Evaluation of aluminum speciation in surface waters in China and its environmental risk assessment

S.P. Bi · N. Gan · X.C. Lu · H.Y. Ni · H. Lin · X.L. Wang · Z.B. Wei

Abstract As the ongoing global research on acid precipitation is developing in depth, more and more attention has been paid to the ecological effects of aluminum (Al) due to its toxicity to plants and animals, which is caused by acid precipitation. As a very serious problem of terrestrial and aquatic environmental acidification occurs in China, especially in southwestern China, a systematic investigation of Al speciation in these regions is very important. In this paper, the Al speciation results of surface waters in China are reported and its ecological impacts is evaluated. More than 100 water samples were collected from about twenty provinces of China. Driscoll's Al speciation scheme combined with the modified MINQEL computer model is used for speciation of Al. This study shows that the ecological impacts of acidification are quite different between China and Western countries, because of different geographical environments and geological settings. In Western countries, acidification is mainly caused by NO_2^-. Due to low concentrations of K^+, Na^+, Ca^{2+}, Mg^{2+}, the buffer capacities of soil and water are weak. Therefore, natural waters can be acidified to pH<5 very easily, resulting in a considerable mobilization of Al and worsening of the ecological environment. In China, acid precipitation is mainly in the form of sulfuric acid. In northwestern China, concentrations of K^+, Na^+, Ca^{2+}, Mg^{2+} are high in soil and surface waters. This leads to much higher capacity and a high resistance ability to acidification. The pH values of waters in this region are high (around 7) and no serious Al toxicity is found at present. However, in northeastern and southeastern China, the soil is rich in Al (unsaturated aluminosilicates in northeastern China, saturated aluminosilicates in north and central China, aluminum-rich soil in southeastern and southwestern China). The concentrations of K^+, Na^+, Ca^{2+}, Mg^{2+} in soil and waters are lower than those of northwestern China. Therefore the buffer capacity is limited. Numerous surface waters have already been acidified and pH values declined to 5. The impacts of Al toxicity on ecological systems in these regions are very serious, especially in Jiangxi, Hubei Provinces and Chongqing Municipality.

Keywords Aluminum speciation · Surface water · Risk assessment

Received: 28 October 2002 / Accepted: 6 May 2003

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Introduction

Environmental acidification with its associated high aluminum (Al) concentrations in soils and surface waters is one of the most important global problems (Sposito 1996). Al represents an important biogeochemical linkage between terrestrial and aquatic environments exposed to acid precipitation (Gensemer and Playle 1999; Benyahya and Garnier 1999). Atmospheric inputs of sulfuric acid and nitric acid to soil lead to comparatively high concentrations of dissolved Al in surface waters. Elevated Al concentrations are harmful to fish and biota (De la Fuente JM and others 1997). As Al toxicity is dependent on its speciation rather than the total concentration, it is critical to obtain speciation information when evaluating the ecological effects of this element.

During the last two decades, there have been substantial studies on Al speciation and its ecological effects for Western countries, such as the United States, Canada, Norway, Sweden and Germany (Sposito 1996; Bi 2000; Ludwig and others 1997). As ongoing research on acid precipitation develops in depth in China, more and more attention is being paid to environmental risk assessment of Al. This is because a serious problem of terrestrial and aquatic environmental acidification continues to occur in China, particularly in southwestern China (National Science Foundation of China 1996). However, the systematic investigation of Al speciation in surface water in China is

DOI 10.1007/s00254-003-0847-5

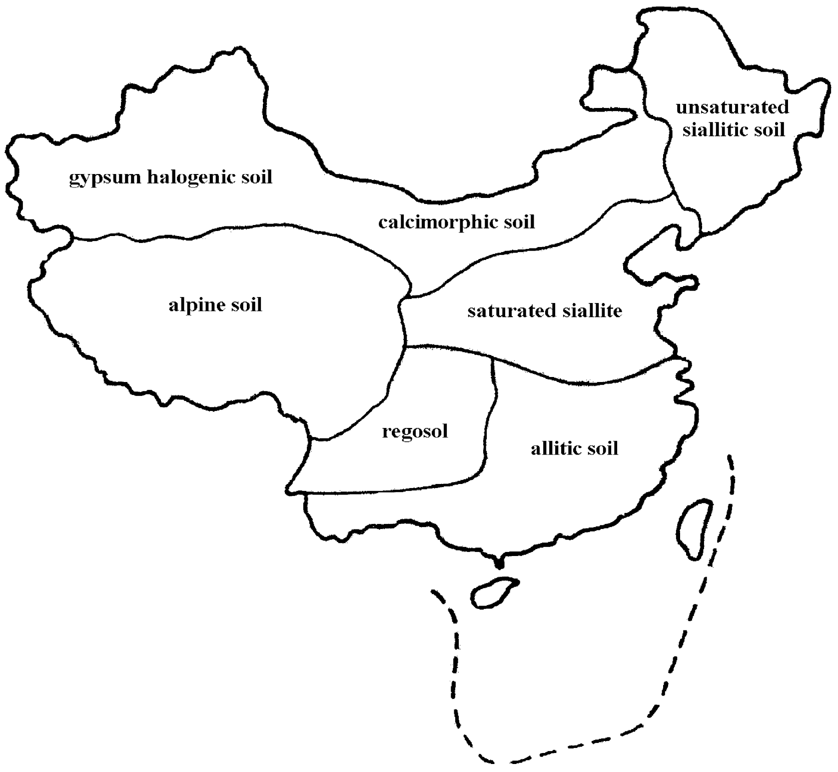

Fig. 1
Map of China showing the different geological settings with different types of soils

still lacking. The geology in Western countries differs from that of China. It is important therefore to consider the geological differences when comparing the characteristics of Al speciation in surface waters among these areas. It will be helpful to gain insight into the mechanism of Al mobilization from soils and transportation into surface waters. Figure 1 is a map showing the seven types of soil in different geological settings in China: unsaturated siallite soil, saturated siallite soil, alpine soil, calcimorphic soil, allitic soil, regosol soil, and gypsum halogenic soil (Nanjing University 1980; Xia 1987; Wei et al. 1992). In this paper, the authors report the distribution of Al species in surface waters in China and assessment of its environmental risk. Comparisons of the chemical parameters in surface waters of China and Western countries are carried out.

Experimental

Apparatus

A Varian AA-475 atomic absorption spectrometry (GF/AAS) with GTA 95-graphite furnace (Varian Company, USA) was used to analyze Al concentrations. A Beckman 900 carbon analyzer (Beckman Company, USA) was used to determine the total dissolved organic carbon (TOC). An Orion-1 ion analyzer (Orion Company, USA) was used to measure the pH values. An 1100 ICP-AES spectrometer (Jarrell-Ash Company, USA) was used to measure the basic cations (Na^+, K^+, Ca^{2+} and Mg^{2+}). A Dionex^R Ion Chromatography was used to determine anions (Cl^-, F^-, SO_4^{2-}, and NO_3^-).

Chemicals

Al stock solution 10^{-2} mol/l was prepared by dissolving adequate amounts of high-purity Al powder in 1:1 HCl. Working standards were prepared by diluting stock solution. The other solutions were: 0.1 mol/l NaCl solution, 1 mol/l HAc-NH_4Ac (pH 5.8) buffer solution, 1 mol/l NaOH, 2% 8-HQ+1 mol/l HAc solution and 1 mol/l NaCl+1 mol/l HCl solution. All chemicals were of analytical reagent grade. The water used for preparing solutions was doubly distilled quartz water.

A cation-exchange resin (732 H^+ form, 14–52 mesh) was used in this study. It was first cleaned by soaking it in 20 mL 5 mol/l HCl for 24 h, and then was converted into the Na^+ form by soaking it in 1 mol/l NaOH for another 2 h, followed by rinsing in a beaker with distilled water. The cation-exchange column was 0.7 cm in diameter and 15 cm in length and contained 10 cm 732 cation-exchange resin. Before analysis, the resin was equilibrated with 0.1 mol/l NaCl solution at the pH of the particular sample analyzed to minimize the change of pH when samples pass through the exchange column.

Sample collection and speciation procedure

A total of 50 surface water samples (from river, stream or lakes) were collected from about twenty provinces of China. The samples were collected in individual 500-ml bottles. In the laboratory, they were stored in the refrigerator (4 °C). The general procedure used for speciation of

Table 1
Speciation of Al in surface waters by Driscoll's method in different areas of China (μmol/l)

No.	Site	Total Al	Monomeric Al	Acid soluble Al	Inorganic monomeric Al	Organic monomeric Al
	Gypsum Halogenic soil (Xinjiang Province)					
1	Yili River, Xinjiang	7.41	4.29	3.12	2.28	2.01
2	Talimu River, Xinjiang	7.78	4.88	2.90	3.01	1.87
3	Wulumuqi River, Xinjiang	7.41	6.20	1.21	5.30	0.90
	Average	*7.53*	*5.12*	*2.41*	*3.53*	*1.59*
	Alpine soil (Xizhang and Qinghai Provinces)					
4	Niyang River, Xizhang	2.59	2.50	0.09	2.30	0.20
5	Moucu River, Xizhang	8.88	8.80	0.08	8.30	0.50
6	Lasha River, Xizhang	5.93	5.60	0.33	5.60	0.00
7	Yagong River, Xizhang	5.56	5.50	0.06	5.30	0.20
8	Yaluzhangpu river, Xizhang	15.6	14.3	1.30	12.1	2.20
9	Xining River, Qinghai	6.59	6.20	0.39	5.10	1.10
	Average	*7.53*	*7.15*	*0.38*	*6.45*	*0.70*
	Calcimorphic soil (Gansu,Ningxia and Neimenggu Provinces)					
10	Qilan mountain, Gansu	10.10	9.80	0.30	9.80	0.00
11	Hegu River,Yingcuan, Gansu	9.26	0.96	8.30	0.63	0.33
12	Dunhuang Spring, Gansu	8.15	0.88	7.27	0.63	0.25
	Average	*9.17*	*3.88*	*5.29*	*3.69*	*0.19*
	Regosol (Sichuan,Guizhou, Yunnan Provinces and western Chongqing,					
13	Mianyang, Sichuan	7.03	4.44	2.59	2.65	1.79
14	Jiuzhai channel,Sichuan	5.93	5.31	0.62	5.10	0.21
15	Guiyang River, Guizhou	7.03	4.46	2.57	3.25	1.21
16	Kunming River,Yunnan	4.81	2.39	2.42	1.38	1.01
	Average	*6.20*	*4.15*	*2.05*	*3.10*	*1.06*
	Unsaturated siallitic soil (Heilongjiang, Jinlin Provinces)					
17	Changbai sky pool, Jilin	4.63	2.48	2.15	2.43	0.05
18	Changbai Spring, Jilin	5.13	3.45	1.68	3.38	0.07
19	Changchun	5.92	4.00	1.92	3.55	0.45
20	Songhua river, Jinlin	3.52	3.59	0.00	3.35	0.24
	Average	*4.80*	*3.38*	*1.44*	*3.18*	*0.20*
	Saturated Siallitic soil (Liaoning, Shanxi,Sanxi, Shandong, Henan, Jiangsu, Anhui Provinces and eastern Chongqing, Beijing)					
21	Jiuhua mountain, Anhui	3.73	3.70	0.03	3.20	0.50
22	Cao lake, Anhui	8.52	4.88	3.64	1.49	3.39
23	Xiangshui River, Anhui	4.81	4.07	0.74	4.04	0.03
24	Crescent Lake, Nanjing	6.56	4.91	1.65	3.79	1.12
25	Wuxi, Jiangsu	4.30	4.13	0.17	3.07	1.06
26	Nantong river, Jiangsu	6.67	6.43	0.24	6.00	0.43
27	Huaian River, Jiangsu	5.96	5.78	0.18	4.53	1.25
28	Yuyuan pond, Beijing	5.19	3.90	1.29	2.95	0.95
29	Suining River, Jiangsu	12.3	10.8	1.50	7.22	3.58
30	Taiyuan River, Shanxi	11.9	7.96	3.94	4.83	3.13
31	Jining river, Shandong	10.2	8.47	1.73	6.96	1.51
32	Weinan river, Sanxi	12.6	11.4	1.20	10.1	1.34
33	Zhengzhou river, Henan	10.7	5.63	5.20	2.50	3.13
34	Jinzhou in dalian, Liaoning	4.07	3.13	0.94	1.89	1.24
35	Wafangdian, Liaoning	6.30	4.31	1.99	2.80	1.51
	Average	*7.59*	*5.96*	*1.62*	*4.36*	*1.61*
	Allitic soil (Guangxi, Guangdong, Hunan, Jiangxi, Hubei, Fujian Provinces)					
36	Qutang gorge, Hubei	24.1	20.2	3.90	15.2	5.00
37	Gezhouba, Hubei	18.1	14.1	4.00	12.1	2.00
38	Zong county, Chongqing	17.1	16.4	0.70	14.5	1.90
39	Jiujiang, Jiangxi	19.6	13.21	6.40	9.00	4.21
40	Nanchang, Jiangxi	15.2	10.63	4.60	6.44	4.19
41	Linchuan, Jiangxi	11.5	8.47	3.00	7.66	0.81
42	Hong Kong	9.26	6.50	2.76	3.88	2.62
43	Macao River	12.3	10.50	1.75	6.30	4.20
44	Zhuhai, Guangdong	7.78	3.04	4.74	2.02	1.02
45	Hepu, Guangxi	5.10	4.65	0.45	4.40	0.25
46	Guilin, Guangxi	4.61	4.50	0.11	4.20	0.30
47	Xiameng, Fujian	4.44	3.81	0.63	2.40	1.41
48	Zhangjiajie, Hunan	6.30	5.34	0.96	3.32	2.02
49	Changsha, Hunan	4.07	2.16	1.91	1.21	0.95
50	Yueyang, Hunan	6.30	3.78	2.52	2.64	1.14
	Average	*11.1*	*8.49*	*2.56*	*6.35*	*2.13*

Table 2
Speciation of Al by MINEQL computer model for those surface waters with higher inorganic monomeric Al (in µmol/l) (The data in parentheses stand for percentages of Al species)

No.	Sites	pH	Al^{3+}	$AlOH^{2+}$	$Al(OH)_2^+$	$Al(OH)_3$	$Al(OH)_4^-$	Al-SO_4	Al-F	Sum of (Al^{3+}+A-lOH^{2+} +$Al(OH)_2^+$)	C^*_F and C^*_{SO4}[a]
3	Wulumuqi, Xinjiang	6.35	0.004 (0.07%)	0.089 (1.67%)	1.94 (36.58%)	0.754 (14.23%)	0.972 (18.33%)	0.001 (0.03%)	1.54 (29.05%)	2.03	*a
5	Mouchu river, Xizhang	6.62	0.001 (0.02%)	0.054 (0.65%)	2.19 (26.37%)	1.59 (19.1%)	3.80 (45.82%)	0.001 (0.01%)	0.729 (8.79%)	2.25	*a
6	Lasha river, Xizhang	6.53	0.001 (0.03%)	0.054 (0.94%)	1.74 (30.99%)	1.02 (18.25%)	1.99 (35.58%)	0.001 (0.01%)	0.835 (14.92%)	1.80	*a
7	Yagongriver, Xizhang	6.45	0.002 (0.04%)	0.066 (1.24%)	1.80 (34.04%)	0.884 (16.67%)	1.43 (27.04%)	0.001 (0.02%)	1.10 (20.93%)	1.87	*a
8	Yaluzhangpu River, Xizhang	5.89	0.090 (0.74%)	0.712 (5.88%)	5.40 (44.62%)	0.728) (6.02%	0.325 (2.69%)	0.037 (0.3%)	4.84 (39.97%)	6.20	*a
9	Xining, Qinghai	6.73	0.001 (0.01%)	0.019 (0.38%)	1.01 (19.74%)	0.94 (18.42%)	2.90) (56.93%	0.0 (0.0%)	0.248 (4.87%)	1.03	*a
10	Qilian mountain-spring, Gansu	6.5	0.003 (0.03%)	0.105 (1.07%)	3.26 (33.21%)	1.77 (18.25%)	3.25 (33.21%)	0.001 (0.01%)	1.39 (14.2%)	3.37	*a
14	Jiuzai channel, Sichuan	5.38	0.158 (3.10%)	0.388 (7.6%)	0.909 (17.82%)	0.038 (0.74%)	0.005 (0.1%)	0.036 (0.7%)	3.57 (70.03%)	1.46	C^*_F= 2.63 C^*_{SO4}= 22
26	Nantong, Jiangsu	7.73	0.00 (0.00%)	0.00 (0.00%)	0.02 (0.33%)	0.187 (3.12%)	5.79 (96.54%)	0.00 (0.00%)	0.00 (0.00%)	0.02	*a
29	Suining, Jiangsu	7.7	0.00 (0.00%)	0.00 (0.00%)	0.028 (0.38%)	0.241 (3.34%)	6.95 (96.28%)	0.00 (0.00%)	0.00 (0.00%)	0.028	*a
30	Taiyuan, Shanxi	6.85	0.00 (0.00%)	0.009 (0.2%)	0.653 (13.52%)	0.803 (16.63%)	3.27 (67.74%)	0.00 (0.00%)	0.985 (2.04%)	0.662	*a
32	Weinan river,Sanxi	8.2	0.00 (0.00%)	0 (0%)	0.004 (0.04%)	0.115 (1.08%)	10.5 (98.88%)	0.00 (0.00%)	0.00 (0.00)	0.004	*a
36	Qutang gorge,Hubei	5.45	0.530 (3.49%)	1.53 (10.06%)	4.21 (27.71%)	0.206 (1.16%)	0.006 (0.04%)	0.216 (1.43%)	8.47 (55.7%)	6.27	*a
37	Gezoubai, Hubei	5.82	0.114 (0.94%)	0.768 (6.35%)	4.96 (41.0%)	0.570 (4.71%)	0.217 (1.79%)	0.047 (0.38%)	5.43 (44.86%)	5.84	*a
38	Zhong County, Chongqing	5.32	.880 (6.07%)	1.88 (12.98%)	3.84 (26.5%)	0.139 (0.96%)	0.017 (0.12%)	0.360 (2.84%)	7.50 (51.74%)	6.6	*a
39	Jiujiang Jiangxi	5.75	0.175 (1.94%)	1.00 (11.16%)	5.52 (61.35%)	0.54 (5.99%)	0.174 (1.94%)	0.026 (0.29%)	1.58 (17.54%)	6.70	C^*_F=2.63 C^*_{SO4}= 148
40	Nanchang,Jiangxi	5.77	0.110 (1.70%)	0.66 (10.25%)	3.80 (58.98%)	0.389 (6.04%)	0.132 (2.05%)	0.020 (0.32%)	1.37 (21.35%)	4.57	C^*_F=2.63 C^*_{SO4}= 182
41	Linchuan, Jiangxi	5.65	0.174 (2.70%)	0.795 (12.34%)	3.47 (53.87%)	0.27 (4.18%)	0.692 (1.07%)	0.827 (1.28%)	1.57 (24.48%)	4.43	C^*_F=2.63 C^*_{SO4}= 465
43	Mecao	6.75	0.00 (0.00%)	0.02 (0.34%)	1.17 (18.64%)	1.15 (18.22%)	3.71 (58.95%)	0.00 (0.00%)	0.263 (4.17%)	1.19	*a

[a] *a: C^*_F=10 µmol/l, C^*_{SO4}=400 µmol/l

Al in natural waters is similar to that described by Driscoll (1984). Five fractions of Al are obtained as follows:

1. Total reactive Al_T: the original sampled waters were acidified by HNO_3 at pH=1 for 24 h and then determined for Al concentration by GF/AAS.
2. Total monomeric Al_a: to 25 ml of solution ready for determination, 5 ml of 1 mol/l HAc-NH_4Ac (pH 5.8) and 2 ml of 2% 8-HQ were first added, followed by adjustment of the solution pH to 8.5 with 6 mol/l $NH_3{\cdot}H_2O$. Next, 50 ml of MIBK (Methyl Isobutyl Ketone) was added and the solution was shaken for 12 s. After separating aqueous and organic phases, the Al species in chloroform phase were immediately determined by GF/AAS.
3. Organic monomeric Al_o and inorganic monomeric Al_i: The first 50 ml of the sample solutions were passed through the column to replace the eluate and then discarded. Then, 50 ml of sample were passed through the prepared column at a flow rate of 2 ml/min. The elute was collected for determining Al_o species by GF/AAS. Inorganic monomeric Al species retained by the resin were eluted with 10 ml 1 mol/l NaCl-HCl into a plastic beaker at a flow rate of 2 ml/min. The solution was gathered for determining Al_i by GF/AAS. After separation, the column was regenerated with a certain volume of distilled water and 0.1 mol/l NaCl before the next separation.
4. Inorganic monomeric Al_i: it was calculated as the difference between total monomeric Al and organic monomeric Al, namely, Al_a–Al_o.

Table 3
Water compositions in surface waters from different areas of China (mg/l) (ND: not detected)

No.	Sector sites	pH	DOC	Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	Cl^{-}	NO$_3^{-}$	SO$_4^{2-}$
	Gypsum halogenic soil (Xinjiang Province)									
1	Yili River, Xinjiang	6.73	2.72	38.2	5.80	1.30	6.90	7.18	11.9	34.0
2	Talimu River, Xinjiang	6.84	1.90	35.2	6.30	1.50	7.30	17.0	ND	6.06
3	Wulumuqi River, Xinjiang	6.35	6.75	91.2	72.7	0.32	35.2			
	Average	*6.64*	*3.79*	*54.9*	*28.3*	*1.04*	*16.5*	*12.1*	*11.9*	*20.0*
	Alpine soil (Xizhang, Qinghai Provinces)									
4	Niyang River, Xizhang	6.62	0.44	14.2	2.35	0.25	1.99			
5	Moucu River, Xizhang	6.62	0.56	63.7	15.6	1.00	16.3			
6	Lasha River, Xizhang	6.53	0.55	26.7	4.64	0.43	4.36			
7	Yagong River, Xizhang	6.45	0.78	42.3	8.85	0.00	5.91			
8	Yaluzhangpu river, Xizhang	5.89	0.99	35.9	7.41	0.36	8.59			
9	Xining River, Qinghai	6.73	1.28	78.7	15.4	8.27	44.5			
	Average	*6.47*	*0.77*	*43.6*	*9.04*	*1.72*	*13.6*			
	Calcimorphic soil (Gansu,Ningxia,Neimenggu Provinces)									
10	Qilan mountain, Gansu	6.50	0.21	130	52.1	1.02	19.0			
11	Hegu river,Yingcuan, Gansu	6.62	0.08	20.5	3.80	ND	4.80	3.64	ND	19.2
12	Dunhuang spring, Gansu	6.72	3.85	35.1	6.40	0.80	7.20	7.93	9.52	26.6
	Average	*6.61*	*1.38*	*61.9*	*20.8*	*0.91*	*10.3*	*5.79*	*9.52*	*22.9*
	Regosol (Sichuan,Guizhou,western Chongqing, Yunnan Provinces)									
13	Mianyang, Sichuan	6.96	2.16	79.5	13.9	ND	1.57	3.89	48.2	14.6
14	Jiuzhai channel, Sichuan	5.38	1.84	45.9	9.73	2.31	12.4	13.2	12.4	21.1
15	Guiyang River, Guizhou	6.86	2.15	79.8	18.9	0.71	3.42	5.79	ND	39.8
16	Kunming River, Yunnan	7.88	10.4	46.8	10.3	ND	1.05	5.22	1.28	15.0
	Average	*6.77*	*4.14*	*63.0*	*13.2*	*1.51*	*4.61*	*7.03*	*20.6*	*22.6*
	Unsaturated siallitic soil (Heilongjiang, Jinlin Provinces)									
17	Changbai sky pool, Jilin	8.23	0.10	73.2	9.74	4.33	31.7	10.7	1.00	15.1
18	Changbai Spring, Jilin	8.20	1.25	62.5	11.2	3.43	31.5	3.70	1.00	5.40
19	Changchun	7.56	9.61	57.6	13.4	11.2	37.6	13.7	5.46	14.5
20	Songhua river, Jinlin	7.62	27.2	55.8	24.8	2.95	3.47	8.60	6.30	5.00
	Average	*7.90*	*9.54*	*62.3*	*14.8*	*5.48*	*26.1*	*9.18*	*3.44*	*10.0*
	Saturated siallitic soil (Liaoning, Shanxi, Sanxi, Shandong,Henan, Jiangsu,Anhui Provinces and,eastern Chongqing, Beijing)									
21	Jiuhua mountain, Anhui	6.87	5.39	44.3	3.70	0.97	3.52			
22	Cao pool, Anhui	5.67	3.32	18.5	5.63	6.22	14.9	6.61	2.55	20.6
23	Xiangshui river, Anhui	5.75	2.25	49.8	11.1	ND	0.89	3.36	0.20	6.58
24	Crescent Lake, Nanjing	6.10	21.6	23.0	2.80	5.23	29.2	38.2	2.20	6.40
25	Wuxi, Jiangsu	8.15	19.4	16.2	21.9	10.3	2.27	41.0	16.3	56.1
26	Nantong river, Jiangsu	7.73	12.4	74.8	78.1	37.5	40.0	8.70	2.30	4.00
27	Huaian river, Jiangsu	7.55	18.9	67.3	6.30	14.7	43.4	10.7	1.70	2.80
28	Yuyuan pond, Beijing	7.02	11.1	53.5	39.2	2.80	85.1	45.30	ND	78.7
29	Suining River,Jiangsu	7.70	48.4	146	43.1	<0.3	94.4	10.60	1.80	21.9
30	Taiyuan River,Shanxi	6.85	4.41	286	57.1	1.00	58.2	12.30	30.4	21.9
31	Jining River, Shandong	7.15	37.6	85.6	56.1	9.80	189	10.50	0.60	20.5
32	Weinan River, Sanxi	8.20	25.1	41.8	34.6	0.90	90.4	9.50	0.60	2.60
33	Zhengzhou river, Henan	6.87	11.2	29.5	6.20	23.4	80.9	10.20	ND	67.0
34	Dalian, Liaoning	6.27	1.71	39.4	5.30	1.67	6.80	12.80	13.2	15.4
35	Wafangdian, Liaoning	6.97	4.29	54.5	9.98	0.54	12.0	12.80	0.39	8.14
	Average	*6.99*	*15.1*	*68.7*	*25.4*	*8.85*	*50.1*	*16.6*	*6.02*	*23.8*
	Allitic soil (Guangxi, Guangdong, Hunan, Jiangxi, Hubei, Fujian provinces)									
36	Qutang gorge, Hubei	5.45	4.21	49.6	10.4	0.49	11.2			
37	Gezhouba, Hubei	5.82	8.73	49.2	10.2	0.49	10.5			
38	Zong County, Chongqing	5.32	5.68	50.2	10.7	0.64	11.4			
39	Jiujiang, Jiangxi	5.75	5.60	61.5	11.3	1.33	12.4	24.1	0.39	14.2
40	Nanchang pond, Jiangxi	5.77	7.39	32.9	7.67	31.7	29.3	22.8	1.18	17.5
41	Linchuan, Jiangxi	5.65	5.43	40.1	6.20	2.20	9.00	4.71	6.75	44.7
42	Hong Kong	5.61	72.0	26.1	3.00	6.00	19.5	98.6	ND	10.6
43	Macao	6.75	13.2	27.7	79.3	28.4	18.6			
44	Zhuhai, Guangdong	6.37	5.54	86.5	50.3	21.4	42.8	36.1	16.8	20.3
45	Hepu, Guangxi	6.80	6.45	1.64	0.29		2.27			
46	Guilin, Guangxi	5.87	3.46	48.8	3.83		1.25			
47	Xiameng, Fujian	7.13	19.5	16.8	4.60	2.80	19.4	9.21	ND	17.0
48	Zhangjiajie, Hunan	6.17	20.6	72.2	4.23	<0.3	1.08	1.01	ND	0.23
49	Changsha, Hunan	7.17	1.52	39.4	5.14	2.10	6.68	53.0	1.24	14.5
50	Yueyang, Hunan	6.75	4.76	37.1	6.51	1.77	5.90	34.4	1.43	6.63
	Average	*6.16*	*12.3*	*42.7*	*14.2*	*8.28*	*13.4*	*31.6*	*4.63*	*16.2*

Table 4
Comparison of the basic water quality data among China and Western countries (mg/l)

No.	Country	Ca^{2+}	Mg^{2+}	K^+	Na^+	Cl^-	SO_4^{2-}	NO_3^-	pH	C*Al-totle	Reference
1	China	56.7	18.0	3.97	19.2	13.7	19.3	9.35	6.79	0.208	This study (average values)
2	Mount Moosilauke fir zone sites, New Hampshire, USA	0.52	0.23	0.39	0.30	0.25	6.34	0.93	4.66	1.81	Cronan and Schofield 1979
3	Hubbard Brook, New Hampshire, USA	1.65	0.38	0.23	0.88	0.54	6.23	1.93	4.90	0.23	Johnson and others 1981
4	Stream, Pennsylvania, USA	1.63	0.59	0.38	0.95	2.50	3.58	0.72	6.20	0.014	DeWalle and Swistok 1994
5	Stream in Birkenes, Norway	1.34	0.48	0.13	2.83	4.37	14.6	0.43	4.48	0.63	Christophersen and others 1982
6	Hagfor Catchment, Sweden	1.21	0.58	0.16	1.20	1.82	7.30	0.02	4.57	0.386	Fransman and Nihlgard 1995
7	Llyn Brianne reservoir, UK	1.60	0.94				6.60	0.20	5.30	0.169	Goenaga and Williams 1988
8	River Duddon Catchment, UK	0.94	0.50	0.10	3.36	5.43	4.56	0.62	4.80	0.21	Tipping 1989
9	Slavkov Forest Mountains, Czech Republic	1.34	0.44	0.48	1.11	1.65	13.7	1.13	3.55	0.56	Hruska and others 1996
10	Teganuma lake, Japan	24.1	6.8	4.7	24.2	29.2	32.0	6.9		0.062	Naoe and others 1991

5. Acid soluble Al_r: it was calculated as the difference between total reactive Al and total monomeric Al, namely, $Al_T{-}Al_a$.

All experiments were carried out at room temperature. Combined with the modified MINQEL computer model, distribution of Al speciation in water samples may be quickly assessed.

Results and discussion

Total Al concentrations and speciation of Al in surface waters in different geological settings of China

Table 1 gives the results of five fractions of Al concentrations in 50 surface water samples representing different geological settings of China obtained by Driscoll's (1984) method. The result indicates that different geological conditions affect the form and concentrations of Al species in surface waters. Based on these differences, three different regions are noted: (1) region with lower total Al concentration 0.130 mg/l in surface waters with a higher pH value 7.90. It is in the area of northeastern China and the soil type is unsaturated siallitic soil; (2) region of moderate total Al concentration with an average value of 0.195 mg/l and moderate pH value of 6.72. The soil types are gypsum halogenic soil (northwestern China), alpine soil (western China) and calcimorphic soil (north China); and (3) region of higher total Al concentration with an average value of 0.274 mg/l and lower pH 6.39. The soil types are regosol (southwestern China) and saturated siallitic soil (in the middle of China). The five Al fractions exhibit the following regression equations: $[Al_T]$ (μmol/l) $=192.6e^{-0.4641pH}$, $R^2=0.5248$; $[Al_a]$ (μmol/l)$=-3.712pH+32.25$, $R^2=0.5130$; $[Al_i]$ (μmol/l)$=-2.432pH+22.175$, $R^2=0.4937$; $[Al_r]$(μmol/l)$=-6.750Ln(pH)+14.98$, $R^2=0.4496$; and $[Al_o]$ (μmol/l)$=-1.270pH+10.50$, $R^2=0.5035$. Since the waters samples are collected from different regions with different geological settings, the low values of R^2 listed in above equations are reasonable.

The toxicity of Al to fish is dependent on its speciation and therefore is greatly dependent on pH. Al has its maximum toxicity to fish at about pH 5 at the concentration as low as 100 μg/l (Miller and Andelman 1987). It has been identified that the most toxic forms are Al^{3+}, $AlOH^{2+}$ and $Al(OH)_2^+$, but complexing agents, such as organic acids and fluoride, can decrease greatly toxic aquo-and hydroxo-Al. The critical concentration of these toxic forms ($Al^{3+}+AlOH^{2+}+Al(OH)_2^+$) is about 4 μmol/l (Baker and Schofield 1982). To further assess the environmental risk of elevated Al concentrations, the modified computer model MINEQL (Bi and others 1997) was utilized for the speciation of Al in those surface waters with higher inorganic monomeric Al_i concentrations (>5 μmol/l). Table 2 indicates that: (1) Hubei, Jiangxi Provinces, Guangxi regional national autonomy, Hong Kong Special Administration Region, and Chongqing municipality are suffering serious acidification. The pH values of surface waters are below 6 (pH 5.32–5.82. No.36–41), and the sum of toxic form of Al concentrations ($Al^{3+}+AlOH^{2+}+Al(OH)_2^+$) are over 4 μmol/l. Therefore, in these areas the toxicity of Al is serious. It has already been reported that in these areas there have been numerous forests that have declined in the past twenty years due to the Al toxicity caused by acid rain (Bi and others 1997); (2) In other regions with surface waters pH over 6, Al-F or $Al(OH)_4^-$ complexes are the dominant species. The toxic forms of Al concentrations are below the critical value. Therefore, in these areas, the toxicity of Al is not serious.

Comparison between basic water compositions in surface waters of China and Western countries

Tables 3 and 4 give the basic water compositions in 50 typical surface waters and the comparison results for Al concentrations and basic water quality data among China and Western countries. This study shows that the environmental impacts of acidification are quite different between China and Western countries (Sposito 1996; Driscoll and Schecher 1990; Bi 1995) as well as among the various areas in China, because of different geographical environments and geological settings. In Western countries, acidification is mainly caused by NO_2^-. Due to low concentrations of K^+, Na^+, Ca^{2+}, Mg^{2+}, the buffer capacities of soil and water are weak. Therefore, natural waters can be acidified to $pH<5$ very easily, resulting in a considerable mobilization of Al and the worsening of the ecological environment. In China, acid precipitation is mainly in the form of sulfuric acid. Concentrations of K^+, Na^+, Ca^{2+}, Mg^{2+} are high in surface waters. This brings the strong buffering capacity and resistance ability for acidification. Therefore, pH values of surface waters in most regions of China are high (around 7) and no serious Al toxicity is found at present. Only in the south and middle of China, the soil is rich in Al (saturated aluminosilicates and allitic soil). Some surface waters have already been acidified and pH values declined down to 6. The impacts of Al toxicity on ecological systems in these regions are serious, especially in Jiangxi, Hubei Provinces and Chongqing Municipality.

Acknowledgements The project is financially supported by the National Science Foundation of China (Key Project No: 49831005 & 29777013), Research Funding from State Education Ministry of China for Young Teachers, and Visiting Fellowship from Berkeley Lawrence National Laboratory (USA). The authors thank Profs. Xiaorong Wang, Guoliang Ji and Tianren Yu for their encouragement and assistance.

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