

Amelioration of an Ultisol profile acidity using crop straws combined with alkaline slag

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Abstract The acidity of Ultisols (pH <5) is detrimental to crop production. Technologies should be explored to promote base saturation and liming effect for amelioration of Ultisol pH. Column leaching experiments were conducted to investigate the amelioration effects of canola straw (CS) and peanut straw (PS) in single treatment and in combination whether with alkaline slag (AS) or with lime on Ultisol profile acidity. The treatment without liming materials was set as control, and the AS and lime in single treatment are set for comparison. Results indicated that all the liming materials increase soil profile pH and soil exchangeable base cations at the 0–40-cm depth, except that the lime had amelioration effect just on 0 to 15-cm profile. The amelioration effect of the liming materials on surface soil acidity was mainly dependent on the ash alkalinity in organic materials or acid neutralization capacity of inorganic materials. Specific adsorption of sulfate (SO_4^{2-}) or organic anions, decarboxylation of organic acids/anions, and the association of H^+ with organic anions induced a “liming effect” of crop residues and AS on subsoil acidity. Moreover, SO_4^{2-} and chloride (Cl^-) in PS, CS, and AS primarily induced base cations to move downward to subsoil and exchange with exchangeable aluminum (Al^{3+}) and protons (H^+). These anions also promoted the exchangeable Al to leach out of the soil profile. The CS was more effective than

PS in decreasing soil acidity in the subsoil, which mainly resulted from higher sulfur (S) and Cl content in CS compared to PS. The CS combined with AS was the better amendment choice in practical agricultural systems.

Keywords Alkaline slag · Canola straw · Peanut straw · pH · Exchangeable base cations · Column leaching study

Introduction

Acid Ultisol is a kind of highly weathered clayey soils and distributes widely in the tropical and subtropical regions around the world (Qafoku et al. 2004). In the Ultisol profile, toxicity of Al and Mn to plants and deficiencies of Ca, Mg, and K can severely limit root elongation and crop growth and reduce crop yield (Farina et al. 2000; Tang et al. 2003; Brown et al. 2008; Fageria and Baligar 2008). Surface soil acidity is easily corrected by liming, but incorporating lime (CaCO_3) into topsoil has very limited effects on subsoil acidity in the short term due to low solubility of lime and slow downward movement of Ca^{2+} through the soil profile (Carvalho and van Raij 1997; Tang et al. 2003; Fageria and Baligar 2008). Incorporation of lime into the subsoil is effective (Sumner et al. 1986; Shainberg et al. 1989) but economically unfeasible. Thus, alternative technologies should be explored for amelioration of subsoil acidity. Surface-applied amendments are considered practical and cost-effective methods to ameliorate subsoil acidity (Sumner et al. 1986; Farina et al. 2000; Liu and Hue 2001). The amelioration effect depends on transport of bases from the surface horizon and the reaction of these bases with acid in the subsoil horizons. Gypsum and phosphogypsum have been proposed as effective amendments for subsoil acidity when surface-applied, since they are more soluble than

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lime and enable calcium (Ca^{2+}) to move through the soil with SO_4^{2-} in a larger quantity and at greater speed compared with applied lime (Sumner et al. 1986; Shainberg et al. 1989; McLay et al. 1994). SO_4^{2-} leached into subsoil can effectively reduce subsoil aluminum (Al) toxicity by self-liming, formation of nontoxic AlSO_4^+ , or precipitation of Al-OH-SO_4 minerals (Alva et al. 1990; Sposito 1996; Carvalho and van Raij 1997; Sun et al. 2000). Moreover, SO_4^{2-} promotes base cations to leach downward to the subsoil and decreases the Al^{3+} activity in the soil solution through an increase in ionic strength and induces displacement of Al^{3+} off soil colloids by Ca^{2+} and subsequently leaching of Al-SO_4 complexes from the soil (Oates and Caldwell 1985; McLay et al. 1994; Carvalho and van Raij 1997). But, their widespread use can be limited by availability, cost, and even environmental risk. Anions derived from organic materials are expected to produce results analogous to those of gypsum or phosphogypsum in ameliorating acid subsoils. The decomposition of organic materials can release soluble humic molecules and low-molecular-weight organic anions as well as inorganic anions, such as SO_4^{2-} and Cl^- (Haynes and Mokolobate 2001). In addition to SO_4^{2-} , organic anions complex with Al in soil solution and induce Al to become nonphytotoxic species (Sposito 1996; Haynes and Mokolobate 2001). Specific adsorption of soluble humic molecules and low-molecular-weight organic anions to Al and iron oxide surfaces in soils can also displace OH^- off soil surfaces and thus confer a greater negative charge on the soils, which tends to increase the Ca^{2+} adsorption capacity (Xu et al. 2003). Decarboxylation of organic acids/anions and the association of H^+ with organic anions also consume H^+ in the subsoil (Butterly et al. 2011, 2013; Rukshana et al. 2011). Moreover, high mobility of most complexed Ca species means that they are also easily leached downward to the subsoil. For example, citrate and acetate promoted the movement of approximately 44 and 55 % of surface-applied Ca to the subsoil layers of 10–15 cm, respectively (Inoue et al. 2001). Hue and Licudine (1999) suggested that manure-derived organic molecules facilitated the downward movement of Ca as Ca complexes. Along their downward path, these complexes reacted with Al, releasing Ca that would become plant-available and forming complexed Al that may be nonphytotoxic. The organic acids/anions and SO_4^{2-} released from the decomposition of organic materials all contributed to ameliorating subsoil acidity, but the ameliorating effect depends on properties of organic materials.

Crop residues are very important organic materials to cropland to improve soil nutrient and maintain soil quality (Haynes and Mokolobate 2001; Bending et al. 2002; Ogbodo 2011; Yuan et al. 2011). Moreover, crop residues have also proved to be effective amendments for soil acidity in surface soil due to the high content of ash alkalinity (Yan et al. 1996; Xu et al. 2006; Wang et al. 2009, 2012; Butterly et al. 2011). Use of

crop residues is specifically interesting due to huge biomass production of main crops in the agricultural systems. Crop residues with low content of base cations should be coupled with lime materials to increase their ameliorating effects on soil acidity. Many industrial by-products containing calcium and sulfate can act as alternative amendments (Fageria and Baligar 2008; Li et al. 2010). Recently, AS, an industrial by-product produced from ammonia-alkali production of sodium carbonate, has proved very effective in correcting surface soil acidity in indoor incubation and field experiments (Li et al. 2010, 2014; Wang et al. 2012; Masud et al. 2014, 2015). The AS contains calcium carbonate as well as calcium sulfate, which would be beneficial for correcting soil acidity similar to lime combined with gypsum (Li et al. 2010, 2014; Masud et al. 2014, 2015). In order to develop low-input methods for ameliorating subsoil acidity, the current study investigated the ameliorating effect of crop residues combined with AS on soil acidity in the profile of an Ultisol using a column leaching experiment. Lime was used for comparison.

Materials and methods

Soils and amendments

An acid Ultisol (US Soil Taxonomy; Haplic Acrisol in the WRB taxonomy) used in the study was collected from Langxi, Anhui Province, China ($31^\circ 6' \text{N}$, $119^\circ 8' \text{E}$) and derived from quaternary red earth. The soil samples were collected at two different depths, with topsoil collected from 0 to 20 cm and subsoil from 20 to 60 cm. The collected soil was air-dried and passed through a 2-mm sieve. Chemical properties of the original soil are presented in Table 1.

In our previous study, peanut straw (PS) and canola straw (CS) were found to be very effective amendments among the leguminous and nonleguminous crop residues, respectively (Wang et al. 2009). Thus, four kinds of liming materials were selected for this experiment: lime, alkaline slag (AS), PS and CS. Using these materials, nine treatments were established: (1) control without liming materials, (2) lime, (3) AS, (4) PS, (5) PS combined with lime (PS+lime), (6) PS combined with AS (PS+AS), (7) CS, (8) CS combined with lime (CS+lime), and (9) CS combined with AS (CS+AS), each with three replications. Ca^{2+} and magnesium (Mg^{2+}) are two important cations for amendments to exchange with H^+ and Al^{3+} and thus ameliorate subsoil acidity. Thus, the application rates of lime, AS, and PS were based on similar quantities of 25 $\text{mmol}_c \text{ kg}^{-1}$ of Ca^{2+} or the sum of Ca^{2+} and Mg^{2+} together applied in the surface soil, and this application rate of lime was chosen in order to increase the soil pH to about 6.0 based on the preliminary study. The application rate of CS was equal to that of PS. The detailed application rates of amendments (all g kg^{-1}) were as follows: (2) lime 1.25, (3) AS 1.6, (4) PS 20, (5)

Table 1 Selected properties of the Ultisol used in the experiments

Layer	pH (H ₂ O)	CEC	Exchangeable Al ³⁺	Fe ₂ O ₃	Al ₂ O ₃	Exchangeable base cation			
						Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺
		(mmol _c kg ⁻¹)		(g kg ⁻¹)		(mmol _c kg ⁻¹)			
Topsoil	4.90	103.0	33.2	30.6	5.5	18.4	3.4	1.8	2.7
Subsoil	4.65	139.9	49.3	34.2	6.1	10.0	3.2	2.3	4.2

PS+lime 20+1.25, (6) PS+AS 20+1.6, (7) CS 20, (8) CS+lime 20+1.25, and (9) CS+AS 20+1.6. AS was obtained from ammonia–alkali production of sodium carbonate, with major chemical components being calcium sulfate and calcium carbonate. PS and CS were obtained locally in Langxi County, oven-dried at 80 °C, and ground to pass a 1-mm sieve. Lime was the analytic agent CaCO₃.

Chemical analysis for amendments

The acid neutralization capacity of lime and AS was determined by titrating their suspensions to pH 5.0 with 0.1 M H₂SO₄ (Wong et al. 1998). AS was digested by alkaline fusion (Li₂CO₃–H₃BO₃) to determine the contents of major elements. Potassium (K), sodium (Na), calcium (Ca), magnesium (Mg), phosphorus (P), and sulfur (S) were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES, VISTA-MPX, Varian, USA) and Cl⁻ by potentiometric titration with silver nitrate (Li et al. 2010). The ash alkalinity of the plant materials was determined using a modified titration method (Slattery et al. 1991). Two grams of the ground plant material was heated at 200 °C for 1 h and then at 500 °C for 4 h in a muffle furnace. The ash of the sample was dissolved in 25 mL of 1.0 M HNO₃. One part of the solution was titrated against a standardized solution of 0.25 M NaOH to obtain the ash alkalinity. Another part of the solution was used to measure Ca, Mg, K, Na, P, and S with ICP-AES and Cl with potentiometric titration as for the methods provided above. Total carbon (C) and nitrogen (N) of the crop residues were determined using the Leco CN-2000 analyzer (Leco Corp., St. Joseph, Mich., USA) at 1300 °C (Wright and Bailey 2011).

The chemical properties of lime, AS, and crop straws are presented in Table 2.

Column preparation

Polyvinyl chloride (PVC) columns (diameter 7.8 cm and height 50 cm) were used in the leaching experiment (Fig. 1). The PVC columns consisted of two equal halves taped together with a PVC plate used as the bottom. A hole of 4-mm internal diameter in the middle of the bottom plate was used to collect leachates from the columns in 1-L plastic bottles that stood on the ground below the columns. A small hole was made in each bottle cap with size just suitable for the tube, which connected bottles and columns (to minimize water evaporation during collection). Paraffin wax was applied on the soil–tube interface to avoid preferential flow between the PVC cylinder and the soil. A filter paper and a plastic mesh were attached at the bottom of each column to avoid soil losses. Then, 2-cm depth at the bottom of the columns was filled with acid-washed SiO₂, and a plastic mesh was placed above this layer. Next, untreated subsoil was packed over the SiO₂ layer to a bulk density of 1.25 g cm⁻³ in three increments of 10 cm, totaling 30 cm (1795 g of air-dried). Above this subsoil layer, topsoil (574 g air-dried) with amended materials was packed and compressed to 10-cm thickness and a bulk density of 1.2 g cm⁻³. The treated amendments were thoroughly mixed with topsoil (10 cm). Each layer (10 cm) was respectively slowly wetted to adjust to 80 % of the soil water-holding capacity at the filling time. The top part of column was filled with acid-washed SiO₂ in a 2-cm layer and a filter paper placed over it to induce uniform water distribution and avoid water evaporation loss.

Table 2 Chemical properties of alkaline slag, crop straw, and lime

Amendment	Alkali content (mol kg ⁻¹)	C/N ratio	Base cation (mmol kg ⁻¹)				Anion (mmol kg ⁻¹)		
			Ca	Mg	K	Na	P	S	Cl
CaCO ₃	20.0 ^a	–	1000	–	–	–	–	–	–
Alkaline slag	8.22 ^a	–	5406	2447	16.6	246.7	18.7	1265	2197
Peanut straw	0.93 ^b	31.57	375.4	237.0	352.5	17.5	88.9	61.8	224
Canola straw	0.55 ^b	49.54	178.8	46.0	467.5	117.5	15.2	109.1	422

^a Acid neutralization capacity

^b Ash alkalinity

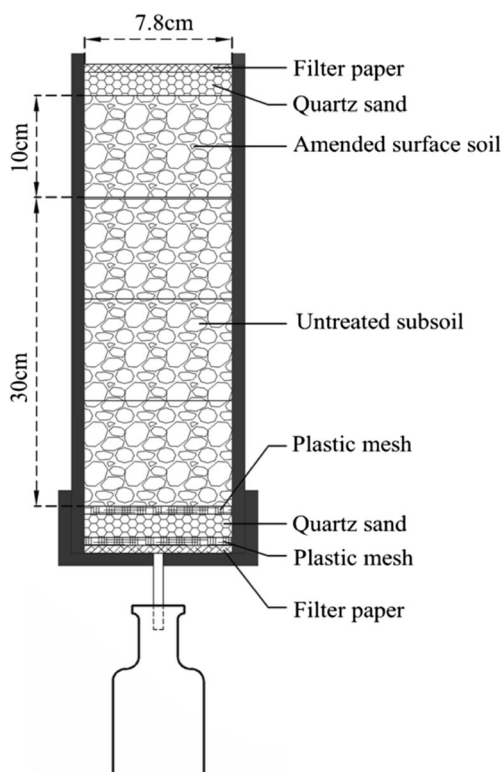


Fig. 1 Schematic diagram of soil column leaching apparatus

Irrigation and leachate analysis

To simulate amelioration effect in the season under actual field conditions, all soil columns were allowed 15 days for reaction of amended materials with soil before the first leaching. The leaching experiment was arranged in a laboratory with summer air temperature (average day 35 °C and night 25 °C in Nanjing, China) in a completely random design with three replications. During the experiment, water was applied to the top of the columns based on the average annual rainfall for the district in the previous 10 years. During the period of leaching, each column received a total of 1632 mm of simulated rainfall divided into ten events in 3 months. Ten milliliters of deionized water was added to each column in 1 h with a peristaltic pump, and the water flow rate was set enough fast but ensured that no water retention occurred on the surface of soil column based on the preliminary experiment. Each leaching event included 78 h of irrigation (780 mL water) and a 9-day interval. The leachates were collected each event and split into two samples. Subsample of leachate was used to measure electrical conductivity (EC) and pH immediately after collection, and the remaining sample was kept in a freezer (−20 °C) until subsequent laboratory analyses for the measurements of Ca, Mg, K, Na, Al, SO₄-S, Cl, ammonium (NH₄⁺)-N, (NO₃⁻ + NO₂⁻)-N, and total organic carbon (TOC). Concentration of Ca and Mg in the leachates was analyzed by atomic adsorption spectrometry (AAS, novAA 350, Analytik Jena AG,

Germany) and the K and Na by flame photometry (FP640, Aopu, Shanghai, China). (NH₄⁺)-N, (NO₃⁻+NO₂⁻)-N, and Cl⁻ were analyzed by UV spectrophotometer, Al and SO₄-S were measured by ICP-AES, and TOC was analyzed by TOC analyzer (Shimadzu, TOC-500).

Soil sampling and analysis

At the end of the leaching experiment, soil columns were separated into two parts from the taped places and were sectioned immediately to seven layers (0–10, 10–15, 15–20, 20–25, 25–30, 30–35, and 35–40 cm) by cutting. The soil samples were air-dried, ground, and passed through 60-mesh sieve for subsequent analysis. Soil pH was measured in a 1:2.5 soil/water suspension. Soil exchangeable base cations were extracted with 1 M NH₄OAc. Ca²⁺ and Mg²⁺ in the extractants were measured by AAS and K⁺ and Na⁺ by flame photometry. Soil exchangeable acidity was extracted with 1 M KCl and then titrated by 0.01 M NaOH to pH 7.0 (Pansu and Gautheyrou 2006).

Statistical analyses

SPSS 15.0 (SPSS Inc., Chicago, IL, USA) was used for statistical analyses. One-way analysis of variance was used to determine differences of soil chemical properties among treatments. Least significant difference test was performed to determine significant differences of each soil property among treatments at every depth level.

Results and discussion

Chemical composition of leachates

The chemical compositions of leachates in different treatments are presented in Table 3. The surface application of amendments significantly increased the leaching of cations and anions along the soil profile. The magnitudes of amendments in promoting the leaching of ions were in the following order: CS>PS≈AS>lime in the sole amendment treatments and CS+AS>PS+AS>CS+lime>PS+lime in the combined treatments. Therefore, CS was more effective than PS in promoting the leaching of base cations and Al³⁺ along the soil profile, whether in sole application or in combination with either lime or AS. Sole applied PS, CS, and AS were less effective than their respective combined amendments in promoting the leaching of base cations and Al³⁺ along the soil profile. The cation leaching pattern can be explained by the principle of electrical neutrality; a cation cannot move down the soil profile unless accompanied by an equivalent anion (Pavan et al. 1984; Cahn et al. 1993). Little phosphate was detected in the leachates due to the strongly specific

Table 3 Chemical compositions of total leachates collected from the Ultisol treated with lime, alkaline slag (AS), peanut straw (PS), canola straw (CS), crop straws combined with lime, or AS after leaching with 1632-mm irrigation with ten events (780 mL event⁻¹)

Treatments	Cations (mM)						Anions (mM)			Total (mM)	
	Al ³⁺	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	NH ₄ ⁺	SO ₄ ²⁻	Cl ⁻	NO ₃ ⁻	Cations	Anions
Control	0.59 e	6.01 e	1.44 g	1.58 f	0.46 g	0.06 c	9.76 f	0.34 f	0.28 c	10.14 g	10.39 h
Lime	0.69 e	6.59 d	1.52 f	1.64 e	0.50 f	0.07 c	10.45 e	0.38 f	0.32 bc	11.00 f	11.16 g
AS	1.20 c	7.85 bc	2.12 e	1.84 d	0.87 d	0.07 c	12.39 bc	1.97 e	0.34 bc	13.96 d	14.69 f
PS	0.96 d	7.79 c	2.12 e	1.85 d	0.51 f	0.20 a	12.02 cd	2.51 d	0.37 bc	13.43 e	14.90 ef
PS+lime	1.17 c	8.01 bc	2.32 c	1.85 d	0.54 e	0.07 c	12.46 b	2.61 d	0.42 ab	13.96 d	15.49 de
PS+AS	1.83 b	8.23 bc	2.88 b	2.10 a	1.01 c	0.15 b	14.71 a	3.72 b	0.52 a	16.19 b	18.95 b
CS	1.08 cd	8.22 bc	2.23 d	1.94 c	1.83 b	0.13 b	11.96 d	3.22 c	0.37 bc	15.44 c	15.54 d
CS+lime	1.26 c	8.34 b	2.37 c	1.99 b	1.85 b	0.14 b	12.45 b	3.95 b	0.35 bc	15.94 b	16.75 c
CS+AS	2.10 a	9.57 a	3.00 a	2.10 a	2.25 a	0.11 ab	14.48 a	4.73 a	0.39 bc	19.13 a	19.60 a

The data followed by the different letters within a row are significantly different at the 5 % level ($P < 0.05$)

adsorption of this anion by the Ultisol (Gimsing et al. 2007). The total amounts of inorganic anions (SO₄²⁻, Cl⁻, and NO₃⁻) and cations (Ca²⁺, Mg²⁺, K⁺, Na⁺, NH₄⁺, and Al³⁺) in the leachates showed a good linear relationship, with correlation coefficient (R^2) of 0.9256 (Fig. 2), suggesting that these inorganic anions were primarily responsible for the leaching of cations along the soil profile. Among the anions leached out, SO₄²⁻ made the greatest contribution to the leaching of cations, followed by Cl⁻, and NO₃⁻ showed the least contribution in each treatment (Table 3). Liu and Hue (2001) also found that downward Ca movement was mainly assisted by SO₄²⁻ when surface-applied compost was used to ameliorate subsoil acidity. The amounts of SO₄²⁻ and Cl⁻ leached out followed the same order as the quantities of these anions applied in different amendment treatments, suggesting that amendments with higher contents of SO₄²⁻ and Cl⁻ were better for ameliorating subsoil acidity.

The highest ECs of the leachates (Fig. 3) were in the second event, generally followed by the fourth event in different

treatments. Since EC primarily represents the concentration of ions in solution, this indicates that high concentrations of cations and anions were leached out mainly in the second and fourth leaching events. The relationships between total cations and total inorganic anions or TOC in the second and fourth leachates (Fig. 4) indicated that total cations were correlated well with inorganic anions ($R^2 = 0.8652$) but correlated poorly with TOC ($R^2 = 0.2176$). The results demonstrated that inorganic anions (SO₄²⁻, Cl⁻, and NO₃⁻) were predominant in promoting the movement and leaching of cations out of the soil profile, while organic anions played minor roles in the moving and leaching of cations. This demonstrated that when crop straws were surface applied to soil, most organic anions released from the decomposition of crop residues were primarily either adsorbed by the Ultisol in the column or completely decomposed into carbon dioxide before leaching out of the soil profile. These results differ from those obtained with crop residues continuously leached in a few days or with fulvate and humate (Liu and Hue 2001; Peiris et al. 2002). When surface-applied crop residues were subjected to continuous leaching over a few days, crop residues were difficult to completely decompose. Fulvate and humate were also not easily decomposed. Thus, organic anions in the previous studies contributed greatly to the leaching of cations along the soil profiles (Liu and Hue 2001; Peiris et al. 2002).

Soil pH in the profile

Figure 5 shows the effect of surface application of sole PS, CS, AS, and lime and their combined application on soil pH in the Ultisol profile. The amendments increased the soil pH in the Ultisol profile to different degrees, and the pH increments decreased from surface horizon to 40-cm soil depth. Sole application of amendments significantly increased the soil pH from 5.05 for control to 5.50 for PS, 5.29 for CS, 5.67 for AS,

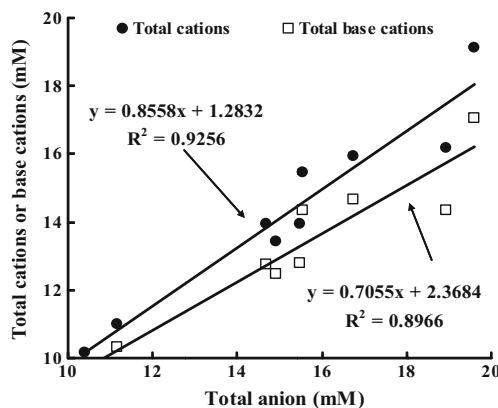
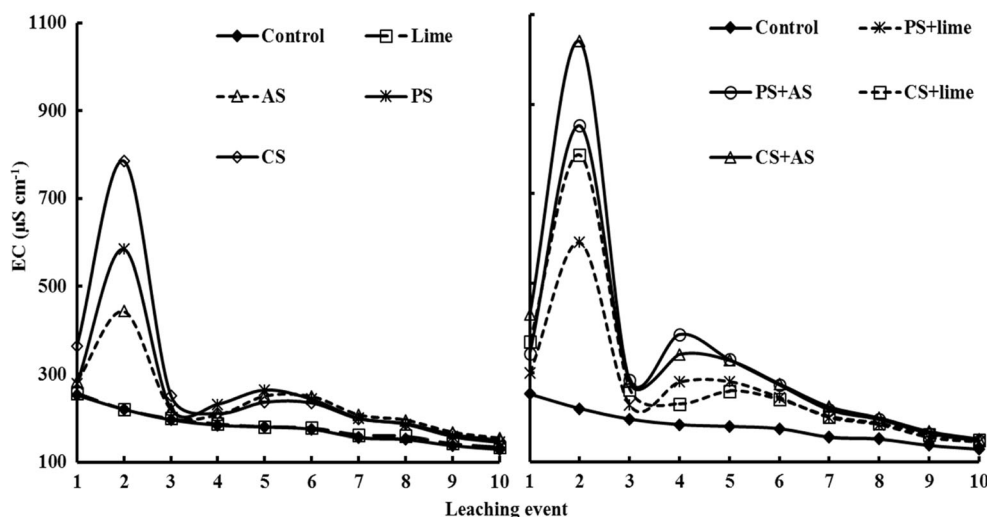


Fig. 2 Relationship between total inorganic anions (SO₄²⁻, Cl⁻, and NO₃⁻) and total cations (Ca²⁺, Mg²⁺, K⁺, Na⁺, NH₄⁺, and Al³⁺) or total base cations (Ca²⁺, Mg²⁺, K⁺, and Na⁺) leached out of soil profile during the leaching experiments

Fig. 3 Dynamics of electrical conductivity (EC) in the leachates of the Ultisol treated with different amendments during the leaching experiments. *AS* alkaline slag, *PS* peanut straw, *CS* canola straw



and 5.74 for lime in the layer of 0–10 cm ($P < 0.05$). The magnitude of amendments in increasing soil pH followed the order: lime>AS>PS>CS, which was generally in agreement with the alkalinity added in the treatments. The amount of alkalinity (calculated from the application rate and acid neutralization capacity for lime and AS, and ash alkalinity for crop straws) added in the amendments was 14.36, 7.55, 10.62, and 6.31 mmol for lime, AS, PS, and CS, respectively. These results suggested that alkalinity in the amendments was the major factor determining the efficiency of crop straws and inorganic amendments in ameliorating surface soil acidity (Sakala et al. 2004; Wang et al. 2009). One exception was that AS was more effective than PS in increasing soil pH in the layer of 0–10 cm, even though less alkalinity was added in AS than PS. Increases in soil pH induced by crop residues are

mainly attributed to the decarboxylation of organic acids/ anions and the association of H^+ with organic anions and other negatively charged chemical functional groups in the crop straws (Yan et al. 1996; Butterly et al. 2011; Rukshana et al. 2011). Specific adsorption of organic anions and SO_4^{2-} also benefits the pH increase due to the ligand exchange between OH^- and these anions (Barrow 1986; Yu 1997). The ash alkalinity for plant material is defined as the sum of cations minus the sum of inorganic anions, and the excess positive charge is balanced by organic anions and is used to estimate the liming potential of a residue. Thus, the ash alkalinity in crop straws only represents the potential alkalinity to neutralize soil acidity but is not available under all conditions (Sakala et al. 2004). Their ameliorating effects are markedly affected by initial soil pH (Xu et al. 2006).

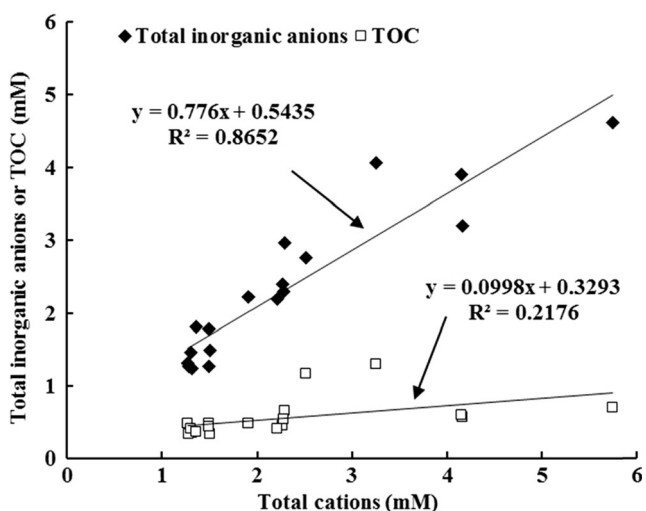
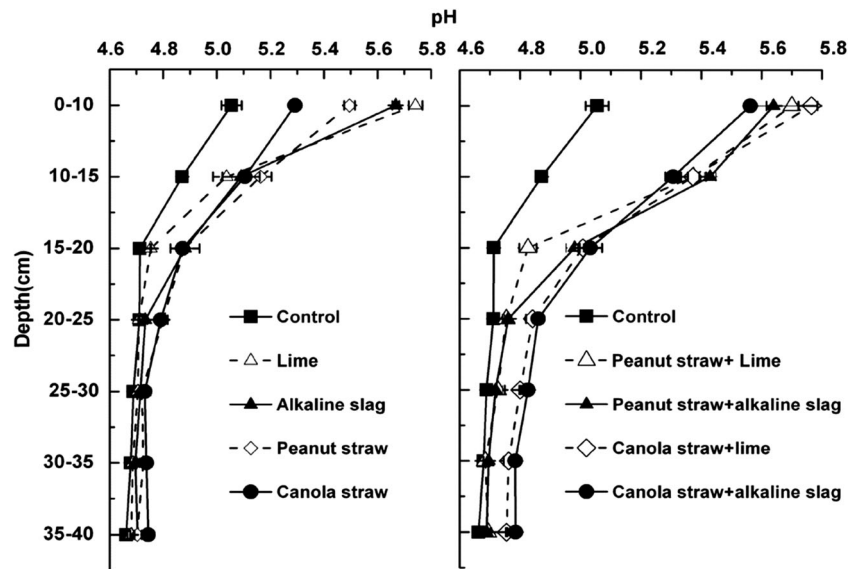


Fig. 4 Relationship between total cations (Ca^{2+} , Mg^{2+} , K^+ , Na^+ , NH_4^+ , and Al^{3+}) and total inorganic anions (SO_4^{2-} , Cl^- , and NO_3^-) or total organic carbon (TOC) leached out of soil profile (data obtained in the second and fourth leaching events)

In the layer of the 10–20-cm depth, surface application of PS, CS, and AS also significantly increased soil pH ($P < 0.05$), while lime significantly increased soil pH only at 10–15 cm ($P < 0.05$). For example, the soil pH was 4.71, 4.78, 4.88, 4.87, and 4.88 in the control, lime, PS, CS, and AS treatments at the 15–20-cm depth, respectively. Lime had little effect in increasing soil pH at 20–40 cm compared to controls. Crop straws and AS also increased the soil pH at 20–40 cm, and CS was the most effective among the different treatments ($P < 0.05$). These results suggested that the amelioration effect of lime had little effect on subsoil below 15 cm. This is due to the lime-released OH^- and HCO_3^- ions being quickly neutralized by topsoil acidity (Hue and Licudine 1999; Liu and Hue 2001; Brown et al. 2008). In the PS and CS treatments, SO_4^{2-} and organic anions, released from crop residue decomposition, could move into the subsoil and be specifically adsorbed by the Ultisol, which replaced OH^- in neutralizing soil acidity (Barrow 1986; Sumner et al. 1986; Alva et al. 1990). Decarboxylation of organic acids/anions and the association of H^+ with organic anions were beneficial for pH increase (Yan et al. 1996; Butterly et al. 2011, 2013; Rukshana et al. 2011). SO_4^{2-}

Fig. 5 Effect of surface application of sole peanut straw and canola straw, lime, alkaline slag, and crop straws in combination with lime or alkaline slag on soil pH in the Ultisol profile



released from dissolution of CaSO_4 in AS also had such a “liming effect” on subsoil acidity (Li et al. 2010).

When crop straws were surface applied in combination with lime or AS, they had more effect than the respective sole applications on soil pH in the Ultisol profiles, especially at the 0–20-cm depth ($P < 0.05$). Since higher content of alkalinity was added in combined amendment treatments than the respective sole treatments, this led to larger pH increases in surface and subsurface soils in the combined amendment treatments. The CS was more effective than PS in increasing soil pH at the 20–40-cm depth when these two crop straws were surface applied in combination either with lime or AS ($P < 0.05$). These results suggested that the property differences between CS and PS were responsible for the pH variations. Higher contents of S and Cl in the CS might have

promoted more base cations to move downward to the subsoil, which exchanged with the exchangeable H^+ and Al^{3+} , and also induced more Al to leach out of the soil profile. This was supported by the observed results presented in Tables 2 and 3 and Figs. 6 and 7. Higher contents of S in the CS benefited the more specific adsorption of SO_4^{2-} and displaced more OH^- in the subsoil (Sumner et al. 1986; Alva et al. 1990). Both mechanisms were responsible for the greater pH increase in subsoil in CS treatments compared with PS treatments.

Soil exchangeable acidity in the profile

Surface-applied amendments decreased the exchangeable acidity in the soil profile to different degrees, and the

Fig. 6 Effect of surface application of sole lime, alkaline slag, peanut straw, canola straw, and crop straws in combination with lime or alkaline slag on soil exchangeable acidity in the Ultisol profile

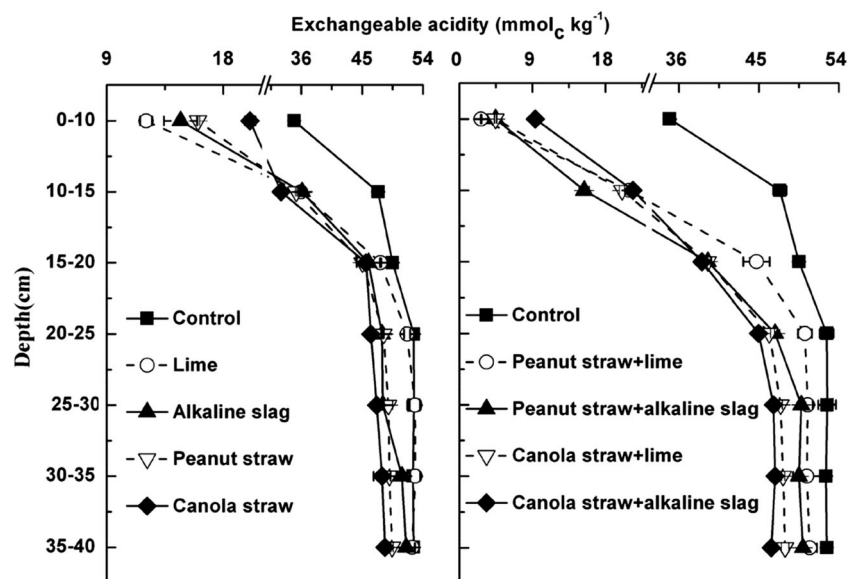
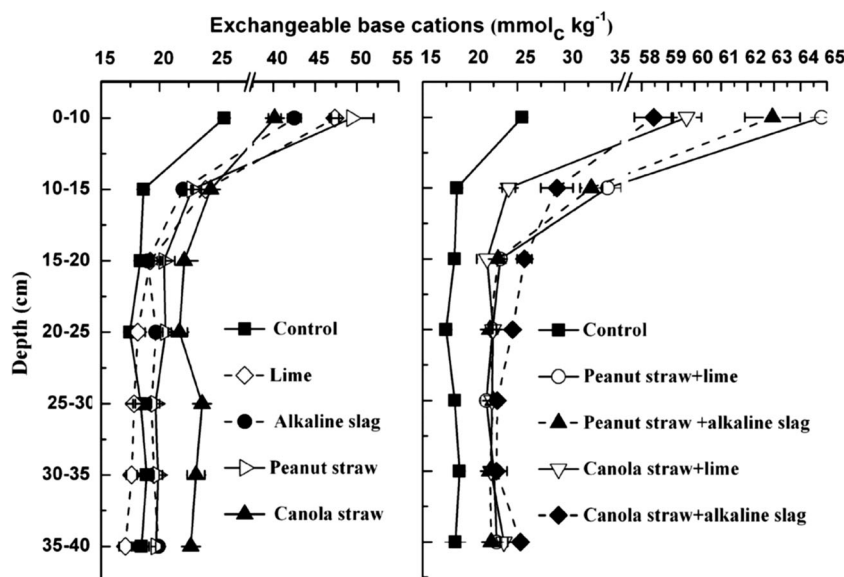


Fig. 7 Effect of surface application of sole peanut straw, canola straw, lime, alkaline slag, and crop straws in combination with lime or alkaline slag on soil exchangeable base cations in the Ultisol profile



amelioration effect was reduced with increasing soil depth (Fig. 6). The effect of amendments in decreasing exchangeable acidity was generally consistent with their effect in increasing soil pH. The CS showed the least effect in decreasing exchangeable acidity in soil at the 0–10-cm depth since CS had the lowest alkalinity among the different treatments. Low alkalinity resulted in a weak ability of CS in neutralizing soil acidity. However, at the 15–40-cm depth, CS was the most effective in decreasing soil exchangeable acidity, followed by PS and AS, and lime had little effect. For example, the soil exchangeable acidity was 52.6, 46.3, 48.2, 47.9, and 51.6 $\text{mmol}_c \text{kg}^{-1}$ in the control, CS, PS, AS, and lime treatments at the 20–25-cm depth, respectively. When crop straws were surface applied in combination with lime or AS, all the combined amendments significantly decreased the soil exchangeable acidity in the soil profile ($P < 0.05$). All the combined amendments had a similar effect in decreasing the exchangeable acidity at the 0–25-cm depth, but PS+lime was less effective than PS+AS, CS+lime, and CS+AS ($P < 0.05$). CS was also more effective than PS in significantly decreasing the exchangeable acidity at the 25–40-cm depth when these two crop straws were surface applied in combination with either lime or AS ($P < 0.05$). The amendments acted mainly through specific adsorption of SO_4^{2-} and organic anions to release OH^- , which induced neutralization of exchangeable acidity and the precipitation of exchangeable Al in the subsoil (Sumner et al. 1986; Alva et al. 1990; Li et al. 2010). The SO_4^{2-} , Cl^- , and even organic anions in the amendments induced base cations to leach downward to subsoil and exchange with exchangeable Al^{3+} and H^+ . These anions also promoted the exchangeable Al to leach out of the soil profile (Table 3). There were good relationships between SO_4^{2-} (or Cl^-) and Ca, Mg, K, Na, or Al (all with $R^2 > 0.75$), which supported the hypothesis that SO_4^{2-} and Cl^- made a significant

contribution in ameliorating subsoil acidity. Therefore, AS was more effective than lime in ameliorating subsoil acidity due to higher contents of SO_4^{2-} and Cl^- in AS compared to lime. The CS treatment contained highest content of SO_4^{2-} and Cl^- and induced the most effective amelioration effect on subsoil acidity among the sole amendment treatments. For the same reason, there were greater amelioration effects of the combined amendments as compared to respective sole amendment treatments.

Soil exchangeable base cations in the profile

The surface application of lime significantly increased the exchangeable base cations only at the 0–15-cm depth ($P < 0.05$) but decreased the exchangeable base cations at the 30–40-cm depth (Fig. 7). All the amendments increased the exchangeable base cations at the 0–10-cm depth in the following order: PS>lime>AS>CS. This was generally in agreement with the quantities of base cations added in each treatment. The quantity of base cations added in each column was 31.9, 25.0, 25.6, and 20.7 $\text{mmol}_c \text{kg}^{-1}$ for PS, lime, AS, and CS, respectively. However, although the smallest quantity of base cations was supplied in the CS treatment, CS was more effective than PS and AS in increasing the exchangeable base cations at the 15–40-cm depth ($P < 0.05$). When crop straws were surface applied in combination with lime or AS, they had more effect than the respective sole applications on soil exchangeable base cations in the Ultisol profiles. Moreover, at the 15–40-cm depth, CS+AS was more effective than the other combined treatments in increasing exchangeable base cations in the subsoil, which was mainly due to the higher contents of SO_4^{2-} and Cl^- in CS+AS treatment. The high contents of anions promoted the moving and leaching of base cations into the subsoil (Table 3) and a subsequent exchange

with the exchangeable acidity (Carvalho and van Raij 1997; Farina et al. 2000; Liu and Hue 2001).

The variation of exchangeable Ca^{2+} , Mg^{2+} , and K^+ in the profile was dependent not only on absolute amounts and relative ratios of these cations in the amendments, but also on amounts and properties of accompanying anions. Surface-applied amendments significantly increased the exchangeable Ca in the soil profile, except lime which only significantly ($P < 0.05$) increased the exchangeable Ca^{2+} at the 0–15-cm depth (Table 4). SO_4^{2-} , Cl^- , and even organic anions promoted the Ca^{2+} in the amendments to move downward to the subsoil in treatments of crop straw or AS, while the effect of lime was confined to the surface and subsurface soils, as no stable anions

could accompany the Ca^{2+} (Carvalho and van Raij 1997; Sun et al. 2000). Combined use of the crop straws with lime or AS induced more increase in soil exchangeable Ca^{2+} at the 0–30-cm depth, because more SO_4^{2-} , Cl^- , and even organic anions in the combined treatments also promoted more Ca^{2+} to move downward to the subsoil (Table 3). There was no evident difference between the combined amendment treatments (Table 4).

The surface application of lime had little effect on the exchangeable Mg^{2+} in the soil profile (Table 4). Surface-applied PS, CS, and AS increased the exchangeable Mg^{2+} at the 0–10-cm depth. PS and AS induced little increase in exchangeable Mg^{2+} at the 15–40-cm depth, while CS gradually increased the exchangeable Mg^{2+} as the depth increased (15–40 cm). There

Table 4 Effect of surface application of lime, alkaline slag (AS), peanut straw (PS), canola straw (CS), crop straws combined with lime, or AS on exchangeable Ca^{2+} , Mg^{2+} , and K^+ of an acid Ultisol after leaching with 1632-cm irrigation with ten events (780 mL/event)

Treatments	Soil depths (cm)						
	0–10	10–15	15–20	20–25	25–30	30–35	35–40
	Exchangeable Ca^{2+} (mmol _c kg ⁻¹)						
Control	17.73 f	11.07 e	10.49 e	9.99 c	10.05 e	9.67 d	9.31 d
Lime	40.71 b	17.38 bc	11.14 de	10.88 c	11.25 de	9.83 e	9.50 d
AS	30.82 d	15.16 cd	12.20 cd	12.61 b	12.30 cd	12.37 b	12.17 c
PS	33.33 d	13.69 d	13.00 c	13.29 b	12.40 cd	12.53 b	12.42 c
PS+lime	45.36 a	21.12 a	13.10 c	12.96 b	12.96 bc	13.46 a	13.63 b
PS+AS	38.52 bc	17.73 b	13.47 bc	13.10 b	13.33 abc	13.09 ab	13.19 bc
CS	26.86 e	15.27 cd	13.90 bc	13.09 b	14.33 ab	13.65 a	13.04 bc
CS+lime	45.93 a	16.12 bc	15.09 b	14.95 a	14.71 a	13.52 c	12.38 c
CS+AS	37.30 c	17.28 bc	17.09 a	14.93 a	13.78 abc	13.40 a	15.21 a
	Exchangeable Mg^{2+} (mmol _c kg ⁻¹)						
Control	3.33 g	3.09 f	3.22 de	3.43 e	3.40 c	3.60 b	3.60 de
Lime	3.30 g	3.38 ef	3.52 c	3.29 e	3.34 c	3.43 b	3.16 e
AS	8.93 e	4.10 de	3.45 cd	3.72 cd	3.46 c	3.59 b	3.99 d
PS	10.12 d	4.75 d	3.62 c	3.47 de	3.69 c	3.97 b	3.93 d
PS+lime	12.73 c	8.08 b	5.36 a	5.27 a	5.02 ab	5.09 a	5.11 c
PS+AS	18.11 a	9.76 a	5.33 a	5.24 a	5.36 a	5.26 a	5.31 bc
CS	6.00 f	3.57 ef	3.37 cde	3.85 c	4.76 ab	5.11 a	5.48 bc
CS+lime	5.88 f	3.42 ef	3.15 e	3.92 c	4.46 b	5.16 a	5.69 ab
CS+AS	13.26 b	6.18 c	4.46 b	4.63 b	4.75 ab	5.25 a	5.97 a
	Exchangeable K^+ (mmol _c kg ⁻¹)						
Control	2.35 ef	2.54 d	2.74 d	3.14 b	3.33 b	3.23 b	3.33 bc
Lime	2.15 f	1.95 e	2.35 e	2.94 b	3.20 bc	3.14 bc	3.14 c
AS	2.54 e	2.54 d	3.14 c	3.14 b	3.53 ab	3.53 a	3.73 b
PS	5.89 c	4.32 bc	3.73 b	3.73 a	3.53 ab	3.33 ab	3.33 bc
PS+lime	5.89 c	4.52 abc	3.33 c	3.14 b	2.94 c	3.14 bc	3.14 c
PS+AS	5.50 d	4.52 abc	3.33 c	2.94 b	2.94 c	2.94 c	2.94 c
CS	6.59 b	4.71 ab	4.12 a	3.92 a	3.73 ab	3.53 a	3.33 bc
CS+lime	7.27 a	4.12 c	3.33 c	3.14 b	3.14 c	2.94 c	4.12 a
CS+AS	7.08 a	4.91 a	4.12 a	3.92 a	3.92 a	3.33 ab	3.33 bc

Statistical analysis was conducted each layer with different treatments. The data followed by the different letters within a row of each item are significantly different at the 5 % level ($P < 0.05$)

was a similar effect on Mg^{2+} distribution in the Ultisol profile for the CS and CS+lime treatments. The CS and lime both contained little Mg but had high contents of Ca. Ca^{2+} released from CS or lime would exchange with soil exchangeable Mg^{2+} and promoted the downward movement of exchangeable Mg^{2+} to deeper layers (Pavan et al. 1984; Liu and Hue 2001). Surface application of CS+AS, PS+lime, and PS+AS significantly increased the exchangeable Mg in the entire Ultisol profile ($P<0.05$). PS+AS was more effective than CS+AS and PS+lime in increasing the exchangeable Mg^{2+} at the 0–15-cm depth, since more Mg was supplied in PS+AS. The difference in exchangeable Mg^{2+} among the combined amendment treatments was not significant at the 15–40-cm depth.

Surface application of PS, CS, lime, and AS also induced variations of exchangeable K^+ in the Ultisol profile (Table 4). Surface application of lime decreased the exchangeable K^+ at the 0–25-cm depth because the Ca^{2+} released from lime exchanged with soil exchangeable K^+ and promoted the leaching of K^+ from topsoil downward to the subsoil (McLay et al. 1994; Sun et al. 2000). AS had little effect on exchangeable K^+ in the Ultisol profile. PS and CS significantly increased the exchangeable K^+ at the 0–25-cm depth but had little effect at the 25–40-cm depth. Crop residues combined with lime and AS increased the exchangeable K^+ at the 0–25-cm depth for CS+AS treatment and at the 0–20-cm depth for the other combined treatments. However, the PS+lime, PS+AS, and CS+lime treatments induced significant decreases in exchangeable K^+ at the 30–40-cm depth because high and unbalanced ratio of Ca^{2+} and K^+ supplied in these treatments promoted the loss of K^+ in the subsoil (McLay et al. 1994; Sun et al. 2000). Therefore, the combined application of CS+AS appears the best with optimal/balanced quantities of exchangeable Ca^{2+} , Mg^{2+} , and K^+ levels and improved soil fertility in the Ultisol profile.

Conclusions

Increased pH and exchangeable base cations and decreased exchangeable acidity in the whole soil profile were observed when crop straws and AS were used to ameliorate soil acidity in an Ultisol profile. However, lime had little amelioration effect on subsoil acidity. Specific adsorption of SO_4^{2-} or organic anions, decarboxylation of organic acids/anions, and the association of H^+ with organic anions induced a liming effect of crop residues and AS on subsoil acidity. SO_4^{2-} and Cl^- were the major anions of amendments that promote base cations to move downward to subsoil and exchange with exchangeable Al^{3+} and H^+ . These anions also promoted some exchangeable Al^{3+} leaching out of the soil profile. CS combined with AS is suggested as a potential amendment to correct soil acidity and improve soil fertility in the whole Ultisol profile.

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