Journal of Environmental Sciences Vol. 6, No.3 pp. 322–329, 1994 ISSN 1001–0742

The research of below-cloud scavenging of rainwater in Guilin City

Bai Yuhua, Yao Rongkui, Li Xin, Tang Xiaoyan

The Department of Technical Physics and The Center of Environmental Science, Peking University, Beijing 100871, China

Abstract— Sequential samples of single precipitation event were collected by the use of specially designed semi-automatic sequential precipitation collector in the spring of 1988 in Guilin City. The pH value and soluble chemical species such as SO_4^{2-}, NO_3^-, NH_4^+, Ca^{2+}, Mg^{2+}, Na^+, K^+, F^- and Cl^- were analyzed. An apparent decrease in the concentration of all ions except H^+ and NO_3^- was observed at the initial portion of the events. The relative acidity increased as the event progress. The concentration of H^+ was the result of comprehensive actions of all ions. The average scavenging ratio of events was calculated and it is found that SO_4^{2-} was the major contributor for acid rain in Guilin and Ca^{2+} was the important neutralizer.

Keywords: acid rain; sequential sample; below-cloud scavenging; precipitation event.

1 Introduction

Since the late 1970s, acid precipitation monitoring studies have been carried out in many provinces and cities of China. However, only a few reports related to the research of sequential sampling. A single sample collected for the duration of the raining event could only indicate the average results. The measurements for sequential rainwater sample can give the information about the change of pH value and chemical components which occurred during the event (Michael, 1983; Ames, 1987; Barrie, 1985; Jaffrezo, 1987).

Guilin is located in northeast Guangxi Province about 65 km south to Maoershan Mountain. The measurement results of rainwater for years have shown that the acid rain pollution around this district was rather serious. This paper presents the results of pH value and chemical components of sequential samples during rainwater events at the Environmental Monitoring Station of Guilin in the spring of 1988 (from March 15 to March 27), mainly discusses below-cloud scavenging procedure of precipitation events.

2 Sampling techniques

The rainwater was collected by semi-automatically sequential samplers designed by ourself. This device consisted of a collection funnel with diameter of 27 cm and eight polyethylene bottles. Each bottle had a cap of manifold and a hollow glass ball. As shown in Fig.1, the bottles entrance was stepped vertically on a frame so that the second bottle was a little lower than first, and so on. All bottles were set inside of a plastic box to keep them from being contamination. The funnel was about 1 m above the box, a teflon tube connected the funnel to the entrance of first bottle. The rainwater collected by the funnel passed through the tube and entered first bottle directly, when first one was full, the hollow glass ball as a check valve floated to the top within the bottle to prevent additional flow into this stage, so that the rainwater could advance to flow second bottle automatically, and so on.

All bottles, funnel and tube were made of polyethylene and were cleaned before use with dilute nitric acid and thoroughly rinsed with distilled deionized water. The funnel was covered between events to eliminate dryfall and the funnel and tubing were cleaned with deionized water shortly before sampling. The analyzing methods of the chemical components and the characterization of Maoershan cloudwater have already been described elsewhere (Yao, 1993).

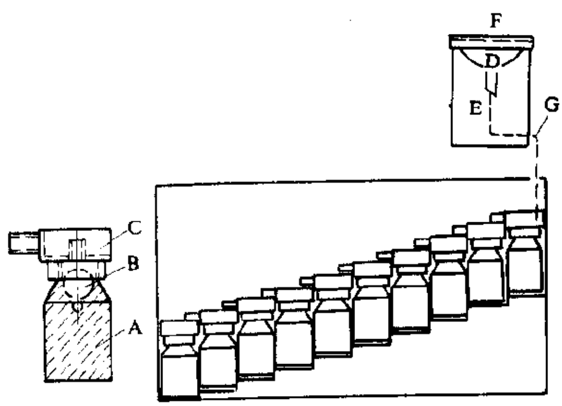

Fig.1 Apparatus of semiautomatic sequential rainwater collector

A: polyethylene bottle
B: hollow glass ball
C: cap of manifold
D: collecting funnel of rainwater
E: plastic tank
F: cover
G: connecting tube

3 Results and discussion

3.1 The variation process of major ions within a single rainfall

Table 1 and Fig.2 show some typical results of rainwater components obtained at Guilin City. In all these cases, sulphate is the dominant anion, Ca^{2-}, NH_4^+ and H, are the main cations. An apparent decrease in the concentration of SO_4^{2-}, Ca^{2-}, NH_4^+

Table 1 The chemical compositions of sequential samples of Guilin rainwater

Unit: μeq/L

Date		pH	F^-	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	H^+
March 23		3.83	35.98	29.91	94.98	292.0	43.06	237.80	46.81	194.1	32.25	147.9
	2	3.82	24.76	35.47	67.90	247.3	26.53	169.60	33.51	122.8	19.09	151.4
	3	3.87	15.84	37.95	64.18	183.8	15.66	178.50	29.16	83.8	13.17	134.9
	4	3.94	30.92	51.16	59.84	137.8	14.79	165.80	26.34	78.8	12.84	114.8
	5	4.00	11.44	15.12	41.86	99.2	0.43	83.15	9.72	47.9	9.63	100.0
	6	3.93	13.31	13.82	42.89	122.9	3.04	102.00	12.02	52.9	11.11	117.5
	7	3.94	8.14	14.42	48.06	115.8	0.43	108.10	14.83	50.4	10.12	114.8
	8	3.93	18.26	31.70	63.15	157.4	6.52	152.40	23.53	78.8	14.73	117.5
	1	3.98	25.31	16.11	41.86	237.0	15.66	151.30	10.74	117.8	20.90	104.7
March	2	3.96	23.66	26.67	41.24	208.0	13.48	158.60	175.50	88.3	16.62	109.6
	3	3.95	16.17	24.25	26.77	184.0	20.88	75.95	20.97	60.9	13.74	112.2
	4	4.06	12.01	18.89	48.27	89.4	2.61	118.10	17.14	44.4	8.64	87.1
	5	4.06	17.71	24.85	49.30	96.5	2.61	97.57	9.21	54.4	12.01	87.1
24–25	6	4.19	16.17	17.90	36.69	61.6	3.04	89.25	13.81	37.4	9.13	64.6
	7	3.99	18.26	18.19	42.07	100.7	−1.00	82.04	10.74	51.4	10.04	128.8
	1	3.24	27.07	21.37	100.40	595.0	40.98	220.60	14.56	235.0	39.58	575.4
March	2	3.27	35.43	21.47	97.25	436.2	22.18	207.30	13.30	147.7	27.98	537.0
	3	3.42	28.17	47.78	91.88	245.6	22.62	171.30	47.06	108.8	22.46	380.2
	4	3.54	14.52	33.09	69.14	145.9	10.87	207.30	29.41	57.4	12.42	288.4
	5	3.63	25.86	39.64	56.61	94.6	21.75	138.00	27.88	54.9	12.42	234.4
26–27	6	3.74	9.35	18.89	52.61	81.1	2.61	119.20	28.39	47.9	9.79	182.0
	7	3.72	18.15	31.60	61.08	108.2	−1.00	120.80	30.69	52.4	10.12	190.5
	8	3.63	57.34	21.57	50.75	171.1	16.96	96.46	15.09	145.2	20.08	234.4

and Mg^{2+} at the first three stages of events can be found except for H^+ and NO_3^-. For the behavior of Ca^{2+}, which may be subjectively related to the presence of dust and the non-reactive aerosol in the large size, is immediately removed by the droplets when the rainfall starts. The relationship between SO_4^{2-} and other cation have been examined and the results have been listed in Table 2. An obvious plus correlation between SO_4^{2-} and all other cation especially with Na^+, Ca^{2+} and Mg^{2+} was obtained. This implied that the SO_2 may be absorbed onto the particles and reacted with soil derived alkaline matter to form the respective sulfate salts. Since large soil derived particles are more rapidly removed by precipitation, the observed rapid decrease of SO_4^{2-}, Na^+, K^+, Ca^{2+} and Mg^{2+} due to washout would

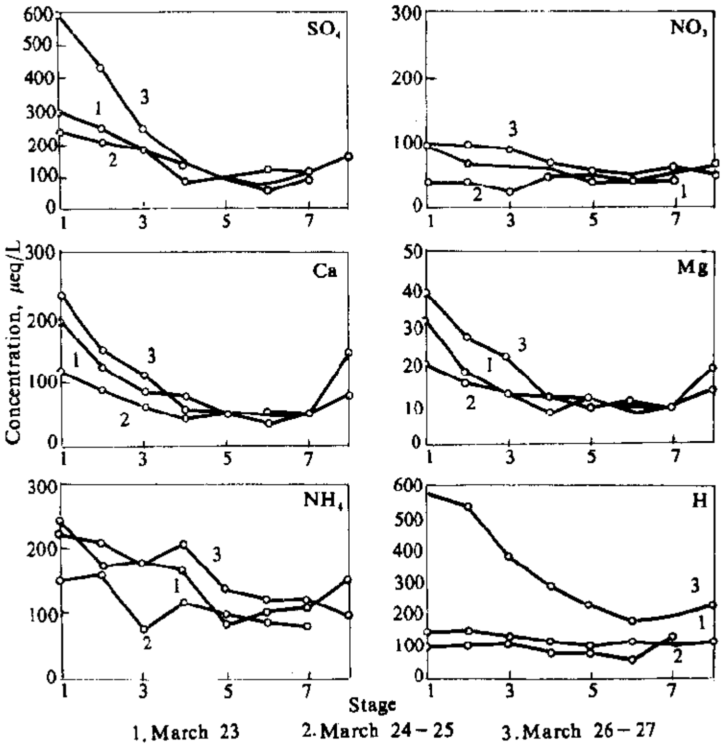

Fig.2 Variation of ion concentration with stages in Guilin rainfall (March, 1988)

be expected (Michael, 1983). The diurnal average concentration of SO_2 over Guilin City is about 0.09 mg/m^3, which also provided a possibility for belowcloud scavenging of SO_2. Moreover, the variation of NH_4^+ also indicated that a significant present of the deposition of NH_4^+ (including gas NH_3) especially NH_4^+ of sulfate occurred in the initial portion of a rainfall event. As shown in Fig.2, the variation in NO_3^- concentration was not as obvious as SO_4^{2-} and other cations, which indicated that the below-cloud scavenging of NO_3^- was not very important.

3.2 The variation of rainwater acidity within rainwater event

3.2.1 The regression result between rainwater acidity and chemical components

It could be seen from Fig. 2, H^+ concentration typically had a slight increase early for two events, then with a slight decrease in the middle and increase again at later events. To investigate the source of acidity and the possible contribution of each chemical components to the acidity, a statistical analysis for Guilin rainwater was carried out. Table 3 shows the results of multiple regression. It indicated that the acidi-

Table 2 The correlation of SO_4^{2-} with other cation in event

Relation	Sampling date	Regression ratio	a	b	s
SO_4^{2-}-Na^+	3/23	0.9622	4.40	108.80	0.51
	3/24–25	0.8554	7.00	82.20	1.90
	3/26–27	0.8203	11.52	37.40	3.30
SO_4^{2-}-NH_4^+	3/23	0.8914	1.21	−11.10	0.25
	3/24–25	0.6338	1.30	−4.20	0.71
	3/26–27	0.7339	2.80	−222.10	1.08
SO_4^{2-}-K^+	3/23	0.9487	5.21	41.80	0.71
	3/24–25	0.4462	0.50	121.20	0.45
	3/26–27	0.4946	−8.12	444.10	5.82
SO_4^{2-}-Ca^{2+}	3/23	0.9621	1.30	51.40	0.15
	3/24–25	0.9205	2.20	−4.61	0.42
	3/26–27	0.9174	2.56	−36.60	0.45
SO_4^{2-}-Mg^{2+}	3/23	0.9268	8.47	39.30	1.38
	3/24–25	0.9419	14.43	−48.14	2.30
	3/26–27	0.9725	17.26	−99.50	1.69
SO_4^{2-}-H^+	3/23	0.8247	3.56	−275.30	0.52
	3/24–25	0.5192	1.68	−27.34	1.24
	3/26–27	0.967	1.16	−146.70	0.13

Notes; a is slope; b is intercept; s is Std. Err. of *X* coefficients

ty of Guilin rainwater were major controlled by mainly the ions such as SO_4^{2-} and Ca^{2+}, secondly by NO_3^- and NH_4^+. SO_4^{2-} and NO_3 made plus contribution to H^+, Ca^{2+} and NH_4^+ made negative contribution.

To examine the reliability of regression results, a cluster analysis of Guilin sequential rainwater ($n=43$) were made (Fig. 3). It could be found clearly that the good correlation occurred between H^+ and all major ions rather than H^+ and any single ion. This result pointed out that the H^+ concentration was the result of comprehensive actions of all ions in rainwater.

3.2.2 The relative acidity of rainwater increased as an rainfall event progressed

The relative precipitation acidity can be examined by the ratio H^+/Sum(−) and $Ca^{2+}+H^+$/Sum(−). Fig. 4 shows that this ratio increases with stages for three events. Such behavior suggested that neutralized compounds or neutralizing agents (such

Table 3 Equations obtained in multiple regression analysis relating H^+ concentration to dissolved ionic concentration in rainwater

$[H^+]=118.7+0.722[NO_3^-]+0.778[SO_4^{2-}]-0.410[NH_4^+]-1.018[Ca^{2+}]$		
$R=0.5913$		
F:	$[NO_3^-]$	4.21
	$[SO_4^{2-}]$	19.32
	$[NH_4^+]$	2.23
	$[Ca^{2+}]$	11.35

F value: Denotes significant level of 0.05

as Ca^{2+} and ammonia) were scavenged early in an event, and acidic SO_4^{2-} and NO_3^- scavenging was more important as the event progress (Chapman, 1986).

3.2.3. The estimation of below-cloud average scavenging efficiency of precipitation

We have obtained the below-cloud scavenging efficiency of species calculated by the following equation using the results of sequential samples of rainwater:

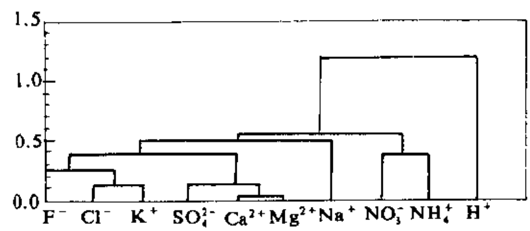

Fig.3 The cluster analysis of the Guilin rainwater

$$\text{Scavenging ratio (j)}=\frac{\text{Sum (1 to 7 stages)} (j)-\text{Min} (j)}{\text{Sum (1 to 7 stages)} (j)}\times 100,$$

where Sum (1 to 7) (j) represents the total concentration of species j in all stages during an event, the Min (j) is the most low concentration of species j in platform, which approximately represents the concentration of species j within the cloud layer near ground, corresponding to the concentration at flat area of curve in Fig. 3. It can be found from above formula that the lesser concentration of Min(j), the higher value of scavenging ratio and the larger contribution of below-cloud scavenging of rainwater.

We calculated the below-cloud average scavenging efficiency and the contribution ratio for 1 to 3 stages of three typical precipitation in Guilin City using above equation and listed the results in Table 4.

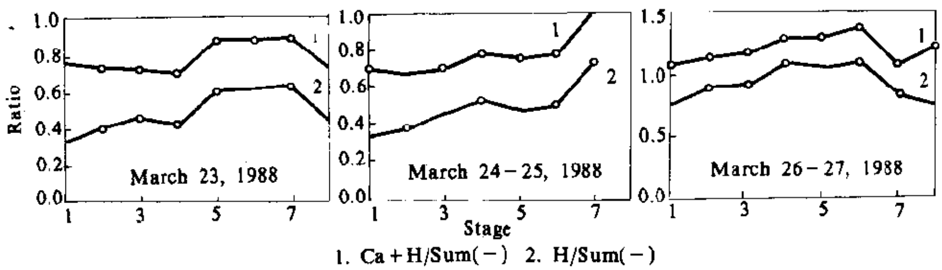

Fig.4 The variation of relative acidity with stages

Table 4 The average scavenging ratio of washout of rainwater events in Guilin City (1988.3)

Unit: μeq/L

Date	F^-	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	H^+
March 23	59.41	48.98	30.19	42.08	97.10	44.30	60.53	46.84	37.70	20.57
March 24-25	35.10	16.53	9.83	57.85	73.13	22.48	77.66	44.35	36.03	31.43
March 26-27	58.72	38.16	30.38	66.73	84.78	29.56	-	52.38	49.15	46.65
March 23*	62.53	61.19	80.10	84.36	83.19	72.68	76.97	87.00	87.30	74.02
March 24-25*	74.70	62.67	35.40	87.62	98.99	76.06	93.48	86.58	86.78	74.68
March 26-27*	67.26	41.60	81.95	90.75	76.62	69.01	-	94.31	91.56	84.98

*The washout for 1 to 3 stages of rainwater events accounted for percentage of total washout amounts.

Although there were different scavenging ratio for different event, which is dependent on many factors such as the time interval between two events act, rain strength and precipitation amount. However the similar role could be found that SO_4^{2-} and Ca^{2+} had the largest scavenging efficiencies, NH_4^+ and Mg^{2+} had secondary. The scavenging ratios of NO_3^- and H^+ were much smaller than others. Approximately 70%-90% of the total SO_4^{2-}, Ca^{2+} and NH_4^+ deposition occurred during the first three stages of the rainwater. This conclusion agrees with the analyzing from Fig.2.

4 Summary

This paper mainly research the chemical characteristic of sequential samples of rainwater events. Several important conclusions were shown as follows: (1) single ion concentrations in the rainwater obviously decrease during the early of the events and keep at a low level later, which represents the ionic concentration in cloud layer near ground; (2) it can be found from the data and figures that there was obvious scavenging action for SO_4^{2-}, Ca^{2+}, Na^+, NH_4^+ and Mg^{2+} in air, with the exception of NO_3^-. This fact was associated with the washout of precipitation; (3) the average scavenging ratio of the rain water (i.e. washout contribute to concentration of j species in rain) in Guilin was to be calculated that SO_4^{2-} and Ca^{2+} were about 50%, NH_4^+ and H^+ about 30%, NO_3^- only 23%; (4) acidic sulfate was the major acidic source, Ca^{2+} and other cations were the neutralizing material of acid in the rainwater, the scavenging action of NO_3^- was not very obvious; (5) the result of multiple regression shows that the concentration of H^+ is the result of comprehensive action of total ions and relative acidity increasing as the rainfall progresses, namely cloudwater of Guilin district are acidic by rainout, but rainwater of Guilin district are more acidic by washout of rain.

Acknowledgments—we thank Prof. Li Jinlong of our division for the help in treatment the data using computer; we thank Assoc. Prof. Zhang Zheng for the help in measuring the pH value and conductivity of rainwater in the field research; thank Environmental Monitoring Station of Guilin City, Guangxi Zhuang Autonomous Region for their closely cooperation with us.

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(Received February 15, 1993)