Environ Monit Assess (2011) 183:581–592
DOI 10.1007/s10661-011-1963-4

Chemical composition of precipitation and its sources in Hangzhou, China

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Received: 11 April 2010 / Accepted: 17 February 2011 / Published online: 8 March 2011

Abstract To understand the origin and chemical characteristics of precipitation in Hangzhou, rainwater samples were collected from June 2006 to May 2008. All samples were analyzed for pH, electrical conductivity, and major ions (NH_4^+, Ca^{2+}, Mg^{2+}, Na^+, K^+, SO_4^{2-}, NO_3^-, F^-, and Cl^-). Acidification of precipitation in Hangzhou was serious with volume-weighted mean pH value of 4.5, while frequency of acid rain was 95%. The calculated SO_4^{2-}/NO_3^- ratio in Hangzhou precipitation was 2.87, which indicated that the precipitation of Hangzhou belonged to sulfate-based acid rain. The results of acid neutralization analysis showed that not all the acidity in the precipitation of Hangzhou was neutralized by alkaline constituents. The results of sea salt contribution analysis showed that nearly all SO_4^{2-}, Ca^{2+}, and Mg^{2+} and 33.7% of K^+ were of non-sea origins, while all Na^+ and Cl^- and 66.3% of K^+ originated from sea sources. The principal component analysis which was used to analyze the sources of various ions indicated that chemical compositions of precipitation in Hangzhou mainly came from terrestrial sources, factory emissions, fuel wood burning, and marine sources.

Keywords Precipitation · Chemical composition · Neutralization factor · Non-sea-salt fraction · Source identification

Introduction

Acidic precipitation is a worldwide atmospheric pollution problem, especially in northeast America, southern China, and North Europe. Acid rain was discovered in 1852 by Robert Smith, an English chemist who first showed the relationship between acid rain and the industrial emissions in the British Midlands (Likens and Bormann 1974). It is a serious threat to human health and ecosystem, such as vegetation, soil, water, and forestry (Likens et al. 1996; Evans et al. 2005). Since the late 1960s scientists had

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begun to research on wet deposition monitoring and its effects on human environment extensively in many countries of the world (Rodhe et al. 2002).

The precipitation chemistry is an indicator of the changes in chemical composition of the atmosphere over time and it is useful to understand the actual status and level of acid rain (Hu et al. 2003). What is more, the rainwater composition data are useful for the validation of Global Chemistry Transport Models and for determining the global cycling of sulfur compounds, oxidized and reduced nitrogen compounds, soil dust, etc. (Rodhe et al. 1995; Langner et al. 1992). The pollutants (SO_2, NO_x, and etc.) emitted from anthropogenic sources, such as power plants, vehicle motors, and other human activities, could affect the precipitation chemistry in different scales through oxidation (Whelpdale et al. 1997; Das et al. 2005). Meanwhile ammonia and alkaline dust are able to neutralize acidic components and thus influence the extent of acidic precipitation (Chabas and Lefevre 2000). Investigation on the precipitation chemistry could provide the knowledge of the changes and other characteristics of local or regional atmospheric pollution. Systematic observations on the chemical composition of precipitation have been carried out for several years in Europe and North America (Galloway et al. 1987; Watmough et al. 2005) and other places. Since the monitoring of acid rain has been conducted in many years, precipitation chemistry measurements during a long-term period can be compared to improve the measurement capabilities (Wetherbee et al. 2010) and investigate the trend of atmospheric pollution (Huang et al. 2008). The origins of acid rain can be obtained through the studies of chemical composition (such as the main cations Ca^{2+}, Mg^{2+}, Na^+, K^+, NH_4^+, and the main anions SO_4^{2-}, NO_3^-, Cl^-, and F^-) in rainwater (Okay et al. 2002), also combined with the meteorological information (Seto and Hara 2006).

Several researches have been conducted to study the chemical composition of precipitation in China since the 1980s (Zhao and Sun 1986; Galloway et al. 1987; Wang 1994; Wang and Wang 1996; Wang and Ding 1997; Huang et al. 2008), especially in southwestern China. It was revealed that in rainwater the main anions SO_4^{2-} and NO_3^- are acidic, while the dominant cations NH_4^+ and Ca^{2+} are important in neutralizing the acidity of precipitation. In recent years, the acidic precipitation in southeastern China has become more serious (Shen and Liu 2009; Fan et al. 2009). Hangzhou, one of the most important cities in this region, which has huge population and highly developed economy and a famous tourism city, suffered serious acid rain in recent years. According to the Environmental Quality Report of Hangzhou (2001–2005), the acidity of the precipitation in this region was very strong with pH of about 4.7 (EAH 2006). Thus systematic observations on the chemical composition of precipitation are needed to learn the changes and other characteristics of atmospheric pollution in this region.

The objectives of this study are to: (1) describe the chemical characteristics of precipitation in Hangzhou, China; (2) identify the sources of the chemical compositions in rainwater by analyzing the precipitation chemistry; and (3) compare the chemistry of precipitation in Hangzhou with that of some other areas in the world.

Experiment and method

Study area

Hangzhou, the capital city of Zhejiang province, China, lies in the east coast of China at 30.3° N and 120.2° E with an area of 16,596 km^2 and a population of ~10 million. It is located in the south of Yangtze River Delta and has a geomorphology of hills and plains with a high elevation in the west and a low elevation in the east. Along its southwest to northeast, Qiantang River, the largest river in Zhejiang Province, flows through most area of the city. Hangzhou is a famous tourism city and its climate belongs to semitropical monsoon type with cold, dry winter and hot, wet summer. The precipitation of Hangzhou is 1,435 mm yearly that mainly happens in summer. The sampling stations of rainwater samples are shown in Fig. 1. The sampling campaigns were carried out at two sampling sites from June 2006 to May 2008. The two sampling sites were both located in the urban area (downtown area) of Hangzhou and have high

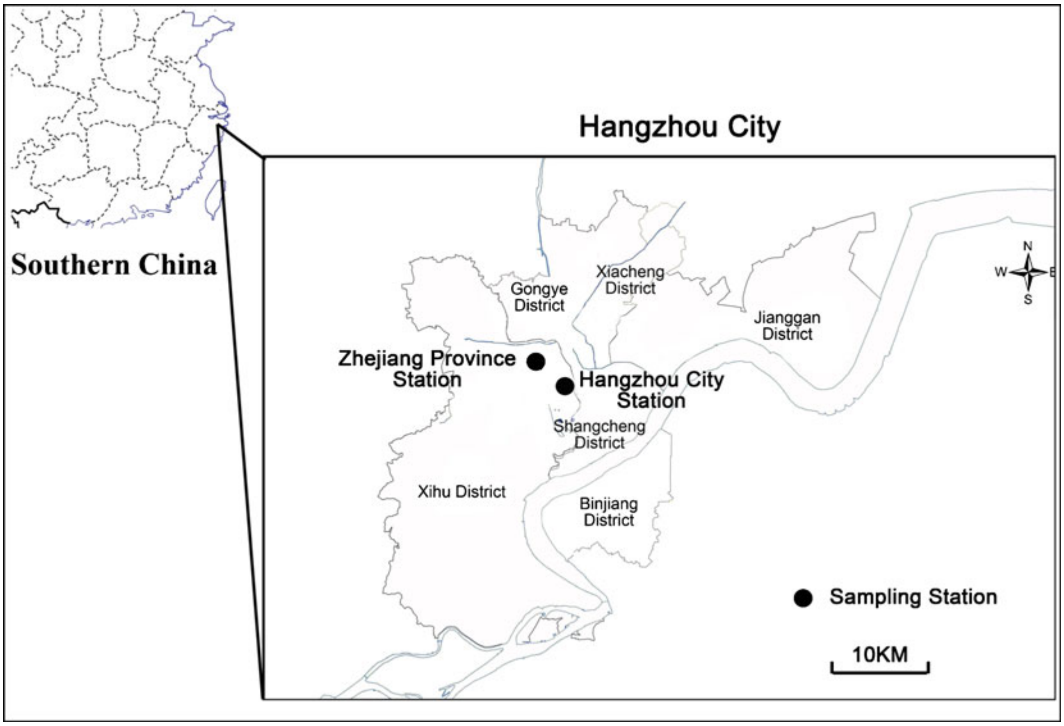

Fig. 1 Location of the precipitation sampling stations in Hangzhou

level of human activities. So, vehicle exhaust and cooking oil might be important source categories in those sampling sites.

Sample collection and analysis

According to Technical Specifications for Acid Deposition Monitoring (SEPA 2004), rain samples were collected every month from June 2006 to May 2008 using an automatic precipitation collector equipped with a polyethylene bucket (SZG-III, China). During the sampling campaign a rain gauge was used to calculate the precipitation amount and conductivity and pH were analyzed promptly. The rain samples were collected on the roof of the buildings at the two monitoring sites where there were no obstructions within 2 m around. A polyethylene bucket with a polyethylene lid was fixed ∼1 m above the roof, which was used to collect the rain samples manually. Before sampling, the bucket was rinsed thoroughly several times with deionized water until the water conductivity was less than 1.5 μS/m. To prevent contamination by dry deposition, the collector was covered by the lid, which was removed prior to each rain event. The collected rainwater was gathered in a 500-ml polypropylene bottle that was washed twice or three times with ultra-pure water till the conductivity was lower than 1.5 μS/m and was filled with pure water for at least 24 h before using it. The pH value was measured immediately after the collection of the samples, and the rain samples were filtered through a 0.45-μm Millipore membrane filter and stored in a refrigerator at 4°C before chemical analysis.

Twenty-one precipitation samples were collected which account for 359.4 mm (15.5%) of a total 2,311.6 mm rainfall during the period in the city. In this study, we focused on the monthly variation of chemical components of rainwater and not all the rain events were collected in the sampling campaign. Four anions (SO_4^{2-}, NO_3^-, F^-, and Cl^-) and five cations (NH_4^+, Ca^{2+}, Mg^{2+}, Na^+, and K^+) were quantitatively measured. The precipitation samples were analyzed according to General Principles for Analytical Methods of The

Wet Precipitation (GB/T 13580.1–13580.13-1992; National Environmental Protection Agency 1992) after they were preserved by adding $\sim$400 mg/L thymol and refrigerated at 4°C. A pH meter (Mettler Delta 320-S) with a flow-type combination electrode was used for pH measurements. The concentration of ammonium was measured using Nessler's Reagent spectrophotometry and the other ions were measured by Ion Chromatography (IC, Dionex 600, USA). Cations were analyzed using a CS12 column, 15 mM MSA eluent, and CAES suppresser and the anions were quantified using an AS11-HC column, 15 mM NaOH eluent, and ASRS suppresser. According to the concentration content of the precipitation samples we prepared the mixed standard solution and drew the standard curve. Then we determined the peak area (A) of the mixed standard solution as well as the blank sample, the slope of the standard curve (S), and the standard deviation (S_A) of seven times. According to the formula $Q_L = 3S_A/S$ (SEPA 2006), the detection limits of F^-, Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, Ca^{2+}, Na^+, Mg^{2+}, and K^+ were 0.01, 0.01, 0.02, 0.04, 0.03, 0.02, 0.01, 0.02, and 0.02 mg/L, respectively. Each rain sample was analyzed for seven times at the same condition. The relative standard deviation for all ions was 1.68%, 2.23%, 0.52%, 0.40%, 2.42%, 1.84%, 1.75%, 1.62%, and 2.21%, respectively, which showed that the analytical data was reliable.

The volume-weighted average concentrations (volume-weighted mean (VWM)) of the major ions in a period (in the entire year or in a month) were calculated with the formula $\overline{C} = \sum_{i=1}^{n} C_i Q_i \Big/ \sum_{i=1}^{n} Q_i$, where Q_i is the rainfall amount in millimeters and C_i is the measured concentration in microequivalents per liter. Accordingly, the average pH in a period could be calculated from the volume-weighted average concentration of H^+, i.e. $pH = -\log\overline{H}^+$ (Tang et al. 2005).

Data quality

The data quality of precipitation samples was assured by ionic balance and by the comparison of measured conductivity with the conductivity calculated according to the Technical Specifications for Acid Deposition Monitoring (SEPA 2004), the manual of EMEP for Sampling and Chemical Analysis (EMEP 1996), and the Technical Manual for Wet Deposition Monitoring in East Asia (EANET 2000).

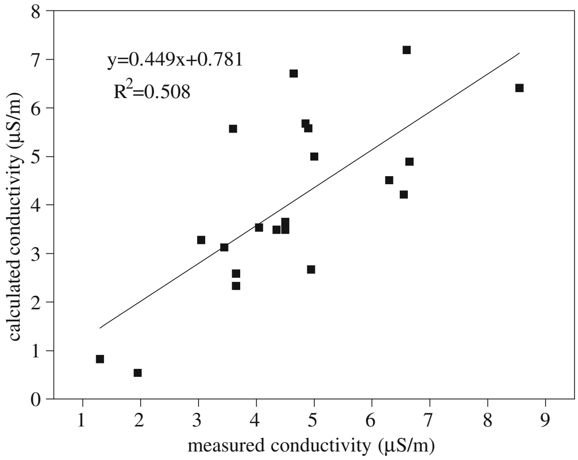

Fig. 2 Linear regression of measured and calculated conductivity. The *dots* in the graph represent the monthly data

As seen in Fig. 2, the linear regression plotted between the calculated and measured conductivity shows that the correlation is relatively weak. Also, the average calculated conductivity, which is 4.06 µS/m, was less than the measured conductivity of 4.62 µS/m, indicating that some ions (e.g., CO_3^{2-} and HCO_3^-) were not analyzed. The evaluation of the sum of cations and anions

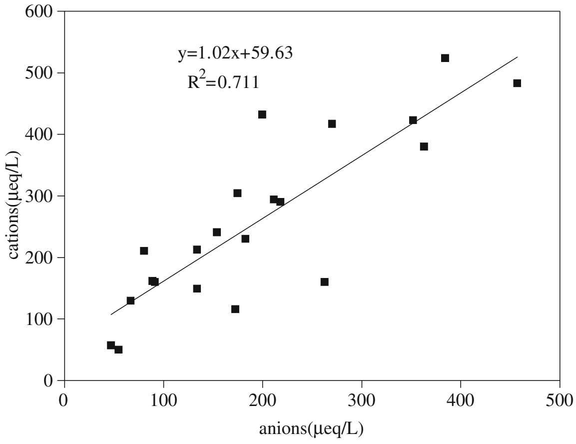

Fig. 3 Linear regression of the cations and anions sum. The *dots* in the graph represent the monthly data

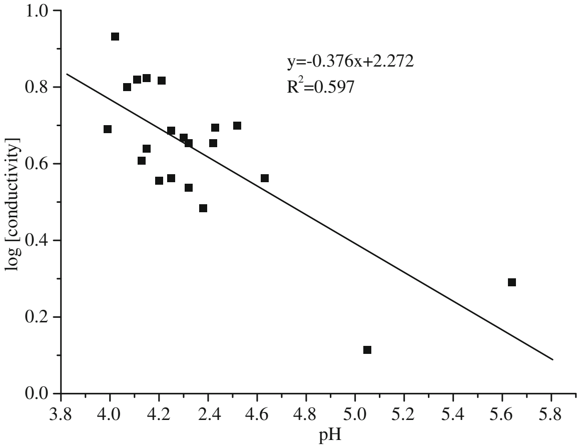

Fig. 4 Linear regression of log [conductivity] and pH. The *dots* in the graph represent the monthly data

shows a good agreement of 0.711 as in Fig. 3, indicating that the majority of ions in precipitation samples had been analyzed. The concentration ratio of cations to anions is 1.11 showing that there were more cations than anions in precipitation, giving the same conclusion with the conductivity comparison, which may be due to the unanalyzed CO_3^{2-}, HCO_3^-, and some organic acids. In Fig. 4 it shows a weak correlation between log [conductivity] and pH. Conductivity is a measure of how well a solution conducts electricity and is often used as an estimate of total dissolved solids content of water samples, whereas the pH specifically tells the concentration of one particular ion, i.e., H^+. But because H^+ has higher ion mobility compared to the rest components, log [conductivity] has relativity with pH.

Results and discussion

The pH value and ionic composition of precipitation

The monthly variations of rainfall and pH are shown in Fig. 5. The pH values of monthly precipitation ranged from 3.99 to 5.64 with a volume-weighted mean of 4.5, and about 95% of the monthly precipitation samples had pH smaller than 5.6. The VWM pH of 4.5 through the study period suggested a strong impact of anthropogenic sources on the acidity of precipitation in Hangzhou. Also, the VWM pH value was lower than that of Beijing (Tang et al. 2005), Nanjing (Tu et al. 2005), Mt. Waliguan (Tang et al. 2000), and Lijiang (Liu et al. 1993) in Yunnan which are background monitoring sites of precipitation chemistry in China, indicating that the pollution of acid precipitation was serious in Hangzhou. Higher values of pH were observed in summer (June, July, and August) and autumn (September, October, and November), and the lower values were in winter (December, January, and February) and spring (March, April, and May). In winter and spring pollutants such as SO_2 and NO_x can be transported to Hangzhou from the northern China, while in summer and autumn the concentration of water-soluble hydrogen ion could be diluted by a larger amount of precipitation. So due to the local and regional impact, the pH of precipitation in Hangzhou presented an obvious seasonal variation. As shown in Fig. 5, the pattern of the time series of pH is different with that of rainfall, and the correlation coefficient between them is 0.42. It implies that the pH value was partially affected by rainfall but there were some other factors influencing pH in precipitation.

The ionic compositions of rainwater samples are listed in Table 1 and Figs. 6 and 7. The monthly concentrations of ions varied greatly and the concentration of total ionic components is highest in autumn, lowest in summer. As seen in Figs. 5 and 6, the months with low ionic concentration

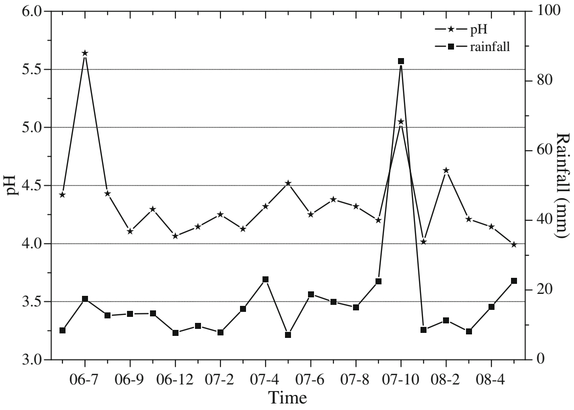

Fig. 5 Monthly variations of pH and precipitation. The *dots* in the graph represent the monthly data

Table 1 Volume-weighted average of pH, ionic concentration (microequivalents per liter), and their percentages in cations and anions comparing with some areas in the world

Area	Hangzhou	Beijing[a]	Nanjing[b]	Jinhua[c]	Guangzhou[d]	Mt. Waliguan[e]	Lijiang[f]	India[g]	Seoul, Korea[h]	Spain[i]	New York[j]
Year	2006.6–2008.5	2001–2003	1992–2003	2004	2005–2006	1997	1993	2001	1996.5–1998.4	1983–1994	1986.7–1988.12
pH	4.5	6.01	5.15	4.54	4.49	6.38	4.96	6.1	4.7	6.4	4.2
SO_4^{2-}	110	249	242	95.2	202	24	10.4	32.4	70.9	46.1	52.8
%	65.5	66.0	54.5	66.1	70.4	62.5	62.3	29.1	59.6	48.4	59.5
NO_3^-	38.4	84.1	39.6	31.2	52	8.3	2.8	10.3	29.9	20.7	29.8
%	22.8	22.3	8.92	21.7	18.1	21.6	16.8	9.26	25.1	21.7	33.6
F^-	5.76	12.9	19.1	9.05	12	–	–		–	–	0.50
%	3.42	3.42	4.30	6.29	4.18	–	–		–	–	0.56
Cl^-	13.9	31.5	143	8.51	21	6.1	3.5	46.8	18.2	28.4	5.6
%	8.24	8.34	8.51	5.91	7.32	15.9	21.0	42.1	15.3	29.8	6.31
NH_4^+	79.9	234	193	81.1	66	45.5	8	12.8	66.4	22.9	19.3
%	42.8	47.9	26.7	42.8	24.9	43.5	26.2	5.57	46.7	19.6	20.8
Ca^{2+}	51.9	191	295	47.9	131	34	4.9	119.2	34.9	57.5	6.5
%	27.8	39.1	40.8	25.3	49.4	32.5	16.0	51.8	24.5	49.2	6.76
Mg^{2+}	7.05	33.8	31.7	3.45	9	12.1	2.1	20.4	6.9	9.8	2.8
%	3.78	6.93	4.38	1.82	3.4	11.6	6.87	8.87	4.85	8.38	2.91
Na^+	12.2	16.3	23	6.27	18	8.7	0.8	40.2	10.5	22.3	3.5
%	6.55	3.34	3.18	3.31	6.79	8.32	2.62	17.5	7.38	19.1	3.64
K^+	4.18	12	12.1	4.73	9.0	3.8	3.9	35.9	3.5	4.0	1.4
%	2.24	2.46	1.67	2.49	3.40	3.64	12.8	15.6	2.46	3.42	1.46
H^+	31.4	0.97	7.02	28.6	32	0.41	10.9	1.4	20	0.4	62.6
%	16.8	0.20	0.97	15.1	12.1	0.39	35.6	0.61	14.0	0.34	65.1
SO_4^{2-}/NO_3^-	2.87	2.96	6.11	3.05	3.88	2.89	3.71	3.14	2.37	2.23	1.77
$(NH_4^+Ca^{2+})/(SO_4^{2-}+NO_3^-)$	0.89	1.28	1.73	1.02	0.78	2.46	0.98	3.09	1	1.2	0.31
$\sum+/\sum-$	1.11	1.29	1.27	1.2	0.92	2.72	1.83	2.07	1.23	1.86	1.08
$\sum$	355	866	1,005	316	552	143	47	341	261.2	212.1	184.8

[a] Tang et al. (2005)
[b] Tu et al. (2005)
[c] Zhang et al. (2007)
[d] Huang et al. (2009)
[e] Tang et al. (2000)
[f] Liu et al. (1993)
[g] Kulshrestha et al. (2003)
[h] Lee et al. (2000)
[i] Avila and Alarcón (1999)
[j] Khwaja and Husain (1990)

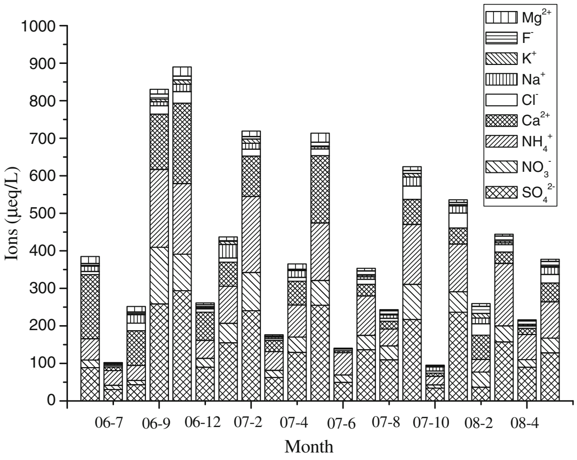

Fig. 6 Time series of ions in precipitation in Hangzhou

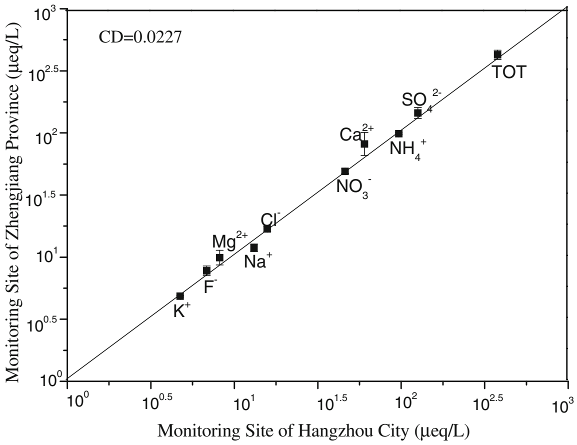

Fig. 8 Concentrations of ionic components in two precipitation monitoring sites. The *dots* in the graph represent the monthly data

happened in July 2006 and October 2007, which had large rainfall. However, the seasonal variation of ionicity had some difference from that of rainfall, i.e., the seasons with large rainfall were summer and autumn, while the rain with highest ionic concentration happened in autumn, lowest in summer. So the factors affecting the ionic compositions in precipitation are complicated. SO_4^{2-} and NO_3^- were the dominant anions which accounted for 88% of total anions, and NH_4^+ and Ca^{2+} were the major cations accounting for 70% of total cations. According to the data in Table 1, the chemical composition distribution in Hangzhou was quite similar to that in other cities in China. But the concentration of these dominant ions in precipitation of Hangzhou was much lower than that of some cities, especially in North China, but higher than that of some other regions in the world. It implicated that the atmospheric pollution in Hangzhou may be less serious than those cities in northern China but is still a big problem.

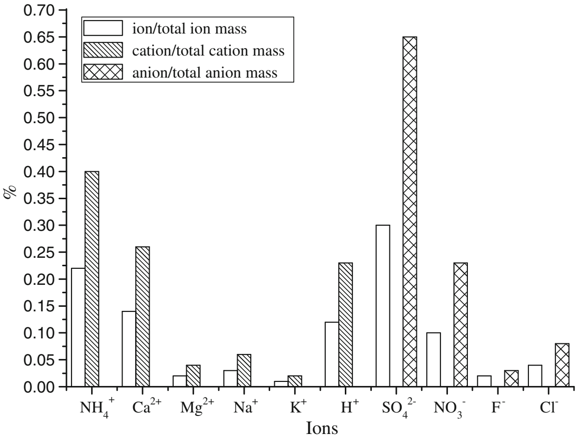

Fig. 7 Distribution of major ions in precipitation

Figure 8 compares the ionic concentration of the monitoring site of Hangzhou city with that of the monitoring site of Zhejiang province. The concentration diagram is a log–log scatter plot of the concentration of the chemical components at one sampling site against those at the other. The diagonal line with unit slope represents a hypothetical case in which the concentrations for each component at the two sampling sites are equal. The coefficient of divergence (CD) (Wongphatarakul et al. 1998) is used to measure the spread of the data points for two databases.

$$CD_{jk} = \sqrt{\frac{1}{p}\sum_{i=1}^{p}\left(\frac{x_{ij}-x_{ik}}{x_{ij}+x_{ik}}\right)^2}$$

Where j and k stand for two sampling sites, p is the number of investigated components, and x_{ij} and x_{ik} present the average concentration of an ionic component i at sites j and k. If the CD approaches zero, the two sampling sites are similar. If the CD approaches one, the two sampling sites are very different (Zhang and Friedlander

2000). In our study, the scatter plot showed a great similarity with the CD value of 0.0227, so the difference of the ionic concentration between the two sampling site is not significant.

SO_4^{2-}/NO_3^- in rainwater of Hangzhou showed a lower value than that of other cities in China except Jinhua, which suggested the different energy consumption patterns of Hangzhou with lower ratio of coal burning to petroleum consumption. Comparing to the former study in 2002, a decrease in SO_4^{2-}/NO_3^- ratio in the precipitation of Hangzhou was found, indicated that HNO_3 made an increasing impact on the acidity of precipitation in Hangzhou.

Acid neutralization

Comparing with some other areas, especially those in the northern part of China, the total ionic concentration in Hangzhou precipitation was significantly lower, while the acidity of precipitation in Hangzhou was rather high. Some studies have proved that the acidity in precipitation depends on the concentrations of acid-forming ions, the concentrations of alkaline species which would neutralize the acidity of rainwater, as well as some meteorological factors rather than only acidic ions (Das et al. 2005; Larssen and Carmichael 2000). So it is necessary to study the formation of acidity in Hangzhou precipitation.

SO_4^{2-} and NO_3^- are the conventional acidic ions in precipitation which can be reacted with alkaline cations. The capacity of acidity neutralization of precipitation was determined by fractional acidity (FA) (Balestrini et al. 2000; Zunckel et al. 2003), which is:

$$FA = \frac{[H^+]}{[SO_4^{2-}] + [NO_3^-]}$$

If FA reaches zero, it is considered that rainwater acidity generated by SO_4^{2-} and NO_3^- will be neutralized completely. The value of FA in Hangzhou ranged from 0.055 to 0.924, with the average of 0.381, indicating that about 38.1% of acidity was not neutralized by alkaline constituents.

The average concentration ratio of measured cations ($\sum +$) to anions ($\sum -$) in rainwater samples was 1.11 which was lower than most areas in Table 1. The equivalent ratio of $(NH_4^+ + Ca^{2+})/(SO_4^{2-} + NO_3^-)$ in Hangzhou precipitation was 0.89 which was lower than that in Beijing, Nanjing, Jinhua, and some cities in other countries. The relative low ratio indicated that the alkaline cations which restrained acidity could not neutralize acidic anions completely. The low acid-neutralizing capacity could explain why the precipitation in Hangzhou had lower ionic concentration but higher acidity.

Neutralization factors (NF) can be used to evaluate the relative neutralization of precipitation by crustal components and ammonia (Possanzini et al. 1988; Kulshrestha et al. 1995, 1996). NF was calculated by the following equations:

$$NF_{NH_4^+} = \frac{[NH_4^+]}{[SO_4^{2-}] + [NO_3^-]},$$

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

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

The factors were 0.577 for NH_4^+, 0.448 for Ca^{2+}, and 0.056 for Mg^{2+}, indicating that NH_4^+ and Ca^{2+} were the dominant neutralization substances. To more clearly demonstrate which cation was the major neutralizing component in the rainwater, a triangular diagram was drawn, showing the

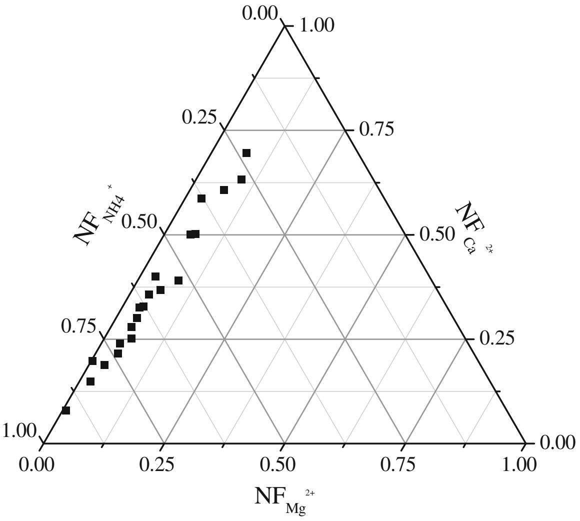

Fig. 9 Triangular diagrams of NFs of dominant alkaline ions. The *dots* in the graph represent the monthly data

Table 2 Major ionic components in rainwater with respect to sea in Hangzhou

	K^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}
Rainwater ratio[a]	0.34	0.58	4.25	1.14	9.02
Seawater ratio[b]	0.227	0.022	0.044	1.167	0.125
EF[a]	1.51	26.3	96.7	0.98	72.1
%SSF	66.3	3.8	1.0	102	1.38
%NSSF	33.7	96.2	99	−2	98.6

EF enrichment factor, *NSS* non-sea salt, *SSF* sea salt fraction, *NSSF* non-sea salt fraction

[a] With respect to Na

[b] Seawater ratio (Keene et al. 1986)

relative proportion of these three NFs. The examination of the NF triangle in Fig. 9 reveals that both NH_4^+ and Ca^{2+} were the predominant neutralizers in rainwater samples, and only about 5% of the neutralization was contributed from Mg^{2+} which could be negligible.

Source analysis of chemical component in precipitation

Sea salt contribution

Ionic species in rainwater had various kinds of sources, and the major natural sources were from marine and from the earth's crust. In order to estimate the marine contribution to different ionic species in rainwater, their respective sea salt fractions (SSF) were calculated (Kulshrestha et al. 1996; Das et al. 2005; Zhang et al. 2007). The rest of the ions were assumed to be non-sea-salt fractions (NSSF). The sea salt fraction of any ionic specie (say X) can be given by

$$\%\ \mathrm{SSF_x} = \frac{100^{*}\ [\mathrm{Na_{rain}}]\,[\mathrm{X/Na}]_{\mathrm{seawater}}}{\mathrm{X_{rain}}},$$

where X_{rain} is the concentration of ionic specie X in rainwater. While the non-sea-salt or sea-salt fractions of X are given by

$$\%\ \mathrm{NSSF_x} = 100 - \mathrm{SSF_x}.$$

Sodium was taken as the best reference element for seawater because it is supposed to be of purely marine origin (Kulshrestha et al. 1996). Enrichment factor (EF) of an ionic specie X is given by

$$\mathrm{EF_X} = [\mathrm{X_{rain}/Na_{rain}}]\,/\,[\mathrm{X_{seawater}/Na_{seawater}}]\,.$$

Table 2 shows the NSSF and SSF ratios of Cl^-, SO_4^{2-}, K^+, Mg^{2+}, and Ca^{2+} with respect to Na^+ in rainwater and seawater as well as their corresponding enrichment factors.

As seen in Table 2, the negative value of NSS Cl^- means that there was no non-sea-salt contribution to it and Cl^- entirely came from marine (Okay et al. 2002; Zhang et al. 2007). The conclusion is further supported by the fact that Cl^-/Na^+ molar ratio of 1.14 in rainwater was similar to the ratio of 1.167 in seawater (Kulshrestha et al. 1996; Chabas and Lefevre 2000) and the EF of 0.98. The ratios SO_4^{2-}/Na^+, Ca^{2+}/Na^+, and Mg^{2+}/Na^+ in rainwater were found to be much higher than the seawater ratios, and the EF analysis gave

Table 3 Principal factor analysis of ionic compositions in Hangzhou precipitation

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Communality
SO_4^{2-}	0.693	0.336	0.568	0.125	0.931
NO_3^-	0.579	0.506	0.473	0.158	0.840
F^-	0.154	0.899	0.027	−0.099	0.842
Cl^-	0.215	0.614	0.317	0.496	0.769
NH_4^+	0.614	0.439	0.559	0.052	0.885
Ca^{2+}	0.921	0.158	−0.046	0.129	0.893
Mg^{2+}	0.929	0.082	−0.084	0.253	0.941
Na^+	0.207	−0.032	0.119	0.937	0.936
K^+	0.177	0.640	0.001	0.583	0.782
H^+	−0.111	−0.010	0.902	0.101	0.837
Eigenvalue	3.06	2.19	1.80	1.61	
Variance %	30.61	21.89	17.98	16.07	
Cumulative %	30.61	52.50	70.48	86.55	

similar results. The high values indicated that these ions mainly came from non-marine origins such as anthropogenic and crustal sources (Huang et al. 2008). Approximately 98.6% of SO_4^{2-}, 99% of Ca^{2+}, and 96.2% of Mg^{2+} in rainwater samples originated from non-marine sources. The K^+/Na^+ ratio in rainwater was also higher than that in seawater, but not so significant comparing to other ratios, and 33.7% of potassium was of marine origin. It is considered that the sources of potassium may be from biomass burning (Calvo et al. 2010).

Principal component analysis

Principal component analysis was used to analyze the relationship between the measured species and to further determine the various sources of chemical composition in precipitation. Table 3 shows the varimax rotated principal component patterns of precipitation. Four major factors were extracted at 95% significance level, accounted for 86.55% of the total variance with the factor loadings greater than 1.0.

The first component had high loadings for Ca^{2+}, Mg^{2+}, SO_4^{2-}, NH_4^+, and NO_3^- and accounted for 30.61% of the total variance of the data. This factor was associated with the earth's crustal source and secondary aerosol source, as Ca^{2+} and Mg^{2+} mainly came from soil dust and road dust, and SO_4^{2-}, NH_4^+, and NO_3^- were trace elements for secondary sulfate and nitrate, which indicates that the first factor might include the secondary sources (Xu et al. 2007). The second component which accounted for 21.89% of the total variance had large loading for F^- and K^+ which came from the mixed sources mostly of the anthropogenic origins (Hu et al. 2003). The ion with the highest loading in factor 3 was H^+ with extremely low loading of other ions. This indicated that H^+ had relatively low correlation with all the other ions and the acidity of precipitation was affected by the comprehensive effect of all factors rather than one single or certain group of ion. The fourth component had high loadings for Na^+ and Cl^- which both came from marine sources (Migliavacca et al. 2005). Similar results have been reported in previous studies on the chemical composition of precipitation (Codina and Lorente 1996; Escarré et al. 1998; Avila and Alarcón 1999; Calvo et al. 2010).

Conclusions

Data from the acid precipitation monitoring in urban area of Hangzhou during the 2-year period from June 2006 to May 2008 were collected and analyzed to characterize the chemical composition of precipitation and identify the possible contributing sources. SO_4^{2-}, NO_3^-, NH_4^+, and Ca^{2+} were the dominant ions in the precipitation samples. The concentration ratio of SO_4^{2-}/NO_3^- was 2.87 which indicated that the precipitation of Hangzhou belonged to sulfate-based acid rain. Fractional acidity was calculated and the results showed that about 38.1% of acidity was not neutralized by alkaline constituents. The average concentration ratio between measured cations ($\sum+$) to anions ($\sum-$) in rainwater samples with the value of 1.11, and the equivalent ratio of $(NH_4^+Ca^{2+})/(SO_4^{2-}+NO_3^-)$ with the value of 0.89 in Hangzhou precipitation were both lower than those in other areas. This observation indicated that the alkaline cations, which restrained acidity, cannot neutralize acidic anions completely in precipitation of Hangzhou. Neutralization factors were calculated to show that NH_4^+ and Ca^{2+} were the predominant neutralizers in rainwater samples, and Mg^{2+} could be negligible. To understand the sources of chemical components in precipitation, sea salt contributions were analyzed, and the calculated SSF, NSSF, and EF showed that nearly all SO_4^{2-}, Ca^{2+}, and Mg^{2+} and 33.7% of K^+ are of non-sea origins, while all Na^+ and Cl^- and 66.3% of K^+ originated from sea sources. Principal component analysis was also performed to find possible sources of the major ionic species. Four factors that accounted for 86.55% of the total variance were extracted. The results showed that crustal sources, the secondary aerosol sources, and marine sources were the dominant sources of the chemical components in precipitation of Hangzhou.

Acknowledgements This study was supported by key projects in the science and technology pillar program of Tianjin (09ZCGYSF02400).

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