

CHAPTER 1

LITERATURE REVIEW

1.1 THE GROUNDNUT CROP

1.1.1 ORIGIN, DISTRIBUTION AND STATISTICS

The cultivated groundnut (*Arachis hypogaea* L.) is an ancient crop of the New World, which originated in South America (southern Bolivia/north west Argentina region) where it was cultivated as early as 1000 B.C. Dissemination of the crop to Africa, Asia, Europe and the Pacific Islands occurred presumably in the sixteenth and seventeenth centuries with the discovery voyages of the Spanish, Portuguese, British and Dutch (Krapovickas, 1969, 1973; Gregory *et al.*, 1980; Hammons, 1982; Isleib *et al.*, 1994). Today, it is grown in areas between 40 degrees South and 40 degrees North of the equator, where average rainfall is 500 to 1200 mm and mean daily temperatures are higher than 20°C. The groundnut crop is cultivated in 108 countries on about 22.2 million hectares, of which 13.69 million ha are in Asia (India 8 million ha; China 3.84 million ha), 7.39 million ha in Sub-Saharan Africa, and 0.7 million ha in Central and South America. Average pod yields on a global scale increased slightly from 1.08 Mt ha⁻¹ in the 1980's to 1.15 Mt ha⁻¹ in the 1990's (Carley & Fletcher, 1995), and the global production is 29 million tonnes of pods. India, China, and the United States are the leading producers and grow about 70% of the world's groundnuts (FAO, 1995-2001; CGIAR Research, 2000).

1.1.2 UTILISATION

The uses of groundnut are diverse; all parts of the plant can be used. The nut (kernel) is a rich source of edible oil, containing 36 to 54% oil and 25 to 32% protein (Knauff & Ozias-Akins, 1995). About two thirds of world production is crushed for oil, which makes it an important oilseed crop (Woodroof, 1983). The oil is used primarily for cooking, manufacture of margarine, shortening and soaps. Seeds are consumed directly either raw or roasted, chopped in confectioneries, or ground into peanut butter. Young pods may be consumed as a vegetable,

while young leaves and tips are utilized as a cooked green vegetable (Martin & Ruberte, 1975). Scorched seeds may serve as a coffee substitute (Duke, 1981).

Nonfood products such as soaps, medicines, cosmetics, pharmaceuticals, emulsions for insect control, lubricants and fuel for diesel engines can be made from groundnut. The oil cake, a high-protein livestock feed, may be used for human consumption. The haulms are excellent high protein hay for horses and ruminant livestock. Groundnut shells may be used for fuel (fireplace "logs"), as a soil conditioner, for sweeping compounds, as a filler in cattle feed, as a raw source of organic chemicals, as an extender of resin, as a cork substitute, and in the building trade as blocks or hardboard (Gibbons, 1980).

In folk medicine, groundnut is used for aphrodisiac purposes, inflammation, cholecystosis, nephritis and decoagulant. In China, the oil is taken with milk for gonorrhoea, and used externally for rheumatism, while in Zimbabwe the groundnut is used in folk remedies for plantar warts (Duke & Wain, 1981; Duke & Ayensu, 1985).

1.1.3 BOTANY

The groundnut belongs to the family *Leguminosae*, subfamily *Papilionoidae*, tribe *Aeschynomeneae*, sub-tribe *Stylosanthinae*, genus *Arachis* and species *hypogaea* (Isleib *et al.*, 1994). The genus name *Arachis* stems from a-rachis (Greek, meaning without spine) in reference to the absence of erect branches. The species name *hypogaea* stems from hupo-gè (Greek, meaning below earth) and relates to the gynophore (flower stalk or peg) that grows downward into the earth so that the pod develops underground. Remarkably *A. hypogaea*, the only cultivated species, is not known in its wild state. Subspecific and varietal classifications are mostly based on location of flowers on the plant, patterns of reproductive nodes on branches, number of trichomes and pod morphology (Krapovickas & Gregory, 1994). There are two major subspecies of *A. hypogaea* that mainly differ in their branching pattern (Gibbons *et al.*, 1972): ssp. *hypogaea* with alternate branching and subspecies *fastigiata* with sequential branching (Table 1.1). Within the *hypogaea* ssp. are two botanical varieties; var. *hypogaea* (Virginia and runner types) and var. *hirsuta* (Peruvian humpback and Chinese dragon). Subspecies *fastigiata* is also

divided into botanical varieties *fastigiata* (Valencia type) and *vulgaris* (Spanish type) (Chapman, 1990; Singh & Simpson, 1994).

Table 1.1 Subspecies of *Arachis hypogaea*

| Subspecies | Site of flowering and pod production | Growth habit | Botanical variety and market type | Seed dormancy | Maturation time |
|-------------------|--------------------------------------|--------------|-----------------------------------|---------------|----------------------|
| <i>Hypogaea</i> | Lateral branches | Spreading | <i>Hypogaea</i> runner | Present | Long 145-165 days |
| | | Bunching | <i>Hypogaea</i> Virginia | Present | |
| | | | <i>Hirsuta</i> | | |
| <i>Fastigiata</i> | Main stem | Erect | <i>Fastigiata</i> | Low or | Short |
| | | | Valencia | absent | 90-120 days |
| | | | <i>Vulgaris</i> | Low or | |
| | | | Spanish | absent | |

Source: Singh & Simpson, 1994; Shokes & Melouk, 1995

1.1.4 MORPHOLOGY AND DEVELOPMENT

Groundnut seed consists of two cotyledons, stem axis and leaf primordia, hypocotyls and primary root. The function of the hypocotyl is to push the seed to the soil surface during germination, and its length is determined by planting depth. The hypocotyl stops elongating as soon as light strikes the emerging cotyledon. Thus, groundnut emergence is intermediate between the epigeal (hypocotyl elongates and cotyledons emerge above ground) and hypogeal (cotyledons remain below ground) types. The taproot grows very fast, reaching a mean length of 10 – 12 cm within four to five days. Lateral roots appear about three days after germination (Gregory *et al.*, 1973). Initial plant growth is slow, with more rapid growth being observed between 40 and 100 days after emergence (Ramanatha Rao, 1988).

Groundnut is a self-pollinating, annual, herbaceous legume growing upright or prostrate, and has an indeterminate growth habit. Natural cross pollination occurs at rates of less than 1% to greater

than 6% due to atypical flowers or action of bees (Duke, 1981; Coffelt, 1989). The plant is sparsely hairy and generally grows 12 to 65 cm high. Plants develop three major stems; the main stem develops from the terminal bud on the epicotyl while the two lateral stems equal in size to the central stem develop from the cotyledonary auxiliary buds. Groundnut produces a well-developed taproot with many lateral roots. The taproot has four series of spirally arranged lateral roots with abundant branching and usually with a large number of nodules. Roots do not have conventional root hairs; clumps of hairs are formed in the axils of lateral roots (Moss & Ramanatha Rao, 1995).

Groundnut plants start flowering about 30 to 40 days after planting and maximum flower production occurs 6 to 10 weeks after planting. The flowers are self-pollinated around sunrise, and wither within 5-6 hours. Within one week of fertilization, the tip of the ovary bearing from 1–5 ovules, grows out from between the floral bracts, bearing with it the dried petals, calyx lobes and hypanthia; creating a unique floral structure - the carpophore, commonly known as a peg or gynophore (Ramanatha Rao, 1988). The peg quickly elongates, and growth is positively geotropic until it penetrates several centimeters (5-10 cm) into the soil when the tip becomes diageotropic, and the ovary starts developing into a pod (Ramanatha Rao, 1988). Because flowering continues over a long period, and because of the relationship between the number of pods per plant and rainfall pattern, pods are in all stages of development at harvest. Pegs near the taproot that enter the soil early in the season require a longer period of time to reach maturity than pegs located farther away from the plant (Ramanatha Rao, 1988; Stalker, 1997).

The pod is an elongated sphere with different reticulation on the surface and /or constriction between the seeds, and contains one to five seeds (Gregory *et al.*, 1973; Ramanatha Rao, 1988; Stalker, 1997). Pods reach maximum size after 2 to 3 weeks in the soil, maximum oil content in 6 to 7 weeks, and maximum protein content after 5 to 8 weeks (Ramanatha Rao & Murty, 1994).

Considerable variability exists in groundnut morphological traits: seed size, (0.15 to more than 1.3 g seed⁻¹), seed color (white, light rose, rose, red, purple, white blotched with purple red), number of seeds pod⁻¹ (1-5), pod length (11-83 mm) and pod breadth (9-27 mm) (Krapovickas & Gregory, 1994; Ramanatha Rao & Murty, 1994; Retamal *et al.*, 1990; Stalker & Simpson, 1995).

1.1.5 ECOLOGY AND FERTILITY REQUIREMENTS

Groundnut requires abundant sunshine and warmth for normal development, but does not appear to be especially sensitive to day-length, though it generally produces more flowers under long day conditions (Stalker, 1997). Temperature significantly influences the rate of development and growth of groundnut, the optimum range for vegetative and reproductive growth being between 25 and 30°C (Cox, 1979; Leong & Ong, 1983). Groundnut grows in regions with an average annual rainfall of 500 – 1200 mm; thrives best when more than 500 mm of rain is evenly distributed during the growing season (Sellschop, 1967). Moisture stress during reproductive development causes embryo abortion, reduces seed development by restricting calcium uptake by the pods, and increases aflatoxin contamination of the seeds (Stalker, 1997).

Groundnut is grown mostly on light-textured soils ranging from coarse and fine sands to sandy clay loams with moderately low amounts of organic matter (1 – 2 %) and good drainage (Henning *et al.*, 1982). The well-drained soils provide good aeration for the roots and nitrifying bacteria. Groundnut does not grow well in soils with a high water retention capacity (Stalker, 1997), and grows best in slightly acidic soils with optimum pH ranging from 5.5 to 6.2 (Gibbons, 1980).

Groundnut requires considerable amounts of nutrients for high yields, however, responses to applied fertilizers have been observed to be very erratic, justifying the name of “the unpredictable legume”. It has often been accepted that groundnut has the ability to utilize soil nutrients that are relatively unavailable to other crops, and can therefore make good use of residual fertility (Sellschop, 1967; Reid & Fox, 1973; Cox *et al.*, 1983). An effective fertilization programme should take into cognizance the levels of nutrient removal. Thus, the estimated amounts of nutrients removed by the groundnut crop, the partitioning of total uptake of macronutrients by growth stage and sufficiency ranges of the nutrients are given in Tables 1.2, 1.3 and 1.4, respectively.

Table 1.2 Nutrient uptake/removal in groundnuts (kg ha⁻¹)

| Plant Part | Yield | N | P | K | Ca | Mg | S |
|------------|----------------------|-----|----|----|----|----|----|
| Pods | 3 t ha ⁻¹ | 120 | 11 | 18 | 13 | 9 | 7 |
| Haulms | 5 t ha ⁻¹ | 72 | 11 | 48 | 64 | 16 | 8 |
| | Total | 192 | 22 | 66 | 77 | 25 | 15 |

Source: Gascho, 1992

Table 1.3 Partitioning of total uptake of macronutrients by growth stage

| Growth stage | Percentages (%) of total uptake | | | | |
|--------------|---------------------------------|----|----|----|----|
| | N | P | K | Ca | Mg |
| Vegetative | 10 | 10 | 19 | 10 | 11 |
| Reproductive | 42 | 39 | 28 | 53 | 48 |
| Ripening | 48 | 51 | 53 | 37 | 41 |

Source: Longanathan & Krishnamoorthy, 1977

Table 1.4 Sufficiency levels of nutrients in groundnut leaf dry matter

| Macronutrients | % of dry matter | | | | | | |
|---|--------------------------------|-----------|---------|---------|----------|-----------|---------|
| Sampling period | N | P | K | Mg | Ca | S | |
| 7 th leaf at 40 days after planting | 3.3-3.9 | 0.15-0.25 | 1.0-1.5 | 0.30 | 2.0 | 0.19-0.25 | |
| Upper mature leaves at bloom | 3.0-4.5 | 0.2-0.5 | 1.7-3.0 | 0.3-0.8 | 1.25-2.0 | 0.20-0.35 | |
| Micronutrients | mg kg ⁻¹ dry matter | | | | | | |
| | Mn | Fe | B | Cu | Zn | Al | Mo |
| Upper mature leaves at bloom | 20-350 | 50-300 | 20-60 | 5-20 | 20-60 | <200 | 0.1-5.0 |

Source: Plank, 1989

Calcium

The most critical element in the production of groundnuts is calcium, and in many regions of the world, it is a major limiting factor to groundnut production. The developing pods require adequate Ca in the surrounding soil for proper pod development and production of high quality seed (Cox *et al.*, 1982; Gascho & Davis, 1994). Because root-absorbed Ca is not translocated to the developing pods after the groundnut peg has entered the soil (Brady, 1947), the Ca required for pod development must be absorbed directly from the soil solution, thereby necessitating high Ca levels in the podding environment (Skelton & Shear, 1971). Soil Ca levels in the range 600 to 800 mg kg⁻¹ in the fruiting zone (0-10 cm) are considered adequate for the production of good quality groundnut kernels (Kvien *et al.*, 1988; Sumner *et al.*, 1988).

The most important morphological attributes that influence Ca uptake by the pods are pod surface area, pod volume, number of days to maturation of a pod, shell thickness and specific shell weight (Boote *et al.*, 1983; Kvien *et al.*, 1988). Smaller-seeded cultivars, because of their larger surface to volume ratio, require lower soil Ca levels than the large seeded types. The soil factors that affect Ca nutrition of groundnut include soil water content, water soluble Ca, exchangeable Ca and the type of soil minerals present (Keisling *et al.*, 1982).

Calcium deficiency results in lower yield, darkened plumules in the seed, empty pods (pops), reduced percentage of sound mature kernels and sometimes plants that stay green and continue to produce flowers and pegs, many of which may be infertile (Cox & Reid, 1964; Sullivan *et al.*, 1974). To avoid Ca deficiency in the pod zone a soluble source of Ca like gypsum can be applied over the row at early flowering stage (Smal *et al.*, 1989), though groundnut cultivars do not always respond to such Ca supplements (Walker, 1975). In acid soils, lime incorporation into the pod zone before planting can correct soil acidity and simultaneously supply adequate Ca for maximum yield of small-seeded cultivars (Gascho & Kidder, 1993).

Magnesium

Magnesium deficiency rarely limits plant growth, however, its necessity for groundnut stems from its role as a carrier of phosphorus in oil formation, and its effect on seed viability (Smith *et al.*, 1994). The supply of Mg to the developing pod is partly from the roots via long distance

transport and partly from direct uptake by pods. Because of this complementarity, Mg supply may be omitted from the pod zone without adverse effects on pod development of some cultivars, provided adequate Mg is supplied in the root zone (Zharare *et al.*, 1993). Because of that, little response to Mg application has been recorded for groundnut, except on excessively drained soils where cations are easily leached, and in acid soils with very low Mg levels (Gascho & Davis, 1994; Smith *et al.*, 1994). When Mg deficiency occurs in acid sandy soils, the deficiency can be corrected by applying dolomitic limestone, which will correct the acidity and supply both Mg and Ca (Sanchez, 1976; Foster, 1981).

Nitrogen, Phosphorus and Potassium

When inoculated with effective strains of Rhizobia, the groundnut is independent of nitrogenous fertilizers because enough N is fixed through symbiotic relations with *Bradyrhizobium* spp. It has been shown that uptake of nitrogen is most intensive during the period between flowering and pod formation. During the reproductive stages, there is continual mobilization of N from leaves to the developing fruit, and this sometimes results in appearance of N deficiency symptoms (Kvien *et al.*, 1986; Cox & Sholar, 1995). On soils in which effective Rhizobia are absent, application of nitrogenous fertilizers increases groundnut yield. In most growing areas of the world application of N to groundnut in order to avoid deficiency is common, and responses to N fertilization have been observed on deep sandy soils (Gascho, 1992).

Groundnut is often grown on P deficient soils in many areas of the world (Cox *et al.*, 1982; Survanvesh & Morrill, 1986). The P deficiency can be easily corrected by application of P fertilizers, since groundnut is normally grown on sandy soils with low amounts of clay and P fixation is generally not a problem. Also, P requirements and removal by groundnut is low, and very little P leaches (Gascho & Davis, 1994). Although groundnut is largely unresponsive to P application, large responses have been observed in soils with high P fixation, particularly under low fertility conditions.

Generally, it is believed that groundnut requires very little K for its growth and reproduction. The crop removes small amounts of potassium and will only respond to K application when the soil K levels are very low. Although variable effects of K fertilizer on groundnut pod yield have been

reported in literature, the consensus is that there is no advantage in applying K fertilizer directly to the groundnut crop. Consequently, it is usually grown on residual fertility, following a well-fertilized crop (Cox *et al.*, 1982). This is because groundnut roots are efficient in obtaining K from low available levels in the soil. Because of this efficiency in utilization of soil K from soils that are low in available K, groundnut response to K fertilizers is rare (Weiss, 1983).

High levels of soil K in the pod zone are undesirable as they result in pod rot and interfere with the uptake of Ca by pegs and pods, which results in a higher percentage of pops and Ca deficiency in the seeds (Hallock & Garren, 1968; Csinos & Gaines, 1986). The most efficient way to apply K is to the preceding crop, or incorporate it well before planting to allow enough time for K to leach into the root zone before pegging (Walker *et al.*, 1979).

Micronutrients

Availability of micronutrient in soils is governed by soil pH, cation and anion exchange capacity, nutrient interactions, soil physical and chemical properties. Groundnut requires the seven micronutrients known to be essential for plants: boron (B), chlorine (Cl), Copper (Cu), Iron (Fe), manganese (Mn), molybdenum (Mo) and zinc (Zn). The potential for symbiotic assimilation of dinitrogen by groundnut creates special demands not only for molybdenum and cobalt, but also for boron, copper and zinc nutrition. The micronutrient most often limiting for groundnut production is B, because of its role in kernel quality and flavor. Boron deficiency results in "hollow-heart" in groundnut kernels. The inner surfaces of the cotyledons are depressed and darkened, and the kernels are graded as damaged. Zinc and Mn deficiencies can be expected in soils with high lime content, especially when high levels of P have been applied. At low soil pH the availability of Mn and Zn may increase to toxic levels, and liming very acidic soils to pH 5.5 decreases the solubility and uptake of Mn sufficiently to eliminate the toxicity. Molybdenum is an essential element in biological nitrogen fixation, and can be limiting at low soil pH (Gascho & Davis, 1994; Smith *et al.*, 1994; Jordan, 2001).

1.1.6 GROUNDNUT PRODUCTION CONSTRAINTS

Among abiotic stresses drought, low pH, and low temperature are important, and these occur in various combinations in Africa, Asia and the Americas (Duke, 1981). Although the groundnut plant is drought tolerant, inadequate moisture coupled with unreliable and poorly distributed rainfall is the most critical abiotic factor limiting yield in the semi-arid regions (Virmani & Singh, 1985; Stalker, 1997). Low pH and Ca deficiency can be important limiting factors in groundnut productivity, especially on the highly weathered soils of the tropics (Edwards *et al.*, 1981; Cox, *et al.*, 1982; Foy, 1984). Calcium availability may be limited by leaching from sandy soils and by limited moisture availability during pod filling (Stalker, 1997).

Considerable yield losses are caused by pests and diseases and by use of cultivars that are not adapted to local conditions (Cummins, 1985). On a global scale, the leaf spots caused by *Cercospora arachidicola* and *Cercospora personatum* and rust caused by *Puccinia arachidis* are the most destructive pathogens of groundnut, accounting for up to 70% yield losses (Subrahmanyam *et al.*, 1984). The most important pre- and post-harvest insect pests that cause significant economic losses in groundnut include aphids, thrips, jassids and *Spodoptera* (Isleib, *et al.*, 1994). Weeds cause great yield reductions when not controlled early in the growing season; therefore, cultivars that quickly establish full canopy are desirable in order to suppress the weeds (Stalker, 1997).

1.2 SOIL ACIDITY

The concept of an acid soil considers pH (a measure of the activity of H⁺ ions in the soil solution) which is strongly (pH 5.5- 4.5) to extremely acid (pH<4.5), the degree of acid aluminium saturation of the cation exchange capacity (CEC), characteristics such as low concentrations or availability of Ca, Mg, P, B and Mo and high solubility of aluminium (Al) and Mn. Soil acidity is influenced by edaphic, climatic and biological factors of natural occurrence. The association between amounts of basic cations [Ca, Mg, K and sodium (Na)] and the Al species on the cation exchange complex also influences the acidity of a soil (Foy, 1984; Thomas & Hargrove, 1984; Barnard & Folscher, 1988; Ritchie, 1989; Fageria *et al.*, 1991; Carver & Ownby, 1995).

Generally, the total acidity of a soil is equated to the sum of the active (actual) and the potential (or buffer pH) acidity. Active acidity (or soil-water pH) is due to the presence of H^+ ions in the soil solution, whereas the potential acidity (measured in me/100 g soil) is due to H^+ and Al^{3+} ions adsorbed on the exchangers and this becomes active acidity when H^+ and Al^{3+} ions are exchanged to the solution. Active acidity is often used to indicate the need of liming, but it is the potential acidity that determines the amount of agricultural limestone required to neutralize soil acidity (Adams, 1990; Tisdale *et al.*, 1993; USDA Agronomy Technical Note No. 8, 1999).

On a universal scale, soils that are naturally acid or have become acid through agricultural activities comprise about 30% of the arable land (Von Uexkull & Mutert, 1995). In the tropics, approximately 43% of the land is classified as acidic, comprising about 68% of tropical America, 38% of tropical Asia, and 27% of tropical Africa. On the whole, acid soils cover a total of 1660 million hectares in the developing countries (Pandey *et al.*, 1994). The formation and nature of acid soils vary considerably due to different factors in soil formation, especially differences in climate, parent material, topography, vegetation and time of soil formation. Acid soils pose major complexities for agricultural use since they may adversely affect plant growth, but can be very productive if lime and nutrients are constantly applied and appropriate soil management is practiced (Van Wambeke, 1986).

1.2.1 CAUSES OF SOIL ACIDITY

Acidification is a natural soil-forming process caused by the production of H^+ ions. According to generalized views, acidity in soils has several sources: humus or organic matter, aluminosilicate clays, hydrous oxides of iron or aluminium, exchangeable aluminium, soluble salts and carbon dioxide. Naturally occurring elements that contribute in varying degrees to soil acidity include high rainfall which results in leaching of basic cations, low evaporation, and high oxidative biological activity that produces acids (Rowell, 1987; Carver & Ownby, 1995). Human activities such as intensive agriculture and industrialisation can accelerate the rate of acidification (Helyar & Porter, 1989).

Soil acidity may result from parent materials that were acid and naturally low in basic cations (Ca^{2+} , Mg^{2+} , K^+ and Na^+) or because these elements have been leached from the soil profile by

heavy rains. For example, soils that develop from granite parent materials acidify at a faster rate than soils derived from calcareous parent materials. Sandy soils with relatively few clay particles acidify more rapidly due to their smaller reservoir of alkaline cations (buffering capacity) and higher leaching potential. In highly leached soils only Fe^{3+} and Al^{3+} oxides and some of the trace metal oxides, which are highly resistant to weathering, remain from the original parent material (Brady, 1990).

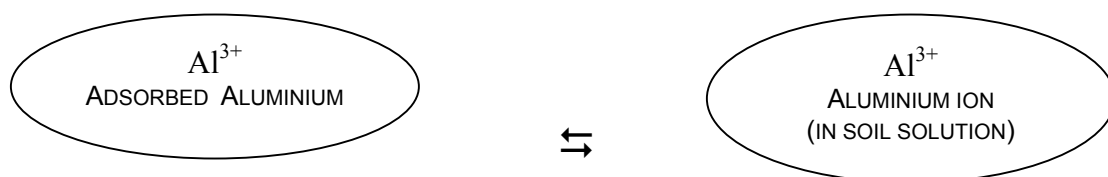
In alkaline or neutral soils, the negatively charged cation exchange complex is dominated by basic cations (Ca^{2+} , Mg^{2+} , K^+ and Na^+) whereas in acid mineral soils, this complex is usually dominated by aluminium ion species [Al^{3+} and $\text{Al}(\text{OH})^{2+}$] formed by the dissolution of soil minerals in acid systems (Reuss & Johnson, 1986; Ritchie, 1989). In acid organic systems, H^+ may be the dominant exchange cation. Each H^+ in the soil competes with other cations to be bonded to the negative exchange surfaces of the soil colloids. As H^+ ions displace the other cations, they are leached from the soil (Singer & Munns, 1996). Processes that would tend to acidify a soil include those that increase the number of negative charges, such as organic matter accumulation or clay formation, or those that remove basic cations, such as leaching of bases in association with an acid anion (Reuss & Johnson, 1986; Ritchie, 1989; Ulrich & Sumner, 1990).

Excessive rainfall influences the rate of soil acidification depending on the rate of water percolation through the soil profile. Water passing through the soil leaches basic cations such as Ca^{2+} , Mg^{2+} and K^+ , which are then replaced by acidic cations such as Al^{3+} and H^+ (Reuss & Johnson, 1986; Ulrich & Sumner, 1990). In addition, the leaching action of CO_2 -charged water percolating through the profile of a base-saturated soil removes free salts very quickly and exchangeable basic cations more slowly. Eventually a soil becomes quite acid, unless bases are replaced by man or nature. For this reason, soils formed under high rainfall conditions are more acid than those formed under arid conditions (Brady, 1990).

Hydrolysis is a molecular phenomenon that is very important to soil acidity. Aluminium and iron as trivalent ions (M^{3+}) take part in hydrolytic reactions, a result of their high ratio of charge to ionic size (Hodges & Zelazny, 1983; Ritchie, 1989). Monomeric aluminium ions (Al^{3+}) can be displaced from clay minerals by other cations and hydrolyze in solution; the hydrolysis products are re-adsorbed on clay, causing increased hydrolysis (Ritchie, 1989). The H^+ ions initially

adsorbed to the cation exchange sites eventually become sufficiently concentrated to attack the clay crystal releasing Si^{4+} and Al^{3+} . The released Al ions partially neutralized as AlOH^{2+} or $\text{Al}(\text{OH})^{2+}$ polymerise in the inter-layers of the clay fraction or become complexed with organic materials, while the Si^{4+} leaches to lower levels in the profile. As the soil becomes still more acid, more Al and Fe are released from the clay minerals, and Al^{3+} remains the dominant exchangeable cation (Hodges & Zelazny, 1983; Lindsay & Walthall, 1989; Zelazny & Jardine, 1989; Brady, 1990).

According to Brady (1990), the mechanisms by which adsorbed H^+ and Al^{3+} ions exert their influence on soil acidity depend on the degree of soil acidity and on the source and nature of the soil colloids. Adsorbed Al^{3+} ions contribute to soil acidity through their tendency to hydrolyse as shown in the following simplified equations:-



The aluminum ions in soil solution are then hydrolysed: $\text{Al}^{3+} + \text{H}_2\text{O} \rightarrow \text{Al}(\text{OH})^{2+} + \text{H}^+$.

The H^+ ions released lower the pH of the soil solution and are the main source of H^+ in most very acid soils. In moderately acid soils (with high percentage of base saturation), the Al can no longer exist as ions, but is converted to aluminum hydroxy ions, some of which are adsorbed and act as exchangeable cations. In the soil solution they produce H^+ ions by the following hydrolysis reactions:-

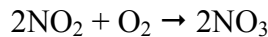
1. $\text{Al}(\text{OH})^{2+} + \text{H}_2\text{O} \rightarrow \text{Al}(\text{OH})^{2+} + \text{H}^+$
2. $\text{Al}(\text{OH})^{2+} + \text{H}_2\text{O} \rightarrow \text{Al}(\text{OH})^3 + \text{H}^+$ (Brady, 1990).

In soils under agricultural production, acidity is often accelerated in the surface layer by certain cropping practices and events.

Fertilizer use

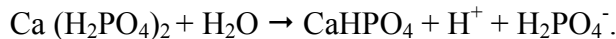
Acidification of soil resulting from the use of commercial fertilizers is claimed to be one of the major reasons for deterioration of soils on a global basis (Stammer, 1992). Both chemical and

organic fertilizers may eventually make the soil more acid because H^+ is added in the form of ammonia-based fertilizers (NH_4^+), urea-based fertilizers [$CO(NH_2)_2$], and as proteins (amino acids) in organic fertilizers. Transformations of these sources of N into nitrate (NO_3^-) release H^+ to create soil acidity. Repeated applications of NH_4 fertilizers in excess of crop uptake, especially on slightly buffered soils, results in net production of H^+ by natural processes (Tisdale & Nelson, 1975; Helyar & Porter, 1989), including nitrification of ammoniacal N:



The resultant pH values can be less than pH 4.0 and rapid loss of exchangeable Ca and Mg can occur. Some of this acidity is neutralized by NO_3^- uptake and the subsequent release of OH. Other compromising factors are the denitrification of NO_3^- , NH_4^+ volatilization or NH_4^+ uptake by the plant. Management practices that increase N-use efficiency and decrease the amount of NO_3^- lost by leaching could slow the rate of acidification (Robson, 1989).

If superphosphate is added to water, an acidic pH is developed as a result of a hydrolysis leading to formation of insoluble calcium monohydrogenphosphate:



The effect is dramatic when the fertilizer is band-applied, but will gradually disappear as diffusion and neutralizing reactions occur (Kennedy, 1986). Superphosphate fertilisers also indirectly add to soil acidity by improving plant growth, which in turn increases the amount of produce that can be removed and also the amount of legume nitrogen available to leach.

Applications of elemental sulphur, especially the reduced forms, also have a soil acidification effect as a result of reactions analogous to those of nitrification, and are catalysed by similar aerobic autotrophs. The oxidation and mineralization of organic matter from biota in ecosystems involves a component of sulphuric acid production from reduced organic sulphur (Kennedy, 1986).

Plant uptake

Uptake by plants of more base cations such as K^+ , Ca^{2+} , and Mg^{2+} than of mineral anions results in increased acidity in the soil due to the release of H^+ ions by plant roots in exchange for base

cations or of OH^- (or HCO_3^-) ions in exchange for anions taken up (Wallace *et al.*, 1976; Haynes 1990). This proton efflux can have greater consequences than the differential cation-anion uptake. When legumes and other plants obtain nitrogen through symbiotic fixation of N_2 , there is less base release into the soil than when nitrate is the N source, with the net result of increased release of H^+ ions to the soil (Chesseman & Enkoji, 1984).

Repeated cultivation and harvest removal

The acidification of soils due to cultivation is a consequence of a number of processes. Improved aeration promotes rapid bacterial oxidation of soil organic matter, resulting in net production of organic acids (Beukes, 1987). Soil organic matter derived from the lignin of plants contains a significant number of reactive carboxyl, phenolic, and amino groups that are capable of bonding H^+ ions (Tisdale & Nelson, 1975). Such H^+ -saturated groups behave as weak acids and the covalently bound H^+ will dissociate. When soil organic matter is mineralized, the nitrogen is released as NH_4OH or equivalent, which means that soil acidification can result. The NH_4OH can be oxidized to HNO_3 (Mengel & Kirkby, 1982). Any conditions that affect the quantity of organic matter in soil will affect the degree of acidification (Tisdale & Nelson, 1975).

Soil acidification in the surface layer is also accelerated by the removal of basic cations (Ca, Mg, K and Na) in the harvested product. Removal of straw depletes basic cations to the greatest extent and actually enhances acidification by nitrification (Wallace, 1989). The severity of soil acidity increases as yields of vegetative or grain dry matter increase (Carver & Ownby, 1995).

1.2.2 ACID SOIL INFERTILITY

It is now realised that acid soil infertility problems are not only restricted to low pH and high solution Al and Mn levels *per se*. High soil acidity reduces the availability of P to plants via fixation by a number of processes (Sample *et al.*, 1980; Sanchez & Uehara, 1980; Fageria *et al.*, 1990; Sanyal & de Datta, 1991) and reduces Mo availability to plants due to reduced solubility (Barnard & Folscher, 1988; Brady *et al.*, 1994). On soils with low pH values, the levels of exchangeable Ca and Mg in relation to Al and Mn activities in the soil solution strongly affect toxicities of Al (Ca and Mg) or Mn (Ca) to plants.

Unlike some of the more obvious forms of land degradation such as erosion, soil acidification is viewed as a hidden problem with the potential to greatly affect yields and to increase the risk of other forms of land degradation (Van Wambeke, 1986). The major factors that constitute acid infertility and adversely affect sensitive plants in acid soils include direct and indirect effects of H^+ ions. The indirect effects of H^+ ions on plant growth include the following:

- a) impaired absorption of several elements, especially Ca, Mg, K and P;
- b) increased soil availability of Mn, Al, sometimes Fe, and possibly heavy metals including Cu and Ni, leading to uptake of toxic quantities;
- c) reduced availability of P when fixed by Al or Fe before or after absorption; reduced solubility of Mo and Zn;
- d) low actual concentration or inhibition in the uptake of Ca, Mg, K, B and sometimes Cu or other micronutrients as a result of prolonged leaching of the soil profile at low pH;
- e) unfavourable biotic conditions such as impaired N fixation, reduced activity and survival of beneficial soil micro-organisms (e.g. rhizobia and mycorrhizae) and increased infection by some soil pathogens;
- f) water and nutrient deficiencies as a result of reduced root growth;
- g) accumulation of organic acids and failure of micro-organisms to decompose toxic residues and production of unfavourable redox balance resulting in reducing conditions; and
- h) increased plant uptake of the toxic heavy metal cadmium, to the extent that this may accumulate to harmful levels in the kidneys of some classes of grazing animals (Hewitt & Smith, 1975; Clark, 1984; Marschner, 1995).

Each of these factors is of different comparative importance depending upon soil pH, soil type and horizon, aeration, clay mineral types and amounts, organic matter contents and kinds, levels of salts, plant species and genotype (Clark, 1984; Marschner, 1995). Acid soil infertility factors may act somewhat independently, or more often together, to affect the growth of plants (Foy *et al.*, 1978; Kamprath & Foy, 1984).

1.2.3 TOXICITY PROBLEMS IN ACID SOILS

Acid soil toxicity is not a single factor but a complex of factors that may affect growth of different plants through different physiological and biochemical pathways (Foy, 1983). Toxicity in acid soils is attributed to enhanced solubility of certain metal cations, particularly Al and Mn. In most acid soils (pH<4.0), Al and Mn toxicities are probably more important than H⁺ ion toxicity in limiting the growth of higher plants, particularly the non-legumes (Moore, 1974; Kamprath & Foy, 1985).

Hydrogen ion (H⁺) toxicity

Solution pH in acid soils is the result of the distribution of H⁺ ions between soil surfaces and the soil solution. In the presence of a given number of H⁺ ions, the pH buffering capacity is the major soil property that determines the soil solution pH and the possibility to manipulate the pH of acid soils economically (Ritchie, 1989). The soil solution not only contains a certain quantity of H⁺ ions, but also has the ability to resist pH changes (pH buffering): the greater the ability of an element to repel H (hydrolyse), the stronger its acidity. Buffering of pH by the solid phase may arise from the dissolution of minerals such as kaolinite or calcite, and buffering will depend on the type and concentration of the ions on the surface and in solution as well as the type, structural characteristics and relative affinity of the surface for different ions (Adams & Moore, 1983).

The direct effects of the H⁺ ion on plant growth are difficult to determine in acid soils because of the varying interrelationships that occur between pH, Al, Mn and other mineral elements that may be soluble in toxic concentrations (Kennedy, 1986). Additionally, the availability of essential elements particularly Ca, Mg, P and Mo may be sub-optimal (Fageria *et al.*, 1990).

Excess H⁺ ions have marked effects on root membrane permeability. They compete with other cations for absorption sites, interfere with ion transport, and cause root membranes to become leaky. Roots may lose previously absorbed cations as well as organic substances, and prolonged exposure to low pH may reduce their capacities for subsequent absorption of nutrients. Because of their effect on nutrient uptake and retention by plant roots, excess H⁺ ions can increase plant requirements for Ca, and perhaps other nutrients in a growth medium (Foy, 1992).

Aluminum toxicity

The chemistry of soil Al is fundamental to the fertility of highly weathered acid soils since in many such soils the concentrations of Al in soil solution are known to be toxic to crops (Kamprath, 1978). Because Al is tightly held to exchange sites, the total soluble Al (Al_T) in the soil solution is usually quite low, ranging between 10-350 μM , and levels $>1000 \mu M$ occur only in exceptional circumstances such as in acid sulphate soils (Kamprath, 1978; Adams & Moore, 1983; Curtin & Smillie, 1983). The level of soluble species of Al is influenced by competition between Al and other cation species. Cations that form weaker complexes with the ligand than Al (e.g. Ca and Mg) can only compete effectively with Al at Al: cation ratios <1 . On the other hand, cations such as Fe^{3+} that form stronger complexes with the ligand can compete even when Al: cation ratios are >1 . The hydrogen ion may also compete with Al for a ligand (Ritchie, 1989).

Soluble Al species in soil solutions may be broadly divided into two groups: monomers and polymers. The total concentration of monomeric Al in acid soils is the sum of the concentrations of the various monomeric species, i.e., Al^{3+} , $Al(OH)^{2+}$, $Al(OH)_2^+$ and $Al(OH)_3$. With sulfate in solution, an additional species (i.e. $AlSO_4^+$) is also present, while complex ions of Al with SO_4^{2-} and F^- also occur when these anions are present in soil solution (Fageria *et al.*, 1990; Kinraide, 1991). The monomeric hydrolysis of Al is significant at pH 4.0, and more than 80% of total soluble Al is hydrolysed by pH 4.9. In the soil solution, the extent of hydrolysis may be reduced by the presence of other anions, particularly nitrate, chloride and sulphate (Curtin & Smillie, 1983). Aluminium can also form soluble polymers with hydroxyl ions alone or in conjunction with phosphate or silicon ions.

The concentration of soluble Al in acid soils may be controlled (i.e. buffered) by the dissolution of inorganic compounds, adsorption onto inorganic minerals or by reactions with solid organic matter. The effect of Al adsorption on pH depends on the type of clay, the hydroxyl: Al ratio in solution and the time of ageing. Removal of hydrolysed Al species from solution induces further hydrolysis of Al and consequently a lowering of the pH. If Al^{3+} were the major species adsorbed then a pH increase would be expected, although the pH increase may be temporary and will decrease with time because of buffering by surface reaction with H^+ and OH^- till a new

equilibrium is established. In some cases, pH increases due to proton uptake are counterbalanced by the adsorption of Al-hydroxyl species and so only a small change may be observed (Hoyt, 1977).

Soluble monomeric Al complexes with organic anions depending on the type and concentration of organic ligand, the proportion of charged sites that are dissociated, pH, ionic strength and the presence of competing ions (Ritchie, 1989). Evidence is mounting that the toxicity of Al is reduced in the presence of inorganic and organic complexing anions and that the activity of Al^{3+} and/or the Al-hydroxyl species are the forms of Al that are most correlated with depressed yields of several plant species (Helyar, 1978; Blamey *et al.*, 1983; Ahmad & Tan, 1986; Wright, 1989; Hue, 1992; Haynes & Mokolobate, 2001).

Aluminium may form soluble or insoluble complexes with organic matter (OM) or it may be non-specifically adsorbed onto exchange sites. Aluminium in a form complexed to soluble OM is not toxic to plants (Kinraide, 1991) and this complexation seems to be a vital mechanism of detoxifying solution Al (Kochian, 1995). The addition of organic matter to a soil or solution can decrease or increase the level of soluble Al depending on the concomitant changes in pH (Haynes & Mokolobate, 2001). Increases in soluble Al could be explained by the high pH of the soil causing some dissociation of H^+ from the organic matter that lowers the soil pH and results in the dissolution or release of Al. The reactions of Al with soluble organic material can also increase the level of Al in the soil by retarding precipitation of Al oxides (Hoyt, 1977; Adams & Moore, 1983). On the other hand, the addition of organic matter can decrease soluble Al because the extent of Al binding by the OM more than counterbalances any increased Al dissolution caused by pH decreases (Hargrove & Thomas, 1981; Hue *et al.*, 1986).

The removal of Al from solution by organic matter adsorption and a concomitant increase in pH buffering capacity can have a confounding effect by increasing exchangeable acidity. Hoyt (1977) observed that even though the addition of organic matter reduced concentrations of soluble and exchangeable Al, there was an increase in exchangeable acidity (i.e. buffer capacity). In some cases, therefore, the benefits from reducing Al toxicity may be counter-balanced by an increase in the lime requirement of the soil.

Since most plants are sensitive to micromolar concentrations of Al, its toxicity is the major limiting factor for plant productivity on many acid soils (Kinraide, 1991). In the tropics, Al toxicity has been identified as a major constraint for the production of maize (*Zea mays* L.), sorghum (*Sorghum bicolor*.) and rice (*Oryza sativa*) (De La Fuente-Martinez & Herrera-Estrella, 1999). The most easily recognised symptom of Al toxicity is the inhibition of root growth, and this has become a widely accepted measure of Al stress in plants. The root system of plants severely affected by Al toxicity is often collaroid in appearance, with many stubby lateral roots and no fine branching (Kamprath & Foy, 1984; Delhaize & Ryan, 1995; Kochian, 1995). The toxic effect of Al on roots has a clear effect on plant metabolism by decreasing mineral nutrition and water absorption. Aluminium has been shown to interfere with cell division in plant roots; inhibit the respiratory activity of mitochondria; increase pectin, hemicellulose and cellulose contents of root cell walls; reduce DNA replication; decrease cell permeability by coagulating protein and inhibiting cell division; reduce root respiration; precipitate nucleic acid by forming strong complexes; inhibit cation transport across the plasma membrane; block K^+ uptake in root hairs; interfere with uptake, transport, and use of several nutrients (P, K, Ca, Mg, Zn and Fe) and water by plants (Kamprath & Foy, 1984; Keltjens, 1990; Keltjens & Dijkstra, 1990; Baligar *et al.*, 1993; Delhaize & Ryan, 1995; Kochian, 1995). Therefore, crop production in acid soils is largely affected by limited water and nutrient uptake caused by the inhibition of root growth and function that result from the toxic effects of Al. In addition to direct effects on plants, Al complexes with some nutrients such as P, reducing their availability for root uptake (Haynes & Mokolobate, 2001).

Manganese toxicity

Manganese in soils may be adsorbed onto the surface of hydrous oxides, clay particles and organic matter, or exists as discrete Mn compounds. Although it may exist in more than one oxidation state under conditions naturally found in soils (Graham *et al.*, 1988), Mn^{2+} is the only oxidation state that has been identified in the soil solution, and it may react with several inorganic and organic ligands to form soluble complexes. In contrast to Al, it forms much weaker complexes, with hydrolysis becoming significant only at $pH > 9$. For that reason the inorganic complexes in acid soils will not be major forms of Mn unless if extremely high levels of sulphate or chloride are present (Graham *et al.*, 1988; Ritchie, 1989).

Mn^{2+} is weakly adsorbed onto clay minerals, and this is attributed to its inability to hydrolyse under acidic conditions. The amount of Mn available to plants in a soil depends on Mn distribution between the soil surfaces and the soil solution and how that is modified by the difference in the rates of oxidation and reduction, which are governed by environmental conditions, soil properties and microbial activity. Thus, soluble Mn levels are ultimately controlled by buffering from the solid phase, and only modified by redox reactions. Oxidation and reduction of Mn can be by both chemical and microbial pathways. Reduction, both microbial and chemical, may be enhanced by an increase in readily oxidisable organic matter, moisture content or temperature and a decrease in redox potential. Oxidation is also affected by the same factors (Nelson, 1977; Curtin & Smillie, 1983; Graham *et al.*, 1988; Ritchie, 1989).

In soils high in Mn minerals, dissolution of Mn at low pH may result in Mn toxicity. Manganese toxicity is perhaps the second major growth-limiting factor after Al toxicity in acid soils (Sanchez & Salinas, 1981). Plants absorb Mn primarily as the Mn^{2+} ion. Decreasing soil pH below 5.5 increases the concentration of Mn^{2+} ions in the soil solution and, consequently, increases the likelihood of Mn toxicity (Kamprath & Foy, 1985). Manganese toxicity can also occur at higher soil pH values (up to 6.0) in poorly drained or compacted soils where reducing conditions favour the production of divalent Mn which plants absorb. The solubility and potential toxicity of Mn to a given crop depends on many soil properties, including total Mn content, pH, organic matter level, aeration and microbial activity (Foy, 1984; 1992; Foth & Ellis, 1997).

Excess Mn seems to affect plant tops more directly than roots. Manganese produces more definitive symptoms in plant tops than Al does, and for a given plant, Mn accumulates in proportion to plant injury. Plant symptoms of Mn toxicity include marginal chlorosis and necrosis of leaves, and leaf puckering (Foy, 1984; 1992). In severe cases of Mn toxicity, plant roots turn brown, usually after the tops have been severely injured. Plant symptoms of Mn toxicity are often detectable at stress levels that produce little or no reduction in vegetative growth (Foy *et al.*, 1978).

Manganese toxicity alters the activities of enzymes and hormones in plants; causes the destruction of indole-3-acetic acid (IAA) through increasing the activity of IAA oxidase, amino

acid imbalance, lower respiration rate, reversal of growth inhibition of roots caused by enhanced auxin production (Robson, 1988). Manganese toxicity is often associated with a decrease in Ca concentration of plants, and supplying additional Ca to the growth medium sometimes reduces Mn accumulation, decreases the severity of Mn-induced chlorosis and alleviates growth reductions (Smith, 1979).

Manganese toxicity is frequently induced or exacerbated by N fertilization, which lowers soil pH (Nelson, 1977). The addition of organic matter can reduce Mn toxicity, probably by chelating excess divalent Mn that plants absorb, and also because microorganisms can oxidise the soluble and toxic divalent Mn to the tetravalent, non-toxic form (Graham *et al.* 1988). Manganese has been reported to interact with Fe, Mo, P, Ca and Si in affecting toxicity symptoms and plant growth (Borkert & Cox, 1999). It appears, therefore, that the toxicity of a given level of soluble Mn in the growth medium, or even within the plant, depends on interactions between Mn and several other mineral elements, particularly Fe and Si (Foy *et al.*, 1978; Foy 1984; 1992).

1.2.4 DEFICIENCIES OF ESSENTIAL NUTRIENTS

Calcium and magnesium

Calcium and Mg deficiencies are key limitations to plant growth in many acid soils, especially in highly leached, sandy soils. With increasing soil acidity, Al and/or Mn replace exchangeable Ca and Mg, and in soils with low CEC the resultant low levels of Ca and Mg may cause deficiency problems with some crops (Foy, 1984; Fageria *et al.*, 1991). Crops remove between 20 and 150 kg ha⁻¹ Ca and 10 to 80 kg ha⁻¹ Mg (Sanchez, 1976). The availability of Ca and Mg to plants is influenced by the percentage Ca and Mg saturation, the total Ca and Mg supply, the concentration of Ca and Mg in the soil solution, and by the presence of ions such as Al³⁺ and Mn²⁺, which inhibit Ca²⁺ and Mg²⁺ absorption. While inadequate soil Ca levels in the topsoil are noticeably manifested on plant growth, inadequate Ca levels in the subsoil may be invisible (Adams, 1984). For root growth, Ca deficiency is discernible by the death of the meristematic root tissue. Because of the incapability of plants to translocate Ca within the phloem tissue, roots cannot grow in a soil zone that is Ca deficient (Adams, 1984).

Absolute Ca deficiency is difficult to identify within the acid soil complex except in the most highly leached acid soils with low CEC (Foy, 1984; Kamprath & Foy, 1985). This is because the levels of Ca required for essential growth functions are so low as to approach those of micronutrients (Wallace *et al.*, 1966), therefore the majority of the Ca in soils and in plants serves as an excluder or detoxifier of other elements, such as Al and heavy metals that might otherwise be toxic (Foy, 1992). While absolute deficiencies of Ca have been attributed to possible Al-Ca antagonism rather than to low Ca supply *per se*, recent evidence suggests that Ca deficiency can be a worse growth-limiting factor than Al toxicity (Foy, 1992). This is because some of the acid soils can be particularly low in exchangeable Ca without a concurrent phytotoxic level of soluble Al (Spain *et al.*, 1975).

Magnesium deficiency may limit plant growth on acid, sandy, highly leached soils having low CEC values and possibly high Al saturations. The uptake of Mg is antagonized by high Al saturations, and because Mg is a poor competitor with Al and Ca for exchange sites, it is often deficient in the topsoil because of acidification, or because of application of large quantities of soluble Ca. Thus, liming to near neutrality with calcitic lime in acid soils low in available Mg can exacerbate Mg deficiency, so can application of high levels of K (Kamprath & Foy, 1985). The critical Mg saturation levels have been reported as 5 to 10% of CEC, with a Mg/K ratio of at least 0.5 (Mayland & Grunes, 1979).

Nitrogen, Phosphorus and Potassium

Nitrogen deficiency is more widespread than the deficiency of any other nutrient mainly because plants take up relatively large amounts of N while soils contain relatively small amounts of N. Thus in acid soils of the tropics, N deficiency is a major limitation to plant growth, and is exacerbated by lower rates of N application *vis a vis* the amount removed in harvested crops or lost by other processes, and the decreases in organic matter content with successive harvests. A decline in organic matter content results in a decrease in effective CEC and the capacity of the soil to retain plant-available nutrients (Fageria *et al.*, 1990).

In low fertility acid soils, P deficiency is a major limiting factor to plant growth. The occurrence of P deficiency in acid soils is attributed to low native soil P content and high P fixation capacity (Marschner, 1995). In acid soils the major inorganic P fractions include phosphate ions adsorbed

to Al- and Fe-oxyhydroxides and P precipitated as amorphous and crystalline Al and Fe minerals, and these transform with time from sparingly soluble into increasingly insoluble crystalline forms such as variscite (Al-P) and strengite (Fe-P) from which the P is unavailable for uptake by the plants (Sample *et al.*, 1980). Consequently, plant available P is insufficient in most acid soils even though the total amount of P may greatly exceed crop requirements. In the soil solution of most acid soils the concentrations of inorganic P are low, ranging between 1-5 mmol m⁻³ (Bielecki, 1973). As a result, fertilizer P has to be applied to most acid soils in order to provide soluble P close to the roots to meet plant requirements.

Potassium deficiency in acid soils is not as widespread as P deficiency (Fageria *et al.*, 1991). However, the more acid a soil becomes, the less K is retained on exchange sites, thereby subjecting K to downward movement by leaching. In addition, increased levels of soluble Al would stunt the roots, further exacerbating the reduced K supply to the plants (Barnard, 1986; Sumner *et al.*, 1991). Because high-yielding crops remove large amounts of K, failure to replace the K removed in the harvested crop results in K deficiency becoming a limiting factor in crop production (Sanchez, 1976). The increased incidence of K deficiency in Australia has been attributed to improved P status of the soils and increased yields (Leach & Easton, 1991). Management practices to alleviate K deficiency in crops include application of K fertilizers at judicious rates that replace K lost through crop removal and leaching, incorporation of crop residues or use of K-efficient cultivars (Fageria *et al.*, 1991).

Micronutrients

While the solubility of other micronutrients generally increases with increasing acidity, the availability of molybdenum is reduced with decreasing pH. Molybdenum is required in greater quantities by legumes for the process of nitrogen fixation. The problem of Mo availability to plants growing in acid soils is compounded by the fact that it is a trace element, and is highly insoluble in acid soils (Fageria *et al.*, 1990). Liming, or treating seeds with Mo can rectify the problem. Deficiencies of other micronutrients on acid soils can occur because of leaching losses (Spencer, 1966; Fageria *et al.*, 1990)

1.2.5 SOIL ACIDITY CONSTRAINTS TO GROUNDNUT PRODUCTION

Although soil acidity can affect groundnut growth indirectly by creating nutrient toxicities and deficiencies (see sections 1.2.3 and 1.2.4) the high H^+ activity at low pH can directly affect legume growth in a number of ways. Tang & Thomson (1996) found that root elongation and shoot growth of a number of grain legumes supplied with mineral N declined at pH below 5.0 in the nutrient solution. The depressions in root elongation and shoot growth associated with high concentrations of H^+ were related to decreased proton extrusion from roots which in turn caused limited nutrient uptake and disturbed cytoplasmic pH regulation (Schubert *et al*, 1990a; Marschner, 1995). The H^+ ion can also adversely affect the growth of legumes grown without N-fertilizer application through its detrimental effects nodulation (Schubert *et al*, 1990; Schubert *et al*, 1990b; Tang & Thomson, 1996). High H^+ concentration impairs rhizobial survival and multiplication in soils, root infection, nodule initiation and legume rhizobial efficiency (Andrew, 1978) that can lead to reduced plant growth as a result of nitrogen deficiency. These effects of the H^+ ion are, however, complex and often overshadowed by Al toxicity, Mn toxicity and deficiencies of Ca, Mg and P (Foy, 1984). Helyar (1978) categorized the toxic effects of Al on legume growth in terms of toxic substrate levels, ion uptake and transport, and toxicity and tolerance mechanisms. At substrate levels of Al sufficient to cause some toxic effects, growth declines in a logarithmic fashion. Studies with soybean have shown that toxic levels of Al inhibit root elongation and decrease the adsorption and translocation of nutrients to plant tops (Sanzonowicz *et al.*, 1998). Inhibition of cell division by high concentrations of Al^{3+} is the prime cause for restricted root elongation in some grain legumes. The symptoms of Al toxicity indicate that the toxic effect is mainly through interference in the P metabolism of the plant, and the plant tops in general appear typically P deficient. Reduced growth of legumes in the presence of Al is not only due to toxicity *per se* but also because of the inhibitory effect of Al on uptake and translocation of Ca. Therefore, one of the primary reasons for response of legumes to liming of acid soils is the neutralization of exchangeable Al (Kamprath, 1978). In the pod environment of groundnut Al toxicity may inhibit Ca uptake by developing groundnut pods leading to an increase in pod rot and in the production of empty pods (pops).

The common symptoms of Mn toxicity in grain legumes are inter-veinal chlorosis and crinkle leaf in young leaves (e.g. soybean) and formation of brown speckles in mature leaves. Some of these symptoms are probably related to induced deficiencies of Ca and Mg (Marschner, 1995). Apart from the interferences with Ca and Mg nutrition, excess Mn disrupts phytohormone balance, certain enzyme activities and membrane functions in leaf tissues. For groundnut, shoot Mn concentrations in the region of 600 - 700 mg kg⁻¹ are sufficient to cause toxicity symptoms or a small (about 10 percent) yield decline (Helyar, 1978).

Deficiencies of Ca, Mg and Mo, and decreased P uptake are important limitations to groundnut growth in many acid soils. In soils with low CEC, low Ca levels may cause deficiency problems with groundnuts. The sensitivity of groundnut to low Ca levels is attributed to its unusual fruiting habit, as more Ca is needed for the pod-filling process (Adams, 1984). Mo deficiency may particularly affect growth of legumes because of the high requirements for it by plants dependent on biological nitrogen fixation (Coventry & Evans, 1989). Hafner *et al.*, (1992) observed large improvements in groundnut response to application of Mo in acidic soils deficient in Mo.

1.2.6 MANAGEMENT OF ACID SOILS

Knowledge of why soil acidity increases, and how acid soils affect plant growth is crucial in devising management options to remedy the acid soil infertility barrier to productivity of crops on acid soils. Accurate identification of the extent and severity of the soil acidity problem would assist in deciding on the best management option. Factors taken into account when choosing the best management option include rainfall availability, rate of acidification, type of land use, capability of the land and soil, and cost of the management option. Thus, within the agricultural context, a number of management options to deal with acid soils are commonly advocated.

Curbing soil acidification by using less acidifying management practices

The use of management practices and cropping systems that aim to reduce the acidifying effects of the carbon and nitrogen will ultimately reduce the rate of soil acidification. In this respect, the ideal management practices include (i) use of less acidifying nitrogen and elemental sulphur

fertilizers (ii) split applications of nitrogenous fertilizers to reduce leaching of N (iii) use of deep-rooted crops to utilise N leached into the lower horizons (iv) inclusion of fewer legumes in rotation, (v) returning of crop residues to avoid major cation removal. While these practices can reduce the rate of acidification, ultimately they will not stop it (Van Wambeke, 1976; Helyar & Conyers, 1997).

Cultivation of acid-tolerant species

The basis of this option is that plant species have widely differing tolerances to acidity and nutritional requirements; therefore crops that are adapted to acid conditions (calcifuges) can be used for cultivation on acid soils in order to avoid yield losses from soil acidity. For example, acid tolerant crops such as buckwheat, cassava, cotton, pineapples, sugarcane, and sweet potatoes can be used to increase returns while acidity is being corrected (Kellogg, 1966). Since the pH will continue to decline if unchecked, eventually all plant species will be affected by soil acidity, thus rendering this option a short-term solution.

Use of more nutrients

In an effort to maintain productivity levels, higher rates of fertiliser can be applied to compensate for a retarded root system and fewer available nutrients. With a continued decline in pH levels, more fertiliser will need to be applied to avoid nutrient deficiencies. This option increases production costs, and is not sustainable.

Neutralising soil acidity

Addition of acid reducing (liming) materials offers a longer-term control of soil acidity. Lime materials containing various proportions of carbonates, hydroxides, and oxides of Ca and Mg, have been used for centuries to increase the pH of agricultural soils (Adams, 1980). Liming acid soils is known to improve crop growth by reducing the harmful effects of low pH, decreasing the amount of exchangeable Al or Mn, and increasing the supply of nutrients such as Ca, Mg, Mo (Ahmad & Tan, 1986)

1.2.7 AMELIORATION OF SOIL ACIDITY BY LIMING MATERIALS

On soils with a low buffering capacity, routine application of lime is a basic principle of good farming. The lime programme is usually determined by the neutralizing value of the liming material, current and target soil pH, the pH-buffering capacity of the soil, plans for future production and anticipated fertiliser use. The application method of the liming material will depend on whether the aim is to maintain or lift the pH in the topsoil (0-10 cm) or subsoil (10-20 cm). The species of plant to be grown and the soil type largely determine the target pH (Adams, 1980).

Amelioration of acid soils has generally been accomplished by the application of agricultural limestone (CaCO_3) or dolomitic limestone ($\text{MgCO}_3 \cdot \text{CaCO}_3$). Other ameliorants that have been used include dusts from cement works, lime kilns and marble works, residues from water and sewage treatment plants, crushed shellfish shells, spent lime from ammonia works, blast furnace slags, wood stove or fireplace ashes (Adams, 1980; Clapham & Zibilske, 1992). In addition, it has been shown that gypsum can improve acid soils that have subsoil acidity problems (Shainberg *et al.*, 1989; Sumner, 1993; Carvalho & van Raij, 1997).

The effectiveness of applied lime depends on the quality of the material, the amount applied, the soil pH, the uniformity of spread, and the extent of soil-lime mixing. The chemical potential of liming materials for neutralizing soil acidity is determined in terms of the CaCO_3 equivalence, i.e. grams of CaCO_3 required to equal the reactivity of 100 g of material (Adams, 1980). Generally, the neutralizing capacity of a liming material is related to its effectiveness in removing H^+ and Al^+ off exchange sites (potential acidity) and neutralizing H^+ in solution (active acidity). The effectiveness of the lime material also depends on the size distribution of lime particles, whose rate of dissolution is dependent upon the amount of contact between lime-particle surface and the acid soil solution. The extent of soil-lime mixing also affects the rate at which lime reacts in the soil; ideally, each lime particle should be surrounded by soil particles (Adams, 1980; Tisdale *et al.*, 1993).

The amount of lime needed to achieve a certain pH depends on (a) the pH of the soil and (b) the buffering capacity of the soil, which is related to the cation exchange capacity (CEC). The higher the CEC, the more exchangeable acidity (hydrogen and aluminum) is held by the soil colloids. As with CEC, buffering capacity increases with the amounts of clay and organic matter in the soil, and soils with a high buffering capacity require larger amounts of lime to increase the pH than soils with a lower buffering capacity (Adams, 1980; Tisdale *et al.*, 1993).

Gypsum (Ca SO_4) can be a valuable soil amendment, as it supplies a large amount of Ca ions deep into the soil where increased concentrations of this nutrient are needed. The dissociated sulfates (SO_4^{2-}) from gypsum combine with the detrimental Al^{3+} ions to form aluminium sulfate, which is less phytotoxic than Al^{3+} (Evanylo, 1989; Ismail *et al.*, 1993; Sumner, 1993).

Surface-applied gypsum is an effective ameliorant of soils with acid subsoils since the dissolved gypsum is leached into the subsoil where various chemical reactions take place (Shainberg *et al.*, 1989, Sumner, 1993). Gypsum can increase the pH of some acid soils by hydroxyl replacement from clay by sulfate (Sumner *et al.* 1986; Farina & Channon, 1988; Shainberg *et al.* 1989; Alva *et al.* 1990; Sumner 1993 & 1994). Even though the change in the pH is usually very small, the effect on crop yields is often large because of the decrease in levels of soluble Al^{3+} ions and increase in soluble Ca. Significant yield responses (7-200%) to applications of gypsum on the soil surface or incorporated into the plow layer have been obtained in experiments conducted in Brazil, South Africa, and the United States on maize, soybeans, alfalfa, wheat, rice, beans and cotton (Sumner 1993). Evanylo (1989) reported the beneficial effects of gypsum to be increased rooting proliferation and alleviation of drought stress in deep-rooted crops.

Soil characteristics affecting response to liming in acid soils

McLean (1971) has summarized the most important soil properties that determine the liming effects in acid soils (Table 1.5).

Table 1.5 Soil attributes pertinent to liming effects (source: McLean, 1971)

| Attribute | Description |
|---|--|
| <i>Permanent charge form of acidity</i> | A change in net CEC of a soil occurs when the negative charge on the surfaces of the clay crystals is partially neutralized by AlOH ions. These ions vary in positive charge depending on whether they adsorb additional OH ions from lime, or lose them by neutralization with H ⁺ . Continued leaching and greater concentration of H ions results in the neutralisation of OH ions associated with the Al ions, leaving Al ³⁺ as the predominant form of exchangeable acidity. |
| <i>Type and crystallinity of clays</i> | Continued weathering causes the gradual removal of K from crystalline clay materials, exposes the interlayers to further weathering and removal of silica, which causes destruction of the 2:1 type clays, eventually leaving hydrous oxides of Fe and Al, with some residual kaolinite as the predominant forms of clay. |
| <i>Potassium release tendency</i> | Large quantities of non-exchangeable K can be released from parent materials containing micaceous clays during the weathering process, but as smaller amounts of micaceous clays remain, less K of this type can be released. However, with increases in the H ion concentration, relatively more K is weathered from primary minerals, and a more rapid turnover of that in the plant residues also helps replenish the soil supply. |
| <i>Phosphate fixing tendency</i> | Al and Fe released from mineral crystals by weathering are accessible in soil solution, on exchange sites, or as constituents of exposed surfaces. Each ion reacts with soluble phosphate forming relatively insoluble compounds. Once the Al and Fe are released in large quantities and coat most of the exposed surfaces of individual particles and granules, lime may not favourably affect the availability of P that they retain. |
| <i>Ionic exchange capacity</i> | Because the total CEC of soils is roughly proportional to concentrations of OM and of clay, the CEC of soils increases as K is weathered from micaceous clays, and as plants grow, producing OM in the soil. However, as OH-Al accumulates and polymerises on clay surfaces or is complexed by the COOH groups of OM, the effective CEC decreases. Conversely, the gradual increase in hydrous oxide clays concomitantly increases the anion exchange capacity (AEC). The dependence of a higher proportion of the total CEC on pH is a result of a high pH-dependence of the negative charges on both OM and hydrous oxide clays. |

Table 1.5 contd. Soil attributes pertinent to liming effects (source: McLean, 1971)

| | |
|---------------------------------------|---|
| <i>Base saturation (Ca).</i> | There exists an inverse relationship between exchangeable Ca, Mg or total bases, and exchangeable Al. Ca and other basic cations are removed from the soil by weathering process, resulting in decreased saturation of the CEC with bases, thereby causing the soil to become progressively more acid. |
| <i>Natural stability of structure</i> | In highly weathered soils, solubilization of Al and Fe results in the formation of Fe- and Al-complexes and oxide or hydrous oxide coatings that stabilize the soil aggregates. In less weathered soils, the structure of the surface horizon is stabilized by Ca- and OM- stabilized aggregates, which can only be destroyed by excessive cultivation, erosion, leaching or residue removal. |

Benefits from lime application

In general, liming acid soils increases yields because of the increase in soil pH to the crop's most favorable range for growth. The other beneficial effects of liming are mainly a reversal of the processes associated with the chemistry of acid soils, namely:

- a) an increase in soil pH that affects the solubility of various compounds;
- b) acid weathering of primary and secondary minerals is curtailed by the decreased concentration of H^+ ;
- c) inactivation or neutralisation of toxic concentrations of Mn^{2+} , Al^{3+} (the major limiting factors on acid soils) and other substances;
- d) alteration in ratios of basic cations adsorbed and in solution: base saturation, particularly Ca increases ;
- e) an increase in pH-dependent CEC, and a decrease in pH-dependent AEC;
- f) improvement of the environment for beneficial soil microorganisms, thereby increasing microbial activity;
- g) encouragement of a more rapid breakdown of organic materials in the soil, releasing nutrients for growing plants;
- h) improvement of nitrogen mineralization and symbiotic N-fixation by legumes; this can improve palatability of forages;
- i) provision of an inexpensive source of Ca^{2+} and Mg^{2+} when these nutrients are deficient at lower pH;
- j) an increase in electrolyte concentration due to dissolution of lime; and

- k) may improve the activity of some herbicides (Adams, 1981b; Ahmad & Tan, 1986; Tisdale *et al.*, 1993; Foth & Ellis, 1997).

Benefits from gypsum application

Application of gypsum on acid soils has a broad range of benefits for plant nutrition and yield, and for soil improvement. Some of the major benefits as documented by Carvalho *et al.* (1986), Farina & Channon (1988), Shainberg *et al.* (1989), Wallace (1989), de Silva & van Raij (1992), Sumner (1993) and Rengasamy *et al.*, (1993) are summarized below.

- a) Corrects subsoil acidity by increasing exchangeable Ca and decreasing Al^{3+} and H^+ , resulting in deeper root penetration and improved plant use of water and nutrients in the subsoil. Crops can better withstand periodic droughts during the season, which translates into increased yield.
- b) Decreases toxicity of Al by formation of $(\text{AlSO}_4)^+$ complex or by releasing hydroxyl ions from clay as replaced by sulfate. Decreases H^+ toxicity by replacing H^+ on clay surfaces that can then be leached away, thereby increasing the pH.
- c) Supplies electrolytes that are needed to stabilize soil structure. In highly dispersive clays gypsum application promotes flocculation, thereby increasing infiltration and decreasing runoff.
- d) Provides soluble Ca needed to prevent physiological disorders such as bitter pit, scald internal breakdown, and cork spot in fruit; pod rot and empty pods in groundnut.
- e) Provides Ca to improve stability of soil organic matter.
- f) Can improve S and Ca nutrition in acid soils, especially in highly weathered soils where they can be limiting factors for legume crops.
- g) Gypsum application on acid soils can decrease acid stress on nodulating bacteria.

Harmful effects of liming

Too much lime may curtail acid weathering or compound solubility so as to cause deficiencies of Mn, Z, Cu or B. These deficiencies are mainly a result of excessive raising of the soil pH. Other negative effects of liming can include reduced phosphate availability, and suppressed availability of Mg and K. Thus, injury to crops due to overliming results primarily from changes in the availability of these nutrients, and to Mo toxicity at times. Overliming can be a problem when

soils have a low CEC and a small buffer capacity, and the pH can be increased easily. This is most likely on sandy soils with permanent charge clays. Adverse effects may result from applying more than 2 t ha^{-1} on light-textured soils (Foy, 1984; Ahmad & Tan, 1986; Tisdale et al., 1993; Foth & Ellis, 1997).