Asian Journal of Chemistry;   Vol. 26, No. 15 (2014), 4794-4800

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.16229

Interactions Between Acidic (Al^{3+}, Fe^{2+}) and Basic (Ca^{2+}, Mg^{2+}) Cations in Oxisol and Ultisol under Acidification Induced by Simulated Acid Rain

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Received: 24 August 2013; *Accepted*: 15 November 2013; *Published online*: 16 July 2014; AJC-15574

This study focuses on the interactions of aluminum and iron with exchangeable bivalent base cations (Ca^{2+} and Mg^{2+}) at different acidity levels in soils treated with acidic solutions. Acidic (pH 5.0, 4.0, 3.5, 3.0, 2.5, 2.0) and non-acidic (7, control) solutions were applied to the soil columns for 45 days representing average annual rainfall. Soil samples from different depths were analyzed for soil pH (acidity) and target elements (Ca^{2+}, Mg^{2+}, Al^{3+} and Fe^{2+}). The extractable aluminum and iron increased with a decrease in the concentration of exchangeable calcium and magnesium as the soil pH drops to 5 or low particularly in the upper layers of the investigated soils. The concentrations of soluble base cations increased as soil pH became moderately acidic and decreased as soil pH became highly acidic. However, concentration of exchangeable base cations decreased at higher levels of acidity due to accelerated transformations of exchangeable forms into soluble ones.

Keywords: Soil acidity, Base cations, Trace elements, Acidic deposition, Southeast Asia, Thailand.

INTRODUCTION

The depletion of acid neutralizing capacity (ANC) of soil due to inputs of H^+ is called soil acidification, while an increase in acid neutralizing capacity due to consumption of H^+ is known as soil alkalinization. There is a variety of processes that add H^+ ions to the soil system and therefore contribute to acidification. Although most of these processes occur naturally, human activities have a major impact on some of them. The sources of H^+ ions in the soils include acid deposition, biological metabolism and accumulation of organic matter, oxidation of sulfur and nitrogen and plant uptake of soil base cations[1]. Soil acidity affects several chemical and biological properties and reactions that control availability of plant nutrients and toxicity of certain elements[2,3]. The availability of plant nutrients (N, P, K, S and Mo) increases, while availability of Fe, Zn, Mn, Co and Cu increases as the soil becomes more acidified. Soil acidity also affects the microbial activity in soils[1].

Agricultural soils in the Northeast region of Thailand belong to oxisols and ultisols soil orders. Kaolonite is the most important clay mineral in the soils of the study area[4]. Such soils are very highly weathered soils, often rich in Al and Fe oxide minerals, having low cation exchange capacity and occupying 7.5 and 8.1 % of the land area, respectively. These soils are strongly leached soils with low fertility and are found in inter-tropical regions (oxisols) and humid temperate and tropical areas (ultisols) of the world[5]. Leaching of base cations and quantification of soil acidification under simulated acid rain have already been studied on these highly weathered soils of Northeast region of Thailand[6,7]. The main objective of this paper was to find out the interactions between soil base cations and extractable aluminum and iron at different acidic conditions in oxisol and ultisol treated with acidic solutions.

EXPERIMENTAL

Soil samples of oxisol (Pak Chong) and ultisol (Korat) soils were collected from agricultural fields in the Northeast region of Thailand. Samples were prepared for the laboratory experiments by air drying, mixing thoroughly and sieving (2 mm). Samples were analyzed in the laboratory for soil pH, particle size distribution by hydrometer method[8], soil organic matter by wet-oxidation method[9], cation exchange capacity (CEC) by 1N ammonium acetate[10] and extractable aluminum by 1N KCl[11]. PVC plastic cylinders (height = 30 cm × diameter = 15 cm) were used to prepare soil columns for the leaching experiments.

Nitric acid and sulfuric acid were used to simulate acidic solutions with pH 5.0 (T2), 4.0 (T3), 3.5 (T4), 3.0 (T5), 2.5 (T6) and 2.0 (T7). To represent unpolluted rain, de-ionized water with pH 7.0 (T1) was used as control treatment. The radius of soil column (r) and average annual precipitation (h) were used to calculate the volume of the applied solutions (V), by an equation *i.e.* $V = \pi r^2 h$. The experiments were carried out on 42 soil columns *i.e.* 2 soil × 7 pH levels of applied solutions × 3 replications for each treatment.

Application of treatment solutions to soil columns: The simulated solutions were applied to the soil columns for a period of 45 days representing average annual rainfall (1379.1 mm). Effluent samples were collected at regular intervals and were analyzed for base cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) and aluminum (Al^{3+}) using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES).

Sample preparation and chemical analysis: Soil was removed from the columns after experiments. Samples were prepared for cations and aluminum and iron extraction. Soluble and exchangeable forms of cations were extracted from soil samples by water[12] and 1N ammonium acetate[13], respectively. Aluminum and iron were extracted by 1N KCl[11] and 0.01 N $CaCl_2$[14], respectively. The target cations in the extract samples were determined by ICP-OES.

RESULTS AND DISCUSSION

Table-1 shows the selected physical and chemical properties of the investigated soils. Oxisol (Pak Chong soil) with clayey texture has higher CEC due to more clay and organic matter contents as compared to ultisol (Korat soil) having sandy texture. Pak Chong soil also has higher amounts of total exchangeable bases (TEB) contributing to its higher base saturation (BS) and consequently, lowering sensitivity to acid deposition. Both soils are slightly acidic in nature.

Interactions of extractable aluminum with exchangeable bivalent base cations: Figs. 1 and 2 show the relationships of extractable soil aluminum with exchangeable calcium and

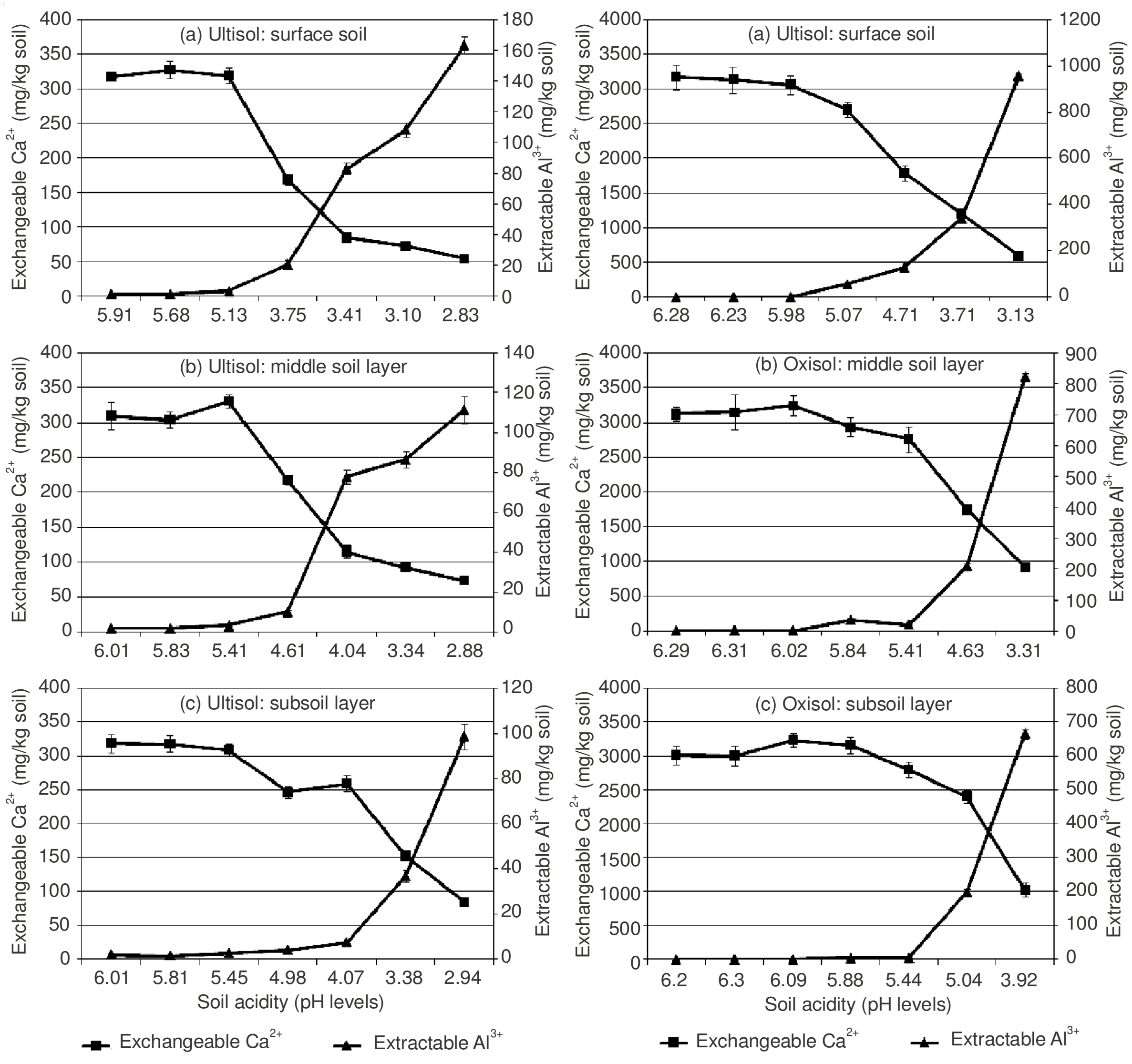

Fig. 1. Interactions between extractable aluminum and exchangeable calcium at different acidic conditions in surface, middle and sub-surface layers of oxisols and ultisols

magnesium at different levels of soil acidity in different soil layers of the investigated soils. The concentration of aluminum increased with a decrease in the concentration of exchangeable calcium and magnesium particularly when the soil pH drops to 4.5 or low in almost all the soil layers of Korat soil. The concentration of Al^{3+} in the upper layer reached 83.2, 108.6 and 163.7 mg/kg soil at 21.1, 85.3, 73.2 and 55.0 mg Ca^{2+}/kg soil and 20.3, 13.3, 14.8 and 9.3 mg Mg^{2+}/kg soil as soil pH dropped to 3.8, 3.4, 3.1 and 2.8, respectively. In case of Pak Chong soil, similar trend has been observed starting at lower acidity level (pH 5) particularly in the surface soil layer. However acid rain with pH 2.5 and 2 caused mobilization of aluminum even in middle and subsoil layers. The concentration of Al^{3+} in the surface layer reached 57.0, 130.8, 341.8 and 957.4 mg/kg soil at 2707.4, 1792.7, 1205.7 and 602.7 mg Ca^{2+}/kg soil and 226.3, 152.1, 103.2 and 52.1 mg Mg^{2+}/kg soil as soil pH dropped to 5.1, 4.7, 3.7 and 3.1, respectively. These large amounts of aluminum in oxisol and ultisol are due to

TABLE-1
BASIC PROPERTIES OF THE INVESTIGATED SOILS

Soil type	Depth (cm)	Bulk density (Mg m^{-3})	Particle size distribution (%)			Soil texture	pH (1:1)	SOM (%)	TEB (cmol kg^{-1})	CEC (%)	BS (%)
			Sand	Silt	Clay						
Kr	0-30	1.53	80.30	12.43	7.27	Loamy sand	5.82	0.19	2.23	2.75	80.94
Pc	0-30	1.18	34.30	18.43	47.27	Clay	6.31	2.94	17.23	17.72	97.27

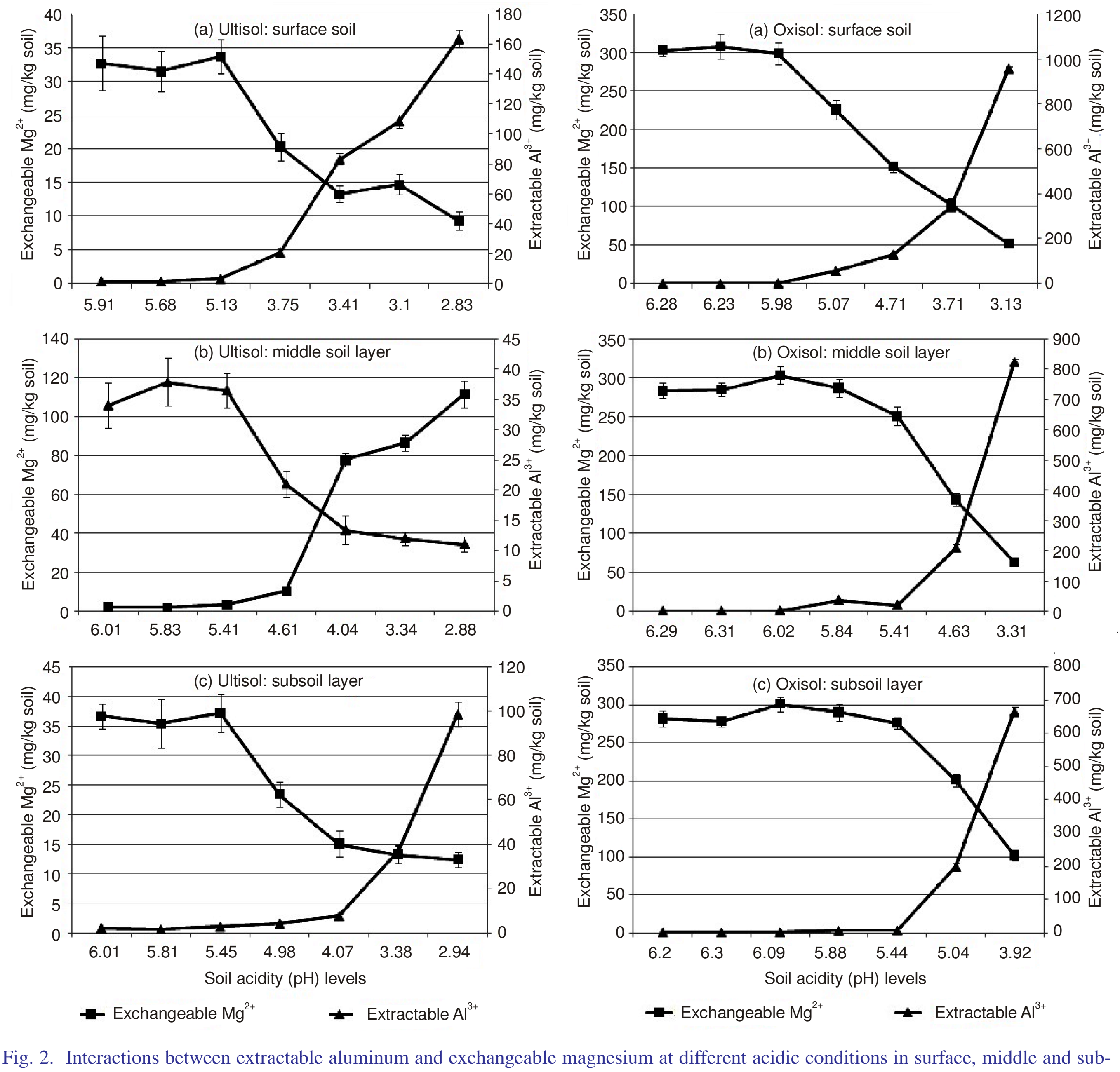

Fig. 2. Interactions between extractable aluminum and exchangeable magnesium at different acidic conditions in surface, middle and subsurface layers of oxisols and ultisols

development of soil acidity because of significant and profound leaching of calcium from the soil receiving acid rain with pH 3.5. Calcium plays a primary role in the amelioration of pH and aluminium-toxicity through Al-Ca interactions improving physiological and biochemical processes in plants. As a result of the negative effects of toxic aluminium, root metabolic processes, such as water and nutrient absorption, are disturbed with an associated decrease in calcium uptake[15]. Aluminum in the soils increased due to the mobilization as the pH of simulated acid rain and soil decreased[16].

Interactions of extractable iron with exchangeable bivalent base cations: Figs. 3 and 4 show the relationships of extractable soil iron with exchangeable calcium and magne-sium at different levels of soil acidity in different soil layers of the investigated soils. Significantly increased concentration of extractable iron has been observed in all the layers of both the soils having higher acidic conditions. Such conditions were induced by higher acidic treatments (pH 2.5 and 2.0) 6. In Pak Chong soil, the concentration of Fe^{2+} reached 8.6 (pH 3.7) and 15.5 (pH 3.1) in upper, 5.8 (pH 4.6) and 6.4 (pH 3.3) in middle and 2.8 (5.0) and 4.5 (pH 3.9) in lower layers. In case of Korat soil, the concentration of Fe^{2+} reached 10.6 (pH 3.1) and 21.2 (pH 2.8) in upper, 13.2 (pH 3.3) and 51.4 (pH 2.9) in middle and 42.8 (3.4) and 54.7 (pH 2.9) in lower layers. At highly acidic conditions, exchangeable bivalent cations in three soil layers dropped to 55.0, 74.5 and 84.8 mg Ca^{2+}/kg and 9.3, 11.1 and 12.4 mg Mg^{2+}/kg soil in Korat soil and 602.7, 924.8 and 1029.9 mg Ca^{2+}/kg soil and 52.1, 63.2 and 102.2 mg Mg^{2+}/kg soil Pak Chong soil. Strong interactions of extractable Fe^{2+} with exchangeable Ca^{2+} and Mg^{2+} was found at higher acidity levels caused by acid rain with pH 2.5 and 2.0. Iron in the soils increased due to its mobilization as the pH of simulated acid rain and soil decreased[16].

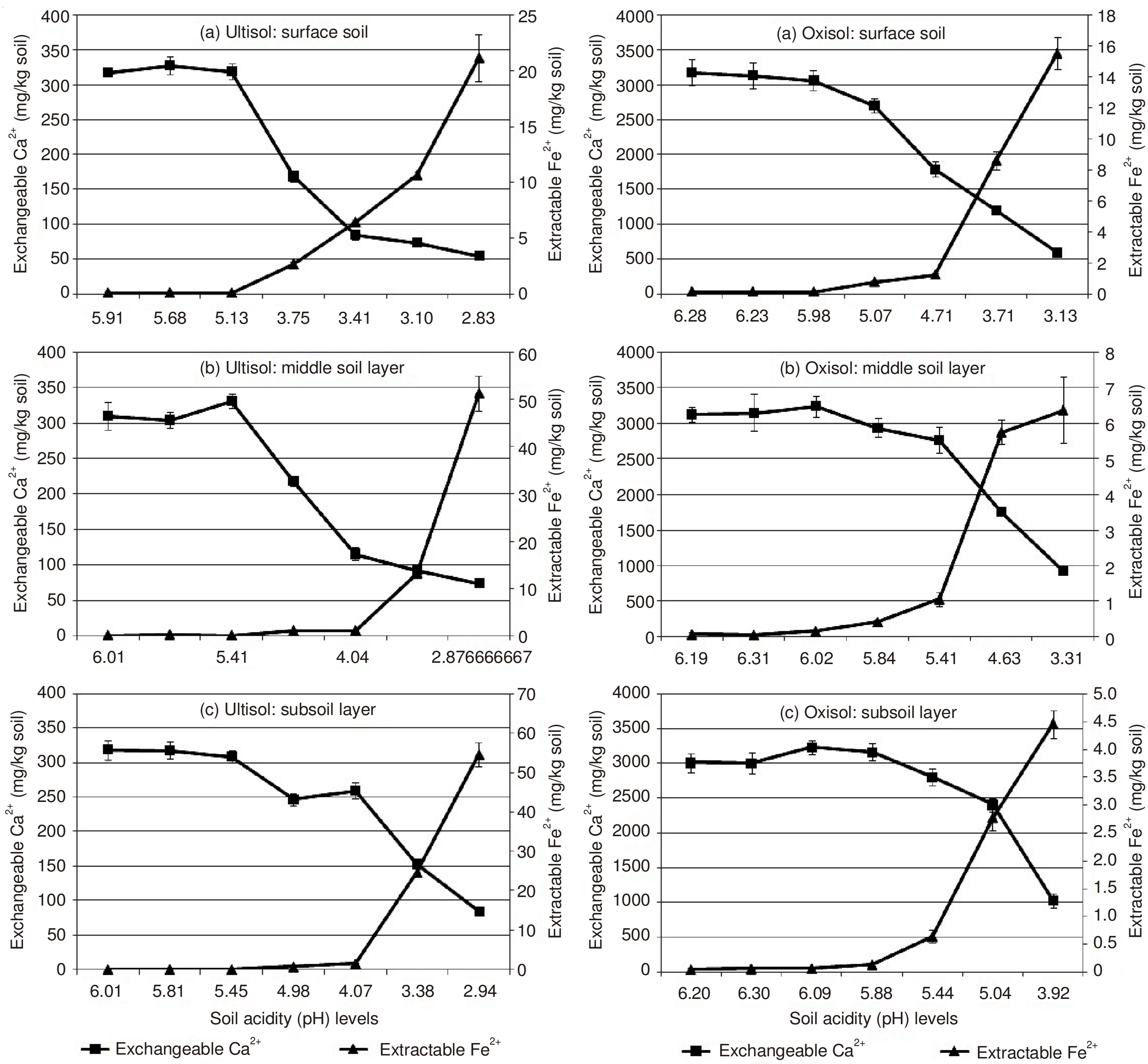

Fig. 3. Interactions between extractable iron and exchangeable calcium at different acidic conditions in surface, middle and sub-surface layers of oxisols and ultisols

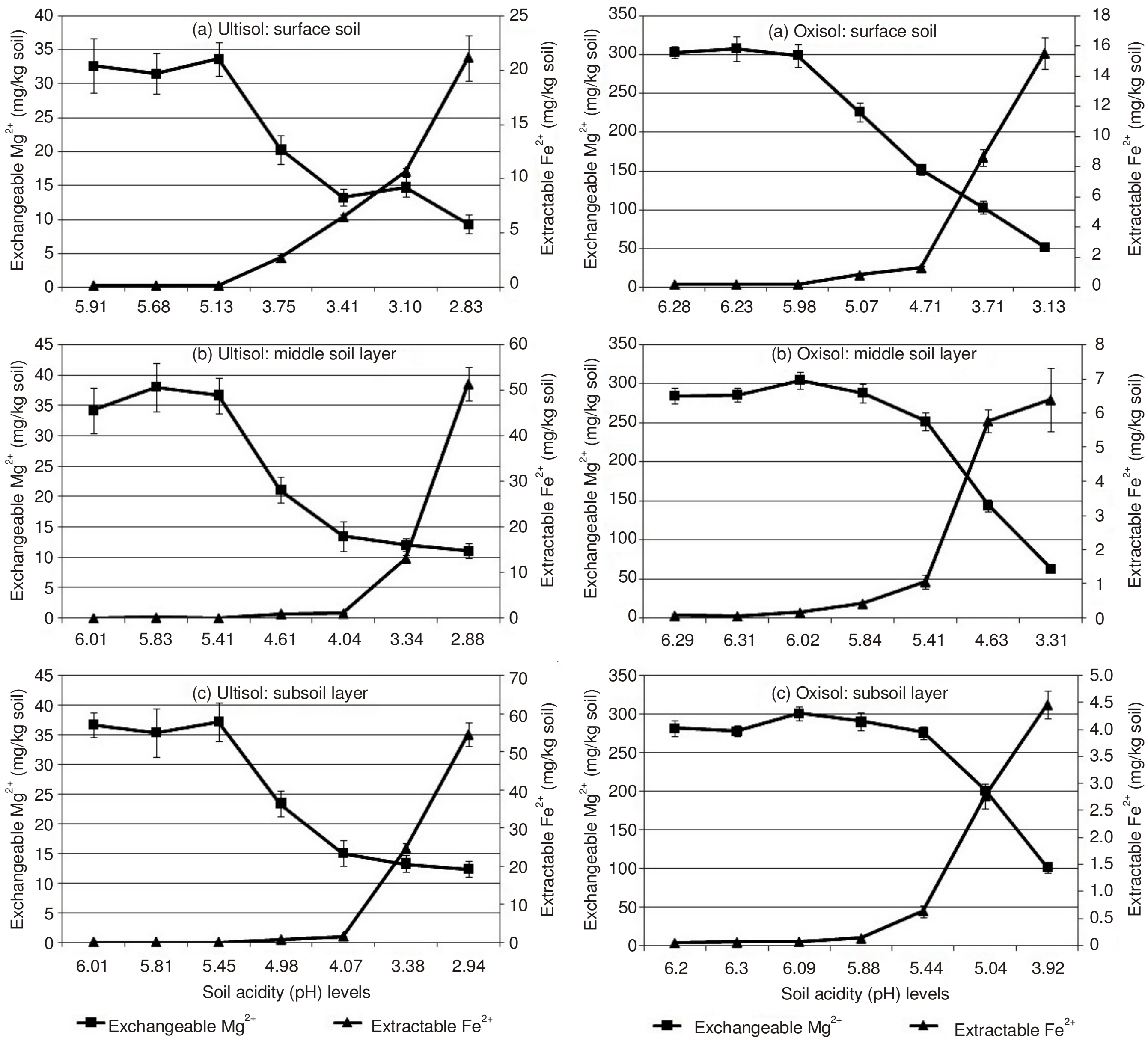

Fig. 4. Interactions between extractable iron and exchangeable magnesium at different acidic conditions in surface, middle and sub-surface layers of oxisols and ultisols

Interaction between total exchangeable base cations and total trace elements: Fig. 5 shows the relationships between total extractable trace elements (Al^{3+}, Fe^{2+} and Mn^{2+}) and total exchangeable base cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) at different levels of soil acidity at different soil depths of the investigated soils. Very strong interaction of trace elements has been found with total exchangeable base cations in almost all the soil layers of both soils investigated, particularly under higher acidity levels caused by higher acidic treatments due to significant leaching of base cations out of the soil column and increased mobilization of trace elements in the soils. The concentration of trace elements increased with a decrease in concentration of exchangeable base cations as the soil pH dropped to 3.8 (upper), 4.6 (middle) and 5.0 (lower layer) in Korat and 5.1 (upper), 5.8 (middle) and 5.0 (lower layer) in Pak Chong soil. Decreased concentration of base cations was due to their leaching under higher acidic treatments[7].

Interaction between total soluble and exchangeable base cations: Fig. 6 shows the relationships between total amounts of different forms (soluble and exchangeable) of soil base cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) at different levels of soil acidity in different soil depths of the investigated soils. No significant change has been observed in the concentration of total exchangeable base cations under slightly acidic conditions in both soils. This is because of smaller leaching of base cations under lower acidic treatments[7]. However, a sharp and continuous decrease in the exchangeable base cations occurred as the soils became moderately and highly acidic due to very high leaching and depletion of base cations under higher acidic treatments.

Soluble base cations also did not show significant change in their concentrations at slightly acidic conditions of both the soils. However, contrary to exchangeable form, concentrations of soluble base cations increased as soil pH became moderately

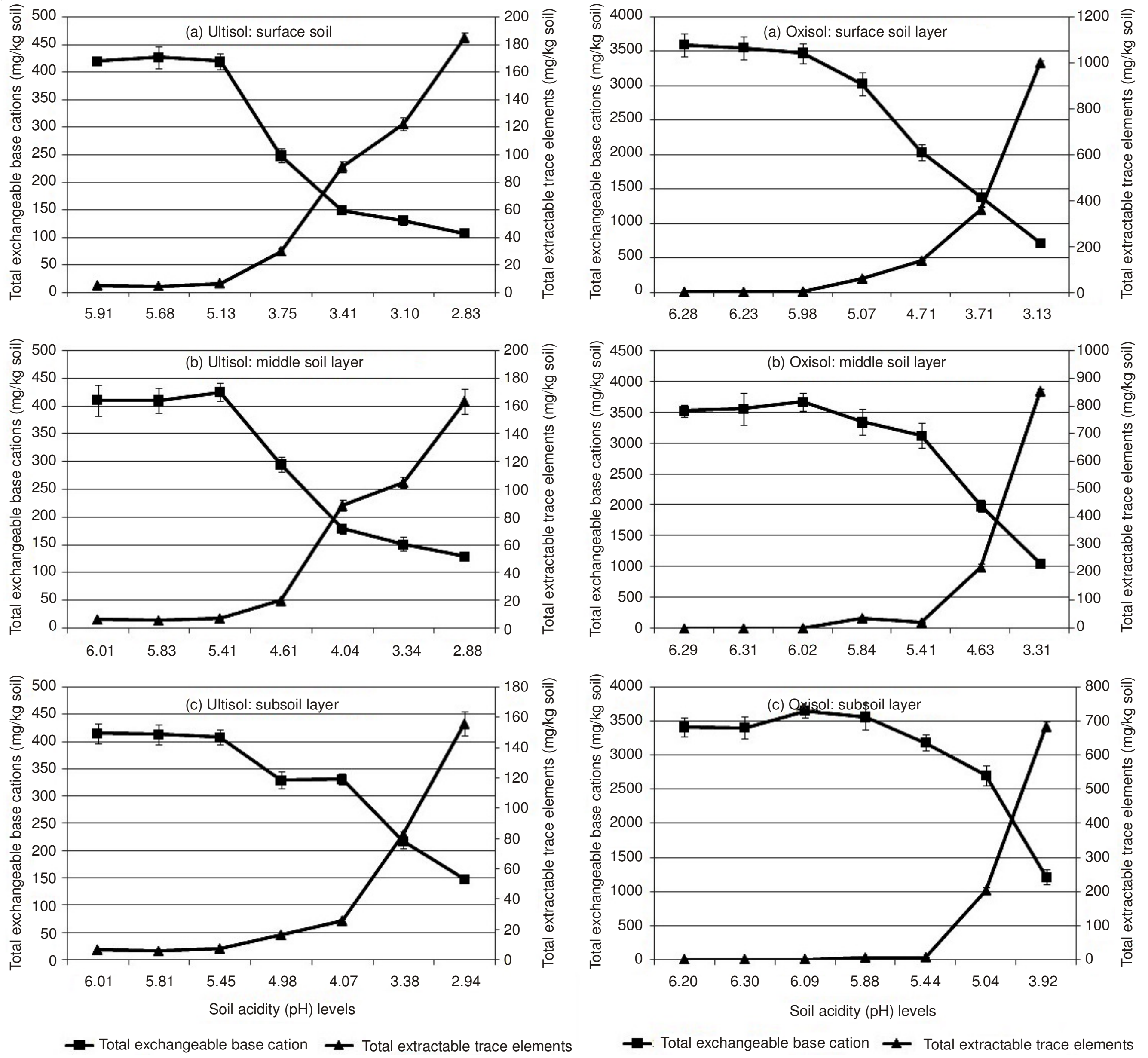

Fig. 5. Interactions between total exchangeable base cations and total extractable trace elements at different acidic conditions in surface, middle and sub-surface layers of oxisols and ultisols

acidic and decreased as soil pH became highly acidic. This is because of transformations of exchangeable base cations into soluble ones at moderate acidic treatments and accelerated leaching and depletion of exchangeable forms of base cations from the soils under higher acidic treatments.

In Korat soil, soluble base cations increased from 74.8 (original, pH 5.8) reaching 113.7 (pH 3.4), 123.3 (pH 4.0) and130.5 mg/kg soil (pH 4.1) in upper, middle and lower layer, respectively. In Pak Chong soil, soluble base cations increased from 162.5 (original, pH 6.3) to 284.8 (pH 4.7), 281.3 (pH 5.4) and 302.4 mg/kg soil (pH 5.4) in upper, middle and lower layer, respectively.

Conclusion

The extractable acid cations (aluminum and iron) increased with a decrease in the concentration of exchangeable base cations (calcium and magnesium) as the soil pH drops to 5 or low particularly in the upper layers of the investigated soils. It can be concluded that acidic and basic cations in soils have antagonistic interactions under higher acidic conditions. Soluble base cations increased under moderate acidic soil pH and decreased under highly acidic soil pH. Exchangeable base cations decreased at higher acidic conditions due to accelerated transformations of exchangeable base cations into soluble forms.

ACKNOWLEDGEMENTS

Thanks are extended to Higher Education Commission of Pakistan (HEC) and Environmental Research and Training Centre (ERTC), Thailand for financing the research work.

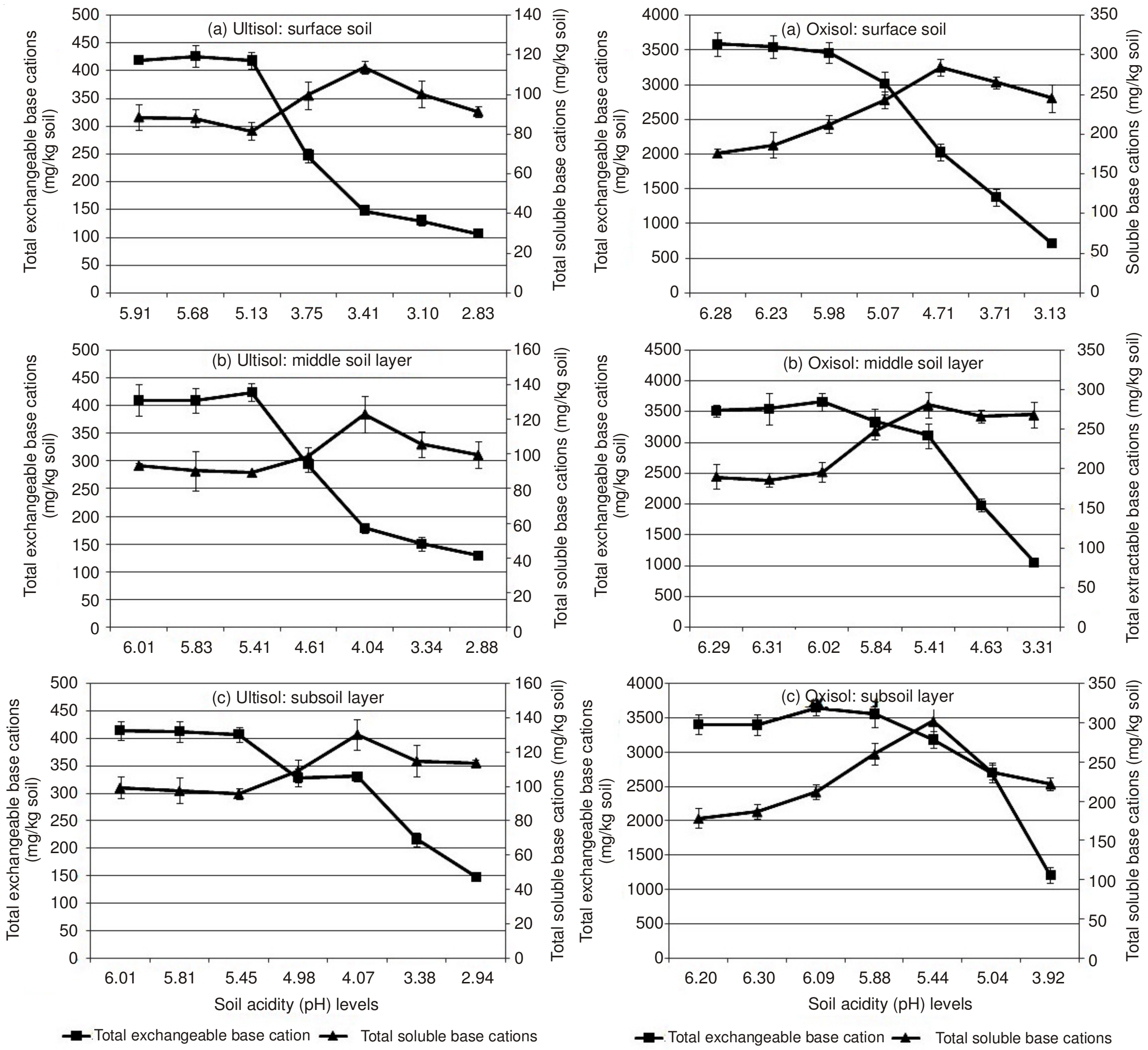

Fig. 6. Interactions between total exchangeable base cations and total soluble base cations at different acidic conditions in surface, middle and sub-surface layers of oxisols and ultisols

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