figure 4c). The ion concentrations remained low, but there was a sharp rise in the Ca^{2+} concentration. Ca^{2+}, NH_4^+, NO_3^- and SO_4^{2-} concentrations in Chongqing exhibited consistent patterns of annual concentration (Figure 4d). SO_4^{2-}/Cl^- displayed an initial increase followed by a decreasing trend, whereas NO_3^-/Cl^- exhibited an overall upward trend (Figure 5b). The proportion of SO_4^{2-} in 2001 was 1.2 times greater than in 2020, indicating a declining trend over time. In contrast, the proportion of NO_3^- in 2020 was 3 times higher than that in 2001, reflecting a drastic rise over time.

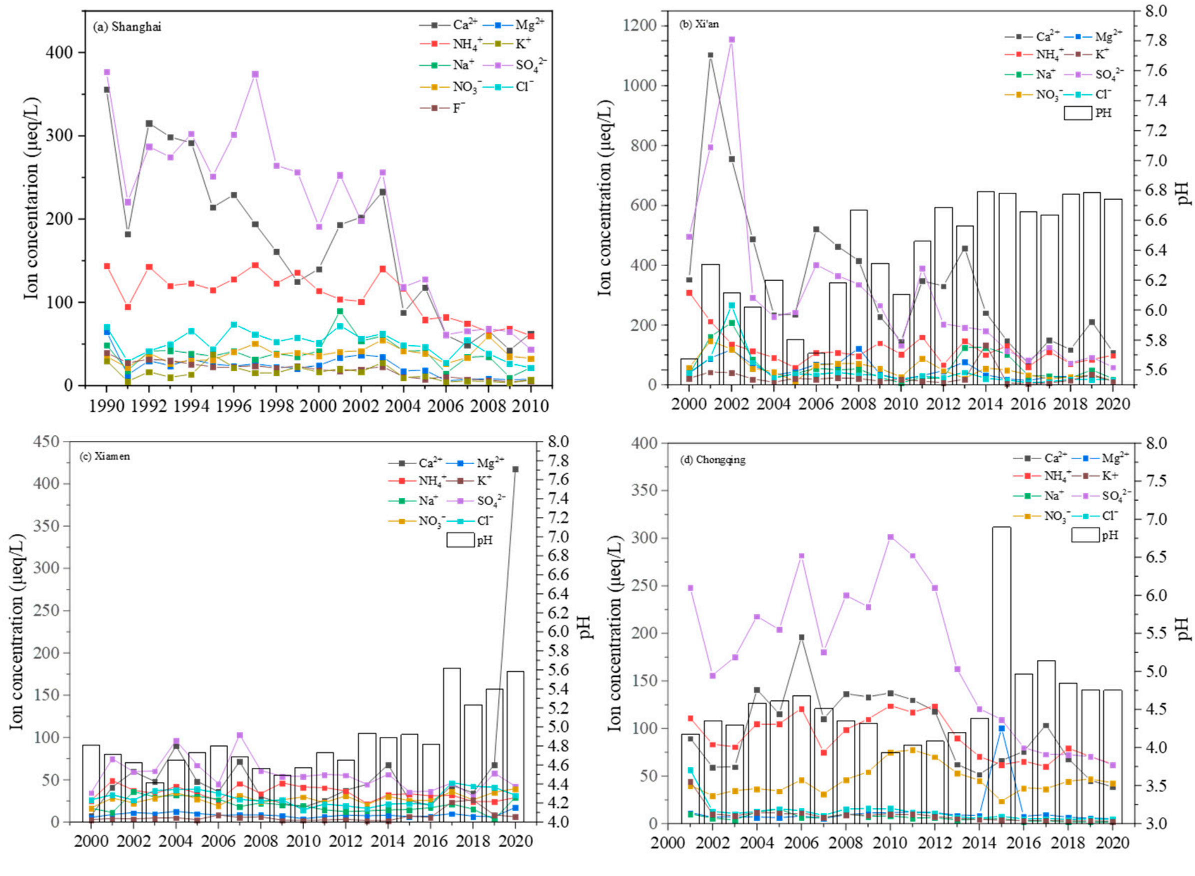

Figure 4. Temporal variations of rainwater chemical ions in several locations (Shanghai, Xi'an, Xiamen, and Chongqing).

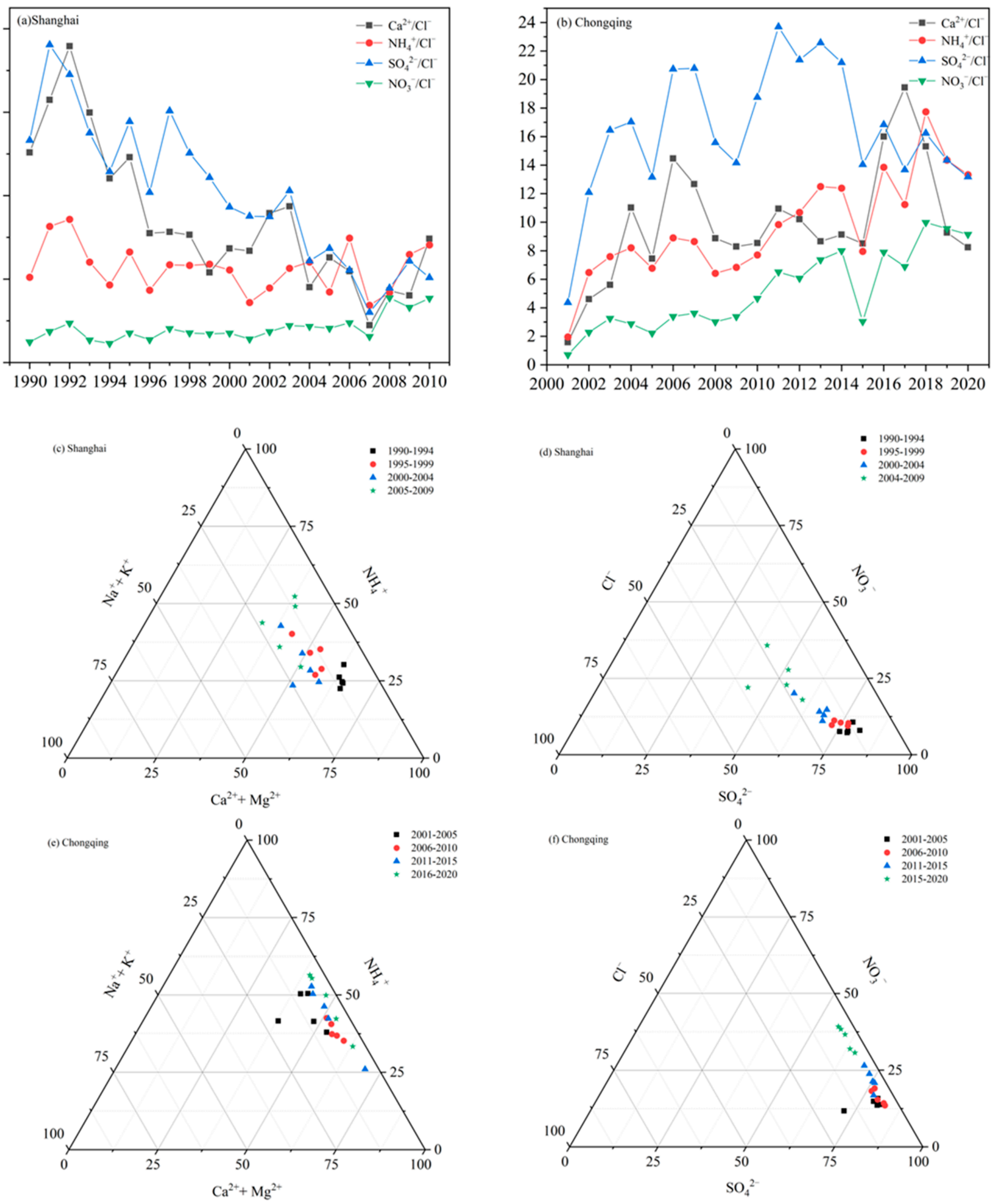

Figure 5. Temporal variations of Cl-normalized equivalent unit ratios and triangular diagrams of rainwater chemical ions in Shanghai and Chongqing.

3.3. Socioeconomic Indicators

The averages of the socioeconomic data are shown in Figure 6. Among all the sites, Lasa has the lowest population, GDP, and GDP per capita. In contrast, Chongqing had the highest population and industrial SO_2 emissions. Shanghai exhibited the highest discharges of SO_2, wastewater, and industrial wastewater, with the second highest GDP. Wuhan displayed the highest GDP during the period with data, while its pollution emission remains below average.

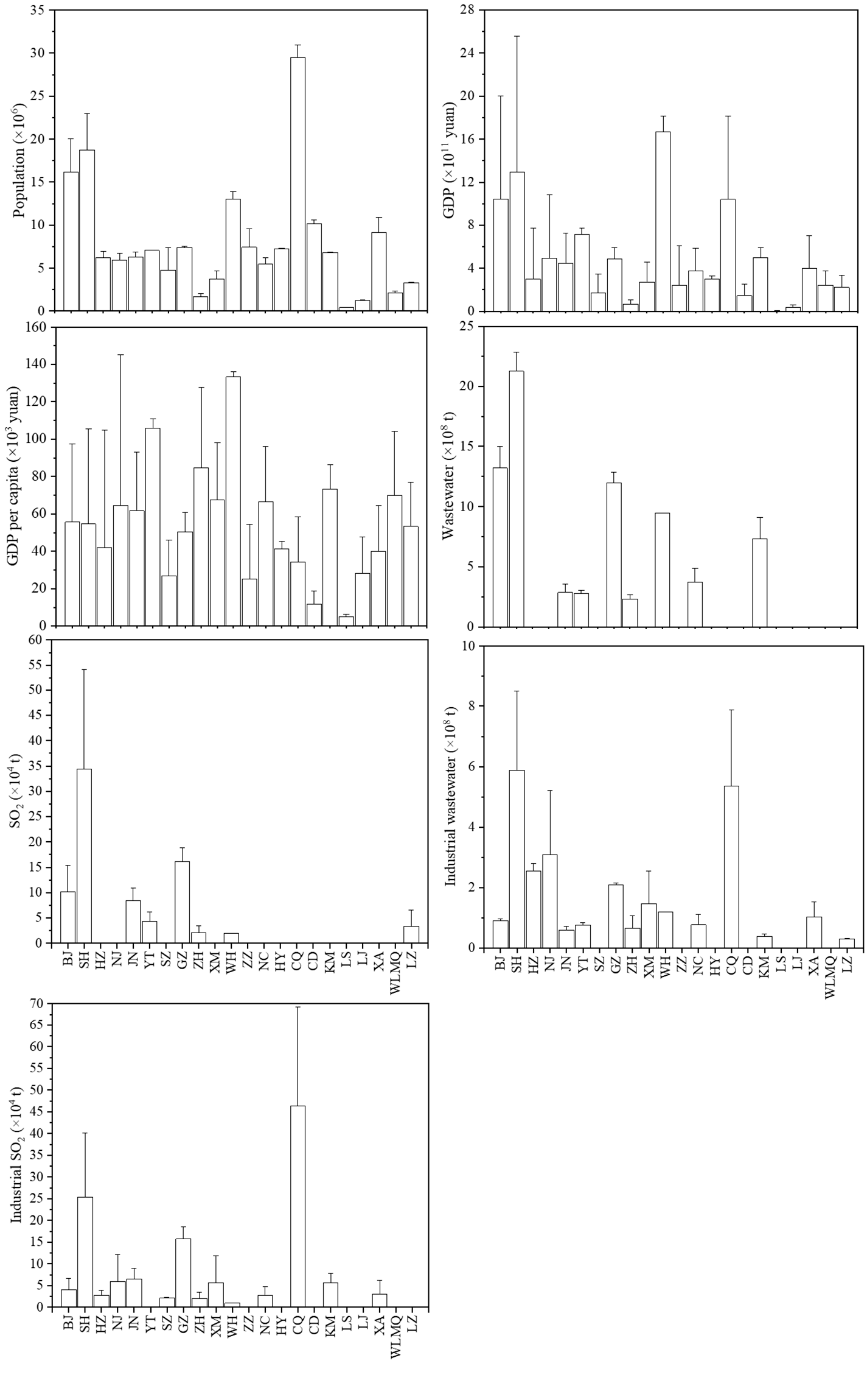

Figure 6. Socioeconomic status at each site.

3.4. Correlation Analyses

Table 1 shows the correlation matrix between rainwater chemical ions and socioeconomic indicators. There were significant positive correlations among chemical ions. Typical acid-causing ions SO_4^{2-} and NO_3^- had strong correlations with the basic cations Ca^{2+}, NH_4^+, and Mg^{2+} ($p < 0.01$), and there were also mutual correlations among these ions. K^+, Na^+, and Cl^- were found to be related to other ions. F^- was solely correlated with NH_4^+ and pH was only related to Ca^{2+} and industrial wastewater. It should be noted that Mg^{2+}, NH_4^+, SO_4^{2-}, NO_3^-, and F^- had correlations with population, while SO_4^{2-} and NO_3^- were relevant to GDP. In addition, there was a correlation between population and GDP. Wastewater was associated with F^-, population, and GDP, suggesting interrelationships among these variables.

Table 1. The Spearman correlation coefficients of socioeconomic indicators and various ionic concentrations in precipitation across China.

	Ca^{2+}	Mg^{2+}	NH_4^+	K^+	Na^+	SO_4^{2-}	NO_3^-	Cl^-	F^-	pH	Population	GDP	GDP per Capita	Wastewater	Industrial Wastewater	SO_2	Industrial SO_2
Ca^{2+}	1.00	0.87 **	0.60 **	0.79 **	0.66 **	0.72 **	0.60 **	0.63 **	0.22	0.52 **	0.31	0.27	−0.08	0.12	−0.33	0.19	0.22
Mg^{2+}		1.00	0.72 **	0.88 **	0.75 **	0.80 **	0.77 **	0.77 **	0.25	0.37	0.47 *	0.41	0.11	−0.05	−0.42	−0.12	0.12
NH_4^+			1.00	0.80 **	0.49 *	0.90 **	0.95 **	0.66 **	0.54 *	−0.06	0.60 **	0.39	−0.09	0.33	−0.09	−0.05	0.39
K^+				1.00	0.73 **	0.79 **	0.83 **	0.76 **	0.36	0.22	0.41	0.38	0.07	0.12	−0.09	−0.36	0.20
Na^+					1.00	0.53 **	0.55 **	0.84 **	0.10	0.28	0.06	0.08	0.11	−0.28	−0.35	−0.05	0.15
SO_4^{2-}						1.00	0.91 **	0.68 **	0.36	−0.02	0.63 **	0.45 *	−0.07	0.23	−0.23	0.24	0.51
NO_3^-							1.00	0.70 **	0.38	−0.04	0.58 **	0.46 *	0.07	0.17	−0.30	−0.10	0.35
Cl^-								1.00	0.30	0.01	0.23	0.21	0.15	0.07	−0.18	0.24	0.29
F^-									1.00	−0.25	0.56 **	0.22	−0.06	0.88 **	0.29	0.39	−0.08
pH										1.00	−0.24	−0.05	0.14	−0.12	−0.54 *	−0.48	−0.26
Population											1.00	0.73 **	−0.05	0.87 **	0.49	0.57	0.43
GDP												1.00	0.49 *	0.67 *	0.38	0.21	0.27
GDP per capita													1.00	−0.62	−0.41	−0.67	−0.49
Wastewater														1.00	0.73 *	0.75	0.48
Industrial Wastewater															1.00	0.52	0.65 *
SO_2																1.00	0.94 **
Industrial SO_2																	1.00

Notes: * indicate significance at $p < 0.05$ level, ** indicate significance at $p < 0.01$ level.

3.5. Source Contributions

The PMF model was employed to diagnose the main sources of pollution and their relative contributions. Five factors were identified, and their profiles and contributions are shown in Figure 7. Factor-1 was characterized by a large portion of Ca^{2+} (49.4%) and Mg^{2+} (57.7%), a tracer of crustal dust. Factor-2 was regarded as a natural source, including terrestrial and marine sources, which are characterized by a high portion of K^+ (74.3%) and Na^+ (43.0%). Factor-3 was interpreted as an anthropogenic sources with a high fraction of $NH_4{}^+$ (72.8%) and $NO_3{}^-$ (76.1%). It also had a considerable contribution from K^+ (16.5%) and $SO_4{}^{2-}$ (29.1%). The dominant components of factor-4 were Ca^{2+} (44.1%) and $SO_4{}^{2-}$ (57.7%), indicating anthropogenic sources. Factor-5 was enriched with Na^+ (60.0%) and Cl^- (79.6%), implying a source of sea salts.

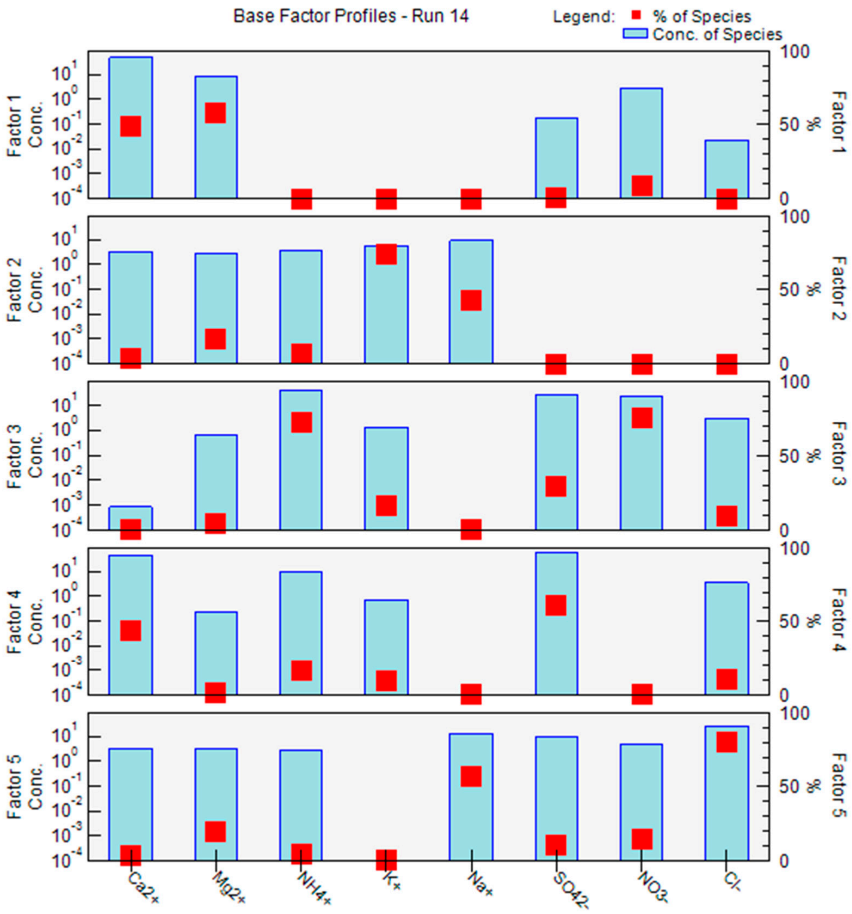

Figure 7. Five source profiles (bar, left y-axis) and their contribution percentages (the red square, right y-axis). F1-crustal dust, F2-natural sources (terrestrial and marine sources), F3-anthropogenic source (fossil fuel, agricultural activity, and biomass burning), F4-anthropogenic source (fossil fuel and industrial dust), F5-marine source.

3.6. Comparison with Other Countries

The concentrations of Ca^{2+}, $SO_4{}^{2-}$, and $NO_3{}^-$ in China were clearly higher than those in Mexico [31], Singapore [32], Tokyo [33], Adirondack [3], Guaiba [34], Poland [35], and Mondy (EANET), but were comparable to those in Thessaloniki [36], Tirupati [12], and Paris [37] (Table 2). The concentrations of Na^+ and Cl^- in China were close to those observed in Tokyo. The concentration of $NH_4{}^+$ was much higher than that in Tirupati, Singapore, Adirondack, Guaiba, Tokyo, and Mondy. The pH in China was found to be higher compared to Singapore, Adirondack, Poland, Guaiba, Tokyo, and Mondy, but lower than Thessaloniki, Tirupati, and Paris.

Table 2. The comparison of the mean pH values and ion concentrations with other countries.

City	Ca^{2+} (μeq/L)	Mg^{2+} (μeq/L)	NH_4^+ (μeq/L)	K^+ (μeq/L)	Na^+ (μeq/L)	SO_4^{2-} (μeq/L)	NO_3^- (μeq/L)	Cl^- (μeq/L)	F^- (μeq/L)	pH	Period	Reference
China	169.9	26.8	86.8	15.3	37.1	135.4	47.8	54.2	13.0	5.86	1980–2020	This study
Tirupati, India	151.0	50.5	20.4	33.9	33.1	128.0	40.8	33.9	4.7	6.78	2000–2001	[12]
Mexico	26.4	2.5	92.4	2.2	7.0	61.9	42.6	9.6	-	5.10	2001–2002	[31]
Singapore	16.1	6.5	19.1	7.2	32.8	83.5	22.3	34.2	-	4.20	1999–2000	[32]
Tokyo, Japan	24.9	11.5	40.4	2.9	37.0	50.2	30.5	55.2	-	4.52	1990–2002	[33]
Adirondack, New York	3.6	1.0	10.5	0.3	1.	36.9	22.6	2.1	-	4.45	1988–1999	[3]
Guaiba, Brazil	9.8	4.6	30.5	3.2	10.9	15.9	2.7	9.2	5.0	5.71	2002	[34]
Poland	64.2	19.2	-	41.0	14.6	88.4	32.1	19.1	-	4.53	1996–1999	[35]
Thessaloniki, Greece	256.0	30.5	116.0	16.4	44.5	134.0	41.2	57.1	-	6.60	2003–2004	[36]
Paris, France	152.5	14.2	-	17.4	47.8	77.1	66.1	73.2	3.2	6.10	2011–2012	[37]
Mondy, Russia	13.8	3.2	11.2	2.6	2.5	11.4	6.4	3.7		5.40	2006–2020	EANET

4. Discussion

4.1. Regional Difference in Precipitation Chemistry

There were obvious regional differences in the acidity and ion concentrations of rainfall across China (Figure 2). The ion concentrations at the northern sites were higher than those in the southern cities overall, which is attributed to different climates and energy structures. For example, surrounded by coal-burning cities, Beijing is greatly affected by the sand and dust source areas in the northwest of China, which results in serious air pollution. What's more, Beijing belongs to a semi-arid climate regime with less annual precipitation. Under the combined effect of these factors, various air pollutants are easy to accumulate in the atmosphere, resulting in high ion concentrations of precipitation [38].

The findings revealed higher pH values in rainwater in northern China compared to the southern region. For instance, acid rain generally occurs in southern cities such as Shenzhen, Guangzhou, Zhuhai, Xiamen, and Chongqing (Figure 2). It is noteworthy that, regarding the remote mountain areas, the pH value of rainfall in mountains in northern China was higher than that of mountains in southern China (Table S3). The main causes could be the development of the economy and industry, climate, local topography, geomorphological features, and the pH of the soil. The details are as follows: (1) The more developed economy and industry in southern cities result in more emissions of pollutants, such as sulfur dioxide and nitrogen oxides. (2) The southern region receives more rainfall, which can dissolve acidic gases such as sulfur dioxide and nitrogen oxides caused by the development of the economy and industry, and cause them to fall along with the precipitation. (3) The great fluctuation of terrain in southern China impedes atmospheric circulation and thus results in increased rain acidity. This is due to the fact that pollutants that are released into the atmosphere are not dispersed as effectively, leading to their accumulation in certain areas. (4) The soil in northern China is classified as alkaline, and the basic dust particles in the air can neutralize acidic gases, leading to a higher pH in rainwater. The neutralization capacity of alkaline cations also decreased from north to south (Table S4). Overall, the complex interplay of variable factors discussed above has contributed to the differences observed in rainwater pH between northern and southern China.

4.2. Temporal Variations of the Acidity and Ion Concentration

The decrease in the ion concentrations of precipitation has witnessed the success of Shanghai's Clean Air Action Policy in 2000. The policy has eliminated the use of polluting fuels and strongly recommends the use of clean energy while reducing the volatilization of agricultural ammonia sources. which has contributed to the continuous decline in the emission of major pollutants [39]. The low value of atmospheric precipitation ions in 2010 may be related to the holding of the Shanghai World Expo when a series of ambient air quality improvement measures were implemented aiming at reducing the emission of pollution sources (Figure 4a). A significant decrease in SO_2 emissions in 2006 gave credit to the implementation of pollution emission reduction, desulfurization, denitrification, and other related measures in the Shannxi province. This also led to the decrease in the concentration of Ca^{2+}, SO_4^{2-}, and NO_3^- observed in Xi'an since 2006 (Figure 4b).

The ion concentrations of precipitation in Xiamen were not very high, but precipitation is characterized by severe acidification (Figure 4c). The influence of marine-land breeze circulation is conducive to the accumulation of acid pollutants [40]. Previous research ascribed the acid rain in Xiamen to external sources, with the influence of local sources superimposed [41]. There was a sharp rise in alkali metals such as Ca^{2+} concentration; however, there was improved pH in rainwater [42]. Chongqing's promotion and use of clean energy and control of waste emissions have greatly reduced the concentration of SO_4^{2-} (Figure 4d). However, the increase at a rate of 15% annually since 2012 in motor vehicles has contributed to an augment in nitrogen oxides [43]. The issue of acid rain in Chongqing is still serious.

It is noteworthy that the relative importance of ions has clearly shifted. For instance, the reduction in the proportion of SO_4^{2-} and the simultaneous increase in the percentage of NO_3^- in anions were both observed in Shanghai and Chongqing (Figure 5). This phenomenon can be attributed to the effective implementation of environmental measures targeted at reducing sulfur dioxide (SO_2) emissions, coupled with the increase in the number of vehicles on the roads. Furthermore, this also led to an increasing impact of NH_4^+ on the neutralization process in metropolises such as Shanghai [42].

4.3. Ionic Sources and Socioeconomic Factors

There existed positive correlations among all precipitation ions (Table 1). Anthropogenic emissions, biogenic materials, and atmospheric aerosols are considered to be the main origins of rainwater chemistry [13,14]. The main origins of precipitation ions in China included anthropogenic sources, crustal sources, and marine sources (Figure 7 and Table S6). NH_4^+, SO_4^{2-}, and NO_3^- are markers of secondary aerosol particles such as ammonium sulfates and nitrates [44,45]. SO_4^{2-} and NO_3^- originate mainly from thermal power and the combustion of fossil fuel from industry (as reflected by F3 and F4), while NH_4^+ originates from agricultural activity and biomass burning (as indicated by F3), and they usually refer to anthropogenic sources [46,47]. Ca^{2+} is mainly attributed to the crustal factor, which includes industrial dust and crust (as represented by F1 and F4) [48]. Na^+, K^+, and Cl^- are traceable from marine sources (as reflected by F2 and F5) [21] while Mg^{2+} originates from crust origin (as presented by F1 and F2) [49]. K^+ is also from biomass burning (as indicated by F3) [49]. If there is no contamination during the conveying process, the Na^+/Cl^- molar ratio ought to be 0.86 [50]. The ratio in several acid rain cities like Hengyang, Chengdu, and Chongqing was close to 0.5, indicating severe pollution like Cl_2 and HCl from non-ferrous metals, metallurgical, and other industries (Table S5). Mg^{2+}, NH_4^+, SO_4^{2-}, NO_3^-, and F^- had correlations with population, while SO_4^{2-} and NO_3^- were relevant to GDP. F^- was associated with wastewater, which may be linked to the production of brick and tiles from clay with high fluoride contents [47]. The pH shows a negative relationship with the industrial wastewater (Table 1). The chemical behavior of SO_4^{2-} and NO_3^- in rainwater and atmospheric particles is similar, and they share a common source with their precursors SO_2 and NO_x, namely coal combustion [44].

During the years of substantial economic growth, there has been a parallel escalation in energy consumption, utilization of coal combustion, and a subsequent rise in pollutant emissions, especially acidic gases like NO_X and SO_2. This, in turn, exacerbates the occurrence of acid rain [51]. Shenzhen is a typical example, which became the first Special Economic Zone in 1980 and is noted for its economic development. However, the precipitation in Shenzhen has undergone rapid acidification since the 1980s [21]. Compared to the period of 1980–1985, the concentration of nss-SO_4^{2-} in rainwater increased by 63% during the period 1986–2006; this was attributed to the growing emissions of SO_2 during the economic boom [21]. The study highlighted that the increasing pollutant emissions caused by economic growth and industrial development considerably shifted the chemical characteristics and intensified the acid rain in China. It is worth noting that the Chinese government has implemented measures to relieve these issues [52,53].

4.4. The Potential Impact of Acid Rain on Aquatic Dissolved Carbon

Based on our findings, urbanization largely shifted several major ions and increased rainfall acidity. Atmospheric acid deposition, in conjunction with surface runoff over urban surfaces as well as urban waste discharges through the urban drainage system [54], therefore dedicatedly contributed to dissolved inorganic carbon species. Acidification of lakes and streams has occurred in geologically sensitive areas of North America that receive precipitation polluted with strong acids [55]. The growing acid deposition in China, especially in the southeast region, can lead to river water acidification while pH decreases [56]. This process can directly affect the dynamic equilibrium of CO_2 and carbonate and bicarbonate ions in water [57]. The input of acidity can largely increase dissolved CO_2 and thus carbon emissions from these rivers. For example, a previous study showed a decrease in pH from 8 to 7.5, pCO_2 could have a three-fold increase in the

Longchuan River (a tributary in the Yangtze), while pCO_2 had a ten-fold increase when pH showed a unit decrease from 8 to 7 [58,59].

5. Conclusions

Rainwater acidity and chemistry were analyzed in 24 sites (mainly cities) across China. The main cation and anion chemistry of precipitation in China were Ca^{2+} and SO_4^{2-}, with an average concentration of 169.9 μeq/L and 135.4 μeq/L, respectively. The main ion concentrations in precipitation were generally higher in the northern sites than in the southern cities; however, the acidity of precipitation decreased gradually from south to north. The long-term analysis of precipitation chemistry in four cities demonstrated that policy concerning the reduction of emissions of pollutants had an impact on concentrations of precipitation ions. In the main cities of Shanghai and Chongqing, there was a notable rise in the proportion of NO_3^-, accompanied by a noteworthy decrease in the proportion of SO_4^{2-} in anions. Strong correlations were found in all precipitation ions, with NH_4^+, SO_4^{2-}, and NO_3^- primarily originating from anthropogenic sources such as fossil fuel combustion, vehicle exhaust emissions, agricultural fertilization, and industrial emissions. Ca^{2+} mainly contributes to crustal factors. Na^+ and Cl^- were traceable from marine sources while Mg^{2+} originated from crust origin. K^+ was mainly from crust origin, marine sources, and biomass burning. Additionally, Mg^{2+}, NH_4^+, SO_4^{2-}, NO_3^-, and F^- had correlations with population, while SO_4^{2-} and NO_3^- were relevant to GDP. The pH in precipitation was negatively correlated with industrial wastewater. The study indicated that increasing pollutant emissions like NO_X and SO_2 caused by economic growth and industrial development have the potential to alter the chemical characteristics of the rainwater, leading to an increase in precipitation acidity in China. According to the precipitation chemical characteristics and sources of major ions, policymakers should pay more attention to the reduction of pollution emissions like SO_2 and NO_X based on the local topography and geomorphological features, meteorological conditions, and energy structure.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w16020193/s1, Table S1: The mean of pH and ion concentration in rainwater of each site in China; Table S2: The Spearman correlation coefficients of socioeconomic indicators and Cl-normalized equivalent unit ratios in precipitation in China; Table S3: The comparison of the mean pH values with other mountains; Table S4: The value of nss-Ca^{2+}, nss-SO_4^{2-}, NP, AP, and NP/AP of rainwater from 24 sites; Table S5: Cl-normalized equivalent unit ratios in rainwater; Table S6: Principal component analysis (PCA) of the major ions. (Maximum variance method was used); Figure S1: Temporal variations of Cl-normalized equivalent unit ratios and triangular diagrams of rainwater chemical ions in Xiamen and Xi'an. References [59–106] are cited in the Supplementary Materials.

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