Characteristics and Source Analysis of Water-Soluble Inorganic Ions in PM$_{10}$ in a Typical Mining City, Central China

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Abstract: A total of 61 PM$_{10}$ samples in Huangshi (HS), Central China, were collected every sixth day from April 2012 to March 2013 and were analyzed for water-soluble inorganic ions (WSIIs) by ion chromatography. The sum of three major ions (SO_4^{2-}, NO_3^-, and NH_4^+) accounted for 75.8% of the total WSIIs on average. The results of a non-parametric test (Kruskal-Wallis) show that, except for Na^+ ($p > 0.05$), the other ions present a distinctly seasonal variation with a statistically significant difference ($p < 0.05$). The minimum concentrations of all ions were found in summer, while the maximum values presented in autumn (for Ca^{2+}) and winter (for Cl^-, NO_3^-, SO_4^{2-}, K^+, NH_4^+, Mg^{2+}). Based on the highest ratio of Cl^-/Na^+ (3.02) and the highest concentration of K (4.37 $\mu g \cdot m^{-3}$), Ba (0.37 $\mu g \cdot m^{-3}$), and Sr (0.07 $\mu g \cdot m^{-3}$) in February 2013, it can be concluded that firework powders have aggravated the haze weather during the Spring Festival of 2013. The micro-equivalent concentrations of cations and anions were calculated and the comparisons between the calculated and measured NH_4^+ concentrations were conducted. The results illustrate that aerosol particles in HS are acidic and there may exist some other cationic ions not detected in this study. An obvious positive correlation and good linear regression among WSIIs suggest that the chemical forms in HS aerosols show a great variety of combinations, such as NH_4NO_3, NH_4HSO_4, $(NH_4)_2SO_4$, NH_4Cl, KCl, KNO_3, $NaCl$, $NaNO_3$, $Ca(NO_3)_2$, $CaSO_4$, $MgCl_2$, $Mg(NO_3)_2$, and $MgSO_4$. The WSIIs have large positive correlation and linear regression with the elements, suggesting that WSIIs in mining cities are strongly influenced by element constituents. Principal component analysis implies that WSIIs in PM$_{10}$ are probably from three sources. NH_4^+, Mg^{2+}, NO_3^-, K and K^+, Cl^- and Cl, SO_4^{2-}, and S accounted for 46.9% of the total variances, suggesting likely anthropogenic sources, especially coal combustion, vehicular exhaust, and biomass burning. Mg accounted for 23.3% of the total variances and Ca^{2+} and Ca explained 18.1% of the total variances, demonstrating that another important source is mineral dust from both natural and anthropogenic sources.

Keywords: water-soluble inorganic ions; urban aerosols; characteristics; source analysis; central China

1. Introduction

Water-soluble inorganic ions (WSIIs) are major components of atmospheric aerosols, which have a direct effect on the acidity of atmospheric precipitation [1] and enhancing the harmfulness of pollutants [2,3]. Prior studies have shown that different regions presented different characteristics of WSIIs relating to the kinds of pollution sources and meteorological conditions [4,5]. Therefore, observations on WSIIs can not only reflect the quality of the atmospheric environment, but also provide a scientific basis for understanding the source, formation mechanism, and transmission processing of aerosols [6,7]. Aerosol WSIIs have been studied extensively in China, especially in large cities, such as Beijing and Tianjin [8], Shanghai [9], Guangzhou [10], Xi'an [11], and Xining [2]. The results illustrate that WSIIs can account for one-third, or more, of aerosol mass in urban regions and act as an important factor in the increase of particulate mass concentrations [4]. However, little is known about aerosol WSIIs in small and medium-sized cities, especially in Central China.

Located in the southeast of Hubei province and the middle and lower reaches of the Yangtze Rivers, Huangshi (HS, 30.12° N, 115.06° E) is a representative mining and industrial city known as the "Hometown of Chinese Bronze" and the "Cradle of the Nation's Iron and Steel industry". Using coal as its main energy, HS is also an important industrial base of raw materials in central China. The rapid development of HS's heavy industry has caused high energy consumption and severe environmental pollution. In recent years, with the expansion of industrial scale (at an average annual growth rate of 12%) and increase of urban vehicles (at an average annual growth rate of 20%) (http://www.huangshi.gov.cn), atmospheric particulates have become the major pollutants that affect air quality and endanger human health [12,13]. HS is more than 4500 square km (1700 square miles) in area and has a population of more than 2 million. It belongs to a subtropical humid monsoon climate with abundant rainfall and sufficient sunshine. Moreover, it has four distinct seasons with high temperature and abundant precipitation in the summer, and is moist and slightly cold in winter. In this study, PM_{10} samples were successively collected in HS for a whole year. Chemical characteristics, temporal variation, and the source of WSIIs are reported for the first time. The results could provide a more accurate understanding of urban aerosols in Central China, and provide a theoretical foundation for the control and treatment of air pollution in HS.

2. Methods

2.1. Sample Collection

The sampling site (30°12′35.34″ N, 115°01′30.17″ E) is located on the rooftop of the School of Environmental Science and Engineering building (about 20 m above the ground level) at the Hubei Polytechnic University campus. The site is surrounded by residential areas and is about 1.5 km away from a major road with busy traffic, including a variety of vehicles, such as natural-gas-fueled city buses, gasoline-fueled cars and motorcycles, and diesel-fueled trucks, passenger cars, and agricultural vehicles.

The 24 h PM_{10} sampling was performed once every sixth day from April 2012 to March 2013. Additionally, eight parallel samples were collected in the four seasons. A total of 61 samples were gained without any operational error. Detailed sampling information is illustrated in Table 1. To account for any artifacts introduced during the sample collection and handling, field blank filters were also collected in each season. Sampling equipment used included an Airmetrics Tactical Air Sampler using quartz microfiber filters (47 mm, British Whatman Company, Maidstone, UK). Before sampling, quartz membranes were baked at 800 °C for 3 h to remove organic artifacts or impurities. After sampling, samples were frozen at −20 °C until further analysis. Simultaneously, Teflon filters for analyzing elements were sampled in order to better understand the source of mining aerosol in HS. Detailed sampling processing was exactly the same as quartz filters.

In Table 1, the study period was classified into the four seasons, such as spring (April, May, June), summer (July, August, September), autumn (October, November, December), and winter (January,

February, March). During the sampling period, the temperature in summer was high (31.0–37.2 °C) and precipitation was concentrated (with the average monthly rainfall of 301 mm) while, in winter, the weather was moist (with the relative humidity of 87.1–94.0%) and slightly cold (3.1–7.2 °C). Specifically, the monthly average highest temperature (37.2 °C) appeared in July 2012 (summer), whereas the lowest (3.1 °C) appeared in February 2013 (winter). May 2012 (spring) was recognized as the driest month (relative humidity of 66.7%) and February 2013 (winter) was the most humid (relative humidity of 94.0%). The monthly highest wind speed (m/s) was observed as 3.0 m/s in May, June, and July of 2012, and no sustained wind was observed in January, February, and March of 2013.

Table 1. Summary of the sampling information and meteorological conditions from April 2012 to March 2013 in Huangshi.

Season	Sampling Time	Sampling Number	Temperature (°C)	Relative Humidity (%)	Remarks
Spring	2012/4/3–2012/6/26	15 *	23.5 ± 1.9	78.4 ± 11.1	sunny with gentle breeze
Summer	2012/7/2–2012/9/30	16 **	33.0 ± 2.5	87.0 ± 15.0	moderate rain to showers with light breeze
Autumn	2012/10/6–2012/12/29	15 *	19.1 ± 3.0	85.4 ± 6.3	clear to cloudy with level 4 of the north wind
Winter	2013/1/4–2013/3/29	15 *	4.2 ± 2.0	88.3 ± 5.1	Overcast with rain and snow, no sustained winds

* Two samples were destroyed because of operational error. ** One sample was destroyed because of operational error.

2.2. Chemical Analysis

WSIIs were analyzed by an ion chromatograph (Dionex Inc., Sunnyvale, CA, USA). A quarter of the quartz filter after sampling was extracted with Milli Q water under ultrasonication for 1 h, filtered using a 0.45 μm microporous filter to remove insoluble material, and injected into the ion chromatograph. Cations were analyzed with 20 mmol·L^{-1} methane sulfonic acid, whereas anions were analyzed with 25 mmol·L^{-1} KOH. We used standard reference materials which were produced by the National Research Center for Certified Reference Materials (Beijing, China). The quality control standard of the Desert Research Institute was used to control ion concentrations. One sample was rechecked among every 10 samples. The allowable variation for ion concentrations should be in the range of 10–15%.

Teflon filters were analyzed for the presence of 51 elements (from Na to U) by energy-dispersive X-ray fluorescence spectrometry (the PANalytical Epsilon 5 ED-XRF analyzer, PANalytical, Almelo, The Netherlands) at the Institute of Earth Environment, Chinese Academy of Science. Detailed measurements, characteristics, and temporal variation of elements in these samples will be published elsewhere.

3. Results and Discussion

3.1. Chemical Characterization

The average mass concentration of WSIIs in HS aerosols are shown in Table 2. The sequence of the mean concentrations of WSIIs in descending order was SO_4^{2-} > NO_3^- > NH_4^+ > Cl^- > Ca^{2+} > Na^+ > K^+ > Mg^{2+} > F^-. The three ions SO_4^{2-}, NO_3^-, and NH_4^+ were the main species, which were secondarily converted from gas precursors SO_2, NO_x, and NH_3, respectively [4,14]. Among cations, NH_4^+ had the highest mean concentration (7.77 μg·m^{-3}) followed by Ca^{2+} (5.29 μg·m^{-3}) and Na^+ (5.25 μg·m^{-3}) while, among anions, SO_4^{2-} had the highest mean concentration (30.9 μg·m^{-3}), followed by NO_3^- (21.1 μg·m^{-3}) and Cl^- (5.32 μg·m^{-3}).

It can be seen from Table 2 that, apart from Tianjin and Shijiazhuang, China, the mean concentration of SO_4^{2-} was higher than other sites. The mean concentrations of NO_3^-, Cl^-, NH_4^+,

and K^+ were higher than other areas, except Beijing, Tianjin, and Shijiazhuang, China, respectively. Aside from Shijiazhuang, China, the mean concentration of Ca^{2+}, Na^+, Mg^{2+} and F^- was greater than other areas, respectively. Thus, we can find that the pollution of WSIIs in HS aerosols is much more serious with increasing industrial development and urbanization [12,13].

Table 2. Average mass concentration ($\mu g \cdot m^{-3}$) of water-soluble ions in Huangshi and other sites around the world.

Location	Period	F^-	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	Reference
Huangshi, China	2012/4–2013/3	0.57	5.32	21.1	30.9	5.25	7.77	2.10	0.58	5.29	This study
Yichang, China	2012/12	n.a.	1.75	9.91	24.6	4.60	3.85	n.a.	n.a.	6.25	[7]
Beijing, China	2013/1–2013/12	0.35	6.44	31.1	23.2	1.92	13.5	2.27	0.52	4.38	[8]
Tianjin, China	2013/1–2013/12	0.38	10.6	37.8	36.7	1.92	18.5	2.63	0.57	5.07	[8]
Shijiazhuang, China	2013/1–2013/12	1.66	17.3	42.3	40.2	4.01	23.2	4.01	1.03	13.0	[8]
Shanghai, China	2009/5–2009/6	n.a.	3.53	32.9	28.7	0.60	19.3	3.00	0.23	2.97	[9]
Taipei, Taiwan	2011/5–2011/11	n.a.	0.54	1.32	6.30	0.65	1.49	0.22	0.20	0.37	[15]
Ishikawa, Japan	2001/1–2003/12	n.a.	2.77	1.77	4.49	1.86	1.31	0.12	0.23	0.25	[16]
Southern Spain	2004/12–2005/11	n.a.	0.60	3.76	4.36	0.99	1.10	0.28	0.16	2.29	[17]
Mohal, India	2009/9–2011/12	0.34	3.16	2.67	5.56	1.14	0.84	0.50	0.09	1.51	[18]
Auchencorth Moss, UK	2013/1–2013/12	n.a.	1.11	1.86	1.43	0.84	0.98	0.07	0.06	0.06	[19]

n.a.: not available.

3.2. Temporal Variation

3.2.1. Seasonal Variation

The sequence of the total mass concentration of WSIIs in the four seasons was winter ($375.2 \mu g \cdot m^{-3}$) > autumn ($229.7 \mu g \cdot m^{-3}$) > spring ($200.6 \mu g \cdot m^{-3}$) > summer ($144.9 \mu g \cdot m^{-3}$), presenting distinctly seasonal variation. The result states that less rainfall, low temperature, higher relative humidity, and no sustained wind in HS winter (Table 1) can easily strand atmospheric pollutants. In addition, increasing coal use for resident's daily life and industrial production in winter in HS may cause high concentrations of total WSIIs.

A non-parametric test (Kruskal-Wallis) was applied to verify that if the seasonal difference for the ions was statistically significant. The specific significance level (p) is 0.84 for Na^+, 0.01 for Ca^{2+}, and 0.00 for SO_4^{2-}, NO_3^-, Cl^-, F^-, NH_4^+, K^+, and Mg^{2+}. The results show that, except for Na^+ ($p > 0.05$), the other eight ions present distinctly seasonal variation with statistically significant differences ($p < 0.05$). As shown in Figure 1, there was no obvious seasonal trend for Na^+. The seasonal cycle of SO_4^{2-}, NO_3^-, Cl^-, F^-, NH_4^+, K^+, and Mg^{2+} appeared to trend high in winter, moderate in autumn and spring, and low in summer, which is similar to the seasonal variation of the total WSIIs. Interestingly, the ratio of winter concentration to summer concentration was 5.74 (for NO_3^-), 4.20 (for NH_4^+ and K^+), and 4.10 (for Cl^-), respectively, greater than the ratio for total WSIIs (2.59). The result implies that, in addition to environmental meteorological factors, some other factors may increase the concentrations of these ions. It will be discussed in a later section. It is noteworthy that, as a typical ion of flowing dust [13,20], Ca^{2+} decreased in the order of autumn > spring > winter > summer. The result illustrates that Ca^{2+} concentration is immensely influenced by anthropogenic activities, especially in periods of moderate weather, such as autumn and spring [4,21]. It can be confirmed that, with accelerating urbanization processes in recent years in HS, a large number of surfaces from construction operations are emerging every year, thus increasing dust sources and resulting in the rise of Ca^{2+} concentrations due to a lack of necessary enclosed structures and watering measures.
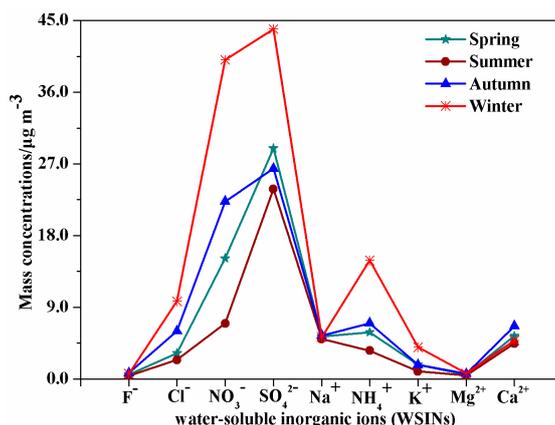
Figure 1. Seasonal variation of nine water-soluble ions in Huangshi aerosols during the observation period.

3.2.2. Monthly Variation

The monthly variation of the concentration of nine water-soluble ions in PM_{10} in HS city is shown in Table 3 and Figure 2. All of the ions appeared at the lowest concentrations in July 2012, suggesting that high temperature (average 37.2 °C), frequent rainfall, and more wind with an average speed 3.0 (m/s) (Table 1) have promoted diffusion and dilution of particulates in HS.

The highest concentration of Na^+ and Ca^{2+} presented in December 2012. The ratio of the highest concentration to the lowest value in July 2012 was 1.41 for Na^+ and 2.45 for Ca^{2+}, respectively, showing the comparatively modest monthly change. The highest concentrations of all of the other six ions were found in February 2013. The ratio of the highest concentration to the lowest value in July 2012 was 4.48 for SO_4^{2-}, 9.05 for Cl^-, 15.44 for NO_3^-, 3.27 for Mg^{2+}, 19.06 for K^+, and 28.09 for NH_4^+, respectively. The above results illustrate strong monthly change, suggesting that a pollution episode is to be certain during the Spring Festival of 2013 in HS.

Table 3. The average monthly concentrations of water-soluble ions and selected elements in PM_{10} from Huangshi ($\mu g \cdot m^{-3}$).

Composition	Apr.	May	Jun.	Jul.	Aug.	Sep.	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.
					Inorganic ions							
F^-	0.84	0.41	0.36	0.31	0.41	0.38	0.70	0.70	0.79	0.84	0.59	0.55
Cl^-	4.10	3.23	2.31	1.71	2.62	2.96	6.47	6.01	5.42	7.79	15.5	6.88
NO_3^-	20.1	16.6	8.97	3.19	7.61	10.5	22.2	22.8	21.9	49.2	39.7	31.3
SO_4^{2-}	30.2	28.3	28.2	11.7	29.4	30.8	29.9	24.6	24.1	49.9	52.5	30.8
Na^+	5.61	5.47	4.95	4.07	5.43	5.20	5.57	5.01	5.75	5.51	5.05	5.12
NH_4^+	6.41	6.33	4.92	0.65	4.40	6.20	7.76	7.46	5.59	18.1	16.7	10.2
K^+	1.38	2.56	1.51	0.44	1.23	1.30	1.93	1.54	1.78	2.65	8.30	1.69
Mg^{2+}	0.76	0.56	0.40	0.27	0.50	0.50	0.67	0.56	0.65	0.67	0.89	0.58
Ca^{2+}	6.66	4.48	4.83	3.05	5.29	4.93	6.66	5.76	7.47	5.59	3.26	5.37
Total	76.1	68.0	56.5	25.4	56.8	62.7	81.8	74.5	73.4	140.3	142.5	92.4
Cl^-/Na^+	0.73	0.59	0.47	0.42	0.48	0.57	1.16	1.20	0.94	1.41	3.07	1.34
NO_3^-/SO_4^{2-}	0.66	0.59	0.32	0.27	0.26	0.34	0.74	0.92	0.91	0.99	0.76	1.01
					Selected elements							
K	1.55	2.09	1.34	0.52	1.05	1.22	1.98	1.64	1.92	2.11	4.37	1.39
Al	0.71	0.39	0.37	0.34	0.42	0.34	0.64	0.55	0.72	0.45	0.57	0.49
Mg	1.90	0.72	0.72	0.50	0.63	0.77	1.18	1.45	1.87	1.10	1.34	1.30
Pb	0.31	0.22	0.25	0.13	0.44	0.19	0.40	0.19	0.28	0.42	0.41	0.23
Ba	0.11	0.08	0.09	0.08	0.13	0.09	0.13	0.11	0.10	0.11	0.37	0.09
Sr	0.03	0.02	0.02	0.02	0.02	0.02	0.03	0.02	0.03	0.03	0.07	0.02
Total	4.61	3.50	2.79	1.58	2.68	2.63	4.36	3.95	4.92	4.22	7.12	3.53
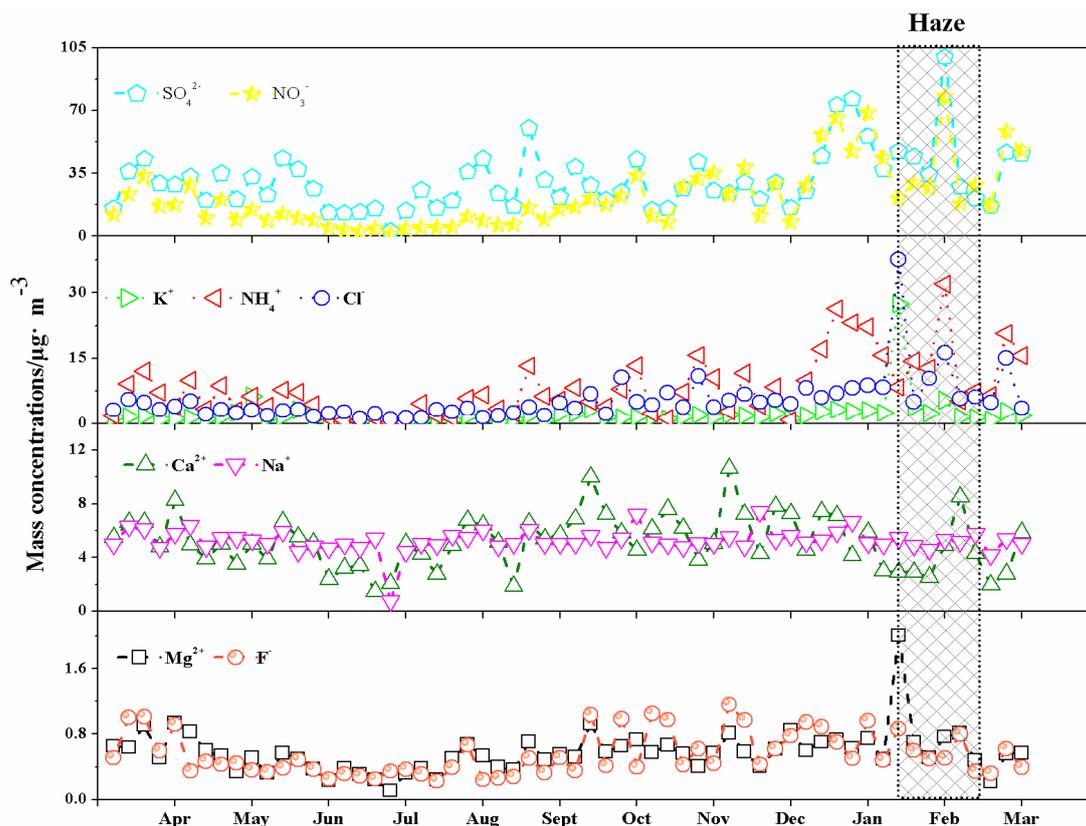
Figure 2. Monthly variation of water-soluble inorganic ions in Huangshi aerosols during the observation period. The shadowed areas show the pollution episode.

3.3. The Pollution Episode in February 2013

In China, frequent haze events have attracted much attention because of poor air quality across the country [11,22]. According to the China Weather Website (www.weather.com.cn) reports, Hubei province suffered haze weather during the Spring Festival of 2013. HS, located in southeast of Hubei province, had issued a yellow warning in February because of the haze weather continuing for ten days. It can be concluded that low temperature (average 3.1 °C), high relative humidity (average 94.0%), and no sustained wind in February 2013 (Table 1) could be the crucial meteorological factors which prevented the diffusion and dilution of particulates, making it easy to form haze.

Concentrations of total WSIIs and respective ions (SO_4^{2-}, Cl^-, NO_3^-, Mg^{2+}, K^+, and NH_4^+) in February 2013 were generally higher than those in other months (Table 3), indicating that firework displays could influence atmospheric particle levels during the Spring Festival in HS [23]. Tsai et al. [24] demonstrated that the ratio of Cl^-/Na^+ can be used as the indicator of firework burning. As shown in Table 3, the Cl^-/Na^+ ratio (average 0.85) was slightly lower during the sampling periods, but it significantly rose up to 3.07 in February 2013, which was similar to that in Taiwan (3.20) during Taiwan's Lantern Festival [24], verifying that Cl^- comes from the chlorine contents of firework powders.

Interestingly, it can be seen from Table 3 that the total concentration of elements in February 2013 showed the highest value (7.12 $\mu g \cdot m^{-3}$). This may be due to the setting off of fireworks that caused the elevated levels of metallic elements [23,25]. The highest concentrations of K (4.37 $\mu g \cdot m^{-3}$), Ba (0.37 $\mu g \cdot m^{-3}$) and Sr (0.07 $\mu g \cdot m^{-3}$) occurred in February 2013 (Table 3), which were related to the raw materials in firework powders (e.g., KNO_3, $Ba(NO_3)_2$, $Sr(NO_3)_2$, etc.) [23,25]. Thus, the results can be concluded that firework powders had emitted a significant amount of aerosol particles containing metals and ions into the atmosphere, and then aggravated the haze in February 2013.

In addition, we investigated the difference among WSIIs characteristic in different days. The specific days were the Spring Festival day (9 February 2013), haze day (15 February 2013), and a normal day in spring (9 May 2012), summer (18 September 2012), autumn (17 November 2012) and winter (5 March 2013). As shown in Figure 3, the percentages of K^+ (24.5%) and Cl^- (17.9%) in the Spring Festival day were clearly higher than other days, verifying that firework displays could influence atmospheric particle levels. And the total percentages of the major species K^+, Cl^-, SO_4^{2-} and NO_3^- in the Spring Festival day reached 84.1%. In haze day, the main ions were SO_4^{2-} (38.5%), NO_3^- (34.7%) and NH_4^+ (13.8%), accounting for the percentage of 87.0% of the total WSIIs. However, apart from SO_4^{2-} and NO_3^-, there were other major ions in normal day in spring (Na^+ and Ca^{2+}), summer (NH_4^+), autumn (NH_4^+ and Ca^{2+}) and winter (Ca^{2+}, Cl^-, NH_4^+ and Na^+).
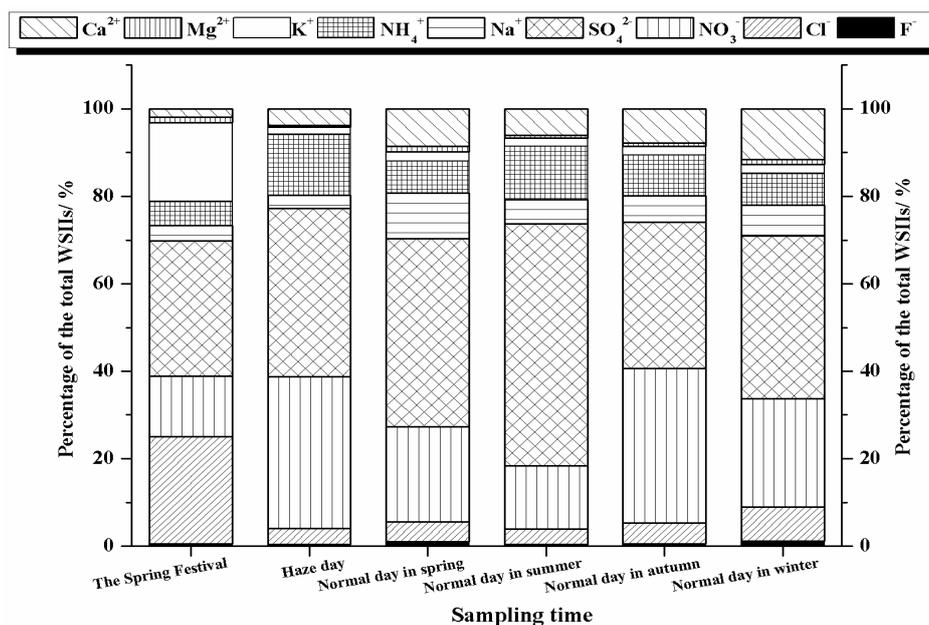
Figure 3. The mass percentage of water-soluble inorganic ions in Huangshi aerosols in the Spring Festival day, haze day, and a normal day in spring, summer, autumn, and winter.

3.4. Charge Balance Analysis of WSIIs

The micro-equivalent concentrations of cations and anions in PM_{10} were calculated by the corresponding equations [21,26,27]. The linear relationship between cation and anion equivalents in the four seasons in HS is drawn in Figure 4. The correlation coefficients (R^2) reached 0.98, 0.97, 0.96, and 0.96 in spring, summer, autumn, and winter, respectively. The results suggest that the cation and anion equivalents were strongly correlated in the four seasons. The slope (cation/anion) of the linear regression was 0.78, 0.85, 0.64, and 0.59 in spring, summer, autumn, and winter, respectively. All of the slopes are significantly lower than 1, which could be best explained by the presence of hydrogen ions (H^+) [20,28], implying that the aerosol particles in HS are acidic. Moreover, all of the slopes have a relatively large gap with 1, indicating that there are some other cationic ions not detected except those had been measured in this study (Na^+, K^+, NH_4^+, Mg^{2+}, and Ca^{2+}), such as H^+ [28], organic cations, or heavy metal ions (Zn^{2+}, Cu^{2+}, etc.) [4]. Especially, compared with other seasons, the lowest slope appeared in HS in winter, which carries a certain probability that PM_{10} in HS contains organic cations or heavy metal ions in winter. This is one of the reasons that the days of heavy pollution weather in winter were more than the days in the other three seasons, such as the pollution episode in February 2013 in HS.
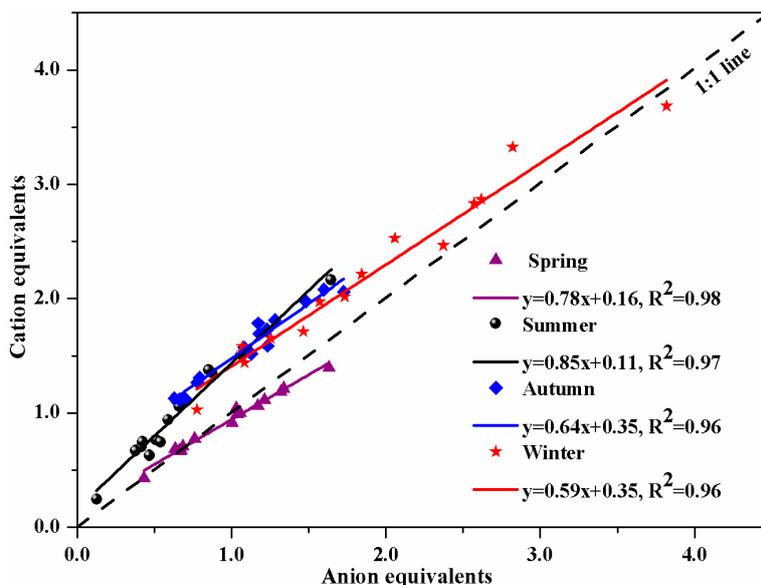
Figure 4. The charge balance of anion and cation water-soluble ions in Huangshi in the four seasons.

Comparisons between the calculated and measured NH_4^+ concentrations were conducted to evaluate the formation of ions. NH_4^+ concentrations can be calculated based on the stoichiometric ratios of the major compounds (i.e., $(NH_4)_2SO_4$, NH_4HSO_4, and NH_4NO_3), which assumed that NO_3^- is in the form of NH_4NO_3 and that SO_4^{2-} is in the form of either $(NH_4)_2SO_4$ or NH_4HSO_4. Figure 5 shows good correlation ($R = 0.98$) between calculated and measured NH_4^+ concentrations. The slope was 1.56 when $(NH_4)_2SO_4$ was assumed and 1.13 when NH_4HSO_4 was assumed. This suggests that the aerosol particles in HS are acidic because of the existing available NH_4^+ is not fully neutralized. The similar conclusion can be found in many studies [20,26,27].
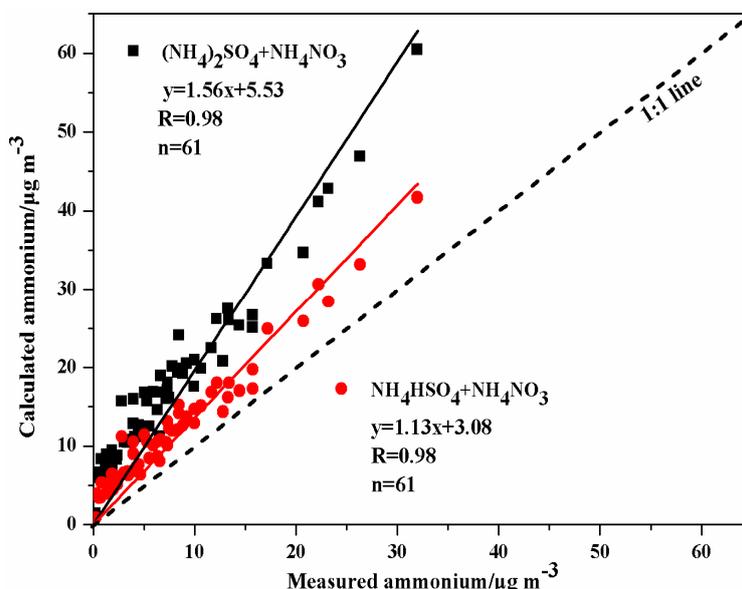
Figure 5. Comparison between calculated and measured ammonium in PM_{10} samples in Huangshi (calculated NH_4^+ = 0.38 $[SO_4^{2-}]$ + 0.29 $[NO_3^-]$ in the form of $(NH_4)_2SO_4$ and NH_4NO_3) and NH_4^+ = 0.19 $[SO_4^{2-}]$ + 0.29 $[NO_3^-]$ in the form of NH_4HSO_4 and NH_4NO_3).

3.5. Source Identification

3.5.1. The Ratio of NO_3^-/SO_4^{2-}

The mass concentration ratio of NO_3^-/SO_4^{2-} can be used as a significant index to measure the relative contribution of mobile sources and stationary sources for nitrogen pollution and sulfur pollution in the atmosphere [4,29]. We found that the ratio in HS aerosols was 0.26–1.01 with an average of 0.65 (Table 3), implying that ion pollution largely comes from stationary sources. The ratio in HS aerosols was lower than those from Beijing (1.34), Tianjin (1.03) and Shijiazhuang (1.05) [8], Shanghai (1.15) [9], China, and Southern Spain (0.86) [17], but higher than those from Yichang, China (0.40) [7], Taipei, Taiwan (0.21) [15], Ishikawa, Japan (0.39) [16], and Mohal, India (0.48) [18].

3.5.2. Correlation Analysis

Table 4 shows the Pearson correlation coefficients among these WSIIs in the PM_{10} samples. NH_4^+ was strongly correlated with SO_4^{2-} in spring ($R = 0.90$), summer ($R = 0.95$), autumn ($R = 0.87$), and winter ($R = 0.92$). Additionally, good linear regression was performed for NH_4^+ and SO_4^{2-} in spring ($R^2 = 0.81$), summer ($R^2 = 0.90$), autumn ($R^2 = 0.75$), and winter ($R^2 = 0.90$). The result suggests that $(NH_4)_2SO_4$ and NH_4HSO_4 are the major chemical fractions. The linear (micro-equivalent vs. micro-equivalent) fits of the data were described as $[NH_4^+] = 0.82\,[SO_4^{2-}] - 0.16$ in spring, $[NH_4^+] = 0.63[SO_4^{2-}] - 0.11$ in summer, $[NH_4^+] = 1.18[SO_4^{2-}] - 0.27$ in autumn, and $[NH_4^+] = 0.85[SO_4^{2-}] + 0.07$ in winter. Since the equivalent ratio of NH_4^+ to SO_4^{2-} in NH_4HSO_4 and $(NH_4)_2SO_4$ is 0.50 and 1.00, respectively, both NH_4HSO_4 and $(NH_4)_2SO_4$ were the major chemical forms of WSIIs in spring, summer, and winter, while $(NH_4)_2SO_4$ was completely formed in autumn.

The strong correlation was found between NH_4^+ and NO_3^- in spring ($R = 0.85$), summer ($R = 0.88$), autumn ($R = 0.86$), and winter ($R = 0.95$), and good linear regression was obtained for NH_4^+ and NO_3^- in spring ($R^2 = 0.73$), summer ($R^2 = 0.77$), autumn ($R^2 = 0.74$), and winter ($R^2 = 0.87$). Thus, it can be implied that NH_4NO_3 was another major compound in HS.

According to the significant correlation and good linear regression, other chemical species in the aerosol particles were also found. Among them, Na^+ mainly constituted NaCl ($R = 0.78$) and $NaNO_3$ ($R = 0.77$) in spring. K^+ formed KCl ($R = 0.90$) and KNO_3 ($R = 0.91$) in summer, and KCl ($R = 0.94$) in winter. Mg^{2+} comprised MgF_2 ($R = 0.74$) and $Mg(NO_3)_2$ ($R = 0.79$) in spring, $MgSO_4$ ($R = 0.85$) in summer, and $MgCl_2$ ($R = 0.87$) in winter. Ca^{2+} composited CaF_2 ($R = 0.72$) in spring, $Ca(NO_3)_2$ ($R = 0.71$) and $CaSO_4$ ($R = 0.76$) in summer. Additionally, NH_4Cl came into being in spring as a compound of NH_4^+ with correlation coefficient (R) reached 0.72.

Pavuluri et al. [30] had verified that mineral dust can add aerosol complexity because of its important role in radiative forcing. Considering that HS is a typical mining and industrial city, the relative correlations between elements and inorganic ions were analyzed (Table 4). We found that inorganic ions had good positive correlation with corresponding elements. Strong correlations were observed for SO_4^{2-} and S in spring ($R = 0.84$), summer ($R = 0.88$), autumn ($R = 0.87$), and winter ($R = 0.85$). And good linear regression was conducted for SO_4^{2-} and S in spring ($R^2 = 0.70$), summer ($R^2 = 0.78$), autumn ($R^2 = 0.76$), and winter ($R^2 = 0.73$). Ca^{2+} and Ca had strong correlation in spring ($R = 0.88$), autumn ($R = 0.85$), and winter ($R = 0.95$). Additionally, good linear regression was performed for Ca^{2+} and Ca in spring ($R^2 = 0.77$), autumn ($R^2 = 0.72$), and winter ($R^2 = 0.91$). Moreover, strong correlations were often observed for Mg^{2+} and Mg in spring ($R = 0.74$), autumn ($R = 0.80$), and winter ($R = 0.83$) with great linear regression in spring ($R^2 = 0.55$), autumn ($R^2 = 0.64$), and winter ($R^2 = 0.69$), for Cl^- and Cl in spring ($R = 0.81$), summer ($R = 0.74$), and winter ($R = 0.97$) with great linear regression in spring ($R^2 = 0.66$), summer ($R^2 = 0.55$), and winter ($R^2 = 0.93$), and for K^+ and K in spring ($R = 0.95$), summer ($R = 0.88$), and winter ($R = 0.99$) with great linear regression in spring ($R^2 = 0.91$), summer ($R^2 = 0.77$), and winter ($R^2 = 0.98$). These results further illustrate the characterization of aerosol WSIIs in mining cities are strongly influenced by elemental constituents.

Table 4. The Pearson correlation coefficients (R) of water-soluble ions in PM_{10} in Huangshi City during the observation period ($n = 61$).

Spring	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	F^-	Cl^-	NO_3^-	SO_4^{2-}
element [#]	0.36 (Na)	n.a.	0.95 ** (K)	0.74 ** (Mg)	0.86 ** (Ca)	n.a.	0.81 ** (Cl)	n.a.	0.84 ** (S)
Na^+	1.00								
NH_4^+	0.62 *	1.00							
K^+	0.04	0.18	1.00						
Mg^{2+}	0.65 *	0.53 *	−0.04	1.00					
Ca^{2+}	0.54 *	0.47	0.06	0.77 **	1.00				
F^-	0.49	0.43	−0.10	0.68 *	0.72 **	1.00			
Cl^-	0.78 **	0.72 **	0.04	0.74 **	0.58 *	0.68 *	1.00		
NO_3^-	0.77 **	0.85 **	0.03	0.79 **	0.53 *	0.62 *	0.87 **	1.00	
SO_4^{2-}	0.55 *	0.90 **	0.30	0.48	0.65 *	0.40	0.57 *	0.65 *	1.00
Autumn	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	F^-	Cl^-	NO_3^-	SO_4^{2-}
element [#]	−0.27 (Na)	n.a.	0.45 (K)	0.80 ** (Mg)	0.85 ** (Ca)	n.a.	0.20 (Cl)	n.a.	0.87 ** (S)
Na^+	1.00								
NH_4^+	0.04	1.00							
K^+	−0.04	0.26	1.00						
Mg^{2+}	0.06	−0.40	0.26	1.00					
Ca^{2+}	−0.30	−0.53	0.44	0.73 **	1.00				
F^-	−0.21	−0.42	0.16	0.53	0.65 *	1.00			
Cl^-	0.03	0.39	0.27	−0.07	−0.10	0.38	1.00		
NO_3^-	−0.09	0.86 **	0.30	−0.14	−0.20	−0.20	0.23	1.00	
SO_4^{2-}	0.16	0.87 **	0.48	−0.19	−0.30	−0.41	0.34	0.67 *	1.00
Summer	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	F^-	Cl^-	NO_3^-	SO_4^{2-}
element [#]	0.25 (Na)	n.a.	0.88 ** (K)	0.24 (Mg)	0.68 * (Ca)	n.a.	0.74 ** (Cl)	n.a.	0.88 ** (S)
Na^+	1.00								
NH_4^+	0.45	1.00							
K^+	0.44	0.71 **	1.00						
Mg^{2+}	0.66 *	0.81 **	0.74 **	1.00					
Ca^{2+}	0.46	0.69 *	0.54 *	0.86 **	1.00				
F^-	0.09	0.47	0.68 *	0.68 *	0.60 *	1.00			
Cl^-	0.36	0.47	0.90 **	0.59 *	0.30	0.61 *	1.00		
NO_3^-	0.49	0.88 **	0.91 **	0.86 **	0.71 **	0.64 *	0.75 **	1.00	
SO_4^{2-}	0.60 *	0.95 **	0.62 *	0.85 **	0.76 **	0.41	0.36	0.80 **	1.00
Winter	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	F^-	Cl^-	NO_3^-	SO_4^{2-}
element [#]	0.16 (Na)	n.a.	0.99 ** (K)	0.83 ** (Mg)	0.95 ** (Ca)	n.a.	0.97 ** (Cl)	n.a.	0.85 ** (S)
Na^+	1.00								
NH_4^+	0.40	1.00							
K^+	0.12	−0.12	1.00						
Mg^{2+}	0.23	−0.06	0.95 **	1.00					
Ca^{2+}	0.31	0.17	−0.20	0.07	1.00				
F^-	0.05	0.02	0.30	0.50	0.54 *	1.00			
Cl^-	0.12	0.07	0.94 **	0.87 **	−0.28	0.24	1.00		
NO_3^-	0.34	0.95 **	−0.16	−0.08	0.32	0.16	−0.03	1.00	
SO_4^{2-}	0.52 *	0.92 **	0.15	0.23	0.21	0.05	0.23	0.79 **	1.00

[#] represents the Pearson correlation coefficients between element and its corresponding ion; ** represents the significant correlation ($p \leq 0.01$); * represents significant correlation ($p \leq 0.05$); and "n.a" represents data that is not available.

3.5.3. Principal Component Analysis

A preliminary source identification study of WSIIs was carried out by principal component analysis (PCA, SPSS version 17.0, SPSS Inc. 2008, Chicago, IL USA). We chose these species because of their higher concentrations or strong influence on other species. The three major factors (F1–F3) in the PM_{10} samples accounted for 88.3% of the total variance in the concentration data (Table 5). F1 accounted for 46.9% of the total variances, which was strongly loaded with NH_4^+, Mg^{2+}, NO_3^-, K and K^+, Cl^- and Cl, and SO_4^{2-} and S, suggesting likely origins from anthropogenic sources, especially coal combustion, vehicular exhaust, and biomass burning. Mg was dominant as F2 accounted for 23.3% of the total variances, and Ca^{2+} and Ca were identified as F3, which explained 18.1% of the variances, demonstrating that another important source is mineral dust from both natural and anthropogenic sources.

Table 5. Principal component factor analysis of water-soluble ions in PM_{10} in Huangshi city.

Factors	F1	F2	F3	Communalities
Cl^-	0.86	0.04	−0.42	0.92
NO_3^-	0.66	−0.56	0.27	0.82
SO_4^{2-}	0.72	−0.58	0.26	0.91
NH_4^+	0.66	−0.70	0.21	0.97
K^+	0.79	0.24	−0.50	0.93
Mg^{2+}	0.87	0.38	0.03	0.90
Ca^{2+}	0.25	0.40	0.82	0.89
K	0.79	0.39	−0.33	0.89
Mg	0.48	0.76	0.20	0.85
Cl	0.85	0.12	−0.24	0.80
Ca	0.23	0.57	0.75	0.93
S	0.65	−0.48	0.37	0.78
Characteristic value	5.62	2.80	2.18	
Contribution rate/%	46.9	23.3	18.1	
Cumulative contribution rate/%	46.9	70.2	88.3	

4. Conclusions

Water-soluble inorganic ions (WSIIs) were reported, for the first time, in Huangshi (HS) which is a representative mining and medium-sized city in Central China. The three ions (SO_4^{2-}, NO_3^-, and NH_4^+) were the main components according to the descending mean concentration order of $SO_4^{2-} > NO_3^- > NH_4^+ > Cl^- > Ca^{2+} > Na^+ > K^+ > Mg^{2+} > F^-$. The inorganic ions had obvious positive correlation and good linear regression with relevant elements, showing that WSIIs in mining cities are strongly influenced by elemental constituents.

The sequence of the total mass concentration of WSIIs in four seasons was winter > autumn > spring > summer, illustrating that winter can easily strand atmospheric pollutants. The results of a non-parametric test (Kruskal-Wallis) show that, except Na^+ ($p > 0.05$), the other ions present distinctly seasonal variation with statistically significant differences ($p < 0.05$). The minimum concentrations of all ions were found in summer, while the maximum values presented in autumn (for Ca^{2+}) and winter (for Cl^-, NO_3^-, SO_4^{2-}, K^+, NH_4^+, Mg^{2+}). Based on the highest ratio of Cl^-/Na^+ (3.02) and the highest concentration of K (4.37 $\mu g \cdot m^{-3}$), Ba (0.37 $\mu g \cdot m^{-3}$), and Sr (0.07 $\mu g \cdot m^{-3}$) in February 2013, it can concluded that firework powders have aggravated the haze during the Spring Festival of 2013.

The micro-equivalent concentrations of cations and anions were calculated and the comparisons between the calculated and measured NH_4^+ concentrations were conducted. The results suggest that aerosol particles in HS are acidic, and there may be some other cationic ions not detected in this study. An obvious positive correlation and good linear regression among WSIIs suggest that chemical forms in HS are a great variety of combinations, such as NH_4NO_3, NH_4HSO_4, $(NH_4)_2SO_4$, NH_4Cl, KCl, KNO_3, NaCl, $NaNO_3$, $Ca(NO_3)_2$, $CaSO_4$, $MgCl_2$, $Mg(NO_3)_2$, and $MgSO_4$.

The mass concentration ratio of NO_3^-/SO_4^{2-} in HS aerosols implies that ion pollution largely comes from stationary sources. Compared with other studies, the results show that, except for the major contribution from stationary sources, caution should be applied to mobile sources, along with economic development and urbanization in HS. Principal component analysis implies that WSIIs in PM_{10} are probably from three sources. NH_4^+, Mg^{2+}, NO_3^-, K and K^+, Cl^- and Cl, SO_4^{2-}, and S accounted for 46.9% of the total variances, suggesting likely anthropogenic sources, especially coal combustion, vehicular exhaust, and biomass burning. Mg accounted for 23.3% of the total variances and Ca^{2+} and Ca explained 18.1% of the total variances, demonstrating that another important source is mineral dust from both natural and anthropogenic sources.

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