# EFFECT OF APPLICATION OF DIFFERENT LEVELS OF UREA AND AMMONIUM SULPHATE AT DIFFERERNT PROPORTIONS ON SOIL pH, SOIL PHOSPHORUS AND MICRO-NUTRIENTS AVALABILITY IN TEA SOIL

By T.M.M.M.Tennakoon 04/AS/083

This thesis is submitted in partial fulfillment of the requirement for the Degree of Bachelor of Sciences in Physical sciences of the Faculty of Applied Sciences, Sabaragamuwa University of Srilanka

> Department of Physical Sciences and Technology, Faculty of Applied Sciences, Sabaragamuwa University of Sri Lanka, Belihuloya, Sri Lanka.

> > .

April 2009.

#### DECLARATION

I certify that the research connected to this dissertation was conducted by me at the Soils and Plant Nutrition Division of the Tea Research Institute of Sri Lanka, Talawakelle and the Faculty of Applied Sciences under the supervision of Drs. A K N Zoysa and C P Udawatthe respectively. This dissertation does not incorporate any material previously submitted for a degree or diploma in any other university and to the best of my knowledge and belief, this dissertation does not contain any material previously published in writing or orally communicated by another person. Also due reference is made to the relevant work where appropriately.

T.M.M.M.Tennakoon (O4/AS/083)

Date: 06-04-2009

**Certified by:** 

#### **Internal Supervisor.**

Dr.C.P.Udawatte, Head/Dept.of Physical Sciences and Technology, Faculty of Applied Sciences, University of Sabaragamuwa, Belihuloya E-mail: chand@sab ac.lk. Tel No: 045-2280285

#### **External Supervisor.**

Dr.A.K.N Zoysa, Head/Soils and Plant Nutrition Division, Tea Research Institute of Sri Lanka, Talawakalle. Tel No. 077-3291076 E-mail: kapilatri@yahoo.com

Śignature

Date: 2009.04.21

Signature

Date: 26/04/ 2009

Affectionately

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Dedicated

To My Parents

and

To All My Teachers

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#### ABSTRACT

Soil samples were collected at a depth of 0-15 cm and 15-30 cm from experimental plots of a long term field trial carried out at the Tea Research Institute of Sri Lanka, Talawakelle to investigate the performance of ammonium sulfate (SA) and urea at two rates (240 and 360 kg N ha<sup>-1</sup> yr<sup>-1</sup>) in five combinations of SA and urea (urea : SA = 100:0, 75:25, 50:50, 25:75 and 0:100). The samples were analyzed for soil pH, Borax extractable phosphorus, DTPA extractable Mn, Cu, Fe and Zn.

The results indicate that the soil pH (water and  $0.01^{\circ}$  M CaCl<sub>2</sub>) decreased linearly with the proportional increase of ammonium sulfate in the SA/Urea combination at both (0-15 and 15-30 cm) depths. There is a decreasing trend of soil phosphorus with the decrease in soil pH at both depths at both N levels. However these changes are not statistically significant.

DTPA extractable Iron availability was linearly increased as soil pH (water and 0.01 M CaCl<sub>2</sub>) decreased at both (0-15 and 15-30 cm) depths at both N levels (240 and 360 kg N). Further zinc, copper and manganese concentration also linearly increased (not statistically significant) as soil pH (water, 0.01 M CaCl<sub>2</sub>) decreased, at (0-15 and 15-30 cm) depths at both levels of N (240 N and 360 N).

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## LIST OF ABRIVIATIONS

<sup>0</sup> C	-	degrees of Celsius
G	-	gram
Cm	-	centimeter
рН	-	Power of hydrogen
a.i	-	Active ingredient
et al	-	and other
рр	-	Pages
mg/kg	ι –	milligram per kilogram

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# CHAPTER 1 INTRODUCTION

#### **1.1 Introduction**

Tea (*Camellia sinensis* (l.) O.kuntze) is grown for its young shoots and it is used for making beverage tea. Tea plants grow well in acid soils of pH ranging from 4.5 to 5.5. The shoots having bud and two to three succulent leaves are generally plucked at regular intervals of 5-7 day depending on the elevation where it is grown for making tea.

The first commercial planting of tea in Sri Lanka was undertaken by James Taylor in 1867, on 19 acres of land at Loolecondera Estate, Hewaheta. This first tea project was carried out with the idea of testing tea as a possible alternate crop for coffee which was facing an economic slump at that time. Tea proved to be a timely venture as the coffee leaf rust disease (*Hemelia vastatrix*) made its appearance about 18 months after 1869 and completely destroyed the entire coffee plantations in the country.

The recommended quantities of N, P and K fertilizers to mature tea vary from country to country (Willson, 1992). At present, 90-220 and 270-400 kg of N ha<sup>-1</sup> yr<sup>-1</sup> is recommended for applying N fertilizer for seedling and vegetative propagated mature tea fields respectively in Sri Lanka, depending on the potential yield. The total quantity of N to be given is recommended solely as urea (Anon, 2000). However, from the national statistics on the fertilizer use, it appears that a considerable quantity on ammonium sulfate has been used for mature tea despite the recommendation of 100% urea by the Tea Research Institute in 1983 (Anon, 2003). The use of ammonium sulphate is mainly owing to grower's preference for ammonium sulphate.

Tea grows in a wide range of soil types derived from diverse parent materials in tropical and temperate climates (Child, 1953; Eden, 1976; Harler, 971; Mann, 1935). Most tea soils are highly weathered and strongly acidic. Generally, tea prefers a deep, permeable and well-drained soil. In a given locality, soil characteristics such as soil depth, gravel content, and rockiness on surface, impose severe limitations for

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successful growth of tea. The most important for good growth of tea is pH. The maintenance of soil pH between 4.5-5.5 is recommended in Sri Lanka (Anon, 2000). The major impact of pH on plant growth is related to its plant nutrient availability and the concentration of elements in the soil to become toxic concentration for plants. Adjustments can be made for soil pH values by application of soil amendments.

The maintenance of soil fertility is important in achieving sustainable yields in tea plantations. The level of fertilizer application for tea is based on the results of field experiments, analyses of soil/foliar and symptoms of mineral deficiency in plants. In 1928, the Tea Research Institute decided to resort to uniformity trials to derive accurate information on the best plot size to use, number of plots per treatment and best arrangement of plots with a view of establishing correct fertilizer practices for Ceylon tea (now Sri Lanka).

Fertilizers are sources of plant nutrients that can be added to soil to supplement its natural fertility. They are applied to the soil to supply plant needs directly rather than indirectly through modification of soil properties such as soil pH and structure. The basic principle of fertilizer application will vary from region to region according to the local conditions (Wilson and Clifford, 1992). Application of chemical fertilizers seems to be the surest and quickest way of increasing nutrient supply to the soil to ensure higher productivity. Nitrogen fertilizers are best applied in small quantities at short intervals to avoid leaching losses.

Nitrogen is one of the major nutrients for tea and it is absorbed by plants as nitrate  $(NO_3)$  and ammonium  $(NH_4^+)$  ions. Nitrogen is available in different forms such as urea and ammonium sulphate. Depending on the form of the N, some of these fertilizers are more acidifying than others. Ammonium sulphate has been an important N fertilizer for over 100 years and has been the dominant form for a long time. It is now becoming obsolete because the ammonium sulphate is costly or difficult to supply because of its low N content. Often ammonium sulphate is preferred in climates such as the humid tropics, where its physical properties make it handle better than  $NO_3^-$ . The strong acid forming reaction of  $(NH)_2SO_4$  in soil can be advantageous in high-pH soils and for acid requiring crops. Chenery (1967) made provisional recommendations for use of urea for tea as it is having lesser degree of

soil acidifying properties. The cost benefit analysis of using urea or ammonium sulphate in tea is presented in Table 1.1.

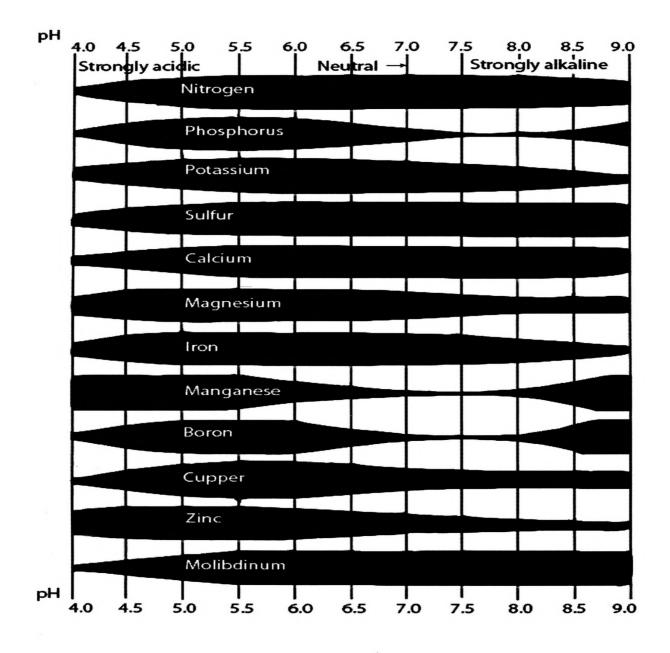
	UREA 100 %	SA 100%	Urea: SA (75:25)%
	(Rs/ha/yr)	(Rs/ha/yr)	(Rs/ha/yr)
VP/UM 910	88,020	124,200	97,065
Benefit		36,180	9,045

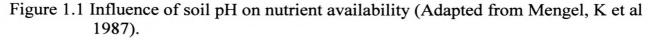
Table 1.1 Cost benefit analysis

The cost per unit of Urea was less and cost of transport, storage and even application, would be halved. In addition to the marked improvements in size, strength and density of granular urea, it has a number of other noteworthy characteristics. The strong acid-forming reaction of  $(NH_4)_2SO_4$  in soil can be advantageous in high pH soils and for acid requiring crops. But it is generally expensive as use as N source.

Phosphorous is an essential element and it is a macro nutrient, hence required in relatively large amounts by plants. Phosphorous is essential for a wide range of plant metabolic function (Mengel and kirkby, 1987), and most importantly carbon fixation during photosynthesis. It has been shown to influence growth yield and quality of tea (Gogoi *et al.*, 1993; Ranganathan *et al.*, 1982; Yongming *et al.*, 1989; Zoysa, 1997). The ultic soils on which tea is commonly grown contain very low concentration of plant available P in their native, unfertilized status (borax-extractable p: 1-4 g g<sup>-1</sup>. In nature, systems like soil and water, phosphorous will exist as phosphate. In water orthophosphate mostly exist as  $H_2PO_4$  in acid conditions or a  $HPO_4^{-2}$  in alkaline condition. Absorption of  $H_2PO_4^{-1}$  is great at low pH values, whereas the uptake of  $HPO_4^{-2}$  is greater at higher soil pH.

The essential micronutrients for plants are Cu, Fe, Mn and Zn. These are needed only in very small quantities but are considered as essential for normal plant growth. They are extremely important in the formation of amino acids and enzymes systems that allow for transferring energy in both the soil and plant. The pH of the soil also affects the mobility of soil nutrients. As the pH of soil falls below 6.0 the availability of nutrients such as P, Cu, and Zn starts to fall off, and above pH of 7.0, Cu, Zn, Mn, and Fe all slow down very quickly (Figure 1.1).





#### 1.2 Overall objective:

To identify the effect of application of different levels of urea and ammonium sulphate and their proportions on soil pH and availability of phosphorous and micronutrients (Fe, Cu, Mn and Zn) in tea soils.

### 1.3 Specific objectives:

- 1.3.1 To identify the effect of different levels and proportion of urea and ammonium sulphate on soil pH.
- 1.3.2 To identify the optimum combinations of urea and ammonium sulfate on P and micro-nutrient availability in soil.
- 1.3.3 To compare control treatment (no fertilizer application) with fertilizer application (different proportions of urea and ammonium sulfate) on soil acidity and its effect on P and micro nutrient availability.

# CHAPTER 2 LITERATURE REVIEW

#### 2.1 Tea

Tea is the third largest agricultural industry and most importantly it is our second largest foreign exchange earner. Sri Lanka's tea industry represents 1.2% of the GDP and employs approximately 1 million people, of whom about 600,000 are directly employed. The tea extent in Sri Lanka as determined by the tea land survey undertaken in 1994/1995 was 187,971 ha, and this increased to 210,621 ha by the year 2002, a 12% increase within a period of 8 years, as revealed by the census department (Anon, 2002).

#### 2.1.1 Tea Soils

The soils of the agro-ecological regions suitable for tea in Sri Lanka fall in to three major soil groups. Red Yellow Podsolic soils, Reddish Brown Latosolic soils and Immature Brown Loams, of which the largest extent is Red Yellow Podsoile soil. The primary requirement for good growth of tea is generally satisfied by these three major soil groups as they are all acidic in nature (De Alwis et al, 1972).

#### 2.2 Fertilizing of Tea

Although Tea was introduced to Sri Lanka in the 1860s, fertilization of tea plantations, on a regular and organized was basis developed only at the beginning of the 20th century. Basically in fertilizing a crop, all that needs to be done is to add nutrients needed by the crop as an inorganic fertilizer and/or as green manure, crop residues, compost or animal manure. Application of chemical fertilizers seems to be the surest and quickest way of increasing the nutrient supply of the soil for better crop production. However due to the complex and dynamic nature of the soil-plant interactions, it is not easy to determine the exact quantity of fertilizers that should be applied for optimum plant growth.

There are several methods for determining the fertility status or plant nutrient supplying capacity of soils. Recent advances in scientific and technological disciplines help in the assessment of the dynamic behavior of plant nutrients in soil and crop growth responses to applied fertilizers.

#### 2.2.1 Urea [CO (NH<sub>2</sub>)<sub>2</sub>]

Chenery (1967) made provisional recommendations for use of urea for tea with the prospect of it being cheaper than the other N fertilizers, in addition to having a lesser degree of soil acidifying properties. The cost per unit of N was less, and the cost of transport, storage and even application would be halved. Bhavanadan (1970), Wickremasinghe (1986) explained the history of urea use as a fertilizer, and its chemistry and behavior in the soil and tea plant, along with preliminary observations from experiments carried out with it on tea soils.

Practical experience of using urea during the past 30 years has shown that it is as good as any other N fertilizer if used properly. They are the fewer tendencies for stickiness and cakiness than NH<sub>4</sub>NO<sub>3</sub>, lack of sensitivity to fire and explosion, and less corrosiveness in handling and application equipments.

#### **2.2.1.2 Behavior of Urea in Soil**

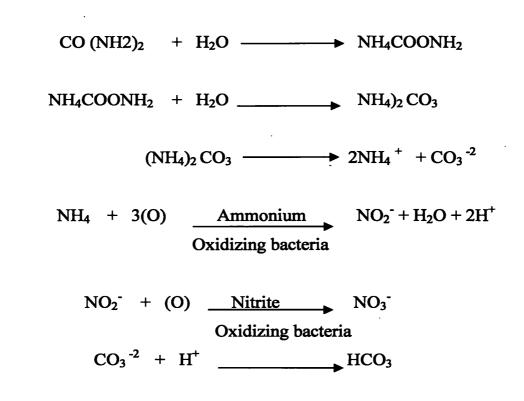
When applied to soil, urea is hydrolyzed by the enzyme urease to  $NH_4^+$ . Depending on soil pH,  $NH_4^+$  may form  $NH_3$ , which can be volatilized at the soil surface and it is represented in the following equations.

$$CO(NH)_{2} + H^{+} + 2H_{2}O \longrightarrow 2NH_{4}^{+} + HCO_{3}^{-}$$

$$NH_{4}^{+} \longrightarrow NH_{3} + H^{+}$$

The  $NH_3$  released will react in soil the same way as  $NH_3$  from anhydrous and aqua  $NH_3$ . There is also a marked rise in soil pH in close proximity to urea particles. These changes in soil properties influence N transformations and crop development just as they do in the vicinity of an anhydrous  $NH_3$  retention zone. In the presence of

adequate water or other  $H^+$  donors,  $NH_4^+$  is retained in the soil. Urea hydrolysis proceeds rapidly when soil conditions are favorable for crop growth. In warm moist soils, most the urea will be transformed to  $NH_4^+$  in several days.



#### 2.2.1.3 Urease activity in acid Tea soil

Net acidity =  $2H^+$  per urea molecule. i.e.  $1H^+$  per N atom

Urease, which catalyses the hydrolysis of urea is abundant in soils. Large number of bacteria, fungi and actinomycetes in soils posses urease. A small group of bacteria, known as urea bacteria, have exceptional ability to decompose urea. Activity of urease increases with the size of soil microbial population and with organic matter content. Although temperatures up to 37  $^{0}$ C favor urease activity, hydrolysis of urea occurs at temperatures down to 2  $^{0}$ C and lower. This evidence of urease functioning at low temperatures combined with urea's ability to melt ice at temperatures down to  $-12 \, ^{0}$ C) suggests that a portion of fall-or early winter applied urea may be converted to NH<sub>3</sub> or NH<sub>4</sub><sup>+</sup> prior to the spring.

The effect of soil moisture on urease activity is generally small in comparison to the influence of temperature and pH. Hydrolysis rates are probably highest at soil

moisture contents optimum for plant. Soil moisture content between 24 and 100% has little effect on the hydrolysis rate of Urea.

Free ammonia inhibits the enzymatic action of urease. Since significant concentration of free ammonia can occur at pH values above 7 causing temporary inhibition of urease. High rates of urea fertilization and its confinement to bands and other methods of localized placement could thus create conditions restrictive to the enzymatic action of urease.

#### 2.2.2 Ammonium Sulfate [(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>]

Ammonium sulphate is one of the oldest N fertilizers. The main advantages of ammonium sulfate are low hygroscopic nature and chemical stability. It is a good source of both N and S. Its' use can be undesirable in acidic soils that are already in need of liming.

$$(NH_4)_2SO_4$$
 \_\_\_\_\_  $2NH_4^+ + SO_4^{--}$ 

 $NH_4 + 3 (O)$  Ammonium  $NO_2 + H_2O + 2H^+$ oxidizing bacteria

 $NO_2^- + (O)$  <u>Nitrite</u>  $NO_3^$ oxidizing bacteria

Net acidity  $4H^+$  per  $(NH_4)_2SO_4$  molecule. i.e.  $2H^+$  per N atom

The main disadvantage of ammonium sulphate (SA) is its relatively low N content (21% N and 24 % S) and it is generally expensive for use as an N source. It can however be an economical source of N when transportation cost is low. The potential acidification of soil with SA is 50 per cent more than with Urea (Wickramasinghe 1985). The results from almost all the fertilizer trials show that soil pH of plots treated with SA consistently and significantly lower than those treated with urea,

confirming the acidification of soils treated with SA (Bhavanandan et al, 1971; Sandana et al, 1980; Wickramasinghe et al., 1985).

#### 2.3 Phosphorus

Phosphorus does not occur abundantly in soils as N and K. Total concentration of P in surface soils varies between about 0.02 and 0.1%. The quantity of total P in soil has little or no relationship to the availability of P for plants. Although prairie soils are often high in total P, many of them are characteristically low in plant-available P. This condition is often aggravated by low soil moisture and low soil temperatures early in the growing season. Therefore, understanding the relationships and interactions of the various forms of P in soils and the numerous factors that influence P availability is essential for efficient P management.

The plant available P in Sri Lankan soils refers to borax–extractable P (Beater, 1949). Plant available P concentrations in tea soils vary widely with location, reflecting changes in soils and management practices. The plant-available soil P concentrations in Sri Lankan tea soils (depth: 0-15 cm) as determined by borax extraction (Beater, 1949) varies from 17 to 170  $\mu$ g g<sup>-1</sup>soil (Wickramasinghe, 1986). Phosphorus in soil is generally considered to be made up of three fractions in dynamic equilibrium, as shown in the following equation (Mengel et al, 1987);

 Labile P
 Labile P
 Non - Labile P

 (Soil solution P)
 (Forms other than Soil solution P)

The soil solution P fraction is the immediate source of P available for uptake by plant roots. The solid phase and labile P fraction is held on soil colloidal surfaces, and this fraction is in rapid equilibrium with soil solution phosphate.

#### 2.3.1 Soil Solution P

P is absorbed by plants largely as orthophosphate ions ( $H_2PO_4^-$  and  $HPO_4^{-2}$ ). The ratio of these two ion species in soil solution is pH dependent. At pH 7.2, there are

approximately equal amount of  $H_2PO_4^-$  and  $HPO_4^{-2}$ . Below this pH,  $H_2PO_4^-$  is the major form in soil solution, whereas  $HPO_4^{-2}$  is the predominant form above pH 7.2.

 $HPO_4^{-2} + H^+$   $H_2PO_4^-$ 

Figure (2.1) shows that at a pH 5,  $HPO_4^-$  is almost absent whereas at pH 7.2, both phosphate species are present in fairly equal proportions.

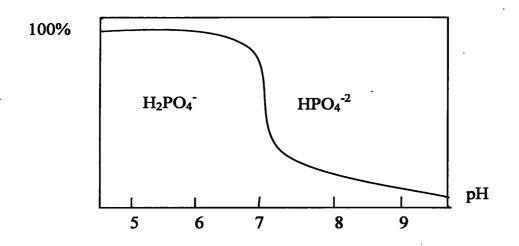


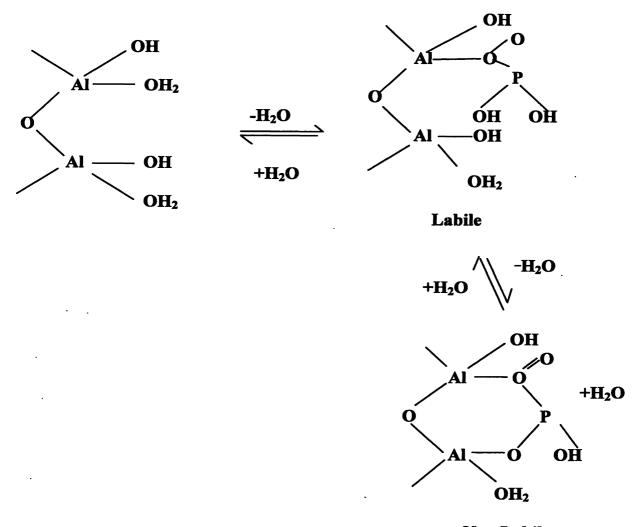
Figure 2.1 Ratio between  $H_2PO_4^{-2}$  and  $HPO_4^{-2}$  in relation to pH availability (Adapted from Mengel, K et al 1987).

Plant uptake of  $HPO_4^{-2}$  is much slower than with  $HPO_4^{-1}$ . Some low molecular weight soluble organic P compounds exist in soil solution and may be absorbed, but generally they are of minor importance. The average soil solution P concentration is about 0.05 ppm and varies widely among soils. The solution P concentration is required by most plants varies from 0.003 to 0.3 ppm and depends on the crop species and level of production. As roots absorb P from soil solution, diffusion and mass flow mechanisms transport additional P to the root surface.

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#### **2.3.1.2** P adsorption reaction

Labile inorganic P represents  $H_2PO_4^-$  and/or  $HPO_4^-$  adsorbed to mineral surfaces. In acid soils, Al and Fe oxide and hydroxide minerals are primarily involved in adsorption of inorganic P. Since the soil solution is acidic the surface of these minerals has a net positive charge, although both (+) and (-) sites exist. The predominant of (+) charges readily attracts  $H_2PO_4^-$  and other anions. P ions adsorb to the Fe/Al oxide surface by exchanging with OH<sup>-</sup> and /or OH<sup>2+</sup> groups on the mineral surface (Figure 2.2). When the orthophosphate ion is bonded through one Al-O-P bond, the  $H_2PO_4^-$ -considered labile and can be readily desorbed from the mineral surface to soil solution. When 2 Al-O bonds with  $H_2PO_4^-$ , a stable 6-member ring is formed. Another proposed mechanism for P adsorption on Fe or Al oxide surfaces is shown in Figure 2.3.



Non Labile

Figure 2.2 Mechanism of P adsorption to Al or Fe oxide surface availability (Adapted from Parfitt, 1978).

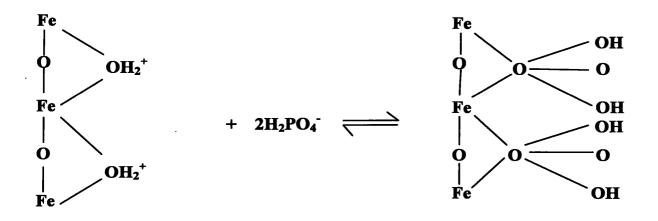


Figure 2.3 Another possible mechanism of P adsorption to Fe and/or Al oxide surfaces (Adapted from Parfitt, 1978).

Many soil physical chemical properties influence P solubility and adsorption reactions (P Fixation) in soils. Consequently, those soil properties also affect soil P concentration availability to plants and recovery of P fertilizer by crops.

#### 2.3.2.1 Nature and amount of soil minerals

Adsorption and desorption reactions are affected by the type of mineral surfaces in contact with P in the soil solution. Although present in most soils, they are most abundant in weathered acid soils. Al and Fe oxides can occur as discrete particles in soils or films on other particles.

#### 2.3.2.2 Soil pH

Soil pH has a profound influence on the quantity of P adsorption and precipitation in soils. Adsorption of P by Fe and Al oxides declines with increasing pH. Gibbsite [ $\gamma$ -Al(OH)<sub>3</sub>] adsorbs the greatest amount of P at pH 4 to 5. P adsorption by goethite [ $\alpha$ -FeOOH] decreases steadily between pH 3 and 12.

P availability in most soils is at maximum in the pH range of 5.5 to 6.5. At low pH, the retention is largely from the reaction with Fe and Al and precipitation as  $AlPO_4$ 

and FePO<sub>4</sub> oxides. As pH increases, the activity of Fe and Al decreases, which results in lower P adsorption/precipitation and higher P concentration in solution. The precipitation of Ca phosphates is promoted by high  $Ca^{+2}$  concentrations in the soil solution and by high pH conditions. High soil pH can thus be associated with dramatically opposite effects on phosphate availability. On the other hand, precipitation of Ca phosphate is favored by desorption of adsorbed phosphate is enhanced.

#### 2.4 Available micronutrients in Soil

Since 1965, numerous studies have been conducted to find a suitable extract for simultaneous extraction of available Zn, Mn, Cu, and Fe in soils. Lindsay and Norvell (1978) developed a method using Diethylene Triamine Penta Acidic Acid (DTPA) which was found useful for separating soils in to deficient and non-deficient categories for Zn, Cu, Mn, and Fe by using atomic absorption spectrophotometer. This method has been adopted in all the laboratories engaged in the analysis of available Zn, Cu, Mn, and Fe in soil.

Critical limits of soil Zn, Cu, Mn, and Fe which separate deficient from non-deficient soils vary with the soil, crop and the extractant used. These variations are to some extent related to their differential sensivity to nutrient stress. Even for the same crop, critical limits are not universal for different soil, since several factors modify availability of the micronutrients. Therefore, critical limits should be used with reference to a crop and established to match the local soil and environmental conditions.

#### 2.4.1 Principal

Chelating agents offer great promise for assessing readily available micro nutrient cations in soils. These agents combine with free metal ions in solution to form soluble complexes. DTPA offers most favorable combination of stability constants for the simultaneous complexing of Zn, Cu, Mn, and Fe. To avoid excessive dissolution of CaCO<sub>3</sub> can release occluded micronutrients (not available for plants) the exractant is

buffered in a slightly alkaline pH range and in part by including soluble  $Ca^{+2}$ . Triethanolamine (TEA) is used as buffer because it burn cleanly during atomization and has a pKa =7.8. At the selected pH of 7.3, three fourth of TEA is protonated and is present as HTEA<sup>+</sup>. When the extractant is added to the soil, additional  $Ca^{+2}$  and some Mg<sup>+2</sup> enter the solution, largely because the protonated TEA exchange with  $Ca^{+2}$  and Mg<sup>+2</sup> from soil exchange sites. This raises the concentration of ionic  $Ca^{+2}$  by two to three fold and aids in suppressing the dissolution of CaCO<sub>3</sub> in calcareous soils with a 2:1 solution to soil ratio. The capacity of DTPA to complex each of the micronutrients cations is 10 times its atomic weight and ranges from 550 to 650 ppm depending on the micronutrient cation. Thus DTPA is present in excess of the micronutrient metal cations that are normally solubilized during on extraction. This excess reduces the possibility that the extraction of one micronutrient might significantly affect the amount of other micronutrient extracted. (Parfitt, 1978).

# 2.4.2 Micronutrient in soil

All plant nutrients present in soils in mineral and organic fractions. However, quite often, one or more nutrients are not present in plant-usable forms in adequate amounts. The result is that the soil may be deficient in a nutrient in spite of containing large amounts of it. Fe for example is a case of scarcity among plenty .It is the fourth most abundant element on earth, yet many soils can vary by a factor of several hundreds. The available nutrient content at a given time is only a very small fraction of the total amount present. (Parfitt, 1978).

# 2.4.3 Fe in soil

Fe presents in the soil in higher concentrations than any other nutrient. It may be present in the soil as oxides, hydroxides and silicate minerals, amorphous oxides, adsorbed iron, Iron complexes by organic materials, and iron in solution. Iron is present in the oxidation states  $Fe^{+2}$  and  $Fe^{+3}$ . The amount of iron present as  $Fe^{+2}$  and  $Fe^{+3}$  in the soil solution depends on the hydroxide forms present in the soil, which in turn, depends on pH, a parameter related to the redox potential. Plant Primary primarily absorbs  $Fe^{+2}$ , but Fe may occur in solution as  $Fe^{+2}$  or  $Fe^{+3}$ . The relation between  $Fe^{+2}$  and  $Fe^{+3}$  in solutions depends on the oxidizing or reducing status of the soil. The oxidation reduction of Iron is,

$$Fe^{+3} + e^{-}$$
  $Fe^{+2}$ 

The soil solution's iron concentration can be increased by both reducing soil pH and adding reducing agents that reduce  $Fe^{+3}$  to  $Fe^{+2}$ .

# 2.4.3.1 Interaction with other nutrients

Metal cations can interact with Fe to induce Fe stress in plants. Fe deficiencies can result from an accumulation of Cu after extended periods of Cu fertilization. In addition to Fe deficiencies caused by excess Cu, Mn, Zn, and Mo, Fe-P interaction have been observed some plants, probably related to precipitation of Fe-P minerals. In addition, plants can be more tolerant of low Fe when P is also low.

#### 2.4.4 Mn in Soil

Mn is the eleventh most common element in the earth's crust, with an average concentration of 0.09% or 900 mg/kg. Mn is present primarily as oxides and sulfides and it often occurs in association with iron. Soil manganese exists in 3 oxidation states. Oxidation-reduction reactions in the soil influence the amount of each oxidation state present. The predominant oxidation states in most soils are  $Mn^{+2}$  and  $Mn^{+4}$ , with much more as  $Mn^{+4}$  than  $Mn^{+2}$  in soils.

Total soil Mn may be divided in to mineral Mn, organic complexes of Mn, exchangeable Mn, and solution Mn. The equilibrium of Mn between these forms is influenced greatly by soil pH and redox condition. Mn deficiency in plants occurs in some soils when the pH is increased above 6.2. For other soils, Mn is adequate even though the pH is 7.5 or higher.

# 2.4.4.1 Interaction with other nutrients

High levels of Cu, Fe, or Zn can reduce Mn uptake by plants. Addition of acidforming  $NH_4^+$  to soil will enhance Mn uptake. Neutral KCl, NaCl and CaCl<sub>2</sub> applied to acid soils also can increase the Mn availability and its concentration in plants. The relative order of the salt effect on increasing available Mn is KCl >KNO<sub>3</sub>>K<sub>2</sub>SO<sub>4</sub>.

# 2.4.5 Zn in soil

Relatively insoluble mineral forms account for more than 90% of the Zn in soils. Zn mineral that may occur in the soil include sphalerite (ZnS), smithsonite (ZnCO<sub>3</sub>), and hemimorphite  $[Zn_4(OH)_2Si_2O_7.H_2O]$ . Zn present in the soil in only the divalent form. Zinc that may become available for plant uptake is present as  $Zn^{+2}$  in the soil solution, exchangeable Zn on the cation-exchange sites, organically complexes Zn in solution, and organically complexes in the soil solid phase. Zn may be displaced by Cu, however, which has a higher stability constant. Complexed Zn can also be removed by treating the soil with a soluble complexing compound, such as Diethylene Triammine Penta Acetic acid (DTPA), since the added complexes are present in larger amounts and usually have higher stability constants than do soil derived solutes.

Soil pH has a strong effect on Zn adsorption. The level of Zn in solution at a specific soil pH depends on the nature of soil surfaces and the level of Zn in the soil. Where hydrous oxide surface are present, the Zn level in solution is usually lower. At high pH levels, if calcium carbonate is present, the solution Zn level will also be lower. At pH value above 7.5, the level of complexes of Zn in solution will depend on the solubility of organic matter, which in turn depends on the presence of calcium and other cations that may suppress its solubility.

#### 2.4.5.1 Interaction with other nutrients

Other metal cations, including  $Cu^{+2}$ ,  $Fe^{+2}$  and  $Mn^{+2}$ , inhibit  $Zn^{+2}$  uptakes possibly because of competition for the same carrier site. High P availability can induce Zn deficiency commonly in soil that is marginally Zn deficient. The popularly held belief that P-Zn reaction in soil, such as the formation of insoluble  $Zn_3(PO_4)_2.4H_2O$ , are responsible for P-induced Zn deficiency should be discounted. Solubility of this compound is sufficiently high that it will readily provide Zn to plants. Application of N fertilizer can stimulate plant growth and increase Zn requirements. Acid-forming N fertilizers will increase the uptake of both native and supplemental Zn.

#### 2.4.6 Cu in soil

Soils contain a total of 1 to 50 mg Cu/kg. This relatively small amount could all be present as substitutions in no cupric minerals or adsorbed copper on mineral surfaces and organic matter. Cu in soil can occur in soil solution, both in ionic and complexed and as exchangeable cation on the exchange complex; as a specifically adsorbed (nonexchangeable)ion; in organic matter; in occluded oxides; and in minerals. Cu specifically adsorbed by inorganic sites was less than 1.9%, while that specifically adsorbed by organic sites varied from 13.1 to 46.9% of the total.

#### **2.4.6.1 Interaction with other nutrients**

There are numerous interactions involving Cu and other nutrients. Application of N-P-K fertilizers can induce Cu deficiency. Cu deficiency following the use of acidforming N fertilizers may be related to increase  $Al^{+3}$  levels the soil solution. Furthermore, increased growth resulting from the application of N or other nutrients may be proportionally greater than Cu uptake, which dilutes Cu concentration in plants. High concentrations of Zn, Fe, and P in soil solution also can depress Cu adsorption by Plant roots and may intensity Cu deficiency.

# CHAPTER 3 MATERIALS AND METHODS

#### 3.1 Materials/Equipments used:

- pH meter equipped with glass electrode.
- Atomic absorption spectrophotometer
- Small beakers and stirring rods
- Polythene distilled water wash bottle
- Digital balance
- Spatula and Funnels.
- Volumetric Flask(25 ml)
- Pipettes

#### **3.2 Methods:**

As treatments N is given at 2 rates viz. 240 and 360 Kg N ha<sup>-1</sup>yr<sup>-1</sup> in the form of urea (U) and sulfate of ammonia (SA), in five combinations. Combinations are urea SA, 100:0; 75:25; 50:50; 25:75; 0:100. Each plot consisted of 80 buses at a spacing of 1.2 by 0.6 m and the treatments were replicated thrice and the design is completely randomized block. The soil belongs Red Yellow Podzolic and it is categorized as Rhodustult according to the USDA soil classification (De Alwis et al, 1972). The soil is characterized as Mattakelle Series (Agro-ecological region-Up Country wet Zone 2). The soil is well drained and the texture of surface soil is clay loam and subsurface soil is loam to clay. The structure in the surface soil is weak to moderate Sub- angular blocky (Dassanayake et al, 1999).

#### **3.2.1 Soil sampling**

To obtain a representative sample of surface/top soil for element analysis, numbers of soil cores are mixed to provide a composite sample. At least 10-25 cores (sub samples) taken randomly constitute a representative sample from the area which

received uniform treatment. Sub samples were taken with an auger to a uniform depth (0-15 cm and 15-30 cm). The collected soil samples were thoroughly mixed on a clean polythene sheet and it was kept in a polythene bag with suitable description and identification marks.

#### **3.2.2 Preparation of Sample for analysis**

Samples were brought to the laboratory and spread on an aluminum tray. Coarse concretions, stones and pieces of roots, leaves and other undecomposed organic residues were removed. Then it was kept to air dry at 20-25°C temperature. After air drying, soil samples were crushed gently in mortar and sieved through a 2 mm sieve for certain analysis. They were transferred into plastic bags immediately after collection.

#### 3.2.3 Determination available micronutrients (Fe, Cu, Zn and Mn)

#### **3.2.3.1 Extracting Solution**

13.1 ml reagent TEA (Triethanolamine), 1.967 g DTPA and 1.47 g of  $CaCl_2$  were added to 100 ml of glass distilled water to prepare 2 liter of DTPA (Diethylene Triammine Pentaacitic Acid) extracting solution. Then it was allowed to stay for sometimes for the DTPA to dissolve and dilute approximately to 1000 ml. The pH was adjusted to 4.7 with 6 N HCl and it was marked up to 2 liter with distilled water.

#### **3.2.3.2 Extraction and Determination**

10 g of air dried soil samples were weighed and 20 ml of the DTPA extracting solution were added them. Then it was placed on a horizontal shaker for 2 hours with a speed of 120 cycles per minute. The suspensions were filtered through the filter paper (542) and the filtrate in polypropylene bottles used to determine the trace elements (Zn, Cu, Mn and Fe) using Atomic Absorption Spectrophotometer (AAS).

#### **3.2.4 Determination available soil Phosphorous**

12 g of Antimony Potassium Tartrate, 0.2908 g of Ammonium molybdate and 148 ml of  $H_2SO_4$  were added to glass distilled water (approximately to 900 ml.) to prepare 1 liter of SCR (Single Color Reagent) solution. After cooling it was marked up to 1 liter with distilled water. Then 2.112 g of Ascorbic acid and 500 ml of SCR were mixed for the analysis of Phosphorous.

2.5 g of air dried soil samples were weighed and 25 ml of the Borax extracting solution were added them. Then it was placed on a horizontal shaker for 1/2 hours with a speed of 120 cycles per minute. The suspensions were filtered through the filter paper (542) and the 3 ml of filtrate were taken to 25 ml of volumetric flask. Then 4 ml of mixture (SCR + Ascorbic acid) were added to each flask and it was volume to 25 ml with distilled water. This was used to determine the Phosphorous using Spectrophotometer.

#### 3.2.5 Determination of Soil pH

Soon after drawing soil samples, pH was monitored. The soil pH was determined using 2 methods.

#### 1. Distilled water method

10 g of soil sample was weighed and added 25 ml of distilled water and allowed to leave for 30 minutes. Then the solution was stirred and the measurement was read by using the pH meter equipped with glass electrode.

#### **2.** $0.01 \text{ M CaCl}_2 \text{ Method}$

This was done as the above method replacing 0.01 M CaCl<sub>2</sub> instead of distilled water.

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# **CHAPTER 4 RESULTS AND DISSCUSSION**

# 4.1 Effect of N levels and Proportions of Urea and SA on Soil P and

The effect of N levels and proportions of urea and SA on soil P at 0-15 cm and 15-30 cm depths at both levels of N (240 N and 360 N) are shown in figure 4.1).

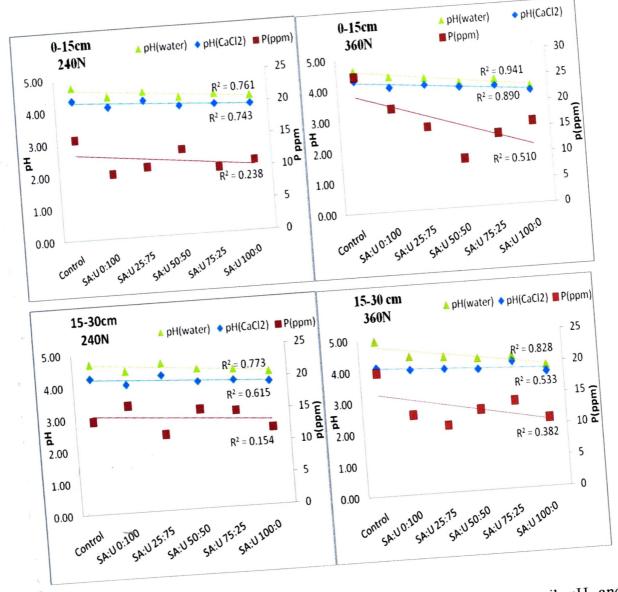


Figure 4.1: Effect of urea and SA with different proportion on soil pH and Phosphorous concentration at (0-15 and 15-30 cm) depths at two N (240 N and 360 N) levels

The soil pH (water and 0.01 M CaCl<sub>2</sub>) decreased linearly as the proportion of SA increased in the urea: SA combination at both (0-15 and 15-30 cm) depths (Figure 4.1). This is mainly due to H<sup>+</sup> release from SA and urea due to hydrolysis. When SA is added to the soil, cation exchange reaction takes place instantaneously, wherein the NH<sub>4</sub><sup>+</sup> ions enter the exchange complex displacing metallic ions mainly Ca and Mg. When urea is added to the soil, it undergoes chemical transformation and (NH<sub>4</sub><sup>+</sup>) is formed. Soil moisture determines how rapidly this transformation takes place. Fertilizers that contain (NH<sub>4</sub><sup>+</sup>) or which converts (NH<sub>4</sub><sup>+</sup>) during nitrification to NO<sub>3</sub><sup>-</sup> release H<sup>+</sup> enhancing acidity. The decrease in pH is more when N fertilizer (SA and urea) is added compared to no N fertilizer treatments (control). As mentioned earlier, urea acidifies the soil less compared to SA. During chemical transformation of urea and SA the net hydrogen produced per 1 molecular of urea and SA is 2H<sup>+</sup> (1H<sup>+</sup> per N atoms) respectively and it is the reason for more acidification in SA treated plots with higher rates of N application (360 kg N). The decrease in pH was significantly more for both sours of N.

The concentration of Borax-extractable P was found to be more in the 15-30 cm depth than at 0-15 cm depth. The P concentration in 0-15 cm was relatively higher compared to 15-30 cm depth in all the treatments. When SA component in the combination of urea: SA mixture is increased, the pH in the soil decreases causing a reduction in P concentration in the soil. The available P concentration in soil is largely dependent on the reaction of soluble Fe and Al oxides and precipitation reactions to form Fe and Al phosphate and this P fixation reduces the P concentration in soil. As tea soils are rich in Al and iron, the P concentration in solution is largely controlled by the solubility of inorganic P minerals in soil (Al and Fe-P minerals in acid soils. Each P mineral will support specific ion concentrations that depend on the solubility products of minerals.

$$FePO_4.2H_2O + H_2O = H_2PO_4 + H^+ + Fe(OH)_3$$

÷

This reaction shows that as  $H^+$  increases (decreasing pH); the  $H_2PO_4^-$  concentration decreases. Therefore, the specific minerals present in soil and the concentration of solution P supported by these minerals are highly dependent on solution pH. As pH

increases, the activity of Fe and Al decreases resulting lower P adsorption/precipitation and higher P concentration in solution.

# **4.2 Effect of N levels and Proportions of Urea and SA on** Micronutrient Concentration in Tea soil

The concentration of DTPA-extractable micronutrients such as Zn, Mn, and Cu linearly increased (not statically significant) with the decrease in pH (water, 0.01 M  $CaCl_2$ ) and this trend was seen at both depths (0-15 and 15-30 cm) and at both N (240 N and 360 N) levels (Fig. 4.2, 4.3, 4.4 and 4.5).

# 4.2.1 The effect of N levels and Proportions of Urea and SA on Mn availability

The Mn concentration range from 1.0 to 2.2 ppm at 0-15 cm and 0.8 to 2.4 ppm at 15-30 cm depth (Figure 4.2). The Mn availability is higher in acid soils at both depths (0-15cm and 15-30 cm) due to the higher solubility of Mn compounds under low pH condition. In extremely acid soils, Mn solubility could be higher causing it toxic to sensitive plant species. On the other hand, low Mn availability in soils with high pH (calcareous soils) and over-limed soils is apparently low and this condition can be largely overcome by using acid-forming N or S containing fertilizers.

Under high pH conditions, Mn availability can be inadequate to meet the plant demand. Lindsay (1974) found that the affinity of  $Mn^{+2}$  for synthetic chelates is comparatively low and complexed Mn can easily be replaced by  $Zn^{+2}$  and  $Ca^{+2}$ . So the levels on Mn is soil solutions are considerably higher than those of Cu and Zn and also water logging of soil could reduce O<sub>2</sub> concentration which lower the redox potential, increases the soluble  $Mn^{+2}$ , especially in acid soils.

Mn availability can be increased by poor aeration in compacted soils and due to local accumulations of  $CO_2$  around roots and other soil micro-sites. Under very dry conditions, Mn salts in the soil can be irreversibly dehydrated and become less

Mn availability can be increased by poor aeration in compacted soils and due to local accumulations of  $CO_2$  around roots and other soil micro-sites. Under very dry conditions, Mn salts in the soil can be irreversibly dehydrated and become less available. The effect of N levels and proportions of Urea and SA on Mn availability at 0-15 cm and 15-30 cm depths are shown in Figure 4.2.

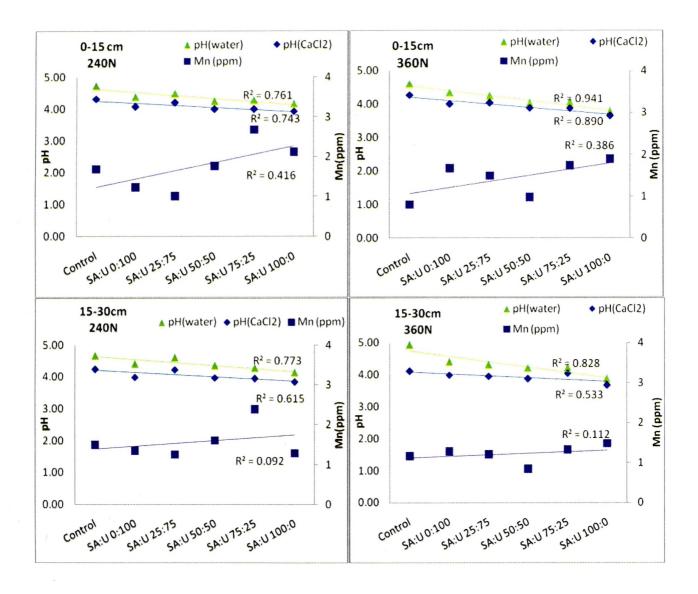


Figure 4.2: Effect of urea and SA with different proportion on soil pH and Mn concentration at (0-15 and 15-30 cm) depth and two N levels (240 N and 360 N)

## 4.2.2 The effect of N levels and Proportions of Urea and SA on Soil Zn Concentration

The effect of N levels and proportions of urea and SA on soil Zn concentration at (0-15 cm and 15-30 cm) depths at both N levels (240 and 360 kg N ha<sup>-1</sup> yr<sup>-1</sup>) are shown in Figure 4.3.

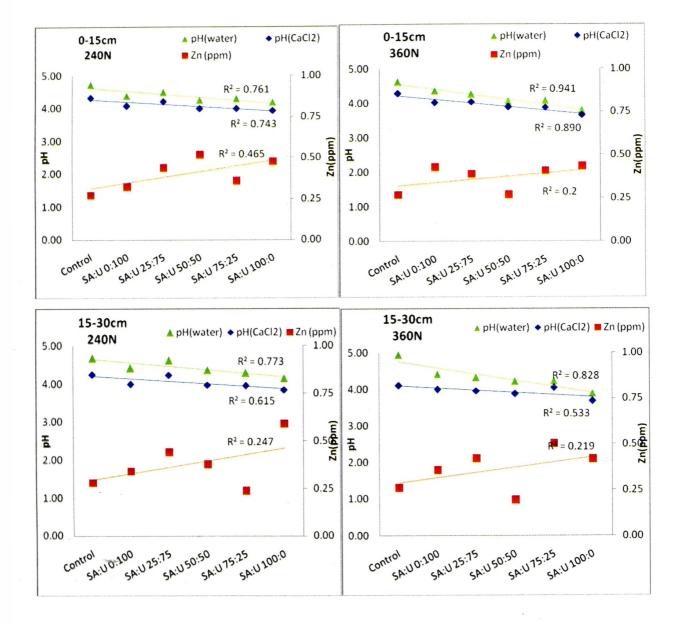


Figure 4.3: Effect of urea and SA with different proportion on soil pH and Zn concentration at (0-15 and 15-30 cm) depth and 2 N (240 N and 360 N) levels

The concentration of Zn in the soil range from 0.2 to 0.5 ppm at 0-15 cm and 0.2 to 0.6 ppm at 15-30 cm depths (Figure 4.3). The availability of  $Zn^{+2}$  decreases with increased soil pH (water, 0.01 M CaCl<sub>2</sub>) at both combinations (not significant) and N (240 N and 360 N) levels, because the  $Zn^{++}$  is strongly adsorbed on cation-exchange sites of silicate clays. Carbonates and perhaps some other soil minerals containing Al and Fe oxides and organic matter adsorb Zinc. Zn adsorption is one of the factors that limit Zn concentration in soil solution, but it is also a source of replacement when more readily available Zn supply is depleted.

Other metal cations including  $Cu^{+2}$ ,  $Fe^{+2}$ , and  $Mn^{+2}$  inhibit  $Zn^{+2}$  uptake by plants possibly because of competition for the carrier site. High P availability can induce Zn deficiency in soils that are marginally Zn deficient. Increasing soil temperature also increases the availability of Zn to crops by increasing solubility and diffusion of  $Zn^{+2}$ . On the other hand, several Zn hydrolysis species exist in solution with  $Zn^{+2}$ predominating below pH 7.7. Also at high pH, Zn precipitates as insoluble amorphous soil Zn, ZnFe<sub>2</sub>O<sub>4</sub>, and/or ZnSiO<sub>4</sub>, which reduces Zn<sup>+2</sup> concentration in soils.

## 4.2.3 The effect of N levels and Proportions of Urea and SA on Soil Cu Concentration

The Cu concentration range from 0.5 to 1.2 ppm at 0-15 cm depth and 0.5 to 1.2 ppm at 15-30 cm depth (Figure 4.4). The concentration of soil solution Cu decreased with increasing pH (water, 0.01 M CaCl<sub>2</sub>) (not statistically significant). Copper is more strongly bound to organic matter than other micronutrient cations (e.g.  $Zn^{+2}$ ,  $Mn^{+2}$ ). In comparison with other cations, Cu is held very tightly on inorganic exchange sites (Grimme, 1968). When soil pH is increased, Cu availability generally declines in both depths (0-15 cm and 15-30 cm) and at both N levels (240 N and 360 N). This is mainly due to strong Cu adsorption. The presence of carbonates or oxides in the soil plays no restriction on Cu availability.

On the other hand, Cu adsorption increases with increasing soil pH due to increasing pH depending sites due to clay minerals and organic matter, reduced competition with  $H^+$ , and a change in the hydrolysis state of Cu in solution. When the pH is raised, hydrolysis of Cu<sup>+2</sup> and increase in chemisorbed Cu (i.e. decreasing  $H^+$  shifts

equilibrium to the right.) A significant fraction of Cu in soil is occluded or buried in various mineral structures, such as clay minerals and Fe and Mn oxides. It is present as an impurity within CaCO<sub>3</sub> and MgCO<sub>3</sub> minerals in acid soils, and within Al(OH)<sub>3</sub> and Fe(OH)<sub>3</sub> in acid soil.

The effect of N levels and proportions of urea and SA on soil Cu concentration at (0-15 cm and 15-30 cm) depths at both N levels (240 and 360 kg N ha<sup>-1</sup> yr<sup>-1</sup>) are shown in figure 4.4.

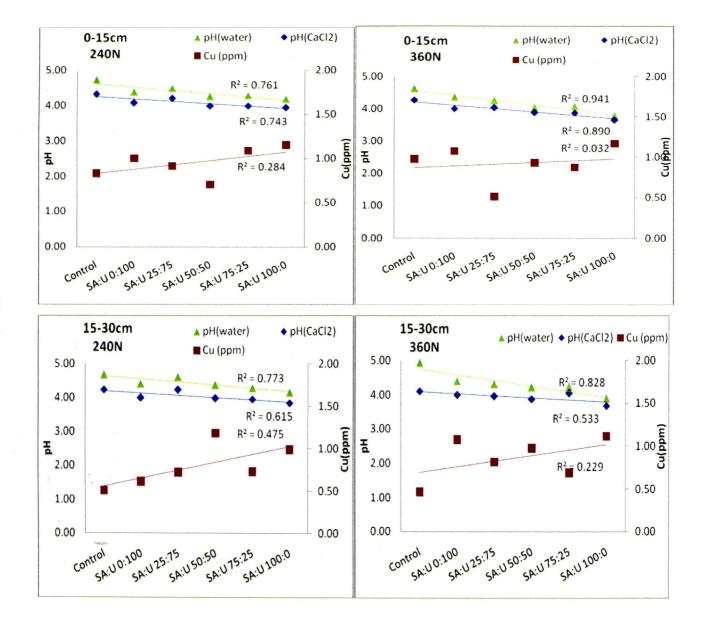


Figure 4.4: Effect of urea and SA with different proportion on soil pH and Cu concentration at (0-15 and 15-30 cm) depth and 2 N (240 N and 360 N) levels

# 4.2.4 The effect of N levels and Proportions of Urea and SA on Fe concentration

The effect of N levels and proportions of Urea and SA on Fe content at (0-15 cm and 15-30 cm) depths at both N levels (240 and 360 kg N ha<sup>-1</sup> yr<sup>-1</sup>) are shown in figure 4.5.

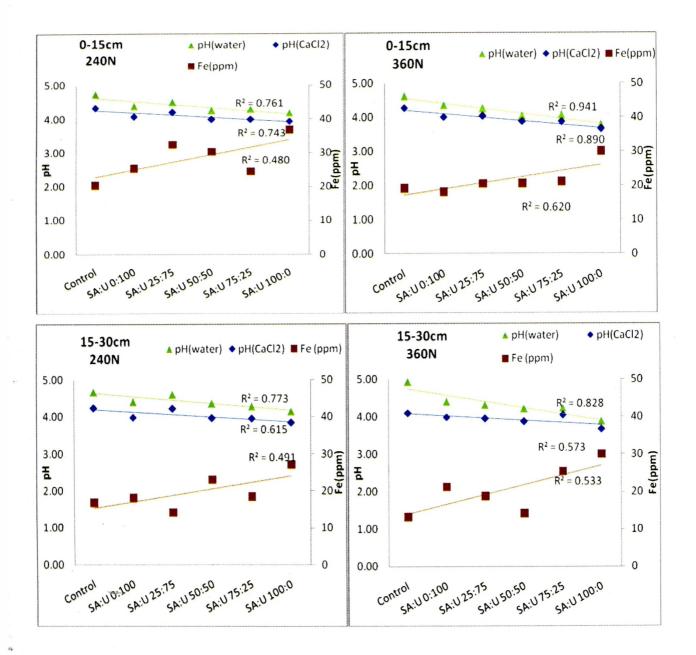


Figure 4.5: Effect of urea and SA with different proportion on soil pH and Fe concentration at (0-15 and 15-30 cm) depths and two N (240 N and 360 N) levels

The Fe concentration range from 18.0 to 37.0 ppm at 0-15 cm depth and 13.7 to 30.1 ppm at 15-30 cm depth (Figure 4.5). The availability of Fe decreased with increased soil pH (water, 0.01 M CaCl<sub>2</sub>) at both combinations and two N levels (240 N and 360 N) because the solubility of Ferric and Ferrous ion are much lower at high pH than at low pH. Both Fe(OH)<sub>3</sub> and Fe(OH)<sub>2</sub> have low solubility and can be precipitated at high pH because OH<sup>-</sup> ions become more abundant when pH rises. Other Fe compounds also becomes less soluble at higher pH.

High pH levels (neutral or alkaline) in soil also can similarly reduce Fe availability and contribute to Fe deficiency (Brown and Jones, 1975). Iron deficiencies also can result from an excess of either Mn or Cu. Mn and Cu can serve as oxidizing agents to convert ferrous ions into more insoluble ferric form. The provision of irrigating water high in bicarbonate or soils that are high in bicarbonate (HCO<sub>3</sub>) may aggravate Fe deficiencies probably because of the high pH levels associated with HCO<sub>3</sub><sup>-</sup> accumulation. The pH of most soils containing CaCO<sub>3</sub> falls in the range 7.3 to 8.5, which coincides with the greatest incidence of Fe deficiency as the solubility of soil Fe is lowest under such conditions.

## CHAPTER 5 CONCLUSION

The following conclusions could be drawn from the study:

- 1. The increasing levels of N (240 and 360 N) increased soil acidity and lowered soil pH significantly when the proportion of sulphate of ammonia is increased in the urea: sulphate of ammonia combination.
- 2. The Borax-extractable phosphorus concentration in soil significantly decreased when the proportion of sulphate of ammonia is increased in the urea: sulphate of ammonia combination at both soil depths and two N levels. Also it was evident that the P concentration was higher in the surface soil (0-15 cm) than 15-30 cm depth. This should be due to accumulation of P in the surface soil.
- The concentration of micronutrients (Zn, Cu and Mn) were linearly decreased (not statistically significant) with the increase in soil pH (water, 0.01M CaCl<sub>2</sub>) at both 0-15 and 15-30 cm depths at both levels of N levels (240 N and 360 N).
- 4. Unlike other micro nutrients, the concentration of Fe decreased significantly with the increase in soil pH due to both depths.

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#### **APPENDIX 1**

Effect of urea and SA with different proportion on soil pH and Phosphorous concentration at (0-15 and 15-30 cm) depths and two N (240 N and 360 N) levels.

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		o-6Cm	o-6Cm	0-6Cm
	Treatments	P(ppm)	pH(water)	pH(CaCl2)
	Control	16	4.74	4.32
<b>N</b> 1	SA:U 0:100	10	4.39	4.07
240N	SA:U 25:75	11	4.5	4.20
_	SA:U 50:50	13	4.26	3.99
·	SA:U 75:25	10	4.30	3.99
	SA:U 100:0	11	4.19	3.93
			-	
	Control	27	4.62	4.27
N2	SA:U 0:100	20	4.36	4.00
360N	SA:U 25:75	16	4.26	4.03
	SA:U 50:50	9	4.05	3.88
	SA:U 75:25	14	4.08	3.87
	SA:U 100:0	16	3.8	3.65
		6-12Cm	6-12Cm	
	Treatments	P(ppm)	pH(water)	pH(CaCl2)
	Control	15	4.68	4.24
	SA:U 0:100	17	4.42	3.99
	SA:U 25:75	12	4.62	4.23
N1	SA:U 50:50	16	4.37	3.97
240N	SA:U 75:25	15	4.29	3.95
	SA:U 100:0	12	4.15	3.84
	Control	20	4.94	4.10
	SA:U 0:100	13	4.41	3.99
	SA:U 25:75	11	4.32	3.95
N2	SA:U 50:50	13	4.22	3.87
360N	SA:U 75:25	14	4.24	4.04
	SA:U 100:0	11	3.89	3.67

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### **APPENDIX 5**

Effect of urea and SA with different proportion on soil pH and Fe concentration at (0-15 and 15-30 cm) depths and two N (240 N and 360 N) levels.

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		0-6 Cm	o-6Cm	o-6Cm
Level	Treatments	Fe(ppm)	pH(water)	pH(CaCl2)
	Control	20.40	4.74	4.32
	SA:U 0:100	25.42	4.39	4.07
N1	SA:U 25:75	32.40	4.5	4.20
240 N	SA:U 50:50	30.33	4.26	3.99
	SA:U 75:25	24.55	4.3	3.99
	SA:U 100:0	36.86	4.19	3.93
		-		
	Control	19.23	4.62	4.27
	SA:U 0:100	18.09	4.36	4.00
N2	SA:U 25:75	20.53	4.26	4.03
360 N	SA:U 50:50	20.59	4.05	3.88
	SA:U 75:25	21.10	4.08	3.87
	SA:U 100:0	30.10	3.8	3.65
		6-12Cm	6-12Cm	6-12Cm
Level	Treatments	Fe (ppm)	pH(water)	pH(CaCl2)
	Control	16 <b>.</b> 96	4.68	4.24
	SA:U 0:100	18.21	4.42	3.99
N1	SA:U 25:75	14.30	4.62	4.23
*	SA:U 50:50	23.06	4.37	3.97
• .	SA:U 75:25	18.54	4.29	3.95
	SA:U 100:0	27.11	4.15	3.84
• •	Control	12 24	4.04	4.10
	SA:U 0:100	13.34 21.32	4.94	4.10
N2	SA:U 25:75	18.92	4.41 4.32	3.99 3.95
	SA:U 50:50	14.33	4.32 4.22	3.95 3.87
	SA:U 75:25	25.49	4.22	4.04
	SA:U 100:0	30.05	3.89	3.67
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