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ORIGINAL ARTICLE

Chemical characteristics of rainwater in karst rural areas, Guizhou Province, Southwest China

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Abstract The chemical composition of rainwater has been studied in a karst rural area from September 2012 to August 2013 in Guizhou Province, Southwest China. The results indicated that the VWM value of pH was 5.4, varied from 4.6 to 6.9. Ca^{2+} and NH_4^+ were the major cations, and SO_4^{2-} was the dominant anion. Neutralization factors show that the acid was mainly neutralized by Ca^{2+}, NH_4^+ and Mg^{2+}. Investigations of correlation coefficients and enrichment factors revealed that Ca^{2+} and Mg^{2+} were mainly crust origins, and NH_4^+ was from agriculture and livestock manure. SO_4^{2-} and NO_3^- were mainly from anthropogenic sources.

Keywords Chemical composition · Rainwater · Karst rural area · Southwest China

1 Introduction

In recent decades, the rapid development of economy in China has aroused increasing use of fossil fuels and consequently lead to a noteworthy atmospheric pollution. The decrease of air quality has displayed a significant impaction on the occurrence of acid rain. The chemical compositions have emerged as an effective proxy to distinguish the sources of ions in the rainwater. In the last few decades, It has been suggested that the impaction of big cities has expanded from the urban to rural areas (Wu et al. 2012).

Some studies have been conducted to investigate chemical characteristics of rainwater in urban areas of Southwest China (Han et al. 2011; Wang and Han 2011; Xiao et al. 2013; Yu et al. 2015; Wu et al. 2012). It has been reported that rainwater chemistry of remote or rural areas in Guizhou Province had been in seriously influenced by anthropogenic sources in nearby large cities (Wu et al. 2012).

Southwest China is one of the fastest growing economies in China in the past 5 years, which also result in severe haze in big cities. In this study, we report the chemical compositions of rainwater in Puding eco-station. The purpose is to present and to discuss the chemical characterization of rainwater, to identify possible sources of the rainwater and finally to evaluate the changes of quality of the atmospheric environment in the remote area, which would possibly help to understand the influence of dramatic deterioration of air quality.

2 Materials and methods

2.1 Study area

The study was conducted in Puding County, located in the west of Guizhou Province, Southwestern China (Fig. 1). It belongs to subtropical humid monsoon climate, with a mean annual temperature of 15.1 °C and an average annual precipitation of 1397 mm. This area is dominated by Permian–Triassic carbonate rocks and the main soil type is

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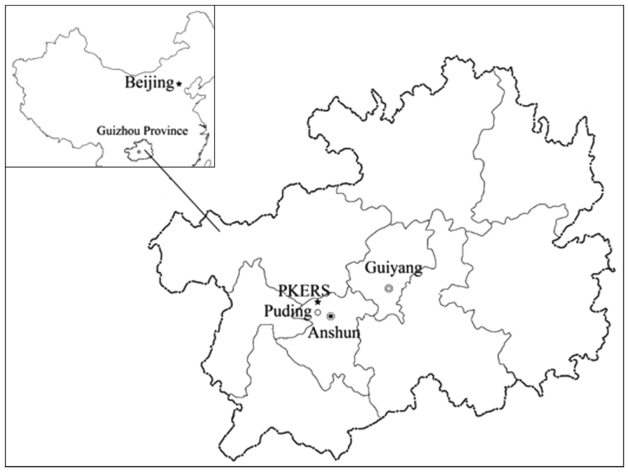

Fig. 1 A sketch map showing Puding Karst Ecosystem Research Station (PKERS)

black limestone soil rich in nutrients and calcium. With a total area of 1079.9 km^2 in this county, karst rock desertification areas account for 21.5% (Wu et al. 2012). It represents a type of the degraded secondary forest ecosystem in karst mountainous rural area of Yunnan–Guizhou Plateau.

2.2 Sampling and analysis

The sampling site was on a building roof of Puding Karst Ecosystem Research Station (PKERS), which is 5 km north of Puding City and surrounded by farmland (26°22′07″N, 105°45′06″E). A total of 25 rainwater samples were collected from September 2012 to August 2013 (no winter samples due to insufficient rainfall). Temperature, pH and electrical conductivity (EC) were measured on site using a portable pH and conductivity meter. After collection, the samples were immediately filtered through 0.45 μm pore size membrane filters to remove the insoluble particles. HCO_3^- was titrated by dilute HCl within 24 h. Major ions were quantitatively determined by ion chromatography (Dionex ICS-1100, USA, columns IonPac AG19 for cations and IonPac CS-12A for anions). NH_4^+ was measured by spectrophotometry using the Nessler method. The analytical precision of data was better than ±5%.

3 Results and discussion

3.1 Variation of pH and conductivity

As is presented in Table 1, the pH values of rainwater samples ranged from 4.6 to 6.9, with a volume-weighted mean (VWM) of 5.4. 60% of the pH values were below 5.6 (the pH of cloud water with atmospheric CO_2 equilibrium) and 28% were below 5.0. Compared to the previous data (Wu et al. 2012), the pH values were similar but the frequency of acid rain increased. The EC values varied between 11 and 306 μS/cm, with VWM values of 65, 28 and 96 μS/cm in spring, summer, and autumn, respectively, indicating an apparent seasonal variation of atmospheric particulate matter pollution.

3.2 Ionic composition of rainwater

The average ratio of cationic charge number to anionic charge number ($\Sigma_{cations}/\Sigma_{anions}$) was 1.05 indicating that almost all ions were measured and analyzed. In general, the VWM concentrations of ions were found to be lower than the mathematic means, suggesting that the lower rainfalls are usually accompanied by higher concentrations. The major ion concentrations in rainwater followed the descending sequence of $SO_4^{2-} > Ca^{2+} > NH_4^+ > Mg^{2+} > Cl^- > NO_3^- > Na^+ > K^+$. In detail, Ca^{2+}, NH_4^+ and Mg^{2+} were the predominant cations, accounting for more than 93% of the total cations mass. SO_4^{2-} was the dominant anion and contributed approximately 85% of the total mass of anions.

A comparison of the major ion concentrations in Puding with other karst-dominated areas is shown in Fig. 2. Puding had much higher concentrations of total ions (373.2 μeq/L) than that in Maolan (109.3 μeq/L), which represents the background atmosphere of Southwest China, a karst area dominated by virgin forest (Han et al. 2010). The

Table 1 pH, EC (μS/cm) and chemical composition of major ions (μeg/L) along with statistical results in rainwater samples

	pH	EC	K^+	Na^+	Ca^{2+}	Mg^{2+}	NH_4^+	Cl^-	SO_4^{2-}	NO_3^-
VWM	5.40	37.5	4.3	7.4	112.9	18.5	32.1	17.0	168.7	12.3
Mean	5.48	70.2	8.8	21.8	228.6	41.4	50.6	16.0	292.7	25.0
Min	4.57	11.0	1.0	1.0	32.4	0.2	13.7	2.0	14.5	0.9
Max	6.87	306.0	25.5	132.9	640.4	126.6	231.0	132.5	1082.8	90.9
S.D.	0.68	63.4	7.0	36.5	193.8	34.5	49.4	25.7	250.8	31.7
%	–	–	2.5	4.2	64.4	10.6	18.3	8.6	85.2	6.2

VWM volume-weighted mean, *Max* maximum, *Min* minimum, *S.D.* standard deviation; % proportion in total cations/anions

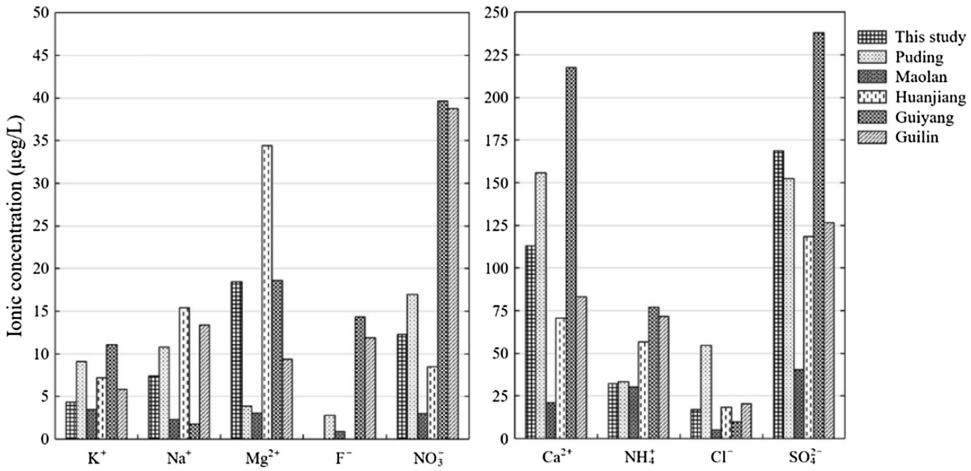

Fig. 2 Comparison of the major ion concentrations (μeg/L) in Puding with other karst-dominated areas. Other area data come from Han et al. (2010), Wu et al. (2012), Ding et al. (2013), Yu et al. (2015)

concentration of NO_3^- and SO_4^{2-} in Puding are lower than other city sites such as Guiyang. The high concentration of NH_4^+ in Puding coincides with the fact that the emission of ammonia from agricultural activities is enormous in Asian regions, especially in Southwest China (Li et al. 2016). SO_4^{2-} is about 10% higher than the data reported 5 years ago in the same area (Wu et al. 2012). Such variations could be caused by the development of industry at the surroundings, such as Guiyang, Chongqing, and Chengdu, etc.

3.3 Acid neutralization

The FA ($[H^+]/([SO_4^{2-}]+[NO_3^-])$) value was 0.025, indicating that approximately 97.5% of acidity in the local rainwater was neutralized by alkaline constituents. Neutralization factors (NF) can be used to evaluate the neutralization of rainwater by cations, which are calculated by the following equation: $NF_{Xi} = [Xi]/[NO_3^- + SO_4^{2-}]$ (Wu and Han 2015). The NF values for K^+, Ca^{2+}, Mg^{2+} and NH_4^+ in rainwater samples were 0.02, 0.62, 0.10, and 0.18, respectively. These results reveal that the main neutralization was occurred due to Ca^{2+} followed by NH_4^+ and then Mg^{2+}, whereas the neutralization by K^+ was negligible.

3.4 Correlation analysis

Significant correlations were observed between soil-derived species such as Ca^{2+}, Mg^{2+} and K^+, which is consistent with the wide distribution of carbonate rocks in other karst-dominated areas (Ding et al. 2013; Wu et al. 2012). The association of SO_4^{2-} with Ca^{2+}, Mg^{2+} and K^+, as well as NO_3^- with Ca^{2+} and K^+, may be attributed to the reactions of acids H_2SO_4 and HNO_3 with alkaline compounds (Table 2). In addition, it is notable that NH_4^+ had no correlations with other ions, suggesting atmospheric ammonia emissions from local agriculture and livestock manure (Wu et al. 2016). Similarly, there was no correlation between sea-salt specie Na^+ and Cl^-. The Na usually from sea salt in the rainwater, while Cl affected by human activities, which lead to the uncorrelation (Wu et al. 2012).

3.5 Enrichment factors and source contributions

Enrichment Factors (EFs) was usually employed to explore the possible sources: anthropogenic, marine or crust origins (Wu et al. 2012). In this study the EF values were

Table 2 Correlation coefficients of ionic concentrations (in μeq/L) in rainwater samples from Puding

	K^+	Na^+	Ca^{2+}	Mg^{2+}	NH_4^+	Cl^-	SO_4^{2-}	NO_3^-
K^+	1.00							
Na^+	0.55**	1.00						
Ca^{2+}	0.75**	0.31	1.00					
Mg^{2+}	0.87**	0.33	0.81**	1.00				
NH_4^+	0.39	0.13	0.39	0.36	1.00			
Cl^-	0.07	0.06	0.08	0.08	0.07	1.00		
SO_4^{2-}	0.41*	0.19	0.60**	0.53**	0.33	0.05	1.00	
NO_3^-	0.49*	0.72**	0.41*	0.32	0.26	0.06	0.28	1.00

** Correlation is significant at 0.01 level (two-tailed)

* Correlation is significant at 0.05 level (two-tailed)

Table 3 Enrichment factors and contribution of various sources to major ions

	$EF_{seawater}$	EF_{soil}	SSF (%)	CF (%)	ASF (%)
K^+	26.9	0.1	3.7	96.3	
Mg^{2+}	11.0	0.3	9.1	90.9	
Ca^{2+}/Na^+	347.5	0.1	–	–	–
Cl^-	2.0	48.4	50.7	2.1	47.3
SO_4^{2-}	188.6	79.5	0.5	1.3	98.2
NO_3^-	–	51.8	–	1.9	98.1

calculated by using Ca as a reference element for crust origin and Na as a reference element for marine origin as follows:

$$EF_{seawater} = [X/Na^+]_{rainwater}/[X/Na^+]_{seawater}$$

$$EF_{soil} = \left[X/Ca^{2+}\right]_{rainwater}/\left[X/Ca^{2+}\right]_{soil} \text{ (Tiwari et al. 2012).}$$

The sea salt fraction (SSF), the crust fraction (CF) and the anthropogenic fraction (AF) are calculated using the following equations:

$$SSF = [X/Na^+]_{seawater}/[X/Na^+]_{rainwater} \times 100\%$$

$$CF = \left[X/Ca^{2+}\right]_{soil}/\left[X/Ca^{2+}\right]_{rainwater} \times 100\%$$

$$ASF = 100\% - SSF - CF.$$

According to the rules of Poissant et al. (1994), EFs between 1 and 10 suggest the major influence of marine or crustal sources; when EFs range between 10 and 500, moderate enrichments are indicated, while when EFs are over 500, extreme enrichments exist (Song and Gao 2009). As show in Table 3, Both EF_{soil} and $EF_{seawater}$ of SO_4^{2-} was higher than 50, which indicated that the SO_4^{2-} was mainly from anthropogenic sources. Anthropogenic activities were also considered as the main sources of NO_3^-, suggested by the EF_{soil}. The $EF_{seawater}$ of Cl^- was 2, which suggest that the Cl^- has anthropogenic sources besides sea salt. K^+ and Mg^{2+} seem to be concentrated by soils and diluted by seawater, which were partly from the marine source and the contribution of soil source was also considerable.

4 Conclusions

The chemical composition of rainwater has been studied in a karst rural area from September 2012 to August 2013 in Guizhou Province, Southwest China. The VWM value of pH was 5.40, varied from 4.6% to 6.9%. 60% of the pH were lower than 5.6. The EC values varied between 11 and 306 μS/cm, with a significant seasonal variation. The major ion concentrations followed the sequence of $SO_4^{2-} > Ca^{2+} > NH_4^+ > Mg^{2+} > Cl^- > NO_3^- > Na^+ > K^+$. Ca^{2+}, NH_4^+ and Mg^{2+} were the most dominant cations, while SO_4^{2-} was the most abundant anion. The acidity of rainwater was neutralized by Ca^{2+} followed by NH_4^+ and then Mg^{2+}. Investigations of correlation coefficients and enrichment factors (*EF*) among major ionic constituents revealed that Ca^{2+}, Mg^{2+} and K^+ were were primarily of crust origin, and NH_4^{2-} was from human activities. SO_4^{2-} and NO_3^- were highly enriched relative to crustal sources, suggesting anthropogenic contributions. The comparison of ions show that the decrease of air quality has led to the higher SO_4^{2-} in the rainwater of the study area.

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References

Ding H, Lang YC, Liu CQ, Liu TZ (2013) Chemical characteristics and $\delta^{34}S$–SO_4^{2-} of acid rain: anthropogenic sulfate deposition and its impacts on CO_2 consumption in the rural karst area of southwest China (special issue: recent progress in environmental hydrogeochemistry). Geochem J 47:625–638

Han GL, Yang T, Wu QX, Qiu T (2010) Chemical and strontium isotope characterization of rainwater in karst virgin forest, Southwest China. Atmos Environ 44:174–181

Han G, Wu Q, Tang Y (2011) Acid rain and alkalization in southwestern China: chemical and strontium isotope evidence in rainwater from Guiyang. J Atmos Chem 68:139–155

Li YC, Zhang M, Shu M, Ho SS, Liu ZF, Wang XX, Zhao XQ (2016) Chemical characteristics of rainwater in Sichuan basin, a case study of Ya'an. Environ Sci Pollut Res 23:13088–13099

Poissant L, Schmit JP, Béron P (1994) Trace inorganic elements in rainfall in the Montreal Island. Atmos Environ 28:339–346

Song F, Gao Y (2009) Chemical characteristics of precipitation at metropolitan Newark in the US East Coast. Atmos Environ 43:4903–4913

Tiwari S, Chate DM, Bisht DS, Srivastava MK, Padmanabhamurty B (2012) Rainwater chemistry in the North Western Himalayan Region, India. Atmos Res 104–105:128–138

Wang H, Han G (2011) Chemical composition of rainwater and anthropogenic influences in Chengdu, Southwest China. Atmos Res 99:190–196

Wu Q, Han G (2015) Sulfur isotope and chemical composition of the rainwater at the Three Gorges Reservoir. Atmos Res 155:130–140

Wu Q, Han G, Tao F, Tang Y (2012) Chemical composition of rainwater in a karstic agricultural area, Southwest China: the impact of urbanization. Atmos Res 111:71–78

Wu Y, Xu Z, Liu W, Zhao T, Zhang X, Jiang H, Yu C, Zhou L, Zhou X (2016) Chemical compositions of precipitation at three non-urban sites of Hebei Province, North China: influence of terrestrial sources on ionic composition. Atmos Res 181:115–123

Xiao HW, Xiao HY, Long AM, Wang YL, Liu CQ (2013) Chemical composition and source apportionment of rainwater at Guiyang, SW China. J Atmos Chem 70:269–281

Yu S, Kuo YM, Du W, He S, Sun PA, Yuan Y, Li R, Li Y (2015) The hydrochemistry properties of precipitation in karst tourism city (Guilin), Southwest China. Environ Earth Sci 74:1061–1069