J Soils Sediments (2012) 12:876–887
DOI 10.1007/s11368-012-0514-0

SOILS, SEC 3 • REMEDIATION AND MANAGEMENT OF CONTAMINATED OR DEGRADED LANDS • RESEARCH ARTICLE

Iron oxides serve as natural anti-acidification agents in highly weathered soils

Jiu-Yu Li · Ren-Kou Xu · Hong Zhang

Received: 25 October 2011 / Accepted: 22 March 2012 / Published online: 3 April 2012

Abstract

Purpose The effect of Fe oxides on the natural acidification of highly weathered soils was investigated to explore the natural acidification process in variable charge soils

Materials and methods A variety of highly weathered soils with different Fe oxide contents were collected from the tropical and subtropical regions of southern China to investigate the soil acidity status. Electrodialysis experiments were conducted to simulate natural acidification process and promote accelerated acidification in a variety of systems such as relatively less weathered soils, mixtures of goethite with montmorillonite or kaolinite, an Alfisol, a limed Ultisol, and Fe oxides coated montmorillonite. The objective was to gather evidence for the occurrence of Fe oxide inhibited natural acidification in highly weathered soils.

Results and discussion Highly weathered soils with free $Fe_2O_3<100$ g/kg (17 soils) had an average pH=4.64±0.06, while the soils with free $Fe_2O_3>100$ g/kg (49 soils) had an average pH=5.25±0.04. A significant linear relationship was found between the soil pH and Fe oxide content of these soils. Similar results were obtained in electrodialysis experiments, i.e., in soils that underwent accelerated acidification. A negative correlation was found between the Fe oxide content and exchangeable acidity or effective cation exchange capacity, respectively. In another set of experiments, goethite slowed down acidification in experiments conducted with this Fe oxide and montmorillonite, or kaolinite, or an Alfisol, or a limed Ultisol. The overlapping of the electrical double layers on the positively charged Fe oxide particles and negatively charged minerals may have caused the release and subsequent leaching of the base cations, but inhibited the production of exchangeable acidity cations. In addition, when montmorillonite or Fe oxide-coated montmorillonite were electrodialyzed in another set of experiments, exchangeable acidity of the former was much greater than that of the latter, suggesting that the positively charged Fe oxide coatings on montmorillonite have partially neutralized the permanent negative charge on montmorillonite surfaces, decreasing exchangeable acidity.

Conclusions Fe oxides may function as natural “anti-acidification” agents through electric double-layer overlapping and coating of phylliosilicates in highly weathered soils.

Keywords Acidification · Electric double layers · Highly weathering soils · Iron oxides · Particle interaction

1 Introduction

Highly weathered soils are widely distributed in subtropical and tropical regions. They contain large amounts of Fe and Al oxides that possess surface charges variable with soil pH and ionic strength (Sposito 1989; Theng 1980; Yu 1997). These soils are often subject to iso-electric weathering; as a result, they contain large amounts of kaolinite, gibbsite, and Fe oxides (e.g., goethite and hematite) and only small amounts of permanent charge minerals (Jackson 1965; Mattson 1932;

Responsible editor: Willie Peijnenburg

J.-Y. Li · R.-K. Xu (✉)
State Key Laboratory of Soil and Sustainable Agriculture,
Institute of Soil Science, Chinese Academy of Sciences,
P.O. Box 821, Nanjing, People’s Republic of China
e-mail: rkxu@issas.ac.cn

H. Zhang
Department of Chemistry, Tennessee Technological University,
Cookeville, TN 38505-0001, USA

J.-Y. Li
Graduate University of the Chinese Academy of Sciences,
Beijing 100049, People’s Republic of China

Qafoku et al. 2004). Hence, highly weathered soils contain two solid phases that carry opposite surface charges (negative and positive). The coexistence of the oppositely charged inorganic particles can result in different patterns of chemical and physical behavior of the soils, as compared to the soil systems of like charges (Chorover and Sposito 1995; Yu 1997).

Highly weathered soils result from intensive weathering and leaching under hot and humid climate conditions and they can also undergo a natural acidification process (Thomas and Hargrove 1984; Ulrich and Sumner 1991). Two principal mechanistic processes underlie the current understanding of natural soil acidification. In the initial stage, prolonged intensive leaching and abundant precipitation deplete cations (especially base cations such as Na^+, K^+, Ca^{2+}, and Mg^{2+}) adsorbed on negatively charged soil particles; the leached ions are then replaced by protons (H^+) originating from H_2O, H_2CO_3, or organic acids to balance the surface charges. The exchangeable H^+ on soil minerals are reactive and can dismantle the mineral lattices by reacting with structural Al^{3+}, which eventually leads to the release of Al^{3+} ions from mineral structure to soil surface cation exchangeable sites (Coleman and Craig 1961; Huang 1997; Jackson and Sherman 1953; Reuss and Johnson 1986). The Al^{3+} ions generated in this process may fully and/or partially neutralize the surface negative charge. Exchangeable Al^{3+} is the main form of exchangeable acidity (EA) in acidic soils (Yu 1997).

This widely accepted soil acidification principle works well with soils in temperate regions (permanent charge soils) that primarily contain negatively charged 2:1 soil minerals. In addition, this principle predicts that the soils in subtropical and tropical regions would become highly acidic as a result of intensive leaching under hot and humid conditions. However, we discovered an interesting trend in some soils from southern China. By examining soil acidification features of a large number of highly weathered soils with high contents of free, positively charged Fe oxides, we found that these severely weathered and leached soils did not become highly acidic, which is inconsistent with the traditional acidification principle. The positively charged Fe oxides that are common in variable charge soils have been shown to play an important role in the particle–particle interactions and the salt adsorption/desorption phenomenon; a mechanism which involved overlapping of diffuse layers on positively charged Fe/Al oxides and negatively charged soil minerals provided a satisfactory account for salt adsorption and desorption that occurs in variable charge soils (Li et al. 2009; Qafoku and Sumner 2002; Qafoku et al. 2004; Wang et al. 2011). The overlapping mechanism was invoked in additional studies published recently in the literature (Hou et al. 2007a, b; Li and Xu 2008). This mechanism might also explain the inconsistency mentioned above.

Electrodialysis (ED) has been used in the past to extract exchangeable cations from soil samples (Puri and Hoon 1938; Wilson 1929). These researchers found that K^+ and Ca^{2+} were easily extracted from soils, while the extraction of higher valence cations, such as Al^{3+}, depended on their ion activities, although, in general, they were not easily extracted from soils. Electrodialysis was used to simulate the slow natural soil acidification process occurring in tropical and subtropical regions because it causes a removal of the exchangeable cations in a similar way as natural acidification, although this process is much faster (Mattson 1933).

In this paper, we describe soil acidification and present results from a study conducted with a variety of highly weathered soils from the tropical and subtropical regions of southern China. We also present results from electrodialysis experiments conducted to promote accelerated acidification of relatively less weathered soils, and results from experiments conducted in systems of goethite and montmorillonite or kaolinite, or an Alfisol, or a limed Ultisol. We propose a mechanistic explanation of the phenomenon based on diffuse layer overlapping of the electric double layers on oppositely charged particles present in these soils and/or systems.

2 Materials and methods

2.1 Survey of soil acidity status of highly weathered soils

In order to understand the process of acidification in highly weathered soils, 66 of these soils, including Oxisols, Ultisols, and Alfisols, were collected from soil profiles in undisturbed natural areas with minimum human disturbance. These are distributed in the provinces of Hainan, Guangxi, Guangdong, Yunnan, Hunan, Jiangxi, Guizhou, and Anhui in the southern China. The soil samples were air-dried and ground to pass a 60-mesh sieve. The soil pH was measured in suspensions at a soil/water ratio of 1:2.5 using deionized water. The free Fe oxides were determined by the sodium dithionite–citrate–bicarbonate method. The cation exchange capacity (CEC) was determined by the ammonium acetate method. The exchangeable base (EB) cations were extracted with 1.0 M ammonium acetate, and Ca^{2+} and Mg^{2+} were analyzed by the atomic adsorption spectrophotometry and K^+ and Na^+ by the flame spectrophotometry. EA (sum of exchangeable Al^{3+} and H^+ extracted with 1 M KCl) was determined using the alkaline titration method. The effective cation exchange capacity (ECEC) is given as the sum of EA and EB, which represents the negative counter-ion charge of soils since these soils contain very little soluble salts (Pansu and Gautheyrou 2006). Selected properties of these soils were listed in Table 1 with numbers from 1 to 66.

2.2 Simulation of natural acidification

Because natural acidification caused by intensive leaching is a very slow process in the tropical and subtropical regions, the ED experiments were conducted to promote accelerated acidification of relatively less weathered soils by increasing the rate of base cation desorption from soil surfaces through applied electrical field (Mattson 1933; Wilson 1929). The ED apparatus was composed of three chambers, with the middle chamber for soil samples and the cathode and anode chambers filled with deionized water on the two sides, respectively; the two adjacent chambers were separated by a cellophane membrane. During eletrodialysis, cations in soil solution and on the surface exchange sites migrated to the cathode (pH increases), and anions migrated to the anode (pH decreases), and mobile anions and cations are being replaced by H^+ and OH^-. The water in the two side chambers was renewed frequently until a constant and low EC of the suspensions was reached (Cornfield and Pollard 1952). Therefore, the electrodialyzed alumino-silicates of soil were more or less saturated with H^+ containing few other exchangeable base cations (Mattson 1933; Wilson 1929). And exchangeable H^+ on clay minerals is reactive and can dismantle the mineral lattices by reacting with structural Al^{3+}, which eventually leads to the release of Al^{3+} ions to soil surface cation exchangeable sites (Coleman and Craig 1961; Zhang et al. 1991). Exchangeable Al^{3+} is easily hydrolyzed, which would release H^+ into soil solution and thus result in soil acidification. The whole process is identical to that of soil natural acidification that occurs slowly in the tropical and subtropical regions (Yu 1997).

To study the acidification of the soils, 35 soils with different free Fe oxide contents and CEC, including Oxisol (n=24), Ultisol (n=6), Alfisol (n=4), and Mollisol (n=1) soil types (soils with letter b in Table 1), were selected to undergo ED. Their Fe oxide contents ranged from 10.3 to 220.3 g kg^{-1} and CEC ranged from 4.25 to 24.97 $cmol_c$ kg^{-1}. For the ED experiments, 50 g of the soil samples were first dispersed ultrasonically at a frequency of 40 kHz and a power of 300 W in 500 mL deionized water for 30 min and then electrodialyzed at a potential gradient of 7.5 V cm^{-1}. The treated samples were dried at 60 °C under an IR lamp and ground to pass a 60-mesh sieve. Then the soil pH, EA, EB, and ECEC were determined using the methods mentioned above.

To study the effect of Fe oxides on the soil acidification, samples of two soils with relatively low contents of free Fe oxides and two mineral samples were selected to react with various amounts of goethite and then the treated samples were electrodialyzed to simulate natural acidification of these mixtures. Subsoil samples of an Ultisol (soil number 63 in Table 1) collected from Jinxian, Jiangxi Province (116° 17 E, 28° 23′ N) with 32.6 g kg^{-1} of free Fe oxides was limed with $Ca(OH)_2$ to pH 6.8 first and then air-dried and ground to pass a 60-mesh sieve. Subsoil samples of an Alfisol (soil number 67 in Table 1) with 22.3 g kg^{-1} of free Fe oxides were collected from Nanjing, Jiangsu Province (118° 49′ E, 32° 3′ N). The kaolinite and montmorillonite used were collected from Suzhou and Nanjing, Jiangsu Province of China, respectively. The clay fractions (<2 μm in diameter) of the soils and minerals were obtained by the sedimentation method (Pansu and Gautheyrou 2006). The goethite used was synthesized following published procedures (Atkinson et al. 1967). Briefly, the goethite was made by adjusting the pH of a 0.5 M $Fe(NO_3)_3$ solution to 12 with NaOH under stirring; the precipitate was aged at 60 °C in an oven for 24 h and then the synthesized goethite was electrodialyzed. Finally, the treated samples were dried at 60 °C under an IR lamp and then ground to pass a 60-mesh sieve. The samples of the kaolinite, montmorillonite, limed Ultisol, and Alfisol were mixed with different amounts of the synthesized goethite, dispersed ultrasonically, electrodialyzed, and finally dried as described above. The soil pH and EA were determined using the methods mentioned above.

2.3 Validation of reversibility of diffuse layer overlapping

When the mixtures of kaolinite and montmorillonite with goethite were electrodialyzed, base cations were removed from surfaces of kaolinite and montmorillonite and the overlapping of the diffuse layers on negatively charged kaolinite or montmorillonite and on positively charged goethite occurred. This process leads to the decrease in ECEC of kaolinite and montmorillonite which is similar to the overlapping of diffuse layers on oppositely charge particles in variable charge soils under strongly leaching conditions (Qafoku et al. 2000; 2004; Qafoku and Sumner 2001, 2002). If the diffuse layer overlapping (DLO) is reversible, the ECEC of mixtures of kaolinite and montmorillonite with goethite will increase with addition of an indifferent electrolyte, because the counter ion from electrolyte will adsorb in the diffuse layers with decreasing DLO.

The electrodialyzed kaolinite and montmorillonite samples with 20 % of goethite were used to validate the reversibility of the DLO. Of each sample, 1.00 g in four replicates was weighed into plastic bottles. These samples were equilibrated with 50 mL of 1.0 mM $Ca(NO_3)_2$ as the supporting electrolyte for 2 h and then washed once first with 70 % ethanol and then with 17 % glycerol (Gillman and Sumpter 1986). The supernatants were discarded after centrifugation for each treatment. Two replicates were used to measure the exchangeable Al and the other two were used to determine the EB cations. The exchangeable Al was extracted with 1 M KCl and analyzed spectrophotometrically using 8-hydroxyquinoline at pH 8.3 (Barnes 1975). The EB cations

Table 1 Basic properties of soils tested in this study

No.	Soils	Location	Profile	Depth (cm)	pH	Fe_2O_3 (g kg^{-1})	CEC (cmol kg^{-1})	OM (g kg^{-1})
1[a]	Oxisol	Kunming, Yunnan	1	0–20	4.87	164.4	11.89	42.51
2[a]				20–40	4.98	173.4	11.82	28.77
3[a,b]				50–150	5.17	173.0	10.27	15.21
4			2	0–20	5.04	140.5	13.60	36.42
5				20–40	5.19	129.1	12.14	24.15
6				50–110	5.48	185.8	11.88	12.89
7[a]	Alfisol	Guiyang, Guizhou	1	0–20	4.48	49.0	13.12	27.97
8[a]				80–100	4.95	84.4	20.15	7.05
9[a,b]			2	110–130	4.97	85.5	12.79	7.30
10[a]	Ultisol	Shaoyang, Hunan	1	0–20	4.36	51.56	12.88	42.04
11[a]				20–60	4.48	54.0	9.70	15.42
12[a,b]				60–160	4.74	57.3	7.50	15.55
13[a]		Changsha, Hunan	1	0–20	4.36	42.7	10.41	9.66
14[a]				20–60	4.52	44.0	9.88	8.95
15[a,b]				60–160	4.60	44.2	9.48	7.42
16[a]	Oxisol	Wenchang, Hainan	1	0–20	4.86	149.2	7.91	30.09
17[a]				20–50	4.63	149.9	9.23	15.55
18[a,b]				60–120	4.96	154.2	9.70	12.09
19[a]			2	0–20	4.76	168.6	9.15	29.29
20[a]				20–60	4.93	171.3	6.19	16.35
21[a]		Kunlun, Hainan	1	0–20	4.52	21.2	4.43	17.29
22[a]				20–50	4.64	24.9	4.25	11.60
23[a]				50–140	4.84	33.8	5.12	8.42
24[a]	Ultisol	Liuzhou, Guangxi	1	20–60	4.92	110.1	4.86	5.05
25[a,b]				60–120	5.15	104.7	4.49	3.48
26[a,b]	Oxisol	Leizhou, Guangdong	1	90–130	4.86	124.8	6.39	10.25
27[a]		Xuwen, Guangdong	1	0–20	5.49	132.4	14.61	16.35
28[a,b]				40–70	5.51	139.7	8.02	13.84
29[a,b]				80–130	5.16	141.9	7.15	7.00
30[a,b]			2	80–110	5.13	141.3	10.46	17.63
31				110–140	5.46	135.5	11.12	12.52
32[a,b]				140–170	5.23	138.6	10.86	13.52
33[a,b]				205–240	5.29	135.6	11.04	5.82
34[a,b]			3	3–18	5.38	140.9	9.97	38.35
35[a,b]				38–70	5.10	152.4	8.45	13.61
36[a,b]				70–100	5.49	220.3	6.43	9.97
37				100–120	5.76	205.4	6.87	9.74
38				120–160	5.66	147.9	8.34	9.02
39[a,b]				190–220	5.63	149.2	10.12	7.80
40[a,b]			4	70–105	5.74	128.2	13.06	7.00
41[a,b]			5	80–120	5.63	160.3	7.74	8.86
42[a,b]		Haikou, Hainan	1	0–16	5.82	113.30	24.28	84.31
43[a,b]				16–40	5.83	130.4	18.56	36.98
44[a,b]				40–60	5.78	122.4	16.38	27.32
45				Under 60	5.79	126.8	16.07	26.28
46			2	15–40	5.62	142.2	9.26	20.06
47[a,b]				40–60	5.54	134.2	7.70	14.2
48				60–90	5.21	146.3	7.28	11.41
49				90–118	5.32	141.0	7.80	5.75

Table 1 (continued)

No.	Soils	Location	Profile	Depth (cm)	pH	Fe_2O_3 (gkg^{-1})	CEC ($cmolkg^{-1}$)	OM (gkg^{-1})
50			3	18–37	5.32	189.8	5.79	15.61
51[a,b]			4	70–100	5.27	133.4	14.27	7.09
52		Chengmai, Hainan	1	0–20	5.04	141.2	5.95	11.89
53				20–60	4.97	133.2	5.82	8.74
54[a,b]				60–120	5.38	145.9	5.62	7.86
55[a,b]			2	100–120	5.2	138.4	10.11	8.06
56				120–150	5.35	122.8	10.78	6.58
57			3	20–50	4.97	150.6	5.37	19.08
58[a,b]				50–80	5.08	158.2	5.11	10.57
59				80–120	5.22	158.9	5.11	8.13
60[a,b]				160–210	5.2	156.3	7.14	5.08
61[a,b]				210–240	5.21	153.8	8.33	5.95
62	Ultisol	Jinxian, Jiangxi	1	40–70	4.28	24.8	8.43	4.85
63				50–100	4.70	32.6	10.60	1.70
64[a,b]			2	80–130	4.73	51.1	9.81	4.40
65[a,b]		Lechang, Guangdong	1	60–130	4.62	73.4	6.50	7.27
66[a,b]		Langxi, Anhui	1	60–120	5.13	58.3	12.40	4.96
67[b]	Alfisol	Nanjing, Jiangsu	1	87–150	6.54	22.3	21.84	3.67
68[b]		Weihai, Shandong	1	40–70	6.7	24.0	14.41	7.00
69[b]		Heilongjiang	1	50–70	5.26	10.3	15.84	10.20
70[b]	Mollisol	Haerbin, Heilongjiang	1	80–110	6.86	11.4	24.97	13.60

[a] Data of soil properties were collected and shown in Fig. 2

[b] Soils were selected for electrodialysis experiment

were analyzed using the method described above. The ECEC is given as the sum of the exchangeable Al and the exchangeable Ca^{2+}, Mg^{2+}, K^+, and Na^+, since the exchangeable H^+ only accounts for less than 5 % of EA in the mineral soils and thus was neglected here (Yu 1997).

2.4 Effect of Fe oxide particles or coatings on acidification

In highly weathered soils, Fe oxides may exist as separate particles or as coatings on other minerals surfaces, phyllosilicates included. Experiments were conducted with systems composed of montmorillonite coated with layers of Fe oxides and montmorillonite mixed with particles of Fe oxides to evaluate the effects of Fe oxides particles or coatings on acidification.

The montmorillonite samples coated with Fe oxides were prepared by suspending montmorillonite in solutions of Fe salts followed by alkaline precipitation (Zhang et al. 1991; Zhuang and Yu 2002). Briefly, 40 g of the montmorillonite was added into 1 L of 0.2 M $Fe(NO_3)_3$ solution in a beaker. The suspension was continually stirred while titrating with a 2 M NaOH solution at pH 7.0. The precipitates were then aged at 60 °C in an oven for 24 h. The samples were then electrodialyzed at a potential gradient of 7.5 V/cm until a constant specific EC was reached. The electrodialysis was used to remove free ions from the system and base cations from the montmorillonite surface to accelerate acidification of montmorillonite as mentioned above. Finally, the treated samples were dried at 60 °C under an IR lamp and then ground to pass a 60-mesh sieve.

Samples of montmorillonite mixed with Fe oxides were prepared as follows: 1 L of 0.2 M $Fe(NO_3)_3$ was continuously titrated with 2 M NaOH to pH 7.0 while stirring. The precipitates were aged at 60 °C in an oven for 24 h. Then 40 g of the montmorillonite was added into the suspension of the synthesized Fe oxide and the mixture was stirred thoroughly and allowed to stand for 24 h. The mixed suspension was then electrodialyzed, dried at 60 °C under an IR lamp, and then ground to pass 60-mesh sieve.

The pH and EA of the electrodialyzed montmorillonite, montmorillonite coated with the Fe oxides, and montmorillonite mixed with the Fe oxides were measured using the methods mentioned above. The colloid suspensions containing 0.25 g L^{-1} of these samples with 0.1 mM $NaNO_3$ as the background electrolyte were prepared for measuring the zeta potentials as follows: The suspensions were dispersed ultrasonically at a frequency of 40 kHz and a power of 300 W for 1 h at 25 °C. Finally, the suspension pH was adjusted to the desired values with dilute HCl or NaOH solution. The suspensions were then shaken for 2 h at 25 °C. The pH was checked again and adjusted if necessary. Furthermore, the suspensions were equilibrated for 24 h before zeta potential measurement; during this period, the colloid suspensions were stirred manually several times. The zeta potentials were measured using a commercial microelectrophoresis instrument (JS94G + microelectrophoresis apparatus, China) following the procedures reported by Li and Xu (Li and Xu 2008).

3 Results and discussion

3.1 Acidification in naturally weathered soils

Seventeen highly weathered soils with contents of free Fe oxides below 100 g kg^{-1} have an average pH of 4.64, while 49 soils with contents of free Fe oxides over 100 g kg^{-1} have an average pH of 5.28. We also found a positive linear relationship between the soil pH and free Fe oxide content in different soils (Fig. 1). The data presented in Fig. 2 show that the ratios of EA to the ECEC vary only from 1 to 55 %, which decrease with increasing free Fe oxide content. The results presented in Figs. 1 and 2 demonstrate that the highly weathered soils with higher free Fe oxide content were less acidic.

3.2 Changes of soil properties after electrodialysis

In order to study the effect of Fe oxides on natural soil acidification, soils with different contents of Fe oxides were selected to undergo ED. The results of these experiments (Fig. 3a and b) indicate that the ratios EA/ECEC of the electrodialyzed soils increased, while the soil pH decreased when compared with the corresponding values in the original soils. The magnitude of the changes in pH and the ratio of EA/ECEC of the permanent charge soils (soils number 67–70 in Table 1) with Fe oxide contents less than 30 g kg^{-1} were larger than those for the highly weathered soils with Fe oxide contents over 40 g kg^{-1} (soils with letter b from no. 1 to 66 in Table 1). For example, the average ratios of EA/ECEC for the permanent charge soils were 0.03 and 0.76 before and after the ED, respectively, while the average pH of these soils decreased, being 6.34 and 4.24 before and after the ED, respectively. Yet, the average ratios of EA/ECEC for the highly weathered soils were 0.11 and 0.37 before and after the ED, respectively, and the average pH of the soils was 5.25 and 5.02 before and after the ED, respectively. These results suggest that the ED can release EB ions from the soils, generate EA, decrease the soil pH, and thus cause soil to acidify. This effect was more evident for the permanent charge soils than for the highly weathered soils since the latter had undergone intensive leaching naturally.

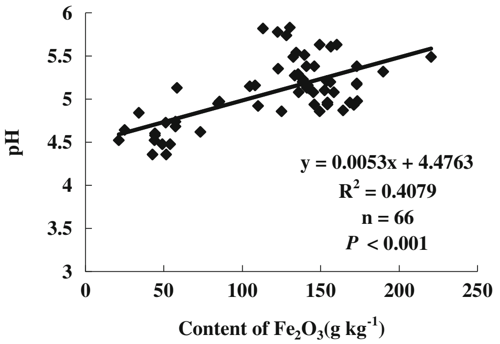


Fig. 1 The relationship between pH and content of Fe oxides for the highly weathered soils tested in this study (data were collected from soil samples of no. 1–66 in Table 1)

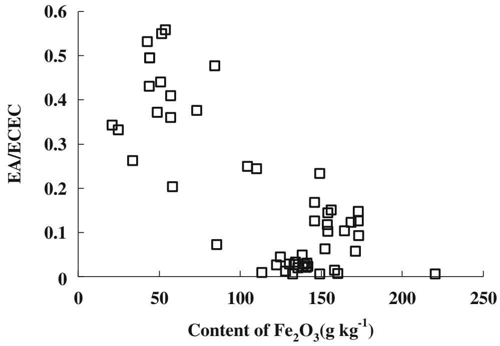


Fig. 2 The relationship between the ratio of exchangeable acidity (EA) to effective cation exchange capacity (ECEC) and content of Fe oxides for the highly weathered soils tested in this study (data were collected from soil samples with letter a in Table 1)

The results presented in Table 2 show that the soil pH relate linearly to the content of Fe oxides, while EA and ratio of EA/ECEC correlate inversely with the content of Fe oxides. The observation that the soils with higher contents of Fe oxides exhibited higher pH with lower EA indicates that these soils were acidified to a lesser degree. EA was nearly undetectable for some electrodialyzed soils with high contents of Fe oxides. The same phenomenon was also observed for some of the untreated samples of the highly weathered soils (see Fig. 2). Our study thus demonstrated that these soils were not strongly acidified although they underwent an accelerated acidification process via electrodialysis.

To retain electroneutrality, the negative charges of soil particles must be balanced by an equivalent amount of indifferent cations present in the outersphere and diffuse layer of the particles. The sum of the indifferent cations is defined as the counter-ion charge. The soil CEC determined using the ammonium acetate extraction method represents the amount of the total negative counter-ion charge at pH 7.0. This quantity is commonly used to compare the contents of the negative counter-ion charges for various soils. The ECEC is the sum of the EB cations plus EA

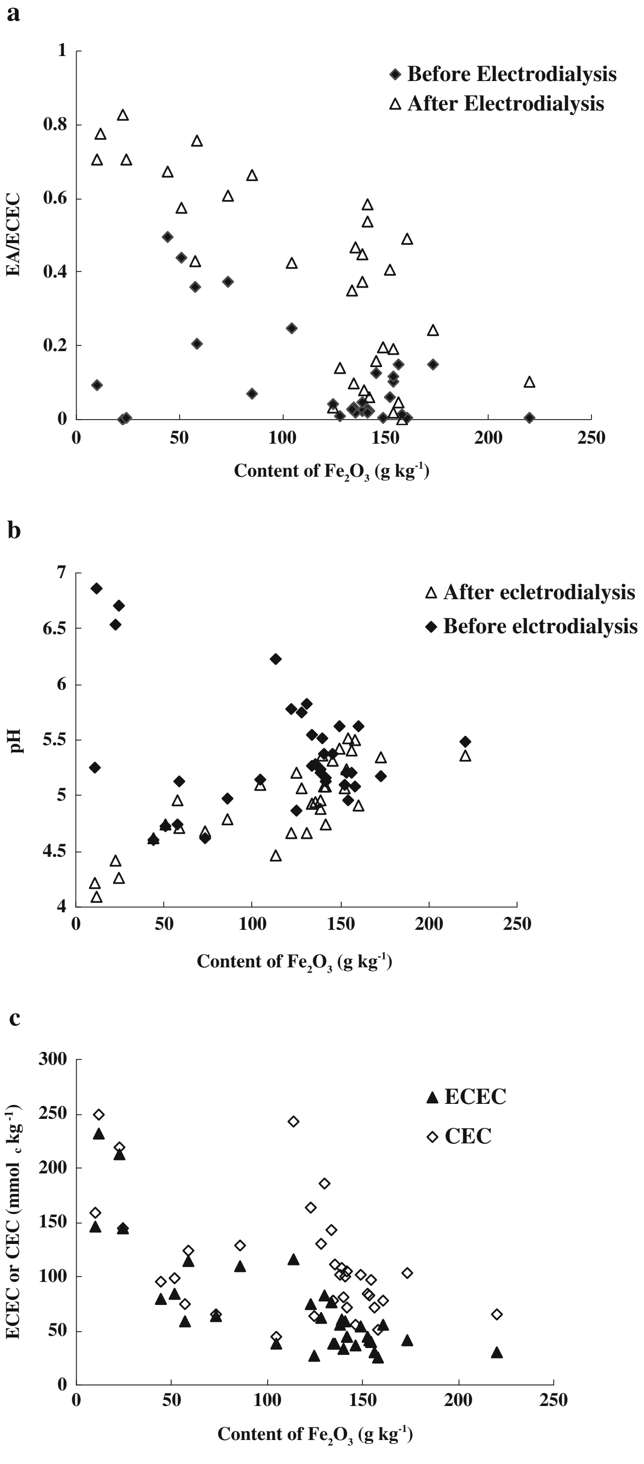


Fig. 3 A comparison of **a** the ratio of EA to ECEC, **b** the pH of the soils before and after electrodialysis, respectively, and **c** the ECEC for the electrodialyzed soils and CEC for the original soils, including 31 highly weathered soils (soils with letter b from no. 1 to 66 in Table 1) and four constant charge soils (no. 67–70 in Table 1) with different contents of Fe oxides

(i.e., exchangeable Al^{3+} and H^+) and thus represents the actual amount of the negative counter-ion charges. Figure 3c shows that compared to the soil CEC, the soil ECEC decreased and furthermore higher contents of Fe oxides led to greater decrease in the ECEC of the electrodialyzed soils. For example, the average ratios of the ECEC for the electrodialyzed soil samples to the CEC for the corresponding untreated soil samples were 0.95, 0.87, and 0.51 for the samples with the contents of Fe oxides at <30, 30–100, and >100 g kg^{-1}, respectively. Table 2 shows that the ECEC correlates negatively with the content of Fe oxides. This suggests that the higher content of Fe oxides in the soils is probably responsible for the larger decrease in the negative counter-ion charge during the ED process.

As shown in Fig. 4a, soil EA increases with the increase in the soil CEC and EA relates linearly to the CEC of the electrodialyzed soil samples. The correlation analyses were also conducted separately for the soil samples with their contents of Fe oxides over 100 g kg^{-1} and for those below 100 g kg^{-1}. The resultant correlation coefficients (R^2) were found to increase from 0.6676 for the case of all the soil samples combined together to 0.9687 and 0.7614 for the soils with their Fe oxides below 100 and over 100 g kg^{-1}, respectively(see Fig. 4b). Evidently, the linear relationship between the soil EA and CEC is more prominent. Moreover, lower EA was found for the soils with their Fe oxides over 100 g kg^{-1} than those below 100 g kg^{-1}. The slope of the correlation line for the soils with their Fe oxides over 100 g kg^{-1} is much lower than that for the soils with their Fe oxides below 100 g kg^{-1} (see Fig. 4b). Our results thus support the idea that higher CEC and higher content of Fe oxides led to greater inhibition of the soil acidification (see Fig. 4b), while higher CEC and lower content of Fe oxides led to lower pH and stronger acidification of the electrodialyzed soils (Fig. 5). Similar linear correlations between the soil ECEC and CEC were also observed for the soils; higher CEC led to greater difference in the soil ECEC between the soils with their Fe oxides over 100 g kg^{-1} and those below 100 g kg^{-1} (Fig. 6). This suggests that some negative charges were balanced by the Fe oxides in these soils. These results indicate that higher contents of Fe oxides would result in a lower EA and negative counter-ion charge, but also higher pH values and thus weaker acidification. The pH, EA, ECEC, and EA/ECEC for the soils studied were found to correlate not only with CEC but also with the content of Fe oxides (see Table 2).

3.3 Effect of goethite on acidification of the soils and minerals during electrodialysis

In order to probe the role of Fe oxides in inhibiting soil acidification, samples of kaolinite, montmorillonite, a limed Ultisol (soil number 63 in Table 1), and an Alfisol (soil number 67 in Table 1) were selected to study the effect of added goethite on the acidification of the soils and minerals

Table 2 The linear equations for correlations between various parameters for the 31 soils including highly weathered soils (soils with letter a from no. 1 to 66 in Table 1) and four constant charge soils (no. 67–70 in Table 1) with different contents of Fe oxides after electrodialysis

Y	*X*	
	Fe_2O_3 (g kg^{-1})	CEC ($mmol_c$ kg^{-1})
pH	$Y = 0.006X + 4.2415, R^2 = 0.661, P < 0.001$	$Y = -0.0052X + 5.5088, R^2 = 0.525, P < 0.001$
EA	$Y = -0.7459X + 126.46, R^2 = 0.657, P < 0.001$	$Y = 0.728X - 42.102, R^2 = 0.668, P < 0.001$
EA/ECEC	$Y = -0.004X + 0.830, R^2 = 0.504, P < 0.001$	$Y = 0.003X + 0.026, R^2 = 0.447, P < 0.001$
ECEC	$Y = -0.7663X + 159.32, R^2 = 0.637, P < 0.001$	$Y = 0.7975X - 17.122, R^2 = 0.692, P < 0.001$
pH	$Y = 0.003X_{Fe2O3} - 0.0036X_{CEC} + 4.963, R^2 = 0.664, P < 0.001$	
EA	$Y = -0.460X_{Fe2O3} + 0.5032X_{CEC} + 36.081, R^2 = 0.866, P < 0.001$	
EA/ECEC	$Y = -0.003X_{Fe2O3} + 0.0022X_{CEC} + 0.455, R^2 = 0.625, P < 0.001$	
ECEC	$Y = -0.362X_{Fe2O3} + 0.6207X_{CEC} + 52.917, R^2 = 0.879, P < 0.001$	

during the ED process. The pH values of the tested samples before and after the ED were 8.26 and 3.18 for montmorillonite, 6.34 and 5.10 for kaolinite, 6.72 and 4.34 for the Alfisol, and 6.58 and 4.65 for the Ultisol, respectively. Furthermore, EA for these samples was found to increase as a result of the ED process. The EA values of the tested samples before and after the ED were 0.0 and 408.1 for montmorillonite, 0.94 and 33.47 for kaolinite, 0.78 and 127.8 for the Alfisol, and 1.58 and 71.64 $mmol_c$ kg^{-1} for the limed Ultisol, respectively. Evidently, the ED process resulted in stronger acidification of the treated samples. This is similar to the natural acidification of most field soils exposed to prolonged intensive leaching. The EA contents of the four samples followed the order of montmorillonite> Alfisol>Ultisol>kaolinite, which is in accordance with the order for their CEC. The corresponding CEC values were 73.5, 21.8, 10.6, and 6.4 $cmol_c kg^{-1}$, respectively. This trend is consistent with that predicted by the traditional soil acidification theory.

However, the ED-induced acidification of the mineral and soil samples was clearly inhibited when goethite is added to the systems. Figure 7 shows that after the addition of goethite, the pH of the electrodialyzed samples increased while EA decreased. For example, the treatment of incorporation of 20 % goethite led to the increase in the pH of the systems of kaolinite, montmorillonite, the limed Ultisol, and

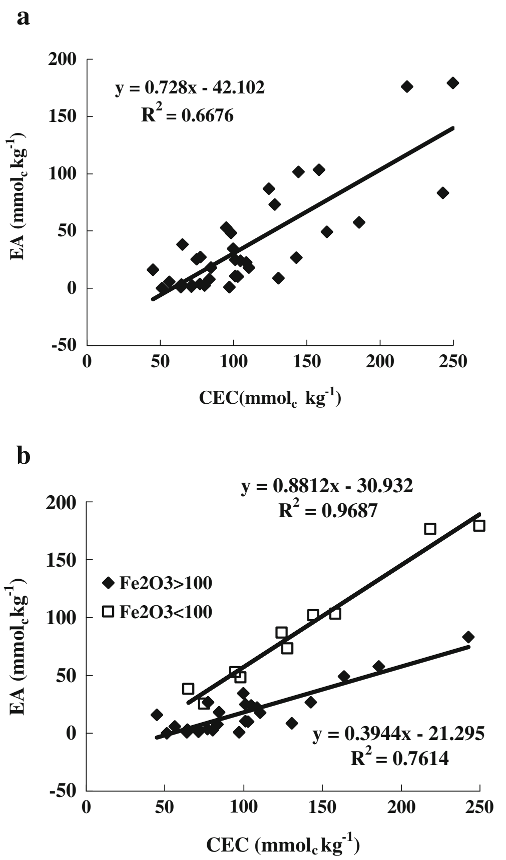


Fig. 4 The relationships **a** between EA and CEC for all electrodialyzed soils combined together and **b** between EA and CEC for the electrodialyzed soils with Fe_2O_3>100 and<100 gkg^{-1} separately, including 31 highly weathered soils (soils with letter b from no. 1 to 66 in Table 1) and four constant charge soils (no. 67–70 in Table 1) with different contents of Fe oxides

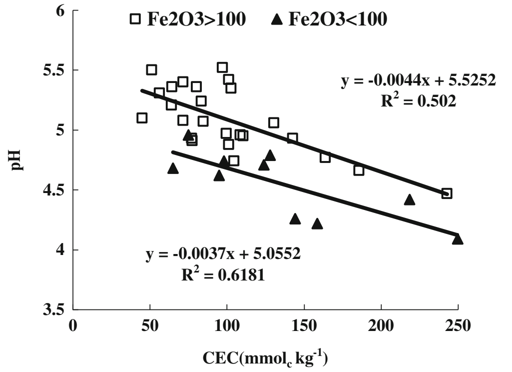


Fig. 5 The relationships between pH and CEC for the electrodialyzed soils with Fe_2O_3 >100 and <100 g kg^{-1} separately, including 31 highly weathered soils (soils with letter b from no. 1 to 66 in Table 1) and four constant charge soils (no. 67–70 in Table 1) with different contents of Fe oxides

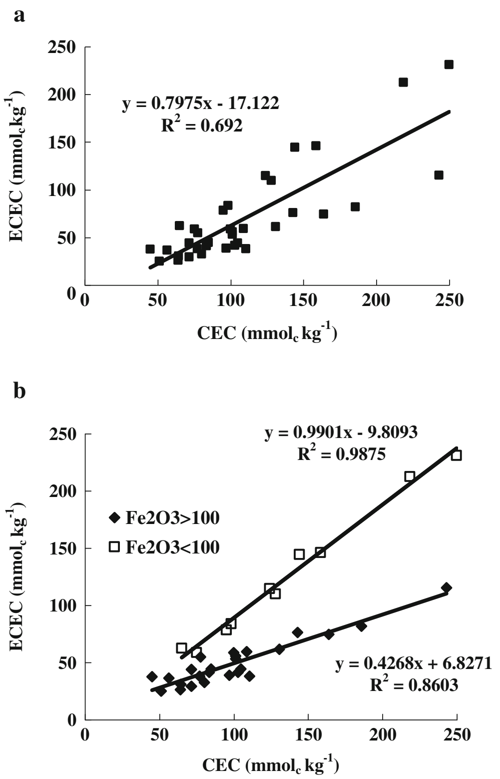


Fig. 6 The relationships **a** between ECEC and CEC for all eletrodialyzed samples combined and **b** between ECEC and CEC for the electrodialyzed soils with Fe_2O_3 >100 and <100 g kg^{-1} separately, including 31 highly weathered soils (soils with letter b from no. 1 to 66 in Table 1) and four constant charge soils (no. 67–70 in Table 1) with different contents of Fe oxides

Alfisol by 0.94, 0.97, 1.01, and 0.76 units, respectively, while their EA decreased by 100, 24, 99, and 66 %, respectively. Moreover, this effect was intensified as the content of goethite was increased. In the two binary systems of (a) the kaolinite and limed Ultisol with 20 % goethite and (b) Alfisol with 33 % goethite, EA was nearly undetectable. This was also observed for both the electro-dialyzed and untreated highly weathered soils. All these results confirm that the addition of goethite inhibited the generation of EA, thus increased the pH, and decreased the acidity of the samples. These experiments evidently support our hypothesis that Fe oxides play a special and important role in natural anti-acidification process which occurs in highly weathered soils.

3.4 Possible mechanisms for the role of Fe oxides in anti-acidification in highly weathered soils

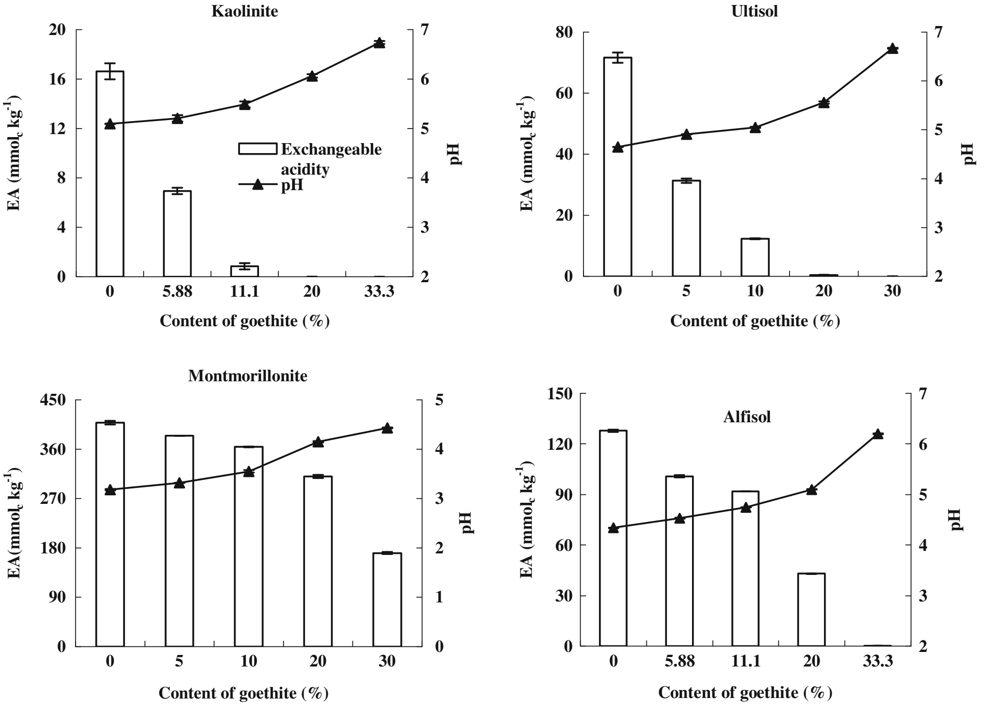
According to the traditional acidification principle described previously in this paper, after subject to intensive leaching, highly weathered soils are characterized by low concentrations of Na^+, K^+, Ca^{2+}, and Mg^{2+}, low ionic strength, and the presence of Fe and Al-hydroxyl polymers; they should contain large amounts of EA ions on the negatively charged sites and thus become strongly acidic (Huang 1997; Jackson and Sherman 1953; Reuss and Johnson 1986; Seaman et al. 1995). Yet, our results show that this is clearly not the case for the highly weathered soils from the field tested in this study and also for the electrodialyzed soil and mineral samples that reached the extreme acidification state, including permanent charge soils (phyllosilicates) with high contents of goethite.

When these soils undergo intensive leaching or ED, their negative charge sites were more or less saturated with EA containing few other exchangeable base cations (Mattson 1932). Therefore, the soil negative charge was an important factor to affect EA. Thus, the EA of the montmorillonite, Alfisol, Ultisol, and kaolinite was in accordance with their CEC (see Fig. 7). In highly weathered soils, clay minerals, such as kaolinite, and organic matter are two major constituents contributing for soil CEC. Kaolinite and organic matter carry variable charge, which magnitude and sign depend on the chemical characteristics of the contact solution (i.e., pH and ionic strength) (Chorover and Sposito 1995; Yu 1997). When these phyllosilicates and soils undergo intensive leaching or ED, the consequent decrease of the pH and ionic strength both would cause the decrease of their negative charges (Yu 1997), and thus smaller amounts of EA ions would be needed to saturate their negative charge sites. This explains why highly weathered soils had lower EA and higher pH as observed in this study.

Mechanistically, how can Fe oxides achieve the anti-acidification through EA reduction? The results in Figs. 3c and 6b suggest that higher contents of Fe oxides can result in less negative counter-ion charges after the ED process. It follows that there must be charge neutralization that causes the apparent negative charge decrease. Fe oxides are amphoteric colloidal components with pH-dependent variable charges and present abundantly in highly weathered soils in subtropical and tropical regions. The point of zero charge of Fe oxides falls between 8 and 9. They commonly carry positive charges in highly weathered acid soils. The positive charges of Fe oxides as variable charge components in the soils can be responsible for the charge neutralization.

Mechanistically, the charge neutralization may occur through overlapping of the double layers of negatively charged mineral particles and positively charged Fe oxides (Hou et al. 2007a; Hou et al. 2007b; Li and Xu 2008; Li et al. 2009; Qafoku and Sumner 2002; Qafoku et al. 2004). Under the conditions of intensive leaching or ED, the ionic strength of the solution in contact with the treated systems was very low. This can cause an expansion of the diffuse layers of the phyllosilicates and Fe oxides particles, which consequently leads to the DLO. The DLO causes charge neutralization and therefore less cations (i.e., Al^{3+}) are required for the charge balance even though large quantities of base cations are released from negative sites of the phyllosilicates. Hence, since

Fig. 7 The effect of goethite on EA and pH for kaolinite, montmorillonite, Ultisol (limed with $Ca(OH)_2$, no. 63 in Table 1), and Alfisol (No.67 in Table 1) after electrodialysis



the soil pH depends mainly on the amount of EA, an occurrence of low EA thus can result in high pH in soils as we observed.

An important feature of the DLO is that it is reversible (Mysels 1959). Once supporting electrolyte concentration becomes sufficiently high, the diffuse layers become compressed, and then the DLO and the resultant charge neutralization would disappear. Consequently, the "lost" negative charges can be restored and the cations are re-adsorbed. We tested the hypothesis that the DLO occurred to the electrodialyzed soil and mineral systems by taking advantage of the reversibility of the DLO and the resultant charge restoration. To conduct the test, we equilibrated an electrodialyzed sample of the mixture of kaolinite and 20 % goethite in a solution of 1.0 mmol L^{-1} $Ca(NO_3)_2$ as the supporting electrolyte and then measured its ECEC. As predicted, the ECEC indeed increased, from 49.20 to 74.71 $mmol_c\ kg^{-1}$ for the tested kaolinite after the treatment. This positive result implicates the occurrence of the DLO to the tested systems during the ED process. We also tested a montmorillonite system with 20 % goethite and found that the ECEC also increased (from 667.02 to 701.59 $mmol_c\ kg^{-1}$). These results evidently substantiate the hypothesis of the DLO-caused charge neutralization that is responsible for the weakened acidification observed for the tested soils and minerals.

Several previous studies showed that Fe/Al oxides increased the zeta potentials and decreased the negatively kinetic surface charge density for the binary systems of the Fe/Al oxides and phyllosilicates when compared to the systems of phyllosilicates only (Hou et al. 2007a, b; Tombácz et al. 2004). This offers another perspective of support for the notion that the DLO occurred between oppositely charged particles in the highly weathered soils. The DLO was intensified with the increase in the amount of the colloid particle charges and was weakened with the increase in the ionic strength of the systems (Li and Xu 2008; Li et al. 2009). This can explain why higher CEC and content of Fe oxides resulted in the larger decrease in the negative counter-ion charge in the electrodialyzed soils (see Figs. 3c and 6b).

In addition to the DLO mechanism for the weakened acidification observed for the highly weathered soils and the simulation systems of the minerals/Fe oxides, coating of Fe oxides on phyllosilicates may also be responsible. Abundant Fe oxides are actually coated on phyllosilicate particle surfaces in highly weathered soils, which can mask the negative charges and affect natural soil acidification. The results in Fig. 8 suggest that the zeta potentials follow the order: montmorillonite coated with Fe oxides>montmorillonite mixed

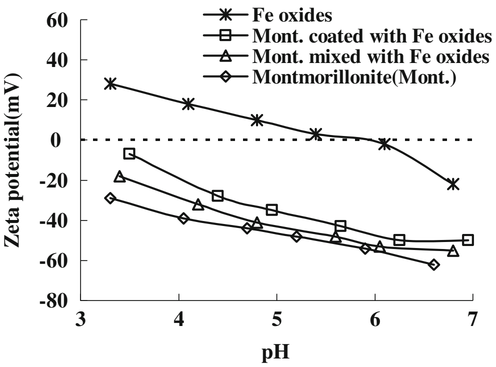


Fig. 8 Changes of zeta potentials after montmorillonite was coated or mixed with Fe oxides

with Fe oxides>montmorillonite. This indicates that Fe oxides can decrease the negative charges in the montmorillonite and the coating of Fe oxides can "mask" negative charges more effectively than the mixtures of Fe oxides. After the ED process, the pH was found to be 4.78, 4.33 and 3.18 for the montmorillonite coated with Fe oxides, the montmorillonite mixed with Fe oxides, and the montmorillonite only, respectively, while their EA values were 76.2, 191.8, and 408.1 $\mathrm{mmol_c kg^{-1}}$, respectively. Consequently, Fe oxides can decrease the negative charges and thus reduce the acidity of the montmorillonite. Therefore, the DLO and Fe oxides coating are both considered important mechanistically in accounting for the decrease in the negative charges and soil acidity of the silicates in highly weathered soils.

4 Conclusions

During this investigation, we observed that the highly weathered acidic soils with free $Fe_2O_3<100$ g/kg (17 soils) had an average pH=4.64±0.06, while the soils with free $Fe_2O_3>$ 100 g/kg (49 soils) had an average pH=5.25±0.04. A significant linear relationship was found between soil pH and the Fe oxide content. To further study this phenomenon and because the natural acidification process is slow in soils, electrodialysis experiments were conducted to promote accelerated acidification of relatively less weathered soils by increasing the rate of base cation desorption from soil surfaces via applied electrical field. The results from these experiments demonstrated that the soils with a free Fe_2O_3 content of <100 $\mathrm{gkg^{-1}}$ (10 soils) reached a different equilibrium pH than the soils with a free Fe_2O_3 content of >100 g $\mathrm{kg^{-1}}$ (25 soils; 4.54±0.06 and 5.08±0.09, respectively), revealing the same trend as the one observed in the naturally weathered soils. Results also showed that the soil pH positively correlated to the Fe oxide content, while the exchangeable acidity and effective cation exchange capacity negatively correlated with the Fe oxide content. Results from another set of experiments showed that goethite slowed down acidification of a system composed of pure minerals, such as montmorillonite or kaolinite, or an Alfisol, or a limed Ultisol. We therefore believe that Fe oxides can function as "anti-acidification" agents in highly weathered soils. The overlapping of the electrical double layers on positively charged Fe oxide particles and those on the negatively charged minerals may have caused the release and subsequent leaching of the basic cations, but inhibit the production of exchangeable acidity cations from these soils. When montmorillonite and Fe oxide coated montmorillonite were electrodialyzed in another set of experiments, exchangeable acidity of the former was much greater than that of the latter. The positively charged Fe oxide thin layers, i.e., coatings, on montmorillonite may have partially neutralized the permanent negative charge on montmorillonite surfaces, decreasing the amount of exchangeable acidity cations. Therefore, it appears that both Fe oxide-induced double layer overlapping and coating are important natural anti-acidification mechanisms for highly weathered soils when they are subject to intensive weathering and leaching.

Acknowledgments This study was funded by the National Natural Science Foundation of China (40901110 and 40971135). The authors would like to express their gratitude to Dr. Nikolla P. Qafoku from Pacific Northwest National Laboratory of USA who edited the manuscript and provided valuable insights which helped in improving the quality of the paper.

References

Atkinson RJ, Posner AM, Quirk JP (1967) Adsorption of potential-determining ions at the ferric oxide-aqueous electrolyte interface. J Phys Chem 71:550–558

Barnes RB (1975) The determination of specific forms of aluminum in natural water. Chem Geol 15:177–191

Chorover J, Sposito G (1995) Surface charge characteristics of kaolinitic tropical soils. Geochim Cosmochim Acta 59:875–884

Coleman NT, Craig D (1961) The spontaneous alteration of hydrogen clay. Soil Sci 91:14–18

Cornfield AH, Pollard AG (1952) The relative rates of release of potassium, calcium and magnesium from soil during electrodialysis. J Sci Food Agric 3:613–615

Gillman GP, Sumpter EA (1986) Modification to the compulsive exchange method, for measuring exchange characteristics of soils. Aust J Soil Res 24:61–66

Hou T, Xu RK, Zhao AZ (2007a) Interaction between electric double layers of kaolinite and Fe/Al oxides in suspensions. Colloids Surf A: Physicochem Eng Aspects 297:91–94

Hou T, Xu RK, Tiwari D, Zhao AZ (2007b) Interaction between electric double layers of soil colloids and Fe/Al oxides in suspensions. J Colloid Interface Sci 310:670–674

Huang PM (1997) Mechanism of soil acidification, in: Dahama AK (ed) Agro's Ann. Rev. of Crop Ecology (Vol). Agro Botanica: Bikaner, India, pp 79–100

Jackson ML (1965) Clay transformation in soil genesis during the quaternary. Soil Sci 99:15–22

Jackson ML, Sherman GM (1953) Chemical weathering of minerals in soils. Adv Agron 53:219–318

Li SZ, Xu RK (2008) Electrical double layers interaction between oppositely charged particles as related to surface charge density and ionic strength. Colloids Surf A: Physicochem Eng Aspects 326:157–161

Li SZ, Xu RK, Li JY (2009) Interaction of electrical double layers between oppositely charged particles in variable charge soils as related to salt adsorption. Soil Sci 174:27–34

Mattson S (1932) The laws of soil colliodal behavior: IX. Ammphoteric reactions and isoelectric weathering. Soil Sci 34:209–240

Mattson S (1933) The law of soil colloidal behavior: electrodialysis in relation to soil processes. Soil Sci 36:149–163

Mysels KJ (1959) Introduction to colloid chemistry. Interscience, New York

Pansu M, Gautheyrou J (2006) Handbook of soil analysis: mineralogical, organic and inorganic methods. Springer, Berlin

Puri AN, Hoon RC (1938) Studies in electrodialysis of soils: part III. Speed of electrodialysis of various cations. Soil Sci 45:309–313

Qafoku NP, Sumner ME (2001) Retention and transport of calcium nitrate in variable charge subsoils. Soil Sci 166:297–307

Qafoku NP, Sumner ME (2002) Adsorption and desorption of indifferent ions in variable charge subsoils: the possible effect of particle interactions on the counter-ion charge density. Soil Sci Soc Am J 66:1231–1239

Qafoku NP, Sumner ME, Radcliffe DE (2000) Anion transport in column of variable charge subsoils: nitrate and chloride. J Environ Qual 29:484–493

Qafoku NP, Ranst EV, Noble A, Baert G (2004) Variable charge soils: their mineralogy, chemistry and management. Adv Agron 84:159–215

Reuss JO, Johnson DW (1986) Acid deposition and the acidification of soils and waters. Springer, New York

Seaman JC, Bertsch PM, Miller WP (1995) Chemical control on colloid generation and transport in a sandy aquifer. Environ Sci Technol 29:1808–1815

Sposito G (1989) The chemistry of soil. Oxford University Press, New York

Theng BKG (1980) Soils with variable charge. New Zealand Society of Soil Science, Lower Hutt

Thomas GW, Hargrove WL (1984) The chemistry of soil acidity. In: Adams F (ed) Soil acidity and liming (2nd ed). Agronomy 12. Am Soc Agron, Crop Sci Soc Am and Soil Sci Soc Am, Madison, WI, pp 3–56

Tombácz E, Libor Z, Illés E, Majzik A, Klumpp E (2004) The role of reactive surface sites and complexation by humic acids in the interaction of clay mineral and iron oxide particles. Organic Geochem 35:257–267

Ulrich B, Sumner ME (1991) Soil acidity. Springer, New York

Wang YP, Xu RK, Li JY (2011) Effect of Fe/Al oxides on desorption of Cd^{2+} from soils and minerals as related to diffuse layer overlapping. Soil Res 49:231–237

Wilson BD (1929) Extraction of adsorbed cations by electrodialysis. Soil Sci 28:411–421

Yu TR (1997) Chemistry of variable charge soils. Oxford University Press, New York

Zhang FS, Zhang XN, Yu TR (1991) Reactions of hydrogen ions with variable charge soils. I. Mechanisms of reaction. Soil Sci 151:436–443

Zhuang J, Yu GR (2002) Effects of surface coatings on electrochemical properties and contaminant sorption of clay minerals. Chemosphere 49:619–628