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Chemical composition of rainwater and anthropogenic influences in Chengdu, Southwest China

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ABSTRACT

A comprehensive study on the chemical compositions of rainwater was carried out from Jan. to Dec. in 2008 in Chengdu, a city located on the acid rain control zone of southwest China. All samples were analyzed for pH and major ions (F^-, Cl^-, NO_3^-, SO_4^{2-}, K^+, Na^+, Ca^{2+}, Mg^{2+}, and NH_4^+). The pH increased due to the result of neutralization caused by the base ions. It was observed that Ca^{2+} was the most abundant cation with a VWM value of 196.6 μeq/L (17.3–1568.7 μeq/L), accounting for 49.7% (9.4%–79.2%) of the total cations. SO_4^{2-} was the most abundant anion with VWM value of 212.8 μeq/L (41.8–1227.6 μeq/L). SO_4^{2-} and NO_3^- were dominant among the anions, accounting for 90.4%–99.1% of the total measured anions.

The concentrations of NO_3^- were higher than the most polluted cities abroad, which indicated Chengdu has been a severe polluted city over the world. The high fuel consumption from urbanization and the rapid increase of vehicles resulted in the high emission of SO_2 and NO_x, which were the precursor of the high concentration of acidic ions NO_3^- and SO_4^{2-}. It was the main reason of the severe acid rain in Chengdu.

The high concentrations of alkaline ions (mainly Ca^{2+}, NH_4^+) in Chengdu city atmosphere have played an important role to neutralize the acidity of rainwater and the pH value has increased by 0.7 units since 1989. It is worth noting that the emission of NO_x from the automobile exhaust is increased and is becoming the important precursor of acid rain now.

1. Introduction

The chemistry of precipitation has been widely investigated in many areas in China, which are significantly affected by acid rain since the last three decades (Zhao et al., 1988; Wang and Wang, 1995; Lei et al., 1997; Yu et al., 1998; Feng et al., 2001; Larssen et al., 2006; Aas et al., 2007; Huang et al., 2008; Xu and Han, 2009; Han et al., 2010). The acid rain is primarily caused by the precursors of strong acids such as H_2SO_4 and HNO_3, resulting from fossil fuel combustion. Moreover, the areas in southwest China affected by acid deposition are gradually expanding due to the rapid economy growth and the increasing fuel consumption (Wang and Wang, 1995; Lei, et al., 1997; Han and Liu, 2006). Great amount of SO_2 released from coal burning and NO_x from traffic emission would result in the corresponding high acidity (Ye et al., 2000). According to the statistical reports, acid precipitation affected about 30% of China and the seriously affected areas are mainly located in the economically developed regions in the east, the south and the center of China (Fig. 1, State Environmental Protection Administration of China, 2008).

Rainwater compositions play an important role in scavenging soluble components from the atmosphere and helping understand the relative contributions of different sources of atmospheric pollutants. The characteristics of rainwater have been studied in Chongqing, Guiyang, Guangzhou (Zhao et al., 1988; Seip et al., 1995, 1999; Lei et al., 1997). However, only limited studies were related to the precipitation in Chengdu (Lei et al., 1997). The composition of the rainwater and sources of the severe acid rain over Chengdu have been

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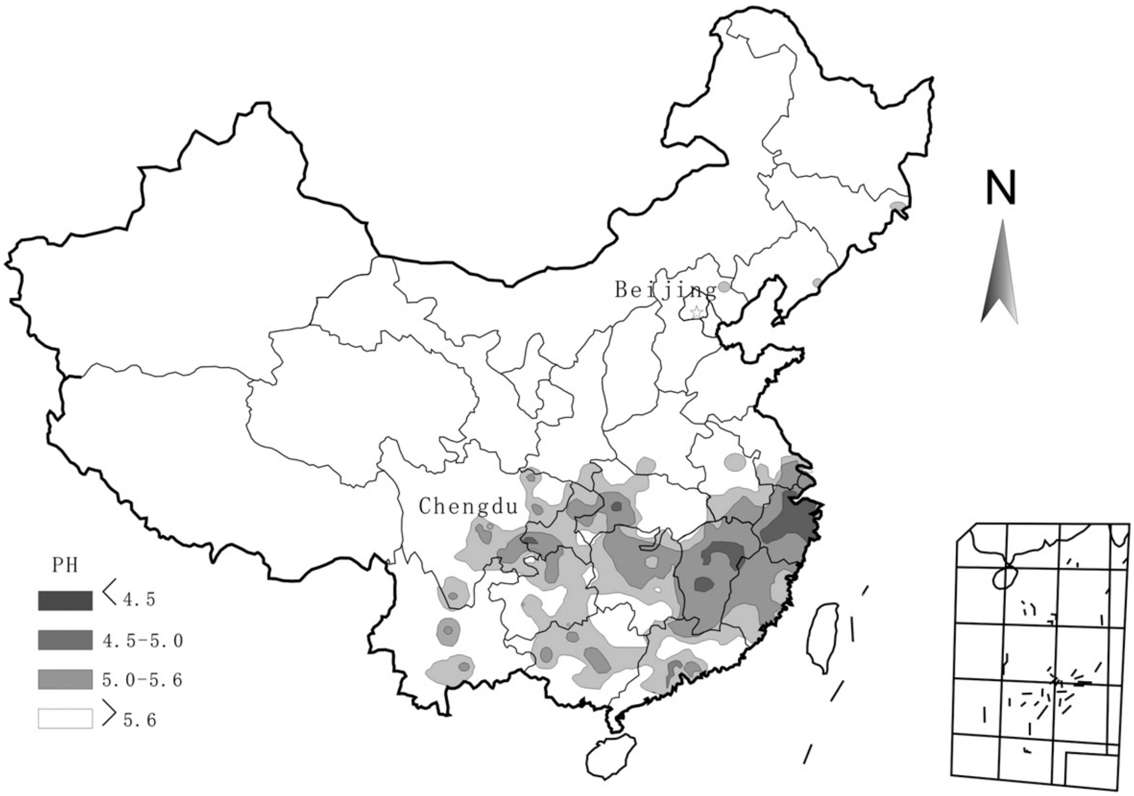

Fig. 1. The location of Chengdu city and the distribution of precipitation acidity during 2008 in China (according to State Environmental Protection Administration of China).

poorly understood to date. In this study we report the severe acid rain over Chengdu, the capital of Sichuan province, based on the continuing sampling rain samples throughout the whole 2008, and address the composition, sources and the formation mechanism of such heavy air-pollution in Chengdu. The results would provide useful information to identify possible sources of the various constituents in precipitation and finally to evaluate the quality of atmosphere in Chengdu city.

2. Sampling site

Chengdu (30°05′ − 31°26′N, 102°54′ − 104°53′E) is located in the southwest of China. Geomorphologically, it is high to the northwest and low to the southeast, not far from the western slopes of the Longmen Mountains. With a typical continental monsoon climate of northern temperate zone, there are four distinct seasons in Chengdu. The average temperature ranges from 5 °C in winter to 26 °C in summer. The average annual precipitation is 918 mm. Rainfall mainly concentrated from July to August. The least rainfall concentrated from December to March.

Chengdu city is one of the most crowded cities in the world. According to Chengdu Economic and Social Development Statistics Bulletin, the population of the city has exceeded 13 million by the end of 2008. The China government has promoted the auto industry and China has been the world's second-largest vehicle market by unit sales, next to the United States. The amount of car has exceeded 1.01 million in Chengdu by the end of 2008.

3. Sampling and analytical procedure

We collected the samples in Chengdu (30°39′12.5 N, 104°00′40.84E) at an elevation of 520 m, southwest of China.

The sampler was placed on the roof of a building about 17 m high from ground level in an office building. The rainwater samples were collected manually from the beginning of each rain event with a funnel sampler that was located approximately 100 cm above the roof. Prior to use, the sampler was cleaned with acid (2–3 N HCl) and soaked in with Milli-Q water (18.2 MΩ cm), then finally rinsed with Milli-Q water and dried. In order to prevent contaminations from dry deposition, special attention was paid to open the sampler as quickly as possible after the onset of rainfall. 44 rainwater samples were collected from Jan. to Dec. in 2008. Most of our samples were collected in the rainy season, from July to August and there are no samples after November due to inadequate amount of precipitation.

The pH values were measured instantaneously at the end of the rain events at sampling sites with a portable pH. All the rainwater samples were filtered through 0.22 μm Millipore membrane filters using a pre-cleaned Nalgene filter apparatus and the filtrate was separated into two aliquots. One was stored in polyethylene bottles for measuring anions and the other was acidified with ultra-purified nitric acid to pH<2 and stored in pre-cleaned polyethylene bottles for measuring cations. Major anions (Cl^-, SO_4^{2-}, NO_3^-) were measured by using an ionic chromatography (Dionex DX-120).The detection limits of Cl^-, NO_3^- and SO_4^{2-} ions were found to be 0.07, 0.07 and 0.10 mg/L, respectively. Reproducibility of results was better than 5% for all major anions. NH_4^+ concentrations were determined by spectrophotometry using the Nessler method. The detection limit of NH_4^+ ion was found to be 0.01 mg/l. Reproducibility of results was better than 3%. Major cations (K^+, Na^+, Ca^{2+}, and Mg^{2+}) were determined by ICP-AES (Thermo's IRIS Intrepid II). The detection limits of K^+, Na^+, Ca^{2+}, and Mg^{2+} ions were found to be 0.004, 0.002, 0.010 and 0.003 mg/L, respectively. Reproducibility of results was better than 5% for all major cations. Reagent and procedural blanks were determined in parallel to the sample treatment using identical procedures and the blanks were all below the detection limit of the measure species. The analytical precision of the data are better than ±5%.

4. Results and discussion

4.1. pH value and ionic composition

The field data and major ions are given in Table 1. According to previous studies, the naturally existing CO_2, NO_x and SO_2 can dissolve into the clouds and droplets, resulting in pH values of the rain in the clean atmosphere to be between 5.0 and 5.6 (Charlson and Rodhe, 1982; Galloway, et al., 1993). Rainwater with pH value below 5.0 is due to the presence of natural H_2SO_4, weak organic acids, or anthropogenic emission of H_2SO_4 and/or HNO_3. The samples with pH values above 6.0 may suggest certain inputs of alkaline species into the precipitation in the study area. The pH values of rain samples from Chengdu city range from 3.7 to 5.8. The

Table 1
Concentrations of major ions (μeq/L) in rainwater from Chengdu, southwestern China.

Sample numbers	Date	pH	NH_4^+	K^+	Na^+	Ca^{2+}	Mg^{2+}	F^-	Cl^-	NO_3^-	SO_4^{2-}
1	2008-3-16	4.00	186.20	11.59	3.80	151.15	13.43	9.18	14.40	108.03	302.95
2	2008-4-1	5.72	172.59	25.84	4.08	357.26	24.06	8.77	36.47	186.01	238.88
3	2008-4-11	5.54	185.58	19.23	2.04	245.04	25.46	5.64	15.81	149.32	298.63
4	2008-4-18	4.05	86.74	7.01	0.91	187.79	16.08	3.39	8.02	112.43	231.10
5	2008-4-21	5.38	153.84	18.72	2.58	531.31	31.61	14.09	24.20	245.75	263.31
6	2008-5-3	5.74	283.52	22.45	11.23	826.73	41.54	10.53	40.96	174.77	391.39
7	2008-5-9	5.54	248.16	13.63	5.16	696.20	46.58	8.73	24.48	292.74	316.14
8	2008-5-21	5.32	280.80	15.49	2.26	384.74	31.89	5.76	13.01	273.35	403.44
9	2008-6-6	5.69	1106.04	58.58	8.42	1568.73	97.91	29.48	78.02	797.79	1227.63
10	2008-6-7	5.19	84.92	1.08	0.72	52.67	5.59	2.11	1.86	42.20	106.71
11	2008-6-11	5.44	359.70	15.15	2.85	256.49	17.62	10.71	19.42	308.77	216.08
12	2008-6-14	4.94	113.03	2.77	0.72	89.31	8.39	5.12	5.11	149.22	220.28
13	2008-6-15	5.38	137.52	8.60	1.92	114.52	15.96	3.57	4.27	135.76	276.12
14	2008-6-19	5.38	135.71	9.56	1.63	272.52	20.42	5.30	7.57	124.29	185.50
15	2008-6-22	5.58	623.59	20.92	4.85	524.44	50.77	14.65	28.27	450.96	678.37
16	2008-7-1	5.32	193.74	15.15	1.90	293.13	24.06	3.37	16.70	137.10	445.38
17	2008-7-9	5.55	421.37	14.82	5.98	858.79	55.67	40.97	39.49	672.23	471.08
18	2008-7-11	5.82	333.40	28.39	4.53	806.12	48.95	10.64	34.07	392.95	432.06
19	2008-7-14	3.94	91.27	4.98	0.63	290.47	35.47	6.52	4.28	198.30	362.77
20	2008-7-15	3.84	118.48	3.52	0.72	36.64	11.48	0.90	1.79	81.05	210.32
21	2008-7-17	5.38	158.62	8.03	3.31	551.92	36.37	22.80	19.77	386.50	312.56
22	2008-7-20	5.74	100.34	1.08	0.36	22.90	3.36	3.77	1.83	42.50	97.68
23	2008-7-24	5.32	127.54	0.91	0.36	52.67	4.90	5.90	3.24	73.29	92.45
24	2008-7-25	5.08	70.41	0.40	0.18	18.32	3.36	5.40	3.02	59.60	93.60
25	2008-7-29	5.54	156.56	4.64	1.00	153.44	11.33	9.15	6.99	166.92	163.42
26	2008-8-1	5.28	152.27	0.74	0.36	20.61	3.36	1.02	1.76	54.45	80.89
27	2008-8-6	5.24	170.41	1.75	0.63	48.09	5.31	2.20	5.89	107.90	165.29
28	2008-8-8	5.49	189.58	6.16	1.63	341.23	17.62	11.15	13.31	226.23	290.31
29	2008-8-9	5.08	35.04	2.94	0.86	171.76	6.29	5.23	4.78	58.95	148.76
30	2008-8-12	5.32	247.25	10.74	2.40	364.13	21.12	15.08	16.43	382.72	278.61
31	2008-8-14	5.38	334.31	13.12	3.67	398.48	29.93	21.92	27.61	554.98	402.69
32	2008-8-19	5.02	454.01	19.90	4.62	812.99	60.56	24.02	28.78	664.38	847.72
33	2008-8-24	5.32	65.88	2.26	1.13	217.56	18.04	5.32	5.72	105.98	93.66
34	2008-8-28	5.44	202.81	8.54	3.35	437.41	38.88	22.11	17.68	272.41	404.89
35	2008-8-29	5.49	83.11	1.58	0.72	93.89	7.83	6.90	4.53	66.81	142.69
36	2008-9-7	3.94	222.76	12.27	2.36	480.92	42.10	13.83	13.01	361.27	550.05
37	2008-9-8	3.71	242.71	23.64	1.49	199.24	26.85	9.91	21.52	253.80	355.22
38	2008-9-9	5.38	59.53	2.09	0.59	54.32	12.90	4.56	1.39	69.51	108.26
39	2008-9-17	5.38	422.27	27.71	6.16	1250.41	67.84	46.53	46.14	469.34	768.80
40	2008-9-23	5.24	97.62	3.79	0.95	167.18	9.79	3.15	3.46	82.19	152.23
41	2008-9-24	5.44	73.13	1.92	0.45	48.09	5.87	1.91	1.87	97.80	142.11
42	2008-9-26	5.38	46.83	1.58	0.68	18.32	2.66	1.05	2.21	38.78	41.81
43	2008-9-28	5.14	159.53	2.43	1.22	17.34	3.92	1.95	4.52	43.98	78.78
44	2008-10-5	5.49	346.10	10.41	4.35	451.15	27.13	16.15	23.33	206.41	362.51

mean pH value observed in Chengdu city was 5.2. The highest acidity was observed on September 8th, 2008 with a pH of 3.7, and the lowest acidity was on July 11th, 2008 with a pH of 5.8. Most samples show pH value from 5.0 to 5.8, while about one tenth rainwater samples have pH value smaller than 4.0.

The equivalence ratio of the sum of anions to that of cations ($\Sigma_{anions}/\Sigma_{cations}$) is usually regarded as an indicator of the completeness of the measured major constituents (Al-Khashman, 2005). The average equivalent sum of anions of that of cations ($\Sigma_{anions}/\Sigma_{cations}$) was 0.94. This suggests that all major ions were measured. The volume-weighted mean (VWM) concentration of the ionic compositions and the statistics analyses are presented in Table 2. VWM was used to calculate the concentrations of ions in one-year period so it is able to account for the effect of precipitation amount on ion concentrations. From Table 2, it can be seen that the concentrations of major ions are in the order of $SO_4^{2-} > Ca^{2+} > NO_3^- > NH_4^+ > Cl^- > Mg^{2+} > K^+ > F^- > Na^+$ (VWM). Ca^{2+} is the most abundant ion among the cations, and its average concentration is 196.6 μeq/L (VWM). Ca^{2+} accounts for 49.7% of the total cations. NH_4^+ is the second abundant cation and contributes 43.8% of the cations measured. SO_4^{2-} and NO_3^- are the dominant anions. SO_4^{2-} is the most abundant anion and its average concentration is 212.8 μeq/L (VWM). SO_4^{2-} accounts for 38.5%–73.9% of the total anions. The second most abundant anion is NO_3^- with mean value of 156.2 μeq/L (VWM). SO_4^{2-} and NO_3^- account for 90.4%–99.1% of the total anions measured. The values of arithmetic mean are higher than those of median, indicating that the frequency distributions are asymmetric and skewed by those high concentration values. The VWM values of rainwater samples are commonly less than the arithmetic means, indicating that the high concentrations of ions are usually associated with low precipitation. The data of the ion concentrations show a high relative standard deviation (from 0.5 to 343.3), indicating a large variability in the cation and anion concentrations in each rain events.

4.2. Correlation factors

Relationships between ionic species are determined by correlation analysis. Table 3 gives the linear correlation coefficients computed. As shown from the inspection of these values, there is no correlation between pH and SO_4^{2-} and NO_3^-. This suggests that SO_4^{2-} and NO_3^- ions in precipitation originate from the ionization of sulfate and nitrate salts, which are produced from neutralizing processes. Positive correlations are obtained between NH_4^+ and SO_4^{2-} and NO_3^- ($R = 0.89$ and 0.84, respectively). This implies NH_3 will first react with H_2SO_4 and then the remaining NH_3 will be taken up by HNO_3 (Seinfield, 1986). Positive correlations are obtained between SO_4^{2-} and Ca^{2+} and Mg^{2+} ($R = 0.88$ and 0.93, respectively) and between NO_3^- and Ca^{2+} and Mg^{2+} ($R = 0.84$ and 0.88, respectively). These correlations indicate that acidic anions are neutralized by base cations.

Table 2
Mean concentration (in μmol/L) of major ionic composition and pH (in unit) along with the statistical results in rainwater.

Component	VWM	Mean	Median	SD	Min	Max
pH	5.1	5.2	5.4	0.5	3.7	5.8
NH_4^+	150.5	216.7	165.0	188.1	35	1106
K^+	6.6	11.0	8.6	11.1	0.4	58.6
Na^+	1.4	2.5	1.8	2.4	0.2	11.2
Ca^{2+}	196.6	339.5	250.8	343.3	17.3	1568.7
Mg^{2+}	16.2	24.8	19.2	20.8	2.7	97.9
F^-	6.2	10.5	6.7	10.2	0.9	46.5
Cl^-	8.9	15.8	13.0	15.8	1.4	78.0
NO_3^-	156.2	225	158.1	188.3	38.8	797.8
SO_4^{2-}	212.8	305.8	269.7	233.4	41.8	1227.6

VWM = volume-weighted mean; mean values are arithmetic values; SD = standard deviation, SD values belong to the "means"; Min = minimum; Mac = maximum.

Table 3
Matrix of correlation coefficients (R) of ionic concentrations (in μeq/L) in rainwater samples from Chengdu.

Ions	NH_4^+	K^+	Na^+	Ca^{2+}	Mg^{2+}	F^-	Cl^-	NO_3^-	SO_4^{2-}
NH_4^+	1								
K^+	0.85	1							
Na^+	0.72	0.76	1						
Ca^{2+}	0.82	0.85	0.86	1					
Mg^{2+}	0.84	0.85	0.80	0.96	1				
F^-	0.65	0.57	0.66	0.81	0.78	1			
Cl^-	0.87	0.93	0.89	0.93	0.89	0.75	1		
NO_3^-	0.84	0.73	0.67	0.84	0.88	0.84	0.82	1	
SO_4^{2-}	0.89	0.84	0.71	0.88	0.93	0.72	0.84	0.86	1

Neutralization factors (NF) can be used to evaluate the neutralization of precipitation by Ca^{2+}, Mg^{2+} and NH_4^+, which are calculated by the following equation (Possanzini et al., 1988; Zhang et al., 2007; Özsoy et al., 2008):

$$NF_{X_i} = \frac{[X_i]}{[NO_3^-] + [SO_4^{2-}]}$$

where X_i is the chemical component of interest, with all the ions expressed in μeq/L. The NF values for Ca^{2+}, Mg^{2+}, K^+ and NH_4^+ in rainwater of the study area are 0.56, 0.04, 0.02 and 0.45, respectively. The results reveal that Ca^{2+} and NH_4^+ are the dominant neutralization substances in the rainwater, whereas the neutralization by Mg^{2+} and K^+ is negligible.

4.3. Origins of major ions in the rainwater

The most usual method of evaluating the contribution of sea salts to ion contents in precipitation is to compare the Cl^-/Na^+ ratio in rainwater to that of seawater. Sea is considered to be the major source of both ions, although they may also be emitted from other natural and industrial sources (Samara et al., 1992). The enrichment factors (EF) for ions (X) have been calculated using Na^+ as the marine reference ($EF = (X/Na^+)_{rain}/(X/Na^+)_{seawater}$) and are given in Table 4. The mean value of Cl^-/Na^+ in rainwater is 6.4. This value is higher than that of 1.17 in seawater, indicating that almost all Na^+ and Cl^- in rainwater derive from the anthropogenic input. The SO_4^{2-}/Na^+ ratio of 174.2 in rainwater with the EF of 1452 for SO_4^{2-} indicated that there was almost no marine contribution of SO_4^{2-}. Coal-fired power stations and traffic emission could account for the highly enrichment of sulfate in rain in Chengdu city. Great enrichment of NO_3^- was attributed to the traffic emission. The marine contribution to Ca^{2+}, Mg^{2+} and K^+ was also negligible based on the high EF of Ca^{2+}, Mg^{2+} and K^+ (Table 4).

Table 4
Ratio of equivalent concentration of ions with reference to Na^+.

	SO_4^{2-}/Na^+	NO_3^-/Na^+	Cl^-/Na^+	Ca^{2+}/Na^+	Mg^{2+}/Na^+	K^+/Na^+
Seawater [a]	0.12	0.00002	1.17	0.044	0.23	0.022
rainwater	174.2	116.0	6.4	135.3	11.9	4.5
EF	1451.7	5,800,000	5.5	3075.0	51.7	204.5

[a] Berner and Berner (1987).

To evaluate the contribution of each source to the total content in precipitation, all the sodium was assumed to be of marine origin while F^-, Cl^-, NO_3^- and NH_4^+ were assumed to have no crustal origin. The proportions of sea salt and terrestrial end–members were therefore calculated using Na as the marine reference species. The contribution of marine component for a given element X (X = Cl^-, NO_3^-, SO_4^{2-}, K^+, Ca^{2+} and Mg^{2+}) is thus:

$$[X]_{marine} = \left[Na^+\right]_{rainwater} \times \left([X] / \left[Na^+\right]\right)_{seawater}$$

The elemental ratios (X/Na) were determined according to the composition of seawater given by Berner and Berner (1987). If Mg^{2+} was assumed to be composed of marine and crustal sources only, the crustal part of Ca^{2+} and K^+ could be estimated by the equivalent $(Ca/Mg)_{crustal}$ and $(K/Mg)_{curstal}$ ratios of 1.87 and 0.48, respectively. Assuming SO_4^{2-} from the crustal source was supplied by gypsum, it could be calculated using the formula $[SO_4^{2-}]_{crustal} = 0.47 [Ca^{2+}]_{crustal}$ (Huang et al., 2008), so the anthropogenic sulfate could be calculated using the following formula: $[SO_4^{2-}]_{anthropogenic} = [SO_4^{2-}]_{rain} - [SO_4^{2-}]_{marine} - [SO_4^{2-}]_{crustal}$. Table 5 showed the estimation of the contributions from different sources to the chemical composition of rainwater (expressed in percentage). The proportion of Cl^- coming from anthropogenic is about 82%. The anthropogenic input of Cl^- could come from various sources of pollution including automobile exhaust, coal combustion and fertilizers (Friedlander, 1973; Fuzzi et al., 1984; Negrel and Roy, 1998). SO_4^{2-} in rainwater may also originate from anthropogenic emissions of SO_2. Aas et al. (2007) suggested that coal combustion accounts for about 70% of the commercial energy production in China, leading to a large amount of SO_2 emissions, which to date has been the most important precursor of acid rain in China. Chengdu city government takes a lot of power measurements to control the emissions of coal combustion since 2000, resulting in the SO_2 and NO_x emissions of coal-fired rapidly decreased. But Chengdu is the capital of Sichuan Province, and the urban road network developed, and the car has exceeded 1.01 million by the end of 2008. Therefore, the emissions of NO_x from fossil fuel combustion would be a new important source of NO_3^- in rainwater. A highly positive correlation between SO_4^{2-} and NO_3^- ($R = 0.84$) indicates that they are from similar sources, and reflects the input of pollutants from fossil fuel combustion in Chengdu city.

Table 5
Proportions (%) of the source contributions in the rainwater samples from Chengdu.

	Marine (%)	Crustal (%)	Anthropogenic (%)
F^-	0.00	0.00	100
SO_4^{2-}	0.08	0.007	99.914
NO_3^-	0.00	0.00	100
Cl^-	18.25	0.00	81.75
Ca^{2+}	0.03	0.31	99.66
Mg^{2+}	1.99	98.01	0.00
K^+	0.47	2.34	97.19
NH_4^+	0.00	0.00	100

The Ca^{2+} in rainwater from Chengdu is likely anthropogenic, coming from soil dust suspended in the lower troposphere due to daytime convection and vehicle/wind-driven roadside dust (Ali et al., 2004). According to Flues et al. (2002), high concentrations of NH_4^+ found in rainwater could be related to gaseous ammonia (NH_3) introduced into the atmosphere, mainly by cattle breeding (80%), fertilizer use (17%) and industrial processes. Chengdu city is the capital in Sichuan Province and therefore gaseous ammonia is the potential NH_3 source. The high level of NH_4^+ in rainwater coincides with the fact that the emission of ammonia to the atmosphere from agriculture activities is enormous in the Asian regions. It is several times higher than that in North America and Europe (Galloway, 1995). Sichuan province is the important grain and vegetable production areas so the agriculture activities are the most important NH_4^+ source. So it can be attributed to the presence of ammonium ions in the samples to a direct input of gaseous ammonia as well as to the input of absorbed ammonia from aerosols. It can be seen from Table 5 that the anthropogenic source dominated over the total ion concentration followed by crustal source, and marine source can be negligible.

4.4. Acid neutralization and rain alkalization

The pH unit alone gives limited information on the acidity of rainwater. Reactions between the acidic and alkaline constituents and water droplets determine the final pH of the rainwater. The concentrations of major ion and pH values in rainwater in Chengdu city have been compared with the available data from other urban areas in China and the world (Table 6). Compared with the megacities in China, the data from Chengdu city show moderate ionic composition. The SO_4^{2-} of rainwater in Chengdu is higher than those from a lot of cities but lower than that of Chongqing and Chengdu (Lei et al., 1997), where both are located in the acid rain central zone in China. Compared with some sites in worldwide, the ion concentrations of Chengdu rainwater, especially SO_4^{2-}, Ca^{2+}, consumedly exceed than those of reference cities in Europe, American and East Asia. These results collectively indicate that Chengdu city is more polluted than most of the megacities of the world. Chengdu city has been a severe polluted city over that world.

Table 6
Comparison of the major ion concentrations (μeq/l) and pH values in Chengdu city with the other sites in China and worldwide.

Site	pH	F^-	Cl^-	NO_3^-	SO_4^{2-}	NH_4^+	K^+	Na^+	Ca^{2+}	Mg^{2+}	references
Chengdu (VWM)	5.1	6.2	8.9	156.2	212.8	150.5	6.6	1.4	196.6	16.2	This study
Chengdu (VWM)	4.4		42.3	30.4	431.5	250.7	20.8	22.6	192	33.2	Lei et al. (1997)
Guiyang city (Mean)	4.5		21.2	48.2	188		11	4	113.2	25.2	Han and Liu (2006)
Beijing (VWM)	5.12	15.7	104	109	316	186	17.7	25	607	40.4	Xu and Han (2009)
Shanghai (VWM)	4.49	11	58.3	49.8	199.6	80.9	14.9	50.1	204	29.6	Huang et al. (2008)
Nanjing (VWM)	5.51		143	39.6	242	193	12.1	23	295	31.7	Tu et al. (2005)
Nanjing (Mean)	5.09		154	34.5	212	289	10.5	13	287	30	Zhang et al. (2007)
Chongqing (VWM)	4.6		40.3	43.2	421.8	386.6	15.2	39.8	207.2	13.2	Lei et al. (1997)
Changsha (mean)	4.3		9.6	21.8	143	70.4	3.8	3.9	62	5.6	Zhang et al. (2007)
South of China (mean)	4.41		16.3	28.2	166.3	61.7	10.8	11.3	82.1	21.5	Aas et al. (2007)
Lhasa (VWM)	7.5	0.4	9.7	6.9	5.2	14.3	5.14	11.2	197	10.9	Zhang et al. (2003a)
Qinghai (VWM)	7.1	46.6	48.8	48.1	84	161	69.2	96.6	314	37.9	Zhang et al. (2003b)
Lanzhou (VWM)	7.7	13.6	27.9	74.4	208	57.2	7.26	12.3	886	46.5	Xu et al. (2009)
Ankara (Turkey)	6.3		20.4	29.2	48	86.4	9.8	15.6	71.4	9.3	Topcu et al. (2002)
Tokyo (VWM)	4.52		55.2	30.5	50.2	40.4	2.9	37	24.9	11.5	Okuda et al. (2005)
Massif (Mean)	5.22		19.6	36.2	22.3		5.7	14.4	14.6	3.4	Negrel and Roy (1998)
Istanbul (VWM)	4.81		124.8	33.4	115.2	12.8	57.4	75.2	285	99.6	Basak and Alagha (2004)
Itatiaia (VWM)	4.94		5.2	11.8	15.5	13.5	1.3	3.9	4.3	2.2	Mello and Almeida (2004)
Mexico (VWM)	5.08		9.6	42.6	61.9	92.4	2.2	7	26.4	2.5	Baez et al. (2007)

In comparison the data of this present study with those suggested by Lei et al. (1997) in Table 6 is noteworthy that the tendency of rain alkalization in precipitation in Chengdu is obvious, and the pH value has been increased by 0.7 units since 1989 (Lei et al., 1997). It is also observed that the concentration of SO_4^{2-} has decreased 1-fold but the concentration of NO_3^- has increased 5-fold. The concentration of Ca^{2+} has almost no change and the concentration NH_4^+ has decreased. The neutralization factors calculation showed that the main neutralization has occurred due to Ca^{2+}. Therefore, Ca^{2+} ions seem to be the major component responsible for neutralization of Chengdu precipitation. It can be concluded that the acidic ions concentrations decreased much more than that of alkaline ions have resulted in the rain alkalization tendency of rainwater in Chengdu.

5. Conclusions

The results of this study clearly showed that acid rain is still taking place in the Chengdu city. In 2008 the acidity of rain in Chengdu decreased compared to 1989, and it is proved that the control policy is taken. In order to improve air quality in Chengdu city, the city government has taken some powerful measures to control SO_2 emissions since 2000. The large emission of SO_2 from coal combustion is still the most important precursor of acid rain in Chengdu, however, according to this study, the increase of NO_x emission from the automobile exhaust is becoming another important cause of the acid rain. The source identification with several different methods indicated that SO_4^{2-}, NO_3^-, NH_4^+ and most Ca^{2+} derived from anthropogenic sources, K^+, Mg^{2+} and partial Ca^{2+} mostly originated from mineral sources. The chemistry of precipitation in Chengdu is influence by local pollutions sources since it locates in a basin.

Chengdu rainwater shows very high concentrations of acidic ions (SO_4^{2-} and NO_3^-). However, the pH value has increased 0.7 units since 1989 (Lei et al., 1997) which shows that the problem of acid rain is not very serious. It showed that the higher concentrations of alkaline ions (Ca^{2+} and NH_4^+) neutralize the acidity of acid rain caused by sulfuric acid and nitric acid from fossil fuel combustion and automobile exhaust. It is noteworthy that the alkalization trend of rainwater in Chengdu is obvious, and the pH value has increased by 0.7 units since 1989. According to this study, the increase of NO_x emission from automobile exhaust is becoming the most important source of acid rain. We think that the only way to solve the problem is to control fossil fuel emissions. Future assessments of acid deposition in megacities require not only consideration of pH values and sulfur input, but also consideration of basic inputs (e.g. Ca^{2+} and NH_4^+).

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