

Chemical characteristics of acidified waters in southwest China

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Abstract—By taking samples of four acidified waters and three contrast waters at outskirts of Chongqing City, chemical characteristics of typical acidified waters in southwest China were investigated.

K^+ , Na^+ , Ca^{2+} and Mg^{2+} are correlated significantly with pH. The change of total concentrations of Ca^{2+} and Mg^{2+} with time is consistent with that of pH. Mg^{2+} and Ca^{2+} played the significant role in buffering active H^+ , and changes of K^+ and Na^+ from rainwater to waters were not significant. There is a linear relationship between logarithm of Al^{3+} concentration and pH.

In the acidified waters, there are high SO_4^{2-} and NO_3^- contents. Sulfate in two typical acidified waters was about 1/3 from rainwater and 2/3 from dissolution of the soil around the waters, and nitrate was mainly from dissolution of the soil, because of a great amount of sulfate and nitrate had been accumulated in the soil.

From correlation analyses among organic nitrogen or carbon and pH, DON, POC and DOC are positively correlated with pH, therefore organic substance do not cause the increase of active H^+ content. The causes of the acidification of the waters are concluded mainly from acid precipitation and weak buffering capacity of the water environment.

Keywords: element; acidified waters; acid rain.

1 Introduction

Southwest China is one of the most serious areas of acid precipitation in China. In past several years, many researches were done on the distribution of acid rain (Chen, 1987), atmospheric transport and deposition of sulfur and nitrogen (Wang, 1989; Liu, 1989), and the effects of acid precipitation on forest (Chen, 1989), but few of researches were done on the chemical characteristics of the acidified waters of the area. By taking samples of several suburban waters of Chongqing City, chemical characteristics of typical acidified waters were studied. Four acidified waters, two waters with pH 4.24 and 4.97 were used for drinking and the other two with pH 5.39 and 5.17 for fishery, and three contrast waters with pH 6.41, 6.90 and 8.45 were investigated. All the waters are formed by rain water, so the studies are important for acid rain and soil background of the area as well as waters acidification. Determined items include pH, conductivi-

ty, transparency, DO, Cl^- , F^- , SO_4^{2-} , DON, PON, NO_3^- , NO_2^- , NH_4^+ , PO_4^{3-} , POC, DOC, PIC, DIC, SiO_2 , K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Al^{3+} and so on. The principal physical and chemical characteristics of the acidified waters, the qualitative and quantitative relation between pH and the chemical components are stated.

2 Methodology

2.1 Collection and analyses of sample

The samples for analyses of Cl^- , SO_4^{2-} , NO_3^- , NO_2^- , NH_4^+ , PO_4^{3-} , SiO_2 , K^+ , Na^+ , Ca^{2+} , Mg^{2+} and Al^{3+} were filtered through 0.45 μm membrane and collected in plastic bottles. The samples for analyses of Cl^- , SO_4^{2-} and NO_3^- were preserved in bucket filled with ice, and analyzed by ion chromatography, NO_2^- , NH_4^+ were determined immediately by spectrophotometry. The samples for analyses of K^+ , Na^+ , Ca^{2+} and Mg^{2+} were preserved with 1.5 ml concentration HNO_3/L sample, and analyzed by atomic absorption spectrophotometry. Al^{3+} was analyzed by colorimetric method with Eriochrome cyanine R as color reagent.

Total kjeldahl nitrogen of samples unfiltered and filtered through 0.45 μm membrane are determined promptly. DON is equal to the total kjeldahl nitrogen of filtered sample minus $\text{NH}_4^+\text{-N}$. PON is equal to total kjeldahl nitrogen of unfiltered sample minus total kjeldahl nitrogen of filtered sample. Total carbon (TC) and total inorganic carbon (TIC) of unfiltered and filtered samples were determined by using Carbon Analyzer (DC-180, USA). $\text{DIC} = \text{TIC of filtered sample}$; $\text{DOC} = \text{TC of filtered sample} - \text{DIC}$; $\text{POC} = \text{TC of unfiltered sample} - \text{TIC of unfiltered sample} - \text{DOC}$; $\text{PIC} = \text{TC of unfiltered sample} - \text{TC of filtered sample} - \text{POC}$.

2.2 Field investigations on typical waters and the chemical composition of the waters

Field investigations were made on two suburban areas of Chongqing, Jinyun Mountain and Nanshan Mountain (Fig. 1). In Jinyun Mountain, there were two small acidified waters which were formed by rain-water of the area and used for drinking. And there were hardly artificial pollution effects on the waters. In the area two contrast waters with different pH were selected for comparison with the acidified waters. In Nanshan Mountain two waters for fishery, which were also formed by rainwater, were acidified. In the area a contrast waters was selected for comparison. Some physical parameters determined on field are listed in Table 1.

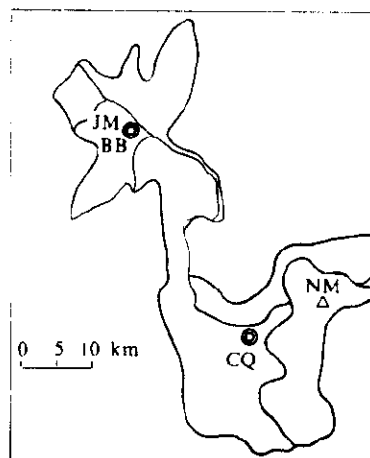


Fig. 1 Sampling sites

JM, Jinyun Mountain BB, Beibei City

CQ, Chongqing City NM, Nanshan Mountain

Table 1 The field determination parameters of some suburban waters of Chongqing

Waters code	Address	pH	Depth, m	Cond, $\mu\text{s}/\text{cm}$	Trans, m	DO, mg/L
01	Jiayun Mountain	4.24	6.5	92	6.0	8.5
02	Jiayun Mountain	4.97	6.0	86	4.5	9.8
03	Jiayun Mountain	6.41	2.0	80	1.2	8.7
04	Jiayun Mountain	6.90	15.0	59	1.2	9.2
05	Nanshan Mountain	5.39	2.0	60	0.3	9.3
06	Nanshan Mountain	5.17	1.8	64	0.4	7.0
07	Nanshan Mountain	8.45	3.0	273	0.6	9.7

The results are average values of three time sampling.

Cond=Conductivity; Trans=Transparency.

The changes of pH in five waters from 1989 to 1992 are showed in Fig. 2. Waters 01, 02 and 04 were in Jiayun Mountain, and there were decreasing tendency of pH with time. Waters 05 and 06 were in Nanshan Mountain, there were increasing tendency of pH possibly because of artificial influence.

To illustrate the characteristics of chemical composition of the acidified waters, the equivalent concentrations of main ions in the waters with different pH are listed in Table 2.

From Table 2, in the two waters with pH 4.24 and 4.97 respectively, the total concentration of three anions is significantly higher than that of seven cations. In the two waters the concentration of Al^{3+}

is about 10 times as those in the other five waters. In fact the analytical results of Al in the two waters are also significantly higher than those reported in other references (Nelson, 1991; Dickson, 1980; Muniz, 1980). Whether Fe, Mn or Zn in the two waters are also as Al with specially high concentrations or not has been known. And in the two waters there are also significantly higher concentrations of SO_4^{2-} and NO_3^- .

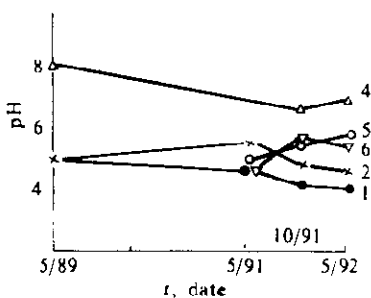


Fig. 2 The changes of pH in five ponds from 1989 to 1992, the codes are stated in the context

Table 2 Chemical composition of seven waters with different pH Unit: $\mu\text{eq}/\text{L}$

Code	pH	H^+	Cl^-	SO_4^{2-}	NO_3^-	NH_4^+	K^+	Na^+	Ca^{2+}	Mg^{2+}	Al^{3+}	HCO_3^-	Σ^+	Σ^-
01	4.01	98	76	416	304	4	30	60	39	116	258	0	605	797
02	4.63	23	34	427	189	16	38	74	110	116	210	0	587	650
03	6.41	0	80	240	60	2	53	176	210	120	21	177	583	557
04	7.02	0	20	329	52	21	51	126	58	133	27	60	415	461
05	5.65	2	106	381	20	91	63	149	53	107	32	12	497	519
06	5.48	3	71	400	20	70	45	100	66	103	35	9	422	499
07	8.09	0	289	1083	71	37	226	828	1103	159	28	981	2381	2424

3 Results and discussion

3.1 Correlation analysis

For studying the relationship of chemical components with pH difference the correlation analyses of 23 parameters was done by using the analytical results of seven waters with different pH (Table 3). In Table 3 significance levels (*P*) of less than 0.1, 0.05 and 0.01 are used for expressing the confidence levels of more than 90%, 95% and 99% respectively.

Table 3 Correlation analysis of parameters of water quality in seven typical ponds taken samples in May 1992

	H ⁺	Cl ⁻	SO ₄ ²⁻	DON	PON	NO ₂ ⁻	NO ₃ ⁻	NH ₄ ⁺	POC	DOC	PIC	DIC
H ⁺	1.000	-0.181	-0.108	-0.218	-0.260	-0.229	0.929	-0.435	-0.528	-0.218	-0.256	-0.347
Cl ⁻		1.000	0.916	0.667	-0.165	0.918	-0.168	0.191	0.800	0.869	0.630	0.926
SO ₄ ²⁻		+++	1.000	0.650	-0.051	0.976	-0.020	0.105	0.811	0.801	0.749	0.855
DON				1.000	0.570	0.770	-0.124	-0.365	0.570	0.822	0.310	0.844
PON					1.000	0.070	-0.152	-0.409	0.286	0.073	-0.260	-0.093
NO ₂ ⁻		+++	+++	++		1.000	-0.104	0.007	0.844	0.897	0.750	0.932
NO ₃ ⁻	+++						1.000	-0.621	-0.525	-0.225	-0.010	-0.257
NH ₄ ⁺								1.000	0.334	-0.140	0.113	-0.038
POC		++	++	+		++			1.000	0.732	0.485	0.819
DOC		++	++	++		+++			+	1.000	0.612	0.984
PIC			++			+			++		1.000	0.595
DIC		+++	++	++		+++			++	+++		1.000
SiO ₂												
HCO ₃		+++	+++	++		+++			++	+++		+++
K ⁺		+++	+++	++		+++			+++	+++	+	+-+
Na ⁺		+++	+++	++		+++			+++	+++	+	+++
Ca ²⁺		+++	+++	++		+++			-+	+++	+	+++
Mg ²⁺		+	++	+++		++			++	++		++
Al ³⁺	+++						+++					
Cond		+++	+++	++		+++			++	+++	+	+++
Trans	+++						+++					
DO											+	
pH	-			++		+			++	+		++

	SiO ₂	HCO ₃ ⁻	K ⁺	Na ⁺	Ca ²⁺	Mg ²⁺	Al ³⁺	Cond	Trans	DO	pH
H ⁺	-0.017	-0.287	-0.340	-0.325	-0.273	-0.205	0.878	-0.096	0.888	-0.104	-0.714
Cl ⁻	0.445	0.935	0.952	0.952	0.937	0.703	-0.294	0.932	-0.333	0.270	0.603
SO ₄ ²⁻	0.591	0.918	0.943	0.933	0.936	0.782	-0.110	0.966	-0.163	0.358	0.545
DON	0.064	0.848	0.782	0.811	0.806	0.952	-0.359	0.768	-0.252	0.402	0.821
PON	-0.086	0.120	0.073	0.086	0.056	0.509	-0.302	0.002	-0.156	0.196	0.533
NO ₂ ⁻	0.445	0.975	0.978	0.979	0.985	0.872	-0.221	0.985	-0.241	0.429	0.678
NO ₃ ⁻	-0.154	-0.187	-0.262	-0.239	-0.155	-0.049	0.960	0.020	0.981	0.149	-0.656
NH ₄ ⁺	0.603	-0.037	0.129	0.068	-0.030	-0.310	-0.471	-0.086	-0.624	-0.230	0.095
POC	0.608	0.850	0.905	0.886	0.827	0.768	-0.624	0.762	-0.645	0.227	0.873
DOC	0.093	0.959	0.909	0.935	0.958	0.818	-0.380	0.907	-0.350	-0.335	0.748
PIC	0.234	0.648	0.693	0.674	0.703	0.535	0.032	0.713	-0.051	0.693	0.320
DIC	0.227	0.987	0.959	0.976	0.979	0.842	-0.419	0.933	-0.400	0.323	0.783

Table 3 (Continued)

	SiO ₂	HCO ₃ ⁻	K ⁺	Na ⁺	Ca ²⁺	Mg ²⁺	Al ³⁺	Cond	Trans	DO	pH
SiO ₂	1.000	0.328	0.447	0.395	0.335	0.201	-0.114	0.383	-0.239	-0.178	0.182
HCO ₃ ⁻		1.000	0.983	0.994	0.996	0.886	-0.342	0.970	-0.333	0.373	0.761
K ⁺			1.000	0.997	0.981	0.847	-0.386	0.952	-0.406	0.391	0.765
Na ⁺				1.000	0.990	0.862	-0.377	0.962	-0.385	0.382	0.768
Ca ²⁺					1.000	0.864	-0.293	0.981	-0.297	0.386	0.718
Mg ²⁺						1.000	-0.237	0.850	-0.168	0.556	0.777
Al ³⁺							1.000	-0.118	0.980	0.115	-0.793
Cond								1.000	-0.130	0.394	0.593
Trans									1.000	0.139	-0.735
DO										1.000	0.286
pH											1.000

Values in the table are correlation coefficients. Signs +, ++ and +++ denote significant positive correlations with $P < 0.1$, $P < 0.05$ and $P < 0.01$ respectively; Signs - and -- denote significant negative correlations with $P < 0.1$ and $P < 0.05$, respectively.

From Table 3 the equivalence concentration of H⁺ is correlated positively with the concentrations of NO₃⁻, Al³⁺ and transparency with $P < 0.01$. The pH is correlated positively with NO₂, DOC and Ca²⁺ at $P < 0.1$, with DON, POC, DIC, HCO₃⁻, K⁺, Na⁺ and Mg²⁺ at $P < 0.05$ and negatively with transparency and Al³⁺ at $P < 0.05$ and 0.1 respectively.

3.2 Properties of K⁺, Na⁺, Ca²⁺ and Mg²⁺

There are significant positive correlation between K⁺, Na⁺, Ca²⁺ or Mg²⁺ and pH (Table 3), which means that the higher the concentrations of the ions in a water body, the more powerful the buffering capacity of the water body. The linear relations between the ions and pH are showed in Fig. 3. In Fig. 3, the four lines show a slope order of Ca²⁺ > Mg²⁺ > K⁺ > Na⁺, the order is consistent with alkalinity difference of the ions.

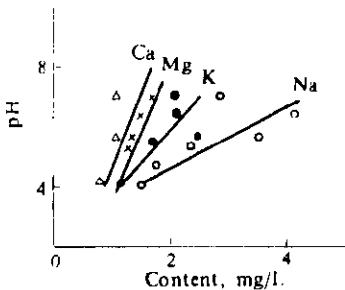


Fig. 3 The relationship between K⁺, Na⁺, Ca²⁺ or Mg²⁺ and pH in several typical ponds

In Jinyun Mountain two acidified waters (waters 01 and 02) were joined with a water - pipe. In 1990, waters 02 was enclosed with stone wall cemented with cement and lime flour, a considerable amount of lime dissolved into water so that pH in the waters in May of 1991 was significantly higher than that in 1989, but the values of pH decreased from 1991 to 1992 due to buffering action of the waters (Fig. 2). And the difference of pH in the two waters is mainly caused by the addition of lime in waters 02. The changes of pH in the two waters from 1991 to 1992 is significantly consistent with changes of total concentration of Ca²⁺ and Mg²⁺ (Fig. 4).

3.3 Properties of Al³⁺

The analytical results of Al³⁺ are given in Table 2, the concentration of Al³⁺ ranges from

0.191 to 2.324 ppm (21–258 $\mu\text{eq/L}$) in seven waters with different pH. Al^{3+} is correlated significantly with H^+ , NO_3^- , and transparency with correlation coefficient 0.878, 0.981 and 0.980 respectively and $P < 0.01$, its pH with a correlation coefficient -0.793 and $P < 0.05$. There is a linear relationship between logarithm of Al^{3+} equivalence concentration and pH with a correlation coefficient of -0.8064 and $P < 0.01$ (Fig. 5). The regression equation is $\log \text{Al}^{3+} = -2.746 - 0.2645 \times \text{pH}$.

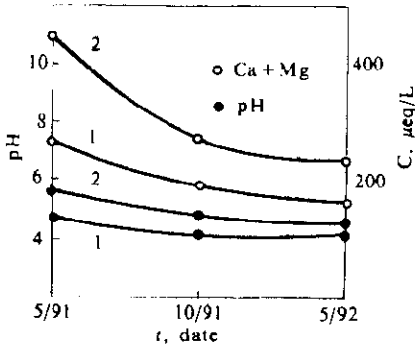


Fig. 4 The consistency of the changes of pH and the total concentration of Ca^{2+} and Mg^{2+} in two acidified ponds from May 1991 to May 1992, the codes are as in Fig.1

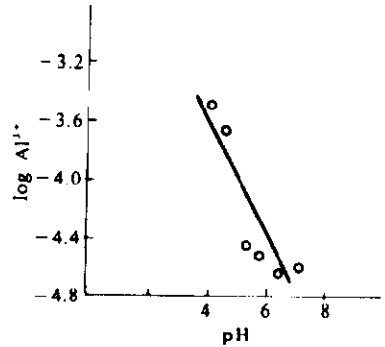


Fig. 5 Plot of $\log \text{Al}^{3+}$ versus pH in six ponds with different pH, Al^{3+} concentration is equivalence concentration

3.4 Sulfate and nitrate

Although the conductivities in the acidified waters are very low, 60–90 $\mu\text{s/cm}$, there are high SO_4^{2-} and $\text{NO}_2^- - \text{N}$ contents in the ranges of 18.3–20.5 ppm and 0.283–4.260 ppm respectively. There are significant positive correlations between NO_3^- and H^+ , Al^{3+} or transparency of the waters with correlation coefficients 0.9294, 0.9595 or 0.9810 respectively.

3.5 Speciation analyses of carbon and nitrogen

The detailed researches are done in the speciation analyses of carbon and nitrogen, and the analytical results are shown in Table 4.

Table 4 The contents of organic nitrogen and inorganic and organic carbon in seven typical waters

Code	pH	PON-N	DON-N	POC-C	DOC-C	PIC-C	DIC-C
01	4.01	0.940	0.440	0.146	2.834	0.042	0.172
02	4.63	0.550	0.220	0.200	3.427	0.286	0.174
03	6.41	1.570	0.690	0.505	5.051	0.066	4.180
04	7.02	4.450	0.760	1.406	3.104	0.051	0.886
05	5.65	0.100	0.220	1.089	2.955	0.167	0.945
06	5.48	0.490	0.180	1.083	3.261	0.053	0.947
07	8.09	1.570	1.190	2.882	7.646	0.342	12.000

Unit: mg/L

From Table 3, DON, NO_2^- , POC, DOC, DIC and HCO_3^- are positively correlated with pH

($P < 0.1$), which means that pH increases with the contents of these species of nitrogen and carbon, and also these species are positively correlated with K^+ , Na^+ , Ca^{2+} , and Mg^{2+} at $P < 0.05$. The PON and PIC show less important in the relationship with water acidification.

3.6 Change in water quality during flowing of mountain stream

In the May of 1991, mountain stream water formed by rainwater and flowing into waters 02 was taken and analyzed (Table 5). Waters 02 and waters 01 in Jinyun Mountain are near away and joined with a water-pipe. The quality of water flowing into waters 01 is assumed to be the same with that flowing into waters 02.

Table 5 Change in chemical composition during flowing of mountain stream

Sample	pH	H ⁺	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	NH ₄ ⁺	K ⁺	Na ⁺	Unnit: $\mu\text{eq/L}$	
									Ca ²⁺	Mg ²⁺
Rainwater	4.36	44	38	148	20	87	24	30	48	12
Mountain stream	4.50	32	89	458	182	3	15	37	80	202
Waters 02	5.60	3	44	472	162	13	44	30	227	219
Waters 01	4.60	25	52	444	198	0	22	24	35	223

3.6.1 Change of H⁺ concentration from rainwater to waters

From Table 5, the concentration of active H⁺ decreases 27% from rainwater to the mountain stream because of the buffering action of soil. And from the mountain stream to waters 01 the concentration decreases 22%, because of the buffering action of the waters. In waters 02 there was a more powerful buffering action because of artificial addition of lime which is stated in Fig. 2 and Fig. 4. Therefore, in 1991 the soil and the acidified waters in Jinyun Mountain could buffer a small part of active H⁺ from rainwater. But in 1992 the values of pH in the two waters decreased continuously to 4.63 and 4.01 respectively (Fig. 2), the buffering capacities had become less than that in 1990. The results also showed that the soil had been acidified seriously.

3.6.2 The changes of sulfate and nitrate

Table 5 shows that the sulfate in rainwater occupied 32% of the total concentration in the mountain stream. 68% of that was from the dissolution from the soil. 11% of nitrate in the mountain stream was from rainwater and 89% from the dissolution of the soil. The results showed that a great amount of sulfate and nitrate had been accumulated by the soil, and the conclusion is consistent within a published paper (Di, 1989). The concentrations of sulfate and nitrate in waters 02 and waters 01 were almost equal to those in the mountain stream, the results showed sulfate and nitrate in the waters were from the mountain stream, hardly from sediment in the waters, and the waters were difficult to adjust the concentrations of sulfate and nitrate.

3.6.3 The changes of NH₄⁺, K⁺, Na⁺, Ca²⁺ and Mg²⁺

There was high content of NH₄⁺ in rainwater in Jinyun Mountain area (Table 5). But the concentrations in the mountain stream and the waters were very low, which showed the soil strongly absorbed or decomposed NH₄⁺, and the denitrification action in waters was weak. The changes of K⁺ and Na⁺ from rainwater to the waters was not significant, it is possibly because of their weak capability of ion-exchange. In waters 02 the concentration of Ca²⁺ was significantly

higher than those in rainwater and mountain stream, which was due to artificial addition of lime that has been stated above in this paper. The concentrations of Mg^{2+} in the mountain stream and waters were very close, but significantly higher than that in rainwater. 94% of Mg^{2+} in the mountain stream was from the dissolution from soil and the aquatic environment of the waters hardly caused the change of the concentration of Mg^{2+} . The result showed Mg^{2+} in soil in Jinyun Mountain area possibly played an important role in adjusting pH of the mountain stream or the waters because of the ion - exchange of a great amount of Mg^{2+} .

4 Conclusion

In suburban areas of Chongqing City there had been some small acidified waters, and the acidification of waters in some areas had been becoming more seriously (for example, that in Jinyun Mountain).

In the acidified waters, there are high SO_4^{2-} and NO_3^- contents, but low TIC, K^+ , Na^+ , Ca^{2+} , Mg^{2+} contents. Sulfate and nitrate in waters are from rainwater and dissolution from the soil around the waters, hardly from sediments. Mg^{2+} and Ca^{2+} in soil around the waters or in the waters played an important role in buffering active H^+ because of ion - exchange or alkalinizing action, and changes of K^+ and Na^+ from rainwater to waters were not significant. The capacities of adjusting pH are $Ca^{2+} > Mg^{2+} > K^+ > Na^+$.

The concentration of Al^{3+} in the waters is mainly controlled by the concentration of active H^+ , hardly correlated with other chemical properties in the waters, and there is significant linear relationship between logarithm of Al^{3+} concentration and pH.

From correlation analyses between organic nitrogen or carbon and pH, organic substance do not cause the increase of active H^+ content. The causes of the acidification of the waters are concluded mainly from heavy acid precipitation and weak buffering capacity of the aquatic environment.

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