Soil Science

Soil Fertility and Nutrient Management

S.N. Sharma
Principal Scientist
Division of Agronomy
Indian Agricultural Research Institute
New Delhi – 110 012

1. History of Plant Nutrition and Soil Fertility

The period of the development of the human race during which it began the cultivation of plants marks the dawn of agriculture. Until then man hunted almost exclusively for his food and was nomadic in his habits. As the years went by man became less of a wanderer and more of a settler. Families, clans, and villages developed, and with them came the development of the skill one calls agriculture. It is generally agreed that one area in the world that shows evidence of a very early civilization is Mesopotamia, situated between the Tigris and Euphrates rivers in what is now Iraq. It is believed that human race invented agricultural practices 8,000-10,000 years ago in the area between Nile Valley in Egypt and Indus in India (Krishna, 2002). Writings dating back to 2500 B.C. mentioned the variation in the fertility of the land. It is recorded that the yield of barley varied from 86-fold to 300-fold in different lands, which means, of course, that for every unit of seed planted 86 to 300 units were harvested.

Theophrastus (327-287 B.C.) recommended the abundant manuring of thin soils but suggested that rich soils be manured sparingly. Theophrastus also suggested that plants with high nutrient requirements also had a high water requirement. Not only did the Greek ancients recognize the merits of manure, but they also observed the effect that dead bodies had an increasing the growth of crops. In Deuteronomy it is directed that the blood of animals should be poured on the ground. The value of green-manure crops, particularly legumes, was also soon recognized. Theophrastus noted that a bean crop (*Vicia faba*) was ploughed under by the farmers of Thessaly and Macedonia. He observed that even when thickly sown and large amounts of seed were produced the crop enriched the soil. Virgil (70-19 B.C.) advocated the application of legumes.

Theophrastus suggested the mixing of different soils as a means of "remedying defects and adding heart to the soil." The addition of fertile soil to infertile soil could lead to increased fertility, and the practice of mixing one soil with another may have provided better inoculation of legume seed on some fields. Again, the mixing of coarse-textured soils with those of fine texture, or vice versa, may have caused an improvement in the water and air relations in the soils of the fields so treated.

The value of marl (a source of lime) was also recognized. The early dwellers of Aegina dug up marl and applied it to their land. The Romans, who learned this practice from the Greeks and Gauls, even classified the various liming materials and recommended that one type be applied to grain and another to meadow. Pliny (A.D. 62 – 113) stated that lime should be spread thinly on the ground and that one treatment was "sufficient for many years, though not 50." Columella also recommended the spreading of marl on a gravelly soil and the mixing of gravel with a dense calcareous soil.

The age of the Greeks from perhaps 800 to 200 B.C. was indeed a Golden Age. Many of the people of this period reflected genius that was unequaled, or at least not permitted expression, for centuries to come. Their writings, their culture, their agriculture were copied by the Romans, and the philosophy of many of the Greeks of this period dominated human thinking for more than 2000 years.

1.1. Ancient Indian Agriculture

Archeological records indicate that agricultural crop production was regularly practiced during the Indus Valley civilization, which began about 25000 to 2000 B.C. (Boltero *et al*., 1965).

Wheat, barley, rice, peas, and pastures were the major crops. Permanent cropping on arable soils, nomadic, tribal agricultural cropping and pastoral nomadism (animal husbandry) were in vogue (Kenoyer, 1995). Whereas, between 2000 B.C. to 500 A.D., the economy of the Rigvedic Indian civilization centred around well developed agriculture. Their cropping zones extended from the present day Multan (Pakistan) in the west to Bengal (India) in the east, covering the entire Indo-Gangetic belt and parts of Peninsular India.

Vedic literature suggests that five basic elements governed the life processes, including plants and agriculture. They are earth, water, air, fire and ether. Two broad divisions of soils are found to occur in the Rigveda: fertile (apnaswati) and barren (astana) in the later vedic literature is expressed as alkaline (usara) and non-alkaline (anusara). Fields with better fertility were classifeed as urvera.

Information on agriculture and soil management and cropping systems followed during late vedic period is available through relics, stone edicts, Sanskrit literature, specialized texts, prose and poetry of called *Samhitas* or *Smriti*. For example, details on crops, their distribution, method of cultivation are mentioned in the *Tagnvalky Smriti* (Yagnavalkya, 320-380 A.D.). Similarly, Varahamihira's Brihatsamhita is a compilation that elaborates on scientific agriculture in addition to other species *Krisiparasara* of the later date (950 A.D.) describes agriculture in greater detail. The weather patterns, cloud classification, to predict rainfall, timing of sowing and other intercultural operations are mentioned in it. It lists a variety of farm implements including the plough (*Sira*), methods of manure preparation, timing of harvests, preservation and even seed stock preparation. It clearly states that agriculture demands total commitment and personal supervision. Agricultural labour and operations, were considered expert professions and were confined to *Krishi thantri* and *Kshudras*.

The yearly cropping pattern of the vedic era was subdivided into wet crops (*Kaidara*), winter crops (*Haimana*), and summer crops (*Graismika*) (Kautilya, 3rd century B.C.). The village economy of the ancient India was mostly subsistent. Food supply by the farmers and cowherds were the mainstay. To ward off the population pressure, Kautilya (3rd century B.C.) the great economist, suggested extending farming areas surrounding the village and demarking extra land area for civilization. Foreign travelers to ancient India expressed that soil fertility was high allowing up to three crop cycles a year (Megasthanes, 3rd century B.C.). Major crops quoted are rice, wheat, barley, millets, pulses, flax, cotton, hemp, grapes and other fruits (Eratosthanes, 3rd century B.C.; Chein Hen Shu, 3rd century B.C.). During the Gupta period (3rd to 5th century A.D.), the science of agriculture was a full-fledged subject of study. It was taught regularly to the pupils at school. The faculty of agricultural expertise was called the *'Krishi thantra gnana'* and the students graduates as '*Krishithanthris'*.

1.2. The Medieval Period

The medieval period has its share of achievements pertaining to the development of agricultural procedures, particularly, soil and crop management. Around 11th to 14th century A.D., the prime tendency of the farming community operating in Europe, Asia and other continents was expansion into newer arable and fertile soils. In Europe, Asia and other continents was expansion into newer arable and fertile soils. In Europe, soils were mended and ploughed using unusually large ploughs drawn by 8 to 12 oxen. Soil fertility replenishments included salt petre, bone meal and phosphate rocks European farming community underwent an agricultural revolution during the middle ages. It was enthused partly because of the enlarged urban population caused by the industrial revolution. It needed extra grain and vegetable sources to feed the growing populations. Medieval scholar paid a lot of attention to soil fertility aspects and the plant growth phenomenon. Palissy (1563) remarked that whenever animal dung was spread or the plant

residues burnt in the field, it amounted to rejuvenation of soil fertility. It was believed that all plants were made up of an assortment of mineral salts.

The medieval agriculture in the Indian subcontinent (South Asia) involved both subsistence and intensive farming practices. It was a well developed enterprise and taxed scrupulously by the monarchs. Documentations indicate that techniques of soil and crop management were fairly refined. In the Indo-Gangetic plains, the Islamic rulers of the medieval period (1300s to 1600s, graded agricultural land based on inherent soil fertility levels and cropping patterns (Abul Fazal, 1595). The soils were classified as: (a) *Polaji* (fertile piece of land cultivated intensively), (b) *Parauli* (areas which needed a fallow period to refresh its fertility), (c) *Cachar* (less fertile soils needing three to four years of fallow), (d) *Banjar* (soils poor in fertility not prone to cultivation without extended durations of fallow). Peanuts used dung and crop waste in different proportions to prepare farmyard manure. Two main cropping seasons were identified, namely, *kharif* (rainy season crop) and *rabi* (crop on stored moisture). This classification continues even today.

Tavernier (1640-67), an European traveler to the Indian plains, mentioned that agricultural fields were irrigated and well manured. Nearly 75% of the populace, the village dwellers were engrossed in cultivation. Horticultural grafting procedures were said to be utilized efficiently to improve crop produce.

Italian traveler Nicolo Conti (1441) reported that the medieval agrarian community in peninsular India recognized the value of soil fertility to crop production immensely. Cropping systems were intensive around the fortress in order to feed the higher population, otherwise subsistent in villages. Farmers grew wetland rice, sugarcane, legumes and several types of fruits.

1.3. Recent History

Russell (1917) classifies the human inquisitiveness and research efforts towards understanding the soil fertility manifestations, during 17^{th} to 19^{th} century into three main aspects.

1.3.1 The search for the "Principle of Vegetation (1630 – 1750)"

Francis Bacon (1561 – 1624) suggested that the principal nourishment of plants was water. He believed that the main purpose of the soil was to keep the plants erect and to protect them from heat and cold and that of each plant drew from the soil a substance unique for its own particular nourishment. Jan Baptiste van Helmont (1577 – 1644), a Flemish physician and chemist, also regarded water as the sole nutrient of plants. Robert Boyle (1627-1691) reported the work of van Helmont several years and confirmed the findings of van Helmont, but he went one step further. As a result of the chemical analyses he performed on plant samples, he stated that plants contained salts, spirits, earth and oil, all of which were formed from water. However, J.R. Glauber (1604 – 1668), German chemist, suggested that saltpeter (KNO_3) and not water was the "principle of vegetation". John Mayow (1643 – 1679), an English chemist, supported the viewpoint of Glauber. About 1700, John Woodward, an Englishman grew spearmint in samples of water obtained from various sources like rain, river, sewage, and sewage plus garden mold and found that the growth of the spearmint was proportional to the amount of impurities in the water and concluded that terrestrial matter, on earth, rather than water, was the principle of vegetation. Arthur Young (1741 – 1820) conducted pot tests to find those substances that would improve the yield of crops. He grew barley in sand with materials such as charcoal, train oil, poultry dung, spirits of wine, niter, gunpowder, pitch, oyster shells and numerous other materials. He published his work entitled *Annals of Agriculture*, in 46 volumes, which was highly regarded and made a considerable impact on English agriculture. Around 1775,

Francis Home stated that there was not only one principle of vegetation but probably many like air, water, earth, salts, oil and fire in a fixed state.

1.3.2. The Phlogistic Period (1750-1800)

During the phlogistic period, the main focus was to search and identify the plant nutrients, either organic or minerals, that are necessary to stimulate plant growth (Russell, 1917). Principles of chemistry were being increasingly applied to explain aspects of crop production. For example, Francis Home (1756), working under the auspices of Ebinburgh Society stated that fertile soils possessed plant food and the whole art of agriculture revolves around discovery of source of nourishment – the minerals and organics. Salt petre, Epson salt, and tartar were known to nourish plant growth. There were further advances in the understanding of both the physiological processes and chemical nature of soil fertility. In 1795, Earl of Dundanland identified and reported that alkaline phosphates too improve plant growth. The interdisciplinary efforts to explain agricultural facts during the 18^{th} century and early 19^{th} century is indeed noteworthy. Wallerius (1761), a professor of Uppsala, analysed plants and soils to conclude that humus being the homogeneous component was the major source of nourishment, while other fractions aided in making appropriately suitable mixtures and soups. Some excellent variations in crop rotations were developed to maximize the utilization of available soil fertility (Lavoisier, 1775). Importance of nitrogen fixing legumes to conserve soil fertility was being increasingly recognized. Experimental analysis by Bousingault (1834) had shown a positive nitrogen balance with crop rotations having legumes.

1.3.3. Liebig's Era: The beginning of agricultural chemistry

Justus von Liebig (1802 – 1873), a German chemist, while present his paper at a prominent scientific meeting made the following statements: (i) Most of the carbon in plants comes from the carbon dioxide of the atmosphere, (ii) Hydrogen and oxygen come from water, (iii) The alkaline metals are needed for the neutralization of acids formed by plants as a result of their metabolic activities, (iv) Phosphates are necessary for seed formation and (v) Plants absorb everything indiscriminately from the soil but excrete from their roots those materials that are nonessential. Liebig firmly believed that by analyzing the plant and studying the elements it contained, one could formulate a set of fertilizer recommendations based on these analyses. It was also his opinion that the growth of plants was proportional to the amount of mineral substances available in the fertilizer. Liebig also stated the *law of the minimum* in 1862 for predicting crop response to fertilization. This law states that every field contains a maximum of one or more and a minimum of one or more nutrients. With this minimum, be it lime, potash, nitrogen, phosphoric acid, magnesia or any other nutrient, the yields stand in direct relation.

J.B. Lawes and J.H. Gilbert in 1843 established an agricultural experiment station at Rothamsted, England and after twelve years they made the points that: (i) Crops require both phosphorus and potash, but the composition of the plant ash is no measurement of the amounts of these constituents required by the plant, (ii) Non-legume crops require a supply of nitrogen. Without this element, no growth will be obtained, regardless of the quantities of phosphorus and potassium present. The amount of ammonia nitrogen contributed by the atmosphere is insufficient for the needs of crops, (iii) Soil fertility could be maintained for some years by means of chemical fertilizers and (iv) The beneficial effect of fallow lies in the increase in the availability of nitrogen compounds in the soil. Development of the modern phosphate fertilizer industry began with the demonstration by Liebig in 1840 that the fertilizer value of bones could be increased by the treatment with sulphuric acid. Shortly thereafter, John B. Lawes patented a

process of phosphate rock acidulation in 1842 which led to commercial production of super phosphate in England in 1845.

1.4. Soil Fertility Research during the Twentieth Century

Ammonia synthesis by the Haber-Bosch process is one of the few most significant discoveries of the early twentieth century which led to a Nobel Prize to Haber for his invention. During early to mid 20th century, soil science (Pedology) became a recognized faculty of agricultural science. Soil fertility laboratories began operating in most universities or research institutes in different parts of the world. In due course, soil scientists understood the essentiality of nutrients and their influence on plant growth. Initially, major nutrients, N, P and K received greater priority, later it was minor and micro-elements. Soil fertility scientists utilized simple extraction media involving either water, weak organic acids or dilute mineral acids to assess nutrient levels in soil and judge corresponding crop yield levels. These were termed crop response curves, which could be mathematically modeled or depicted (Mitcherlich, 1923; Naubauer, 1932). Extraction solutions, which tallied more accurately with the available range of nutrients were prepared. For example, Trougs, Brays, Mehlichs, Olsen, etc. were consistently used to assess the available nutrients in soil. One of the most used techniques in plant and soil analysis was devised by Kjeldahl (1879). Around 1920s and 1940s chemical titration methods were regularly used to assess the quantity of mineral nutrients extracted into solutions. Such methods were best suited to assess elements, such as N, Ca, Mg and S. Devising techniques that assess soil fertility (mineral nutrients) has indeed received high priority during the 20th century. Improvements in instrumentation, its sophistication, accuracy, rapidity and the quantity of samples handled per unit time have been enormous. At present, plant essential nutrients are routinely estimated using automated spectrocolorimetry, atomic absorption spectroscopy, emission spectroscopy, X-ray fluorescence spectroscopy, mass spectroscopy, radio isotope techniques, etc.

2. Soil Fertility and Productivity

A productive soil has to be fertile, while a fertile soil may or may not be productive. A soil is said to be fertile if it contains and can supply all the thirteen essential plant nutrients (N, P, K, Ca, Mg, S, Fe, Mn, Zn, Cu, B, Mo, Cl) in adequate amounts needed by the growing crop plants; the quantities of these essential plant nutrients should neither be deficient nor in toxic amounts. However, for good plant growth and productivity also needed are adequate amounts of water and air in soil. Furthermore for release of several plant nutrients a good activity of many soil microorganisms is also required. Thus for a soil to be productive good soil physical and microbiological properties are also needed in addition to it being fertile. Also a soil to be productive must also needed in addition to it being fertile. Also a soil to be productive must also be safe from natural hazards such as floods and associated erosion.

3. Essential Plant Nutrients

Arnon and Stout (1939) suggested the following criteria for the essentiality of a plant nutrient: (i) A deficiency of the essential element makes it impossible for a plant to complete its life cycle, (ii) The deficiency is specific to particular essential element, (iii) An essential element is directly involved in the nutrition of the plant. To the above 3 criteria may be added a fourth one, which is "The deficiency of an essential element can be overcome only by the supply of that element". Based on the these criteria 16 elements have been so far considered as essential plant nutrients. These are : C, H, O, N, P, K, Ca, Mg, S, Fe, Mn, Zn, Cu, B, Mo and Cl. Of these 3 elements (CHO) are taken from air and soil water, while the rest 13 are taken from the soil through soil solution.

3.1. Classification of nutrients

On the basis of the amounts of these nutrients taken by plants they are classified as: (i) macronutrients and (ii) micronutrients.

3.1.1 Macronutrients (taken up in large amounts, generally in kg per hectare). These can be further sub-divided as (i) Primary nutrients (taken up in large amounts): N, P, K. (ii) Secondary nutrients (taken up in lesser amounts than N and K) : Ca, Mg, S

3.1.2. Micronutrients : These are taken up in very small amounts, generally expressed in g or mg per hectare, these include Fe, Mn, Zn, Cu, B, Mo, Cl.

The ionic form in which different plant nutrients are taken up by crop plants, their functions and deficiency symptoms are given in Table 1.

Table 1. Ionic forms in which taken up by plants, functions and deficiency symptoms of essential plant nutrients.

Nutrients (ionic forms)	Functions	Deficiency symptoms
N (NH_4^+, NO_3^-)	Synthesis of protein, component of chlorophyll, enzymes, nuclei acids	Light green colour of leaves, older leaves show the symptoms first.
P ($H_2PO_4^-$, HPO_4^-)	Component of ATP and ADP and hence involved in energy transfer in photosynthesis, helps in root development	Leaves show purplish to red coloration
K (K^+)	Control stomata opening for photosynthesis, neutralizes organic acids	Scorching and burning of leaf margins
Ca (Ca^{++})	Component of cell wall, involved in cell division and cell growth, co-factor for enzymes	Failure in the development of terminal buds, dead spots in the mid-rib of leaves. In maize the tip of the new leaves may have a sticky material that causes them to adhere to one another
Mg (Mg^{++})	Component of chlorophyll	Light green veination in leaves, cupping of leaves
S (SO_4^-)	Component of proteins – S containing amino acids cystine and methonine	Similarly to N deficiency but seen on top leaves as a contrast to N deficiency symptoms which first appear in lower leaves. In rapeseed mustard young leaves of S deficient plants become pale, chlorotic and cupped
Zn (Zn^{++})	Formation of auxins & chloroplasts; carbohydrate metabolism	Stunted growth, pale to white coloration of young leaves (white bud disease of maize); browning and scorching of leaves (khaira disease of rice)

Nutrients (ionic forms)	Functions	Deficiency symptoms
Mn (Mn^{++})	Photosynthesis-evolution of O_2, oxidation-reduction processes	Green veins against a pale lamina, abscission of leaves, grey speck of oats, marsh spots of beans
Fe (Fe^{++})	Structural component of cytochromes, perichromes and leghemoglobin, involved in oxidation-reduction process in respiration	Yellowing or whitening of leaves; in rice nurseries and sorghum plants may turn pale or white
Cu (Cu^{++})	Constituent of chlorophyll, involved in carbohydrate and protein metabolism catalyst for respiration	Leaf tops become white, leaves narrow and twisted, stunted growth
B (BO_3^-)	Involved in cell division and fruiting and in pollen tube growth	Terminal buds die, rosette formation, flower and fruit setting adversely affected
Mo (Mo^-_4)	Component of nitrate reduction and nitrogenous enzymes; important in N fixation by legumes	Symptoms similar to N deficiency; whiptail disease of cauliflower
Cl (Cl^-)	Involved in photosynthesis II in evolution of O_2 and in cell osmotic pressure	Chlorotic leaves; leaf necrosis

4. How the Nutrients are Held by Soil Clay Particles and Soil O.M.

Ion exchange is a reversible process by which one type of cation or anion held on the solid phase is exchanged with another kind of cation or anion in the liquid phase. The exchange of ions may also take place of two solids if they are in contact. There are two types of ion exchange (i) cation exchange (ii) anion exchange, the cation exchange generally considered to be more important, since the anion and molecular retention capacity of most agricultural soils is much smaller than the cation retention capacity.

4.1. Cation exchange

The seats of ion exchange are the organic and the mineral components of soil with effective particle diameters of less than 20 μm. This includes a portion of the silt and all of the clay fraction (< 2 μm) as well as colloidal organic matter.

The cations being positively charged are attracted to negatively charged surfaces. In the organic fraction the negative charged surfaces are arised from the dissociation of H^+ from certain functional groups particularly from carboxylic (-COOH) and phenolic ($-C_6H_4OH$) groups. Many carboxylic groups will dissociate H^+ at pH values below 7, leaving a negative charge at the site of the functional group, as shown in the following equation.

$$- COOH \rightleftharpoons COO + H^+$$

It has been reported that 85 to 90% of the negative charge of humus is due to these two functional groups alone. Two other groups, enol (─COH = CH) and imide (= NH), also contribute to the negative charge of organic matter.

Negative charges in the inorganic clay fraction generally arise from two sources: (i) Isomorphous substitution in layer silicate minerals such as smectite, and (ii) deprotonation of both (a) hydroxyl – OH groups attached to the silicon atoms at the broken edges of the tetrahedral planes, and (b) exposed AlOH groups in layer silicates. The negative charge resulting from isomorphous substitution by the replacement of a silicon or aluminium atom by an atom of similar geometry but of lower charge (e.g., Mg^{2+} for Al^{3+} or Al^{3+} for Si^{4+}). Isomorphic substitution occurs mainly during crystallization of layer silicate minerals, and once the charge is created it is largely unaffected by future changes in the environment and called permanent charge of soils. Isomorphic substitution is the principal source of negative charge for the 2:1 and 2:1:1 groups of clay minerals but is of minor consequence for the 1:1 group of clays.

Deprotonation or dissociation of H^+ from OH groups at the broken edges of clay particles is the prime source of negative charge in the 1:1 clay minerals. High pH values favour this deprotonation of exposed hydroxyl groups.

The oxides and hydrous oxides abundant in highly weathered soils also have pH-dependent charges. These materials occur as coatings and interlayers of crystalline clay minerals. On exposure to moisture their surfaces become hydroxylated. Charges develop on these hydroxylated surfaces either through amphoteric dissociation of the surface hydroxyl groups or by adsorption of H^+ or OH^- ions. Negative charges at the edge of clay plates increase with increasing pH as shown below.

- $SiOH + OH = \rightleftharpoons SiO + H_2O$
- $AlOH + OH = \rightleftharpoons AlO + H_2O$

4.1.1. Cation exchange capacity (CEC): The negative charge that develops on organic and mineral colloids is neutralized by cations attracted to the surfaces of these colloids. The quantity of cations expressed in milliequivalents per 100 g of oven-dry soil is termed the *cation exchange capacity* (CEC) of the soil.

4.1.2. Measurement of CEC

(i) Principle: A soil sample is extracted with neutral 1 N ammonium acetate. All of the exchangeable cations are replaced by ammonium ions and the CEC becomes saturated with ammonium. If this ammonium-saturated soil is extracted with a solution of a different salt, say 1.0 N KCl, the potassium ions will replace the ammonium ions. If the soil-potassium chloride suspension is filtered, the filtrate will contain the ammonium ions that were previously adsorbed by the soil. The quantity of ammonium ions in the leachate is a measure of the CEC of the soil in question and can easily be determined.

(ii) Procedure: A sample of 20 g of oven-dry soil is extracted with 200 ml of 1 N NH_4OAC (ammonium acetate). The extraction is accomplished by intermittent shaking over a period of 30 minutes. The soil-ammonium acetate solution is filtered and the soil is washed with alcohol to remove the excess solution. The soil containing the adsorbed ammonium ions is next extracted with 200 ml of a solution of 1 N KCl. The soil-potassium chloride solution is filtered and the ammonium contained in the filtrate is determined.

(iii) Calculation: Suppose that 0.072 g of NH_4^+ were found. This was, of course, retained by the 20 g of soil extracted (0.072 g is 4 meq – i.e., 0.072/0.018 = 4, as 0.018 g is the milliequivalent

weight of 1 meq). Because 4 meq were present in 20 g of soil, the CEC of the soil is 20 meq/100 g.

4.1.3. Factors affecting CEC: The CEC of a soil will obviously be affected by the nature and amount of mineral and organic colloid present. As a rule, soils with large amounts of clay and organic matter will have higher exchange capacities than sandy soils low in organic matter. Also, soils with predominantly 2:1 colloids will have higher exchange capacities than soils with predominantly 1:1 mineral colloids.

Generally, 1:1 mineral colloids have CEC values of 1 to 10 meq per 100 g; 2:1 mineral colloids such as montmorillonite and vermiculite, 80 to 150 meq per 100 g; 2:1:1 chlorites and 2:1 micas, 20 to 40 meq per 100 g; and organic colloids, 100 to 300 meq per 100 g.

4.1.4. Base saturation: Base saturation reflects the extent of leaching and weathering of the soil. It is defined as the percentage of total CEC occupied by such basic cations as calcium, magnesium, sodium and potassium.

4.1.5. Measurement of base saturation: Suppose following ion quantities were found in the ammonium acetate extract from the leaching of the 20 g of soil:

Ca	0.01 g
Mg	0.012 g
Na	0.0092 g
K	0.0156 g

The milliequivalents weights of calcium, magnesium, sodium and potassium are 0.02, 0.012, 0.023 and 0.039, respectively. The milliequivalents of each of these ions present in 20 g soil will be:

Ca	=	0.01/0.02	=	0.5 meq
Mg	=	0.012/0.012	=	1.0 meq
Na	=	0.0092/0.023	=	0.4 meq
K	=	0.0156/0.039	=	0.4 meq
Total				2.3 meq

Thus 20 g soil contains 2.3 meq bases will be equivalent to 11.5 meq per 100 g of soil. The total CEC of this soil was 20 meq per 100 g, so the percentage of base saturation is (11.5/20) x 100, or 57.5.

Generally the degree of base saturation of normal uncultivated soils is higher for arid than for humid region soils. The degree of base saturation of soils formed from limestones or basic igneous rocks is greater than that of soils formed from sandstones or acid igneous rocks. Base saturation is related to soil pH and to the level of soil fertility. For a soil of any given organic and mineral composition, the pH and fertility level increase with an increase in the degree of base saturation.

Form any given soil the availability of the nutrient cations such as calcium, magnesium and potassium to plants increases with the degree of base saturation. However the relation between percent base saturation and cation availability is modified by the nature of the soil colloid. As a

rule, soils with large amounts of organic or 1:1 colloids can supply nutrient cations to plants at a much lower degree of base saturation than soils high in 2:1 colloids.

4.2. Anion exchange

Contrary to cation exchange, the capacity for retaining anions increases with a decrease in soil pH. Further, anion exchange is much greater in soils high in 1:1 clays and those containing hydrous oxides of iron and aluminium than it is in soils with predominantly 2:1 clays.

Anions may be retained by soil particles through a number of reactions, some of which are simply electrostatic and are described as being nonspecific. Specific adsorption or chemisorption reactions of a nonelectrostatic nature are also possible. The positive charge sites responsible for electrostatic adsorption and exchange of anions originate in the broken bonds, primarily in the alumina octahedral sheet, exposing OH groups on the edges of clay minerals. Anion exchange may also occur with OH groups on the hydroxyl surface of kaolinite. Displacement of OH ions from hydrous iron and aluminium oxides is also considered to be an important mechanism for anion exchange, particularly in highly leached soils of the tropics and subtropics was anion exchange is greatest. Clay minerals in the montmorillonite group of expansible layer silicates usually where anion exchange capacities of less than 5 meq per 100 g. On the other hand, kaolinites can have an anion exchange capacity as high as 43 meq per 100 g at an acidic equilibrium pH of 4.7.

4.3. Root cation exchange capacities

Soil colloids are not the only component of the soil-plant system to exhibit cation exchange properties. Plant roots themselves may also possess this property. Capacities ranging from less than 10 to almost 100 meq per 100 g have been measured.

The exchange properties of roots appear to be attributable mainly to carboxyl groups (- COOH) present in pectic substances. Such sites may account for 70-90% of the exchange properties of roots. Uptake of exchangeable ions by roots is considered to be a passive process that is distinct from intake into the interior, living portions of cells.

Plants differ considerably in the magnitude of their measured root CEC values. Legumes and other dicotyledons generally have values at least double the capacities reported for monocotyledons, including the grasses. Legumes and other plant species with high CEC values tend to absorb divalent cations such as calcium preferentially over monovalent cations, whereas the reverse occurs with grasses.

5. Movement of Nutrients from Soils to Roots, their Uptake and Translocation

Nutrients must come in contact with the root surface. There are generally three ways in which nutrient ions in soil may reach the root surface: (i) root interception, with the possibility of contact exchange, (ii) diffusion of ions in the soil solution; and (iii) movement of ions by mass movement with the soil solution.

5.1. Root interception

As the root system develops and exploits the soil completely, soil solution and soil surfaces retaining adsorbed ions are exposed to the root mass and adsorption of these ions by the contact exchange mechanism is accomplished. The quantity of nutrients that can come in direct contact with the plant roots is the amount in a volume of soil equal to the volume of roots. It can be assumed that roots usually occupy 1% or less of the soil. Because roots grow through soil pores which may have higher than average nutrient content, it is estimated that roots would contact a maximum of 3 % of the available nutrients in the soil.

5.2. Mass flow

Movement of ions in the soil solution to the surfaces of roots is accomplished largely by mass flow and diffusion. Mass flow, a convective process, occurs when plant nutrient ions and other dissolved substances are transported with the flow of water to the root that results from transpirational water uptake by the plant. Some mass flow can also take place in response to evaporation and percolation of soil water.

Amounts of nutrients reaching roots by mass flow are determined by the rate of water flow or the water consumption of plants and the average nutrient concentrations in the soil water. The level of a particular nutrient around the root will fluctuate depending on the balance between the rate at which it reaches this zone by mass flow and the rate of uptake by the root. Mass flow supplies an overabundance of calcium and magnesium in many soils and most of the mobile nutrients, such as nitrogen and sulphur, if concentrations in the soil solution are sufficient.

5.3. Diffusion: Diffusion occurs when an ion moves from an area of high concentration to one of low concentration by random thermal motion. As plant roots absorb nutrients from the surrounding soil solution, a diffusion gradient is set up. Plant roots absorbing nutrients in this manner thus create a sink to which nutrients diffuse. A high plant requirement or a high root "absorbing power" results in strong sink or a high diffusion gradient, favoring ion transport.

5.4. Back diffusion

Under some conditions the concentration of certain ions may build up at the root surface because the root is unable to absorb them at a sufficiently rapid rate. This results in a phenomenon known as "back diffusion." In which the concentration gradient, and hence the movement of certain ions, will be away from the root surface and back toward the soil solution. Normally such a condition will not occur, but as roots do not absorb all nutrient ions at the same rate, there may on occasion be a buildup of those ions that are less rapidly absorbed, particularly during periods when the plant is absorbing moisture rapidly. It should be noted that elevated levels of one or more nutrients in the rhizosphere can have important effects on the uptake of other nutrients.

5.5 Complementary ion effect

The complementary ion effect is defined as the influence of one adsorbed ion on the release of another from the surface of a colloid. When only a portion of the cations held by soil colloids is being exchanged, the release of a given cation from exchangeable form is easier as the retention strength or the strength of bonding of the complementary exchangeable cations increases. For example ammonium in the soil solution is exchanging with calcium on soil colloids. This exchange will take place more readily when the complementary cation on the exchange complex is aluminium rather than sodium. Ammonium will replace much more sodium than aluminium. The more strongly held trivalent aluminium tends to satisfy a greater part of the cation exchange capacity and permits the exchange of ammonium for calcium to proceed more completely.

6. Nitrogen

Nitrogen occurs in many forms in agricultural ecosystems because it can exist in a number of valence states within an ecosystem. For example, atmospheric N_2 (0 charge) gas is converted by lightening to various oxides and finally nitrate (+5 charge), which falls with the rain and is taken up by growing plants. Also N_2 gas can be converted to ammonia (-3 charge) by microbial fixation, with the NH_3 being used in various biochemical reactions within the plant. When plant residues decompose, eventually much of the N they contain undergoes several microbial conversions and eventually ends up back as nitrates. Also under anaerobic conditions, nitrates

can be reduced to various oxides and ultimately to N_2 gas again. Nitrogen in inputs such as fertilizers and manures is also subjected to these same microbial transformations.

A global inventory of N in the biosphere shows that N is distributed in terrestrial, oceanic and atmospheric components in the ratio 1:70:11818. Thus the bulk of the biospheric N is in the atmosphere. The atmospheric column on an hectare of land will contain approximately 8.4×10^4 Mg* ha^{-1} N (*1 Mg = 1 metric ton = 1000 kg). Yet for growing most cereals and non-legume forage crops, one has to apply large amounts of manure and/or fertilizer N. Total N content in the top 15-20 cm of surface soils ranges from 0.01% (or even less in desert soils) to more than 2.5% in peats. In any soil, N content in the sub-surface is generally less than in the surface layers since most organic residues are deposited on the soil surface.

6.1. Forms of soil nitrogen

There are two major forms of nitrogen in mineral soils: organic nitrogen and inorganic nitrogen.

6.1.1. Organic nitrogen : The bulk of soil N in a surface soil is present in the organic form. Soil organic N consists of proteins (20-40%), amino sugars such as the hexosamines (5-10%), purine and pyrimidine derivatives (1% or less) and complex unidentified compounds formed by reaction of ammonium with lignin, polymerization of quinones with nitrogen compounds and condensation of sugars and amines. A part of the organic N is also present as clay-humus complexes, which are resistant to decomposition. This would also explain why only a very small part of immobilized fertilizer N becomes available to the growing crop plants.

6.1.2. Inorganic nitrogen : Inorganic nitrogen includes ammonium nitrogen fixed by certain clay minerals, exchangeable ammonium and soluble ammonium and nitrate compounds. The amount of ammonium nitrogen fixed varies depending on the nature and amount of clay present; up to 8% of the total nitrogen in surface soils and 40% of that in subsoils may be in the fixed form. The amount of nitrogen in the form of soluble ammonium and nitrate compounds is seldom more than 1-2% of the total N present, except where large applications of inorganic nitrogen fertilizers have been made.

6.2. Nitrogen cycle

The interlocking succession of largely biochemical reactions of intake and loss of nitrogen in the course of time accompanied by many complex transformations is known as nitrogen cycle (Fig. 1). Major components of nitrogen cycle are briefly discussed.

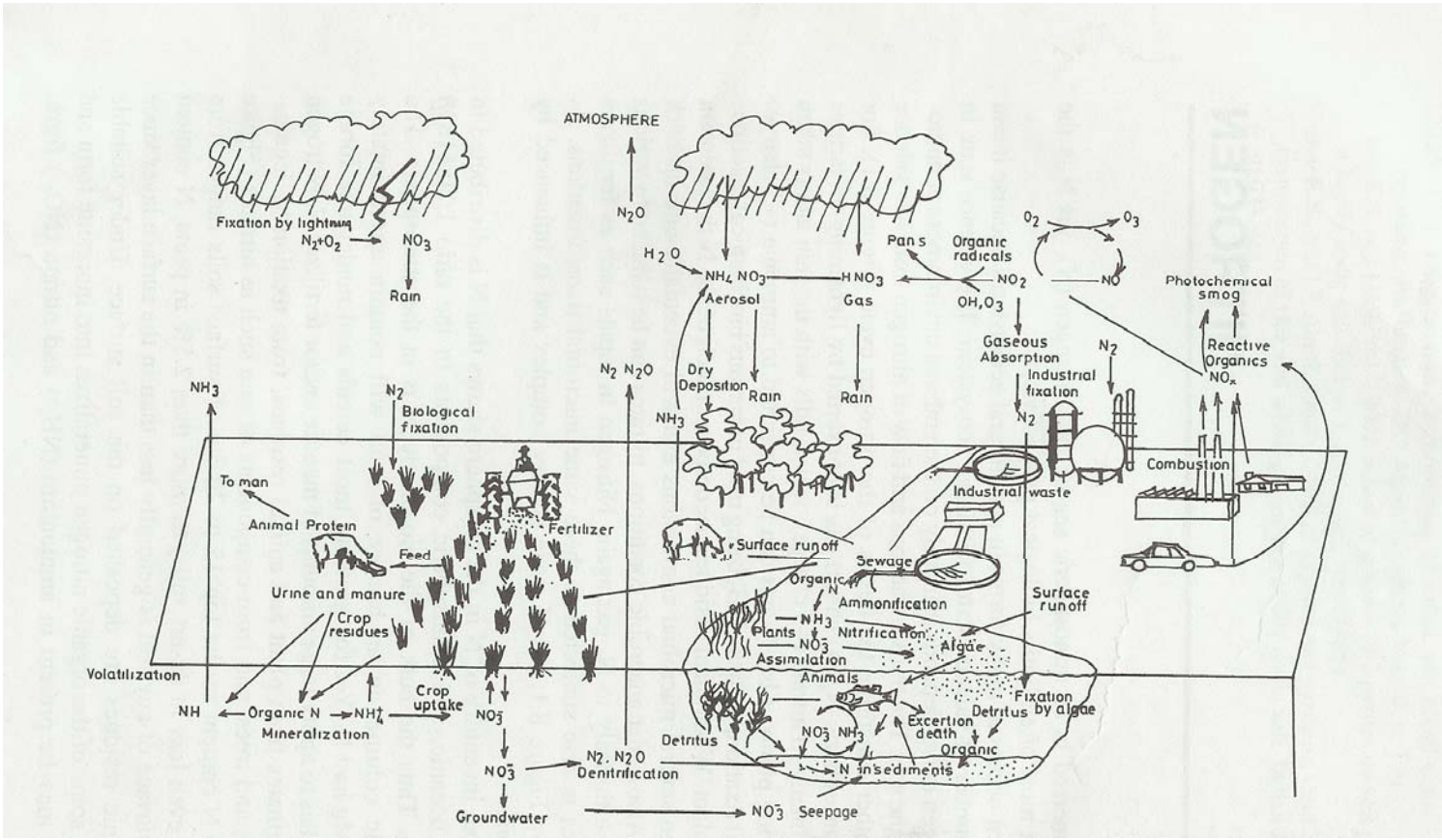


Figure 1. Schematic representation of the nitrogen cycle (adapted from Prasad and Power, 1997)

6.2.1. Immobilization: The process of tying up nitrogen in organic form is called immobilization. During the process of microbial decomposition of plant and animal residues especially those low in nitrogen, the plant inorganic nitrogen as well as that in the soil is converted to organic forms primarily as microbial tissue. The immobilized nitrogen in the microbial tissue becomes an integral part of the soil organic matter.

6.2.2. Mineralization: The conversion of organic nitrogen to more mobile inorganic nitrogen is called nitrogen mineralization. It is microbial process by which about 2-3% of organic nitrogen is mineralized annually. Mineralization takes place in three step-by-step, namely (i) Aminization, (ii) ammonification and (iii) nitrification. Of these three reactions, the first two are carried out by heterotrophic microorganisms, while the third one is carried out by autotrophic bacteria. The heterotrophs derive their energy from oxidation of organic carbon compounds, while the autotrophs obtain their energy from specific inorganic salts and their carbon from the carbon dioxide of the surrounding atmosphere.

(i) Aminization: Aminization is the process of conversion of proteins into amines and amino acids. The protein molecule is composed of a long chain of amino acids, all of which have the general type of structure $H_2N.CH.R$ ─ COOH, where R may be a hydrogen atom, a single methyl group, short carbon chain or a cyclic structure.

In the process of aminization, proteolytic enzymes cleave the protein molecule to polypeptides (long amino acid chains), peptides (short amino acid chains) and finally to the amino-acids.

It may be represented schematically by:

Proteins $\longrightarrow$ $R\text{-}NH_2 + CO_2$ + Energy + other products

Organisms responsible for aminization or proteolytion are bacteria (*Pseudomonas, Bacillus clostridium, micrococccus* and *serratia*) predominantly in neutral to alkaline pH and fungi in acidic pH. Amino acids, thus released, are: (a) taken by microorganisms, (b) taken up by certain plants and (c) further metabolised in to CO_2 and NH_4 etc.

(ii) Ammonification: The amines and amino-acids so released during aminization are further utilized by still other groups of heterotrophs with the release of ammonia or ammonium. This step is termed as ammonification and is represented as follows:

$$R - NH_2 + HOH \longrightarrow NH_3 + R - OH + \text{Energy}$$

$$+ H_2O \searrow$$

$$NH_4^+ + OH^-$$

Organisms responsible for amonifixation are a diverse population of bacteria, fungi and actinomycetes These are both aerobic and anaerobic The ammonium so released (a) may be converted to nitrite and nitrates (Nitrification), (b) may be absorbed directly by higher plants (Uptake), (c) may be utilized by heterotrophic organisms in further decomposing organic carbon residues (Immobilization), (d) It may be fixed in the lattice of certain expanding type clay minerals (Ammonium fixation and (e) It could slowly released back to the atmosphere as elemental nitrogen (Ammonium volatilization)

(iii) Nitrification*: This is a two-step process. In the first step ammonium is converted to nitrite (NO_2^-) and in the second step nitrite is converted to nitrate (NO_3^-).*

$$NH_4^+ + 2O_2 \longrightarrow NO_2^- + 2H_2O$$
$$2NO_2 + O_2 \longrightarrow 2NO_3^-$$

A group of obligate autotrophic bacteria known as Nitrosomonas are responsible for the first step, and another group of obligate autotrophic bacteria known as Nitrobacter for the second step. A few heterotrophs can also carry out nitrification, usually at much lower rates. Nitrates so formed may be: (a) taken up by plants (b) lost by leaching – creating health hazards by increasing nitrate concentration in underground water, (c) under anaerobic conditions lost by denitrification – creating atmospheric pollution problems, (d) immobilized by soil microorganisms. It is obvious that the factors that have a pronounced effect on the activity of nitrifying bacteria will affect nitrification. Some of these factors are: soil water content, aeration, pH, temperature, supply of ammonium and population of nitrifying organisms.

6.2.3. Ammonium fixation (Non-exchangeable ammonium) : Several clay minerals with a 2:1 expanding type structure (illites, montmorillonites etc.) have the capacity to fix ammonium and potassium ions. The 2:1 expanding type clay minerals are known for interlayer expansion, which occurs by swelling when the minerals are wetted, the water entering the interlayer space and forcing the layer apart. In these clay minerals octahedral sheet sandwiched between two tetrahedral sheets are loosely held together by very week oxygen-to-oxygen and cation-to-oxygen linkages, which facilitates expansion of the crystal lattice. Most cations can move freely into and out the crystal. Ammonium and potassium, however, are apparently just the right size ions (radius of NH_4^+ = 1.48 A^o and K^+ = 1.33 A^o) to fit into the "cavities" between the crystal units, thereby becoming fixed as a rigid part of crystal. These prevent the normal expansion of the crystal and in turn are held in a non-exchangeable form, from which these are slowly released for higher plants and micro-organisms as shown below.

$$\underset{\text{(Soil soln.)}}{NH_4^+} \rightleftharpoons \underset{\text{(Exchangeable)}}{NH_4^+} \longrightarrow \underset{\text{(Fixed)}}{NH_4^+}$$

In addition to clay minerals, soil organic matter can also fix NH_4^+ in non-exchangeable forms. Also NH_4-organic matter complexes are extremely resistant to microbial decomposition. Aromatic compounds and their unsaturated alicyclic counterparts are primarily responsible for NH_4-fixation by soil organic matter. Mechanisms responsible for ammonium fixation by soil organic matter are not yet well understood.

Important factors affecting ammonium fixation in soil are: (i) amount of ammonium added, (ii) soil water content, drying and wetting (iii) presence of other ions (especially K^+) and (iv) freezing and thawing.

6.2.4. Mechanisms of N loss: Fertilizer N applied to crop fields if not taken up by the crop plants or immobilized in soil may be lost by: (i) surface runoff, (ii) ammonia volatilization, (iii) ammonium losses from foliage, (iv) denitrified as N_2 or N_2O and (v) nitrate leaching.

(i) ***Surface runoff:*** When heavy rains follow an application of fertilizer N, part may be lost by surface runoff, particularly with urea and nitrates which are very soluble and not retained by soil particles (Prasad and Power, 1997). Moe *et al*. (1968) reported that losses were greater from ammonium nitrate than from urea with a simulated rain storm applying 12.5 cm of rain on a Lanesville silt loam Indiana, having a 13% slope and a fragipan layer at 60 to 95 cm depth.

(ii) ***Ammonia volatilization from soil:*** When urea is used as N fertilizer and applied to a moist soil, it is first hydrolyzed to ammonium carbamate and then to ammonium carbonate by the enzyme "urease", which is generally present in most soils. Ammonium carbonate readily degrades to NH_3 and O_2 gases. The whole process can be represented by equation:

$$CO(NH_2)_2 + 2H_2O \longrightarrow (NH_4)_2CO_3$$

Ammonium carbonate is unstable and decomposes as follows:

$$(NH_4)_2CO_3 + H_2O \rightleftharpoons 2NH_3 + 2H_2O + CO_2$$

$$\downarrow\uparrow$$

$$2NH_4OH$$

The pH of the soil in the vicinity of a urea prill may rise to 8.0 or above due to the formation of ammonium carbonate. This can result in loss of N by ammonia volatilization. Urea hydrolyzes fairly rapidly in soils. Losses of N by ammonia volatilization after fertilizer application to crops range from 0-50% of the N applied. The factors which control ammonia volatilization loss include: fertilizer form, method of application, soil pH, soil water content, cation exchange capacity of soil, wind velocity, crop, and stage of crop growth. Ammonia loss under upland conditions is greatest from ammonium or ammonium producing fertilizers applied on calcareous soils, where ammonium salts react with calcium carbonate to form precipitates of low solubility. Ammonia volatilization losses are very high when prilled urea is broadcast on a wet surface soil or on flood water in rice paddies. Ammonia volatilization losses from rice fields range from 7 to 48% of the quantity of fertilizer N applied, depending upon the dose of N, its method of application, and soil characteristics (Freney *et al*., 1990). Ammonium volatilization losses can be considerably reduced by band, or point placement of fertilizer urea or by use of coated urea or urea super granules (USG – a modified urea form where the size of each granule may be a few mm to 1 cm in diameter (Schnier *et al*., 1990).

(iii) ***Nitrogen losses from foliage:*** The total amount of N in the above ground biomass (grain plus stover) reaches a maximum well before maturity, often followed by a subsequent decline. In perennial species, much of this N is probably translocated and stored in roots as a reserve to initiate growth in the next season. However, for annual species (including most grain crops), there is little evidence of appreciable translocation of N to roots. Post-anthesis N losses from wheat ranged from 5.9 to 80 kg N ha^{-1} (Daigger *et al*., 1976; Harper *et al*., 1987; Papkosta and Gagianas, 1991) due to ammonia volatilization from the above ground biomass. In a recent study in Nebraska (Francis *et al*., 1993) post-anthesis fertilizer N losses ranged from 45 to 81 kg N ha^{-1} for irrigated corn.

(iv) ***Denitrification*****:** Denitrification is the process by which nitrates are reduced to N_2 gas or various gaseous oxides of N. In soils, most denitrification results from action of certain anaerobic and especially facultative microbes. Chemical denitrification can also occur, especially in acid soils. In microbial denitrification, nitrates serve as the oxygen source for the organisms. Soluble organic carbon compounds are used for microbial growth. For denitrification to occur, there are four requirements : (a) anaerobic environment, (b) presence of nitrates, (c) presence of soluble carbons, and (d) presence of denitrifying organisms.

When soils become submerged as in rice paddies or under heavy rainfall or irrigation under upland conditions, oxygen supply is temporarily depleted to the extent that denitrification can occur. Some anaerobic organisms which belong to the genera *Pseudomonas, Bacillus, Chromobacteria* and *Thiobacillus* can obtain their oxygen from nitrates and nitrites and release N_2 and N_2O. The most probable biochemical pathway is shown below:

$$\underset{-2H_2O}{\overset{+4H}{2HNO_3}} \longrightarrow \underset{-2H_2O}{\overset{+2H}{2HNO_2}} \longrightarrow \underset{-H_2O}{\overset{+2H}{2NO}} \longrightarrow \underset{-H_2}{\overset{+2H}{N_2O}} \longrightarrow -N_2$$

Because of the release of N_2O (a green house gas) and its involvement in ozone depletion, the process of denitrification has received considerable attention. The ratio of N_2 to N_2O and other oxides produced by denitrification depends on many environmental factors. However, generally the more anaerobic the environment, the greater the N_2 production. Estimates of N losses by denitrification vary from 3 to 62% of applied N in arable soils (Prasad and Power, 1997). Losses were greater from rice paddies. However, these values were arrived at by substracting ammonia volatilization losses from the unacounted ^{15}N.

While denitrification in soil is primarily controlled by three primary or proximal factors (namely, oxygen, nitrate and carbon), these primary factors are affected by several physical and biological factors (distal factors). Thus it usually becomes necessary to focus on distal rather than proximal factors as controllers of denitrification (Groftman *et al*., 1988). As already pointed out an anaerobic condition is the basic requirement for denitrification to proceed. Therefore, as oxygen concentration decreases denitrification increases. A source of energy (carbon) is essential for denitrification. Consequently denitrification generally increases with an increase in water soluble as well as with mineralizable soil organic C. In addition to oxygen, nitrate and carbon, soil pH also influences the rate of denitrification. Since baterial activity is generally low below pH 5, denitrification losses are very low in soil having pH 4 or less (Bremner and Shaw, 1958). Denitrification is most rapid at pH values 6 to 8. Soil temperatures most suited to denitrification are 25 to 60^oC; it is slow at lower temperatures and may be inhibited at temperatures above 60^oC (Tisdale *et al*., 1985). Denitrification loss was greatest in heavy (clay loam) soil. Also the increase in denitrification due to impoverished drainage was greater in clay loam than in loam soils; and least in sandy loam soil.

(v) ***Leaching:*** Amount and intensity of rainfall, quantity and frequency of irrigation, evaporation rate, temperature effects, soil properties (particularly texture and structure), the type of land use, cropping and tillage practices, and the amount and form of N applied interact in complex ways to determine the amount of nitrates leached through the effective root zone, vedose zone and eventually into the underground water. Nitrate leaching can be accelerated by preferential flow of water through worm or root channels and natural fissures and cracks in soils. This is especially evident in vertisols. Leaching of nitrate is likely to be greatest under bare fallow. Rennie *et al*. (1976) reported that leaching losses ranged between 0 from pasture land and 1082 kg N/ha from continuous fallow from 3.6 m. depth.

6.2 Ways to Reduce N Losses

The efficiency of N use is generally low ranging from 20 to 50 per cent (Subbiah *et al*., 1985; Goswami *et al*., 1988; George and Prasad, 1939). The low efficiency of N utilization by *kharif* cereals, specially rice, is a matter of great concern; rice alone accounts for 40% of the total fertilizer N consumption in India. Even if the fertilizer N efficiency could be increased by 10% it would reduce the N needs of India by about 1.5 million tonnes annually. Since fertilizer N use efficiency is determined by the biomass yield and nitrogen uptake by a crop, all factors that affect biomass yield and nitrogen concentration in plant will affect N use efficiency. These factors can be broadly classified into 5 groups, namely soil factors, crop factors, environmental factors, agronomic practices, and fertilizer management. The discussion on all the factors mentioned above is beyond the scope of this chapter and is restricted to fertilizer N management.

6.3.1. *Rate of nitrogen application*

Fertilizer nitrogen efficiency, in most crops, is generally greater at lower fertilizer levels than at higher levels, and decreases considerably when N rates increase beyond the optimum. Frances *et al*. (1993) reported that increase in fertilizer uptake by corn was greatly reduced beyond 100 kg N/ha. As a consequence much more nitrate N was lost at rates above 100 kg N ha^{-1} than below. Numerous data supporting this conclusion exist for most crops from all parts of the world.

6.3.2. *Methods of application*

Nitrogenous fertilizers are readily soluble in water and move rapidly in all directions from the place of application. Hence nitrogenous fertilizers applied on the soil surface reach the plant roots easily and rapidly. However in some specific situations nitrogenous fertilities have to be placed at an optimum soil depth for higher N use efficiency. For example on calcareous and alkaline soils and in rice paddies part of the N applied as ammonium or ammonium producing fertilizers (urea) is lost through ammonia volatilization. Under such situations the fertilizer placement at a few centimeters depth is considered desirable and profitable. Similarly placement of ammonium or ammonium producing fertilizers in the reduced zone of the submerged rice crop has been found to improve the efficiency of nitrogen (Prasad *et al*., 1970).

6.3.3. *Time of nitrogen application*

Timely fertilizer application is one agronomic technique which has helped considerably in increasing the nitrogen use efficiency. It is now very well established that for most crops, nitrogen must be applied in 2 or 3 split doses coinciding with the crop growth stages when nitrogen requirement is high. However, there may be some variation in the number of splits, stage of crop growth and quantity of N to be applied in each split from crop to crop and agroclimatic condition to condition. *Rabi* crops also responded well to the split application of nitrogen but not to an extent of *kharif* crops.

6.3.4. Nitrogen regulators

The losses of fertilizer nitrogen take place after hydrolysis and nitrification of fertilizer N. There are two types of materials which delay nitrification (i) fertilizer materials that release N slowly in the soil known as slow-release N fertilizers, (ii) nitrification inhibitors.

(i) ***Slow-release N fertilizers*****:** There are basically two groups of slow release fertilizers: (a) chemical compounds which have an inherently slow rate of dissolution such as Oxamide, urea form, isobutylidene diurea (IBDU) and urea acetaldehyde; (b) soluble fertilizers coated with a slowly permeable materials such as sulphur, plastic, wax,

neem extract, lac, cement and resins that regulate the rate of nitrogen release. These materials give 10-15% higher efficiency compared to urea (Prasad *et ali., 1971)*

(ii) Nitrification inhibitors: Nitrification inhibitors selectively retard the bacterial transformation of ammonium ions into nitrate in soil. Unlike ammonium, nitrates are highly susceptible to losses by denitrification, leaching and runoff. Besides reducing recovery of applied nitrogen, these loss mechanisms have adverse impact on the environment. The denitrification gases such as NO and NO_2 have been implicated in acid rain formation and development of photochemical smog, while enrichment of the stratosphere with N_2O leads to depletion of the ozone layer. The nitrates lost via leaching result in contamination of ground and surface water. Hence it is imperative that these loss mechanisms be reduced. Nitrification inhibitors have thus greater role to play, much beyond increasing the fertilizer N use efficiency.

Positive responses from such materials is indicated by slowing down the nitrification processes, retaining N in the ammoniacal form for a longer period and lengthening the period of N availability to crop plants. Use of nitrification inhibitors thus provides a possible approach for the maintenance of a chosen NH_4^+:NO_3^- ratio in soil (Shaviv *et al*., 1987).

Some recommendations on slow release N fertilizers for increasing efficiency are summarized in Table 2.(Source: Tandon (1989)

State	Technique	Situation
Rice		
Andhra Pradesh	Neem cake mixed urea	Top dressing at panicle initiation stage
Kerala	Neem cake mixed urea (1:5 ratio)	Top dressing
Kerala	Soil cured urea (6:1 ratio) stored for 24-48 hours in shade	Top dressing
Karnataka	Soil cured urea (50-100 kg soil) kept for 24 hours	Top dressing
Karnataka	Neem cake blended urea	Basal
Meghalaya	Soil-cured urea (5:1) stored for 48-72 hours	Top dressing
Meghalaya	Rock phosphate coated urea	Basal
Orissa	Coated urea	Basal
Tamil Nadu	Urea mixed with gypsum (1:3)	Basal
Tamil Nadu	Neem cake blended urea (20% cake by weight)	Top dressing
Tamil Nadu	Urea treated with coaltar (100 kg urea, 1 kg coaltar, 1.5 litre kerosene)	Basal
Rajasthan	Soil cured urea (5:1) stored for 24 hours	Top dressing
Rajasthan	Neem cake treated urea (100 kg urea, 0.5 kg coaltar, 1 litre kerosene)	Top dressing
Chillies		
Andhra Pradesh	Neem cake blended urea (150 kg urea plus 27.5 kg neem cake)	3 times at 30, 60, 90 DAT
Banana		
Tamil Nadu	Neem cake coated urea	Top dressing twice in 3rd and 5th month

High concentrations of ammonium in the soil surface or in flood water of rice soil creates the conditions favourable for the loss of applied nitrogen through of ammonia volatilization. Urease inhibitors are chemicals that may be added to urea to prevent or delay hydrolysis of urea and thus decrease nitrogen losses by ammonia volatilization.

6.3.5. Urea supergranules (USG)

Point placement of fertilizer nitrogen has been found to reduce N losses (Cao *et al*. 1984ab). Based on this theory USG were developed in India and their higher efficiency compared to urea prilled was observed in field studies by many workers (Thomas and Prasad, 1982, 1987; Prasad and Prasad, 1980; Savant *et al*., 1983). The higher efficiency of USG as compared to urea is attributed to (i) slower urea hydrolysis most likely because of less contact of urea with soil particles, (ii) retention of N in soil for a longer period due to slower rate of formation of ammonium nitrogen, and (iii) lower nitrite concentration with USG. The creation of a high concentration of ammonia by the placement of USG may act as a nitrification inhibitor (Thomas and Prasad, 1982). The per cent increase in grain yield of rice (Prasad *et al*., 1989) with USG over PU ranged from 3.9 to 30.5, the mean being 10.7% (Table 3).

Table 3. Grain yield (q/ha) of rice as affected by urea and urea supergranules

Sources of N	Year										
	1977[1]	1978[1]	1979[2]	1980[2]	1981[3]	1982[4]	1983[4]	1984[5]	1986[6]	1987[6]	Mean
Urea	39.7	51.7	32.5	41.6	35.4	40.0	38.5	48.0	46.5	43.2	41.7
USG	41.8 (5.3)	56.5 (9.3)	37.3 (14.8)	46.2 (11.0)	46.5 (30.5)	41.9 (4.7)	40.0 (3.9)	52.9 (10.2)	49.5 (6.4)	48.1 (11.3)	46.0 (10.7)
CD at 5%	2.0	1.6	2.4	1.9	3.0	0.5	0.4	NS	3.0	3.7	-

Figures in parentheses indicate per cent increase with USG over urea

1. Prasad and Prasad (1980), 2. Thomas and Prasad (1987), 3. Singh (1985), 4. Sudhakara and Prasad (1986), 5. Prasad and Singh (1984), 6. Pichai (1988)

6.3. Nitrogenous fertilizers

A large number of fertilizers containing nitrogen are available. These can be broadly grouped into four classes, namely ammonium, nitrate, ammonium and nitrate and amide containing fertilizers. These are given in Table 4.

Table 4. Nitrogen content and other characteristics of nitrogenous fertilizers

Fertilizers	Total N (%)	Other nutrients (%)	Equivalent acidity/ basicity (kg $CaCO_3$)	Other characteristics
Ammonium fertilizers				
Anhydrous ammonia	82.2	-	147	Marketed as compressed liquid gauge pressure –75 pounds/sqm at 50°F and 197 pounds/sqm at 100°F
Ammonium sulphate	20	24% S	107-110	Marketed in fine to medium fine crystals, non-hygroscopic

Fertilizers	Total N (%)	Other nutrients (%)	Equivalent acidity/ basicity (kg Ca/CO_3)	Other characteristics
Ammonium chloride	26	-	128	Not widely used, manufactures in white, crystalline form, non-hygroscopie
Nitrate fertilizers				
Sodium nitrate	16	20% Na	29	Naturally occurring chemical. In early 20th century it was prime source of nitrogen. Very hygroscopic, marketed in grey granules
Calcium nitrate	15	19% Ca	21	Available in white crystalline highly hygroscopic and not marketed in India
Ammonium and nitrate fertilizer				
Ammonium sulphate nitrate	26 (19.25% NH_4& 67.5% NO_3)	5-6% S	93	Slightly hygroscopic
Calcium ammonium nitrate	25 (12.5% NH_4 & 12.5% NO_3)	81% Ca	Neutral	Slightly hygroscopic but excellent handling qualities
Amide fertilizers				
Urea	46	-	80	Most popular, cheap. Free flowing fertilizer. It comes in white prilled form
Calcium cynamid	20	54% Ca	-	It is no longer produced

6.5.1. Bulky organic manures: These include FYM, rural compost, town compost, biogas compost, night soil, sludge, green manures and other bulky sources of organic matter.

6.5.2. Concentrated organic manures: These include oil cakes, blood meal, fish manure, meat meal and wool waste.

The application of organic manure improves the physical, chemical and biological conditions of soils besides providing plant nutrients. The humus of organic manures is a colloidal material with negative electric charge and is coagulated with cations. With organic manures soil particles form granules. Soil with more granules is less sticky, have a better permeability, and greater water holding capacity. Organic manures also increase buffering capacity of soils. Soils with higher buffering capacity are capable of regulating the soil pH. Thus addition of organic manures create a good environment for crop growth.

7. Phosphorus

In contrast to nitrogen, which constitutes 78% of the earth's atmosphere, phosphorus is present as mineral deposits, which are a nonrenewable natural resource. Total phosphorus content of soils is generally less than for total N or K; about one-tenth to one-fourth that of

nitrogen, and one twentieth that of K (Brady, 1990). Total P content in surface soil and subsoil may vary from a few mg kg^{-1} soil to over 1 g kg^{-1}soil. Also in contrast to soil N, which is concentrated in surface soil, P content in subsoil may be less, equal or greater than that in surface soil.

7.1. Form of soil phosphorus

Phosphorus is present in soils in both organic and inorganic forms.

7.1.1. Inorganic phosphorus: Inorganic P in soil is mostly present as compounds of Ca, Fe and Al; Ca-phosphates dominate in neutral to alkaline soils, while Fe and Al-phosphates dominate in acid soils. At any specific time very small amounts of phosphate are present in soil solution in equilibrium with the solid inorganic phase. The concentration of P in soil solution is commonly approximately 0.05 mg l^{-1} and seldom exceeds 0.3 mg l^{-1} in unfertilized soils.

The ionic form of inorganic P are pH dependent. Between pH values of 4.0 and 6.0, most of the P in soil solution is present as $H_2PO_4^-$ ion, the form in which it can be readily adsorbed by plant roots. Between pH 6.5 and 7.5, P in soil solution is present partly as $H_2PO_4^-$ and partly as HPO_4^{2-} ion. HPO_4^{2-} ions can also be taken up by the plant roots but not as readily as $H_2PO_4^-$ ions. Between pH 8.0 and 10.0 HPO_4^{2-} ion is dominant. Under such conditions Na^+ ions dominate the soil cation exchange complex and some phosphate is present as sodium phosphate, making HPO_4^{2-} ions available on hydrolysis. Beyond pH 10.0 the dominant ionic form of P is PO_4^{3+} and unless present as sodium phosphate, P is not available to crop plants. On the other extreme i.e., below pH 3.0, which is generally not found in cultivated soils, P would be present as H_3PO_4 (phosphoric acid), a very reactive form. That is why in highly acid ultisols and oxisols, phosphate fixation or reversion is rapid and large amounts of phosphate fertilizers are required to obtain good crop growth.

7.1.2. Organic phosphorus: The amount of P present in organic form in soils varies from a few milligrams to about 0.5 g kg^{-1} soil (20-80% total P), depending upon a number of factors such as climate, vegetation, soil texture, land use pattern, fertilizer practices, drainage and irrigation, etc.; a number of these factors are interdependent. There are three groups of organic-P compounds in soil : (i) inositol phosphates (phosphate esters of inositol $C_6H_6(OH)_6$, (ii) nucleic acids and (iii) phospholipids.

Inositol phosphate: Inositol phosphate is thought to be of microbial origin and can exist in several stereo-isomeric forms; phosphate esters of myo-, scyllo-, neo- and chrio-inositol have been characterized in soil (Cosgrove, 1962). Myo-inositol hexophosphoric acid (phytic acid) is usually a major pool of organic P. It is fairly stable in alkaline medium, but gradually hydrolyzes to a range of intermediate inositol phosphates and finally to inositol, in acid media; the optimum pH for hydrolysis being near 4.0. Enzymes phytases also hydrolyze myo-inositol phosphates. Inositol phosphates make up from less than 1 to 62% of total organic P in soil.

Nucleic acids: Ribonucleic acid (RNA) and deoxyribonulcleic acid (DNA) are found in all living beings. For a time it was believed that at least half of the organic P in soils was present in nucleic acids, but when specific methods of identification and measurements were applied, much lower values were found.

Phospholipids: Most reported values of soil phospholipids fall within the range of 0.2 to 14 mg P kg^{-1} soil (Kowalenko and McKercher, 1971) representing less than 5% of the organic P. Phosphatidyl choline (lecithin) and phosphatidyl ethanolamine are the predominant phospholipids in soil

7.2. Phosphate retention or fixation in soil

Phosphorus is highly immobile in soils and generally is fixed near the point of application. Phosphorus fixation is a serious problem in both acidic and alkaline soil.

7.2.1. Reaction of phosphorus in acid soils: In acidic soils, P is fixed by (i) precipitation of iron, aluminium and manganese ions, (ii) reaction with hydrous oxides, and (iii) reaction with silicate clays.

Precipitation by iron, aluminium and manganese ions : Some soluble iron, aluminium and manganese are usually found in strongly acid mineral soils. Reaction with the $H_2PO_4^-$ ions would immediately occur, rendering the phosphorus insoluble and unavailable to plants. The chemical reactions occurring between the soluble iron and aluminium and the $H_2PO_4^-$ ions would result in the formation of hydroxy phosphates.

Reaction with hydrous oxides : Most typical soils contain appreciable quantifies of hydrous oxides of iron, aluminum titanium and manganese. The oxides are colloidal in nature and are characterized by a surface of negatively charged OH groups. Thus they are amphoteric, having either negative, zero or positive charge, depending on the pH. The pH at which there are equal number of positive and negative charges on the surface defines the point of zero charge (PZC) of the oxide, which is approximately 8.5 and 9, respectively for aluminum and iron oxides. At pH level below the PZC, phosphorus and other anions such as SO_4^{2-} are attracted to the positively charged oxide surface.

H_2PO_4 ion reacts not only with the soluble iron, aluminium and manganese but also with insoluble hydrous oxides of Al and Fe elements, such as gibbsite [$Al_2O_33H_2O$] and goethite [$Fe_2O_3.3H_2O$]. The actual quantity of phosphorus fixed by these minerals in acid soils quite likely exceeds that phosphorus fixed due to chemical precipitation by the soluble iron, aluminum and manganese cations.

The compound formed as a result of fixation by iron and aluminum oxides are likely to be hydroxy phosphates, just as in the case of chemical precipitation described above. Their formation can be illustrated by means of the following equation if the hydrous oxide of Al is represented as aluminum hydroxide.

$$Al(OH)_3 + H_2PO_4 \text{ (Soluble)} \rightleftharpoons Al(OH)_2H_2PO_4 \text{ (Insoluble)} + OH^-$$

(iii) Reaction with silicate clays: Soil clay are composed of layers of silica and alumina which are combined to form silica-alumina sheets. The phosphorus may combine directly with 2:1 montmorillonite and 1:1 kaolinite silicate clays by:

(a) Replacing a hydroxyl group from an aluminum atom.

$$(OH)_8\ Al_4Si_4O_{10} + H_2PO_4 \rightleftharpoons HPO_4(OH)_7Al_4Si_4O_{10} + OH^-$$

(b) Forming a clay-Ca-phosphate linkage: A clay-Ca-H_2PO_4 linkage might occur at pH values slightly less than 6.5.

Phosphate can also participate in single anion exchange. Certain positively charged colloidal particles are the seat of exchange between two anions. This can be illustrated with $AlOH_2^+$ to represent the positively charged particle.

$$\left[AlOH_2^+\right] OH + H_2PO_4 \rightleftharpoons \left[AlOH^+\ H_2PO_4 + OH\right]$$

7.2.2. Retention of phosphate in alkaline soils : An increase in pH of a medium favours the formation of di- and tri-calcium phosphate ions. Solubility of calcium orthophosphate decreases in order mono-, di- and tri- calcium phosphate. While the specific mechanisms for the formation of these compounds are not well established, their relationship to each other can be shown as below.

$Ca(H_2PO_4)_2 + CaCO_3 + H_2O \rightarrow 2CaHPO_4.2H_2O + CO_2$

$6CaH\ PO_4.2H_2O + 2CaCO_3 + H_2O \longrightarrow Ca_8H_2(PO_4)_6.5H_2O + 2CO_2$

$Ca_8H_2(PO_4)_6.5H_2O + CaCO_3 \rightarrow 3Ca_3(PO_4)_2 + CO_2 + 6H_2O$

Thus, phosphate ions coming in contact with solid phase $CaCO_3$ are precipitated on the surface of these particles. Calcium carbonate occurring in soil primarily as the mineral calcite is responsible for phosphorus absorption. This mineral develops a negative charge due to the greater tendency for Ca^{2+} ions than CO_3^{2-} ions to go into solution. Cations such as Mg^{2+} and OH^+ can be absorbed on calcite surfaces but more important, phosphorus ions become chemisorbed at the surface. This reaction of phosphorus with calcite surfaces apparently involves absorption of small amounts of phosphorus followed by precipitation of calcium phosphate at higher concentration.

The initial adsorption is thought to occur at certain sites where phosphate ions form surface clusters. These clusters of amorphous calcium phosphate act as nuclei for subsequent crystal growth. Dicalcium phosphate, octacalcium phosphate and hydroxy apatite are the principal crystalline phosphates that have been identified. The adsorption and precipitation of phosphorus on to calcite appears to be occurred in sequence of dicalcium phosphate and then octa calcium phosphate. The octacalcium phosphate probably occurs as a coating on dicalcium phosphate.

In soils containing large amount of active magnesium, a number of insoluble magnesium phosphate compounds such as dimagnesium phosphate trihydrate, tri-magnesium phosphate and struvite may form. However, these magnesium phosphates are more soluble than dicalcium phosphate and octacalcium phosphate.

7.3. Factors affecting phosphorus retention in soils:

Factors affecting phosphorus retention in soils include hydrous oxides of iron and aluminium, types of clay, clay content, contents of morphous colloids, amount of calcium carbonate, soil pH, (vii) associated cations, associated anions, saturation of sorption complex, organic matter content, temperature, and time of application.

7.3.1. Hydrous metal oxides of iron and aluminum: These substances, particularly hydrous ferric oxide gel have the capacity to sorb very large amount of phosphorus. Crystalline hydrous metal oxides are capable of retaining more phosphorus than layer silitates. Less crystalline oxides, have larger phosphorus fixation capacity because of their greater surface areas.

7.3.2. Types of clay: Phosphorus is retained to a greater extent by 1:1 clay (kaolinite) than by 2:1 clays, probably due to the higher amounts of hydrated oxides of iron and aluminum associated with kaolinitic clays. In addition, kaolinite develops pH-dependent charges on its edges which can enter into sorption reactions with phosphorus. Clays such as kaolinite with a low SiO_2/RaO_3 ratio will fix larger quantities of phosphorus than clays with high ratio.

Kaolinite with a 1:1 silica/alumina lattice has a larger number of exposed hydroxyl groups in the gibbsite layer which can be exchanged for phosphorus.

7.3.3.Clay content: Soil containing large quantities of clay will fix more phosphorus than those composed of small amounts of clay because of large surface area exposed in soils containing large quantities of clay.

7.3.4. Content of amorphous colloids: Soils containing large amount of amorphous colloids fix large amount of phosphorus. Amorphous minerals have great specific surface and high anion and cation-exchange capacity. Amorphous aluminosilicate mineral like allophane have a large negative charge which is likely or entirely balanced by complex aluminum cations. Phosphorus becomes adsorbed by reacting with these aluminum cations.

7.3.5. Amount of calcium carbonate: A minor portion of P sorption capacity of soils originates from $CaCO_3$ and much of the adsorption attributed to it, however, may actually be due to hydrous ferric oxide impurities. Both amount and reactivity of $CaCO_3$ will influence P fixation.

7.3.6. Soil pH : Soil pH has a profound influence on the amount and manner in which soluble phosphorus becomes fixed. Phosphorus availability in most soils is maximum in the pH range 6.0 to 6.5. At low pH values, the retention results largely from the reaction with iron and aluminum and their hydrous oxides. As the pH increases, the activity of these reactants is decreased until, within the pH range just given, the activity of phosphorus is at a maximum. Above pH 8, the ions of Ca and Mg as well as the presence of the carbonates of these metals in the soil, cause precipitation of the added phosphorus and its availability again decreases. However, if a soil is basic due to the presence of cations such as sodium rather than Ca, a decrease in P availability would not necessarily be observed with a continuing increase in soil pH. Hence, the presence of Ca or Mg ions must accompany high pH values for decrease in the solubility of soil phosphorus.

7.3.7. Cation effects : Divalent cations enhance P sorption compared to monovalent cations. For example, clay saturated with Ca^{2+} can retain greater amounts of P than those saturated with Na or other monovalent ions, because the positively charged edge sites of crystalline clay minerals having Ca are more accessible to the phosphorus anions. Concentration of exchangeable aluminum is also an important factor in P retention in soils as evident with following illustrastion.

$$Al + 2\ H_2O \rightleftharpoons Al(OH)_2^+ + 2H^+$$

$$Al(OH)_2^+ + H_2PO_4^- \rightleftharpoons Al(OH)_2H_2PO_4\ (K_{sp}=10^{-29})$$

It has been reported that 1 meq of exchangeable Al per 100 g of soil when completely hydrolyzed may fix up to 102 ppm of P in solution.

7.3.8. Anion effects : Both inorganic and organic anion can compete in varying degrees with P for sorption sites, resulting in some cases in a decrease in the sorption of added P or a desorption of retained P. Weakly held inorganic anions such as NO_3^- & Cl^- are of little consequence, whereas specifically sorbed anions and acids such as hydroxyl, silicic acid, sulphate and molybdate can be competitive. The strength of bonding of the anion with the sorption surface determines the competitive ability of that anion.

The impact of organic anions on reduction of P sorption is related to their molecular structure and the pH of the system. Organic anions which form stable complexes with the iron and aluminum of soil components are particularly effective in reducing P sorption. Oxalate, citrate, and polygalacturonate have been shown to be specifically sorbed at soil surface in a

similar manner to phosphate. Anions of tricarboxylic acids are more effective in reducing phosphate sorption than are those of dicarboxylic and monocarboxylic acids.

7.3.9. Saturation of the sorption complex : Both sorption and desorption of P are strongly influenced by the extent of saturation of the sorption complex. Higher the number of sites available for reaction – more amount of P will be adsorbed. Ease of desorption is greater at higher saturation because P is held less tightly with increasing surface coverage.

7.3.10. Organic matter : The effect on phosphorus availability of different compounds arising from the decomposition of organic residues is attributed to humus extracts. This has been variously described as resulting from: (i) the formation of phosphohumic complexes which are more easily assimilated by plants, (ii) anion replacement of the phosphate by the humus ions, (iii) the coating of sesquioxide particles by humus to form a protective cover and thus reduce the P fixing capacity of the soil. Certain organic anions arising from the stable complexes with iron and aluminum, thus preventing their reaction with P. These complexes release phosphorus previously fixed by iron and aluminum by the same mechanism. The anions that are most effective in replacing phosphates are citrate, oxalate, tartrate, malate, malonate.

The part of favourable effect is likely related to the decomposition of organic residues which is accompanied by the evolution of CO_2. This gas when dissolved in water forms carbonic acid, which is capable of decomposing certain primary minerals. The greatest effect of carbonic acid in dissolving soil phosphorus is probably under slightly acid to alkaline conditions.

7.3.11. Temperature : High temperatures are expected to slightly increase the molar solubility of compounds such as apatide, hydroxy apatide, octacalcium phosphate, variscite and strengite. Mineralization of P from the organic matter is dependent on biological activity and increase in temperatures stimulates biologic activity. Dissolution of granules of water soluble P and resultant reactions with soil components to produce less soluble reaction products are hastened by higher temperatures and thus P retention increases at higher temperatures.

7.3.12. Time of application : The compounds precipitated during the reaction of phosphorus fertilizer salts in soils are metastable and will usually change with time into more stable and less soluble compounds.

7.4. Phosphorus deficiency symptoms in plants

Phosphorus is readily mobilized in plants and when a deficiency occurs, the P contained in older tissues is transferred to the active meristematic region. Darker green colour of small leaves than normal with reddish-purple cast and dying tips indicate P deficiency. Purpling in young plants is more distinct. Other symptoms in small grain crops such as wheat include stunted growth, poor tillering and delayed maturity.

7.5. Phosphate fertilizers

All phosphate fertilizers are produced from phosphate rock; the only exceptions are polyphosphates produced from the elemental P. Global phosphate rock reserves are estimated at 41,000 million Mg. Phosphorus rock basically consists of fluor-, hydroxy-, chlor-, and carbonate apatites; fluroapatite being the dominant mineral. Apatites have insular structure and therefore the phosphate they contain are not available to growing crop plants. This can be achieved by two ways, namely, reacting the phosphate rock with a strong acid such as sulphuric, nitric, hydrochloric or phosphoric acid, or by employing heat (very high temperatures, generally about 1400^oC and high pressure). When an acid is employed it decomposes the mineral and its anionic component such as SO_4^{2-}, PO_4^{3-}, NO_3^- or Cl^- reacts

with calcium in the rock. When heat is employed, the fluoride, chloride, hydroxy or carbonate ions present in the mineral are released as F, Cl or CO_2 gases or water vapours, and the crystal structure of mineral is broken down. When finely ground rock phosphate is applied to acid soils, soil acids decompose the apatite minerals in the same way as strong acids, but the slower rate of reaction depends upon soil pH and potential acidity. There are number of P fertilizers manufactured and used in crop production. These are given in Table 5.

Table 5. Composition of phosphatic fertilizers

Fertilizers	Phosphorus (P_2O_5) (%)			Nitrogen (%)				Calcium (CaO) (%)	Magne-sium (MgO) (%)
	Total	Available	Water soluble	Total	Ammoniacal	Nitrate	Amide		
Single super phosphate	18-20	16.5-17	16	-	-	-	-	25-30	0.5
Triple super phosphate	46	43	42.5	-	-	-	-	17-20	0.5
Diammonium phosphate	46	41	41	18	18	-	-	-	-
Ammonium phosphate sulphate (16:20:0)	20	19.5	19.5	16	16	-	-	-	-
Ammonium phosphate sulphate (20+20+0)	20	20	17	20	18	2	-	-	-
Ammonium phosphate sulphate nitrate	20	20	17	20	17	3	-	-	-
Urea ammonium phosphate (28:28:0)	28	28	25,2	28	9	-	19	-	-
Urea ammonium	24	24	20.4	24	7.5	-	16.5	-	-

phosphate (24:24:0)									
Nitro-phosphate (20:20:0)	20	20	5.4	-	-	-	-	-	-
Udaipur rock phosphate	20-35	-	-	-	-	-	-	-	-
Mussoorie rock phosphate	23-34	-	-	-	-	-	-	-	-
Jhabua rock phosphate	31-38	-	-	-	-	-	-	-	-

In addition to the P fertilizers listed in Table 5, mention may be made of poly and thermal phsopahtes.

Ammonium polyphosphate: This product was developed by Tennessee Valley Authority (TVA) of USA by ammoniation of mixtures of electric furnace superphosphoric acid and up to 30% of the P as wet-process orthophoric acid. This results in a granular product with a grade of 15-62-0 (27% P). Both liquid and solid ammonium polyphosphate are available. In addition to high nutrient content, ammonium polyphosphates have the advantage of chelating micronutrients and reduced P-fixation due to time required for their conversion to orthophosphates.

Thermal phosphates: These fertilizers are made by the heat treatment of phosphate rock. There are two processes, namely, "calcinations" and "fusion" by which thermal phosphates are made. In calcinations the heating is done below the melting point of the mixture, while in fusion it is done above the melting point, so that the material fuses together.

7.6. Efficient utilization of fertilizer phosphorus

Due to the fast reactivity of soluble P in fertilizers with the cations in soil solution and cations and anions on the surface of clay and organic matter particles, P does not move far from the point of placement. Therefore the key to efficient P utilization is deep placement near the growing young roots of the crop. Although a few recommendations are available for foliar application of soluble phosphate fertilizers, most fertilizer phosphate is applied to soil before or at seeding of a crop. Deep placement in a standing crop without damaging root system is neither possible nor desirable due to the immobile nature of P. However, in recent years some recommendations have emerged for split application of P in rice; top dressing in such cases has to be quite early in the crop's life span and can provide a solution in situations where phosphate fertilizers are not applied before transplanting.

A knowledge of the early rooting habits of various crop plants is helpful in determining the most satisfactory method of placing phosphate fertilizer. If a vigorous tap root is produced early, such as cotton, tobacco and most grain legumes, application may best be made directly under the seed. If many lateral roots are formed early, such as in cereals, side placement may be best. Increased root growth in the P-fertilized volume of soil compared to unfertilized soil is well known.

A rule of the thumb is that for row sown corps, phosphate must be placed; the wider the interrow spacing, the greater is the advantage of P placement. Only for those corps which are sown broadcast, incorporation in soil may be as good as deep placement. By banding, fertilizer P comes into less direct contact with soil, reducing the opportunity for fixation of soluble P. Likewise, often by using larger fertilizer P particles which are subject to less fixation is sometimes more effective than using finely ground P fertilizer.

In multiple cropping systems the recommendations is to give priority to those crops which are more responsive to P and are poor users of residual P (wheat, potato) as compared to crops which are benefit from residual P (rice, corn).

8. Potassium

In most soils, potassium is present in much larger amounts than nitrogen and phosphorus; the earth's crust contains about 1.9% K. The potassium content in surface soil may vary from a few hundred kilograms per hectare in light sandy soils to about 50,000 kilograms per hectare in heavy clayey soils rich in micas and 2:1 layer silicates. Almost all potassium is present in inorganic form; and is fairly well distributed throughout the profile, and in some cases sub-soils may even have more potassium than surface soils.

8.1. Forms of soil potassium

Potassium is present in soils in four different forms, namely, primary minerals, fixed, exchangeable, and solution K. These four forms of K are interrelated.

8.1.1. Primary mineral K : The potassium bearing minerals in soils are the feldspars orthoclase [K, Na)$AlSi_3O_8$] and microline [(Na, K)AlS_iO_4] and the micas muscovite [$KAl_3Si_3O_{10}(OH)_2$], biotite [K $(MgFe)_3AlSi_3$ O_{10} $(OH)_2$] and phlogopite [KMg_3Al $Si_3O_{10}(OH)_2$]. While feldspars are generally present in the coarser fraction of soil, micas are predominantly in the clay fraction. Potassium in mineral form in soils may vary from 5000 to 25000 mg K kg^{-1} soil (0.5 to 2.5%) (Tisdale *et al*., 1985).

8.1.2. Non-exchangeable or fixed K : Non-exchangeable K is distinct from mineral K in that it is not bonded covalently within the crystal structure of soil mineral particles, instead, it is held between adjacent tetrahedral layers of micas, vermiculites and integrade minerals (Sparks, 1987). Micas (muscovite, biotite and phlogopite) have K fixed in the interlayer spaces. Bonding of K is stronger in dioctahedral mica (muscovite) than in tri-octahedral micas (biotite and phlogopite). Weathering of micas releases K in soils. Due to variation in binding strength, the rate of release of K from different micas differs. Rate of potassium liberation from biotite is 13 to 16 and 75 to 105 times faster than from phlogopite and muscovite, respectively. The sequence of K release from K-bearing minerals by oxalic or citric acid has been found to be: biotite > microline ≈ orthoclase > muscovite.

8.1.3. Exchangeable K : This is the potassium held in exchange complex of 2:1 layer silicates. Thus soils containing smectite have more exchangeable K than those containing illite, which in turn have more than the soils containing kaolinite. The amount of exchangeable K in soils may vary form 40 to 600 mg K kg^{-1} soil (Tisdale *et al*., 1985). Exchangeable K in soils is generally determined by extracting soil with neutral 1 N ammonium acetate and therefore includes water soluble K; the entire value is known as available K in soils.

8.1.4. Soil solution K : This is the potassium present in soil solution and is measured by extracting the soil with distilled water. Water soluble K in soil may vary from 1 to 10 mg K kg^{-1} soil. Solution K concentration is important for successful crop production.

There is a continuous transfer of mineral K to exchangeable K and fixed K and from there to solution K; the process may reverse to the fixed K stage under some soil conditions or when heavy K dressings are made. The entire equilibrium may be represented as below:

Non-exchangeable K ⇄ slow exchangeable K ⇄ rapid exchangeable K ⇄ soil solution K

8.2. Potassium fixation

Potassium fixation is defined as the conversion of soil solution or exchangeable K into non-exchangeable forms and was once considered a negative soil property causing a drastic reduction of plant available K. However, this view is no longer held and K-fixation is considered beneficial, because it reduces K losses by leaching and luxury consumption, yet it maintains a potentially available K pool (Pearson, 1952).

A number of factors such as clay mineral, soil pH, wetting and drying, potassium fertilization, and freezing and thawing affect potassium fixation in soils.

8.2.1. Clay minerals: The amount of K fixed by a soil depends much upon its clay content; both quantity and quality are important. In general, the greater the clay content, greater is the K fixation. As regards the kind of clay minerals, illite, weathered mica, vermiculite, smectite and interstratified minerals fix K, while kaolinite fixes very little.

8.2.2. Soil pH: In acid soils the presence of Al^{3+} and aluminium hydroxide cations and their polymers occupy the K-selective binding sites on clay minerals. Also the presence of hydroxyl aluminum-iron interlayer groups under acid conditions prevents the collapse of silica layers in expanded clay minerals and therefore prevent the entrapment of K. Thus when pH of acid soil is raised, it affects K-fixation in two complementary ways: (i) precipitation of Al^{3+} due to higher OH^- ion concentration and (ii) progressive hydroxylation of monomeric and polymeric forms of hydroxyl-Al ions, whose positive charge is gradually neutralized. Liming will thus increase K-fixation especially in temperate region soils where 2:1 layer silicates having Al^{3+} dominate. Liming may have very little effect on K-fixation in tropical soils where kaolinite dominates (Ritchey, 1979; Malavolta, 1985).

8.2.3. Wetting and drying: Air drying soils high in exchangeable K will result in fixation and a decline in exchangeable K. However, drying of moist soils, particularly subsoils, with low to medium levels of K is reported to increase exchangeable K. This has been attributed to the exfoliation of edge-weathered micas and exposure in interlayer K.

8.2.4. Potassium fertilization: Adding large amounts of fertilizer K generally results in increased K fixation because solution K concentration is greatly increased, pushing the equilibrium between soluble and fixed K towards the fixed K pool.

8.2.5. Freezing and thawing: Alternate freezing and thawing may result in increased exchangeable K in some soils; however, reverse may also happen in illitic soils having high exchangeable K (Tisdale *et al*., 1985).

8.3. Leaching of potassium

Potassium leaching from a soil fluctuates in accordance with the quantity, timing and intensity of rainfall. Despite low K content in tropical soils, considerable K may be lost by leaching due to heavy rains. Liming generally reduces K leaching due to increased K fixation.

8.4. Potassium fertilizers

There are two major potash fertilizers, namely, potassium chloride or muriate of potash (KCl) (50-52% K or 60-63 K K_2O) and potassium sulphate (K_2SO_4) (40-44% K or 48-53% K_2O). Both of these fertilizers are mined as minerals in Canada, USA and Germany. Production of potassium chloride is about 20 times that of potassium sulphate. Potassium chloride therefore makes up the bulk of fertilizer K consumed in the world. Potassium sulphate also contains about 17% S and this is an advantage for areas having sulphur deficiency.

Small amounts of potassium are also marketed as double salts of potassium and magnesium. Kainite (KCl Mg $SO_4 3H_2O$) contains 15.99% K (19.2% K_2O), 9.94% Mg and 13% S. Langbeinite, which is marketed as K-Mag or Sul-Po-Mag, has a theoretical composition of 18.85% K (22.7% K_2O), 11.71% Mg and 23.18% S. These materials have the advantage of supplying Mg and S in addition to K. Very small amounts of potassium are applied as potassium nitrate (36.7% K or 44% K_2O) and potassium phosphate (3-26% P or 30-60% P_2O_5 and 25-41.7% K or 30-50% K_2O).

8.5. Choice of K fertilizers

Potassium is applied to a majority of crops as potassium chloride or muriate of potash. The recognition that Cl^- ion, quite apart from its role in plant nutrition, suppresses some disease organisms, such as those causing take-all of wheat and stalk-rot of corn and may influence the selection of muriate of potash as a source.

Potassium sulphate is commonly applied to tobacco because excessive chloride uptake may impair the burning quality of the cured leaf. Superiority of potassium sulphate for potatoes is suggested for higher specific gravity and starch yields. Potassium sulphate is also preferred on soils having S deficiency.

8.6. Efficient use of potassium fertilizers

For efficient use of potassium fertilizers, one has to consider: (i) soil factors; (ii) weather factors especially precipitation; and (iii) crop factors. Soils having 2:1 layer silicates and interstratified minerals can fix appreciable K and therefore these soils do not pose a serious leaching problem. On the other hand sandy soils and soils having kaolinite as the dominant mineral, as in tropical and subtropical soils and which are also in high rainfall regions, present serious leaching problems. Method and time of potassium fertilizer application therefore assumes considerable importance. Application of K in the planting furrow is advantageous when soils are poor in K and the levels applied are low to moderate; application of high rates in the planting furrow may result in a localized salinity problem, causing seedling injury. On soils susceptible to K leaching, broadcast application followed by incorporation in 20 cm depth is considered superior to band application (Ritchey, 1979). Split application of K (part at planting and part side-dressed later) is recommended to avoid salinity effects and leaching losses both in annual and perennial crops.

9. Calcium

Calcium is a secondary nutrient and has only one active valence 2^+. It is taken up by plants as cation. Calcium is present in cell wall and is involved in cell division and is therefore an important component of plant structure. It is generally considered an immobile element in plants. Calcium in soils serves as an excluder or detoxifier of heavy metals such as Ni as well as other elements that might otherwise be toxic. In addition Ca provides protection against drought, salinity and mechanical stress.

9.1. Calcium in soil

Calcium is present in earth's crust in much larger amounts (3.64%). Highly weathered coarse sandy soils in humid regions may contain 0.1 to 0.3% total Ca, while fine textured clay soils rich in 2:1 layer silicates may contain 0.7 to 3% total Ca. Values greater than 3% total Ca in soils indicate the presence of calcium carbonate. Such soils are known as calcareous soils. These soils may have a hard pan of calcium carbonate and calcium silicate at a rather shallow depth in soil profile.

Calcium in soils is derived from the minerals anorthrite, pyroxenes (augite), amphiboles (hornblende) and albite. Calcite ($CaCO_3$) is the most important source of Ca in calcareous soils; when present, dolomite (Ca, Mg $(CO_3)_2$) also contributes to soil Ca. In arid and semiarid regions gypsum ($CaSO_4 2H_2O$) could be an important source of Ca.

Calcium is present in non-exchangeable and exchangeable forms and in soil solution; the latter two forms remain in a dynamic equilibrium. The optimum range of Ca saturation of the exchange complex (CEC) is varied from 12 to 75%; for temperate regions. However, the suggested optimum for a number of crops is 65% (Eckert and McLean, 1981).

Exchangeable Ca in soils can range from <25 mg kg^{-1} to more than 5000 mg kg^{-1}. Ca in soil solution may range from 68 to 778 mg kg^{-1}. When solution Ca is depleted by leaching or plant uptake, more Ca is released from the solid phase.

9.2. Factors affecting the availability of Ca in soils

Release of Ca from the exchange complex and its availability to crop plants depends upon the following factors; a number of these are independent.

9.2.1. Type of clay mineral present: Soils having 2:1 layer silicates have higher CEC and can thus retain larger amounts of Ca. In such acid soils, however, Ca level may be too low to be available to plants. Smectites require nearly 75% saturation of exchange complex before appreciable Ca is released for plant uptake. On the other hand soils having 1:1 layer silicates (kaolinites) will release exchangeable Ca into the soil solution at only 20 to 40% Ca saturation of the exchange complex.

9.2.2. Soil pH: Soil pH inversely related to exchangeable Ca. In acid soils, which can have high exchangeable Al, Ca concentrations become low. Liming such soils increases soil pH by increasing saturation of exchange complex with Ca, which replaces exchangeable H^+.

9.2.3. Ratio of Ca to other cations in soil solution: Availability of Ca and its uptake by plants is largely influenced by the ratio of this cation with other cations. A Ca/(Ca+Mg+K) ratio in solution of 0.1 to 0.2 is generally considered desirable for adequate Ca uptake.

9.3. Leaching of calcium

Calcium is often the dominant cation in drainage waters, springs, streams, ponds and lakes. Annual leaching loss of Ca from a soil will depend upon the total amounts present in a soil, its CEC, frequency and intensity of precipitation and in irrigated areas on the amount of irrigation water applied and its Ca content. Provision of a plant canopy such as grass cover can greatly reduce the leaching of Ca from a soil. Excessive leaching of Ca is one factor responsible for the development of acidity in oxisols and ultisols. In less humid regions during soil development, some Ca was leached from the surface soil and precipitated mainly as carbonates and sulphates in the subsoil.

9.4. Deficiency symptoms of calcium

Since Ca is generally immobile in plants, there is very little translocation of Ca in phloem. This leads to poor supply and consequent deficiency symptoms often result in storage organs

and fruits. Bitter pit development in apples is a good example of this. Blossom-end rot in tomato and moldy, diseased and low quality soybean are some other examples. Terminal buds and apical tips of roots in plants fail to develop. Acute Ca deficiency in corn prevents the emergence and unfolding of young leaves, the tips of which may be covered with a sticky gelatinous material; the leaves tend to stick together giving a ladder-like appearance.

9.5. Calcium amendments

Most of the Ca amendments are applied as limiting materials on acid soils. In addition to liming materials, gypsum ($CaSO_4$) because of its higher water solubility than limestone, has received special attention for supplying Ca to peanut or groundnut. Calcium absorbed by the roots is not translocated to the developing pods, which therefore, absorb directly from the soil solution the Ca needed for their development during initial pegging and seed development. For this purpose gypsum is generally band applied or broadcast at first bloom stage; the term lime plastering is sometimes used for this practice. Release of Ca from gypsum is influenced by the particle size so finely powdered material is generally used. Gypsum application increased pod yield as well as percentage of sound matured kernels (SMK); crystalline and free powder (wet) and better than other materials.

10. Magnesium

Magnesium is a secondary nutrient and is taken up as cation and has only one active valence 2^+. Magnesium is the core cation in the structure of the chlorophyll molecule and is thus vital to photosynthesis. Magnesium also serves as a structural component in ribosome and thus plays an important role in protein synthesis. It is fairly mobile in plants.

10.1. Magnesium in soil

Magnesium is present in earth's crust at 1.93%. Highly weathered course sandy soils in humid regions may contain 0.1% total Mg, whereas fine textured clay soils such as 2:1 layer silicates may contain 0.7-3% total Mg. Magnesium in soils is derived from minerals biotite, phologpite, hornblende, oliving and serpentine. In calcareous soils dolomite, when present, is an important source of soil Mg. In arid and semiarid regions substantial amounts of mineral epsomite ($MgSO_47H_2O$) may be present and contributes to soil Mg. The range for critical Mg saturation levels is narrow, often 5 to 10% of CEC. Exchangeable Mg generally constitutes 4 to 20% of the CEC and concentration in soil solution may range from 50 to 120 mg L^{-1}.

10.2. Factors affecting the availability of Mg in soils

Availability of Mg in soils depends upon a number of factors described below.

10.2.1. Type of clay minerals: Clay minerals having 2:1 layer structure have higher CEC and can thus retain larger amounts of Mg.

10.2.2. Ratio of Mg to other cations in soil solution: Excess Ca may adversely affect Mg uptake and Ca/Mg ratio in solution greater than 7:1 is not considered desirable (Tisdale *et al*., 1985). This would explain why continuous liming of coarse-textured soils may lead to Mg deficiency (due to increased Ca/Mg ratio). Similarly K antagonizes Mg uptake and this could be a concern in low Mg soils. The recommended K/Mg ratio are: <5:1 for field crops; 3:1 for vegetables and sugarbeets and 2:1 for fruits and greenhouse crops (Tisdale *et al.*, 1985).

10.3. Deficiency symptoms of Mg

Magnesium is fairly mobile in plants and its deficiency symptoms appear first on the lower leaves. In corn Mg deficiency results in interveinal chlorosis of lower leaves, only veins

remain green. In cotton, the lower leaves develop a reddish purple cast. That may gradually turn brown and necrotic.

10.4. Magnesium amendments

Potassium magnesium sulphate, magnesium sulphate, and kieserite are commonly used sources of Mg. Other materials containing significant amounts of Mg are magnesia (MgO, 55% Mg), magnesium nitrate [$Mg(NO_3)_2$, 16% Mg], magnesium silitate (basic slag, 3-4% Mg; serpentine, 26% Mg), magnesium chloride solution ($MgCl_2.10H_2O$, 8-10% Mg), synthetic chelates(2-4% Mg), and natural organic complexing substances (4-9% Mg). Potassium magnesium sulphate, magnesium sulphate, magnesia, magnesium silicate are used as dry fertilizer formulations for direct application, whereas, magnesium sulphate, magnesium chloride, magnesium nitrate and synthetic and natural magnesium chelates are well suited for foliar sprays.

11. Sulphur

Sulphur along with calcium and magnesium is a secondary plant nutrient. The criterion of grouping plant nutrients as primary, secondary or micro-nutrients is based on their amounts removed by crop plants. However, sulphur and magnesium are taken up by the crop plants in about the same amounts as phosphorus.

11.1. Soil sulphur

Total S in soils may vary from a few to 1000 mg S kg^{-1} soil (0.1%); higher values can be encountered in problem soils such as saline and acid-sulphate soils (Takkar, 1988; Ganeshmurthy *et al*., 1989). Sulphur in soils is present both in organic and inorganic forms. While inorganic forms are important because most of the S is taken up by plants as $SO_4^=$ (sulphate), organic forms are important because they often make up the bulk of soil S. Because S is an integral part of soil organic matter, total S is generally greater in fine textured than in coarse textured soils. In general, soils containing greater amounts of organic matter contain a larger fraction of their S in organic form.

11.1.1. Organic sulphur: Well over 90% of the sulphur in surface layers of well-drained non-saline soils is present in organic form. Organic S is divided in two major groups, namely, C-bonded S (amino acids) and non C-bonded S (ester sulphates such as phenolic sulphates and sulphated polysaccharides. Since the bulk of S in plant tissue is present as the S containing amino acids cystine, cysteine and methionine, and plants residue when added to the soil, plant-S therefore becomes an integral part of soil organic matter.

11.1.2. Inorganic sulphur : Inorganic S in most soils is present as $SO_4^=$ ions associated with monovalent (Na, K) and divalent cations (mostly with Ca and Mg; traces with Cu, Mn, Zn and Fe). Sulphate salts presents in the soil solution (soluble S) may be adsorbed on soil colloids or the salts may be present as insoluble compounds. Inorganic sulphur may be further divided into (i) soluble sulphur, (ii) adsorbed sulphur and (iii) insoluble sulphur.

(i) **Soluble sulphur**: Sulphate content of the soil solution (soluble S) is variable and depends upon a number of factors: (a) Weather conditions particularly temperature that determines the rate of mineralization of soil organic matter, (b) Precipitation – heavy rains can lead to excessive leaching, (c) Associated cations – leaching losses are the highest when monovalent cations such as Na and K are mostly associated with sulphate, (d) Soil water content – soil water affects sulphate content in soil solution in two ways. First of all, the sulplhate concentration in soil solution generally decreases as the water content increases (dilution effect). Secondly, as a soil dries out due to high evapotranspiration rates, sulphate from lower soil layers moves upward by capillary action with water, and

increases the concentration of sulphate in the surface layer soil solution. With sufficient drying, sulphates may then precipitate on the soil surface, particularly calcium sulphate, (e) Application of sulphur containing fertilizers – as expected this will increase soil solution sulphur content. A soluble S content of 5 mg kg^{-1} soil is generally adequate for the growth of most crops; *Brassicas* require somewhat more S.

(ii) **Adsorbed sulphur**: Sulphur as $SO_4^{=}$ can be adsorbed on clay minerals by salt adsorption; on hydroxides and oxyhydroxides of iron and aluminium, which acquire a positive charge under low pH conditions; and on soil organic matter which develops positive charges under certain conditions.

(iii) **Insoluble sulphur**: Calcium sulphate can coprecipitate with calcium carbonate and this corecipitated sulphate forms an important fraction of total S in calcareous soils. Unless brought into solution, which is difficult and very slow, this form of S is relatively unavailable to plants. A number of factors, particularly the size of the calcium carbonate particles, common ion effects, and soil water content determine the rate of dissolution of insoluble S. Grinding of soil samples while preparing it for analysis may reduce the particle size of calcium carbonate and may lead to increased dissolution of insoluble S. This results in higher available S values as determined in a soil test.

11.2. Sulphur transformations in soil

Sulphur transformations can be categorized into four process namely, mineralization, immobilization, oxidation, and reduction.

11.2.1. Mineralization : The process of conversion of organic S into inorganic S is known as mineralization. First cysteine is changed to cystine by chemical oxidation. The cystine is oxidized to sulphate with cystine disulphoxide and possibly cystein sulphenic acid as intermediate. In general sulphur mineralization may be represented by a simple expression.

$$R - O.SO_3 + H_2O \xrightarrow{\text{Sulphatase}} R\text{-}OH + HSO_4$$

11.2.2. Immobilization: About 0.1 to 1% of body weight of micro-organisms is made of S. As long as there is less sulphur in the organic matter than required by microbial proliferation, immobilization will be dominant. A content of 0.15% S in dry matter is the minimum requirement for its mineralization and wheat straw contains only one-third of this minimum required, hence wheat straw incorporation results in S immobilization.

11.2. 3. Oxidation of inorganic sulphur : The inorganic compounds of sulphur present in various states of oxidation from -2 of sulphide to +6 of sulphate. In culture, a wide variety of inorganic sulphur compounds are metabolized to sulphate. For example, the soils treated with colloidal sulphur, thiosulphate, trithionate or tetrathionate form sulphate after an initial lag period. These reactions are biological as they are abolished by microbial inhibitors. Sulphides are readily oxidized, although this process may not be entirely microbiological, because sulphides can be converted to elemental sulphur by chemical means. The following pathway has been proposed.

$$S \longrightarrow S_2O_3^{-2} \longrightarrow S_4O_6^{-2} \longrightarrow S_3O_6^{-2} \longrightarrow SO_3 \longrightarrow SO_4$$

Sulphide thiosulphate tetrathionate trithionate sulphite sulphate

Thiobacillus thioxidans, T. thioparus, T. novellas, T. denitrificans and T. ferro-oxidans are responsible for sulphur oxidation.

Oxidation reactions may be illustrated with hydrogen sulphide and elemental S.

$H_2S + 20_2 \longrightarrow H_2SO_4 \longrightarrow 2\ H^+ + SO_4$

$2S + 3O_2 + 2\ H_2O \longrightarrow 2H_2SO_4 \longrightarrow 4H + 2SO_4$

Sulphur oxidation in soil is affected by a number of factors which are given below:

(i) Soil microflora: Sulphur is oxidized by several bacterial spp. of genera *Thiobacillus*. These organisms are obligate, autotrophic aerobics. When the soil or the added sulphur is inoculated with *Thiobacillus* organisms, the oxidation of sulphur is greatly increased.

(ii) Temperature: An increase in temperature up to 40^oC increases the rate of S oxidation in soil. The maximum rate of oxidation is observed between 27 and 35^oC and at temperature of 55 to 60^oC, these organisms are killed.

(iii) Soil moisture: The most rapid oxidation take place at a moisture level near that corresponding to field capacity. When soil are either excessively wet or excessively dry, oxidation is seriously impended. Because the degree of soil aeration is inversely related to soil moisture, at high moisture content, oxygen will be a limiting factor. Organisms are aerobic.

(iv) Soil pH: Thiobacillus thiooxidans is capable of surviving at extremely low pH. Other organisms appear to have different pH requirements but in general oxidation proceeds more rapidly in more acid soils.

(v) Fineness of applied sulphur: Finer the particle size of a given mass of sulphur, the larger the specific surface area and the faster the conversion to sulphate. When elemental sulphur is to be applied as plant nutrient, 100% of material must pass through a 16 mesh screen and that 50% should, in turn, pass through a 100 mesh screen.

11.2.4. Sulphur reduction: Like nitrates, sulphate tend to be unstable in anaerobic environments. They are reduced to sulphides by a number of bacteria of two genera,. *Disulfovibro* (five sps.) and *Disulfotomaculum* (3 sps). In fact SO_4^{2-} present in the soil serves as an electron acceptor for sulphate-reducing bacteria. This reduction of SO_4^{2-} is both redox potential and pH dependent. Little or no SO_4^{2-} accumulate at redox potential above –150 mv or a pH outside the range of 6.5 to 8.5. The organisms use the combined oxygen in sulphate to oxidize organic materials as shown below

$$2R - CH_2OH + SO_4^{-2} \longrightarrow 2R - COOH + S + 2\ H_2O$$

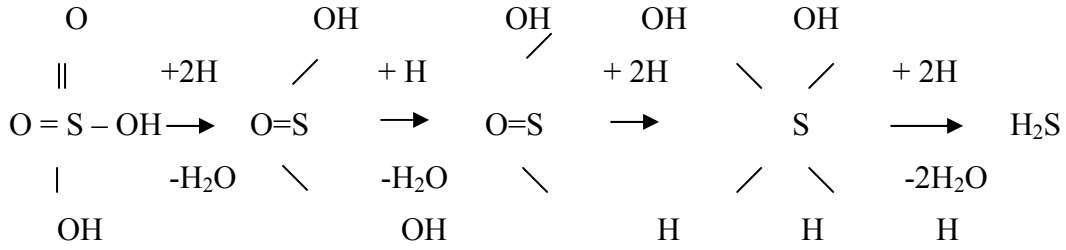
Organic alcohol Sulphate Organic acid Sulphide

In poorly drained soils, sulphides ion would likely react immediately with iron. This reaction may be expressed as follows:

$$Fe^{2+} + S^{2-} \longrightarrow FeS$$

The first iron sulphide precipitate is usually amorphous FeS which undergoes conversion to either pyrite or marcasite both with the formula FeS_2. Mackenawite (FeS) and greigite (Fe_3S_4) may be intermediates in the conversion.

Sulphur reduction also takes place with compounds other than sulphate. Sulphides, thiosulpahte ($S_2O_3^{2-}$) and elemental sulphur (S) are rather easily reduced to the sulfide form. *Desulfovibrio* spp., *Desulfotomaculum* spp., *Clostridium nigrificoms*, *Bacillus megatorium, Pseudomonas zelinskii* participate in sulphur reduction. A likely mechanism involves the stepwise reduction of sulphate to sulphide via sulphite, sulphoxylate and sulphur hydrate as shown below:



Sulphuate Sulphite Sulphoxylate Sulphur hydrate Sulphide

11.3. Sulphur deficiency symptoms in plants

Sulphur deficiency in plants resembles N deficiency and S deficient plants also turn pale-yellow. However, S is less mobile than N in pla nts and the younger leaves may generally turn pale-yellow, while the older leaves may remain green; note that the reverse is the case in N deficiency. There are frequent exceptions to these symptoms, such as stoopy plants with short and slender stalks; these symptoms will not disappear with N application. Plant species differ considerably in expressing S deficiency symptoms.

11.4. Sulphur needs of crops

Crops and cultivars within crops vary considerably in their S requirements. Spencer (1975) has divided crops into 3 broad groups. Group I includes Crucifers and *Brassicas* which have high S requirement (20-80 kg S ha^{-1}). Group II includes plantation crops which have moderate S requirements (10-50 kg S ha^{-1}). Group III includes cereals, forages and other field crops and has low S requirement (5-25 kg S ha^{-1}). As a rule of thumb, Tandon (1991) recommended 3-4 kg S Mg^{-1} grain for cereals, 8 kg S Mg^{-1} grain for legumes (beans) and 12 kg S Mg^{-1} seed for oilseeds (rapeseed mustard, sunflower, groundnut, soybeans, etc.).

11.5. Sulphur fertilization

Sulphur has been applied in the past along with ammonium sulphate, ordinary superphosphate and potassium sulphate. However, with the advent of high analysis fertilizers such as anhydrous ammonia, urea, diammonium phosphate (DAP) and ammonium polyphosphate (APP), application of S has been gradually reduced. Thus, where necessary, additional S may be applied as elemental S, gypsum or pyrite depending on the availability of material and needs of crops and soils.

12. Micronutrients

Micronutrients are required by crop plants in small or micro-amounts (<500 mg/kg dry matter except Fe and Mn), hence are termed as micronutrients. There are seven micronutrients namely Zn, Fe, Mn, Cu, B, Mo and Cl. These are subdivided into micronutrient cations (Zn, Fe, Mn, Cu) and micronutrient anions (B, Mo and Cl) depending upon the form in which they are absorbed by the plants. These micronutrients are discussed separately.

12.1. Iron

In biological systems, especially in animals, Fe is supreme and plays a dominant role (Prasad and Power, 1997) Iron together with Mn provide the key to the establishment of the organic mantle, the humified soil top layer that covers the surface of the earth and serves as the nurturing home for the roots of all plants and carbon-recycling microorganisms (Bartlett and James, 1993).

12.1.1. Amount and forms of Fe in soil: Iron comprises about 50 g kg^{-1} (5%), of the earth's crust. The amounts of Fe in a soil depend upon the kind and degree of weathering the parent material has undergone during soil formation. The amounts of this element are greatest in highly weathered oxisols and ultisols. Fe must exists in +2 valence form to be soluble in soil solution and taken up by plants. Diffusion is the main process by which Fe ions are made available for uptake by plants. The other processes involved in uptake of Fe by plants are mass flow and root interception.

12.1.2. Factors affecting Fe availability: In addition to pH and soil water or aeration as measured by redox potential, soil organic matter and interaction with other ions in soil solution also affect the availability of Fe. Organic materials added to soil produce chelating agents such as simple aliphatic acids, hydroxamate siderophores, phenols and phenolic acids, complex polymeric phenols and components of stable humus such as humic and fulvic acids (Stevenson, 1991). These chelating agents make more Fe available to plants. Excesses of essential nutrients such as P, Cu, Zn and Mo adversely affect the availability of Fe. Phosphorus application at higher rates aggravates Fe deficiency through some poorly defined inactivation reaction. Application of NH_4^+-containing or producing fertilizers are likely to result in less Fe deficiency, while application of NO_3^--containing fertilizers is likely to enhance the deficiency of Fe.

12.1.3. Deficiency symptoms of Fe: Iron is an immobile nutrient in plants. Therefore, its deficiency symptoms show up first in the young leaves of plants. Because 90% of the iron in leaves occurs in chloroplasts and mitochondria, deficiency of Fe results in loss of greenness (chlorophyll) in plants; leaves turn pale green and develop interveinal chlorosis. In severe deficiency the young leaves turn entirely white. Such symptoms are distinctly seen in sorghum, especially when growing on neutral to alkaline soils. Sorghum is an excellent indicator plant for Fe deficiency. Rice nurseries on neutral to alkaline soils and direct-seeded rice crops in early growth stages on similar soils may also show similar symptoms, that is, patches of plants with white young leaves.

12.1.4. Fe fertilizers: Ferrous sulphate is generally used for correcting Fe deficiency in soil. Other than ferrous sulphate, synthetic iron chelates are quite popular. Iron chelates can be applied to soils; HEDTA chelates are good for acid soils, EDTA chelates for neutral soils and EDDHA chelates for alkaline soils. Soil application of Fe fertilizer is of limited help in rectifying an iron deficiency because applied Fe^{2+} is rapidly oxidized. Foliar application to field crops and injection of Fe^{2+}-salts directly into trunks and limbs of fruit trees is preferred. In field corps a single or several spray applications (at weekly or fortnightly intervals) of 2 to 3% solution of ferrous sulphate (650 to 700 l ha^{-1}) is generally required.

12.2. Manganese

Mn is secondary to Fe and displays some toxicity tendencies. In the oxidation-reduction reactions of soils, however, Mn is first to Fe in importance. Manganese provides O_2 to the poorly ventilated interior soil pores, where Fe^{2+} and complex organic molecules would otherwise tend to remain unoxidized.

12.2.1. Amount and forms of Mn in soil : Mn is present at about 1 g kg^{-1} (0.1%) of earth's crust. Like, Fe, Mn also exits in +2 valence form to be soluble in soil solution and taken by plants. Similarly Mn is taken by plants by diffusion, mass flow and root interception.

12.2.2. Factors affecting Mn availability: A number of chelating agents like aliphatic acids, hydroxamate, siderophores, phenols and phenolic acids, complex polymeric phenols and components of stable humus such as humic and fulvic acids increase the availability of Mn. Neutral chloride-containing salts when applied also increase Mn availability.

12.2.3. Deficiency symptoms of Mn: Manganese is an immobile nutrient in plants and deficiency symptoms show up in younger leaves as in the case of Fe. In some wide-leaved plants such as corn or soybean, interveinal chlorosis, similar to that in the case of Fe-deficiency, is seen. In other crops symptoms are different such as gray speck of oats, marsh spot of peas and speckled yellow of sugarbeets.

12.2.4. Mn fertilizers: Manganese sulphate is best source of Mn. Manganese fertilizers can be applied to soil or directly to the crop as a foliar spray. Soil application of manganese sulphate may range from 5 to 25 kg ha^{-1} depending upon soil and crop. For foliar application generally a 0.2 to 0.5% solution of manganese sulphate is used.

12.3. Copper

Copper, like Fe, participates in oxidation-reduction processes in plants. Copper is associated with enzymes that can hydroxylate monophenols, oxidizing them to create complex polymers such as lignin and melanin, detoxify superoxides, oxidize amines, terminate electron transfer chains and act generally as cytoplasmic oxidases (Tisdale *et al*., 1985).

12.3.1. Amount of Cu in soil : The Cu content in soils ranges from nearly 5 to 60 mg kg^{-1}, although both lower (<2 mg kg^{-1}) and higher values are not uncommon (Stevenson, 1986). The average value of Cu in soils is about 9-10 mg kg^{-1}. The most widely occurring copper mineral is chalcopyrite ($CuFeS_2$). Other Cu-bearing minerals are chalcocite (Cu_2S) and bornite ($CuFeS_4$).

12.3.2. Cu in soil solution: The concentrations of Cu in soil solution remain very low, approximately 0.5 to 70 mg Mg^{-1} (ppb). Plant uptake of Cu is mostly by root interception. Cu is present in three ionic forms – Cu^{2+}, $Cu(OH)^{+}$ and $Cu(OH)_2^{0}$. At pH <6.0 nearly all Cu is present as Cu^{2+}. As pH approaches neutrality nearly half the Cu in soil solution is hydrolyzed to $Cu(OH)_2^{0}$ and the change to this form is 92% at pH 8. The change to this form reduces Cu availability to plants.

12.3.3. Factors affecting the availability of Cu: The availability of Cu to plants is affected by a number of factors such as pH, kind and amount of organic matter, interaction with other elements in soil solution, fertilizer practices, soil amendments, flooding (as in rice culture), environmental factors, and plant factors. In general, increase in soil pH above 6.0 decreases the availability of Cu due to: (i) change in the hydrolysis status – e.g., at pH 8 $Cu(OH)_2^{0}$ is the dominant ionic species, which have less solubility (activity) than Cu^{2+}, (ii) increased sorption on Al and Fe oxides and hydroxides, clay minerals and soil organic matter due to increased pH dependent charge, (iii) reduced competition with H^{+} for the adsorption sites. High concentrations of Zn, Al, P and Fe in soil solution restrict Cu absorption by plants.

12.3.4. Deficiency symptoms of Cu in plants : Symptoms of Cu deficiency appear first at the top of the plant with youngest leaves becoming yellow and pale and as the deficiency advances, eventually dead tissue appears along the tips and edges of leaves as in the case

of K. In vegetables the leaves lack turgor and develop a bluish green cast (Tisdale *et al*., 1985). Crops most susceptible to Cu deficiency are alfalfa, wheat, barley, oats and onions.

12.3.5. Cu fertilizers : The most popular and widely used source of Cu is $CuSO_4.5H_2O$. Generally a dose of 10 to 25 kg ha^{-1} $CuSO_4$ is recommended on Cu deficient soils, depending upon soil texture; the heavier the texture greater the dose. In general, soil application of Cu is considered more effective. When a deficiency is observed in a standing crop, foliar applications can also be made. A 0.5% w/v solution of $CuSO_4$ is recommended with a small amount of slaked lime (0.5 kg 100 l^{-1}); this practice prevents scorching of leaves. Dosages are much less when chelates are used and these are preferably used for foliar application.

12.4. Zinc

Zinc ion (Zn^{2+}) is formed by the loss of the two electrons 4s sub shell and reactions tend to be similar to those of Ca (Harter, 1991). Zinc is involved in a diversity of enzymatic activities such as auxin metabolism, dehydrogenase, phosphodiesterase and promotion of synthesis of cytochrome C. Zinc deficiencies are more prevalent than other micronutrients and are virtually global in nature. In India most states are now recognize the need for supplemental Zn for one or more crops. Analysis of about 40 thousand soil samples from different parts of India showed 50% of the samples to be deficient in plant available Zn (Katyal and Sharma, 1979).

12.4.1. Amounts of Zn in soil : Total Zn content in soils ranges from 10-300 mg kg^{-1} soil with an average of 50 mg kg^{-1} soil. The Zn content in various rocks varies from 4 to 100 mg kg^{-1}. General values (mg kg^{-1}) are: basalt 100, shale 45, granite 10, limestone 4 and sandstone 30 mg kg^{-1} (Tisdale *et al*., 1985; Stevenson, 1986). The most important minerals are sphalerite (ZnS), smithsonite ($ZnCO_3$) and hemimorphite ($Zn_4(OH)_2Si_2O_7.H_2O$).

12.4.2. Zn in soil solution: Concentration of Zn in soil solution ranges from 0.5 to 7 mg Mg^{-1}. At any time the concentration of Zn in the soil solution is generally greater than that of Cu. Like Cu, Zn is present in three ionic form – Zn^{2+}, $Zn(OH)^+$ and $Zn(OH)_2^0$. At pH <6 nearly all Zn is present as Zn^{2+}. $Zn(OH)_2^0$ begins to appear only at pH 8. Reduction in the divalent form of Zn^{2+} to the hydrolyzed form is slower. At pH 7 about 83% is still present as Zn^2, and 31% at pH 8. At pH 8 about two-thirds of Zn may be present as $Zn(OH)^+$, which is less available to plants. It may vary from 0.5 to 70 mg Mg^{-1}. Plant uptake of Zn is mostly through diffusion.

12.4.3. Factors affecting the availability of Zn: Cu, Fe and Mn inhibit uptake of Zn (Kausar *et al*., 1976; Giordano *et al*., 1974). This is possibly due to competition for the carrier sites on roots. The most frequently reported and researched interaction is P x Zn, namely, phosphorus induced Zn deficiency. Application of high rates of P enhances the adsorption of Zn in some soils, especially those rich in Fe and Al oxides and hydroxides (Saeed and Fox, 1979). This could be due to additional negative charge or complexation sites created due to sorption of PO_4 into oxides surfaces (Bolland *et al*., 1977). Furthermore, physiological research has brought out that high P rates increase the amount of Zn in the ethanol-soluble and pectate fraction of root cell walls and this binding of Zn results in reduced amounts of Zn available for transport to the plant shoot (Youngdahl *et al*., 1977). An alternative hypothesis suggests that what is generally considered a Zn deficiency is in reality P-toxicity due to higher uptake of P (Webb and Loneragan, 1988). Whatever many be the explanation, large amounts of data (Adams, 1980) suggest the presence of a negative P x Zn interaction under field conditions.

12.4.4. Deficiency symptoms of Zn in plants: Since Zn is highly immobile in plants, its deficiency symptoms are seen on the growing points and young leaves. In corn the young leaves become yellow to white (sometimes stripped) and the plant has stunted growth; therefore, the name "white bud". Zinc deficiency in rice fields is indicated by spots of chocolate brown-burned up plants, hence the name "Khaira" disease. In citrus the deficiency is indicated by a cluster of leaves (rosette) at the top of mainly bare branches; referred to as "mottle leaf" or "frenching". Some other zinc deficiency diseases are "little leaf" in cotton, and "fern leaf" in Russet Burbank potato.

12.4.5. Zinc fertilizers: $ZnSO_4.5H_2O$ is most widely used source of Zn. A dose of 20-25 kg $ZnSO_4$ is generally recommended on Zn deficient soil depending upon the texture of soil. Soil application of Zn is considered more effective. However, the deficiency of Zn can be corrected by spraying of 0.5% w/v solution of $ZnSO_4$ with small amount of slaked lime. Dipping of rice seedlings or cut potato seed pieces in a 2% $ZnSO_4$ or ZnO suspension or slurry is an economical way of applying Zn to crops on Zn deficient soils; only 2 to 5 kg $ZnSO_4$ or ZnO is required this way.

12.5. Boron

Boron is taken up by the plants as an anion.

12.5.1. Amount of B in soils: The total concentration of boron in most soils varies between 2 and 200 mg kg^{-1} and less than 5% is generally available to plants (Tisdale *et al*., 1985). Boron-containing minerals in soils are tourmaline, axenite, ulexite, colemenite and kermite; tourmaline is the most important. Boron-containing minerals are quire resistant to weathering and most plant available B comes from the decomposition of soil organic matter and from B adsorbed and precipitated onto the surface of soil particles.

Boron is highly mobile in soils and highly immobile in plant. Consequently both B deficiencies and toxicities are of concern. Soils of humid regions such as sandy podzols, vertisols, alluvial soils and organic soils have low amounts of plant available B due to leaching of B.

Boron, like sodium and chloride, is soluble and tends to accumulate where salts accumulate. Thus, B may be found in toxic levels in saline and sodic soils, in low lying areas with impeded drainage and in areas with a shallow water table. Irrigation water high in B content is a major cause of B toxicity.

12.5.2. Forms of B in soils : In addition to being present as a component of minerals and rocks, B exists as : (i) adsorbed on surfaces of clay minerals and hydroxides of Al and Fe; (ii) complexed with soil organic matter, and (iii) in the soil solution as soluble B, either as free non-ionized H_3BO_3 or as ionized $B(OH)_4^-$ forms.

12.5.3. Factors Affecting B availability: Soils having a relatively high content of micaceous clay minerals (such as illite) and organic matter contain greater amounts of total and available B. On the other hand coarse, well drained, low-organic matter sandy soils usually have less total and available B.

Soil pH and liming, interactions with Ca, K and other nutrients and weather factors influence B availability to plants. Liming of strongly acid soils frequently induces at least a temporary B deficiency in susceptible plants, which is believed to be caused by increased adsorption of B on freshly formed $Al(OH)_3$ (Tisdale *et al*., 1985). As a corollary moderate liming can be used as a corrective treatment on soils containing excess B.

The most well known of the B interactions with other nutrients is that with Ca, as seen in liming. This effect is probably related to the Ca:B ratio in plants. For example Ca:B ratios of 10-45 were toxic to barley, a ratio of 180 was optimal, and ratios greater than 697 may produce B deficiency.

High levels of K accentuate B deficiency as well as toxicity symptoms mainly by affecting Ca concentration. Liberal N applications decrease the severity of B toxicity symptoms in citrus and cereals (Gupta, 1985).

Environmental factors can influence B availability to plants. For example in areas of adequate precipitation, B deficiency is observed only in dry seasons or in late summer when water availability is low. Plants can tolerate higher B concentrations without experiencing harmful effects during cooler weather than during warmer humid conditions (Eaton, 1935). B toxicity can be exacerbated by high light intensity.

12.5.4. Boron deficiency symptoms in plants : Boron plays an essential role in the development and growth of new cells in the meristematic tissue and imparts stability to the pollen tubes. It is also involved in the germination and growth of pollen. Boron also facilitates the translocation of sugar through the phloem.

Boron is one of the least mobile of the micronutrients in plants and is not readily translocated from old to young plant parts. The first symptoms of B deficiency therefore appears in the growing points and meristematic tissue – the stem tips, root tips, new leaves and flower buds. Boron deficiency symptoms include thickened, creaked and wilted leaves, petioles and stems; discoloration, cracking or rotting of fruits, tubers or roots. In cotton square or boll shedding may take place due to B deficiency.

12.5.5. Boron fertilizers : Boron is applied to both soils and foliage. When applied to soil, B-fertilizers should be uniformly banded or broadcast and incorporated in the soil. Foliar application of B is practiced in orchards and also in field crops such as cotton, which need insecticidal sprays; B can be easily mixed with insecticides. Method of application has an important bearing on the rate at which B is applied. A dose of 0.5 to 1 kg B ha^{-1} is recommended for soil application; it may be increased when B is broadcast. For foliar application a dose of 0.1 to 0.5 kg ha^{-1} is generally recommended.

12.6. Molybdenum

Molybdenum, like B, is taken up by the plants as an anion.

12.6.1. Amounts of Mo in soils: Molybdenum content in soils ranges from 0-.2 to 5 mg kg^{-1} and averages about 2 mg kg^{-1} (Tisdale *et al*., 1985). Like any other nutrient, Mo in soils is present in the crystal lattice of primary and secondary minerals, bound to Al and Fe hydroxides and oxides, complexed with soil organic matter, held as an exchangeable anion and dissolved in soil solution.

In soil solution Mo is present the following ionic species – MoO_4^{2-}, $HmoO_4^{-}$ and $H_2MoO_4^{0}$. The concentration of these 3 species is highly pH dependent. $M_oO_4^{2-}$ is the most prevalent species followed by $HmoO_4^{-1}$. The availability (solubility) of both MoO_4^{2-} and $HmoO_4^{-}$ and thus of Mo increases with pH. At pH 6.5 the concentration of $MoO4^{-2}$ is $10^{-7.5}$ M. The concentration of Mo in soil solution is generally 2 to 8 mg Mg^{-1} (2 parts per billion). When the concentration is less than 4 mg Mg^{-1}, diffusion is the main mechanism of Mo uptake by plants. When the concentration exceeds 4 mg Mg^{-1}, considerable Mo is transported to plant roots by mass flow.

12.6.2. Factors affecting Mo availability in soils: Soil pH, content of Fe and Al hydroxides and oxides, interaction with other ions in soil solution and environmental factors affect Mo availability in soils. In general, there is a 10-fold increase in MoO_4^{-2} for each unit increase in soil pH. Limiting will improve Mo availability because pH is reduced. On the other hand acid forming fertilizers such as ammonium sulphate are likely to decrease Mo availability. Large and continuous application of such fertilizers will increase Mo deficiency. Fe oxides (and Al oxides to a lesser degree) can sorb large quantities of MoO_2^{-2}, particularly under acid conditions when these oxides acquire a positive charge.

Of the anions, phosphate increases and sulphate decreases Mo uptake by plants. The decrease in Mo uptake by plants due to phosphate may result from increased release of absorbed MoO_4^{2-} or from the formation of a complex phosphomolybdate ion, which is more soluble and adsorbed more readily by plants (Barshad, 1951). The inhibitory antagonistic effects of SO_4^{-2} on Mo content have been suggested to occur primarily during the absorption process, with some antagonistic mechanism involved during translocation form roots to shoots (Gupta and Lipsett, 1981).

Of the cations Mg has been reported to increase Mo uptake, while Cu and Mn have antagonistic effects (Tisdale *et al*., 1985). Molybdenum deficiency is more severe under dry weather conditions which reduce soil water content and reduce the mobility of Mo in soil solution.

12.6.3. Molybdenum deficiency symptoms in plants : The symptoms of Mo deficiency are closely related to N metabolism since most of the Mo in plants is concentrated in the nitrate reductase enzyme. Deficient plants are suffering essentially from a shortage of protein due to the failure of the initial process of nitrate reduction. These specific symptoms commonly involve deformation of leaves, as in "whiptail" of cauliflower. In wheat the symptoms are yellowing of older leaves and, in acute deficiency, presence of empty heads. In clovers and legumes also yellowing of leaves is the most common symptom.

12.6.4. Molybdenum fertilizers : The commonly used Mo fertilizers are ammonium molybdate ($(NH_4)_6Mo_7O_{24}.2H_2O$, containing 54% Mo), sodium molybdate ($Na_2MoO_4.2H_2O$, containing 39% Mo), molybdenum trioxide (MoO_3, containing 66% Mo) and molybdenum frits (1-30% Mo).

Molybdenum may be applied to soil, foliage or put on seed prior to sowing. Coating or soaking seeds with Mo is the easiest method and involves the least amount of Mo fertilizers. When applied to soil the doses vary from 345 to 350 g ha^{-1} depending on the soil and crop.

13. Soil Fertility Evaluation and Fertilizer Recommendations

In the modern agriculture, the addition of plant nutrients is increasing but most crops continue to be grown on the basis of mining the soil for some or more nutrients. The selection of the proper rate of plant nutrients is influenced by a knowledge of the nutrient requirement of the crop and the nutrient-supplying power of the soil on which the crop is to be grown. When the soil does not furnish adequate quantities of the elements necessary for normal development of plants, it is essential that the required amounts be supplied. This necessitates finding a method that will permit the determination of those deficient elements.

The problem of predicting plant-nutrient needs has been under study for many years. In 1813, Sir Humphry Davy stated that if a soil is unproductive the cause of unproductivity can be determined by chemical analysis. Since then much work has been done on soil analysis and

other techniques, and gradual improvement in methods of predicting the soil fertility status of the soil has become evident. The techniques commonly employed to assess the fertility status of a soil are : (i) nutrient-deficiency symptoms of plants, (ii) analyses of tissue from plants growing on the soil, (iii) biological tests in which the growth of either higher plants or certain micro-organisms is used as a measure of soil fertility and (iv) chemical soil tests.

13.1. Nutrient-deficiency symptoms of plants

Plants act as integrators of all growth factors and are the products in which the grower is interested. An abnormal appearance of the growing plant may be caused by a deficiency of one or more nutrient elements. If a plant is lacking in a particular element, more or less characteristic symptoms may appear. This visual method of evaluating soil fertility is unique in that it requires no expensive or elaborate equipment and can be used as a supplement to other diagnostic techniques.

Some times plants possess hidden hunger symptoms. Hidden hunger refers to a situation in which a crop needs more of a given element, yet has shown no deficiency symptoms. The content of an element is above the deficiency symptom zone but still considerably below that needed to permit the most profitable crop performance. Because agriculture has changed from a way of life to a business, the grower will make a determined effort to avoid obvious deficiency in his crops. However, he may not add quantities sufficient to obtain the most profitable yield or maximum economic yield. With most nutrients on most crops, significant responses can be obtained even though no recognizable symptoms have appeared.

13.2 Plant analysis

Two general types of plant analysis have been used. One is the tissue test which is customarily made on fresh tissue in the field. The other is the total analysis performed in the laboratory with precise analytical technique.

13.2.1. Tissue tests: Rapid tests for the determination of nutrient elements in the plant sap of fresh tissue have found an important place in the diagnosis of the needs of growing plants. In these tests the sap from ruptured cells is tested for unassimilated nitrogen, phosphorus and potassium. These are semiquantitative tests intended mainly for verifying or predicting deficiencies of nitrogen, phosphorus, or potassium. The results are read as very low, medium or high. Through the proper application of tissue testing it is possible to anticipate or forecast certain production problems – while still in the field. Although not as widely used, similar on-the-spot tissue tests have been developed for other nutrients, including sulphur, magnesium, manganese and zinc.

13.2.2. Total analysis: Total analysis is performed on the whole plant or on plant parts. Precise analytical techniques are used for measurement of the various elements after the plant material is dried, ground, and ashed. Simultaneous analysis of up to 22 elements is possible by inductively coupled plasma optical emission spectrometry. This method is at least as sensitive as older but less automated techniques such as flame atomic absorption spectrometry. The spectrograph can also be used for the simultaneous determination of several elements. Electron microprobes and microscopes also are being developed. Analytical results from these various instruments are often compiled and reported by computer.

13.3. Biological tests

Use of the growing plant understandably has much appeal in the study of fertilizer requirements, and much attention has been devoted to these methods for measuring the fertility status of soils. Biological tests include following tests:

13.3.1. Field tests: The field-plot method is one of the oldest and best known of the biological tests. The series of treatments selected depends on the particular question the experimenter wishes to have answered. The treatments are then randomly assigned to an area of land, known as a replication, which is representative of the conditions. Several such replications are used to obtain more reliable results and to account for variations in soil and management. These experiments are helpful in the formulation of general recommendations. Field tests are expensive and time consuming, and one is unable to control climatic conditions and other limiting factors. They are valuable tools, however, and are widely used by experiment stations, although they are not well adapted for use in determining the nutrient status of large numbers of soils. Rather, they are used in conjunction with laboratory and green house studies as a final proving ground and in the calibration of soil and plant tests.

13.3.2. Strip tests on farmers' fields: Strips of fields are being treated with fertilizer by extension, industry, and growers alike to check on recommendations based on soil or plant tests. The results of these tests must be interpreted with caution if they are unreplicated and use of two or three replicates is recommended. Repetition of strip tests at several locations is also helpful.

13.3.3. Laboratory and greenhouse tests: Similar and more rapid biological techniques which will involve higher plants but utilize small quantities of soil have been developed. These methods have met with wide acceptance on the European continent and have frequently been employed in the United States.

13.3.4. Microbiological methods: Winogradsky was one of the first to observe that in the absence of mineral elements certain microorganisms exhibited a behaviour similar to that of higher plants. It was shown that the growth of *Azotobacter* served to indicate the limiting mineral nutrients in the soil, especially calcium, phosphorus, and potassium, with greater sensitivity than chemical methods. Since that time several techniques which employ different types of microorganisms have been developed and a few are described here.

(i) Sackett and Stewart technique: The Sackett and Stewart technique is based on Winogradsky's work and was used to study the phosphorus and potassium status of Colorado soils. A culture is prepared of each soil, phosphorus is added to one portion, potassium to another, and both elements to a third portion. The cultures are then inoculated with *Azotobacter* and incubated for 72 hours. The soil is rated from very deficient to not deficient in the respective elements, depending on the amount of colony growth.

(ii) Aspergillus niger: To determine phosphorus and potassium small amounts of soil are incubated for a period of four days in flasks containing the appropriate nutrient solution. The weight of the mycelial pad or the amount of potassium absorbed by these pads is used as a measure of the nutrient deficiency.

(iii) Mehlich's Cunninghamella-Plaque method for phosphorus: The soil is mixed with the nutrient solution, a paste is made, spread uniformly in the well of a specially constructed clay dish, inoculated on the surface in the center of the paste, and allowed to incubate for four and half days. The diameter of the mycelial growth on the dish is used to estimate the amount of phosphorus present.

13.4. Soil testing

A soil test is a chemical method for estimating the nutrient-supplying power of a soil. Although biological methods for evaluating soil fertility have certain advantages, most of these tests have the disadvantages of being time consuming, hence, not well adapted for use with large numbers of samples. A chemical soil test, on the other hand, is much more rapid and has the added advantage over deficiency symptoms and plant analyses in that one may

determine the needs of the soil before the crop is planted. A soil test measures a part of the total nutrient supply in the soil. The values are of little use in themselves. To employ such a measurement in predicting nutrient needs of crops the test must be calibrated against nutrient rate experiments conducted in the field and in the greenhouse.

13.5. Fertilizer recommendations

There are several ways for making fertilizer recommendations to different crops and each method has some advantages and disadvantages which are discussed here.

13.5.1. Fertilizer recommendations on the basis of soil test data: Soil test interpretation involves an economic evaluation of the relation between the soil test values and the fertilizer response. However, the potential response may vary due to several factors among which are the soil, weather, and management ability of the farmer. Hence the soil test data have to be calibrated against the crop responses to the application of nutrients in question. This information is obtained from field and green house fertility experiments conducted over wide range of soil. The yield responses to the applied nutrients can then be related to the quantity of available nutrients in the soil. A calibrated soil test value for a particular nutrient will indicate the degree of deficiency of that nutrient, expected per cent increase on fertilizer application to correct the deficiency. The present system of calibrating the soil values as low, medium and high has a handicap for varying interpretation of such terms by different research workers. For its better use cooperative efforts among the workers in different parts of the country are necessary. To calibrate test values, they should be expressed in terms of relative yield or percentage sufficiency to describe degree of deficiency. It has also been suggested that the relative yield percentage at any soil test value may be termed as fertility index.

13.5.2. Fertilizer recommendations on the basis of soil test crop response (STCR) and targeted yield : In recent years systems of soil test rating are being modified incorporating crop response data available from systematic field experiments. Any soil test method intended for use in advisory work needs to be correlated with actual crop response obtained under field conditions and the success of the fertilizer recommendations programme will depend on the accuracy of the calibrations obtained in this way.

13.5.3. Fertilizer-recommendations on the basis of fertilizer-crop price ratios (FCPR) : This is useful parameter to judge the effectiveness of fertilizer use. The FCPR means kg of crop produce to pay for 1 kg of fertilizer nutrients e.g. if a farmer pays Rs 10/- per kg N and receives Rs 5/- per kg of his produce, then he needs 2 kg of produce to pay the cost of fertilizer. He will start making profit if each kg N produces more than 2 kg yield. If fertilizer prices go up, more yield will be needed to pay for 1 kg nutrient, and fertilizer use profitability will fall. If the produce prices go up, then less of it can pay for a unit of fertilizer and the profitability improves. Increase in fertilizer prices will result in lowering of the profit-maximizing dose because the marginal rate of return declines, whereas the nature of response curve remains unaffected by price changes.

13.5.4. Fertilizer recommendations on the basis of value:cost ratio (VCR) : This gives the value of crop per Re spent on fertilizer or the gross financial returns on every Re invested in fertilizers. It is very often used as an index of profitability of fertilizer use. Sometimes, the people say that a farmer should aim at the highest VCR i.e. the highest rate of return. This is not the right advice because the highest VCR is usually obtained at low application rates when the yield of crop is low. A farmer is interested in maximizing his returns in absolute terms. A VCR tells some other things also. A VCR of <1.0 means a loss i.e. the money spent on fertilizer is more than what can be earned by selling extra crop. A VCR of 1.0 indicates no profit, no loss. This is also known as the break-even point. On the other hand, a VCR of 2.0

means 100% profit and so on. The VCR is an index of gross rate of returns. The net rate of returns is given by benefit:cost ratio (BCR). The BCR gives net profitability after deducting the fertilizer cost.

13.5.5. Real time management of nitrogen : In many field situations up to 50% of the applied N is lost because of lack of synchrony of plant N demand with N supply. There are large site-to-site variations in N supplying capacity of soil to meet crop demand. The IRRI has identified crop demand indicators namely chlorophyll meter and leaf colour charts to regulate the timing of N application in rice.

(i) Chlorophyll meter : This is also known as Soil-Plant Analysis Development (SPAD) meter. This is a non-destructive method to determine the right time of N top dressing for rice. This concept is based on the results that show a close link between leaf chlorophyll content and leaf N content. The chlorophyll meter can provide a quick and accurate measurement of the leaf N status of rice plants *in situ* in the field. The SPAD threshold or critical values indicate critical N content in rice leaves. When SPAD readings fall below the critical SPAD values, the crop will suffer from N deficiency and yields will decline if N fertilizer is not applied immediately e.g. SPAD threshold value of 35 is equal to 1.4-1.5 g N/m^2 of leaf area of semi-dwarf varieties. Different SPAD threshold values are needed to optimize rice yields in different conditions e.g. wet season 30-35, dry season 30-37. The threshold values for wheat are in the range of 43-45. These can be refined by 1-2 seasons of testing for locally adopted important varieties. The SPAD technique indicates higher agronomic efficiency and partial factor productivity, and saving in N fertilizer dose without reducing grain yield.

(ii) Leaf colour charts: Chlorophyll method is a costly method as the SPAD meter costs about US $ 1000 and therefore, its use is restricted at the farmers' level. A simple technique is to use the green colour of leaf as an indicator of plant N status. The leaf colour chart has been developed at IRRI to measure leaf colour intensity and relate it to plant N status. It is ideal tool to optimize N use in rice, irrespective of the source of N application – inorganic, organic or biofertilizers. It is an eco-friendly tool in the hands of farmers. It costs about US $ 1.0 a piece. In India, the LCC is manufactured by M/s Protech Plast Pvt. Ltd., # 25/5 Jaraganahalli, J.P. Nagar Post, Bangalore 560 078. The LCC contains six green strips with the colour ranging from yellowish green (No. 1) to dark green (No. 6). The critical leaf colour chart reading for N top dressing in transplanted rice ranges from 3 for varieties with higher green foliage (aromatic rice) to 4 for semi-dwarf indica rice varieties and hybrids.

The colour of the youngest fully expanded leaf (second from the top) of 10 randomly selected disease-free rice plants/hill starting from 2 weeks after transplanting till initiation of flowering is matched with LCC. When greenness of 6 or more out of 10 leaves is less than the shade 4 on the LCC, the N application is made. The colour of the leaf is always compared under the shade of the body and around the same time (9-10 AM or 4-5 PM of the day), preferably by the same person.

14. Biofertilizers

The bio-inoculants or preparations containing microorganisms that supply nutrients especially nitrogen and phosphorus are known as biofertilizers. On the basis of nutrients supply, these are broadly classified in four groups: (i) nitrogen fixers, (ii) phosphorus solubilizers, (iii) plant growth promoters (iv) organic matter decomposers.

14.1. Nitrogen fixers

Certain micro-organisms like bacteria and blue-green algae have the ability to use atmospheric nitrogen and made available this nutrient to the crop plants. Some of these 'nitrogen fixers' like rhizobia are obligate symbionts in leguminous plants (Tilak and Saxena,

1996), while others colonize root zones and fix nitrogen with loose association with plants. A very important bacterium of the latter category is *Azospirillum*, which was discovered by a Brazilian scientist in the mid 1970s. The third group includes free-living nitrogen fixers such as blue-green algae and *Azotobacter.*

14.1.1. Legume Inoculants : The most widely used biofertilizer for pulse crops is *Rhizobium* which colonizes the roots of specific legumes to form turmour like growth called root nodules. The *Rhizobium*-legume association can fix up to 100-200 kg N/ha in one crop season and in certain situations can leave behind substantial nitrogen for the following crop.

The range of nitrogen fixed per hectare per year by different legumes is 100-150 kg for clover, 53-85 kg for cowpea, 68-200 kg for pigeonpea, 46 kg for peas, 35-106 kg for lentil, 112-152 kg for groundnut, 49-130 kg for soybean, 50-55 kg for mungbean and 37-196 kg for guar (Tilak, 1998). Stem nodulating legumes such as *Sesbania rostrata, Aeschynomene* sp. and *Neptunia oleracea* have become popular in improving soil fertility. The N-fixing bacteria associated with such stem nodulating legumes belong to *Azorhizobium,* a fast growing species of *Rhizobium*. The N-acumulating potential of stem nodulating legumes under flooded conditions ranges from 40-200 kg N/ha (Rao *et al*., 1994).

14.1.2. *Azotobacter and Azospirillum* : The beneficial effects of *Azotobacter* on cereals, millets, vegetables, cotton and sugarcane under both irrigated and dryland conditions have been well substantiated and documented. Application of this biofertilizer has been found to increase the yield of wheat, rice, pearlmillet and sorghum by 0-30% over control. Apart from nitrogen, this organism is also capable of producing antibacterial and antifungal compounds, hormones and siderophores (Tilak, 1993).

Azospirillum, an associative microareophilioc organism living in association with diverse group of plants consists of 5 species namely, *A. brasilense, A. lipoferum, A. amazonense, A. halopreference* and *A. irkense.* Associative nitrogen fixation, capability to produce plant growth promoting antifungal, antibacterial substances and their effect on root morphology are the principal mechanisms responsible for the increase in crop yields (Tilak and Annapurna, 1993). Inoculation with *Azospirillum* results in enhanced assimilation of mineral nutrients (N, P, K, Rb^{+}, Fe^{2+}), and offers resistance to pathogens (Wani, 1990).

A new bacterium *Herbaspirillum* taxonomically closely related to *Azospirillum* has also been isolated from forage grasses (Indira and Bagyaraj, 1996). *Acetobacter diazotrophicus* is a saccharophilic bacterium and is associated with sugarcane, sweet sorghum and sweet potato. Reports from Brazil indicate that this bacterium fixes around 150-250 kg N/ha/year in case of sugarcane.

14.1.3. Blue-green algae : A judicious use of blue green algae could provide to the country's entire rice acrease as much nitrogen as obtained from 15-17 lakh tonnes of urea. Methods have been developed for mass production of algal biofertilizers and it is becoming popular among the rice growers in many parts of the country (Ventakaraman and Tilak, 1990). Recent research has shown that algae also help to reduce soil alkalinity, and this opens up possibilities for bioreclamation of such inhospitable environments. This area is of particular relevance, because 7 million hectares of arable land in our country are salt affected.

14.1.4. *Azolla* : *Azolla* is known as a floating nitrogen factory in low land rice fields and in shallow fresh water bodies. The *Azolla anabaena* association use the energy from photosynthesis to fix atmospheric nitrogen amount to 100-150 kg/ha/year from about 40-60 tonnes of biomass (Singh, 1998). An integrated system of rice-*Azolla*-fish has been developed in China. We need to give greater thrust on this system.

14.2. Phosphate solubilizers

14.2.1. Phosphorus solubizing bacteria : Bacteria such as *Pesudomonas* and *Bacillus* excrete acids into the growth medium and hence solubilize bound phosphorus (Gaur, 1985). These organisms are quite useful in the utilization of rock phosphate with low content of P. Field experiments conducted with P-solubilizers like *Aspergillus awamori, P. striata* and *B. polymyxa* significantly increased the yields of various crops like wheat, rice, cowpea, etc. Use of rock phosphate with phosphate solubilizing bacteria resulted in a saving of 30 kg P_2O_5/ha (Gaur, 1985).

14.2.2. Mycorrhizae : Recent research has shown the possibility of domesticating mycorrhizae in agricultural systems. They also ubiquitous in geographic distribution occurring with plants growing in all environmental conditions. VA-mycorrhizal fungi occur over a broad ecological range from aquatic to desert environments. These fungi belonging to the genera *Glomus*, *Gigaspora, Acaulospora, Entrophosphora, Modicella, Sclerocystis* and are obligate symbionts. These fungi have been cultured on nutrient media using standard microbiological techniques. They are multiplied in the roots of host plants and the inoculum is prepared using infected roots and soil.

Crop responses to VAM inoculation are governed by soil type, host variety, VAM strains, temperature, moisture, cropping practices and soil management practices. The major constraint for using VAM has been the inability to produce 'clean pure' inoculum on large scale. Field trials indicated that VAM inoculation increased yields at certain locations and the response varied from soil type, soil fertility particularly with available P status of soil and VAM culture (Tilak, 1993). Mycorrhizal fungi assists in the uptake of phosphorus and trace metals and positively influences water and nutrient status via hormonal influences. However, lack of suitable inoculum production technology is the major limitation for the commercial exploitation of this system.

14.3. Plant growth promoting Rhizobacteria

A group of rhizosphere bacteria (rhizobacteria) that exerts a beneficial effect on plant growth is referred to as Plant Growth Promoting Rhizobacteria or PGPR (Schroth and Hancock, 1981). PGPR belongs to several genera, namely, *Actinoplanes, Agrobacterium, Alcaligenes, Amorphosporangium, Arthrobacter, Azotobacter, Bacillus, Bradyrhizobium, Cellulomonas, Enterobacter, Erwinia, Flavobacterium, Pseudomonas, Rhizobium, Streptomyces* and *Zanthomonas* (Weller, 1988). *Bacillus* sp. are appealing candidates as PGPR because of their endospore producing ability which make them ideal inoculants for dry areas. Currently *Pseudomonas* spp. are receiving much attention as PGPR, because of their multiple effects on plant growth promotion.

PGPR are believed to improve plant growth by colonizing the root system and pre-emptying the establishment of suppressing Deleterious Rhizosphere Micro Organisms (DRMO) on the root (Schroth and Hancock, 1981). Inoculating planting material with PGPR presumably prevents or reduces the establishment of pathogens (Suslow, 1982). Production of siderophores is yet another molecular weight high affinity Fe^{+3} chelators that transport iron into bacterial cells and are responsible for increased plant growth by PGPR (Kloepper *et al*., 1980). Under Fe-deficient conditions, fluorescent Pseudomonas produce yellow-green fluorescent siderophore-iron complex (Hohnadel and Meyer, 1986) which creates an iron deficient environment deleterious to fungal growth.

14.4. Organic matter decomposers

With increasing need to conserve natural resources and energy, recycling of organic wastes assumes major importance. Further, in the wake of serious pollution problems and

biomagnification of toxic chemicals in the various biological systems, 'Organic farming' is a right approach. Agricultural wastes including cereal straw/stalk/stover, animal wastes, by-products of food processing industry etc. are available in large quantity and contain valuable plant nutrients. These can be converted into useful compost products. Composting offers several advantages as a waste disposal method, including increased availability of plant nutrients, destruction of pathogens, elimination of unfavourable odours and easy handling. The humus material formed influences the physical, chemical and biological characteristics of the soil and improves crop growth (Gaur and Sadasivam, 1993).

15. Integrated Nutrient Management (INM)

The concept of INM is the rationalization of plant nutrient management in order to upgrade the efficiency of plant nutrient supply to the crops through the adequate association of local and external plant nutrient sources accessible and affordable to the farmers resulting ultimately in higher productivity and income to the farmers. In INM, better management results in plant nutrient gains, which are reinvested in the plant nutrient cycle in order to gradually upgrade the plant nutrient capital on the farm (soil reserves, crop residues, manures etc.) in an economically justified, socially acceptable and ecofriendly manner. This should also increase the cash flow for the purchase of chemical fertilizer.

INM firstly operates at the field level, optimizing the stocks and flows of plant nutrients from the diverse sources in order to increase the uptake of plant nutrients by the crops, the agronomic and physiological efficiency and at the same time to reduce losses of plant nutrients from the soil.

At the farm level INM is the combination of plant nutrition practices and allocation of plant nutrient sources optimizing the flows of nutrients passing through the soil/crop/livestock system and increasing both the stock of plant nutrients in the system and income of the farmers. INM aims at the accumulation of the production capacity of the farmers through accurate and profitable investments in external plant nutrient sources and amendments, efficient processing and recycling of crop residues and onfarm organic wastes. An inventory has to be made for the entire farming system involving seed, irrigation, manure, residues, animals on the farm etc. Only a careful periodic study of the inventory permits the proper implementation of INM.

The concept of INM can then be extended to the entire village or a district or a state. This will then involve making of inventories beyond the cropped areas and should list the source and amount of irrigation water, its quality including plant nutrient content, sediments provided by floods, plant nutrients removed by cutting of trees, contribution of pasture land if any and loss of gains of nutrients by rains, floods and storms. When planned and proceed well, INM leads to the betterment of soils, pasture and forest lands animal stock, people and area as a whole.

15.1. Components of INM

The major components of INM are as follows:

15.1.1. Fertilizers: Fertilizers are concentrated source of one or more plant nutrients. The nutrient supply through fertilizers during 2004-2005 was 18.4 million tonnes consisting of 11.7, 4.6 and 2.1 million tonnes of N, P_2O_5 and K_2O, respectively (FAI, 2005). In contrast, nutrient removal by crops was 8-10 million tonnes higher than nutrient addition through fertilizers. This gap needs to be bridged through organics and biofertilizers.

15.1.2. Organic manures: Among the organic manures, the most common is the compost/farmyard manure (FYM). Organic manures not only supply plant nutrients in

balanced proportion but also improve, physical and biological properties of soil and thus make the system sustainable.

15.1.3. Green manures: Green manuring with legumes has long been known to be beneficial for sustainable crop productivity. In several studies conducted in India green manure was able to replace 60 kg N/ha. A fertilized green manure crop would substitute more mineral fertilizer N than an unfertilized green manure crop (Sharma and Mittra, 1988). A wide variability in N substitution through green manuring to the order of 45-120 has been reported. However, most commonly observed N additions through an array of green manures are in the range of 40-60 kg N/ha.

15.1.4. Crop rotation: To overcome the ecological diseases of monoculture, the first solution that man found was the changing of crops from one to another or from one season to another. Even before the modern agriculture was established the farmer had discovered the restorative power of legumes. For example, Vigil as early as 70-19 BC advocated the application of legumes and indicated in the following passage.

"Or, changing the season, you will sow these yellow wheat, wherever before you have taken up joyful pulse, with resulting pods".

Thus the key to successful crop rotation was a soil restorer legume such as beans (*Vicia faba* L.), clover, lupins (*Lupinus album* L.) and Vatch (*Vicia savita* L.). The famous English Norfold rotation popular in 18^{th} Century in England was turnip, barley, clover and wheat in a 4 year sequence. Thomas Jefferson followed a 5 year rotation of wheat-corn/potato-pea (*Pisum sativum* L.) – rye (*Secale cereals* L.)/wheat-clover/buck wheat (*Fagopynum esculentum* Moench). Even today only 20% of the corn in the United States is grown in continuous monoculture, while the remaining 80% is grown in a 2 year rotation with soybean or in short (2-or-3 year rotation) with alfalfa, cotton, dry bean or other crop. The legumes restore soil fertility in many ways. Some of them are: (i) they fix atmospheric N_2 and leave part of it in soil, (ii) their deeper tap root system absorbs moisture and nutrients from deeper soil layers and some of the nutrients absorbed are left in the root mass in the surface soil, (iii) improve soil permeability, (iv) lesser disease and pest problem and (v) better weed control.

15.1.5. Crop residues : Substantial amounts of crop residues are produced in India every year. Five major crops namely rice, wheat, sorghum, pearlmillet and maize alone yield approximately 225 MT straw/stover with an average composition of about 0.5% N, 0.5% P_2O_5 and 1.5% K_2O (Table 6)

Table 6. Estimate of the availability of some crop residues in India and their plant nutrient potential

Crop	Residue to economic yield ratio	Residue yield* (,000 tonnnes)	Nutrient (%)				Nutrient potential ('000 tonnes)	
			N	P_2O_5	K_2O	Total	Utilizable**	Fertilizer equivalent***
Rice	1.5	110,495	0.61	0.18	1.38	2,398	799	399
Wheat	1.5	79,631	0.48	0.16	0.18	1,504	501	250
Sorghum	1.5	12,535	0.52	0.23	1.34	262	87	43
Maize	1.5	11,974	0.52	0.18	1.35	252	84	42
Pearl millet	1.5	9,967	0.45	0.16	1.14	121	40	20
Total		224,602				4,537	1511	754

***** Arrived at by multiplying the economic yield by the given residue:economic yield ratio.

****** One third of the total NPK potential assuming that two thirds of the total residue is used as animal feed on national basis

******* Fifty per cent of the utilizable NPK, assuming 50% mineralization of NPK per season

Source: Bhardwaj (1995)

The nutrient potential of these five crops alone thus comes to 4.537 MT including 1.23, 0.39 and 2.91 MT of N, P_2O_5 and K_2O, respectively (Table 2). Assuming that two-third of the total residues is used as animal feed, one third of the total NPK potential would be 1.51 MT of N + P_2O_5 + K_2O. Assuming 50% mineralization of NPK per season, the nutrient supply as fertilizer equivalent would be 0.75 MT. In addition to this, contribution of the residues of pulses, oilseeds, sugarcane etc. towards nutrient supply would be substantial. The beneficial effect of residue incorporation on soil productivity is attributed to over all improvement in physical, chemical and biological properties of soils. Regular return of residues to soil contributes to the build up of soil nutrient pool over a period of time.

15.1.6. Biofertilizers: Biofertilizers by rendering unavailable sources of elemental nitrogen, bound phosphates and decomposed plant residues into available forms help enhancing soil fertility and crops yields. The details of benefits from biofertilizers have been discussed under Section 14.

References

1. Abul Fazal. 1595. Ain-I-Akbari. Cited in: A new Advance History of India. P.N. Chopra,
2. B.N. Puri, M.N. D as and A.C. Pradhan (Eds.). Prentice-Hall of India, New Delhi. p. 329.

3. Adams, F. 1980. Interaction of phosphorus with other elements in soils and plants. **In** The Role of Phosphorus in Agriculture. F.E. Khasawneh, E.C. Sample and E.J. Kamprath (eds.). American Society of Agronomy, Madison. pp. 655-680.

4. Arnon, D.I. and Stout, P.R. 1939. The essentiality of certain elements in minute quantity for plants with special reference to copper. *Plant Physiology* **14**:371-375.

5. Bacon, Francis. 1561-1624. Cited in: A History of Agriculture Science in Great Britain. E.J. Russell (Ed.) 1951. George Allen and Henwein Ltd. London. pp. 1-18.

6. Barshad, I. 1951. Factors affecting the molybdenum content of pasture plants. 1. Nature of soil Mo, growth of plants and soil pH. *Soil Science* **71**:387-398.

7. Bartlett, R.J. and James, B.R. 1993. Redox chemistry of soils. *Advances in Agronomy* **50**:151-208.

8. Bolland, M.D.A., Posner, A.M. and Quirk, J.P. 1977. Zinc adsorption by goethite in the absence and presence of phosphate. *Australian Journal of Soil Research* **15**:279-286.

9. Botterro, I., Elena, C. and Vercontter, J. 1965. The Nearest: The early civilization. Weidinfield and Nicolson, London, p. 782.

10. Boussingault, J.B. 1834. Cited in Soil Conditions and Plant Growth. E.J. Russell (Ed.) Longmans Green & Co. London.

11. Boyle, R. 1627-1691. Cited in: Soil Fertility and Fertilizers. S.L. Tisdale, W.L. Nelson and J.D. Beaton (Eds.), MacMillan Pub. Co. New York. pp. 3-18.

12. Brady, N.C. 1990. The Nature and Properties of Soils. 10th Ed. John Wiley and Sons, New York.

13. Bremner, J.M. and Shaw, K. 1958. Denitrification in soil. II. Factors affecting denitrificaiton. *Journal of Agricultural Science*, *Cambridge* **51**:40-45.

14. Cao, Z.H. DeDatta, S.K. and Fillery, I.R.P. 1984a, Labelled nitrogen fertilizer research with urea in the semi-arid tropics. I. Greenhouse studies. *Plant and Soil* **80**:3-19.

15. Cao, Z.H., De Datta, S.K. and Fillery, I.R.P. 1984b. Effect of placement methods on recovery of applied N (^{15}N-labelled urea) in wetland. *Soil Science Society of America Journal* **48**:196-203.

16. Chien Hen Shu. 3rd century B.C.. Cited in: Foundation of Indian culture. G.C. Pande (Ed), 1989. Motilal Banarasidas Pub. Delhi. p. 89.

17. Cosgrove, D.J. 1962. Forms of inositol hexaphosphate in soils. *Nature* (London) **194**:1265-1266.

18. Daigger, L.A., Sander, D.H. and Peterson, G.A. 1976. Nitrogen content of winter wheat during growth and maturation. *Agronomy Journal* **68**:815-818.

19. Eckert, D.L. and McLean, E.O. 1981. Basic cation saturation ratios as a basis for fertilizing and liming agronomic crops: I. Growth chamber studies. *Agronomy Journal* **75**:795-799.

20. Empedocles. 495 B.C. Cited in: Soil Conditions of Plant Growth. E.J. Russel (Ed.), 1917, Longmans Green and Company, London, pp. 1-18.

21. Erathothenes 3rd century B.C. Cited in: Foundations in Indian Culture. G.C. Pandey (Ed.) 1989. Motilal Banarsidas Pub., Delhi. p. 89.

22. FAI. 2005. Fertilizer Statistics. Fertilizer Association of India, New Delhi.

23. Francis, D.D., Schepers, J.S. and Vigil, M.F. 1993. Post-anthesis nitrogen loss from corn. *Agronomy Journal* **85**:659-663.

24. Freney, J.R., Trevitt, A.C.F., De Datta, S.K., Obcemea, W.H. and Real, J.G. 1990. The interdependence of ammonia volatilization and denitrification as nitrogen loss processes in flooded rice fields in the Philippines. *Biology and Fertility of Soils* **9**:31-36.

25. Ganeshmurthy, A.N., Mongia, A.D. and Singh, N.T. 1989. Forms of S in soil profiles of Andaman and Nicobar Islands. *Journal of Indian Society of Soil Science* **37**:825-829.

26. Gaur, A.C. 1985. Phosphate solubilizing microorganisms and their role in plant growth and crop yields. Proceedings of Soil Biology Symposium, held at Hisar, India. M.M. Mishra and K.K. Kapoor (Eds.). pp. 125-138.

27. Gaur, A.C. and Sadasivam, K.V. 1993. Theory and practical considerations of composting organic wastes. **In** Organics in Soil Health and Crop Production. P.K. Thampan (Ed.). Peekay Tree Crops Development Foundation, Cochin, Kerala, pp. 69-86.

28. George, M. and Prasad, R. 1989. Studies on the effect of legumes on fertilizer N utilization by rice using ^{15}N technique in rice based cropping system. *Research and Development Agriculture* **8**:115-118

29. Giordano, P.M., Noggle, J.C. and Mortvedt, J.J. 1974. Zinc uptake by rice as affected by metabolic inhibitors and competing cations. *Plant and Soil* **41**:637-648.

30. Glauber, J.R. 1604-1668. Cited in: Soil Fertility and Fertilizers. S.L. Tisdale, W.L. Nelson and J.D. Beaton (Eds.), MacMillan Pub. Co. New York. pp. 5-18.

31. Goswami, N.N., Prasad, R., Sarkar, M.C. and Singh, S. 1988. Studies on the effect of green manuring in nitrogen economy in rice-wheat rotation using ^{15}N technique. *Journal of Agricultural Science* **111**:413-417.

32. Groftman, P.M., Tiedje, J.M., Robertson, G.P. and Christensen, S. 1988. Denitrification at different temporal and geographical scales: proximal and distal control. p. 174-192. **In** Advances in Nitrogen Cycling in Agricultural Ecosystems. J.R. Wilson (Ed.). C.A.B. International, Wallingford, U.K.

33. Gupta, U.C. 1985. Boron toxicity and efficiency: A review. *Canadian Journal of Soil Science* **65**:381-409.

34. Gupta, U.C. and Lipsett, J. 1981. Molybdenum in soils, plants and animals. *Advances in Agronomy* **34**:73-113.

35. Harper, L.A., Sharpe, R.R., Langdale, G.W. and Giddens, J.E. 1987. Nitrogen cycling in a wheat crop: Soil, plant and aerial transport. *Agronomy Journal* **79**:965-973.

36. Harter, R.D. 1983. Effect of soil pH on adsorption of lead, copper, zinc and nickel. *Soil Science Society of America Journal* **47**:47-51.

37. Hohandel, O.B. and Meyer, J.M. 1986. Pyoverdine-facilitated iron uptake among *fluorescent Pseudomonas*. **In** Iron Siderophores and Plant Diseases. T.R. Swinburne, (Ed.). Plenum Press, New York, USA, pp. 119-129.

38. Home, Francis. 1767. The principles of agriculture and vegetation. Cited in Soil Conditions and Plant Growth. E.J. Russell (Ed.). Longmans Green & Co. London, pp. 1-8.

39. Indira, B.N. and Bagyaraj, D.J. 1996. *Herbaspirillum* associated with forage grasses. Proc. Indian National Science Academy **63**:25-30.

40. Jan Baptiste Van Helmont . 1577-1644. Cited in: Soil Fertility and Fertilizers (S.L. Tisdale, W.L. Nelson and J.D. Beaton (Eds.), MacMillan Pub. Co. New York. pp. 5-18.

41. Katyal, J.C. and Sharma, B.D. 1979. Role of micronutrients in crop production. *Fertilizer News* **24**(9):33-50.

42. Kausar, M.A., Chaudhary, F.M., Radhid, A., Latif, A. and Alam, S.M. 1976. Micronutrient availability to cereals from calcareous soils. I. Comparative Zn and Cu deficiency and their mutual interaction in rice and wheat. *Plant and Soil* **45**:397-410.

43. Kautilya. 3rd century B.C. Arthashastra. Cited in: Foundation of Indian culture. G.C. Pande (Ed), 1989. Motilal Banarasidas Pub. Delhi. p. 89.

44. Kenoyer, M.J. 1995. Interaction system, specialized crafts and cultural change: The Indus Valley tradition and the Indo-Gangetic traditions in South Asia. **In** Indo-Aryans of Asian South Asia: Language, material, culture and ethnicity. G. Erdosy (Ed.). Munshiram Manohar Lal Pub., New Delhi.

45. Kjeldahl, J.Z. 1879. A new method for the determination of nitrogen in organic bodies. *Z. Anal. Cheno*. **22**:366.

46. Kloepper, J.W., Leong, J., Teintze, P., Arayangkool, T., Sintwongse, P., Siripaibool, C., Wadisirisuk, P. and Boonkerd, N. 1988. Nitrogen fixation (^{15}N dilution) with soybeans under Thai field conditions. II. Effect of herbicides and water application schedules. *Plant and Soil* **108**:87-92.

47. Kowalenko, C.G. and McKercher, R.B. 1971. Phospholipid P content of Saskatchewan soils. *Soil Biology and Biochemistry* **3**:243-247.

48. Krishiparasara. 950 AD. Cited in Foundations of Indian culture, Vol. 2. Dimensions of Ancient Indian History. G.C. Pande (Ed), 1989. Motilal Banarasidas Pub. Delhi. p. 96.

49. Krishna, K.R. 2002. Soil Fertility and Crop Production. Oxford & IBH Pub. Co., New Delhi.

50. Lavoisier. 1775. Cited in: The Principles and Practices of Agricultural Research. S.C. Salman and A.A. Hanson (Eds.) 1964. Leonard Hill, London, pp. 1-44.

51. Lawes, J.B. and Gilbert, J.H. 1843. Cited in: Soil Fertility and Fertilizers. S.L. Tisdale, W.L. Nelson, J.D. Beaton (Eds.). Macmillan Pub. Co., New York. pp. 5-18.

52. Liebig, J.V. 1802-1873. Cited in: Cited in: Soil Fertility and Fertilizers. S.L. Tisdale, W.L. Nelson, J.D. Beaton (Eds.). Macmillan Pub. Co., New York. pp. 5-18.

53. Malavolta, E. 1985. Potassium status of tropical and subtropical region soils. **In** Potassium in Agriculture. R.D. Munson (Ed.), American Society of Agronomy, Madison, Washington. pp. 163-200.

54. Mayow, John 1643-1679. Cited in: Soil Fertility and Fertilizers. S.L. Tisdale, W.L. Nelson and J.D. Beaton (Eds.), MacMillan Pub. Co. New York. pp. 5-18.

55. Megasthanes. 3rd. century B.C. Cited in: Foundation in Indian Culture. G.C. Pande (Ed), 1989. Motilal Banarasidas Pub. Delhi. p. 89.

56. Mitcherlich, E.A. 1923. Das gaset, des Minimums and Das Gazets des abnchenerelon Bodenestrages, London, Fehrb. XXXVIII:537-552.

57. Moe, P.G., Mannering, J.V. and Johnson, C.B. 1968. A comparison of nitrogen losses from urea and ammonium nitrate in surface runoff water. *Soil Science* **105**:428-433.

58. Naubauer, H. 1932. Ein Vereinfachtes verfehaem Bestimmung Von phosphorsaure, Kalium, Natrium, Calcium and Magnesium in Salzsauren, Bodenauszngen. Lvi:203 Landw., Versucks-Stat.

59. Nicolo Conti. 1441. Travels in India. Cited in: Mughal Economy: Organization and Working. B.N. Sarkar (Ed.) 1987. Noya Prakash, Calcutta. pp. 1-42.

60. Palissy 1563. Cited in Soil Conditions and Plant Growth. E.J. Russell (Ed). 1917. Longmans Green and Co., London. pp. 1-18.

61. Papkosta, D.K. and Gagianas, A.A. 1991. Nitrogen and dry matter accumulation, remobilization and loss for Mediterranean wheat during grain filling. *Agronomy Journal* **83**:864-870.

62. Pearson, R.W. 1952. Potassium supplying power of eight Alabama soils. *Soil Science* **74**:301-309.

63. Pichai, S. 1988. Ph.D. Thesis, Division of Agronomy, Indian Agricultural Research Institute, New Delhi.

64. Pliny. 62-113 AD. Cited in: Soil Fertility and Fertilizers. S.L. Tisdale, W.L. Nelson, J.D. Beaton (Eds.). Macmillan Pub. Co., New York. pp. 5-18.

65. Prasad, M. and Prasad, R. 1980. Yield and nitrogen uptake as affected by variety, method of planting and new nitrogen fertilizers. *Fertilizer Research* **1**(4):207-214.

66. Prasad, R. and Power, J.F. 1997. Soil Fertility Management for Sustainable Agriculture. CRC Boca Raton, New York.

67. Prasad, R., Rajale, G.B. and Lakhdive, B.A. 1970. Effect of time and method of application of urea and its treatments with nitrification inhibitors on the yield and nitrogen uptake by irrigated rice. *Indian Journal of Agricultural Science* **40**:1118-1127.

68. Prasad, R., Rajale, G.B. and Lakhdive, B.A. 1971. Nitrification retarders and slow-release nitrogen fertilizers. *Advances in Agronomy* **29**:337-383.

69. Prasad, R., Sharma, S.N., Singh, S. and Prasad, M. 1989. Relative efficiency of prilled urea and urea supergranules for rice. **In** *Soil Fertility and Fertilizer Use* Vol. III Urea Supergranules for Increasing Nitrogen Use Efficiency. IFFCO, New Delhi. pp. 36-46.

70. Rao, V.V.R., Adhya, T.K., Patnaik, G.K., Kanungo, P.K. and Ramakrishan, B. 1994. Associative nitrogen fixation in rice: potentials and limitations. **In**: Biology and Application of Nitrogen Fixing Organisms: Problems and Prospects. A.B. Prasad and A. Vaishampayan (Eds.), Scientific Publishers, Jodhpur, India. pp. 129-138.

71. Rennie, D.A. Racz, G.J. and McBeath, D.K. 1976. Nitrogen losses. Proc. Western Canada Nitrogen Symp., Alberta, Edmonton, pp. 325-353.

72. Ritchey, K.D. 1979. Potassium fertility in oxisols and ultisols of humid tropics. Cornell Institute of Agriculture Bulletin 37, Cornell University, Ithaca, New York.

73. Russell, E.J. 1917. Soil Conditions and Plant Growth. Longmans Green & Co., London.

74. Saeed, M. and Fox, R.L. 1979. Influence of phosphate fertilization on zinc adsorption by tropical soils. *Soil Science Society of America Journal* **43**:683-686.

75. Savant, N.K., Craswell, E.T. and Diamond, R.B. 1983. Use of urea supergranules for wetland rice. A review. *Fertilizer News* **28**(8):27-35.

76. Schnier, H.F., Dingkuhn, M., DeDatta, S.K., Marqueses, E.P. and Faronilo, J.E. 1990. Nitrogen –15 balance in transplanted and direct-seeded flooded rice as affected by different methods of urea application. *Biology and Fertility of Soils* **10**:89-96.

77. Schroth, M.N. and Hancock, J.G. 1981. Selected topics in biological control. *Annual Review of Microbiology* **35**:453-476.

78. Shavir, A., Hagin, J. and Nelson, P.M. 1987. Effects of nitrification inhibitor on efficiency of nitrogen utilization by wheat and millet. *Communication of Soil Science and Plant Analysis* **18**:815-833.

79. Singh, P.K. 1998. *Azolla* biofertilizer production. **In** Mass production of Blue-Green Algal production (eds. P.K. Singh and S. Pabbi), National Centre for Conservation and Utilization of BGA, Indian Agricultural Research Institute, New Delhi, India. pp. 39-42.

80. Singh, S. 1985. Ph.D. Thesis, Division of Agronomy, Indian Agricultural Research Institute, New Delhi.

81. Sparks, D.L. 1987. Potassium dynamics in soils. *Advances in Soil Science* **6**:1-63.

82. Spencer, K. 1975. Sulphur requirements of crops. **In** Sulphur in Australian Agriculture. K.D. McLachlan (Ed.). Sydney University Press, Sydney. pp. 98-198.

83. Stevenson, F.J. 1986. Cycles of soil. Role of micronutrients in crop production. John Wiley and Sons, New York. pp. 380.

84. Stevenson, F.J. 1991. Organic matter – nutrient reactions in soils. **In** Micronutrients in Agriculture. J.J. Mortvedt, F.R. Cox, L.M. Shuman and R.M. Welch (Eds.). Soil Science Society of America, Madison, WI. pp. 145-186.

85. Subbiah, B.V., Sachdev, M.S., Arora, R.P. and Sud, Y.K. 1985. Efficiency of fertilizer use in multiple cropping system – studies with isotope techniques. *Fertilizer News* **30**(2):45-48.

86. Sudhakara, K. and Prasad, R. 1986. Ammonia volatilizatin losses from prilled urea, urea supergranules (USG) and coated USG in rice fields. *Plant and Soil* **94**:293-295.

87. Suslow, T.V. 1982. Role of root colonizing bacteria in plant growth. **In** Phytopathogenic prokaryots. M.S. Mount and G.H. Lacy (Eds.), Academic Press, London, pp. 187-223.

88. Takkar, P.N. 1988. Sulphur status of Indian soils. Proceedings of the Sulphur Institute – Fertilizer Association of India Symposium, "Sulphur in Indian Agriculture" held at New Delhi. p. 5/1/12/1-31.

89. Tandon, H.L.S. 1989. Nitrogen recommendations for higher fertilizer efficiency. *Fertilizer News* **34**(12):63-77.

90. Tandon, H.L.S. 1991. Sulphur Research and Agricultural Production in India. 3rd edition, The Sulphur Institute, Washington, D.C. pp. 140.

91. Tavernier, Jean Baptiste. 1640-67. Original in French. Translated by John Phillips as Tavernier Travels in India. Cited in: Mughal Economy: Organization and Working. B.N. Sarkar (Ed.) 1987. Noya Prakash, Calcutta. pp. 1-42.

92. Theophrastus. 327-287 B.C. Cited in: Foundation of Indian culture. G.C. Pande (Ed), 1989. Motilal Banarasidas Pub. Delhi. p. 86.

93. Thomas, J. and Prasad, R. 1982. On the nature of mechanisms responsible for the higher efficiency of urea supergranules for rice. *Plant and Soil* **69**:127-130.

94. Thomas, J. and Prasad, R. 1987. Relative efficiency of prilled urea, urea supergranules, sulphur coated urea and nitrification inhibitor N-Serve blended urea for direct seeded rice. *Journal of Agronomy and Crop Science* **15**:302-307.

95. Tilak, K.V.B.R. 1993. Associative effects of vesicular-arbuscular mycorrhizae with nitrogen fixers. Proceedings of Indian National Science Academy. B59 (3&4):325-332.

96. Tilak, K.V.B.R. 1998. Bacterial Fertilizers, Publications Division, Indian Council of Agricultural Research, New Delhi, India, pp. 1-63.

97. Tilak, K.V.B.R. and Annapurna, K. 1993. Role of *Azospirillum* in the improvement of crop production and plant nutrition. Proceedings of Indian National Science Academy. B59 (3&4):315-324.

98. Tilak, K.V.B.R. and Saxena, A.K. 1996. Biofertilizers – their role in crop production. Fertilizer Industry, Annual Rev. pp. 187-194.

99. Tisdale, S.L., Nelson, W.L. and Beaton, J.D. 1985. Soil Fertility and Fertilizers, 4th Ed. Macmillan Publ. Co., New York.

100. Venkataraman, G.S. and Tilak, K.V.B.R. 1990. Biofertilizers in sustainable agriculture. **In** Soil Fertility and Fertilizers Vol. IV, Nutrient management and supply system for sustaining agriculture in 1990's. V. Kumar, G.C. Shrotriya and S.V. Kavre (Eds.) Indian Farmers Fertilizers Cooperative Ltd., New Delhi, pp. 132-148.

101. Virgil 70-19 B.C.. Aeniel Cited in: Revised Websters Encyclopedia of the English Language. Gramercy Books, New York. p. 1587.

102. Wallerious. 1761. Cited in: Soil Conditions and Plant Growth. E.J. Russel (Ed.). Longmans Green & Co. London. pp. 1-18.

103. Wani, S.P. 1990. Inoculation with associative nitrogen fixing bacteria: Role of cereal grain production improvement. *Indian Journal of Microbiology* **30**:363-393.

104. Webb, M.J. and Loneragan, J.F. 1988. Effect of zinc deficiency on growth, phosphorus concentration and phosphorus toxicity of wheat plants. *Soil Science Society of America Journal* **52**:1676-1680.

105. Weller, D.M. 1988. Biological control of soil borne plant pathogens in the rhizosphere with bacteria. *Annual Review of Phytopathology* **26**:379-407.

106. Woodward, John 1700. Cited in: Soil Fertility and Fertilizers. S.L. Tisdale, W.L. Nelson and J.D. Beaton (Eds.), MacMillan Pub. Co. New York.

107. Yagnavalkya 300-380 A.D. Yagnavalkya Smriti-II 200-03. Cited in: The age of Guptas R.W. Dandekar (Ed.) 1986. Ajantha Pub. (India) pp. 42-43.

108. Young, Anthur. 1971-1820. Cited in: Soil Fertility and Fertilizers. S.L. Tisdale, W.L. Nelson and J.D. Beaton (Eds.), MacMillan Pub. Co. New York. pp. 5-18.

109. Youngdahl, L.J., Svec, L.V., Leibhardt, W.C. and Teel, M.R. 1977. Changes in $Zinc^{65}$ distribution in corn root tissue with a phosphorus variable. *Crop Science* **17**:66-69.