

Mechanism of aluminum release from variable charge soils induced by low-molecular-weight organic acids: Kinetic study

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Abstract

The kinetic curves of aluminum release from two variable charge soils and a kaolinite within 48 h can be divided into three stages: the first stage located within the initial 30 min, at which the release rate of Al was the fastest one and the released Al dominantly originated from exchangeable Al and amorphous Al pools. The Elovich equation fit the kinetics data at this stage fairly well. The moderate and the slow stages occurred within 0.5–2 and 2–48 h, respectively. During these two stages, the released Al was mainly attributed to Al oxides, poorly crystalline kaolinite and easily weathered hydrous mica. The different linear equations also fit the kinetics data at these two stages well. The rate of Al release decreased sharply with time during the fast stage, but the rate remained constant during the moderate and slow stages. In Ultisol, Al oxides were the more important pool for Al release than poorly crystalline kaolinite and easily weathered hydrous mica during the latter two stages. In Oxisol, poorly crystalline kaolinite was the more important Al pool. Compared to the control system, the presence of organic acids increased the rate and quantity of Al release from variable charge soils. The ability of organic acids to accelerate Al release followed the order: oxalic acid > citric acid > malic acid > lactic acid. This is generally in consistent with the magnitude of the stability constants of the Al–organic complexes. The release rate of Al also increased with the rise in concentration of organic acids.

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1. Introduction

Soil acidification induced by acid precipitation is a global ecological and environmental problem. Dissolution of Al from solid phases is an important acid buffering process in acidic soils containing few base cations (Ritchie, 1994; Zysset et al., 1999), but leads to an increase in Al concentration in soil solution. The high concentration of soluble Al is a measure of Al toxicity in the terrestrial and aqueous systems (Parker et al., 1988; Hunter and Ross, 1991; Spósito, 1996; Beyrouty et al., 2000).

Research on Al release has mainly focused on two aspects in the past. One was the dissolution kinetics and mechanism of Al oxides and aluminosilicates. The influence of pH and

organic acids on dissolution rate of Al oxides and aluminosilicates (viz., kaolinite and feldspar) was usually interpreted on the basis of a surface-reaction model (Wieland et al., 1988; Drever and Stillings, 1997). This model contended that the dissolution rate was proportional to the concentration of surface species (protonated sites, deprotonated sites, and/or organic complexes at the mineral surface), which were precursors to the activated complex. The framework for the most commonly applied surface-controlled model was established by Furrer and Stumm (1986) for the dissolution of simple oxides δ -Al₂O₃ and BeO. They explained the mechanism involved at the interfacial region between hydrous oxides and aqueous solution as characterized by adsorption of H⁺, OH⁻, cations, anions, and weak acids to specific surface sites on the oxide surface.

The second aspect was the mechanism of Al release and the control of Al solubility in soils. The sources, their

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capacities and release kinetics for Al release in different conditions have gained more attention recently. Most hydrochemical models assumed that Al^{3+} is in an equilibrium state with a single $\text{Al}(\text{OH})_3$ mineral phase such as gibbsite. This assumption appears valid for a number of soil solutions, especially in highly weathered soils with low organic matter contents, such as soils in Australia (Conyers, 1990). However, under certain conditions, natural solutions may significantly depart from the equilibrium with $\text{Al}(\text{OH})_3$.

Some workers have attempted to explain field observations of aluminum in terms of kinetically constrained dissolution of minerals (Matzner and Prenzel, 1992), but a growing body of evidence suggested that in temperate zones the labile aluminum pool in soil was largely associated with organic matter, even in many acid mineral soils (Bloom et al., 1979; Mulder and Stein, 1994; Skyllberg, 1999); and, that on a short timescale, organic complexation controlled aluminum chemistry in such soils (Dahlgren and Ugolini, 1989; Walker et al., 1990; Berggren and Mulder, 1995). Therefore, different Al pools could control Al solubility at different conditions. For example, the Al solubility was controlled by different Al pools in different horizons of the profile in a podzol (Zysset et al., 1999).

Low-molecular-weight (LMW) organic acids are the most active part in organic matter and exist widely in soils, especially in the rhizosphere. These acids possess one or more carboxyls and hydroxyls functional groups that can form complexes with metals in soils and thus play an important role in soil processes such as mineral weathering, nutrient mobilization and Al detoxification (Boyle et al., 1974; Hue et al., 1986; Bolan et al., 1994; Han and Jordan, 1995; Xu et al., 2002; Feng et al., 2004).

Some authors have shown that organic acids could promote Al dissolution by proton-promoted and ligand-promoted mechanisms. Proton-promoted mechanism mostly involves the Si centered sites, and this effect becomes more predominant as pH decreases. For the ligand-promoted mechanism, there are two possible interpretations. Some scientists suggested that organic acids could form surface complexes with Al in the solid phase and decreased the activation energy of the rate-limiting step for Al dissolution (Furrer and Stumm, 1986; Amrhein and Suarez, 1988; Welch and Ullman, 1993). However, in recent years, Kubicki et al. (1999) found that although strong, inner-sphere surface complexes of organic acids form on mineral surfaces, they may actually strengthen Al bonds to the rest of the mineral rather than weaken them. They suggested that the reason for the increase in dissolution rate of Al was the decrease in ΔG associated with lowering the activity of Al in solution due to complex formation. Similar phenomenon was observed in goethite system (Cheah et al., 2003). For this system, adsorption of oxalate at lower concentration did not result in an increased dissolution rate of Fe(III). The dissolution rate increase was not seen until the affinity of the reaction was increased either by increasing the oxalate solution concentration or adding siderophore (Cheah et al., 2003).

Soils on earth may be broadly classified into two basic categories: constant charge soils and variable charge soils. Owing to the characteristics of variable charge soils in chemical and mineralogical compositions, these soils possess remarkable chemical properties different from that of constant charge soils. Variable charge soils are acid soils distributing widely in the tropical and subtropical regions of south China, where Al toxicity is the main cause of the unfavorable effect of acid soils on plants (Feng et al., 1999).

Although the mobilization of Al in variable charge soils as affected by organic acids has been studied extensively, little information is available on the kinetics of Al release induced by organic acids. The mechanism involved in the release of Al from mineral samples in the presence of organic acids was also extensively studied; but few reports have appeared on these complex soils. To our knowledge, soils composed of several kinds of minerals may have different mechanism of Al release. Therefore, the objective of this paper is to investigate the effects of LMW organic acids on the kinetics and mechanism of Al release in short timescale and to evaluate the relative contribution of different Al pools to Al release in variable charge soils.

2. Materials and methods

2.1. Soils and organic acids

Two variable charge subsoils, Oxisol (located at $110^{\circ}10'E$, $20^{\circ}20'N$) and Ultisol (located at $116^{\circ}17'E$, $28^{\circ}23'N$) were collected, respectively, from Xuwen, Guangdong Province and Jinxian, Jiangxi Province, China. These two soils, occupying large areas, are representative of major types of soils in these regions. The soil samples were taken from a depth of 70 to 100 cm. The organic matter content was very low (Table 1). Selected properties of these soils are given in Table 1. Similarly, the kaolinite samples were collected from Suzhou, Jiangsu Province, China. The X-ray diffraction pattern and chemical analysis showed that this kaolinite had good crystalline properties and high degree of purity. The kaolinite has a CEC of $5.58 \text{ cmol kg}^{-1}$. The samples were air-dried and ground to pass a 60-mesh sieve.

Table 1
Selected properties of the tested soils

Soil	pH ^a	Apparent CEC ^b (cmol kg^{-1})	Fe_2O_3^c (mmol kg^{-1})	O.M ^d (g kg^{-1})	Dominant clay mineral ^e
Oxisol	5.6	7.15	979.3	7.0	K,G,H
Ultisol	4.8	8.91	320.0	4.4	K,I(V)

^a Soil:water1:2.5.

^b Ammonium acetate method.

^c DCB method.

^d Dichromate method.

^e K, kaolinite; G, gibbsite; H, hematite; I, hydrous mica; V, vermiculite.

Lactic acid, oxalic acid, malic acid and citric acid were used for the study because they occur naturally in soils. All the acids used were AR or equivalent grade reagents.

2.2. X-ray diffraction analysis

For X-ray diffraction analysis, the kaolinite sample was pressured in the hole of an aluminum frame to form powder samples, and the XRD spectrum was recorded using a D/max-IIIc X-ray diffractometer (made in Japan) with $\text{CuK}\alpha$ radiation.

2.3. Preparation of K-saturated soil

To investigate the effect of exchangeable Al on the Al release in soils, K-saturated samples were prepared to depress the content of exchangeable Al with 1.0 mol L^{-1} KCl by soaking the samples in the KCl solution with a soil-to-solution ratio of 1:5 for 5 days and equilibrium solution was changed every day. After saturation, the excessive KCl was removed by washing with deionized water until no Cl^- ion in the supernatant solution was detected with 0.1 mol L^{-1} AgNO_3 (Li et al., 2005).

2.4. Preparation of $\text{H}^+ - \text{Al}^{3+}$ saturated soil

Some samples were electro-dialyzed to make them $\text{H}^+ - \text{Al}^{3+}$ saturated as the soils were ultrasonically dispersed in 0.1 mol L^{-1} NaOH medium for 25 min, and then electro-dialyzed at a potential gradient of 15 V cm^{-1} until a constant specific electric conductance of the suspension was achieved (Ji and Kong, 1992). The treated sample was dried at 60°C using an IR lamp and reground to pass a 60-mesh sieve.

2.5. Removal of amorphous Al oxides and free Al oxides

In order to investigate the effects of aluminum oxides on Al release from the soils, amorphous Al oxides and free Al oxides were removed from the Oxisol with acid ammonium oxalate method (AAlreOxisol) and DCB method (FAlreOxisol), respectively (Hseung, 1985). For the removal of amorphous Al oxides, soil samples were mixed with the 0.2 mol L^{-1} ammonium oxalate (pH 3.0) with a soil-to-solution ratio 1:50, and the suspension was shaken for 2 h. The solid was then separated from the solution by centrifugation at 3880g for 10 min and the treated sample was electro-dialyzed to make $\text{H}^+ - \text{Al}^{3+}$ saturated. For removal of free Al oxides, 5.0 g of soil sample was taken into 250 ml centrifuge tube, and 100 ml of 0.3 mol L^{-1} citrate and 12.5 ml of 1 mol L^{-1} NaHCO_3 were added into this sample. The temperature of the suspension was increased to 80°C in a water bath and then 2.5 g sodium dithionite was added, and the mixture was stirred constantly for 15 min in the water bath. The solid was then separated from the solution by centrifugation at 3880g for 10 min. The same procedure was repeated for three times. The solid

in centrifuge tube was washed with 1.0 mol L^{-1} NaCl at least two times, and finally the sample was electro-dialyzed to make it $\text{H}^+ - \text{Al}^{3+}$ saturated as described above. The operational extraction technique is not exclusively selective; however, it does provide a means of comparison for the relative distribution of Al between the various extractable Al pools.

2.6. Experimental procedure

The ability of acetate to complex with Al is very weak (Sposito, 1996); hence, acetic acid/sodium acetate (0.01 mol L^{-1}) buffer was chosen as pH buffer solution. An appropriate quantity of each organic acid, 0.5 mol L^{-1} acetic acid/sodium acetate and deionized water were added into a flask to obtain the mixed solutions containing 0.01 mol L^{-1} acetic acid/sodium acetate and varying concentrations of organic acid (0.2, 0.5, and 1.0 mmol L^{-1} for concentration-effect experiment and 1.0 mmol L^{-1} for other experiments). All solutions contained 0.01 mol L^{-1} sodium nitrate as supporting electrolyte. In the control treatment, acetic acid/sodium acetate (0.01 mol L^{-1}) and sodium nitrate (0.01 mol L^{-1}) were used. One liter of the sample solution or the control solution was taken in a 1.25 L beaker and the solution pH was adjusted to its required value with 1:1 (v/v) HNO_3 or 5.0 mol L^{-1} NaOH. The beaker with its content were placed in a constant temperature water-bath at $28(\pm 1)^\circ\text{C}$. Then, 10.0 g of soil sample or kaolinite sample was added to the beaker and the suspension was stirred with a mechanical stirrer. 15 ml suspension in duplicate was taken at certain intervals through a 48-h period and the suspension was filtered through a $0.45 \mu\text{m}$ membrane filter by applying vacuum through a pump system. The filtrate was taken for measuring Al and Si. Al was determined by the 8-hydroxyquinoline method at pH 8.3, using butyl acetate as an extractant (Xu et al., 2002; Li et al., 2004) and Si was measured by ICP-spectroscopy.

The pH values for all the solutions obtained during the kinetic experiments were determined. The results obtained indicated that the change of pH was less than 0.1 pH unit during the experiments. Therefore, the initial pH value of suspension systems was presented in the figures and tables.

3. Results and discussion

3.1. Kinetics and mechanisms of Al release in the presence of citric acid

The release rate of Al from well crystalline minerals is very slow. Hence, two typical variable charge soils, Oxisol and Ultisol, and a well crystalline kaolinite were chosen for the investigation. Fig. 1 shows the kinetic curves of Al release in the presence of citric acid. The data demonstrate that the release rate of Al from variable charge soils was faster than that from kaolinite, especially in the initial 2 h of reaction time. Several empirical equations were used to

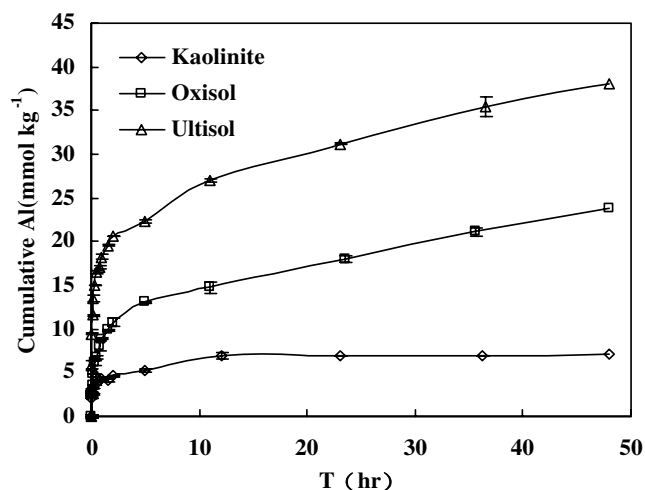


Fig. 1. The plot of cumulative Al vs. time in Oxisol, Ultisol, and kaolinite in the presence of citric acid at pH 4.0 (Initial concentration of citric acid was 1.0 mmol L^{-1}).

describe kinetics of Al release. The data within 0–0.5 h fit the Elovich equation $Y = A \ln(t) + B$ fairly well, where Y is quantity of cumulative Al of release and A and B are constants. The Elovich equations fitted $Y = 0.918 \ln(t) + 4.618$ for kaolinite, $Y = 1.229 \ln(t) + 5.712$ for Oxisol and $Y = 3.161 \ln(t) + 19.241$ for Ultisol, and the correlation coefficients (R^2) for kaolinite, Oxisol, and Ultisol were 0.986, 0.966, and 0.989, respectively. From the Elovich equation, the rate equation for Al release was obtained by $dY/dt = A/t$. The plot of dY/dt versus time is shown in Fig. 2, where dY/dt is release rate of Al from soils and kaolinite. The results shown in Fig. 2 clearly suggest that the rate and the quantity of Al release from different soils and kaolinite followed the order: Ultisol > Oxisol > kaolinite and decreased sharply with the lapse of time, which reflects the order of the release rate of Al for Oxisol, Ultisol and kaolinite was in agreement with that of A values in Elovich equation. Thus the A value can be used to compare the relative rate of Al release.

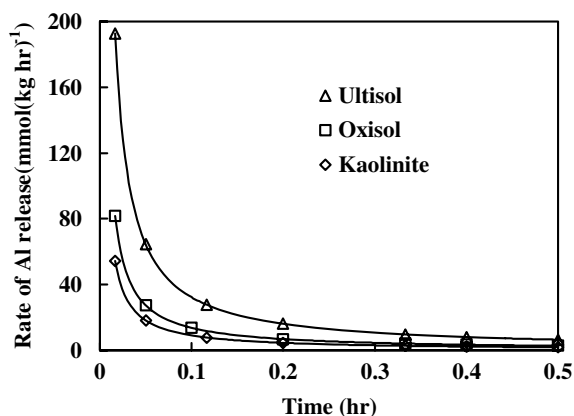


Fig. 2. The plot of release rate of Al vs. time in Oxisol, Ultisol, and kaolinite at fast stage in the presence of citric acid at pH 4.0 (Initial concentration of citric acid was 1.0 mmol L^{-1}).

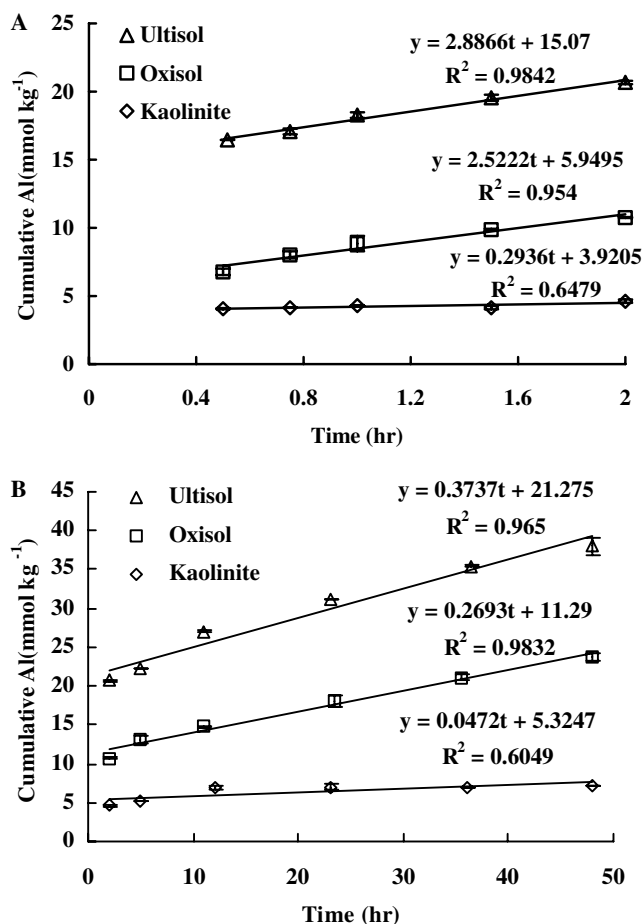


Fig. 3. The plot of cumulative Al vs. time and fitted linear equations in Oxisol, Ultisol, and kaolinite at (A) moderate stage and (B) slow stage in the presence of citric acid at pH 4.0 (Initial concentration of citric acid was 1.0 mmol L^{-1}).

The data in the intervals between 0.5–2 and 2–48 h fit linear equations well (Fig. 3). The slopes of these lines within the two intervals represent the release rate of Al. Results suggest that the release rate of Al within 0.5–2 h was higher than that within 2–48 h. Further, based on the results from fitting of empirical equation for the kinetics of Al release, the kinetic curves within 48 h can be divided into three stages: the first stage within 30 min, the second stage within 0.5–2 h and the third stage within 2–48 h. The rates of Al release at different stages were different, and they were termed the fast, the moderate, and the slow stages.

The release rate of Al from Ultisol during the fast stage was much higher than that from Oxisol and kaolinite (Fig. 2). The faster rate may be due to the higher content of exchangeable Al in Ultisol than in Oxisol and kaolinite (Table 2). The exchangeable Al can release to the solution through ion exchange. The exchange reaction of Al on clay mineral surfaces is extremely fast; hence, the exchangeable Al may release from the clay mineral surface within few minutes (Walker et al., 1988; Dahlgren and Walker, 1993).

In order to verify the importance of exchangeable Al to Al release at the fast stage, Ultisol, electro-dialyzed Ultisol, and K-saturated Ultisol were chosen for the investigation.

Table 2

Contents of exchangeable Al and amorphous Al of different kinds of soils and Elovich equations fitting the kinetics of Al release from these soils within 0–0.5 h

Soil	Exchangeable Al (mmol kg ⁻¹)	Amorphous Al (mmol kg ⁻¹)	Elovich equations fitted for the data within 0–0.5 h
Kaolinite	5.02 ± 0.07	19.31 ± 1.23	$Y = 0.908 \text{Ln}(t) + 4.618, R^2 = 0.987$
Electro-dialyzed Kaolinite	15.30 ± 0.06	50.81 ± 1.12	$Y = 2.214 \text{Ln}(t) + 12.570, R^2 = 0.994$
K-saturated Oxisol	1.06 ± 0.09	88.69 ± 2.82	$Y = 1.927 \text{Ln}(t) + 9.417, R^2 = 0.921$
Oxisol	1.11 ± 0.07	78.56 ± 2.81	$Y = 1.229 \text{Ln}(t) + 6.712, R^2 = 0.966$
Electro-dialyzed Oxisol	0.84 ± 0.02	87.19 ± 1.31	$Y = 2.192 \text{Ln}(t) + 11.851, R^2 = 0.972$
AAlreOxisol	8.82 ± 0.08	ND	$Y = 1.949 \text{Ln}(t) + 13.015, R^2 = 0.988$
FAlreOxisol	21.44 ± 0.00	ND	$Y = 1.807 \text{Ln}(t) + 21.670, R^2 = 0.973$
K-saturated Ultisol	1.95 ± 0.04	69.75 ± 1.12	$Y = 2.033 \text{Ln}(t) + 11.333, R^2 = 0.958$
Ultisol	13.49 ± 0.07	81.19 ± 0.94	$Y = 3.161 \text{Ln}(t) + 19.241, R^2 = 0.989$
Electro-dialyzed Ultisol	15.27 ± 0.19	82.13 ± 4.50	$Y = 3.641 \text{Ln}(t) + 21.796, R^2 = 0.958$

ND, not determined.

The main difference among these soil samples was in the content of exchangeable Al (Table 2). The contents of exchangeable Al in electro-dialyzed Ultisol, Ultisol and K-saturated Ultisol were 15.30, 13.50, and 1.95 mmol kg⁻¹, respectively, which agreed with the order of the quantity of released Al at the same reaction time and the magnitude of *A* values in the Elovich equation for these soils (Fig. 4). The *A* values were 3.64, 3.16, and 2.03 for electro-dialyzed Ultisol, Ultisol, and K-saturated Ultisol, respectively. Due to the high degree of saturation of Al in Ultisol, the exchangeable Al did not increase much more after electro-dialysis treatment. However, the comparison among electro-dialyzed Ultisol, Ultisol, and K-saturated Ultisol implied that the exchangeable Al was an important Al pool for Al release at the fast stage. The results for kaolinite and electro-dialyzed kaolinite also supported this point of view. The rate of Al release from electro-dialyzed kaolinite was larger than that from kaolinite, which also coincided with their exchangeable Al contents (Table 2 and Fig. 5).

Amorphous Al oxides are also important Al pools to Al release in soils in addition to exchangeable Al during the fast stage. The contents of exchangeable Al in Oxisol and K-saturated Oxisol were 1.11 and 1.06 mmol kg⁻¹, respec-

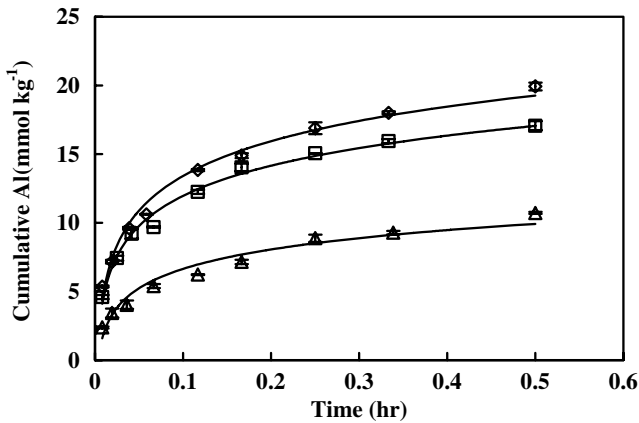


Fig. 4. The plot of cumulative Al vs. time at fast stage in electro-dialyzed Ultisol, Ultisol, and K-saturated Ultisol in the presence of citric acid at pH 4.0 (Initial concentration of citric acid was 1.0 mmol L⁻¹); ◇, electro-dialyzed Ultisol; □, Ultisol; Δ, K-saturated Ultisol).

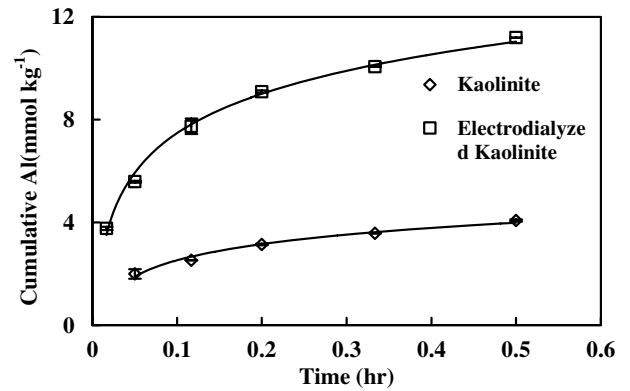


Fig. 5. The plot of cumulative Al vs. time at fast stage in electro-dialyzed kaolinite and kaolinite in the presence of citric acid at pH 4.0 (Initial concentration of citric acid was 1.0 mmol L⁻¹).

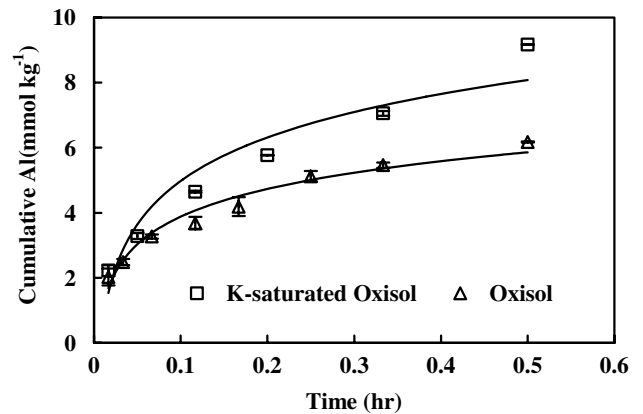


Fig. 6. The plot of cumulative Al vs. time at fast stage in Oxisol and K-saturated Oxisol in the presence of citric acid at pH 4.0 (Initial concentration of citric acid was 1.0 mmol L⁻¹).

tively (Table 2). But the quantities of released Al during the fast stage were larger than the contents of exchangeable Al, especially for K-saturated Oxisol (Fig. 6). This is mainly due to the fact that the content of amorphous Al oxides in K-saturated Oxisol was higher than that in Oxisol (Table 2). Hence, the release rate for K-saturated Oxisol was higher than that for Oxisol, with the *A* values 1.93 and 1.23, respectively. Similar results were also found for K-saturat-

ed Ultisol. Although the content of exchangeable Al of this sample was only $1.95 \text{ mmol kg}^{-1}$, the quantity of released Al was found larger than the content of exchangeable Al. Thus, the released Al mainly came from amorphous Al oxides (Fig. 4). To sum up, the amorphous Al oxides were also important Al pools to Al release during the fast stage, especially in soils with low content of exchangeable Al.

In addition to exchangeable Al and amorphous Al oxides, both soils contain other oxides and minerals containing aluminum such as poorly crystalline kaolinite, gibbsite, hydrous mica and small amounts of vermiculite in Ultisol (Table 1). They may also be potential Al pools to Al release during the fast stage. Primary minerals, crystalline layer silicates, and gibbsite have low dissolution rate and could not contribute to the rapid reactions (May et al., 1986; Bloom and Erich, 1987). Layered aluminosilicates in this study, such as hydrous mica and vermiculite, are short-range-order materials. The quantity of released Si should likely be larger than that of Al in such hydrous mica and vermiculite in which the stoichiometry of Si to Al was greater than 1:1. However, when the quantity of released Si was compared with that of Al in Fig. 7, it was

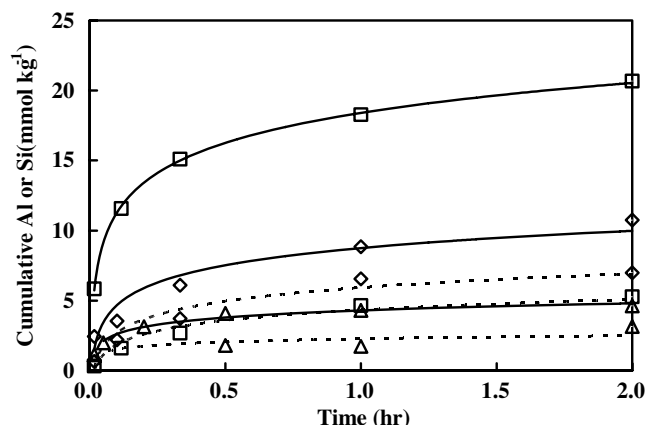


Fig. 7. The plot of cumulative Al or Si vs. time in Oxisol, Ultisol, and kaolinite in the presence of citric acid at pH 4.0 (Initial concentration of citric acid was 1.0 mmol L^{-1} ; \square , Ultisol; \diamond , Oxisol; Δ , kaolinite; —, Al;, Si).

found that not only for the variable charge soils was the quantity of released Si smaller than that of released Al, but for kaolinite (with a stoichiometry of Si to Al 1:1) it was also true. Therefore, it is possible that aluminosilicates could not release significant amount of Al during the initial few minutes of the experiment. Another possible reason for this phenomenon is aluminosilicates to preferential leach Al and leave behind Si as they dissolve (Hellmann et al., 1997). In Fig. 7, the released Si during the fast stage was derived mainly from the active Si and amorphous Si of soils.

In order to find out the Al sources of release Al in the moderate and slow stages, the kinetic data of Al release were also fitted by empirical equations. All data fit linear equations well except for kaolinite (cf. Table 3). The slope of these lines is the measures of release rate of Al. Results obtained clearly suggest that the release rate of Al at the moderate stage was much higher than that at the slow stage.

It can be seen from Table 3, that at the moderate stage, when T was 0.5 h, the quantity of released Al (Y_1) was equal to the total amount of released Al at the fast stage. When the Y_1 was compared with the exchangeable Al in Table 2, it was found that the Y_1 is larger than the corresponding quantity of exchangeable Al except in kaolinite system. These results suggest that the contribution of exchangeable Al to the Al release was less at the moderate stage.

It has been reported that the dissolution rate of kaolinite was slow in the presence of malonate, and that the high initial dissolution rate was likely due to the different processes involved such as dissolution of fine-grained materials, highly strained area on large grains of defects (Huertas et al., 1999). Table 3 also shows that the release rate of well crystalline kaolinite was much lower than that of electro-dialyzed kaolinite and soils, which demonstrates that the well crystalline kaolinite contributed little to the Al release at the moderate and slow stages. Similarly, the vermiculite has slow dissolution rate and lower content in the studied soils, so it should also contributed little to the Al release. After treated by DCB method, the main composition of Oxisol was kaolinite. During the moderate stage, the rates

Table 3

Linear equation fitting the release kinetics of Al or Si within 0.5–2 and 2–48 h from different soils in the presence of citric acid at pH 4.0 (initial concentration of citric acid : 1.0 mmol L^{-1})

Treatment	Linear equations fitted for data within 0.5–2 h	Linear equations fitted for data within 2–48 h
Al in kaolinite	$Y = 0.437t + 3.894, R^2 = 0.686$	$Y = 0.047t + 5.325, R^2 = 0.605$
Al in electro-dialyzed kaolinite	$Y = 1.359t + 10.83, R^2 = 0.930$	$Y = 0.161t + 14.072, R^2 = 0.896$
Al in K-saturated Oxisol	$Y = 2.346t + 8.077, R^2 = 0.991$	$Y = 0.375t + 12.832, R^2 = 0.987$
Al in Oxisol	$Y = 2.522t + 5.950, R^2 = 0.954$	$Y = 0.269t + 11.290, R^2 = 0.896$
Al in electro-dialyzed Oxisol	$Y = 2.670t + 9.453, R^2 = 0.963$	$Y = 0.331t + 15.433, R^2 = 0.966$
Al in AalreOxisol	$Y = 2.036t + 11.009, R^2 = 0.952$	$Y = 0.238t + 15.000, R^2 = 0.988$
Al in FalreOxisol	$Y = 1.871t + 19.428, R^2 = 0.819$	$Y = 0.120t + 22.508, R^2 = 0.987$
Al in K-saturated Ultisol	$Y = 2.291t + 8.470, R^2 = 0.978$	$Y = 0.368t + 13.280, R^2 = 0.963$
Al in Ultisol	$Y = 2.887t + 15.070, R^2 = 0.984$	$Y = 0.374t + 21.275, R^2 = 0.965$
Al in electro-dialyzed Ultisol	$Y = 3.613t + 16.736, R^2 = 0.971$	$Y = 0.331t + 24.916, R^2 = 0.961$
Si in Oxisol	$Y = 1.833t + 3.715, R^2 = 0.753$	$Y = 0.199t + 7.900, R^2 = 0.938$
Si in Ultisol	$Y = 1.483t + 2.559, R^2 = 0.870$	$Y = 0.124t + 15.026, R^2 = 0.998$

of Al release from FAlreOxisol and AAlreOxisol accounted for 70% and 76% of that from electro-dialyzed Oxisol, respectively. These results suggest that amorphous Al oxides and free Al oxides were important Al pools for Al release whereas, poorly crystalline kaolinite was a significant Al pool in Oxisol. The difference between the release rates of Al and Si from the Oxisol further confirmed these conclusions. The release rate of Si accounted for 72.7% of that of Al, which generally correlated with the ratio of Al release rate from FAlreOxisol to that from electro-dialyzed Oxisol, because the stoichiometry of Si and Al is 1:1 in kaolinite.

During the moderate stage, the release rates of Al for different treated Ultisol followed the order: electro-dialyzed Ultisol > Ultisol > K-saturated Ultisol, which was in agreement with the magnitude of the content of amorphous Al oxides in these soil samples. We concluded that amorphous Al oxides were also important Al pools for Al release in Ultisol. The release rate of Si accounted for 51.4% of that of Al in this soil sample, which demonstrates that Al oxides and aluminosilicates, such as hydrous mica and poorly crystalline kaolinite, also significantly contributed to the Al release in Ultisol.

Table 3 also shows that the release rate of Al at the slow stage was much smaller than that at the fast and moderate stages. The release rate of Si in Oxisol and Ultisol accounted for 74.2% and 33.1% of that of Al, respectively. As the Si came mainly from aluminosilicates, therefore the Al pools contributed to Al release were Al oxides, poorly crystalline kaolinite and hydrous mica only. The release rates for different treated Oxisol followed the order: electro-dialyzed Oxisol > AAlreOxisol > FAlreOxisol, which further confirmed the relative contribution of Al oxides to Al release at the slow stage.

In general, there are various kinds of Al pools in variable charge soils. Apart from the well crystalline aluminosilicates, there are exchangeable Al, Al oxides, and poorly crystalline aluminosilicates. This is the reason that the release rate of Al in variable charge soils was much faster than that in pure minerals, which is also in a line with the results for Spodosol reported by Dahlgren and Walker (1993) and Zysset et al. (1999). Furthermore, different kinds of Al pools cannot detach simply but mix together and the release mechanisms of different kinds of Al pools also differ from each other, which may result in overlapping of Al release from different kinds of Al pools and make the release mechanisms much more complicated in variable charge soils. In the cumulative release process within 48 h, the release rate of Al in Ultisol was greater than that in Oxisol. This phenomenon can be explained from two different aspects, one is that the content of exchangeable Al in Ultisol was much higher than that in Oxisol (Table 2) as mentioned above and the other is that the weathering extent of Ultisol was much weaker than that of Oxisol and thus the crystallization of Al oxides in Ultisol was poorer than that in Oxisol. Therefore, the Al oxides in Ultisol were the more important Al pools for Al release

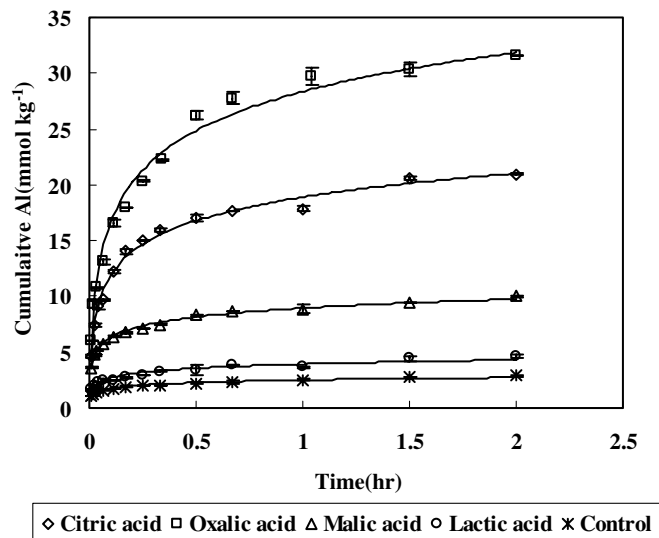


Fig. 8. Effect of organic acids on kinetics of Al release from Ultisol at pH 4.0 (Initial concentration of organic acid was 1.0 mmol L⁻¹).

than aluminosilicates, whereas the contribution of the poorly crystalline kaolinite in Oxisol to Al release was greater than that of Al oxides, especially at moderate and slow stages.

3.2. Effect of kind and concentration of LMW organic acids on the kinetics of Al release from variable charge soils

Because the release rate of Al at the slow stage was so small, the fast and moderate stages were chosen to investigate the effect of kind and concentration of LMW organic acids on the rate of Al release from variable charge soils. Kinetic curves of Al release from Ultisol in four organic acid systems are presented graphically in Fig. 8. The results show that organic acids accelerated the release of Al and the accelerating ability of different organic acids followed the order: oxalic acid > citric acid > malic acid > lactic acid. The Elovich equation and linear equation were used to fit the experiment data at the fast stage and moderate stage, respectively, and the results were listed in Table 4. With the help of *A* value of Elovich equations and the slope of fitting lines, enables the comparison of the release rate of Al in different systems. It shows that the organic acids increased the release rate of Al from Ultisol and the effect extent followed the same order as the increase in quantity of Al release induced by organic acids, which was in agreement with the order of stability constants of the complexes of these organic acids with Al. Because organic acids accelerated the Al release through the formation of soluble complexes of Al-organic anion, thus the larger the stability constant, the greater the ability of organic acid to release Al.

One exception was the effect of citric acid. The stability constant of complexes of citric acid with Al (7.98) is larger than that of oxalic acid with Al (6.16), whilst the ability of oxalic acid to release Al is greater than that of citric acid

Table 4
Elovich and linear equations fitting the kinetics of Al release from Ultisol in the systems of different organic acids at pH 4.0 (Initial concentration of organic acid : 1.0 mmol L⁻¹)

Organic acid	Elovich equations fitted for data within 0–0.5 h	Linear equations fitted for data within 0.5–2 h
Control	$Y = 0.268 \text{Ln}(x) + 2.349, R^2 = 0.990$	$Y = 0.459x + 2.025, R^2 = 0.955$
Lactic acid	$Y = 0.428 \text{Ln}(x) + 3.611, R^2 = 0.968$	$Y = 0.791x + 3.126, R^2 = 0.870$
Malic acid	$Y = 1.074 \text{Ln}(x) + 8.749, R^2 = 0.992$	$Y = 1.083x + 7.834, R^2 = 0.989$
Oxalic acid	$Y = 4.716 \text{Ln}(x) + 27.286, R^2 = 0.969$	$Y = 3.313x + 25.362, R^2 = 0.901$
Citric acid	$Y = 3.161 \text{Ln}(x) + 19.241, R^2 = 0.989$	$Y = 2.887x + 15.700, R^2 = 0.984$

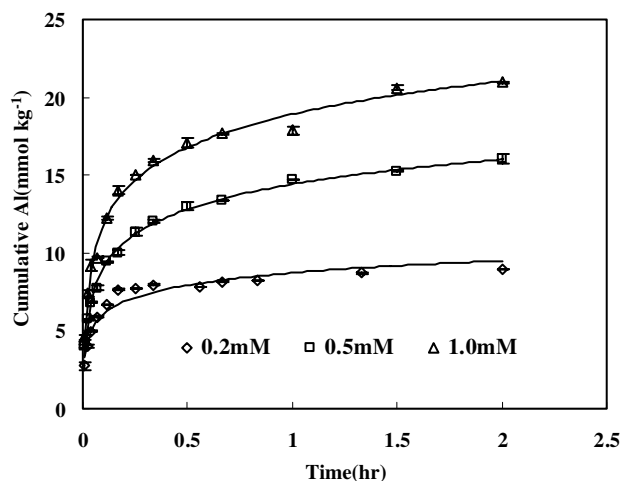


Fig. 9. Effect of citric acid concentration on Al release from Ultisol at pH 4.0.

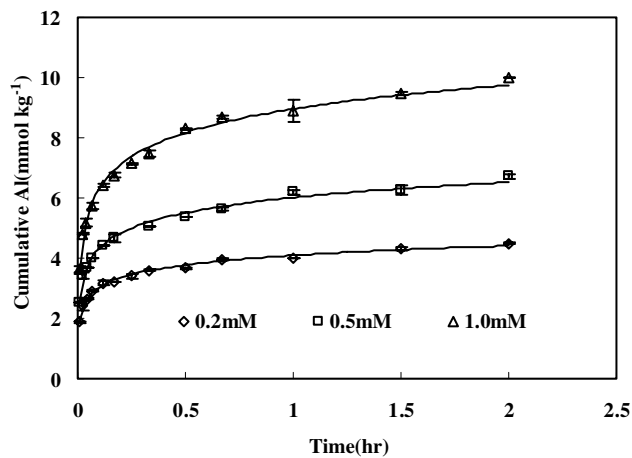


Fig. 10. Effect of malic acid concentration on Al release from Ultisol at pH 4.0.

Table 5
Elovich and linear equations fitting the kinetics of Al release from Ultisol in the systems of malic and citric acids at pH 4.0

Organic acid	Concentration (mmol L ⁻¹)	Elovich equations fitted for data within 0–0.5 h	Linear equations fitted for data within 0.5–2 h
Citric acid	0.2	$Y = 1.369 \text{Ln}(t) + 9.412, R^2 = 0.952$	$Y = 0.710t + 7.611, R^2 = 0.886$
	0.5	$Y = 2.270 \text{Ln}(t) + 14.319, R^2 = 0.989$	$Y = 2.009t + 12.210, R^2 = 0.940$
	1.0	$Y = 3.161 \text{Ln}(t) + 19.241, R^2 = 0.989$	$Y = 2.887t + 15.070, R^2 = 0.984$
Malic acid	0.2	$Y = 0.439 \text{Ln}(t) + 4.038, R^2 = 0.992$	$Y = 0.520t + 3.498, R^2 = 0.943$
	0.5	$Y = 0.680 \text{Ln}(t) + 5.852, R^2 = 0.998$	$Y = 0.821t + 5.103, R^2 = 0.909$
	1.0	$Y = 1.074 \text{Ln}(t) + 8.749, R^2 = 0.992$	$Y = 1.083t + 7.834, R^2 = 0.989$

(Fig. 8 and Table 4). One possible reason for this phenomenon is the value of the first dissociation constant ($\text{p}K_{a1}$) of citric acid (3.13) is greater than that of oxalic acid (1.25), and at pH 4.0 only 89.7% of citric acid is dissociated into citrate ion, while the corresponding figure for oxalic acid is 100%. The higher concentration of oxalate could increase the formation of complexes of Al–oxalate, thus accelerate Al release. Another possibility is that oxalate might form Al–dioxalate or Al–trioxalate complexes with Al besides Al–oxalate complexes, whereas citrate could only form Al–citrate complexes. This effect might also lead to an increase in the ability of oxalate to release Al. In conclusion, the ability of LMW organic acids to promote Al release was related not only to the stability constants of Al–organic acid complexes ($\log K_s$), but also to the first dissociation constant ($\text{p}K_{a1}$) of organic acids, i.e., the effective concentration of organic ligand.

The effect of the concentration of organic acids on Al release further confirmed the conclusion mentioned above. The quantity of released Al from Ultisol increased with the increase in concentration of malic and citric acids (cf. Figs. 9 and 10). Based on the values of A in Elovich equations and slopes of lines in Table 5, it can be found that the release rate of Al also increased with the increase in concentration of organic acids. As the concentration of organic acids rose, accordingly the concentration of effective organic ligands increased hence, the effect of organic acid through ligand-promoted mechanism was also intensified.

The ligand-promoted mechanism involves the complexation of organic acid with Al in solution, which reduces the activity of free Al^{3+} and disturbs the dissolution equilibrium of Al. Some authors suggested that the formation of Al–organic acid complexes polarized and thus weakened the Al–O bonds. However, Kubicki et al. (1999) found that the inner-sphere surface complexes of organic acids formed on mineral surface might actually strengthen Al

bonds to the rest of the mineral surfaces rather than weaken them.

In a previous study, we found that when the concentration of oxalic acid or citric acid was lower than 0.2 mmol L^{-1} , increased dissolution of Al from the variable charge soils was not observed due to the adsorption of almost all the added organic acids by the soils (Li et al., 2005). The dissolution of Al increased sharply with the increase in concentration of the two organic acids (Li et al., 2005). The results in Table 5 also show that the dissolution rate of Al also increased with the concentration of organic acids. These results were consistent with that obtained by Cheah et al. (2003) for the dissolution of iron in oxalate-goethite system. It can be considered that the increase in concentration of organic acids could increase the affinity of organic acid for Al in solution, thus decrease the activity of Al^{3+} and consequently accelerate the dissolution of Al from soils.

3.3. Implications

The results obtained from solution culture experiments suggest that LMW organic acids could alleviate Al toxicity to plants. However, the presence of LMW organic acids induced the increase in Al release from minerals and soils. In this investigation, the results show that the LMW organic acids accelerated the Al release from variable charge soils to some extent. The results also indicated that exchangeable Al played an important role in Al release. Therefore, the high content of exchangeable Al in acidified soils may accelerate Al migration from soils to aquatic environment and cause an increased risk factor of Al to the ecology and the environment. Although Al-organic acid complexes are less toxic to plants, when they are decomposed by microbe, the released aluminum will increase toxicity of Al to plants. On the other hand, Al-complexation to higher molecular weight natural organic matter (i.e., humic matter) may sequester the Al in the soil and keep it out of the soluble and bioavailable pool, thus partially reduce its migration and toxicity in the ecology and environment.

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