Evaluating Controlling Factors to $Al_i/(Ca + Mg)$ Molar Ratio in Acidic Soil Water, Southern and Southwestern China: Multivariate Approach

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Abstract $Al_i/(Ca + Mg)$ molar ratio in soil water has been used as an indicator to the effects of acid deposition on terrestrial ecosystems. However, the main factors controlling this ratio have not been well documented in southern and southwestern China. In

this study, we presented the variation in inorganic aluminum (Al_i) and $Al_i/(Ca + Mg)$ molar ratio in different sites and soil horizons based on two to three years monitoring data, and evaluated the main factors controlling $Al_i/(Ca + Mg)$ molar ratio using principle component analysis (PCA) and partial least square (PLS) regression. Monitoring data showed although $Al_i/(Ca + Mg)$ molar ratios in most soil water were lower than assumed critical 1.0, higher molar ratios were found in some soil water at TSP and LXH site. Besides acid loading, both soil properties and soil water chemistry affected the value of $Al_i/(Ca + Mg)$ molar ratio in soil water. Partial least square (PLS) indicated that they had different relative importance in different soil horizons. In A-horizon, soil aluminum saturation (AIS) had higher influence on $Al_i/(Ca + Mg)$ molar ratio than soil water chemistry did; higher soil aluminum saturation (AIS) led to higher $Al_i/(Ca + Mg)$ molar ratio in soil water. In the deeper horizons (i.e., B₁-, B₂- and BC-horizon), inorganic aluminum (Al_i) in soil water had more and more important role in regulating $Al_i/(Ca + Mg)$ molar ratio. On regional scale, soil aluminum saturation (AIS) as well as cation exchange capacity (CEC) was the dominant factor controlling $Al_i/(Ca + Mg)$ molar ratio. This should be paid enough attention on when making regional acid rain control policy in China.

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1 Introduction

Acid deposition as well as soil acidification has been recognized as a potential environmental problem in China since last 1980s (Seip et al., 1999; Zhao & Sun, 1986). High aluminum concentration induced by acid inputs was also reported in several experimental and field studies (Guo et al., 2004; Larssen et al., 1998, 1999; Liao, Larssen, & Seip, 1998; Liao, Seip, & Larssen, 1997; Zhu, Jiang, & Ji, 2004). Many studies have shown that elevated concentrations of Al in soil water could cause potential damage to vegetation, while Ca and Mg could counteract this toxic effect (e.g., Anandi, Thangavel, & Subburam, 2002; Anderson, 1988; Gensemer & Playle, 1999; Leblanc & Loehle, 1993; Lydersen & Lofgren, 2002; Silva, Smyth, Israel, Raper, & Rufty, 2001; Yang, Cheng, & Abdullahi, 2001). Therefore, various molar ratios between aluminum and base cations in soil water have been used as indicator to toxicity effects of acidification (e.g., Cronan & Grigal, 1995; de Vries, Reinds, & Vel, 2003; Norton, Kahl, & Fernandez, 1999; Stutter, Smart, Cresser, & Langan, 2001). For example, a molar $Al_i/(Ca + Mg)$ ratio of 1.0 was generally assumed to be a critical limit when calculating the critical loading of acid deposition (e.g., Akselsson, Ardo, & Sverdrup, 2004; Kumar, Gough, Karagatzdies, Bolton, & Tsuji, 2001; Sverdrup & de Vries, 1994; Sverdrup, Warfvinge, & Nihlgard, 1994; van der Salm & de Vries, 2001). Although the rationale and relevance of these ratios have been highly disputed (e.g., Løkke et al., 1996), many work still thought these ratios as reasonable risk implication of acid deposition, especially in comparing the potential effects of acid deposition between different regions (e.g., Larssen et al., 1998; Liao et al., 1997, 1998; Stutter et al., 2001). In China, the distribution and controlling factors of these critical ratios are still not well understood due to lack of relevant study, especially the regional field monitoring studies. Although many relevant studies have been conducted in North America and Europe, applicability of these experiences in Chinese subtropical regions should be carefully tested mainly due to the difference in climate, soil and vegetation between China and other regions.

At present, about one third of Chinese country area receives various acid depositions. Soils in these regions are highly heterogeneous, which brings big difficulties in evaluating the effects of acid deposition

on terrestrial ecosystems. Sino-Norwegian cooperated IMPACTS (Integrated Monitoring Program on Acidification of Chinese Terrestrial Systems) project selected and established five monitoring sites in southern and southwestern China; long-term monitoring on deposition, soil, soil water, stream water as well as vegetation has been conducted. These sites varied in atmospheric deposition, soil properties and vegetation, and are thought to be representative in Chinese acid rain zone (IMPACTS, 2004; Tang et al., 2001). One objective of this article is to investigate the potential effects of acid deposition in different sites and soil horizons using $Al_i/(Ca + Mg)$ molar ratio as a general risk parameter, based on IMPACTS monitoring data. Soil–soil water system is extremely complicate due to the co-linearity between the parameters, which makes it difficult to identify the dominant influencing factors and to evaluate their relative importance, especially on the regional scale. Therefore, another objective of this article is to distinguish and assess the main factors controlling this $Al_i/(Ca + Mg)$ molar ratio in Chinese acid forest soils using multivariate methods.

2 Materials and Methods

2.1 Site description

All studied five sites are located in southern and southwestern China, where acid rain has been thought as a serious problem. Climate in these regions is subtropical and monsoonal. These sites are forested and practically undisturbed by land-use activities. The forests are mixed deciduous and conifer dominated by the coniferous species. Much of the forests were replanted in the 1960s. Sulphate is the dominating anion in precipitation; calcium and/or ammonium are the main cations. Beside wet deposition, dry deposition is another important contributor to the acid loading on terrestrial ecosystem. IMPACTS field monitoring indicated that dry deposition was about equal to (even larger than) the wet deposition (IMPACTS, 2004). Dominant soil types in these sites are *haplic acrisol/ferric acrisol*, and are representative for southern and southwestern China. Soil acidity ranges from moderate to strongly acidic. Some basic information of these sites is listed in Table I; detail information of these sites can be found in IMPACTS annual report (IMPACTS, 2004) and some specific papers (e.g.,

Table 1 Basic information of IMPACTS sites

Sites	Location	Wet deposition ^a					Bedrock	Mineral	Dominant forest
		Precipitation (mm)	pH ^b	S (g m ⁻² year ⁻¹)	N (g m ⁻² year ⁻¹)	Ca (g m ⁻² year ⁻¹)			
TSP (Tie Shan Ping)	106°41'E, 29°38'N	1,228	4.11	3.47	1.93	1.27	Sandstone	Kaolinite	Mason pine
LCG (Lu Chong Guan)	106°43'E, 26°38'N	703	4.63	2.40	0.70	1.87	Sandstone	Kaolinite	Mason pine
LGS (Lei Gong Shan)	108°11'E, 26°22'N	1,615	4.75	1.40	0.93	0.70	Shale	Kaolinite, semetite, illite	Armandi pine
CJT (Cai Jia Tang)	112°26'E, 27°55'N	1,251	4.40	2.50	2.07	1.13	Sandstone/shale	Illite	Mason pine/Chinese fir
LXH (Liu Xi He)	113°35'E, 23°33'N	1,434	4.43	1.90	0.95	1.85	Granite	Illite	Machilus broadleaves

^aData for wet deposition is average in monitoring period.

^bpH is average of annually volume weighted in the monitoring period.

Larssen et al., 1998, 1999; Tang et al., 2001; Zhao et al., 2001).

2.2 Sampling and analysis

In each site there were four intensive plots (i.e., well defined 10 × 10 m squares in the watershed) and one to several additional soil water plots. In each of these plots, four to five ceramic tension lysimeters (approx. 0.5 vacuum atm.) were installed down soil profile according to genetic horizons. Soil waters were weekly sampled, and four weekly samples from the same lysimeter were pooled into one sample for chemical analysis. Soil samples close to each lysimeter were also collected for chemical analysis.

Water and soil samples were analyzed by IMPACTS local and central laboratories. Analytical quality was well controlled by frequently inter-calibrations between laboratories in China and Norway. Major anions (SO₄²⁻, NO₃⁻, Cl⁻, F⁻) and cations (Ca²⁺, Mg²⁺, K⁺, Na⁺, NH₄⁺) in soil water were determined by Ion Chromatography (Dionex DX 120). UV-absorbency at 254 nm was chosen as the proxy of dissolved organic carbon. The factor between UV-absorbency and DOC was found to be 30.2 (Guo & Vogt, 2004). The monomeric fraction of aluminum (Al_a) was determined using the 8-hydroxy-quinoline method (Barnes, 1975). Organic fraction (Al_o) was determined by first passing the sample through an Amberlite IR-120 cation exchange column. Inorganic fraction (Al_i) was calculated as the difference between Al_a and Al_o.

(Driscoll, 1984). Soil cation exchange capacity (CEC) was measured using the BaCl₂ extraction method (Hendershot & Duquette, 1986). Metal cations in the BaCl₂ extracts were determined using ICP-AES, H⁺ activity was determined using a pH combination electrode. Sum of exchangeable cations (i.e., H, Al, Fe, Mn, K, Na, Ca and Mg) was calculated as CEC. Fraction of Al and base cations (i.e., K, Na, Ca and Mg) in CEC were calculated as soil aluminum saturation (AIS) and soil base saturation (BS), respectively. Other parameters were determined using the Chinese national or international commonly used methods and can be found in the IMPACTS manuals (<http://folk.uio.no/rvogt/Impacts/>).

2.3 Statistics and data compiling

There are complicate interrelationships among the chemical parameters of soil and soil water. This made it difficult to distinguish and evaluate the relative influences of certain parameters on the other(s). Therefore, principal component analysis (PCA) and partial least square (PLS) regression were introduced in our study, to deal with the co-variances among the parameters. Principle component analysis describes the correlations of multiple variables (x-matrix) by extracting number of principle components that bring statistically significant variance of original dataset. This dimension-lowering treatment of multivariable dataset provides a powerful tool to understand the correlations among the interested variables. Based on the PCA method, partial least square

(PLS) regression finds the linear (or polynomial) relationship between multiple independent variables (x -matrix) and dependent variables (y -matrix). A PLS model, therefore, geometrically corresponds to fit a line, plane or hyper plane between two spaces by extracting number of principal components bringing maximum variances of two spaces. The loadings of variables in established PLS model show their relative importance in modelled plane. In this study, we carried out PCA and PLS analysis using SIMCA-P 10.0 software (Umetrics AB, Sweden).

Three years (2001–2003) monitoring data from TSP, LCG, LGS, CJT site and two years (2002–2003) data from LXH site were included in present study. In five IMPACTS sites, there were 103 lysimeters installed in four soil horizons (i.e., A-, B₁-, B₂- and BC-horizon), respectively. Data for each lysimeter were treated as one observation in PCA and PLS analysis. For each observation, each soil water parameter was its average during monitoring period; each soil parameter was its average of several soil samples close to the same lysimeter.

3 Results and Discussions

3.1 Soil and soil water chemistry characteristics

Both soil and soil water chemistry varied significantly in different sites and horizons (IMPACTS, 2004).

Since chemical parameters of soil and soil water are usually correlated, principle component analysis (PCA) was used to maximally understand the chemical differences among the sites and soil horizons. Major soil water compounds, fraction of soil exchangeable cations, cation exchange capacity (CEC), dissolved organic carbon (DOC) and soil organic carbon (SOC) were included in the PCA model. The loading plot of variables on the first two components is shown in Figure 1a. Scores of soil horizons in five sites on these two components is accordingly plotted as Figure 1b. For clarity, the error bars were not presented in Figure 1b. The first principle component (PC1) with 33% of dataset variance describes ionic strength and acidity of soil solution (i.e., intensity factor), while the second component (PC2) with 19% of dataset variance mainly indicates soil acidity (e.g., AIS virus BS) as well as soil richness (e.g., CEC; i.e., capacity factor).

It is easier to find the major chemical difference among different sites and soil horizons, based on the comparison between Figure 1a and b. TSP site had higher score on both components in Figure 1b, which indicated highest ionic strength and acidity in soil water, and higher soil acidity (i.e., AIS). In Figure 1b, LCG and CJT site were plotted closely, indicating the similar situation between two sites. These two sites had similar ionic strength in soil water, but acidity of soil water in LCG site was higher than that in CJT site. Also, soil cation exchange capacity was higher than that of CJT, mainly due to higher clay content.

Figure 1 Variable loading (a) and soil horizon score (b) on the first two principal components.

All LXH horizons located in the top left section of Figure 1b, suggesting lower ionic strength and acidity in soil water, and lower soil CEC but higher aluminum saturation. In LXH site, ionic strength as well as acidity in soil water was the second lowest besides LGS site. However, soil cation exchange capacity (CEC) in LXH was the lowest in five sites. Furthermore, much of soil exchangeable sites were occupied by acid aluminum with soil aluminum saturation (AIS) of 78.2% ($\pm 3.75\%$) in four horizons. In five IMPACTS site, LGS catchment located in remote Leishan Mountain area was regarded as background site due to lower acid loading. Soils were moderate acidic with pH (water) ranging from 4.04 (10 percentile) to 5.67 (90 percentile). Soil base saturation (BS) was higher than 20% with median value of 32.5% for four horizons. Ionic strength as well as acidity of soil water was the lowest in all five sites. Therefore, four soil horizons of LGS site were plotted in the bottom left in Figure 1b.

In each site, wet-only deposition (WO) was weekly collected and analyzed during the monitoring period. However, there was only one deposition chemistry, but more than 10 soil water chemistry data in each site. Due to this inequality in the number of deposition and soil water, deposition data were not able to be included in the PCA analysis. However, comparison between soil water intensity factor (i.e., ionic strength and acidity, Figure 1b) and wet-only deposition (Table I)

showed that the order of water intensity factor was as same as the deposition intensity for five sites. This supported the conceptual linkage between acid deposition and soil water chemistry. We could say that the variations in intensity factor of soil water among different sites were mainly due to the difference in acid deposition intensity.

3.2 Inorganic aluminum (Al_i) and $Al_i/(Ca + Mg)$ molar ratio

In IMPACTS sites, inorganic aluminum (Al_i) was absolutely dominant fraction in monomeric aluminum (Al_a); organic aluminum (Al_o) in most soil waters was less than 10%. Also, organic aluminum is thought as less toxicity than inorganic aluminum. Therefore, only inorganic aluminum (Al_i) variation was presented. In Figure 2a, aluminum (Al_i) variations between sites exactly agreed with their water ionic strength shown in Figure 1b along the second component. In TSP site with highest acid loading, aluminum (Al_i) was the highest in five sites, with average of 236 and 328 $\mu\text{mol l}^{-1}$ in A and BC horizon, respectively. While in LXH and LGS site with lower acid loading, higher aluminum was not observed over three-year monitoring.

Variations of $Al_i/(Ca + Mg)$ molar ratio are shown as Figure 2b. For most soil water samples, molar ratios were generally lower than the critical value of

Figure 2 Distribution of inorganic aluminum (Al_i) and $Al_i/(Ca + Mg)$ molar ratio in different sites and soil horizons: (a) inorganic aluminum (Al_i); (b) $Al_i/(Ca + Mg)$ molar ratio.

1.0. Even in TSP site that received most high acid loading, there only were 15% to 34% samples with molar ratio higher than 1.0 in A- and BC-horizon, respectively. Comparison between Figure 2a and b indicated that variation in $Al_i/(Ca + Mg)$ molar ratio did not fully agree with that of inorganic aluminum (Al_i). In soil water of LXH site, $Al_i/(Ca + Mg)$ molar ratios were significantly higher than other sites (even higher than TSP site), despite of lower acid loading (Table I) and inorganic aluminum (Al_i) concentration (Figure 2a).

Decrease in pH resulted from acidic deposition have been regarded as the important reason for aluminum release (e.g., Berggren, Mulder, & Westerhof, 1998; Dahlgren & Walker, 1993; Larssen et al., 1999; Mulder & Stein, 1994). So decrease in soil water pH would lead to increase in $Al_i/(Ca + Mg)$ molar ratio. In Figure 3a, $Al_i/(Ca + Mg)$ molar ratios were exponentially related with solution pH in all four horizons ($P < 0.01$). Compared with other horizons, molar ratios were less dependent on pH in A-horizon. On the other hand, $Al_i/(Ca + Mg)$ molar ratio in soil water was also regulated by soil properties (i.e., capacity factor). In Figure 3b, $Al_i/(Ca + Mg)$ molar ratios were exponentially related with soil base saturation (BS; $P < 0.01$). Therefore, both soil property (i.e., capacity factor) and soil water chemistry (i.e., intensity factor) had influences on $Al_i/(Ca + Mg)$ molar ratio. However, their relative importance to $Al_i/(Ca + Mg)$ molar ratios were difficult to be evaluated in above discussion.

3.3 Partial least square (PLS) regression

To distinguish relative importance of controlling factors to $Al_i/(Ca + Mg)$ molar ratios in soil water, partial least square (PLS) regression was introduced instead of complicate chemical mechanisms. In the PLS analysis, 25 possible influencing parameters from both soil and soil water were treated as x -variables (Table II). $Al_i/(Ca + Mg)$ molar ratio in soil water was thought as y -variable. All variables used in PLS analysis were centered and scaled to unit variance. For clarity, only the first two principle components were discussed.

The loading plot of variables for A-horizon is shown as Figure 4a. The first component mainly describes soil capacity properties (e.g., AIS, BS and CEC). Soil water acidity (i.e., intensity factor) is also partly reflected by the first principle component, because of higher loadings of water alkalinity (Alk), aluminum (Al_i) as well as hydrogen (H^+) on it. The second principle component did not bring statistically significant dataset variances, mainly describing the relative distribution of cation distribution (e.g., Al_i versus Ca and Mg) in soil water. $Al_i/(Ca + Mg)$ molar ratio (ratio in Figure 4a) was more heavily loaded on the first component, which indicated that both soil properties and soil water acidity was the main factor influencing molar ratio in A-horizon. For soil properties, higher soil aluminum saturation (AIS), lower soil base saturation (BS) as well lower would increase $Al_i/(Ca + Mg)$ molar ratio in soil water. For soil water chemistry, higher acidity (i.e., H^+ and Al_i) would lead

Figure 3 Relationships of $Al_i/(Ca + Mg)$ molar ratio with water pH (a) and soil base saturation (b).

Table II Basic information of partial least square (PLS) regression analysis

Horizon	Number of observation	Optimal components numbers	x-variance explained by the first two components (%)	y-variance explained by the first two components (%)
A	34	1	45	72
B ₁	24	3	51	82
B ₂	24	2	50	76
BC	21	2	48	90
x-variables in PLS regression				
Soil		H _f ^a , K _f , Na _f , Mn _f , Fe _f , Ca _f , Mg _f , CEC, AIS, BS, SOC		
Soil water		H ⁺ , K ⁺ , Na ⁺ , Ca ²⁺ , Mg ²⁺ , NH ₄ ⁺ , SO ₄ ²⁻ , NO ₃ ⁻ , Cl ⁻ , F ⁻ , DOC, Si, Alk, Al _i		

^af means the fraction of exchangeable cations in soil CEC.

higher Al_i/(Ca + Mg) molar ratio in soil water. A closer look at Figure 4a indicated that absolute loadings of soil aluminum saturation (AIS) on Al_i/(Ca + Mg) molar ratio (a thought line from origin to ratio in Figure 4a) were higher than the loading of soil water acidity (Al_i and H⁺). This suggested that soil aluminum saturation had higher influence on Al_i/(Ca + Mg) molar ratio in A-horizon. This was also consistent with less dependence of molar ratio on water pH in A-horizon (Figure 3a). In LXH site, Al_i/(Ca + Mg) molar ratio were higher than other sites, despite of lower acid loading and lower soil water intensity properties (i.e., ionic strength and acidity). This should be attributed to the influence of soil aluminum saturation.

Loading plots of variables are presented as Figure 4b–d for B₁-, B₂- and BC-horizon, respectively. Compared with A-horizon, there were several differences in deeper horizons. Firstly, loadings of soil aluminum saturation (AIS) and base saturation (BS) on the first component tended to be smaller; ions in soil water had higher loadings on the first component. Therefore, soil water ionic strength and acidity were mainly reflected by the first principle component. Secondly, absolute loading values of aluminum (Al_i) and base cations (Ca and Mg) in soil water on the second principal component increased significantly compared with A-horizon. This indicated that cation distribution in soil water was described by the second

Figure 4 Loading plots of PLS regression ((a) A-horizon (b) B₁-horizon (c) B₂-horizon (d) BC-horizon).

principal component. The first two components described simultaneously the aqueous chemistry, which suggested that soil water chemistry was the dominant factor controlling $Al_i/(Ca + Mg)$ molar ratio in soil water. Thirdly, in all variables inorganic aluminum (Al_i) had the highest loading on molar ratio (a thought line from origin to ratio in Figure 4). Therefore, aluminum (Al_i) in soil water was the dominant factor controlling the value of $Al_i/(Ca + Mg)$ molar ratio in deeper soil horizons. Any factor increasing aluminum concentration would increase the molar ratio in soil water. $Al_i/(Ca + Mg)$ molar ratio also had higher loading on the first component that indicated ionic strength and acidity of soil water. The reason for this is that these two factors can accelerate the release of aluminum from soils. Studies showed that higher ionic strength increased the concentration and percentage of aluminum in water (Guo et al., 2004; Matschonat & Vogt, 1998; van Hees, Lundstrom, Danielsson, & Nyberg, 2001). Comparing loading plot in Figure 4, we could find that influence of inorganic aluminum (Al_i) on $Al_i/(Ca + Mg)$ molar ratio increased with soil depth (i.e., from A-horizon to BC-horizon). Therefore, vertical variation in inorganic aluminum (Al_i) would strongly affect $Al_i/(Ca + Mg)$ molar ratio changes down soil profile.

In Figure 4, soil properties (i.e., AIS, BS as well as CEC) had significant loadings on molar ratio in all four horizons, despite of clear decrease along soil depth. So soil capacity properties may determine the value of $Al_i/(Ca + Mg)$ molar ratio on the regional scale. Regions with higher soil aluminum saturation and lower soil cation exchange capacity usually had higher $Al_i/(Ca + Mg)$ molar ratio in soil water, even though with lower acid loading. In Figure 2b, regional variations in $Al_i/(Ca + Mg)$ molar ratio among five sites were in the same order as their difference in soil aluminum saturation (AIS) (i.e., along the second component in Figure 1b). Stutter et al. (2001) reported an exponential relationship between Ca/Al_i molar ratio and stream pH in sub-catchments of River Dee, northeast Scotland. They attributed it to the influence of catchment characteristics. In this study, LXH site may serve as an example for such sensitive regions. Soils in these regions are called red soil in Chinese classification system (ferric Acrisol in FAO system). These soils are widely distributed in Chinese acid rain control zone, covering about 1/5 of country area. Therefore, special measure should be taken to avoid serious aluminum toxicity in these regions.

4 Conclusions

$Al_i/(Ca + Mg)$ molar ratios in soil water varied significantly in all investigated sites and horizons. In most cases, molar ratio was still lower than thought critical 1.0, except in some soil waters of TSP and LXH site. Both soil properties and soil water chemistry affected $Al_i/(Ca + Mg)$ molar ratio in soil water, but they had different relative importance in different horizons. In A-horizon, soil aluminum saturation (AIS) had more important role than soil water intensity factor (i.e., acidity and ionic strength) in controlling $Al_i/(Ca + Mg)$ molar ratio in soil water. In the deeper horizons, inorganic aluminum (Al_i) in soil water had more and more important role in regulating $Al_i/(Ca + Mg)$ molar ratio. Variation in inorganic aluminum (Al_i) led to the vertical changes in $Al_i/(Ca + Mg)$ molar ratio down soil profile. On regional scale, soil aluminum saturation (AIS) as well as soil cation exchange capacity (CEC) was the dominant factor controlling the value of $Al_i/(Ca + Mg)$ molar ratio in soil water. Red soils widely distributed in Chinese acid rain zone are highly sensitive to acid deposition, carefully attentions should be paid on these regions in Chinese acid rain controlling policy making.

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