Aluminium Mobilization from Acidic Forest Soils in Leigongshan Area, Southwestern China: Laboratory and Field Study

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Abstract. Aluminium mobilization from acidic forest soils in the remote Leigongshan area in southwestern China was investigated in the field and by a laboratory batch experiment using sequential extractions with HCl solutions with pH of approximately 3.4. Experimental data showed that strongly organically bound aluminium (Alp-Alcu) decreased significantly after sequential extraction, whereas exchangeable aluminium (Alex) increased in all three horizons. In the A-horizon with higher base saturation (BS), dissolved aluminium exchanged with base cations (BCs) on soil complex, causing lower aluminium release but significant leaching of BCs. In AB- and B-horizon with lower BS, more dissolved aluminium remained in solution. Al^{3+} activities in both experimental soil extracts and field soil waters strongly deviated from those predicted by the gibbsite model (i.e., $\text{pAl} = \text{pKsp} + 3.0 \text{ pH}$) despite a significant increase in Al^{3+} with a decrease in pH. The soil organic-bound aluminium model, using Alcu and Alp to account for differences in the size of available Al pools in the soil, gave considerably better fits to both experimental and field data. SOM-Al model, approved by using Alex instead of organically bound aluminium (i.e., Alp and Alcu), could depict the changes in Al activities most successfully. We have concluded that Alp-Alcu is the main source of aqueous aluminium, whereas Alex plays an important role in regulating aluminium solubility during soil acidification.

Enhanced dissolution of soil aluminium is one of the most severe effects of acid deposition on a terrestrial ecosystem and an important process by which soils buffer the external H^+ input. The process consumes H^+ but increases aluminium concentrations in soil water. Studies in Europe and North America have shown that high concentrations of certain aluminium species could be toxic to both terrestrial vegetation and aquatic organisms (Andersson 1988, Rosseland *et al.* 1990). Clarifications of the processes that control aluminium release and sol-

ubility have therefore been regarded as crucial in predicting the impact of acidification on terrestrial and aquatic ecosystems (Mulder *et al.* 1989; Mulder and Stein 1994; Zhu *et al.* 1994).

Acid rain has been recognized as a potential environmental problem in China since the late 1980 s, especially in its southern and southwestern parts. In some areas, soil pH values were reported to have decreased by 0.1 to 1.0 during the course of approximately 30 years, mainly because of acid deposition (Pan 1992; Dai *et al.* 1998). Later studies in China showed that soil acidification is a major problem in some areas although acidification of surface water is not likely to become a regional problem in the near future (Larssen *et al.* 1999a; Seip *et al.* 1999).

The understanding of Al mobilization mechanisms in acidic Chinese ecosystems is still far from adequate. Based on studies conducted in Europe and North America, models have been developed to simulate the mobilization of aluminium from soils. However, testing these models under Chinese conditions is necessary because of differences in soil, climate, and vegetation between China and these other regions.

In the Leigongshan (LGS) catchment area, located in the remote LGS mountain area in Guizhou province, sulfur deposition is low. Therefore, it was selected as the background site of five IMPACTS (Integrated Monitoring Program on Acidification of Chinese Terrestrial Systems) catchments (Tang *et al.* 2001). Better understanding of aluminium release and solubility in this pristine catchment has special importance for interpret aluminium solubility in other more acidified soils. Furthermore, there is a lack of such studies in remote areas in China. In this article, Al release mechanisms and solubility in soils were investigated based on IMPACTS field data in 2003 and results from a laboratory experiment using soils collected from the LGS catchment.

Materials and Methods

Site Description

LGS, also called Leishan (26°10'N, 108°10'E), is located approximately 140 km to the east of Guiyang at an elevation of

Table 1. Some basic properties of soils in LGS catchment

Soil horizons	pH (H ₂ O)	PH (BaCl ₂)	Organic matter (%)	CEC (meq/kg soil)	BS (%)	AIS (%)	Alcu (mmol/kg soil)	Alp (mmol/kg soil)
A	4.42 (± 0.03)	3.86 (± 0.05)	14.5 (± 1.55)	184.3 (± 6.65)	31.92 (± 5.21)	59.8 (± 7.34)	43.7 (± 2.89)	92.8 (± 5.36)
	4.07 (± 0.58)	3.54 (± 0.58)	11.8 (± 3.12)	156 (± 48.7)	52.5 (± 23.0)	35.0 (± 17.9)	42.4 (± 15.6)	95.1 (± 36.7)
	n = 50	n = 50	n = 50	n = 50	n = 50	n = 50	n = 5	n = 5
AB	4.65 (± 0.06)	4.24 (± 0.03)	9.6 (± 0.47)	55.8 (± 5.56)	19.08 (± 3.42)	73.9 (± 6.31)	23.8 (± 2.50)	57.2 (± 4.65)
	4.38 (± 0.56)	3.87 (± 0.38)	5.89 (± 3.38)	56.1 (± 27.3)	43.76 (± 23.7)	50.0 (± 25.2)	22.3 (± 10.36)	72.6 (± 32.1)
	n = 26	n = 26	n = 26	n = 26	n = 26	n = 26	n = 7	n = 7
B	4.81 (± 0.05)	4.45 (± 0.04)	5.5 (± 0.26)	33.9 (± 3.67)	16.16 (± 1.68)	72.9 (± 2.37)	16.5 (± 3.76)	49.0 (± 3.03)
	4.39 (± 0.52)	3.96 (± 0.53)	3.34 (± 1.91)	42.5 (± 29.0)	32.5 (± 28.3)	61.7 (± 26.4)	20.2 (± 7.84)	60 (± 17.4)
	n = 20	n = 20	n = 20	n = 20	n = 20	n = 20	n = 6	n = 6

For each horizon, the values in the first line are properties of soil samples used in experiment. Data in the second line are median values of available data; number of sample is listed in the third line.

Alcu = Weakly organically bound aluminium.

Alp = Strongly organically bound aluminium.

AIS = Soil aluminium saturation.

BS = Base saturation.

CEC = Cation-exchange capacity.

approximately 1500 meters. The climate is mild and humid with an annual precipitation of approximately 1300 mm. The annual average temperature is 11.7°C. In 2000, the IMPACTS project established a small catchment for integrated monitoring of atmospheric chemistry, precipitation, soil, water, and vegetation. The SO₄²⁻ concentration in precipitation is lower than at the other IMPACTS sites with an annual volume-weighted average of approximately 52.27 µmol L⁻¹ in 2003. The annual volume-weighted average pH for precipitation is approximately 4.44 with lime potential (= pH - ½ pCa) of approximately 2.13 in the same year. The soil type is yellow according to the Chinese classification system (*Haplic Acrisol* in the Food and Agriculture Organisation system). As reported by Lydersen *et al.* (1997) soil properties vary widely. Some basic soil chemical properties in the LGS catchment are listed in Table 1. The alkalinity of surface water is approximately 88.25 µeq L⁻¹ (± 37.18, n = 47), which indicates high sensitivity to acid deposition despite a quite high pH (Lydersen *et al.* 1997).

Equipment Installations and Sampling

The procedures used for equipment installation and sampling of throughfall, litterfall, and soil water in LGS have been described in Vogt *et al.* (2001). Equipment for soil water sampling was located in four intensive macroplots (i.e., well-defined 10 x 10 m squares randomly selected within the watershed) and one additional soil water-only macroplot (Fig. 1). In each of these five macroplots, four soil water lysimeters and four soil temperature sensors were located at different soil depths according to genetic horizons.

Soil water samples from all lysimeters were sampled weekly, and samples for 4 weeks were pooled. Main components were analyzed in a provincial standard laboratory, which was quality approved by the IMPACTS project. In this article, >100 soil water samples with ion balance (= (Σanion-Σcations)/(Σanions + Σcations)*100%) <10% were included. These samples were collected from 15 lysimeters located in the A-, AB-, and B-horizons. There were significant temporal and spatial variations in sample composition (Table 2). In addition, soil samples for the A-, AB- and B-horizons were collected within the site to conduct laboratory batch experiments after analysis of main soil parameters.

Fig. 1. Map of Leigongshan (LGS) catchment. LGS = Leigongshan

Batch Experiment

An artificial acidic solution was prepared by diluting hydrochloric acid to pH of approximately 3.42. This H⁺ concentration is nearly four times higher than the average value in precipitation in areas in China receiving heavy loads of acid rain (i.e., pH 4.1 to 4.2). The high concentration was chosen to accelerate aluminium release processes to make the changes clearer. Furthermore, the acid solution used in this experiment contained only HCl instead of H₂SO₄, which is typical for acid rain. This was done to avoid the disturbance of coadsorption between aluminium and sulfate on the soil as well as complexation between aluminium and sulfate.

Table 2. Chemical composition of soil water in LGS catchment in 2003

LGS (2003)	N	pH	Ali (μeq L ⁻¹)	Ca ²⁺ (μeq L ⁻¹)	Mg ²⁺ (μeq L ⁻¹)	Na ⁺ (μeq L ⁻¹)	K ⁺ (μeq L ⁻¹)	NH ₄ ⁺ (μeq L ⁻¹)	SO ₄ ²⁻ (μeq L ⁻¹)	NO ₃ ⁻ (μeq L ⁻¹)	Cl ⁻ (μeq L ⁻¹)	Total F (μeq L ⁻¹)	H ₄ SiO ₄ (μmol L ⁻¹)
A	51	4.93 (4.48–5.23)	12.96 (0.00–51.06)	101.80 (40.42–763.51)	45.25 (28.79–79.55)	8.26 (4.78–21.14)	6.91 (1.28–45.78)	0.00 (0.00–2.86)	92.35 (68.61–476.55)	46.05 (7.14–395.38)	12.13 (2.26–40.34)	0.53 (0.00–3.16)	28.2 (0.00–43.4)
AB	46	4.79 (4.62–4.89)	24.72 (0.00–40.87)	59.73 (25.05–224.79)	30.48 (16.78–60.88)	10.00 (4.63–30.45)	7.42 (0.51–15.11)	0.00 (0.00–1.04)	110.40 (61.94–191.80)	24.27 (0.00–170.99)	10.65 (0.45–25.81)	0.00 (0.00–3.16)	195 (0.00–38.8)
B	47	5.24 (4.90–6.14)	4.01 (0–19.33)	52.40 (22.58–295.27)	26.32 (19.09–69.12)	11.74 (4.57–30.80)	2.56 (1.02–18.61)	0.00 (0.00–1.00)	62.38 (31.81–108.53)	10.00 (0.00–272.73)	5.08 (0.03–17.77)	0.00 (0.00–0.63)	27.5 (5.72–34.5)

For each horizon, data in the first line are median concentration. Data ranges are shown in the second line (10 percentile – 90 percentile).

Ali = Inorganic Al fraction.

LGS = Leigongshan.

The soils used in the batch experiment were air dried and passed through a 2.0-mm sieve. The samples, 150 g, were then mixed thoroughly before they were evenly divided into 10 subsamples. Each subsample was transferred to a 250-mL Erlenmeyer bottle. The 10 subsamples were extracted with the acid (HCl) solution, the first sample just once, the second twice, and so on until the last sample had been extracted 10 times. Acid solution, 150 mL, was used in each extraction. The slurry was shaken for 30 minutes every 4 hours for 2 days. This shaking time was assumed sufficient to reach equilibrium because it is considerably longer than time shaken in other soil experiments found in the literature (e.g., Liao *et al.* 1998; Zhu *et al.* 2004). After the last acidification of each subsample, the supernatant was decanted, centrifuged, and passed through a 0.45-μm filter membrane (Millex-HV Millipore) before it was stocked in a polyethylene bottle for chemical analysis. Soil sediments were washed using 500 mL ion-exchanged water, dried at 40°C, and stored to measure soil parameters.

Analytic Methods

pH values in soil solutions were measured potentiometrically by a pH combination electrode (Rex E-201-C-9, Rex, Shanghai). Major anions (SO₄²⁻, NO₃⁻, Cl⁻, F⁻) and cations (Ca²⁺, Mg²⁺, K⁺, Na⁺, NH₄⁺) were determined by ion chromatography (Dionex DX 120 with IonPac AS14A and CS12 columns, Dionex, America). Silicon in the leachates was analyzed by a molybdosilicate colorimetric method (Goltermann *et al.* 1978). Organic matter anion was detected using colorimetric method at 253.7 nm (McMurry 1990). In most samples, the concentrations were near 0 mg C/L. The monomeric fraction of aluminium (Ala) was determined using the 8-hydroxy-quinoline method (Barnes 1975). The organic fraction (Alo) of the Ala was determined by first passing the sample through an Amberlight IR-120, Amberlight, Germany cation exchange column. The inorganic Al fraction (Ali) was calculated as the difference between Ala and Alo (Driscoll 1984). The concentrations of different Al species were calculated from Ali using the computer program Alchemi (Schecher and Driscoll 1987). For the samples from the laboratory experiment, the temperature was assumed constant at 20°C, whereas for the field samples the speciation was conducted using field soil temperatures.

The soil pH values were determined by mixing 5-g soil sample with 25 mL deionized water and shaking for 30 minutes. The effective cation-exchange capacity (CEC_E) was measured at soil pH using the BaCl₂ extraction method (Hendershot and Duquette 1986). Extractants—0.1 M Na₄P₂O₇, 0.1 M BaCl₂, and 0.5 M CuCl₂—were used to determine the strongly organically bound (Alp) and exchangeable (Alex) and weakly organically bound (Alcu) aluminium, respectively (McKeague 1967; Hendershot and Duquette 1986; McKeague and Day 1966; Jou and Kamparth 1979; Kaiser and Zech 1996). Metal cations in the extracts were determined using inductively coupled plasma–atomic emission spectrometry. H⁺ activity was determined using a pH combination electrode (Rex E-201-C-9, Rex, Shanghai). Soil organic matter was analyzed using the K₂CrO₇ oxidization method (Anonymous 1998).

Results and Discussion

Aqueous Chemistry

The distributions of cations in experimental extracts were quite different for the three soil horizons studied. The equivalent charges of the cations in the extracts were divided into three fractions: H⁺, the equivalent charge of Al species (A_{eq}), and base cation (BC = the sum of Ca, Mg, Na, K, and NH₄). BC

was the dominating cation fraction in all extracts from the A-horizon, whereas equivalent aluminium (A_{eq}) was less important (percentage <25%). In the extracts from the AB- and B-horizons, A_{eq} was the main cation fraction and increased with extraction time. A_{eq} represented 55% and 66% in the last extracts, respectively (Fig. 2).

Concentrations in field soil-water were, as expected, lower than in extracts in the laboratory experiment because the mobile anion (Cl⁻) concentration in experiment was much higher than the anion concentration in field soil-water. In all field soil-water samples, Al_i concentration was lower compared with BCs (median percentage 7.05%, 18.5%, and 6.67% for A-, AB- and B-horizons, respectively [Table 2]).

At present, BCs dominate in soil solution in all three horizons. However, it does not necessarily mean that significant aluminium mobilization will not occur in the short term. In other Chinese regions with higher sulfur loading, such as Guizhou and Chongqing, soil waters with high aluminium and considerable BCs are quite common (Larssen *et al.* 1998; Zhao *et al.* 2001). According to the concepts described by Ruess and Johnson (1986), high sulfur deposition can cause aluminium mobilization at higher soil-base saturation. Sulfur deposition fluxes in the LGS area were 0.7, 1.1, and 1.2 g S m⁻² yr⁻¹, and annual volume-weighted pHs of precipitation were 5.17, 4.97, and 4.44 in 2001, 2002, and 2003, respectively (IMPACTS, unpublished data). Therefore, the worsening acid deposition probably will cause aluminium mobilization in the near future.

Soil Aluminium Release

Soil aluminium pools are important sources of aqueous aluminium in acidified soils. Figure 3 shows that different pools have different change during acidification extraction. After sequential acidification extractions, strongly organically bound aluminium (Alp-Alcu) decreased in all three soil horizons (i.e., A-, AB-, and B- horizons). CuCl₂-extractable aluminums (Alcu) were not significantly larger than Alex, especially in A-horizon soil. Moreover, no clear change was observed in weakly organically bound aluminium (Alcu-Alex) in three soil horizons during 10 extractions. Compared with the decreases in Alp-Alcu, Alex increased in three soil horizons, indicating that part of aluminium released from the Alp-Alcu pool was adsorbed on soil-exchanging sites, especially in soils with higher BS. These results agree with similar studies in northern Europe and China (Mulder *et al.* 1989; Mulder and Stein 1994; Zhu *et al.* 2004). Aluminium budgets between solid soils and solutions are listed in Table 3. Accumulative aluminums dissolved in solutions are higher than accumulative aluminums released from solid soils after 5 and 10 acidification extractions, which should be attributed to some undetermined aluminium pools in soil. Zhu *et al.* (2004) found that acidic oxalate-extractable aluminium (Alex) was also an important contributor to aqueous aluminium in some acidified soils.

Considering the changes both in experimental solutions and in aluminium pools, we conclude that Alp-Alcu is the important source of aqueous aluminium and that Alex plays a significant role in regulating aluminium in soil water. In soils with higher BS, most of the dissolved Al exchanges with BC on the soil complex, whereas in soils with lower BS, dissolved Al remains in solution.

Fig. 2. The changes in cations in extracts after 5 and 10 extractions: for each horizon, left bar is the extracts after 5 extractions; right bar is the extracts after 10 extractions

Fig. 3. The change in aluminium pools after 0, 5 and 10 extractions

Possible Processes Controlling Aluminium Activity

Theoretical review. Many models commonly used for soil and soil-water acidification assume that Al activities in soil solution are in equilibrium with a gibbsite-like (Al(OH)₃) phase (Tiktak and Van Grinsven 1995). Such equilibria with gibbsite phase can be expressed as:

$$\text{Log}\{\text{Al}^{3+}\} = \text{logKsp} - 3\text{pH} \quad (2)$$

where { } denotes activity in solution, and Ksp is the solubility product of the gibbsite phase.

Table 3. Accumulative aluminium released from solid soil and accumulative aluminium in solution

Soil horizon	Al released from solid soil (mmol/kg)		Dissolved Al in solution (mmol/kg)	
	5 extractions	10 extractions	5 extractions	10 extractions
A	1.58	4.36	2.84	4.91
AB	1.69	6.00	1.84	6.96
B	3.38	8.11	3.44	8.26

Instead, several investigators have postulated that the complexation reaction between H^+ and aluminium bound to soil organic matter is the dominating process controlling Al activities in soil-waters (Mulder and Stein 1994; Berggren and Mulder 1995):

$$\{Al^{3+}\}/\{H^+\}^x = K_{org}RAI^{(3-x)+}/RH_x \quad (4)$$

$$(RAI^{(3-x)+})/(RH_x) \approx Al_{org}/C \quad (5)$$

$$pY = pK^*_{org} + xpH, \quad (6)$$

$$\text{where } pY = p(\{Al^{3+}\}C/Al_{org})$$

In the previously mentioned equations, $(RAI^{(3-x)+})$ and (RH_x) denote the activities of aluminium and protons bound to soil organic matter, and K_{org} represents the equilibrium constant. In practice, the activity ratio $RAI^{(3-x)+}/RH_x$ is assumed to be proportional to the ratio between an extractable organically bound aluminium pool (e.g., Alp or Alcu) and the organic carbon content of soil (i.e., Al_{org}/C) because the number of total and aluminium-occupied binding sites at soil organic matter is difficult to assess. As discussed in a previous section of this article, Alex plays an important role in regulating the aluminium in solution. Here we investigate the possible use of Alex to predict the aluminium activity in soil water in Chinese acidic forest soils. $(RAI^{(3-x)+})/(RH_x)$ is assumed to be assumed to be proportional to the ratio between Alex and soil cation exchange capacity (CEC_E) instead of Al_{org}/C in the following equation:

$$(RAI^{(3-x)+})/(RH_x) \approx Alex/CEC_E \quad (7)$$

$$\text{If } pY = p(Al^{3+} * CEC_E / Alex)$$

$$PY = xpH + pK_{ex}. \quad (8)$$

In Equation 7, $(CEC_E/Alex)$ is inverse of soil aluminium saturation (AIS) and conceptually related with soil acidity. Therefore, using Equation 8 can reflect the influence of soil acidity on aluminium mobilization.

Fig. 4. pH-pAl relationship for experimental and field samples

Gibbsite Dissolution Equilibrium and pAl-pH Relationship. pAl-pH diagrams for both experimental and field data are shown in Figure 4. For comparison, equilibrium lines for crystalline gibbsite ($K_{sp} = 10^{8.11}$) and amorphous aluminium trihydroxide ($K_{sp} = 10^{10.08}$) are included (K_{sp} values from Schecher and Driscoll 1987). As found elsewhere, both field and experimental data deviated from the gibbsite equilibrium. Al^{3+} activities were oversaturated with respect to synthetic gibbsite except for some samples with $pH < 4.2$, whereas the gibbsite model, with respect to amorphous gibbsite (with $pK_{sp} = -10.08$) overestimated Al^{3+} activities in nearly all the samples. The saturation index (SI) with respect to the gibbsite minerals tended to increase with pH.

In some literature, empirical fitted equations and constants have been used to minimize the discrepancies between model-calculated Al activities *in situ* or laboratory values. Such an empirical model, described by Reuss *et al.* (1990), gave satisfactory agreement to both experimental and field data (Table 4). Larssen *et al.* (1999b) presented pK values optimized for the Chinese soils they studied ($pK = -9.01$). However, such empirically fitted constants and equations are known to show large spatial variation and are therefore of limited value in different regions.

SOM-Al model. In Figures 5a and 5b, data are plotted according to the SOM-Al model (Equation 6) using both Alp and Alcu. Results of linear regressions are listed in Table 4. The SOM-Al model fitted both experimental and field data

Table 4. Linear regression and model test results of different equilibriums

Data	Model	<i>n</i>	Intercept, pK	Slope <i>x</i>	<i>R</i> ²	<i>p</i> ^a
Experimental data	Gibbsite pK = -8.11	30				18.41
	Gibbsite pK = -10.8	30				38.53
	Empirical pAl-pH	30	-1.02 (± 0.46)	1.29 (± 0.10)	0.78	5.27
	SOM-Al with Alcu	30	-2.29 (± 0.64)	1.13 (± 0.15)	0.68	14.6
	SOM-Al with Alp	30	-1.63 (± 0.69)	1.11 (± 0.16)	0.64	6.40
	SOM-Al with Alex	30	-0.90 (± 0.58)	1.24 (± 0.13)	0.76	5.87
Field data	Gibbsite pK = -8.11	100				29.34
	Gibbsite pK = -10.08	100				19.25
	Empirical pAl-pH	100	-2.75 (± 0.63)	1.69 (± 0.13)	0.64	6.74
	SOM-Al with Alcu	100	-5.86 (± 0.69)	1.85 (± 0.18)	0.52	15.46
	SOM-Al with Alp	100	-6.13 (± 0.97)	2.01 (± 0.20)	0.51	10.72
	SOM-Al with Alex	100	-3.33 (± 0.66)	1.76 (± 0.14)	0.64	7.65
Data in Reference	Wesselink <i>et al.</i> 1996 (Al _p)	29	-2.09 (± 0.40)	1.19 (± 0.10)	0.87	
	Larssen <i>et al.</i> 1999b (Al _p)	119	-2.95 (± 0.56)	1.42 (± 0.11)	0.60	
	Larssen <i>et al.</i> 1999b (Al _{Cu})	119	-3.46 (± 0.56)	1.45 (± 0.10)	0.63	

^a*p* is defined as: $[(\sum(pAl_{\text{measured}} - pAl_{\text{modelled}})^2 / (n-2))^{1/2} / pAl_{\text{avg, measured}}] * 100\%$. *n* denotes the number of samples. Lower *p* values indicate better fits.

Alcu = Weakly organically bound aluminium.

Alex = Exchangeable aluminium.

Alp = Strongly organically bound aluminium.

better than the gibbsite model (Fig. 4), whereas modeling results using Alp and Alcu were not significantly different. Although *R*² for Alcu was slightly higher than for Alp, relative standard deviations (*p*) indicated that the SOM-Al model using Alp predicts Al³⁺ activities somewhat better than Alcu (Table 4). Results for experimental data were slightly better than for field data. The main likely reason is that the field data were from 15 different lysimeters locations, whereas the batch experiment was conducted on only three different soils. Furthermore, the pH in the soil extracts of the batch experiment was lower than in field-soil water. Studies have suggested that model performances are better at pH values <4.3 (Wesselink *et al.* 1996). Coefficients in the linear regression equations of the SOM-Al model vary significantly among the results reported by different investigators (Table 4). These deviations may be caused by differences in soil characteristics influencing the Al mobility and not accounted for by differences in the Alp or Alcu pools. The slopes of our linear regression on the batch titration data were low. This is likely because of the high H⁺ inputs, which made the soils more acidic with low pH and high AIS.

Figure 5c shows diagrams of pY-pH according to Equation 8. The fit is clearly better than for the gibbsite model. The deviations between modeled and measured data (in pAl form) are also smaller than for the original SOM-Al model (Table 4). The fit is slightly better for the laboratory data than for the field data as discussed in previous sections. From Table 4, we see that the slopes for both laboratory and field sample were similar to those of empirical pAl-pH equations.

SOM-Al models using Alp, Alcu, and Alex gave better fits to laboratory and field samples than did the gibbsite model. One possible reason is the reasonable consideration of differences in soil properties such as soil aluminium pools. However, it is difficult to distinguish the roles of different aluminium pools in aluminium mobilization because of extreme complicity of soil systems. Studies conducted in China

and western countries showed that Alp is the important sources and regulator of aqueous aluminium in acidified soils (Mulder *et al.* 1989; Liao *et al.* 1998; Zhu *et al.* 2004). Usually, Alcu was correlated with soil organic carbon (Liao *et al.* 1998; Lydersen *et al.* 1997) and has been considered a better measure than Alp to evaluate soil organically bound aluminium (Jou and Kamprath 1979). Larssen *et al.* (1999) reported the better fits of SOM-Al model using Alcu over Alp in some Chinese acidic soils. In China, especially in southern and southwestern China where the climate is tropical and subtropical, soil organic matter is usually lower than north Europe because of quick decomposition; the roles of organically bound aluminium in controlling aluminium solubility are quite uncertain. Our experimental results showed that Alex can significantly regulate aluminium solubility in soil solution, which also was supported by better fits of SOM-Al models using Alex.

Summary

Experimental data showed that Alp-Alcu decreased significantly after sequential extraction (1500 mL), whereas Alex increased in all three horizons. In the A-horizon with higher BS, dissolved aluminium exchanged with BCs on soil complex, thus causing lower aluminium release but significant leaching of BCs. However, in AB- and B-horizon with lower BS, more dissolved aluminium remained in solution. Al³⁺ activities in experimental soil extracts and field soil-waters strongly deviated from those predicted by the gibbsite model (i.e., pAl = pKsp + 3.0pH) despite a significant increase in Al³⁺ with decrease in pH. The soil organic bound aluminium (SOM-Al) model, using Alcu and Alp to account for differences in the size of available Al pools in the soil, gave considerably better fits to both experimental and field data. The SOM-Al model, approved by using Alex instead of organically bound aluminium (i.e., Alp and Alcu), predicted changes in Al

Fig. 5. Diagrams of SOM-Al model. (a) Using Alp. (b) Using Alcu. (c) Using Alex. Alcu = Weakly organically bound aluminium; Alex = exchangeable aluminium; Alp = strongly organically bound aluminium.

activities most successfully. We conclude that Alp-Alou is the main source of aqueous aluminium, whereas Alex plays an important role in regulating aluminium solubility during soil acidification.

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