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Evaluating main factors controlling aluminum solubility in acid forest soils, southern and southwestern China

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Abstract

The mechanism controlling Al solubility in Chinese acidic forest soils is not clearly understood. This is the main limitation to the ability to generate adequate dose-response prediction models of the ecological effect of acid rain. To evaluate the relative significance of possible processes, soils and soil solutions from five forest catchments, located in southern and southwestern China, were collected and analyzed for chemical parameters. Monitoring showed that inorganic Al (Al_i) was the dominant fraction in most soil solutions; organic Al (Al_o) was usually less than 10% of total monomeric Al (Al_a). Aluminum fractions varied significantly between and within the different sites, though appearing to follow a similar pattern. Over the entire pH range of 3.6–5.6, the pAl (i.e. $-\log$ of the Al^{3+} activity) closely correlated with solution pH, following regression slopes of 1.28 and 2.00 for upper and lower soil horizons, respectively. The variations in Al^{3+} activity could not be explained satisfactorily using mineral dissolution equilibria. Partial least square (PLS) regression showed that soil acidity (quality) and ionic strength (intensity) of the solution were the main explanatory variables for the variation in the concentration of Al fractions. Aluminum in upper horizons originated from both organic and inorganic solid Al pools, while aqueous Al in lower horizons was dominantly of inorganic origin. Aluminum solubility was strongly influenced by cation exchange, especially in the upper horizon. In the upper horizon, ionic strength (I) had a greater influence on Al solubility due to cation exchange reaction. In the lower horizon, dissolution of inorganic Al pools by the elevated H^+ concentrations was the main Al release mechanism. So Al activity was more dependent on H^+ (or pH) in the lower horizon.
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1. Introduction

Acid deposition has been recognized as a critical environmental problem in China for over 20 years

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(Zhao and Sun, 1986; Seip et al., 1999; Larssen et al., 2006). Acidification as well as other potential effects will occur in the coming decades unless scientific and strict measures are taken. There is a strong need to develop models to predict the long-term effect of acid deposition. Studies have clearly suggested that understanding of the related geochemical processes in soil is a prerequisite for the adaptation and development of acid rain prediction models (e.g. Cosby et al., 1985). However, little information exists in China or in other countries with similar subtropical and monsoonal climate conditions and ecosystems. Valuable knowledge has been obtained from studies in Europe and North America, but its applicability in Chinese soils should be rationally tested because large differences exist in climate, soil and biota. This is a major problem for the adaptation of acid rain prediction models established in temperate regions (i.e. Europe and North America) to Chinese conditions.

Aluminum chemistry is a crucial issue in acid rain and acidification research. Release and mobilization of soil Al is not only an important process buffering external H^+ input in acid and moderately acid soils, but also poses a serious effect of acid rain on terrestrial ecosystems (e.g. Reuss and Johnson, 1986; Mulder et al., 1989; Dahlgren and Walker, 1993). Elevated Al concentrations in soils, streams and lakes is a potential threat to both terrestrial and aquatic organisms due to the toxicity of certain Al species (Driscoll et al., 1980; Andersson, 1988). In China, high Al concentrations induced by acid deposition have also been reported (see Guo et al., 2006; Xue et al., 2003). Based on laboratory experiments and limited field monitoring, the significance of some possible influencing factors have been documented by several specific studies (i.e. Larssen et al., 1999; Guo et al., 2004; Zhu et al., 2004). However, the main controlling mechanism of Al solubility is far from clearly understood, especially at the regional scale. Integrated evaluation of these possible factors (or geochemical processes) is strongly needed, especially studies based on long-term regional monitoring.

Since 1999, the Chinese–Norwegian cooperative project IMPACTS (Integrated Monitoring Program on Acidification of Chinese Terrestrial Systems) has established five integrated monitoring sites in southern and southwestern China. At these sites, long-term monitoring of deposition, soil, soil-solution and stream-water as well as vegetation has been conducted (Tang et al., 2001; IMPACTS, 2004).

The objectives of this paper are to test and discuss the applicability of Al equilibrium models for Chinese mature acidic forest soils, and to evaluate the relative importance of influencing factors to Al solubility based on the unique monitoring data of the IMPACTS project.

2. Materials and methods

2.1. Site description

The IMPACTS project includes integrated monitoring at TSP (Tie Shan Ping: 106°41′E, 29°38′N), LCG (Lu Chong Guan: 106°43′E, 26°38′N), LGS (Lei Gong Shan: 108°11′E, 26°22′N), CJT (Cai Jia Tang: 112°26′E, 27°55′N) and LXH (Liu Xi He: 113°35′E, 23°33′N). All five sites are forested and practically undisturbed by land-use activities. The forests are mixed deciduous and conifer forests, dominated by the coniferous species Masson pine (*Pinus massoniana*) and Chinese fir (*Cunninghamia lanceolata*). The forests were re-planted in the 1960s, because large parts of the forests in China were logged between 1958 and 1962 during the Great Leap Forward. All IMPACTS sites are located with in the Chinese acid rain control zone though they have different atmospheric loading. In general, SO_4^{2-} is the dominating anion in precipitation while Ca^{2+} and/or NH_4^+ are the main cations. The sites have also received highly varied N deposition (mainly as NH_4^+), ranging from 0.7 to 2.7 g N m^{-2} a^{-1} in LCG and CJT, respectively. The annual volume weighted pHs for precipitation are acidic (<5.6) and decreased in the order of LGS > LCG > CJT > LXH > TSP (Table 1).

The soil types are yellow/red soils in the Chinese classification system (*Haplic Acrisol*/*Haplic Alisol* in the FAO system). These soils are prone to be sensitive to acidification and as such are representative for southern and southwestern China. Soil structure is rather homogenous, ranging from silty loam to loam, i.e. rich in finer particles. The bedrock is sedimentary, sandstone and shale, except for the southernmost LXH site where there is granite. The pedo unit consists of highly weathered parent materials with some mineral residues of primarily quartz and K-feldspar as well as plagioclase. Secondary minerals are dominated by kaolinite. Other minerals such as illite, smectite and gibbsite are also found in varying amounts at the different sites. The soil acidity differs from moderate to strongly acidic, with average base saturation ranging from 51% in the

Table 1
Basic information on the five IMPACTS sites[a]

Sites	Wet deposition[a]				Soil chemistry											Soil-solution chemistry					
	pH[b]	S (g m^{-2} a^{-1})	N (g m^{-2} a^{-1})	Ca (g m^{-2} a^{-1})	Bedrock	Horizon	Number n	pH (H$_2$O)	SOC (%)	CEC (mmol/kg)	AlS (%)	Alcu (mmol/kg)	Alp (mmol/kg)	Alox (mmol/kg)		Number n	pH	SO$_4^{2-}$ (µmol/L)	NO$_3^-$ (µmol/L)	Ca^{2+} (µmol/L)	DOC (mg/L)
TSP	4.11	3.47	1.93	1.27	Sandstone	Upper	50	4.05 ± 0.13	5.70 ± 5.78	53.5 ± 26.7	76.0 ± 13.3	19.7 ± 9.2	269.0 ± 128.3	98.0 ± 21.5		433	3.90 ± 0.30	809 ± 373	641 ± 354	385 ± 220	5.72 ± 5.31
					Sandstone	Lower	45	4.18 ± 0.13	0.55 ± 0.28	37.0 ± 12.0	82.0 ± 5.84	12.4 ± 2.8	372.3 ± 149.3	117.8 ± 31.7		346	4.17 ± 0.32	532 ± 301	338 ± 262	227 ± 163	1.70 ± 1.26
LCG	4.63	2.40	0.70	1.87	Sandstone	Upper	49	3.86 ± 0.16	7.29 ± 6.87	100 ± 61.8	70.7 ± 17.2	42.4 ± 16.4	125.1 ± 64.0	193.3 ± 161.7		202	4.14 ± 0.14	600 ± 198	77.6 ± 123	318 ± 118	3.99 ± 4.27
						Lower	69	4.00 ± 0.14	0.89 ± 0.66	78.2 ± 17.4	75.5 ± 12.1	38.0 ± 6.2	80.6 ± 15.6	148.2 ± 124.6		148	4.23 ± 0.30	605 ± 129	86.8 ± 100	287 ± 101	1.83 ± 2.30
LGS	4.75	1.40	0.93	0.70	Shale	Upper	48	4.67 ± 0.89	7.68 ± 6.58	103 ± 61.1	42.9 ± 35.9	49.4 ± 23.3	176.6 ± 90.1	349.0 ± 178.3		201	5.16 ± 0.70	80.7 ± 59.4	111 ± 137	152 ± 108	4.50 ± 14.33
						Lower	45	4.98 ± 0.55	4.64 ± 3.32	35.3 ± 14.3	56.2 ± 26.7	48.7 ± 29.5	276.6 ± 146.9	343.1 ± 134.4		128	5.38 ± 0.51	50.2 ± 21.7	56.6 ± 92.4	80.0 ± 64.1	0.70 ± 1.54
CJT	4.40	2.50	2.07	1.13	Sandstone/shale	Upper	50	4.00 ± 0.20	4.43 ± 2.41	48.0 ± 18.9	65.2 ± 13.6	34.7 ± 11.7	192.2 ± 109.4	220.7 ± 80.5		151	4.95 ± 0.21	291 ± 139	392 ± 298	323 ± 108	3.90 ± 4.17
						Lower	48	4.19 ± 0.27	0.75 ± 0.30	26.3 ± 4.43	71.3 ± 13.9	18.2 ± 6.7	84.9 ± 27.0	204.0 ± 96.6		148	4.79 ± 0.64	356 ± 109	393 ± 227	400 ± 73.3	2.08 ± 4.49
LXH	4.43	1.90	0.95	1.85	Granite	Upper	51	4.66 ± 0.17	1.94 ± 1.14	21.5 ± 4.24	78.2 ± 44.7	22.1 ± 10.7	68.1 ± 11.7	221.5 ± 104.0		155	4.39 ± 0.19	40.4 ± 8.87	110 ± 111	30.0 ± 14.3	0.94 ± 0.67
						Lower	45	4.63 ± 0.14	1.38 ± 1.43	15.9 ± 3.50	78.3 ± 25.1	12.2 ± 2.8	61.4 ± 12.7	193.3 ± 161.7		114	4.88 ± 0.35	27.0 ± 26.0	71.0 ± 46.4	29.3 ± 15.3	0.52 ± 0.61

[a] Data for wet deposition is the average of annually volume weighted data during the monitoring period.
[b] pH is the average of annually volume weighted data during the monitoring period.

upper horizon of LGS to 7.6% in the lower horizon of TSP. Effective cation exchange capacity (CEC$_E$; i.e. using an un-buffered BaCl$_2$ extractant) and Al saturation (AlS; i.e. percentage fraction of Al on soil exchanger) varies among sites and horizons (Table 1), reflecting mainly the variation in organic matter and clay content. Detailed information of climate, deposition, soil and vegetation can be found in the IMPACTS annual report (IMPACTS, 2004).

2.2. Sampling and analysis

Equipment for soil solution sampling is located in 4–8 soil water plots in each watershed. In each of these plots, 4–5 ceramic tension lysimeters (Ceramtec, Germany) and four soil temperature sensors are located at different soil depths according to the genetic horizon (i.e. A, AB, B and BC horizons). Soil solutions from all lysimeters were sampled weekly. In many cases the soil solution sample volumes were too small to conduct chemical analysis, so four weekly-samples from the same lysimeter were pooled into one sample. Before pooling, weekly-samples were stored in a refrigerator at 4 °C, so that 4-week storage would not significantly influence the equilibria in soil solution. The chemical composition of the samples was analyzed at local provincial environmental laboratories, which are quality monitored by the EMEP (cooperative programme for monitoring and evaluation of long range transmission of air pollutants in Europe: <http://www.emep.int/>) inter-calibration program (Uggerud et al., 2003). Soil samples close to each lysimeter were collected and analyzed.

pH was measured potentiometrically using a pH combination electrode (Rex, Shanghai). Major anions (SO$_4^{2-}$, NO$_3^-$, Cl$^-$, and F$^-$) and cations (Ca^{2+}, Mg^{2+}, K$^+$, Na$^+$, and NH$_4^+$) were determined by Ion Chromatography (Dionex DX 120). Silicon in the soil solutions was analyzed by a molybdosilicate colorimetric method. UV-absorbance at 254 nm was chosen as the proxy for dissolved organic C. The factor relating UV-absorbance to DOC was found to be 30.2 (Guo and Vogt, 2004). The total monomeric fraction of Al (Al$_a$) was determined using the 8-hydroxy-quinoline method (Barnes, 1975). The organic fraction (Al$_o$) of the Al$_a$ was determined by first passing the sample through an Amberlite IR-120 cation exchange column. The inorganic Al fraction (Al$_i$) was calculated as the difference between Al$_a$ and Al$_o$ (Driscoll, 1984). For each water sample, Al speciation

calculation using the computer program ALCHEMI (Schecher and Driscoll, 1987) was conducted using inorganic Al (Al_i) as input.

Soil chemical parameters were determined using the most commonly used methods. Soil pH was determined in soil extracts after mixing 5 g soil samples with 25 mL deionized water. The effective cation exchange capacity (CEC_E) was measured using the $BaCl_2$ extraction method (Hendershot and Duquette, 1986). Metal cations in the $BaCl_2$ extracts were determined using ICP-AES, while H^+ activity was determined using a pH combination electrode. Aluminum concentration (in meq./kg soil) in $BaCl_2$ extracts was calculated as exchangeable Al (Al_{ex}). Organically bound Al pools were extracted using 0.5 M $CuCl_2$ and 0.1 M $Na_4P_2O_7$, respectively. Amorphous Al was extracted using 0.2 M acidic oxalate. Detailed methodology can be found in IMPACTS manuals (available on: <http://folk.uio.no/rvogt/Impacts>). The amount of oxalate extractable Al (Al_{ox}) was not significantly higher (in some cases it was lower) than $Na_4P_2O_7$ extractable Al (Al_p) in some soils, which had been validated in previous studies (e.g. Liao et al., 1998; Larssen et al., 1999; Xue et al., 2003). This is likely due to the fact that some inorganic Al pools were also extracted by pyrophosphate (Kaiser and Zech, 1996), this is increasingly important in subtropical soils with lower organic contents (cf. Larssen et al., 1999). Therefore, in this study $CuCl_2$ and acid oxalate extractable Al were used as proxies of the organic and inorganic Al pool (i.e. Al_{org} and Al_{inorg}), respectively. Soil organic C (SOC) was analyzed using the $K_2Cr_2O_7$ oxidization method.

2.3. Partial least square (PLS) regression and data compilation

There are complicated inter-relationships among the chemical variables of soil and soil solution. This made it difficult to distinguish and evaluate the relative influences of certain variables on the other(s). Partial least square (PLS) regression is a powerful tool to describe such co-variances between the x matrix of independent variables and y matrix of dependent variables (van Hees et al., 2000; van Hees et al., 2001). Therefore, PLS regression was introduced in this study, to deal with the co-variances among the variables in the soil–soil solution system. A PLS model will contain loadings for the y-variables (Al_a, Al_i, Al_o, and Al^{3+} in this case) and the x-variables, showing their different importance in

constructing the pattern of co-variation. In this study, PLS analysis was carried out using SIMCA-P 10.0 software (UMETRICS AB, Sweden). All variables used in the PLS analysis were centered and scaled to unit variance.

Three years (2001–2003) field monitoring data from the TSP, LCG, LGS, CJT sites and two years (2002–2003) data from the LXH site were included in PLS analysis. Datasets of each lysimeter was treated as one observation in PLS analysis. In each observation, each soil solution variable was its average during the monitoring period; each soil variable was the average of several soil samples close to the same lysimeter. The soil profiles were divided into upper and lower horizons according to soil taxonomy. The upper horizon approximately represents the A and AB horizons, while the lower horizon mainly includes the B and BC horizons. The depth boundary between the upper and lower horizon is about 20 cm in the sites.

3. Results and discussion

3.1. Aqueous aluminum fractions

Distribution of Al fractions in solution at different sites is shown in Fig. 1. The soil solution number (n) at each site can be found in Table 1. Aluminum fractions differed considerably between and within the sites. Monomeric Al (Al_a) was highest in TSP with a median concentration of 260 and 256 $\mu mol\ L^{-1}$ in the upper and lower horizon, respectively. At the LGS, with the lowest mineral acid loading (Table 1), Al_a was less than 10 $\mu mol\ L^{-1}$ in most samples (75% percentile). CJT received higher S and N loading than LCG sites, but higher monomeric Al concentration was still not observed. This is likely due to a substantial dry deposition of alkaline dust and to higher soil base saturation. Variation in the other Al fractions (i.e. Al_i, Al_o and Al^{3+}) between the different sites and horizons followed a similar pattern as for monomeric Al (Fig. 1). The difference between total monomeric Al and inorganic Al was small due to a rather minor percentage (<10%) of organic Al (Al_o). As can be seen in Fig. 1c, the organic Al in almost all samples was less than 50 $\mu mol\ L^{-1}$. This distribution of the Al fraction is different from that which has been found in northern Europe and northern America (e.g. Vogt et al., 1994; van Hees et al., 2000; Dijkstra and Fitzhugh, 2003). This is likely due to the lower organic content (i.e. DOC) in these subtropical soil solutions (cf. Guo and Vogt, 2004). In these five sites,
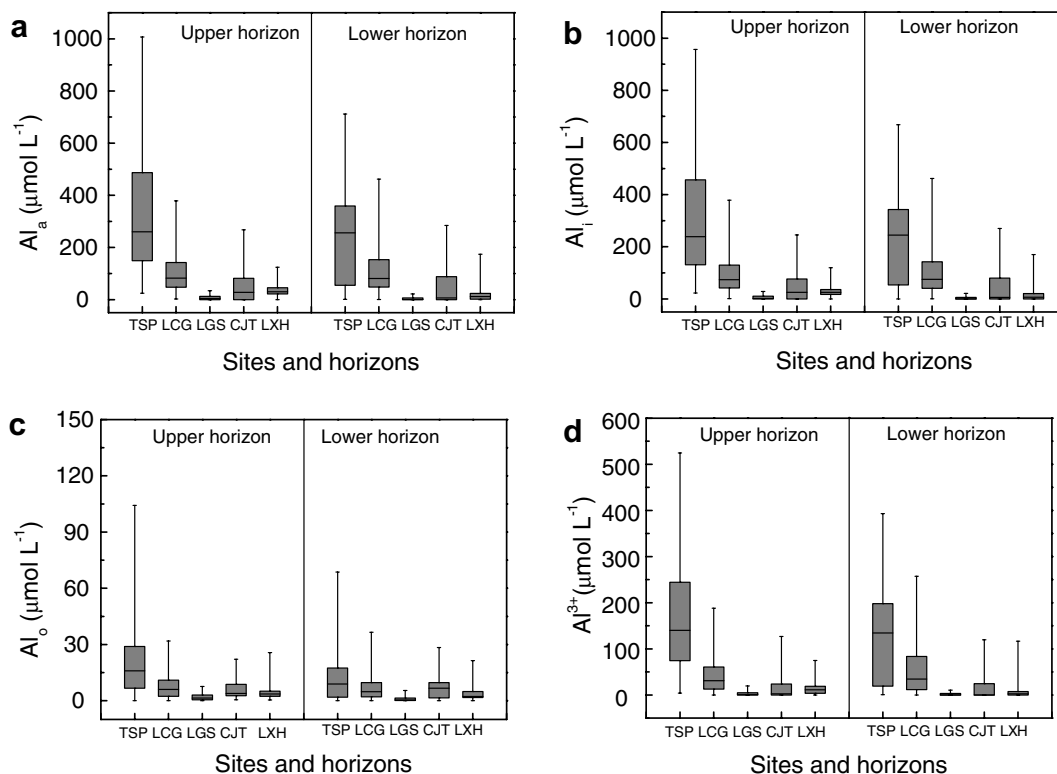
Fig. 1. Distribution of Al fractions in solution at different sites: (a) monomeric Al (Al_a); (b) inorganic Al (Al_i); (c) organic Al (Al_o); (d) Al^{3+}.

free aqueous Al^{3+} ranged from less than 10% to 70% of the monomeric Al mainly due to the variations in solution pH.

3.2. Equilibria with possible mineral phases

In many acidification models, dissolution of gibbsite-like minerals is commonly used as the controlling mechanisms of Al solubility. In Fig. 2a, Al^{3+} activity (presented as pAl) is plotted versus solution pH. As commonly found in many studies in temperate regions, the Al^{3+} activity increased with a decrease in pH ($p < 0.001$ for both horizons). Moreover, a steeper slope of pAl versus pH in the lower horizon implies a stronger dependence of Al on H^+. The saturation index (SI) indicated from Fig. 2a increased with solution pH. In the LGS and LXH sites with higher solution pH, Al^{3+} was over-saturated relative to synthetic gibbsite but under-saturated relative to amorphous gibbsite. In these two sites, gibbsite was also commonly found to be <10% of the clay fraction. The student t-test showed that the pAl–pH pattern deviated from gibbsite equilibrium (the dashed lines) especially at

lower pH ($p < 0.001$). This suggests that dissolution of gibbsite minerals was not the dominant process controlling Al solubility in Chinese acidic forest soil solutions.

Equilibrium with a jurbanite-like mineral ($AlSO_4OH$) has also been suggested as a possible mechanism controlling Al solubility in soils with a high SO_4^{2-} loading, though jurbanite was not found in these soils (van Breemen, 1973; Nordström, 1982; Vogt et al., 1994; Vogt et al., 2001). In Fig. 2b, Al^{3+} activity variation is plotted as jurbanite equilibrium. A reasonable regional agreement with jurbanite equilibrium was not observed among the sites, for either upper or lower horizons (Fig. 2b). Partial correlation analysis showed that the saturation index (SI) of jurbanite was highly dependent on SO_4^{2-} (in pSO_4^{2-}) and pH ($p < 0.01$) instead of being a nearly constant value. In TSP and LCG sites with higher SO_4^{2-} concentration and lower pH, SI was higher than at other sites.

In Fig. 2c and d, Al^{3+} activity is plotted as the function of Si and H^+ according to kaolinite and imogolite dissolution equilibria. Aluminum was over-saturated relative to dominant kaolinite in
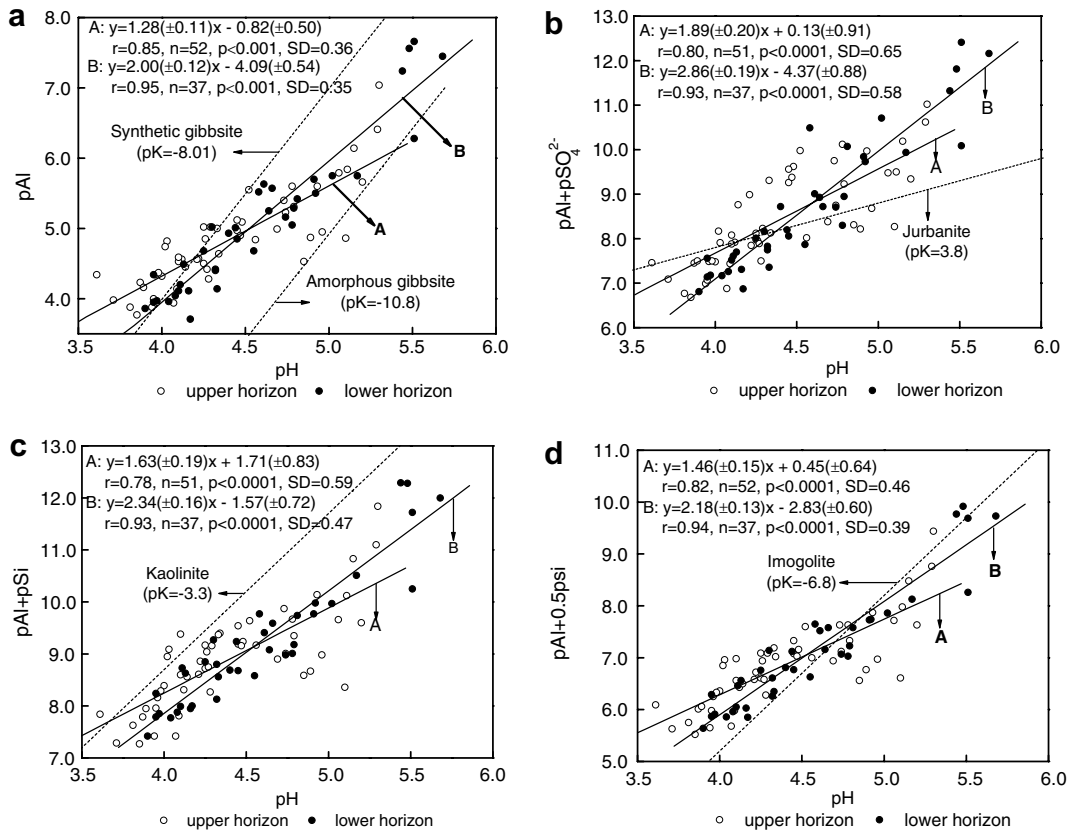
Fig. 2. Equilibria with possible mineral phases: (a) gibbsite; (b) jurbanite; (c) kaolinte; and (d) imogolite. A and B denote the regression line for the upper and lower horizon, respectively. n is the number of the lysimeter.

nearly all soil solutions. Except for some soil solutions from the CJT and LXH sites, Al in most soil solutions was under-saturated relative to imogolite. Mineral analysis showed that the illite content was higher ($13 \pm 8\%$, $n = 20$) in these two sites than other sites. The regression showed a good correlation between Al^{3+} and Si concentration ($p < 0.005$, $n = 52$ and 37 for lower and upper horizons, respectively) and a better slope agreement was achieved with kaolinite and imogolite than with gibbsite dissolution. However, the relationship was different from the theoretical dissolution equilibrium of kaolinite and imogolite ($p < 0.001$), especially for the upper horizon. The saturation index (SI) relative to these two minerals increased with Si concentration and pH ($p < 0.01$).

3.3. PLS regression analysis

It is likely that there were many co-variant factors influencing Al solubility, and it was not possible to distinguish and evaluate their relative significance

using the discussed conceptual chemical mechanisms. Therefore, partial least square (PLS) regression was used to evaluate the relative importance of these factors without basing it on any chemical mechanism. In the PLS analysis, 26 possible influencing factors from both soil and soil solution were treated as the x-variable matrix. Aluminum fractions (Al_a, Al_i, Al_o, Al^{3+}) were studied as the y-variable matrix. There were 47 and 28 observations for the upper and lower soil horizon, respectively (Table 2). These observations with different chemical data constituted a dynamic (i.e. non-equilibrium) system, though soil and soil water were assumed to be in equilibrium for each observation. Therefore, PLS can investigate the co-variances of different variables in this dynamic system and describe the dynamic inter-relationships of these variables.

Variable loadings on the first two principle components that bring significant variance of both x- and y-variable matrix were plotted in Fig. 3. For both upper and lower horizon, the first component

Table 2
Basic information on partial least square regression (PLS) analysis

Horizon	y-Variables	Number of observation	Optimal component numbers	x-Variance explained by first two components (%)	y-Variance explained by first two components (%)
Upper	Al_a, Al_i, Al_o, Al^{3+}	47	5	52	74
Lower	Al_a, Al_i, Al_o, Al^{3+}	28	2	42	88

x-Variables in PLS regression:
Soil: H_{ex}, K_{ex}, Na_{ex}, Mn_{ex}, Fe_{ex}, Ca_{ex}, Mg_{ex}, Al_{ex}, CEC, AlS, BS, SOC, Al_{org}, and Al_{inorg}.
Soil solution: I , H^+, K^+, Na^+, Ca^{2+}, Mg^{2+}, NH_4^+, SO_4^{2-}, NO_3^-, Cl^-, F^-, DOC, and Si.

mainly describes the acidity of soil (quality), while the second axis indicates the acidity of solution (intensity). The first component also brings in the information on ionic strength (I) in soil solution, since all dominant ions had higher loadings on it. All Al fractions were clustered together in Fig. 3. This is mainly due to the co-variations as shown in Fig. 1a–d. They are therefore empirically conceived to be controlled by similar factors. Further-

more, the Al fractions were loaded positively on both components, which indicated that both the soil quality and solution intensity govern the Al release, i.e. the highest mobility of Al is found in acid soils receiving high deposition of acid mobile anions and proton.

The variable loading plot for the upper horizon is shown in Fig. 3a. Both organic and inorganic Al pools (Al_{org} and Al_{inorg}) had strong negative loading on the Al fractions (i.e. having higher negative loadings on the imaginary dashed line from the origin to Al fractions). This means that decrease in Al pools (i.e. Al_{org} and Al_{inorg}) is related to the increase of Al concentration in soil solution. In other words, a decrease in Al pools will enhance Al in soil solution. Therefore, both Al pools are the source of aqueous Al in the upper horizon. The importance of the organic Al pool (Al_{org}) has been addressed by many studies in Europe and North America where the climate is temperate and soil organic content is higher (e.g. Mulder et al., 1989; Walker et al., 1990; Berggren and Mulder, 1995). However, dissolution of the soil inorganic Al pool (Al_{inorg}) is also an important contributor to the Al concentration in these Chinese soils. Although the loading of the organic Al pool (Al_{org}) was slightly higher than the inorganic Al pool (Al_{inorg}), this difference was not significant considering the dominant contribution of the organic Al pool in temperate regions.

It was apparent that cation exchange reactions strongly influenced Al solubility after their dissolution from the organic and inorganic pools. In Fig. 3a, Al fractions were significantly positively related with soil Al saturation (AlS) and negatively with base saturation (BS). This means that higher AlS and lower BS will increase the Al concentration in soil solution. Guo et al. (2006) showed that in soils with lower AlS and higher BS, more mobilized Al was retained in soil as exchangeable Al. With the
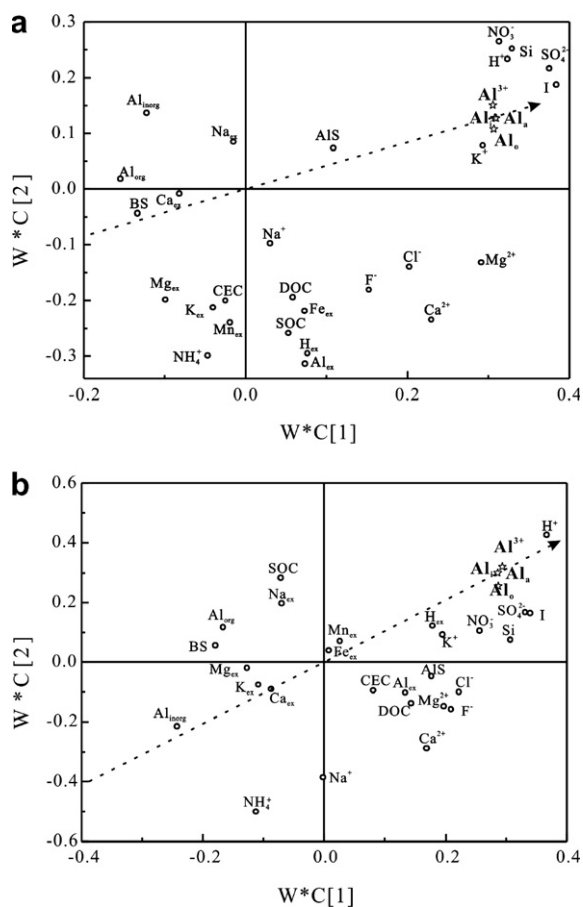

Fig. 3. Loading plots of PLS regression: (a) upper horizon; and (b) lower horizon.

increase in soil Al saturation (AlS), more Al was released to soil solution. Such relationships should be attributed to quick exchange between dissolved Al and base cations (i.e. Na, K, Mg and Ca) adsorbed on soil surfaces, especially in soils with lower Al saturation (AlS). This exchange process is also the important reason for the deviation from mineral phase equilibria (Fig. 2a–d). Ionic strength (I) was closely positively related with and had the highest loading on Al fractions. This indicated their higher influence on Al solubility. Studies have shown that increasing cation charge would increase Al concentration through cation exchange reactions (Matschonat and Vogt, 1998; Guo et al., 2004). Sulfate and NO_3^-, the two dominant mobile anions in precipitation and soil solution, were also closely correlated with Al. However, their influence on Al is mainly limited by increasing the ionic strength, because partial correlation did not show any significant relationship with Al fractions when considering their contribution to ionic strength (not shown). The H^+ was also significantly correlated with Al_a, but its loading on Al fractions was slightly smaller than ion strength. The smaller effect of H^+ was not, however, due to the complexation of DOC as reported in European podzols (van Hees et al., 2000), because a significantly high loading of DOC on Al fractions was not observed in these Chinese sites.

The loading plot for the lower horizon had a similar basic pattern for most variables (Fig. 3b). However, there were at least two contrasting differences with the upper horizon. Firstly, the loading of the inorganic Al pool (Al_{inorg}) on the Al fraction was significantly larger than that of the organic Al pool. Therefore, the inorganic Al pool (Al_{inorg}) became the dominant source of aqueous Al in the lower horizon. Using well controlled laboratory experiments, Zysset et al. (1999) reached a similar conclusion for podzol. Secondly, H^+ became the most important factor controlling Al solubility. Although Al saturation (AlS), base saturation (BS) as well ionic strength had higher loadings on the Al fraction, their impacts were less important than that of H^+ concentration. This is likely due to higher Al saturation in lower horizons; this limited the role of cation exchange reactions in regulating Al concentration. Therefore, dissolution of the inorganic Al pool was the dominant source of aqueous Al in the lower horizon. These were likely the main reasons for the higher dependence of Al^{3+} activity on pH (Fig. 2a–d).

4. Conclusions

Aqueous Al fractions, dominated by inorganic Al (Al_i), varied significantly between different sites and soil horizons. The pAl (i.e. $-\log$ of the Al^{3+} activity) closely correlated with solution pH, with regression slopes of 1.28 and 2.00 for upper and lower soil horizons, respectively. This could not be explained satisfactorily using mineral dissolution equilibria (i.e. gibbsite, jurbanite, kaolinite and imogolite) over the pH range of 3.6–5.6. PLS regression showed that soil acidity (quality) and ionic strength (intensity) of the solution were the main explanatory variables for the variation in Al fractions. Inorganic and organic Al pools almost equally contributed to aqueous Al in the upper horizon. While in the lower horizon, aqueous Al dominantly originated from inorganic pools. After dissolution from various solid pools, Al solubility was strongly regulated by cation exchange reactions. In the upper horizon, ionic strength (I) was the dominant factor empirically explaining the Al concentration. This was thought to be due to the higher influence of cation exchange reactions in the upper horizon. In contrast with the upper horizon, H^+ (or pH) became the dominant controlling factor for aqueous Al in the lower horizon. Furthermore, the regulating role of exchange reactions tended to be smaller compared with the upper horizon, which led to the higher dependence of Al^{3+} activity on H^+ (or pH) in the lower horizon. In these Chinese old acidic forest soils, the significant role of organic matter in controlling Al solubility was not clearly observed.

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