SOIL FERTILITY, PLANT NUTRITION,

AND FERTILIZER MANAGEMENT IN THE

TROPICS

BY

B.R. Singh
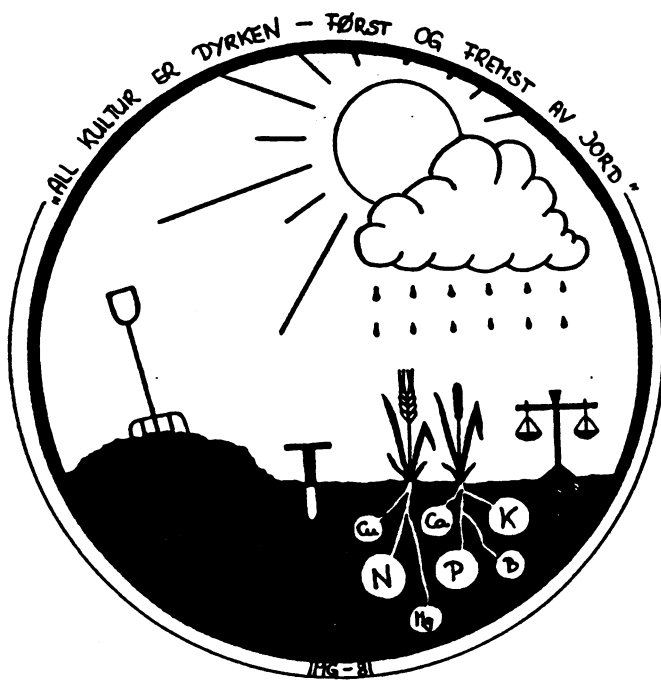
CONTENTS

1 PLANT NUTRIENTS AND FACTORS RELATING TO NUTRIENT AVAILABILITY

1.1 Essential plant nutrients.

The essential nutrients required by green plants are exclusively of inorganic nature. In this respect green plants differ fundamentally from man, animals and a number of microorganisms, which additionally need organic compounds as food stuff.

An essential element may be defined as one, which is required for the normal life cycle of an organism and whose functions cannot be substituted by other chemical compounds. In addition, the element must be shown to be directly involved in nutrition, as for example as a constituent; of an essential metabolite or the element must be required for the action of an essential enzyme system. Based on theis definition, as proposed by Arnon & Stout (1939), the following chemical elements are known to be essential for higher plants.

C, H, O, N, P, S, K, Ca, Mg, Fe, Mn, Cu, Zn, Mo, B, Cl, (Na), (Si), (Co).

The last three elements, shown in brackets, have not been established for all higher plants. In the case of Na there are some plant species, particularly the chenopodiaceae and species adaptable to saline conditions that take up this element in relatively high amounts. The same is true for Si which is an essential nutrient for rice. For some microorganisms, for example, vanadium (V) has now been established as an essential element.

The plant nutriants may be devided into macronutrients viz. C, H, O, N, P, S, K, Ca, Mg (Na, Si) and micronutrients viz. Fe, Mn, Cu, Zn, Mo, B, and Cl. Macronutrients are found and needed in plants in relatively higher amounts than micronutrients. The plant tissue content of the micronutrient N, for example is over a 1000 times greater than the content of the micronutrient Zn. This division of the plant nutrient is somewhat arbitrary and in many cases differences between contents of macronutriants and micronutrients are considerably lower than the example cited above.

From a physiological point of view, plant nutrients may be divided
into four groups as shown in Table 1.1.

Table 1.1 Classification of plant nutrients

Nutrient Element	Uptake	Biochemical Functions
1st group C, H, O, N, S	in the form of CO_2, HCO_3^-, H_2O, O_2, NO_3^-, NH_4^+, N_2, SO_4^{2-}, SO_2. The ions from the soil solution, the gases from the atmosphere.	Major constituent of organic material. Essential elements of atomic groups which are involved in enzymic processes. Assimilation by oxidation-reduction reactions.
2nd group P, B, Si	in the form of phosphates, boric acid or borate, silicate from the soil solution.	Esterification with native alcohol groups in plants. The phosphate esters are involved in energy transfer reactions.
3rd group K, Na, Mg, Ca, Mn, Cl	in the form of ions from the soil solution.	Non-specific functions establishing osmotic potentials. More specific reactions by which the conformation of the enzyme protein is brought into optimum status (enzyme activation). Bridging of reaction partners. Balancing indiffusible and diffusible anions.
4th group Fe, Cu, Zn, Mo	in the form of ions or chelates from the soil solution.	Present predominantly in a chelated form incorporated in prosthetic groups. Enable electron transport by valency change.

(Mengel and Kirkby, 1982)

1.2 Mineral Content of Plant Material.

The material of living plants consists of organic matter, water,
and minerals and their percentage distribution is in the following
order of magnitude.

Water	70%
Organic material	27%
Minerals	3%

The water content of various plant tissues and materials in % of
the fresh weight is shown in Table 1.2. The main factor controlling
the mineral content of plant material is the specific, genetically
fixed nutrient uptake potential for the different mineral nutrients.
This account for the fact that N and K content of green plant
material is about 10 times higher than that of P and Mg which in
turn is about 100-1000 times higher than the content of the
micronutrients. This general pattern accurs in all species of
higher plants. Within plant species, however, considerable diffe-
rences in the mineral content do occur, which is also genetically
determined.

Table 1.2 Water content of various plant tissues and materials in % of the fresh weight

Young green plant material	90–95
Young roots	92–93
Old leaves	75–85
Mature cereal straw	15–20
Hay	15
Cereal grains	10–16
Rape seed	7–10
Tomato fruits	92–93
Oranges	86–90
Apples	74–81
Banana fruits	73–78
Potato tubers	75–80
Sugar beet roots	75–80

(Mengel and Kirkby, 1982)
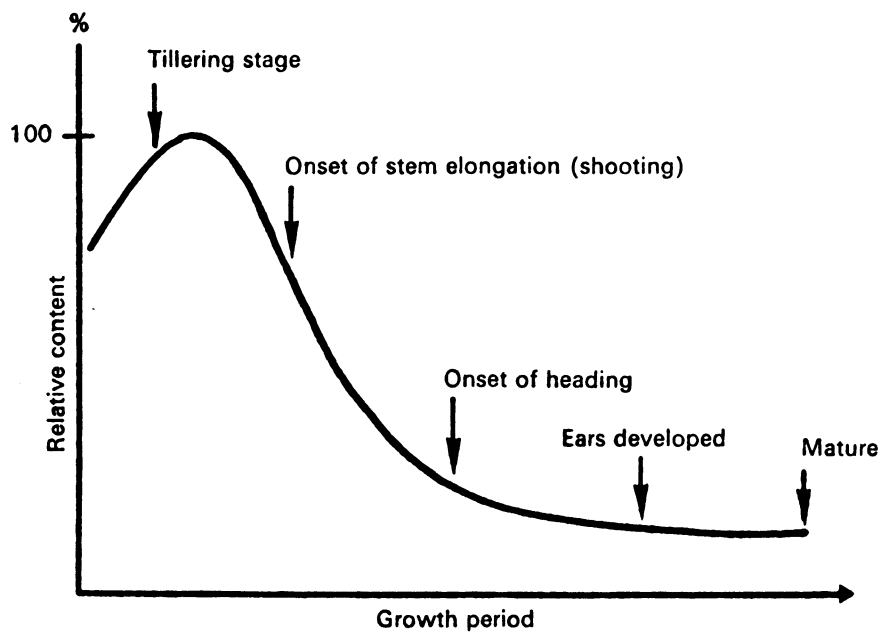
Fig. 1.1   Contents of N, P and K in oats during the course of the growing period (after SCHARRER and MENGEL [1960]).

The second factor controlling the mineral content of plant material is the availability of plant nutrients in the nutrient medium. Mineral contents differ considerably between plant organs. Generally, the vegetative parts of plants such as leaves, stems,and roots vary to a higher extent in their mineral composition than fruits, tubers, and seeds. The mineral content of plant is also very much dependent on age. The tropical variation in the contents of N, P, and K during the growth period of cereals is shown in Fig. 1.1. In the first weeks of growing season the nutrient contents increase, due to a relatively higher nutrient uptake rate as compared with the growth rate. As soon as the tilling stage is completed, the very high growth rate of stem elongation begins. This vigorous growth causes a dramatic reduction in the mineral content of the plant by dilution. Once the ears are fully developed, there is a little change in the content of N, P, and K expressed in terms of the whole plant, within plant itself, however, considerable changes occur between tissues, for during the ripening period high quantities of N and P are translocated from the leaves and stem to the grain.

1.3 Factors Relating to Nutrient Availability.

The term nutrient availability, in a simple way may be considered as that nutrient fraction in the soil which is accessible to plant roots. The term nutrient availability thus encompasses the chemical and physical status of a nutrient in the soil as well as plant root relationships which involve plant metabolism. It is for this reason that in strict sense the amounts of available nutrients in the soil cannot be measured and expressed in quantitative terms. Nevertheless, it is expedient to know the factors and their causal relationships, which contribute to nutrient availability.

1.3.1 Interception and contact exchange.

Jenny and Overstreet (1938) proposed a theory of contact exchange which envisages that a close contact between root surface and soil colloids enabled direct exchange of H+ released from the plant root with cations from soil colloids. It was argued that by releasing H^+ produced in plant metabilosm, plant roots should be able to strip off and mobilize the cationic nutrients adsorbed to clay minerals. This contact exchange process was envisaged as the first step of cation uptake by plants. Undoubtedly H^+ ions are released by plant roots, and they can exchange for the adsorbed cations on the soil colloids. What is in question is whether the process plays a major role in nutrient availability and whether contact exchange is at all important in the ion uptake process by the plant.

Figure 1.2 shows the site and dimensions of contact exchange in relation to the cell wall, and plasma membrane of a root cell. It can be seen immediately that only cations at the very outer surface of the cell wall can exchange for cations adsorbed to the clay mineral. By an exchange of H^+ from the call wall, K^+ can be mobilized from a clay mineral as indicated in Figure 1.2. Even if this does occur, however, the exchanged K^+ is still only at the outer surface of the cell wall. This is very far from the real site of ion uptake. This occurs at the plasma membrane (plasmalemma) and is about 1000 mm distant from the site of contact exchange. There is no evidence that K^+ is able to move across the cell wall by further exchange processes.

| Clay
Mineral | Contact
Zone | Cell Wall | Cell
Membrane | Cytoplasm |

←5nm→←——1000nm——→←8nm→
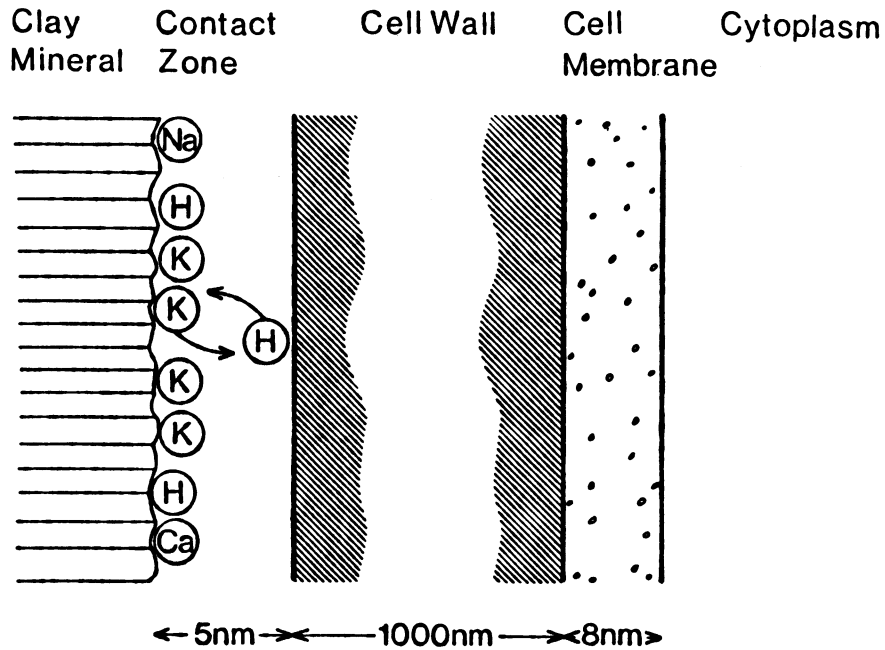
Fig. 1.2 Contact exchange between a clay mineral and an epidermal root cell, showing the
dimensions involved. (Mengel and Kirkby, 1982)

In the contact exchange process it is widely believed that root
surfaces are acid. This is usually held to be the source of
H+ for cation exchange. Generally this is not true. When plants
are supplied with NO_3^- as the N-source, a higher uptake of anions
than cations induces a net release of HCO_3^- from the roots
(KIRKBY (1969), BARBER (1974).

Another point of importance in the contact exchange theory is
the quantitative aspect. DREW and NYE (1969)   found that only
6% of the total K demand of L o l i u m p e r e n n e was
supplied by the soil volume of the root hair cylinder ,94%
of the K taken up therefore orginated from beyond the limit of
the root hairs. It can thus be concluded that the bulk of
macronutrients required by a crop must be transported towards
the roots. For this reason nutrient mobility in the soil medium
is a major factor of nutrient availability.

1.3.2 Mass-flow and diffusion

Nutrients in the soil can be transported by two different mechanisms: by mass-flow and by diffusion. Mass-flow occurs when solutes are transported with the convective flow of water from the soil to plant roots. The amount of nutrients reaching the root is thus dependent on the rate of water flow or the water consumption of the plant and the average nutrient concentration of the water. The level of a particular nutrient around the root may be increased, decreased or remain the same depending on the balance between the rate of its supply to the root by mass flow and the rate of uptake by the root.

Diffusion occurs when an ion is transported from a higher to a lower concentration by random thermal motion. Diffusion comes into operation when the concentration at the root surface is either higher or lower than that of the surrounding solution. It is directed towards the root when the concentration at the root surface is decreased, and away from the roots when it is increased. Diffusion follows F i c k's l a w :

$$F = - D \cdot \frac{dc}{dx}$$

F = Diffusion rate (quantity diffused per unit cross section and per unit time)

$\frac{dc}{dx}$ = concentration gradient c = concentration

D = diffusion coefficient x = distance

Plant roots absorbing nutrients from the adjacent soil can thus create a sink to which nutrients diffuse (Drew et al.(1969)). The nutrient depletion depends on the balance between the supply from the soil and the demand by the plant. Thus a high plant requirement or a high root 'absorbing power' as it has been termed by NYE (1968) gives rise to a strong sink. This indicates that the root itself and its metabolism also influence nutrient availability. When the demand for a nutrient is fairly high and the soil solution concentration is low, mass flow is unable to supply more than a small fraction of the total requirement. Most plant nutrients are therefore supplied by

diffusion. This is typical for K^+ and phosphate which show nutrient depletion patterns around the plant root.(LEWIS and QUIRK (1967), BHAT and NYE (1974).

The relative depletion of plant nutrients declines with increasing distance from the root surface (LEWIS and QUIRK (1967). This is shown in Figure 1-3 for two soils with high and low nutrient levels in the bulk soil. It is clear that the soil with the higher nutrient level has the steeper concentration gradient and therefore the rate of diffusion to the plant roots is greater. The higher nutrient level in the bulk soil also gives a higher concentration at the root surface which causes a more rapid up-take rate and the larger gradient allows this to be maintained. The depletion zone around the root can often be extended in higher nutrient level soils, since the higher nutrient level frequently implies a steeper concentration gradient.

Distance from the Root Surface
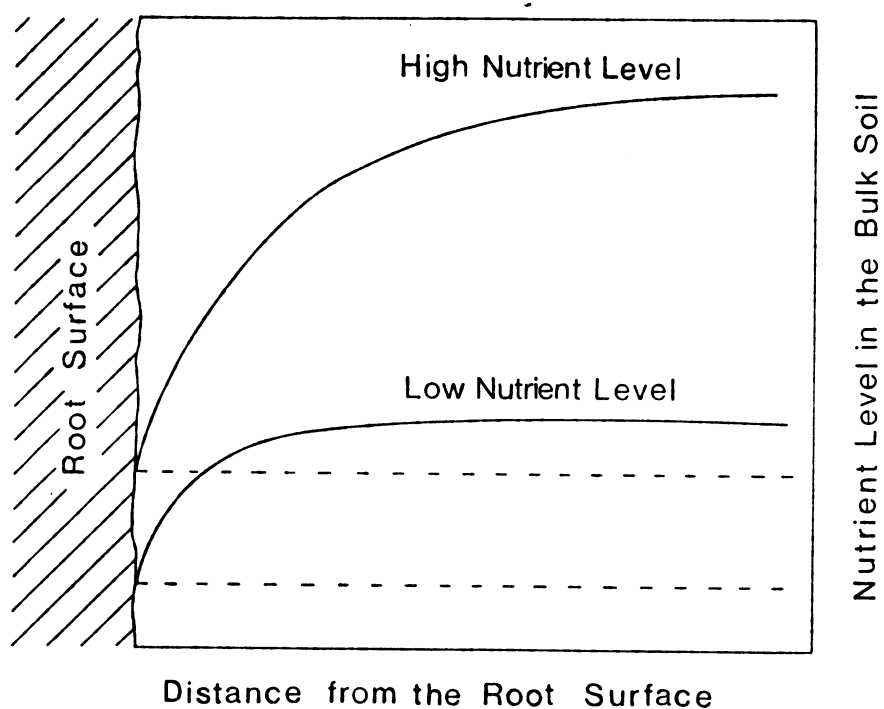
Fig. 1.3 Nutrient depletion pattern at the immediate vicinity of the root for a soil with a high and with a low nutrient level in the bulk soil. (Mengel and Kirkby, 1982)

Concentration gradients are of particular importance when diffusion rather than mass flow is the main process by which the nutrients are transported towards the roots. According to investigations and calculations of BARBER et al. (1963) only a small proportion of the total demand for K^+ and phosphate is provided by mass flow. By far the greater portion of these two nutrients must be transported by diffusion to the plant roots. Diffusion also dominates when the transpiration of the plants is low, whereas under high transpiration conditions considerable quantities of water are translocated to the roots carrying various solutes. If these solutes are not taken up as fast as they are supplied an accumulation occurs in the root vicinity. This occurs particularly with Ca^{2+} which is often present in the soil solution in rather high concentrations and which is only taken up by many plant species at a relatively low rate (BARBER (1974)).

The rate of ion movement in the soil, whether by mass flow or diffusion, depends highly on soil moisture. Within the last decade several investigations have been made showing that soil moisture affects the diffusion rate considerably. GRAHAM-BRYCE (1967) showed that a soil with a water content of 23% had a diffusion coefficient of $1 \times 10^{-7}/cm^2/sec$ for Rb^+. When the water content was decreased to 10% in the same soil, the diffusion coefficient fell to $5 \times 10^{-8} cm^2/sec$. The dependence of ion diffusion on soil moisture is easily understood as the removal of soil water results in an increase in air filled pores.

1.3.3 Soil solution

Nutrient mobility in the soil depends considerably on the nutrient concentration in the soil solution. As already demonstrated in Figure 1.3 the diffusion rate towards the roots is generally faster the higher the concentration of the nutrient in the soil solution.

The soil solution is not homogenous but may differ in its concentration and composition as the water filled spaces and pores of the soil are not completely interconnected. Composition and concentration of the soil solution also depend considerably on soil moisture. In a wet soil (field

capacity) the soil solution is diluted and as the soil dries out the solution becomes more concentrated. Some of its ion species may even reach concentrations higher than their solubility products and precipitation of these ions can occur. Calcium, sulphate and phosphates are particularly susceptible. In order to compare soil solutions they must be based on equivalent soil moisture levels. This is usually taken at field capacity (RICHARDS (1941), MAGISTAD et al. (1945), ADAMS (1974)).

The concentrations of the ion species in the soil solution (water saturated extract) can differ widely depending on the soil properties. Generally, however, the phosphate concentration is very low, the concentration of K^+ and Mg^{2+} medium and the concentration of Ca^{2+} rather high. MENGEL et al. (1969) found mean concentrations in the range of 0.015-0.030 mM P, o.1-1.0 mM K, 0.5-1.0 mM Mg and 1.0-10.0 mM Ca in the upper layer of Central European arable soils saturated with water. Frequently NO_3^- is the anion present in highest concentrations and often occurs at levels in the same order as the sum of Ca^{2+} and Mg^{2+} (LARSEN and WIDDOWSON (1968)).

Table 1.3 shows the concentration of various plant nutrients, found in water saturated extracts (FRIED and SHAPIRO (1961)).

Table 1.3. Ion concentrations in the soil solution (water saturated soil) in mM (FRIED and SHAPIRO [1961])

Element	Range of all soils	An acid soil	A calcareous soil
Ca.......................	0.5–38	3.4	14
Mg	0.7–100	1.9	7
K.................	0.2–10	0.7	1
Na...............	0.4–150	1.0	29
N.................	0.16–55	12.1	13
P.................	<0.001–1	0.007	<0.03
S	<0.1–150	0.5	24
Cl	0.2–230	1.1	20

1.3.4 Intensity and quantity

Plants must be supplied adequately with nutrients during their entire growth period. For this reason the concentration of plant nutrients in the soil solution must be maintained at a satisfactory level for plant growth. Nutrient availability depends therefore not only on the nutrient concentration of the soil solution at any given time but also on the ability of the soil to maintain the nurient concentration. This capability of a soil to ˉbufferˉ the nutrient concentration of the soil solution is a further important factor in nutrient availability.

Generally, those nutrients required by plants in high amounts, are present in the soil solution in relatively small concentrations. This is particularly the case for phosphate and K^+. Calculated on an area basis the soil solution contains in the order of only about 0.5-1.0 kg P/ha and 10-30 kg K/ha, whereas the total demand for these nutrients is considerably higher. A cereal crop for example requires about 20 kg P/ha and 100 kg K/ha. As a cereal crop growing under the soil conditions described does not necessarily become deficient in P or K, this shows that the removal of these nutrients from the soil solution by crop must be accompanied by a substantial replenishment of the soil solution from the solid phase of the soil.

One may thus distinguish between two nutrient fractions in the soil: the quantity factor (Q) represents the amount of available nutrient, whereas the intensity factor (I) reflects the strength of retention by which the nutrient is held in the soil. Considered simply the intensity factor is the concentration of the nutrient in the soil solution. The concept of nutrient intensity and nutrient quantity was first proposed by SCHOFIELD (1955). He compared the availability of soil water. Soil water availability depends not on the total amount of water present in the soil but rather on the strength by which the water is bound to the soil particles. The same holds true for phosphate and also for some other plant nutrients. SCHOFIELD (1947) states: ´It is possible that the potash status of a soil can be better judged by finding the equilibrium concentration of potassium ions ... than by finding the total exchangeable potassium.´

Nutrient intensity and quantity factors are interrelated. The main relationships are illustrated in Figure 1.4. The general concepts shown in the Figure have formed the basis of much of the very useful soil phosphate work of E.G. WILLIAMS. Over the years this study has lead to a much better understanding of the behaviour of phosphate in soils and its availability to plants.
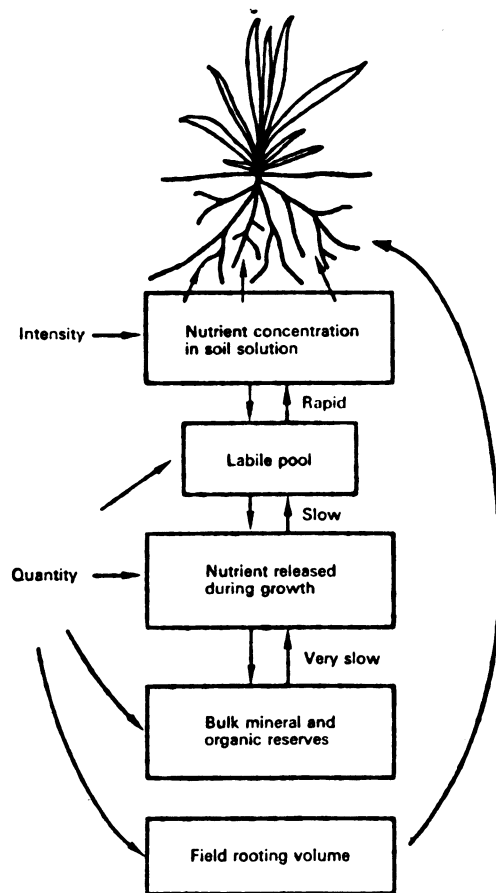
Fig.1.4 Intensity, quantity and nutrient sources (after E.G.WILLIAMS).

Plant roots are dependent on the nutrient intensity or soil
solution concentration. This is usually regulated by a much
larger labile pool of easily exchangeable nutrient. Generally
this represents the main component of the quantity factor.
However, this is not always the case as nutrient release from
the more slowly available forms can sometimes provide a major
source of nutrient supply. The extent to which this occurs
is not only dependent of the particular nutrient. Soil condi-
tions such as pH, temperature, aeration and moisture level
are also important. For example, in tropical soils the rate
of release of nutrients by weathering or by mineralization can
be so rapid that this can form the main nutrient source.
The quantity factor is therefore very much dependent on clima-
tic and soil conditions. In addition it also depends on the
volume of soil which the roots occupy. This means of course
that all factors influencing the distribution of roots in the
profile contribute to the quantity factor.

Another important factor in nutrient availability is the ability
of the soil to maintain intensity (nutrient concentration of
the soil solution). This is the buffer factor and it indicates
how intensity varies with quantity. In Figure 1.5 the quantity
of K is plotted against intensity for two soils of differing K
adsorption capacity, soil A and soil B. For both soils increa-
sing intensity (K concentration of the soil solution) is accompa-
nied by fairly linear increase in quantity. Soil A, however,
shows a steeper rise in the slope than soil B. Where an equal
amount of K^+ is removed from both soils by plants a similar de-
crease in the K quantity results. This is indicated by $\triangle Q$ in
the figure. The consequent reduction in intensity, however,
differs considerably for both soils (compare $\triangle I_A$ with $\triangle I_B$ in
Figure 1.5). This example shows that the two soils differ in
their capability of replenishing the soil solution with K^+.
Soil A is better able to maintain the K concentration in the
soil solution. Soil A is thus more buffered than soil B. In
quantitiative terms the buffer capacity is expressed as the ra-
tio $\triangle Q / \triangle I$.

$$B_K = \frac{\triangle Q}{\triangle I}$$

where B_K = buffer capacity for K^+. The higher ratio of $\Delta Q/\Delta I$, the more the soil is buffered. The importance of soil solution K concentration and the K buffer capacity in relation to crop production has been considered by NEMETH (1975).
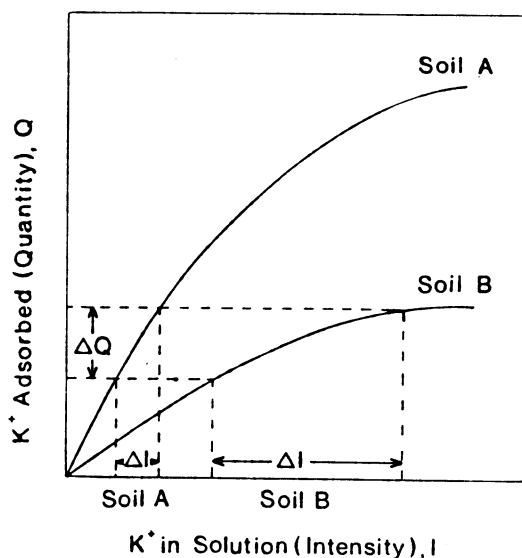
Fig.1.5 Relationship between K^+ intensity and K^+ quantity for two soils with differing adsorbing capacities (Soil A high and Soil B low).

(Mengel and Kirkby, 1982)

As already mentioned the quantity/intensity concept is used in soil phosphate studies. Soils can differ much in their ability to adsorb phosphate. Thus red tropical soils can generally adsorb huge quantities of phosphate whereas the phosphate adsorption potential of podzols is low. The phosphate adsorption isotherms for two such soils are shown in Figure 1.6. It can be seen that the red tropical soil requires a much higher amount of adsorbed phosphate than the podzol in order to maintain the same phosphate concentration in the equilibrated solution. From this it follows that soils with a high phosphate adsorption capacity should contain more adsorbed phosphate than sandy soils and organic soils in order to provide a satisfactory phosphate intensity. The ratio ´adsorbed phosphate/phosphate concentration in solution´usually represents the phosphate buffer capacity. In a detailed study OLSEN and WATANABE (1970) found, that the phos-

phate buffer capacity has a substantial impact on the P supply to plant roots and that soils with a low P buffer capacity require higher P concentrations in the soil solution and vice versa in order to provide adequate P to plant roots.

The quantity/intensity concept cannot be applied to N. By far the greatest amount of soil N is present in organic form. This is biologically converted to NO_3^- which is only weakly held in the soil. The nitrate concentration of the soil solution is thus not buffered and the distinction between quantity and intensity is unimportant. The results of HARMSEN (1959) show that the NO_3^- level in the soil solution can vary enormously during the growing season. This is dependent on a number of factors, including the rates of mineralization and leaching. The rate of NO_3^- supply to plant roots is thus capable of greater fluctuation than other nutrients.
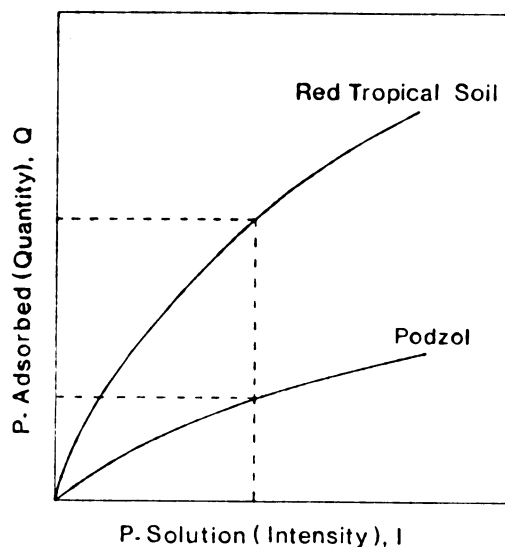
Fig. 1.6 Phosphate adsorption isotherms for two soils differing greatly in ability to adsorb phosphate. (Mengel and Kirkby, 1982)

2.3.6 Root growth and extension

It has been shown that nutrient availability is very dependent
on a number of soil factors. These include the nutrient con-
centration of the soil solution, the capability of the soil
to buffer this concentration and soil diffusion conditions.

These factors are largely, although not totally, controlled
by chemical and physical processes in the soil. In addition,
root growth and development considerably influence nutrient
availability. This is brought about in two ways. In the
first place the root system explores the soil for nutrients
so that the more dense the root system the more nutrients
have an opportunity to reach the roots by mass flow and diffu-
sion. Secondly root metabolism creates a nutrient demand which
also influences availability.

Whatever the detailed relationship between root growth and
nutrient availability is, it is generally accepted that a
well extended root system and a high root density contribute
to nutrient availability, This has been shown by JUNGK and
BARBER (1974), who found a close relationship between P uptake
per plant and root length. The relationship was particularly
clear, when the P concentration of the nutrient was low.
Thus all processes affecting root growth as well as root meta-
bolism have an indirect influence on nutrient availability.

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2. Mechanisms of Nutrient uptake by Plants

2.1 Ion uptake and metabolism

In experimenting with the fresh water alga Nitella and the sea water alga Valonia Hoagland (1948) found that the ion concentrations in the vacuoles of these two algae did not correspond to the concentrations in the respective algal nutrient environments. In the vacuole of Nitella several ion species and particularly $K+$ and $Cl-$ were concentrated to a considerably high degree. The same was also true for Valonia with the exception of $Na+$ where the concentration was higher in the sea water than in the vacuole (see Figure 2.1). From these findings the following important conclusions may be drawn:

1. The plant is able to take up ions selectively. Thus $K+$ which is lowest in concentration of all the cations in the pond water is the cation which is accumulated to the greatest extent by far in the vacuole of Nitella. On the other hand the concentration of $Na+$ in the vacuole of Valonia is kept to a relatively low level even though the concentration of $Na+$ in the sea water is high. These results support the concept that plant cells can take up certain ion species from their environment and transport them into the interior of the cell whereas other ion species are in some way excluded from the cell. This phenomenon is called <u>selective ion uptake</u>

2. Another major conclusion is the fact that the concentrations of several ion species are considerably higher in the vacuole than in the outer medium. This indicates that accumulation has taken place against a concentration gradient.

3. A further important point to be considered from these results is the fact that the uptake process itself requires energy. This is generated by cell metabolism.

The relationship between metabolism and ion uptake is not yet fully understood, although it has been known for many years that ion uptake is closely associated with respiration. An early approach to account for this relationship was put forward
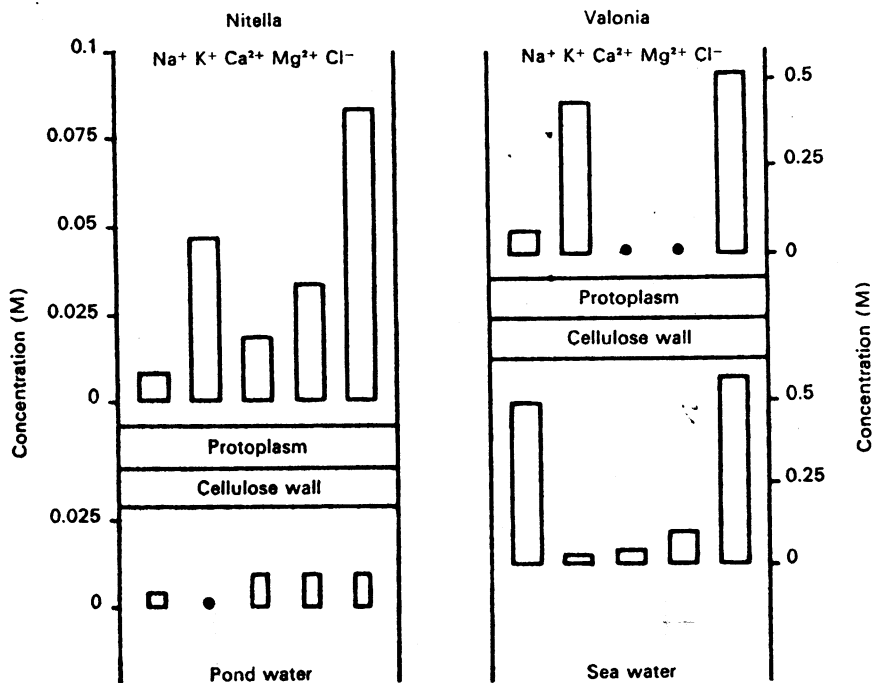
Fig.2. Ion concentrations in the vacuole of *Nitella* and *Valonia* in relation to the ion concentrations in outer medium (after HOAGLAND [1948]).

by Lundegårdh (1932). The main principle of his very sophisticated concept was the linking of ion transport with electron flow in the respiration chain. Lundegårdh's ingenious ideas and experiments contributed much to our present understanding of ion uptake. It is now generally accepted, however, that cytochromes do not play any role in the ion uptake process as they are present in neither the plasmalemma nor the tonoplast.

In aerobic organisms respiration is directly related to ion uptake. This is shown in Figure 2.2 for phosphate (Hopkins 1956). This result demonstrates that O_2 uptake and hence respiration is essential for phosphate uptake. It is of interest that the O_2 tension, at which the maximum phosphate uptake is attained, is rather low (2-3%). The same kind of relationship has also been found for other plant nutrients such as NO_3-, NH_4+, $K+$, Mg^2+ and $Cl-$. Another indication of the significance of respiration on ion uptake is the observation that the rate of uptake of plant nutrients rises as the root carbohydrate content is increased (Mengel 1967).

The major physiological function of respiration is the synthesis of adenosine triphosphate (ATP) from adenosine diphosphate

(ADP) and inorganic phosphate. All biochemical processes which need energy including the synthesis of molecules and the uptake and transport of some ion species depend on the supply of ATP or analogous compounds. ATP consists of adenine (N-base), ribose (pentose) and 3 phosphate groups.
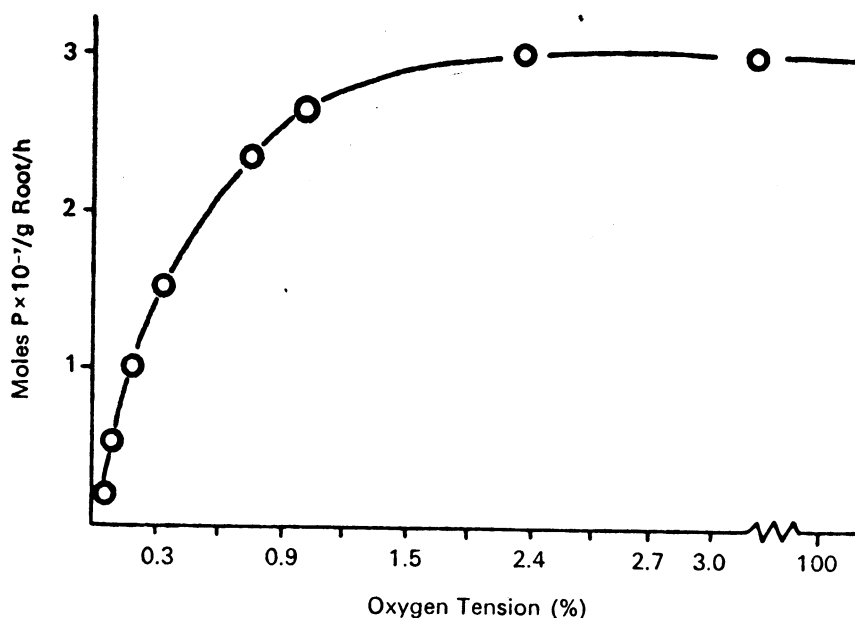
Fig.2.2. Rate of phosphate uptake by excised barley roots in relation to the O_2-tension (after HOPKINS [1956]).

The phosphate groups are bound to each other by energy rich bonds which are indicated by the symbol ($\sim$). This is a high energy bound and during hydrolysis it releases about 7600 cal per mol of ATP.

ATP $\rightarrow$ ADP + P_i + 7600 cal
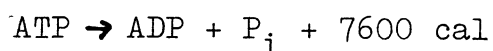
ADP = Adenosine diphosphate

P_i = inorganic phosphate

ATP is not only synthezed during respiration (oxidative phosphory-lation) but also in the glycolytic pathway (anaerobic phosphory-lation) and in photosynthesis.

As outlined above ATP appears to provide the energy for the ion uptake process. Thus when ATP formation is prevented as for example by inhibitors or uncouplers such as CO, CN-, 2,4-dinitro-

phenol (DNP) or arsenate, ion uptake is inhibited. In roots
respiration provides the main source of ATP, but in green plant
tissues photophosphorylation also supplies ATP for the energy
dependet ion uptake mechanism. This is the reason why light
can directly enhance the uptake of ions by photosynthetically
active tissues. This has been shown by various authors (Jeschke
1967, Nobel 1970). The precise mechanism by which ATP drives
the ion uptake process and particularly ion transport across
biological membranes, is not yet completely clear. There are
currently two main although not exclusively independent directions
of thought concerning metabolically driven ion uptake. One
visualizes uptake in terms of carrier transport and is known
as the carrier theory. The other stresses the importance of
ion pumps across the membrane. Both these concepts are con-
sidered below.

2.2 The carrier theory

It is supposed that biological membranes contain certain molecules
which are able to carry ions across the membrane. Such mole-
cules are termed "carriers" and it is believed that they possess
specific binding sites for particular ion species, thus enabling
selective ion transport through the membrane. The generation
of these carriers directly or indirectly requires ATP. Figure 2.3
shows a hypothecial scheme in which the active carrier is
envisaged as a phosphorylated compound. It is suggested that
this carrier is diffusible in the membrane. At the outer
membrane boundary it meets the particular ion species for which
it has affinity. The ion is bound by carrier, thus forming
a carrier ion complex. This diffusible complex then moves
across the membrane to a phosphatase located at the inner
membrane boundary. The enzyme phosphatase splits off the
phosphate group from the carrier complex. By this process the
carrier is believed to lose its affinity for the ion which is
released into the adjacent medium e.g. into the cytoplasm.

Regeneration of carrier selectivety requires ATP. This process
is brought about by a "carrier ATP kinase" which is also located
at the inner membrane boundary. The phosphorylated carrier
compound may then diffuse back to the outher membrane boundary,

Fig. 2.3. Carrier ion transport across a membrane involving energy expenditure.
(Mengel and Kirkby, 1982)

pick up another ion and the uptake cycles is repeated. The ATP
required for the process may originate from respiration (plant
roots), from photophosphorylation and in anaerobic organisms
from glycolysis.

The whole uptake cycle may be described by the following equations:

$$\text{Car} + \text{ATP} \xrightarrow{\text{Kinase}} \text{Car } \textcircled{p} + \text{ADP}$$

$$\text{Car } \textcircled{p} + \text{Ion} \longrightarrow \text{Car } \textcircled{p} - \text{Ion}$$

$$\text{Car } \textcircled{p} - \text{Ion} \xrightarrow{\text{Phosphatase}} \text{Car} + \text{P}_i + \text{Ion}$$

Net: $\text{Ion} + \text{ATP} \xrightarrow{\text{Transport}} \text{Ion} + \text{ADP} + \text{P}_i$
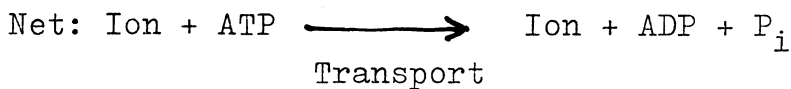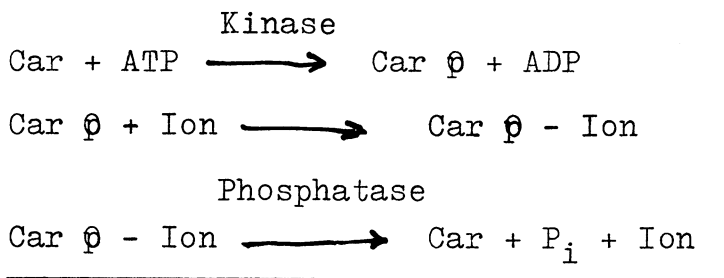
The net equation shows that the transport of 1 ion through the
membrane requires 1 ATP molecule. From an energetic point of
view this would seem to be a reasonable energy demand. If it
is assumed that the uptake of 1 ion requires 1 ATP molecule,

then it follows that the ATP needed for the K uptake by a plant is less than 1% of the quantity of ATP required for CO_2 assimilation.

The concenpt of carrier transport as illustrated in Figure 2.3 is highly hypothetical. It does, however, cover the main experimental facts, implications and conclusions of ion uptake. These are, that energy driven ion uptake is selective, that the energy is probably in the form of ATP and that ion transport takes place against a concentration gradient. Whether a phosphatase and kinase are really involved in the ion uptake is an open question. There is considerable evidence, however, that enzymic processes are associated with ion uptake.

The barrier for hydrophilic particles is the lipid phase of the membrane, so it seems probable that carrier molecules are lipid molecules. As biological membranes are permeable to lipid molecules as carrier of this type would well be able to diffuse in the membrane. The real nature of the carrier, however, is still a matter of speculation. It is possible that carriers are derivatives of phosphatidic acid or peptides of a lipidic character. Investigations of Kilbourn et al. (1967), Mueller and Rudin (1967) and of Dobler et al. (1969) have shown, that organic molecules do exist, which are highly selective in binding inorganic ions.

2.3 Ion pumps

In plants it is known that ATPase activity is associated with the plasmalemma and is cation activated (Hodges et al. 1972). A high correlation has been observed between ATPase activity and the rate of ion absorption (Fisher et al. 1970). Another indication of the importance of ATPase activity in ion uptake is the striking similarity found between the kinetics of the K^+ absorption by the roots themselves (Leonard and Hodges 1973). These observations strongly suggest that ATP provides the energy for transport and that the ATPase of the plasmalemma enables the enrgy coupling in ion transport (Hodges 1973).

Based on the above findings Hodges (1973) has proposed a hypothetical model to account for both cation and anion absorption by

roots. This is shown in Figure 2.4. It is believed that a
membrane bound ATPase splits ATP into ADP⁻ (anion) and a phospho-
ryl cation. The phosphoryl cation is not stable but rapidly
reacts with water generating H^+ according to the following
equation:

$$ATP \rightarrow ADP^- + (O = P(OH)_2)^+$$
$$\text{Phosphoryl cation}$$

$$(O\ P\ (OH)_2)^+ + HOH \rightarrow O\ P\ (OH)_3 + H^+$$

$$O\ P\ (OH)_3 = H_3PO_4$$
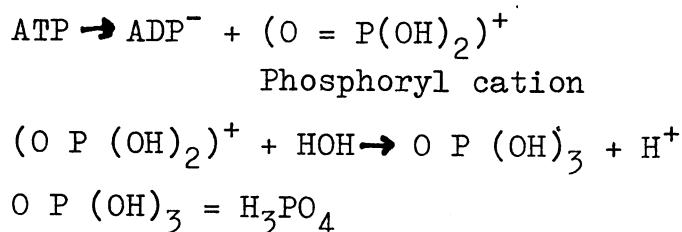
The net ATPase reaction results in the production of an anion
ADP⁻ and a cation H^+. This is released into the outer medioum
(H^+ pump) and a pH gradient is thus generated across the mem-
brane. The anion equivalents remain in the cytoplasm and give
rise to the negative electropotential of the cell as compared
with the outer medium. This is exactly, what has been found in
the living cell: it is negatively charged compared with the
outer solution, the potential difference between cell and medium
being in the order of about 60 to 160 mV.
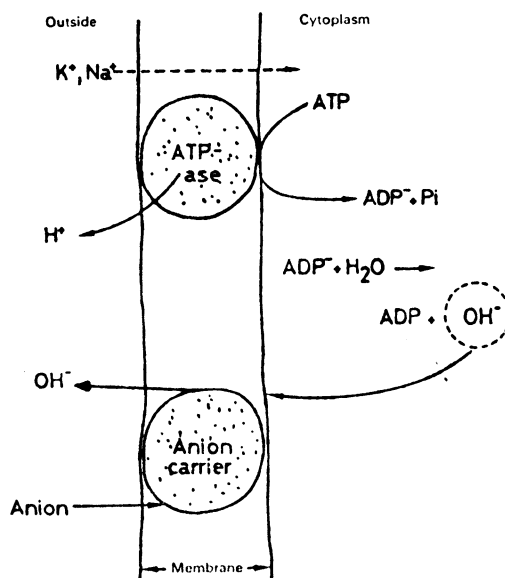
Fig. 2.4. Model of an ATPase driven cation pump coupled with an anion carrier (modified
after HODGES [1973]).

As cells are negatively charged they attract cations in exchange for H^+. Provided that the membrane is not completely impermeable to cation transport, cations may thus diffuse through the channels of the membrane into the cytoplasm (see Figure 2.4). This kind of ion diffusion is called <u>electroosmosis</u> (Higinbotham 1973). Such a mechanism of ATPase driven cation uptake cannot bring about selective uptake, as it does not distinguish between different ion species, e.g. K^+ and Na^+. Provided, however, that membranes possess tunnels built up by macrocyclic antibiotics, which preferentially allow the diffusion of one cation species and exclude another, selective ion uptake can also result from ATPase activity. Such a selective diffusion of K^+ enabled by the presence of valinomycin has been shown by Mueller and Rudin (1967) using an artificial membrane. This selective diffusion is called "facilitated diffusion". Recent experimental data of Ratner and Jacoby (1976) support the view that the high K^+ uptake rates of plant cells can be explained in terms of an ATPase driven facilitated diffusion of K^+.

In the ATPase driven ion pump model of Hodges (1973) it is assumed that the ADP^- produced by splitting ATP and released into the cytoplasm gives rise to an increase in the OH^- concentration resulting from the reaction of ADP^- with H_2O:

$$ADP^- + HOH \rightarrow ADP + OH^-$$

Hodges suggests that the generated OH^- could drive an anion carrier, enabling a selective uptake of anions in exchange for OH^- (see Figure 2.4).

2.4 Active and passive transport

Ions in solution are subjected to two main physical "forces". One arises from the chemical potential gradient and the other from the electrical potential gradient (Dainty 1962). Ions move down a chemical gradient, i.e. from a higher to a lower concentration. For ions acted upon by an electrical gradient, cations are attracted to a negative electropotential whereas anions are attracted to a positive electropotential. Ion move-

ment is thus dependent on an electrochemical potential gradient.
As has been shown above, living cells are negatively charged
as compared with the outer medium. For this reason the passage
of ions through the plasmalemma or tonoplast must also be con-
sidered in relation to the prevailing electrical potential
gradient as well as to the concentration gradient between the
"outer solution" (medium) and "inner solution" (cytoplasm).
"Facilitated cation diffusion" discussed above is a typical
example of where cations are moved along an electrical gradient.
This net inwardly directed movement of cations terminates as
soon as the equilibrium between the electrical and kinetic
driving forces is attained. This equilibrium is described by
the Nernst equation. A simple case may be considered in which
an aqueous solution of KCl is separated by a membrane which
is permeable to both ions, K^+ and Cl^-. Assuming that the
electrical potential across the membrane is E, equilibrium for
K^+ and Cl^- is attained as soon as the concentrations of these
ions at either side of the membrane satisfy the Nernst equation.
This may be described as follows:

$$\Psi_i - \Psi_o = E = \frac{RT}{z.F} \ln \frac{(K_o^+)}{(K_i^+)} = \frac{RT}{z.F} \ln \frac{(Cl_i^-)}{(Cl_o^-)}$$

Ψ_i = electrical charge of the inner medium e.g. cytoplasm

Ψ_o = electrical charge of the outer medium e.g. nutrient solution

R = gas constant

T = absolute temperature

F = Faraday constant

z = valence of the ions

The subscripts i and o designate the inner or outer solution,
the values in brackets indicate the concentrations or more
precisely the activities of the ion species in question. From
this equation it can be derived that when $E < 0$ (the cell is
negatively charged) the term $(K_o^+)/(K_i^+)$ must be < 1. This means
that under equilibrium conditions an accumulation of K^+ occurs
in the inner solution. It further follows that the term
$(Cl_i^-)/(Cl_o^-)$ must be < 1. This implies that under equilibrium
conditions the Cl^- concentration of the outer solution is higher

than that of the inner solution. It thus appears that the
cation concentration in the cytoplasm can be several times higher
than that of the outer solution without requiring an "uphill
transport" of cations, i.e. transport against an <u>electrochemical
gradient</u>. If for example the K^+ concentration of the inner
solution is 10 times higher than that of the outer solution the
term log $(K_o^+)/(K_i^+)$ = -1. The corresponding electrical potential
difference is then -58 mV (Dainty 1962). For living cells
-58 mV is a rather small electrical potential difference. This
example shows that K^+ as well as other cation species may be
accumulated to a considerable extent in the cell merely by
physical forces. Only, where the concentration is higher than
that of the equilibrium condition, must an "uphill transport",
i.e. a transport against an electrochemical gradient, have
occurred. In a strict thermodynamical sense only transport
against an electrochemical gradient is called <u>active transport</u>,
whereas the transport down or along an electrochemical gradient
is <u>passive transport</u>. Active transport needs additional energy
and cannot be brought about merely by kinetic and electrical
forces (Etherton 1963, Etherton and Higinbotham 1961).

In order to test, whether an ion species has been moved actively
or passively into the cell, the concentrations of the particular
ion species in the outer medium and in the cell must be measured
as well as the electropotential (E_m) between the cell and the
outer medium. This can be achieved using a microelectrode.
By substituting the measured ion concentrations into the <u>Nernst
equation</u> an electrical potential difference (E_{cal}) can be cal-
culated. Where E_m designates the measured potential, the differ-
ence between E_m and E_{cal} indicates whether a passive or an
active transport has occurred.

$$E_m - E_{cal} = E_d$$

E_d is the driving force. For cations a negative value of E_d
indicates a passive uptake and a positive value an active uptake.
For anions the reverse is true. A negative value is indicative
of active transport, and a positive value of passive transport.
It must be remembered that the test of whether an ion species
has been transported actively or passively is only valid, if
equilibrium conditions have been maintained in the system.

This is often difficult to achieve in whole plant studies as plant tops provide a very strong sink for ions taken up by roots.

The fact that living cells are always negatively charged implies that anions are more subjected to active transport than cations. Whenever the anion concentration of the cell is in excess of the outer medium, active uptake must have occurred. The major anions NO_3^-, Cl^-, SO_4^{2-} and $H_2PO_4^-$ are thus all apparently accumulated against an electrochemical gradient (Higinbotham 1973). Figure 2.5 shows results from mung bean root tips (Phaseoulus aureus) in which measured Cl^- uptake values are compared with calculated Cl^- uptake levels derived from Nernst equilibrium conditions (Gerson and Poole 1972). As the measured Cl^- concentrations are several times higher than the calculated values it can be concluded that Cl^- must have been taken up actively.
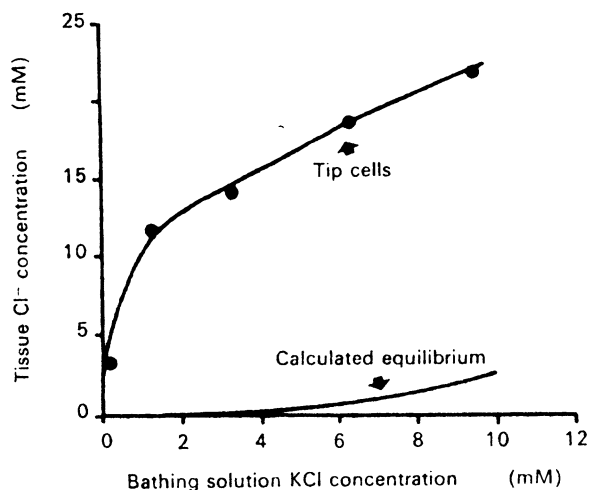
Fig. 2.5. Chloride concentration in mung bean root tips compared with the maximum concentration which could be due to diffusion calculated equilibrium (after GERSON and POOLE [1972]).

above was necessary in the outer solution. This finding suggests that the influence of Ca^{2+} at the outer boundary between the nutrient solution and the plasmalemma is responsible for the Viets effect and not the metabolism of the cell. The Viets effect has been interpreted in a number of ways by different authors. Kahn and Hanson (1957), Foote and Hanson (1964) and Rains and Epstein (1967) suppose that Ca^{2+} enhances carrier meditaed transport. Jacobson et al. (1960), Hooymans (1964) and Pitman (1965) believe that Ca^{2+} removes a H^+ barrier, thus enabling the entry of ions in the cells. According to investigations of Mengel and Helal (1967), Ca^{2+} affects the efflux and not the influx of K^+ and phosphate.

2.6 Ion competition, antagonism and synergism

It has already been outlined in the previous sections that electrogenic pumps (anion carriers, H^+ pumps) generate a negative charge in the cell and that most cation species are attracted by this negative charge and are thus absorbed passively. The absorption of cations is thus more or less a non specific process, depending mainly on the concentration of the cation species in the nutrient medium and in some cases also on the specific permeability of membranes to particular cation species (facilitated diffusion). For this reason nonspecific competition between the cation species for the negative charges of the cell may occur. This is evident from the frequently made observation, that the total sum of cations in a plant or plant tissue is little changed despite variations in the levels of the individual cations in the nutrient medium. Increasing the supply of one cation species in the nutrient medium can thus depress the levels of other cation species in the plant. Table 2.2 shows an example of this kind. Increasing the level of Zn application to maize and barley plants, grown in a soil, resulted in a decrease of Mn in all plant parts. (Singh & Steenberg 1974). Similar results were obtained for major nutrients (Table 2.3). It is the general rule, therefore, that increasing the supply of one cation species results in lowering the concentration of other cation species. This relationship is called cation anatogonism.

TABLE 2.1

The effect of zinc application on the total Mn content of maize and barley plants

Part	Mn rate ppm	Zn rate ppm					
		Maize			Barley		
		0	5	25	0	5	25
Roots	0	31.7	18.1	22.0	70.4	78.2	77.7
	50	51.2	52.6	52.1	199.8	208.3	194.6
	100	131.5	103.1	83.3	243.5	246.6	271.5
Sheaths	0	20.0	8.4	7.4	18.0	16.6	14.0
	50	74.9	27.4	25.6	68.4	49.8	38.5
	100	78.5	57.3	52.7	72.4	84.5	68.4
Blades	0	31.2	16.4	13.4	34.5	29.9	27.3
	50	175.3	53.1	47.8	121.2	72.5	89.5
	100	167.9	82.9	72.4	127.2	104.5	135.2

LSD at 0.05 Part	Maize	Barley
Roots	53.6	—
Sheaths	26.9	31.3
Blades	62.3	56.5

(After Singh & Steenberg 1974).

The physiological background of the finding, that an increase in one cation species reduces the concentration of another cation species is not yet clear. Some investigators explain this effect in terms of carrier competition. If this were true,

Table 2.2. The effect of an increasing Mg application on the content of various cation species in sunflower plants (Scharrer and Jung 1955)

	K	Na	Ca	Mg	Sum
			mg/100g DM		
Mg_1	49	4	42	49	144
Mg_2	57	3	31	61	152
Mg_3	57	2	23	68	150

however, it would mean that the three major cations (Ca^{2+}, Mg^{2+}, K^+) were competing for the same cation carrier binding site. This seems unlikely because of the difference in size and structure of the ions. Moreover in short term experiments such cation competition effects are often not observed (Leggett and Gilbert 1969, Mengel 1973).

As outlined above the cell produces anionic equivalents which attract and retain cations non specifically. This attraction can be likened to race for uptake between the individual cation species. The cation species taken up fastest will neutralize the anion equivalents first and thus reduce the electrostatic attraction for the other cation species. The uptake rate depends on the concentration of the individual cation species in the nutrient solution and also on the uptake mechanism. Potassium, which is taken up actively or at least may enter the cell by facilitated diffusion, is favoured in comparison with the other cation species. This is the reason why K^+ often competes so strongly in cation uptake.

In anion uptake, antagonistic effects are less common although Cl^-, SO_4^{2-} and $H_2PO_4^-$ uptake can be stimulated when NO_3-uptake is strongly depressed (Kirkby and Knight 1977). The most common anion antagonism is between NO_3^- and Cl^-. High Cl^- supply in the nutrient medium lowers the nitrate uptake and vice versa. The effects are particularly marked in plants which accumulate NO_3^- and Cl such as the Chenopodiaceae. The basis of this non specific antagonism is probably analogous to that of cation competition.

In plant nutrition the term synergism is often used to describe the opposite phenomenon of antagonism. Thus a synergistic relationship occurs between two plant nutrients when the uptake of one is stimulated by the other. For example NO_3^- nutrition stimulates the uptake of cations. This effect is non specific. Increasing the level of NO_3^- nutrition enchances cation uptake which is associated with higher levels of organic acid accumulation. Another example of synergism between two cations (Zn and Mn) is shown i Figure 2.6. Increasing the application of Zn in a zinc polluted soil resulted in increased uptake of Mn in barley plants. (Singh & Steenberg 1975). It is, however, not clearly understood whether it is the effect of zinc or associated anions on Mn uptake.
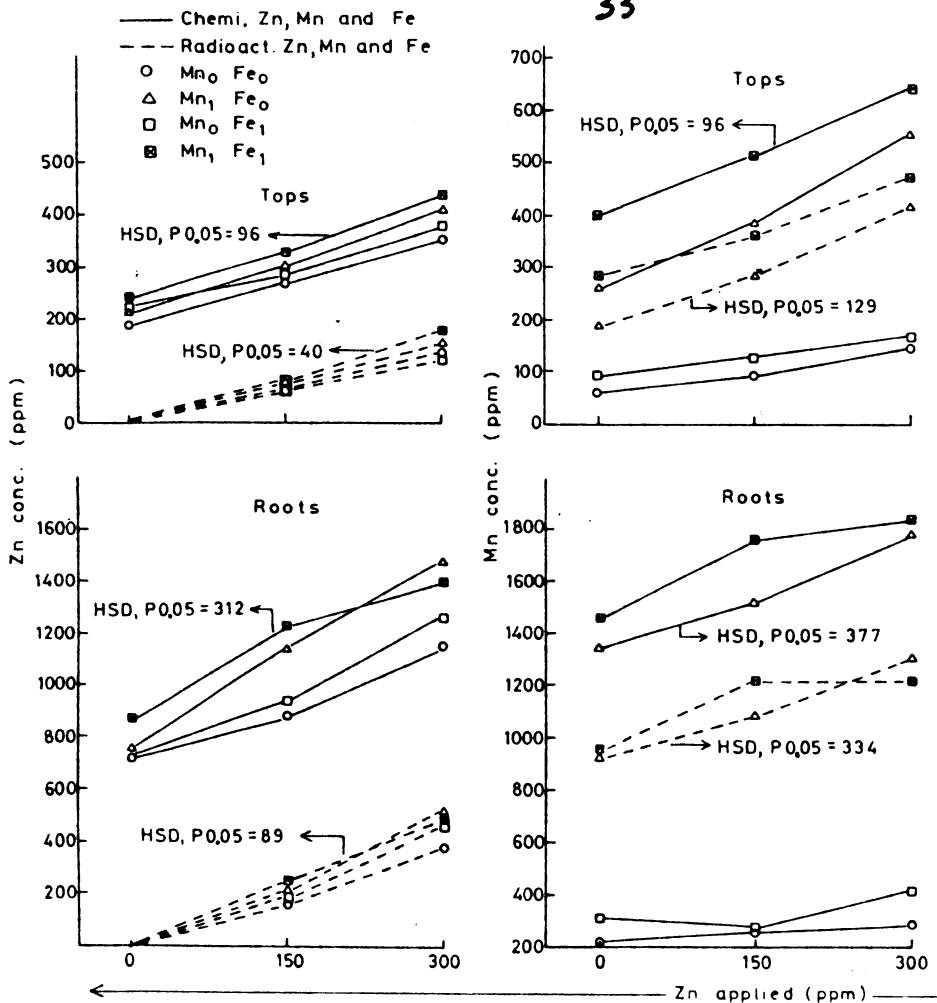
Fig. 2.6.
Effect of Zn, Mn, and Fe application on Zn and Mn concentrations in barle (Singh and Steenberg 1975).

5. Translocation of nutrients in plants

Translocation, transport, or conduction may be defined as "a movement of solutes or water from one part of a plant to another part - generally through specialized conducting tissues". However, substances can move from cell to cell, such as from one parenchymatous cell to another, without moving in specialized conducting tissues (i.e., xylem and phloem). The greater rates and quantities of translocation occur in the specialized conducting tissues.

In general, water and inorganic ions and molecules move in the xylem; organic molecules move in the phloem. There one striking exception:, all substances moving out of leaves - even water - move outward through the phloem. There are cases of unusual events or apparent irregularities in translocation; at least there are exceptions to some of the general scheme of events. For example, some organic compounds may move in the xylem, and at least some inorganic ions apparently move in the phloem (Bollard 1960).

3.1 Theories

3.1.1 Simple diffusion

Ordinary diffusion has long been recognized as inadequate for explaining the rates at which substances diffuse and the amounts that diffuse. For example, within 40 min newly absorbed ^{32}P was detected in the leaves and stem tips of tomato plants over 6 ft tall (Arnon et al. 1940). Radioactive Br⁻ moved from the culture solution to the leaves at the tips of 15-ft-long cucurbits in 5 min (Stout et al. 1947). The observed diffusion constant of sugar in sieve tubes is approximately 40,000 times as great as the diffusion constant for sugar in a 2% solution of sucrose in water (Mason and Maskell 1928).

3.1.2 Protoplasmic streaming

The significance of protoplasmic streaming in circulating and distributing substances within a cell was first suggested by Vries (1885) and was later supported by Curtis (1925, 1935) and Mitchell and Worley (1964). If, for example, a given substance were rapidly distributed uniformly throughout a sieve tube, its movement to the next sieve tube would pressumably be expedited.

Mitchell and Worley (1964) observed rotational streaming of protoplasm in phloem and xylem fibers of bean stems, and in cells that appeared to be fibers in stems of young cucumber, tomato, sunflower, and flax. In immature bean phloem fibers, plastids were carried a distance of approximately 2 mm - the average length of a fiber - in about 3 min (3.6 cm/hr).

It has been suggested by Suteliffe (1960) that protoplasmic streaming probably depends on a rhythmic folding and unfolding of protein molecules. He noted that streaming was stopped by chloramphenicol, whereas salt absorption was not. In view of this observation, this investigator concluded that streaming was not important in salt absorption per se. Although streaming does not appear to be a mechanism of absorption, it could aid in steepening the gradient from outside to the inside of the cell.

There are two main objections to this theory as regards explaining

the observed rates and amounts of translocation of materials throughout the plant. First, protoplasmic streaming has not been universally observed in sieve tubes. Second, this phenomenon would not explain the rapid rates of translocation that have been recorded.

3.1.3 Interfacial diffusion

This theory (Honert 1932) is based on the principle that substances that lower the interfacial tension between two immiscible liquids tend to spread __rapidly__ by diffusional gradients over the interface between them. Substances move in this interface from the region of their introduction or formation, where surface tension is lowered, toward regions not containing the substance or where surface tension is relatively higher. This type of movement is approximately 68,000 times as rapid as that occurring by simple diffusion.

3.1.4 Activated diffusion

Mason and Philis (1937) proposed that transport occurred through stationary cytoplasm by a process they calles "activated diffusion". They proposed that living cytoplasm was capable of hastening diffusion either by activating the diffusing molecule or by decreasing the resistance to diffusion through the cytoplasm.

3.1.5 Mass flow or pressure hypothesis

According to this theory, as orginally proposed by Münch (1927) and most recently championed by Zimmermann (1961) and Crafts (1961), there is a turgor pressure gradient between supplying and receiving cells (or tissues). Sugars are formed in leaves, and the osmotic pressure of the cells is increased; sugars are used by the roots with a concomitant lowering of osmotic pressure. These phenomena, then, tend to establish the gradient on which this theory rests. As water is moved from the roots to the tops, salts would be carried along by the mass flow of solution. Downward movement of this mass flow of solution in the phloem would carry sugars from the leaves to the roots.

There is experimental evidence consistent with the mass flow

hypothesis. In many cases, although not in all, the required
gradient exists and is in the right direction. Phloem cells
have been observed to be under pressure; phloem exudes when it
is pierced; and a volume of exudate from a given sieve tube may
exceed manyfold the volume of the sieve tube cell.

Working with aphids attached to three stems, Zimmermann (1961)
cut off the stylets and collected phloem exudate. He observed
that a single sieve element 20-30 μ in diameter and 0.4 mm long
could be continuously refilled 3 to 10 times per second with a
concentrated sugar solution for hours or days without any visible
injury. He concluded that mass flow was the only reasonable
explanation for this rapid rate of refilling. He also noted
that the exudate concentration decreased approximately 0.01 M
per meter in a downward direction of a normal tree during the
summer. According to Poiseulle's equation, he determined that
pressure gradient, to which this would correspond, was fully
sufficient to force solution at the observed rates through
capillaries of the dimensions of the sieve tube lumen and the
combined sieve pores.

There is some evidence that would appear to discredit mass flow
as a satisfactory ecplanation of translocation. Using an approach
similar to that reported by Trip and Gorham (1968b), Gage and
Aronoff (1960) and Choi and Aronoff (1966) concluded that mass
flow was not a dominant process in the translocation of photo-
synthate in their experiments.

3.1.6 Dual transport

This type of translocation concerns the transport of two sub-
stances simultaneously. For example, although sugars may be
translocated independently, there is considerable evidence that
translocation of applied plant growth regulators (from leaves)
is dependent on simultaneous translocation of photosynthate -
pressumably sugars (Mitchell and Brown 1946, Linder et al. 1949,
Jaworski et al. 1955, Hay and Thimann 1956, Barrier and Loomis
1957, Clor 1959, Mitchell et al. 1960). Phloem transport of
2,4-D, urea, and 3-amino-1,2,4-triazole was greatly reduced in
carbohydrate-starved cotton leaves (Chlor et al. 1963).

Linder et al. (1949) observed that synthetic growth regulators were readily translocated from bean when the latter contained 2,5-3,5% total sugar, but not when they contained only about 2% total sugar. These percentage were determined by methods that depended on reducing properties of sugars, but certain substances other than sugars have a reducing action - the so-called "noncarbohydrate reducing substances". Apparently, these substances are present in relatively high concentration in bean leaves, since Mathes (1961) found by paper chromatography that bean leaves with 2% sugar were in fact essentially devoid of sugars. The report by Mathes thus clarifies why 2% sugar was ineffective in the translocation of synthetic plant growth regulators.

According to Crafts (1961), there is increasing evidence indicating a simultaneous correlated flow of many substances (in the phloem) from source to sink. Viruses, growth regulators, hormones, and photosynthate apparently move together.

Gauch and Dugger (1953, 1954) provided an example of dual translocation involving an inorganic ion and an organic molecule. They obtained evidence which they interpreted as indicating that B was involved in sugar translocation. One of the two mechanisms of action for B which they proposed (Gauch and Dugger 1953) involved the translocation of sugar-borate complexes.

3.2 Tissues involved in translocation

3.2.1 Upward movement

For many years most plant physiologists agreed that upward translocation of water and inorganic ions or molecules occurred in the xylem. Curtis (1925, 1935) contradicted this viewpoint and claimed that phloem was the major pathway for inorganic ions. His research (Curtis 1925) with privet and other stems, in which some were ringed and others were not, indicated that N and ash constituents moved primarily in the phloem. Curtis' experiment were conducted before the interrelationship between salt absorption and respiration was established. Ringing of

stems undoubtedly interfered with translocation of sugars to roots; the normal pathway for translocation could thus have been altered. Clements and Engard (1938) voiced strong opposition to Curtis' conclusions. With the advent of isotopes or tracers, overwhelming evidence was obtained which implicated xylem as the normal pathway for inorganic ions. Leaving the tissues intact, Stout and Hoagland (1939) separated phloem and xylem with a layer of waxed paper and showed clearly that xylem was the major pathway for the upward conduction of inorganic nutrients.

The much higher water solubility of ^{45}Ca in xylem and the known immobility of Ca^{2+} in phloem make it likely that xylem provides the radiocalcium for translocation to dogwood foliage (Thomas 1970). It was concluded that upward movement of ^{45}Ca by exchange reactions in the stems and branches could account for the movement to the tops - a point og agreement with conclusions by Bell and Biddulph (1963).

3.2.2 Downward movement

When inorganic constituents move out of leaves, it is generally agreed that they do so via the phloem and, if these constituents are moving in a downward direction, they continue to move in the phloem. Biddulph and Markle (1944) observed downward movement of radioactive phosphate through phloem at a rate of 21 cm/ hr. Huber (1941) reported that downward movement may be as high as 100 cm/hr in broad-leaved forest trees. In general, velocities of translocation in phloem are of the order of 10-100 cm/hr with extremes ranging up to 300 or even 3000 cm/ hr (Zimmermann 1960).

Movement of materials out of leaves occurs through phloem - as amply demonstrated in the case of SO_4^{2-} and phosphate (Biddulph 1951, 1959; Biddulph and Markle 1944). It was reported that Ca^{2+} is not transported in phloem, hence does not move out of leaves prior to leaf fall - as is the case eith other ions (Sutcliffe 1962). However, Ca^{2+} may move in the phloem, but at a very slow rate. Foliar-applied Ca^{2+} was observed by Biddulph et al. (1959) to move outward in phloem, but at a rate approximately 1/100 that of P. These investigators also noted that Ca^{2+} was translocated from cotyledons of bean plants during

early growth of the seedling, but that later growth depended on external Ca^{2+}, since Ca^{2+} in the cotyledons later became immobile. When Ca^{2+} injected into the stem of a white pine moved into the phloem, the element became immobilized in the form of Ca oxalate crystals (Thomas 1967).

3.2.3 Lateral movement

In stems in which there are xylem and phloem rays composed of parenchymatous cells, there may be lateral movement of inorganic constituents from xylem to phloem, and even to tissues outward from the phloem.

Lateral movement of inorganic solutes is clearly shown in the case of spiral ringing of a tree (apple, for example) in that upwardly translocated ions or salts move laterally around a spirally ringed trunk, emerge at the end of the spiral, and affect the growth or appearance of branches in line with the open end of the spiral.

Ca^{2+} appears to enter bean stem sections in two ways: a reversible exchange phase, and an irreversible accumulation phase in which Ca oxalate is formed. Biddulph et al. (1961) noted that the xylem cylinder operated essentially as an exchange column for Ca^{2+}. Lateral movement was indicated by the fact that Ca^{2+} was tranferred from the xylem of leaf traces to cells of the adjacent phloem.

3.2.4 Simultaneous upward and downward movements in xylem and phloem

Zimmermann and Connard (1934) studied in detail the reversal of direction of translocation of solutes in stems. They reported that the orientation of the (intervening) stem was of no consequence in determining the direction of translocation of water, inorganics, and organics, and that activity at some distant point was the determining factor affecting the direction of translocation of each substance. They therefore concluded that each of these classes of translocatable substances could be moving upward in a given tussue in one part of the stem and downward in this same tissue in another part.

In cotton plants, organic N compounds may be traveling upward at the same time that carbohydrates are moving downward in the phloem (Phillis and Mason 1936).

Translocation of individual nutrients will be discussed under the nutritional aspects of these nutrients.

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4. Nitrogen in the Soil and its Availability to Plants.

4.1. General Aspects

Nitrogen is one of the most widely distributed elements in nature. The highest amount is present in a fixed form in the earth's crust in rocks and sediments. This is in contrast to the commonly held belief that the atmosphere is the largest reservoir of N_2. This ranks second. According to DELWICHE (1970) the atmoshphere contains about 3.8×10^{15} tonnes of molecular N_2 whereas the amount of N present in the lithosphere is about 18×10^{15} tonnes. The soil accounts for only a minute fraction of lithospheric N, and of this soil N, only a very small proportion is directly available to plants. This occurs mainly in the form of NO_3^- or NH_4^+ ions. Nitrogen is a very mobile element circulating between the atmosphere, the soil and living organisms. Many factors and processes are involved in this N-turnover, some of which are physico-chemical, and others biological.

Nitrogen is the nutrient element that most frequently limits yields in the tropics as well as in the temperate region. With the exception of some recently cleared land, most cultivated soils are deficient in this element. The fact that the nitrogen contents of tropical crops and grasses are in general lower than corresponding values in the temperate region (Webster and Wilson, 1966) contributes to the protein deficit so widespread in the tropics.

4.2. Sources of Nitrogen.

4.2.1. Soil Organic Nitrogen.

Additions of nitrogen to soils originate from rain and dust, nonsymbiotic fixation, symbiotic fixation, and animal and human wastes. Losses of nitrogen from the soil are due to volatilization, leaching, denitrification, erosion, and plant uptake. A summary of the relative contribution of each nitrogen

source under four tropical conditions is presented in Table 4.1

Table 4.1. Low and High Estimates of the Relative Annual
Contributions of Different Sources of Nitrogen
in Five Tropical Ecosystems (kgN/ha)

Source	Rain forest	Tall Grass Savanna	Short Grass Savanna	Sugar Cane	Rice Paddy
Rain and dust	4-8	4-8	4-8	4-8	4-8
Nonsymbiotic fixation					
In phyllosphere	12-40	0-12	0-4	0-12	0-4
By blue-green algae	0	0-10	0-10	0-10	14-70
In rhizosphere	0-6	0-13	0-6	0-9	0-10
In litter	0-25	0-10	0-6	12-50	0-10
Symbiotic fixation	34-68	0	0-10	0	0
Total	46-147	4-63	4-44	16-89	18-102

Source: Kass and Drosdoff (1970).

4.2.2. Nitrogen in Rain and Dust

The sources contribute an average of 4 to 8 Kg N/ha
annually. The highest levels, however, are recorded in
tropical areas, perhaps because of intense electrical activity
during thunderstorms. Dust storms from the Sahara contribute
small amounts of nitrogen to the sub-Saharan countries. A
question that has not been studied is whether nitrogen
volatilized when vegetation is burned is brought back to
another spot with rainfall in shifting cultivation areas.
Visual observations indicate that smoke is sometimes intercepted
by localized thundershowers, but no information is available
on this matter.

4.2.3. Asymbiotic Fixation

Asymbiotic nitrogen fixation is known to occur in the phyllosphere (leaf canopy), in the litter, in the soil, and in the rhizosphere. Atmospheric nitrogen is "fixed" by large populations of Azotobacter and Beijerinckia spp in the leaf blades of many tropical species. The annual contribution of this process ranges from 0 to 8 kg N/ha. In rainforests it may supply up to 40 kgN/ha .

Asymbiotic nitrogen fixation in the soil by blue-green algae is a well-known phenomenon thought to be particularly relevant in flooded rice culture, where the blue-green algae population is large. Estimates shown in Table 4.1. indicate generally low levels for the aerobic ecosystems.

4.2.4   Symbiotic Fixation

As in the temperate region, symbiotic nitrogen fixation is the main mechanism for soil nitrogen additions in the tropics. The magnitude of this phenomenon depends on the amount of legume species, certain nonlegumes such as Casuarina, a common coastal pine tree, and some tropical grasses.   The large amounts of nitrogen fixed in tropical forests are probably due to the significant proportion of tree legumes present. Symbiotic nitrogen fixation is of little relevance in cropped fields unless a legume is present. Single legume stands contribute from 16 to over 500 kg N/ha a year (Henzell and Norris, 1962). In many cases, however, nitrogen fixation by legumes is substantially lower than would be expected. This may be due to the low phosphorus or high aluminum levels of many soils, which inhibit Rhizobium activity, to extremes in soil moisture, and to the lack of a specific inoculum for the crop or variety in question. Very little nitrogen is fixed by field beans (Phaseolus vulgaris) in Latin America, partly because of their naturally poor nodulation.

4.3. Total Nitrogen Additions

The annual additions of soil organic nitrogen in several locations are shown in Table 4.2. Like the annual organic carbon additions, they are greater in tropical forests than in temperate forests or savannas. It is because of high rate of organic matter decomposition caused by high temperature.

Table 4.2. Estimates of Annual Soil Organic Nitrogen
Increments in Several Surface Soils

Location	Annual Soil N increments (kgN/ha)	
	Maximum	Minumum
Tropical lowland forests		
1. Ghana	55	22
2. India	60	24
3. Zaire	58	23
4. Indonesia	55	22
5. Columbia (Andept)	30	12
Tropical highland forests		
6. Columbia	57	23
7. Indonesia	45	18
8. Madagascar	38	15
Temperate forests		
9. California (oak)	4	2
10. California (pine)	9	4
Tropical savannas		
11. Ghana (1250 mm rain)	15	5
12. Ghana (850 mm rain)	4	2
Temperate prairie		
13. Minnesota (870 mm)	11	5

Source: Greenland and Nye (1959)

4.4.   Nitrogen Mineralization

The decomposition of soil organic nitrogen into inorganic compounds, called "mineralization", consists of three steps: aminization, the transformation of proteins into amines; the transformation of amines into ammonium (NH_4^+) ; and nitrification, the transformation of ammonium into nitrate (NO_3^-) with a short intermediate stage of nitrite (NO_2^-) formation.

4.4.1.   Ammonification

Soil organic matter primarily contains N in the amino form (protein) and to a lesser extent in the form of a hetero-cyclic N compounds (N bases of nucleic acids). The release of amino N from organic matter is termed proteolysis (aminization) and the reduction of amino Nto NH_3 is called ammonification. These processes may be represented schematically as follows:

$$Soil\ Organic\ N \longrightarrow R\ NH_2\ +\ CO_2\ +\ Additional\ Products\ +\ energy$$

$$RNH_2\ +\ H_2O \longrightarrow NH_3\ +\ ROH\ +\ energy.$$
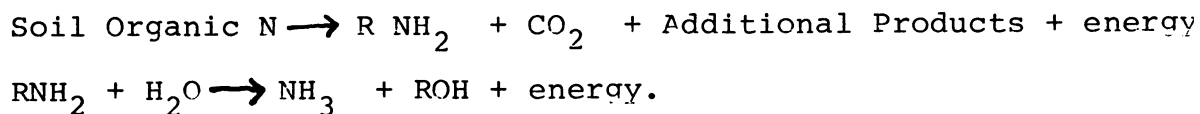
In both processes energy is released and this is utilized by the heterotrophic microorganisms which bring about the reactions.

4.4.2.   Nitrification

The biological oxidation of ammonia to nitrate is known is nitrification. This is a two-step process. Ammonia is first oxidized to NO_2^-.   The process is mediated by auto-trophic bacteria, or in other words by bacteria which obtain energy from the oxidation of inorganic salts and use CO_2 as a source of C. Two very specialized groups of bacteria are involved. The conversion of NH_4^+ to NO_2^- is largely brought about by Nitrosomonas whilst the Nitrobacter effect the oxidation of

NO_2^- to NO_3^-. Both groups are obligately aerobic, so that they can only live in media where O_2 is available. In waterlogged soils the oxidation of NH_4^+ is thus restricted. In addition, the nitrifying bacteria prefer more neutral to slightly acid pH conditions.

The two step oxidation from NH_4^+ to NO_3^- takes place as follows:

$$2\ NH_4^+ \quad + 3\ O_2 \longrightarrow 2\ HNO_2 + 2\ H_2O \ + 2H^+$$

$$2\ HNO_2 \quad + \ O_2 \longrightarrow \quad +2\ H^+ \ + 2NO_3^-$$

$$\overline{\text{Net}\ 2\ NH_4^+ \quad +4\ O_2 \longrightarrow 2\ NO_3^- + 4\ H^+ \ + 2H_2O}$$
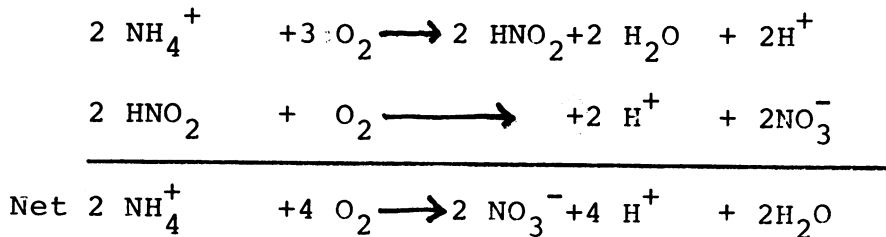
The net equation shows that nitrification is coupled with the release of H^+ and thus results in an acidification of the soil medium. The relationships of NH_4^+ oxidation, pH shift and NO_3^- formation are well demonstrated in an experiment of DUISBERG and BÜHRER (1954) the main results of which are presented in Figure 4.1. In the incubation period of 14 days nearly all the NH_4^+ was oxidized to NO_3^- with a concomitant drop in soil pH. After one week of incubation, a peak in the NO_2^- content occurred, which later disappeared due to the activity of the Nitrobacter. Generally NO_2^- does not accummulate in the soil, because the NO_2^- formed is readily oxidezed by Nitrobacter. Both bacterial groups, Nitrosomonas and Nitrobacter, obviously function "in series". Ammonia is thus rather rapidly converted to NO_3^- , provided that suitable conditions for nitrifying bacteria are present in the soil, as was the case in the example presented in figure 4.1. The soil used was a fertile calcareous sandy loam with a pH of 7.8 and the experiment was carried out in the laboratory with optimum soil water and temperature conditions. In the field, nitrification often occurs at a lower rate and in soils of low pH and in waterlogged soils, nitrification is restricted or even completely inhibited. Under these conditions the soil may thus accumulate NH_4^- N. Nitrification is also depressed in dry soils (Sabey 1969).
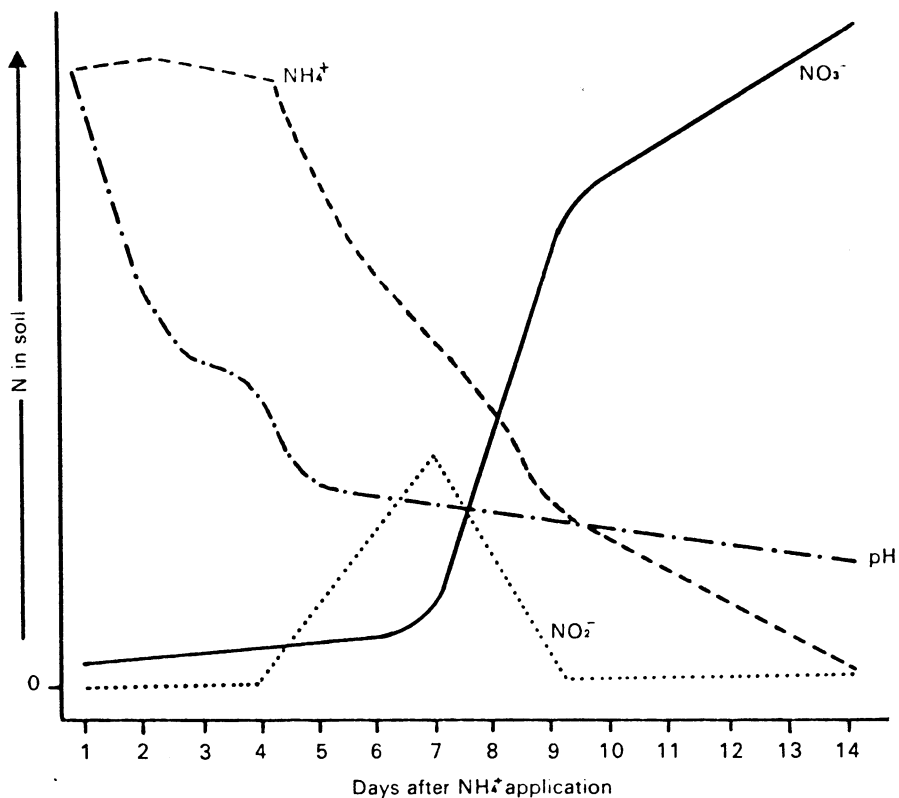
Fig. 4.1. Relationship between microbial NH₄ oxidation, nitrate formation and soil pH (after DUISBERG and BUEHRER [1954]).

Nitrogen mineralization also occurs under flooded conditions, but it stops at the ammonification stage, because only aerobic microorganisms can convert NH_4^+ into NO_3^-. Although the mineralization processes are slower, anaerobic microorganisms apparently can transform organic nitrogen to ammonium at higher C:N ratios than aerobic microorganisms (DeDatta and Magnaye, 1969). The net result is a mineralization rate similar to that in aerobic soils.

Between these two extremes in moisture contents, most tropical soils undergo several periods of alternate wetting and drying. Organic carbon and nitrogen mineralization is faster under alternate wetting and drying than under "optimum" moisture conditions. Furthermore, the critical C:N ratios for mineralization also change under these conditions. Birch (1960) found that drying promotes faster carbon than nitrogen mineralization, thus reducing the C:N ratios. Birch also found that the critical C:N ratio above which mineralization stops is higher under

alternate wetting and drying. For example, a residue material containing 1.5 per cent N was mineralized under alternate wetting and drying but inmobilized under constant moisture. this phenomenon is probably associated with a more active microbial population after drying and rewetting the soil or perhaps an increased accessibility of humus to microogranisms by shringk-swell of clay minerals or thin oxide coats.

Nitrifyers oxidize both NH_4^+ released by ammonification and NH_4^+ applied as fertilizer. Fertilizer NH_4^+ is thus also converted to nitrate. The rate at which this occurs of course depends on prevalent soil conditions (GASSER and IORDANOU (1967)). In practice it is often the case that a soil is treated with NH_4^+-N, but that crop uptake occurs mainly as NO_3^-. Nitrification can be suppressed or even prevented by the so-called nitrification inhibitors (NOWAKOSWSKI and GASSER 1967). A well-known chemical of this kind is 2 chlor-6- (trichlormethyl)-pyridine, known commercially as "N Serve". NIELSEN et al. (1967) reported that application of this inhibitor to soil completely prevented the formation of NO_3^-, and that NH_4^+ accumulation was observed. Nitrification inhibitors have been used in practice so that crops may utilize NH_4 fertilizers more efficiently. By applying the nitrification inhibitor to the soil the conversion of NH_4^+ to NO_3^- is prevented and thus also the loss of N by leaching of the very mobile NO_3^-.

4.5 Denitrification

Many different types of anaerobic organisms are capable of utilizing NO_3^- or NO_2^- as a source of oxygen in place of molecular O_2. This often occurs when soils become waterlogged and anaerobic decomposition takes place. Nitrate is reduced by a series of steps to nitrous oxide and N_2, which are then released into the atmosphere. This process of microbial

denitrification thus results in a loss of N from the soil system. According to ALLISON (1966) these losses of gaseous N can range from about 5 to 50% of the total N applied. Even in aerated arable soils some N losses due to denitrification may occur for O_2 is not uniformly distributed throughout the soil and some anaerobic regions may be present (WOLDENDORP 1968) Denitrification is promoted by high soil moisture conditions, the presence of fresh organic material in the soil and a low O_2 tension in the soil water. Thus on well aerated sandy soils denitrification rates are generally lower than on clay soils .

4.6. Ammonium fixation

In contrast to NO_3^- which is rather mobile in the soil and hardly adsorbed by soil particles, NH_4^+ is strongly adsorbed to negatively charged clay minerals because of its cationic properties. In particular it can be bound rather selectively to 2:1 clay minerals, such as illites, vermiculites and montmorillonites. This process is called NH_4^+ -fixation, and is analogous to K^+-fixation. Ammonium and K^+ thus complete for the same selective binding sites. BARTLETT and SIMPSON (1967) reported, that the fixation of fertilizer K^+ was lowered by NH_4^+ application. According to the investigations of SIPPOLA et al.(1973) on Finnish soils, NH_4^+ is fixed in even larger quantities than K^+ by vermiculities. Because of this fixation, soils rich in 2:1 clay minerals often contain appreciable amounts of NH_4^+ in a fixed form which may range from 2000 to 3000 kg N/ha. In an analysis of a large number of soil samples BREMNER (1959) found that about 5-6% of the total N in the upper soil horizon was present in the form of fixed NH_4^+ whereas in the deeper part of the profile where the clay content was higher, the proportion of fixed NH_4^+ was as much as 20% and more. As a result of adsorption and fixation processes the mobility of NH_4^+ in the soil is essentially lower than that of NO_3^- (DAM KOFOED) and KJELLERUP 1970) and for this reason N is mainly leached out in the form of NO_3^- and only to a very small extent in

the form of NH_4^+. This means that generally the NO_3^- content
in drainage water is about 100 times higher than that of
NH_4^+ (WILLIAMS (1970)). In the soil solution nitrate is also
usually much higher in concentration than NH_4^+, except in acid
soils.

4.7. Nitrogen uptake and translocation.

Both NO_3^- and NH_4^+ forms can be taken up and metabolized
by plants. Nitrate is often a preferential source for
crop growth but much depends on plant species and other
environmental factors discussed below. Arable crops mainly
take up NO_3^- even when NH_4^+ fertilizers are applied because
of the microbial oxidation of the NH_4^+ in the soil. The rate
of uptake of NO_3^- is generally high, and according to the
investigations of ANSARI and BOWLING (1972) with decapitated
sunflower plants, uptake occurs against an electrochemical
gradient, indicating that NO_3^- is actively absorbed. Nitrate
present in the root can readily be exchanged for NO_3^- of the
soil solution. According to MORGAN et al. (1973) the
efflux is a passive process whereas NO_3^- absorption is active.
Further evidence of metabolic control of NO_3^- has been provided
by RAO and RAINS (1976). Whether the uptake of NH_4^+ by plants
is also an active process is still an open question. Investi-
gations of ZSOLDOS (1972) with excised rice roots show that
uptake of NO_3^- depends considerably on temperature (Figure 4.2),
and was approximately zero at $0^\circ C$. However, such clear-cut
effects were not observed with NH_4-N. As NH_3 is a neutral mole-
cule, MOORE (1974) suggests that it can readily cross cell
membranes. The question therefore arises as to whether NH_4-N is
taken up by roots as NH_4^+ or NH_3 or as both. Results of MENGEL
et al. (1976) suppose that NH_3 can be absorbed by plant roots
particularly under conditions of high pH where the presence
of NH_3 is favoured.

A most important difference between NO_3^- uptake and
NH_4-N uptake is in their sensitivity to pH. NH_4-N uptake takes
place best in a neutral medium and it is depressed as the
pH falls. The converse is true for NO_3^- absorption, a more
rapid uptake occurring at low pH values (RAO and RAINS 1976).
These workers suggest that the reduction of NO_3^- uptake at
high pH values may be due to the competitive effect of OH -
ions suppressing the NO_3^- uptake transport system.
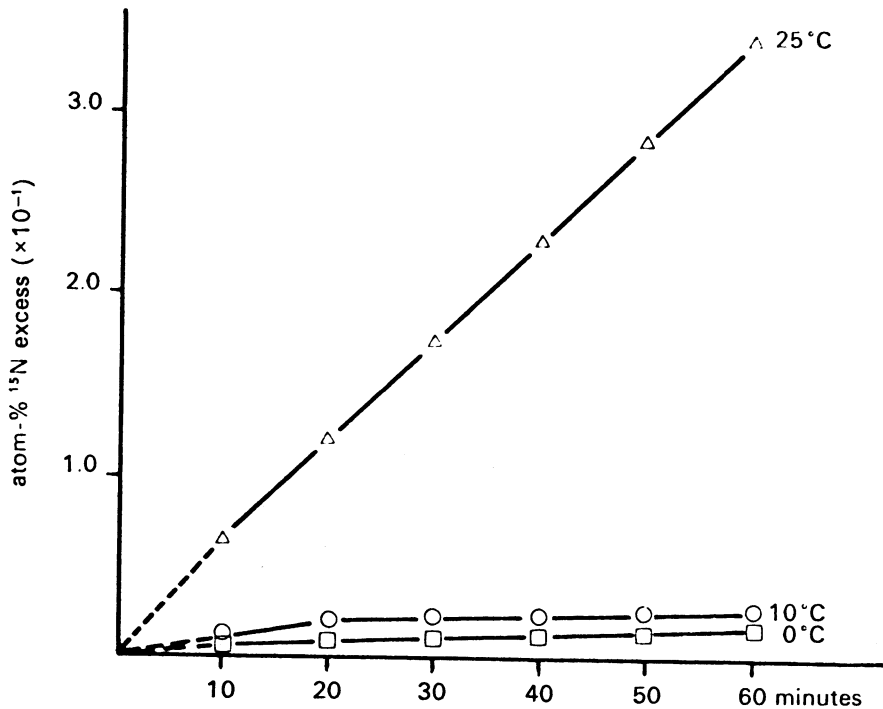
Fig. 4.2 Uptake of labelled nitrate by rice roots at various temperatures (after Zsoldos [1972]).

Nitrogen taken up by plant roots is translocated in
the xylem to the upper plant parts. The form in which N
translocation occurs depends on the N uptake source and
root metabolism. According to MARTIN (1970) nearly all
the NH_4-N absorbed is assimilated in the root tissue and

and redistributed as amino acids. Nitrate-N can be translocated
unaltered to shoots and leaves but this depends on the nitrate
reduction potential of the roots. Nitrate and amino acids
are thus the main forms in which N is translocated in the
vascular system of higher plants. Generally in the xylem sap
70 to 80% of amino acids present are rich in N, with a N/C
ratio greater than 0.4

When the supply of N from the root medium is inadequate,
N from older leaves is mobilized to feed the younger plant
organs. For this reason, plants suffering from N deficiency
first show deficiency symptoms in the older leaves. In
such leaves protein has been hydrolyzed (proteolysis) and
the resulting amino acids have been redistributed to the younger
tips and leaves. Proteolysis results in a collapse of the
chloroplasts and this in a decline of the chlorophyll content.
Hence yellowing of older leaves is a first symptom of
inadequate N nutrition.

4.8. Nitrogen deficiency symptoms.

Nitrogen deficiency is characterized by a poor
growth rate. The plants remain small the stems have a spindly
appearance, the leaves are small and the older ones often fall
prematurely. Root growth is affected and in particular
branching is restricted. The root/shoot ratio, however,
is usually increased by N deficiency (CASPER (1975). Nitrogen
deficiency results in the collapse of chloroplasts and also
in a disturbance of chloroplast development (THOMSON and
WEIER (1962)). Hence leaves deficient in N show chlorosis
which is generally rather evenly distributed over the whole
leaf. Necrosis of leaves or parts of the leaf occurs at a
rather late and severe stage in the deficiency. In this respect
N deficiency differs fundamentally from K and Mg deficiencies,
where the symptoms also begin in the older leaves but where
chlorotic and necrotic spots appear at a rather early stage.
Deficiency symptoms of Fe, Ca, S are also similar to N deficiency
being characterized by yellowish and pale leaves. In these

deficiencies, howere, the symptoms occur first in the younger
leaves. These more general observations may be used to serve
as a first means of distinguishing between these various
nutrient deficiencies.

Plants suffering from N deficiency mature earlier, and
the vegetative growth stage is often shortened. This early
senescence probably relates to the effect of the N supply
on the synthesis and translocation of cytokinins. According
to investigations of WAGNER and MICHAEL (1971) the synhtesis
of cytokinins is depressed when N-nutrition is inadequate.
As these phytohormones promote vigorous growth and the
retention of the plant in a more juvenile stage, cytokinin
deficiency may well result in senescence.

Nitrogen deficiency in cereals is characterized by
poor tillering; the number of ears per unit area and also the
number of grains per ear are reduced. The grains are small,
but often relatively high in protein content, due to a decrease
in the import of carbohydrate into the grains, during the
later stages of grain filling.

4.9. Seasonal Fluctuations of Inorganic Nitrogen.

Inorganic nitrogen in most tropical areas shows a
marked seasonal fluctuation, as illustrated in Fig. 4.3.
The pattern consists of (1) a slow nitrate buildup in the
topsoil during the dry season, (2) a large but short-lived
increase at the onset of the rainy season and (3) a rapid
decrease during the rest of the rainy season. When short-
term droughts occur during the rainy season, they are followed
by sharp but smaller increases in inorganic nitrogen and then
by gradual decreases. These short-term peaks, called "flushes"
were first described by Hardy in 1946. Subsequent work in
Africa by Birch and other workers has substantiated their

existence in a wide range of soil conditions (Birch, 1958, 1960, 1964).
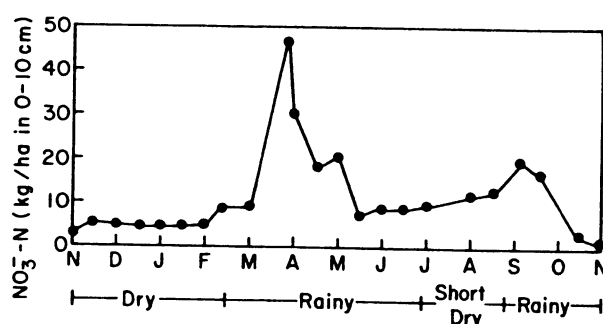
Fig. 4.3. Seasonal pattern of NO$_s$-N fluctuation in the top 10 cm of a cultivated Alfisol in Ghana. *Source:* Adapted from Greenland (1958).

Within a few days after the first heavy rains, dramatic increases in inorganic nitrogen takes place. In the field they may range from 23 to 121 kgN/ha within 10 days (Semb and Robinson, 1969). The sharpness of the peaks is directly proportional to the duration and intensity of the preceding dry period. These sharp increases are accompanied by similarly sharp decreases caused by rapid leaching in the rainy season. Semb and Robinson provided clear evidence of NO_3^- moving into the subsoil after such flushes.

Several reasons were advanced by Birch (1958) to explain these flushes. Active microbial populations build up rapidly when moisture becomes available and easily decomposible substrate is abundant. Intense drying loweres the C:N ratio humus because carbon decomposes at a faster rate than nitrogen in dry periods. Nitrogen mineralization proceeds faster at lower C:N ratios. Also, the dead microbial population provides additional substrate, which stimulates mineralization further.

As the rainy season progresses, the inorganic nitrogen supply is reduced by plant uptake, leaching, and denitrification. Leaching depends on a series of soil factors. For fairly well-aggregated Alfisols of northern Nigeria, Wild (1972b) found that peak NO_3^- concentrations in the profile gradually move down as the rainy season progresses.

4.10. Nitrogen Fertilizer Reactions in Soils

Nitrogen is the fertilizer nutrient applied in largest quantities in the tropics. Nevertheless, the actual amounts used as much lower than in the temperate region. Calculations from FAO (1971) statistics indicate that only 13 percent of the world's total nitrogen production is consumed in the tropics. In 1971, 2.6 million tons of nitrogen were used in tropical Asia, 1.3 million in tropical America, and 0.2 million in tropical Africa. In certain tropical areas, particularly for irrigated rice, sugarcane, other plantation crops, and some pastures, nitrogen use per unit area rates among the highest in the world. In sharp contrast the bulk of subsistence agriculture is just beginning to use fertilizers, particularly in tropical Asia and Latin America.

The most common fertilizer nitrogen sources used in the tropics are urea and ammonium sulfate. In temperate areas like the United States, on the other hand, ammonium nitrate, anhydrous ammonia, and ammonium phosphates tend to predominate.

4.10.1. Urea Hydrolysis

Urea is the most commonly used inorganic nitrogen source in the tropics. Its popularity is partly due to its high content (46 percent N), low unit cost, and availability in the world market. When applied to a moist soil, urea is hydrolyzed into ammonium carbonate by the enzyme urease in the following way:

$$CO(NH_2)_2 + 2H_2O \xrightarrow{\text{urease}} (NH_4)_2CO_3$$

$$(NH_4)_2CO_3 + 2H^+ \longrightarrow 2NH_4 + CO_2 + H_2O.$$
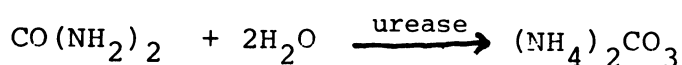
Ammonium carbonate in the presence of water dissociates into the ammonium and carbonate ions. Before hydrolysis, urea is as mobile as nitrate and may be leached down below the root zone with heavy rainfall if soil structure permits. Tamimi and Kanehiro (1962) showed that urea hydrolysis proceeds at about the same speed in the tropics as in the temperate region and is complete within 1 to 4 days. In flooded soils, Delaune and Patrick (1970) found that the rate of hydrolysis is similar to that in well-drained soils. Consequently, the first reaction of urea is no different in the tropics than in the temperate region.

4.10.2. Volatilization Losses of Ammonia

At soil pH values higher than 7, the NH_4^+ ions can be converted to NH_3 (ammonia gas) and lost to the atmosphere if the soil is dry. Volatilization losses of ammonia were first recognized in the tropics by Jewitt (1942), working with Vertisols in the Sudan. Although ammonia volatilization

Losses can occur with both urea and ammonium sources, they
are particularly important with urea since its hydrolysis
increases the pH of the surrounding soil. Broadcast nitrogen
applications to the soil surface are very common in the
tropics; therefore volatilization losses can be of practical
importance in the high-pH soils, particularly when high
nitrogen rates are applied. Shankaracharya and Mehta (1971),
working with a loamy sand of pH 7.1 in Guarajat, India,
measured field volatilization losses of 4 percent when 28 kg N/ ha
were applied as urea to the surface. When the rate was
increased to 277 kg n/ha, volatilization losses increased to
44 percent. Such high rates are common in areas where
high-yielding rice or wheat varieties are planted.

Urea volatilization losses can be drastically reduced
if the material is placed below the soil surface before
hydrolysis. This can be accomplished by incorporation, by
deep placement, or simply by moving the freshly applied
urea down with irrigation water or rainfall.
Table 4.3 shows the reduction in volatilization losses when
irrigation followed a surface application. The irrigation water
simply moved the urea down before it had a chance to be
hydrolyzed. In the presence of moisture, volatilization of
ammonia does not take place. This table also indicates that
urea volatilization losses are essentially eliminated by
incorporating the material to about 5 cm depth. The practical
implication is that urea should be incorporated into the soil
if it is to be applied to a dry calcareous soil.

Table 4.3. Volatilization Losses of Applied Urea as a
            Function of Depth and Timing in Relation to
            Irrigation in a Calcareous Loamy Sand in Gurajat,
            India (N rate: 222 kgN/ha)

| Placement | Percent Loss of Applied N | |
Depth (cm)	Applied before Irrigation	Applied after Irrigation
Surface	8.1	40.2
1.2	1.2	33.4
2.5	0.6	18.1
5.0	0.05	0.5
7.5	0	0

Source: Adapted from Shankarcharya and Meta (1971).

4.10.3 Nitrification of $(NH_4)_2SO_4$ applied as a broadcast or band placement.

Ammonium sulfate when broadcast on the soil surface does not suffer substantial volatilization losses as urea does. The nitrification of NH_4^+ into NO_3^- and the distribution of both ionic species in the profile vary with soil properties and moisture conditions. Wetselaar (1962) followed these changes in Alfisols of northern Australia. Nitrification was very fast in clay loam soils under high rainfall during the rainy season. Most of the applied nitrogen was detected as nitrates in the 60 to 120 cm section of the subsoil.

Banded applications of nitrogen fertilizers are being practiced in mechanized agriculture, primarily when complete fertilizer mixtures are used. The usual justification for this practice is the reduction of phosphorus fixation. Also side-dressed nitrogen applications by hand in traditional systems are localized close to plants. Wetselaar et al. (1972, 1973b) found that banding nitrogen applications affects the rate of nitrification of ammonium sources, and that this practice may result in an increased efficiency of applied nitrogen.

With time the ammonium ion concentration around the band decreases; when the soil pH near the urea band is between 7 and 8, nitrification proceeds to the nitrite stage. Nitrite accumulates in such bands and is toxic to plants. As pH decreases below 7 because of CO_2 increases, nitrates are formed. Nitrite accumulation does not occur with ammonium sulfate, however, because the pH of the band does not rise above 7 in acid soils. These reactions are illustrated in Table 4.4.

Table 4.4. Nitrite and Nitrate formation after Additions
of 1000 ppm N as Urea or Ammonium Sulfate in
Bands as a Function of Time on Calcareous Soil
from northern Australia

Nitrogen Fertilizer		Weeks of Incubation			
		2	4	6	12
Urea	NO_2^- -N(ppm)	170	345	125	0
	NO_3^- -N (ppm)	15	55	330	365
	Soil pH	7.4	7.2	6.0	4.7
$(NH_4)_2SO_4$	NO_2^--N (ppm)	0	0	0	0
	NO_3^- -N (ppm)	25	85	130	140
	Soil pH	6.2	6.4	5.6	4.8

Source: Wetselaar et al. (1972).

4.11   Nitrogen Requirements of Tropical Crops.

In spite of large amounts of research on nitrogen
fertilization, information about nitrogen uptake patterns
of the principal tropical crops is quite limited.
Bartholomew (1972b) has compiled estimates of nitrogen uptake
by corn, wheat, and rice at several yield levels. His results
are reproduced in Fig. 4.4.
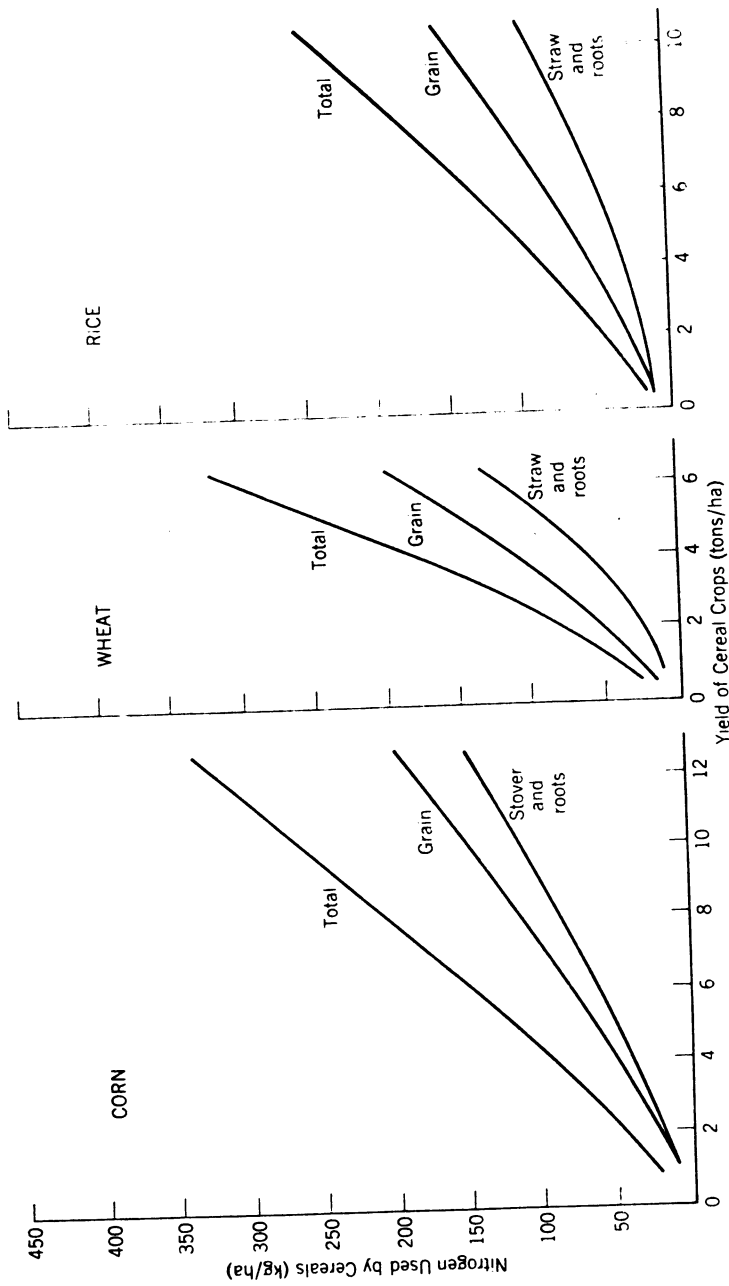
Fig 4.4. A comparison of nitrogen use by corn, wheat, and rice at a range of yield level. Source: Bartholomew (1972b).

4.11.1.   Cereals

At the present average yield levels in the tropics
of about 1 ton of grain/ha, corn, rice, wheat and sorghum
remove around 30 kg n/ha. This is probably in balance with
the nitrogen-supplying capacity of most tropical soils.
At moderatly high yield levels of 4 to 5 tons/ha, nitrogen
uptake is on the order of 100 to 150 kg n/ha. This yield
level is particularly important, because it can be commonly
attained in many tropical areas with new high-yielding
varieties and fertilization. At very high yield levels of
8 to 10 tons/ha, total nitrogen uptake exceeds 200 kg N/ha.

The nitrogen uptake pattern of cereals with time has the
characteristic sinusoid curve. For rice two periods exists
when the nitrogen requirements are highest: at the tillering
stage, when secondary shoots appear, and at the panicle
primordium initiation stage, which marks the start of the
reproductive phase. The number of panicles per unit area is
highly correlated with the nitrogen supply at tillering.
The number of spikelets per panicle is dependent on the
nitrogen supply at panicle initiation   (Sanchez, 1972).
Rice yields are positively correlated with adequate plant
nitrogen levels at these two critical growth stages.

In corn, tillering is an undesirable characteristic and
yields are correlated with a maximum number of kernels per
unit area. Nitrogen requirements are high during the "grand
period of growth" in the vegetative phase and at silking.
The nitrogen uptake pattern of wheat is similar to that of
rice (Srivatsava, 1969), and the pattern of sorghum to that
of corn (Roy and Wright, 1973).

4.11.2. Root Crops

Root crops also remove large quantities of nitrogen.
At presently low yield levels of 8 to 10 tons/ha of fresh roots,
cassava roots and potato tubers remove about 40 kg N/ha.
At the higher yield levels attained with fertilization, these
crops can remove over 150 kg N/ha, including the tops.

The nitrogen uptake pattern of Peruvian potatoes observed
by Ezeta and McCollum (1972) shows that most of the nitrogen
was taken up before tuber initiation. During the grand period
of growth from 97 to 137 days after planting, nitrogen
accumulated at the rate of 2.5 kg N/ha per day.

The nitrogen accumulation pattern in cassava is slow
during the first 2 months, then increases linearly, and reaches
a maximum at 10 months for varieties that mature in 14 months
(Hendershortt et al., 1972).

4.11.3.   Grain Legumes

At presently low yield levels of 0.5 to 1.0 ton/ha beans,
soybeans, and peanuts remove about 30 to 50 kg N/ha. At
higher yield levels Fassbender (1967) has reported removal
rates on the order of 100 to 150 kg N/ha for Phaseolus
vulgaris beans.

4.11.4.   Pastures

Of all tropical crops, tropical grasses are the greatest
annual extractors of nitrogen. At low annual yield levels
(10 tons dry matter/ha) tropical grasses may remove about
100 kg N/ha a year. At high yield levels of 30 to 50 tons,
they may remove from 400 to 600 kg N/ha a year. Since these
are perennial species, the nitrogen requirement patterns varies
with time and height of cutting or grazing (Vincent-Chandler
et al., 1964). When legumes are grown with grasses, the
total uptake may be closer to the legume contribution, which
can reach 200 kg N/ha in some cases.

4.12.   Management of Nitrogen Fertilizers

4.12.1   Determining Application Rates

Since there are no practical soil tests for estimating
the available nitrogen levels in the soil, the determination
of optimum nitrogen rates has to be based on indirect methods,
usually field experience. In areas where organic nitrogen
is supposed to be at equilibrium in the soil because of
similar management for many years, three parameters can be
used to estimate rates of applications: (1) the nitrogen uptake
required by the crop to produce a desired yield level, (2)
the nitrogen supplied by the soil, and (3) the percent recovery
of added nitrogen.

The nitrogen uptake required for optimum yields can be
obtained in the case of rice, corn, and wheat by referring to
Fig. 4.4, by measureing nitrogen uptake in field experiments,
or by calculating the internal nitrogen requirement of the
crop in question. The internal nitrogen requirement is the
minimum amount of nitrogen in the above-ground portions of
the crop associated with maximum yields (Stanford, 1966).
Only a few estimates are available: 0.2 percent N for sugarcane,
1.3 to 2.4 percent for some tropical grasses, 1.4 percent
for wheat, 1.2 percent for corn, and 0.8 percent for rice
(Stanford 1966; Sanchez et al., 1973a). The uptake at the
desired yield level can be obtained by multiplying the internal
nitrogen requirement by the total dry matter produced at the
desired yield levels.

The nitrogen supplied by the soil can be estimated from the
average yield without nitrogen or, preferably, by determining
the nitrogen uptake of the check plots in nitrogen fertilizer
experiments. In equilibrium conditions this is a reliable
measure, but in newly cleared land or in irrigated soils some
chemical methods are preferred (Bartholomew, 1972b).
Measurements of total soil nitrogen, organic matter, and inorganic
nitrogen might be useful at the research level but they are
too expensive or cumbersome for routine soil testing.

The efficiency of fertilizer nitrogen utilization can be calculated as the apparent fertilizer recovery from field experiments with or without the use of N^{15} radioisotopes. By knowing the nitrogen uptake at the certain rates and the uptake without added nitrogen, the percent recovery can be calculated as follows:

$$\text{Percent recovery} = \frac{\text{N uptake at applied rate} - \text{N uptake without added N}}{\text{N rate}} \times 100$$

Recovery ranges from 20 to 70 percent. The higher figure is common for crops with extensive root systems such as pastures (Vicente-Chandler et al., 1964; Henzell, 1971). The lowest recoveries are found in areas of alternate wetting and drying.

The optimum nitrogen rate therefore can be determined by the following equation:

$$\text{N rate} = \frac{\text{N uptake at desired yield level} - \text{N uptake without added N}}{\text{Percent recovery}}$$

4.12.2. Nitrogen Responses in Cereals

Rates. Corn responses to nitrogen are usually positive, except in newly cleared land, when the profile inorganic nitrogen is very high, or when acidity or serious problems with other nutrients exist. Many of the responses in tropical Africa, although positive, increased yields only from 1.2 to 1.4 tons/ha, according to a summary by Richardson (1966). This clearly indicates that either the rates used were too low or some other factor, such as variety or spacing, was inhibiting yields. In tropical America, where yield responses are generally higher, the recommended rates of application range from 60 to 150 kg N/ha (Sanchez, 1973). In addition to soil factors, the shape of the response curve is affected

by variety, plant population, and water regime. For example, the recommended rates of application in Mexico have gradually increased from 40 kg N/ha in the 1940s to 80 kg N/ha in the 1950s and from 80 to 175 kg N/ha in the 1960s (Sanchez, 1973). This is clearly a result of the varietal improvement in that country.

Rice responses to nitrogen are affected more by nonsoil factors than by soil properties. Plant type, solar radiation, spacing, and growth duration essentially determine the shape of the nitrogen response curve (Sanchez, 1972).

Wheat responses to nitrogen are also affected by plant type. Tall, traditional varieties respond positively to relatively low levels of nitrogen. When they receive high rates, they show a yield decrease due to excessive vegetative growth and lodging. On the other hand, the new short, stiff-strawed Mexican varieties respond positively to higher nitrogen rates and produce much higher yields at the optimum application rates. Their stiff straw prevents lodging at higher nitrogen rates. Figure 4.5 illustrates the response pattern of a tall variety (C-306) and a short-statured variety (Sonora 64) in Pantnagar, India.
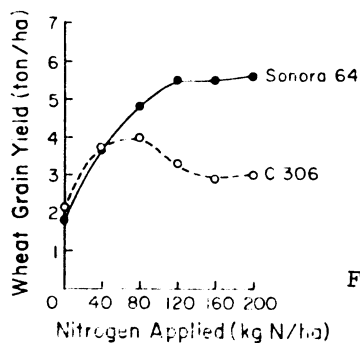
Fig.4.5: Varietal response to nitrogen by wheat in Pantnagar, U.P., India. Source: Sharma et al. (1970).

<u>Sources.</u>   Much research has been conducted to compare urea, ammonium sulfate, and other nitrogen sources on corn, rice, wheat, and sorghum in the tropics. For all crops the overwhelming evidence indicates no differences between urea and ammonium sulfate or other ammonium sources (DeDatta and Magnaye, 1969; International Atomic Energy Agency, 1970 a; Sanchez, 1972, 1973; Khalifa, 1973). In instances where ammonium sulfate was superior to urea, the effect was due to sulfur deficiency or volatilization losses of surface-applied urea. Where urea was superior, differences were due to the acidifying effect of ammonium sulfate in already acid soils or, in the case of rice, to H_2S toxicity in flooded soils very low in iron. The bulk of the evidence indicates few differences in ammoniacal sources when properly applied.

Nitrate sources are usually inferior to ammoniacal sources under conditions favouring leaching or denitrification. Their lower nitrogen content also implies a greater cost per unit of nitrogen.

Organic sources are excellent. However, the quantity required to reach the optimum rates requires a tremendous amount of bulk and may cause problems of incorporation.

Nitrification inhibitors have received much attention recently. A review by Prasad et al. (1971) cites several instances of yield responses throughout the world but no evidence of economical results under field conditions.

<u>Timing and placement</u>. The most practical way of applying any fertilizer is to broadcast it and incorporate it into the soil surface before planting.   For nitrogen this procedure is efficient only if the NH_4^+ and NO_3^- ions released stay in the root zone and are not leached or denitrified to a considerable extent. Since crop nitrogen requirements are low at early growth stages, the optimum timing is that which ensures a good nitrogen supply at the two critical growth stages of the cereals at the lowest possible cost.

Preplant urea or ammonium sulfate applications
incorporated into the soil were found to be as effective
as other timing or placement practices for high-yielding corn
in Samaru, Nigeria, under conditions of little leaching
(Jones, 1973). The same is true of rice under constantly
flooded conditions with essentially no leaching. In most
cases, however, delaying the only nitrogen application
until the first critical stage or splitting applications in
two is more efficient. The work of Fox et al.(1974) in
Puerto Rico shows the substantial benefits of delaying one
application for corn in udic regions of Puerto Rico. They
also obtained the same results with sorghum. Similar results
were found with rice and wheat (Sanchez, 1972;). It is
seldom profitable, however, to have more than two split
applications.

There is no question that incorporating preplant appli-
cations is a good placement practice. Whether the nitrogen
is broadcast or banded depends on how other nutrients are
applied and whether nitrification should be delayed by
locally high rates. Postplant applications are usually broad-
cast or can be incorporated lightly in the process of weeding.
The International Atomic Energy Agency (1970) studies with
corn and rice emphasize the importance of incorporation
whenever possible.

Efficiency of utilization The recovery of applied nitrogen
is higly variable. Bartholomew (1972) estimates a 50 percent
recovery for rice and wheat. These figures are applicable
to the temperate region but to only a few places in the tropics.
Fox et al. (1974) obtained recoveries of 51 percent with the
optimum postplant side-dressed application rate for corn in
Puerto Rico but only 33 percent when the same rate was
incorporated into the soil surface. Jones (1973) reports a
70 percent recovery for corn under conditions of no leaching,
with the nitrogen applied before seeding or side-dressed.

Nitrogen recovery by rice ranges from 30 to 50 percent under constant flooding and from 20 to 30 percent under water management practices conducive to leaching and denitrification. In the latter case use of sulfur-coated urea may increase the recovery rate to 30 to 40 percent (Sanchez et al.,1973 b). Nitrogen recovery by wheat may be as high as 50 percent with the best rate, timing, and placement practices (Hamid, 1972).

4.12.3   Nitrogen Response by Root Crops

Nitrogen responses are often negative for cassava in spite of the high nitrogen requirement of this crop. Nitrogen applications increase the top:root ratio and decrease yields in many cases. In others it increases the tuber yield and protein content but not the starch yield (Sanchez, 1973). Long-term experiments in Brazil by Normanha et al. (1968) emphasize the importance of an appropriate N:K ratio. Nitrogen responses were obtained in the presence of ample phosphorus and potassium supplies. Cassava cutting are very susceptible to salt concentrations when in contact with fertilizers. Nitrogen should be applied to the side of the planting furrow, and the rest side-dressed at later stages.

Potatoes respond to applications of 60 to 120 kg N/ha in southern Brazil and to 160 kg N/ha in the Peruvian Sierra. In Peru, McCollum and Valverde (1968) noted that the magnitude of the response was inversely related to the soil inorganic matter content. They also observed no differences among nitrogen sources, but with organic manure (guano) the quantity needed for optimum rates was too bulky to be practical. The best timing of applications is half at planting and half at later stages.

4.13.   Residual Effects of Nitrogen Fertilization

4.13.1.   Inorganic Nitrogen Supply

If it is assumed that 30 to 50 percent of the added nitrogen is recovered by plants, the rest either stays in

the soil or is lost by leaching and denitrification. The
fate of the leftover nitrogen undoubtedly varies with soil
and climatic conditions. In some cases large quantities are
lost from the profile, and in others a gradual buildup takes
place. Fox et al. (1974) report that some Oxisols and
Ultisols of Puerto Rico contained over 300 kg N/ha as
inorganic nitrogen in their profiles after many years of
continuous fertilization. Yields of 5.8 tons/ha of grain sorghum
were obtained in these soils without additional nitrogen.

The magnitudes of these nitrogen buildups are not well
known or described. They may occur where high rates have
been consistently applied over many years, and all the excess
nitrogen has not been completely lost by leaching or
denitrification.

4.13.2. Changes in Soil Properties.

Ammonium sulfate and urea have a net residual acidity
because of the following reactions:

$$(NH_4)_2SO_4 + 4O_2 \longrightarrow 2NO_3^- + 2H_2O + 4H^+ + SO_4^{2-}$$

$$(NH_2)_2CO + 2H_2O \longrightarrow (NH_4)_2CO_3 + 4O_2 \longrightarrow 2NO_3^- + 3H_2O + 2H^+ + CO_2$$
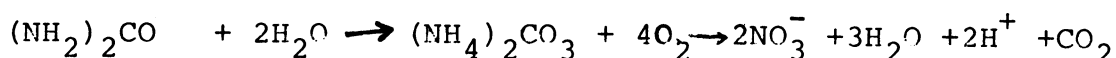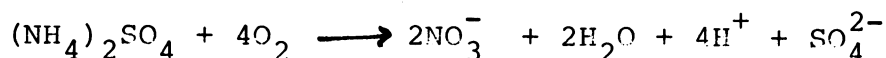
Ammonium sulfate generates 2 moles of H^+ per mole of
NH_4^+ , while urea generates 1 mole of H^+ per mole of NH_4^+ .
In terms of lime values, 7.1 kg of $CaCO_3$ is required to neutralize
1 kg of nitrogen as ammonium sulfate and half that amount when
the source is urea. The nitrification process is the cause
of residual acidity. If the NH_4^+ ions are taken directly,
there is no acidifying affect. The presence of oxygen is
also necessary for residual acidity to occur since denitri-
fication has the opposite effect. Sodium nitrate produces a
net increase in pH because of its sodium content.
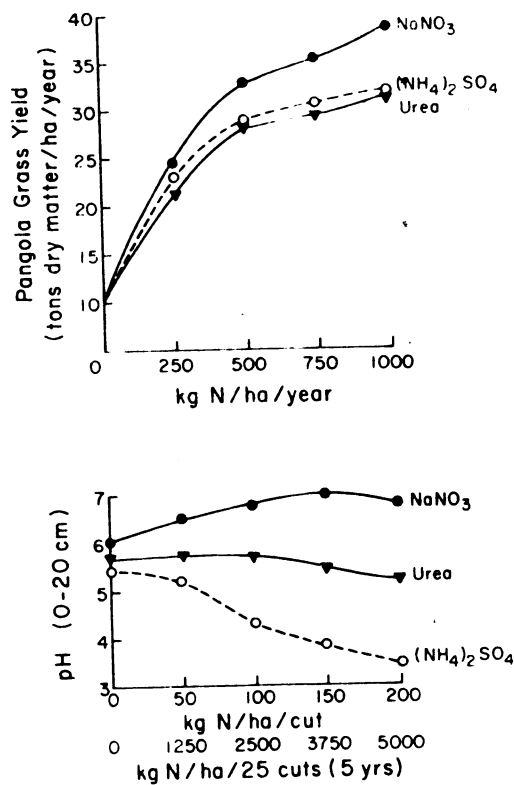
Fig. 4.6. Effects of rates and nitrogen sources on pangola grass yields and changes in soil pH after 5 years in an Andept from Colombia. *Source:* Villamízar and Lotero (1967).

The residual effects of nitrogen fertilizers on chemical soil properties are most common in heavily fertilized pastures. Villamizar and Lotero (1967) evaluated the effects of annual applications of urea, ammonium sulfate, and sodium nitrates at rates up to 1000 kg N/ha a year for 5 years in an Andept from Colombia. The results shown in Fig. 4.6. indicate that optimum yields of 30 tons/ha a year of Pangola grass were obtained at an annual rate of 500 kg N/ha. At this rate the topsoil pH decreased from 5.8 to 4.2 with ammonium sulfate, remained the same with urea, and increased to about 6.8 with sodium nitrate. In view of the similarity in efficiency between urea and ammonium sulfate, urea is definitely the better source.

Heavy ammonium sulfate applications also affect the
base status of the subsoil. Annual rates of 900 and 4000
kg N/ha drastically decreased the pH and base saturation of
two subsoils in Puerto Rico (Abruna et al., 1958) as shown
in Fig. 4.7. When lime was applied in conjunction with these
heavy rates, the base status of acid subsoils increased
dramatically. Pearson et al.,(1962) attributed this
effect to the downward movement of calcium and magnesium
applied to the surface as lime. In such cases Vicente-Chandler
et al. (1964) have recommended the application of a ton of
lime per ton of 10-14-10 fertilizer when ammonium sulfate
is used in heavily fertilized pastures of Puerto Rico.
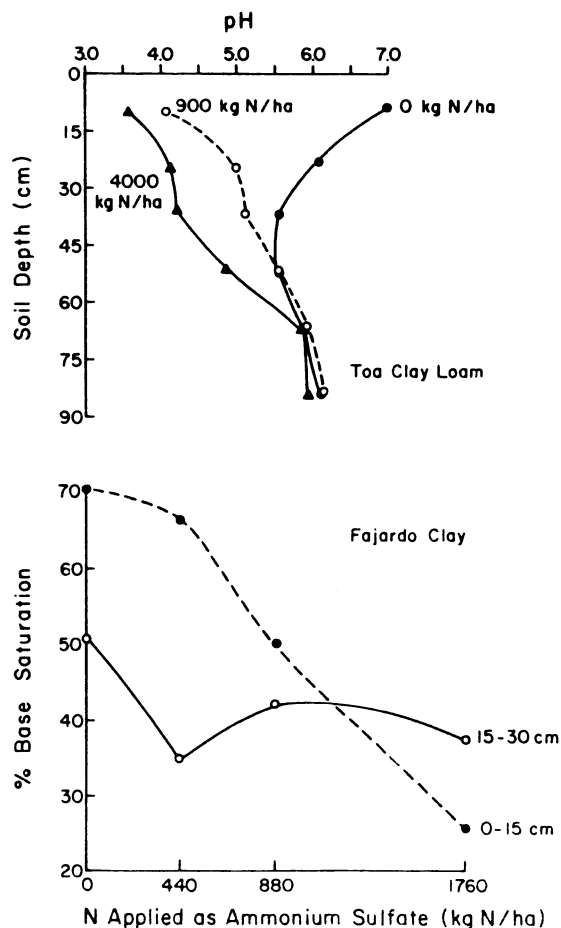
Fig. 4.7. Effects of leaching nitrogen fertilization on pH and base saturation changes in two
soils from Puerto Rico. Source. Abruña et al. (1968).

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5. Phosphorous in Soils and its availability to Plants

Phosphorus deficiencies are very common in highly weathered Oxisols and Ultisols and in slightly weathered Andepts and Vertisols. Many tropical soils have extremely high capacities to immobilize phosphorus. Considerable modification of phosphorus management practices developed for soils with moderate fixation capacity is required for such soils. In addition, significant differences exist between and within species in the ability to tolerate low levels of available soil phosphorus.

5.1. Phosphorus Contents and Forms.

5.1.1. Total Phosphorus

The total phosphorus content of the soil is of no direct practical importance, but it has often been used as a weathering index. Total phosphorus in the topsoil decreases with increasing weathering intensity. This is shown in Fig. 5.1. and Table 5.1.

Table 5.1. Distributions of Topsoil Phosphorus Fractions in some Venezuelan Soils as Related to Their Degrees of Weathering (ppm).

Series	Order	CEC of Clay (meq/100g)	pH	Total P	Organic P	Ca-P	Al-P	Fe-P
Chispa	Mollisol	100	6.9	692	235	70	33	43
Maracy	Entisol	127	5.9	298	79	88	20	33
Paya	Alfisol	50	5.0	144	85	3	14	19
Guataparo	Oxisol	18	4.8	59	11	0	2	17

Source: Adapted from Westin and de Brito (1969).

It can be seen from Fig. 5.1 that the proportion of
organic P in the soil profile reaches a.maximum and falls off
slowly. For most mineral soils, apatites are believed to be
the primary phosphate containing minerals from which the other
P containing soil fractions are derived.   In the diagram
these derived P fractions are shown as "non occluded inorganic
phosphate" and "occluded inorganic phosphate". The non occluded
fraction contains phosphate in solution, phosphate adsorbed
to soil surfaces and some phosphate minerals. The occluded
phosphate is held by Fe and Al minerals, often within a skin
of Fe hydroxy compounds. Figure 5.1 also demonstrates that
during pedogenesis an appreciable amount of phosphate is lost
. from the soil. This results largely from trans-
location of soluble P out of the soil profile. When one considers
the time scale involved, however, it is clear that the annual
rate of leaching of phosphate is extremely low.

In Venezuela, for example, total phosphorus contents are correlated with increasing weathering, as measured by the cation exchange capacity of the clays. These relationships are shown in Table 5.1.

Although Oxisols are generally low in total phosphors (less than 200 ppm), some are extremely high. Moura et al. (1972) reported 3760 ppm total P in a Eustrustox from Brazil. Ultisols and Alfisols are also generally low in total phosphorus, with values mostly below 200 ppm (Nye and Bertheux, 1957; Westin and de Brito, 1969).

5.1.2. Organic Phosphorus

Organic phosphorus normally accounts for 20 to 50 percent of the total topsoil phosphorus. In the more highly weathered Oxisols, Ultisols, and Alfisols it often represents 60 to 80 percent of the total soil phosphorus. African workers consider organic phosphorus to be the main source of phosphorus for plants in no-fertilizer agriculture. Its maintenance, therefore, is of great practical significance in traditional agricultural systems. For example, Smith and Acquaye (1963) observed a high correlation between cacao yield and soil organic phosphorus content. Friend and Birch (1960) obtained a negative correlation between responses to applied phosphorus and organic phosphorus contents in East Africa. Omatoso (1971) found sharp yield increases with phosphorus applications only when the soil organic phosphorus content was less than 150 ppm in cacao plantations of Ghana.

The C:P ratio of organic matter in representative soils of Ghana are on the order of 240:1, according to Nye and Bertheux (1957). This value represents a much lower phosphorus content than in the United States about 9:1. These wide C:N and N:P ratios are indicative of phosphorus deficiency.
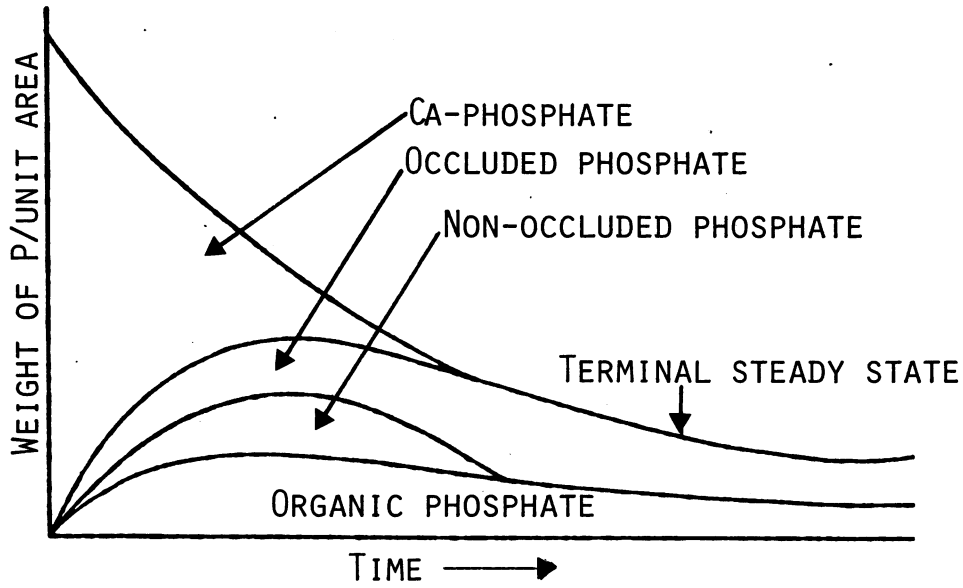
FIG. 5.1. CHANGES OF SOIL PHOSPHATE FRACTIONS DURING PEDOGENESIS (AFTER WALKER AND SYERS 1976). SOILS OF DIFFERENT AGES DEVELOPED ON THE SAME PARENT MATERIAL (CHRONOSEQUENCE).
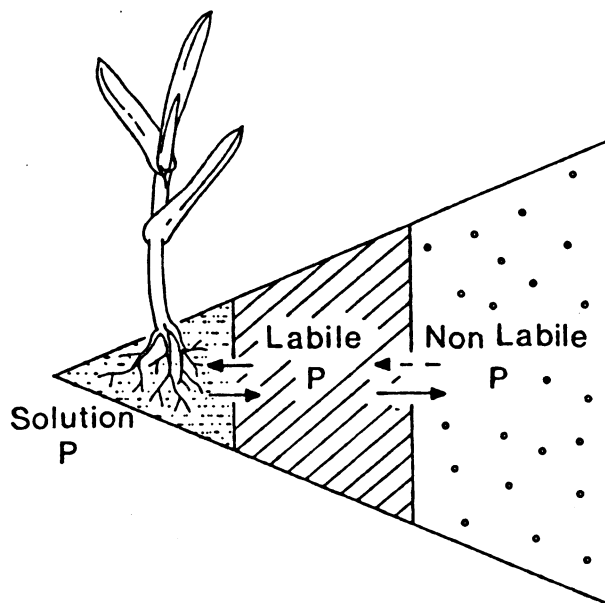
FIG. 5.2. SCHEMATIC REPRESENTATION OF THE 3 IMPORTANT P SOIL FRACTIONS FOR PLANT NUTRITION.

(Mengel and Kirkby, 1982)

Organic phosphorus mineralization is difficult to quantify because the released $H_2PO_4^-$ ions may be quickly fixed into inorganic forms. Laboratory experiments in Ghana suggest that organic phosphorus may release from 2 to 27 ppm P to the soil, according to Acquaye (1963). He also found that nitrogen and phosphorus applications increased organic phosphorus mineralization. Awan (1964), working in Honduras, also found that increased yields of corn sorghum, and cowpeas due to liming were associated with increased mineralization of soil organic phosphorus.

5.1.3. Inorganic Phosphorus Fractions.

The solid inorganic forms of phosphorus are usually divided into three active fractions and two relatively inactive fractions. The active fractions can be grouped into calcium-bonded phosphates (Ca-P), aluminium-bonded phosphates (Al-P), and iron-bonded phosphates (Fe-P). Calcium phosphates are present as films or as discrete particles, while Al-P and Fe-P occur as films or are simply adsorbed on clay or silt surfaces. The relatively inactive fractions are the occluded and reductant-soluble forms. Occluded phosphorus consists of Fe-P and Al-P compounds surrounded by an inert coat of another material that prevents the reaction of these phosphates with the soil solution. Reductant-soluble forms are covered by a coat that may be partially or totally dissolved under anaerobic conditions.

The forms of inorganic phosphorus present in a soil depend on its chemical stage of weathering. This is clearly shown in Table 5.1., where the proportion of iron phosphates increases. Calcium phosphates are more soluble than aluminium phosphates, which are in turn more soluble than iron phosphates.

The transformation of one form of phosphate into another is controlled mainly by soil pH. As soils become more acid, the activity of iron and aluminium increases and the relatively soluble calcium phosphates are converted into less soluble

aluminium and iron phosphates (Kamprath, 1973). These processes are slow enough to permit considerable quantities of calcium phosphates to be present in acid soils with pH values below 5.5.

In highly weathered soils most of the inorganic phosphorus is in the occluded or reductant-soluble form because of the formation of iron and aluminium oxide coatings. Table 5.2 shows that reductant-soluble iron phosphates are the dominant inorganic form of phosphorus in an Oxisol from the Llanos Orientales of Columbia.

Table 5.2.   Soil Phosphorus Fractions in the Profile of an Oxisol of Carimagua, Llanos Orientales, Columbia

Horizon (cm)	(pH)	Organic C (%)	Base Saturation (%)	Total P (ppm)	Percent of total P					
					Organic P	Ca-P	Al-P	Fe-P	Reductant Sol Fe-P	Occluded Al-P
0-6	4.5	2.26	7	185	77	0.9	0.8	10	9	1
6-15	4.6	1.84	7	151	75	0.6	0.9	11	11	1
15-40	4.6	1.13	13	126	73	0.7	1.2	6	17	1
40-70	4.9	0.53	15	114	55	0.8	1.3	7	34	1
70-100	5.1	0.43	29	90	47	0.6	1.0	9	41	1
100-150	5.1	0.24	21	84	35	0.7	1.2	4	53	4

Source: Benavides (1963).

Considered simply from the viewpoint of plant nutrition three main soil phosphate fractions are important:

1.   Phospate in soil solution
2.   Phosphate in the labile pool
3.   Phosphate of the non-labile fraction.

These three fractions are represented schematically in Fig. 5.2. The first fraction is clearly defined and is the phosphate dissolved in the soil solution. The second fraction is the solid phosphate which is held on surfaces so that it is in rapid equilibrium with soil solution phosphate. It can be determined by means of isotopic exchange and is called labile phosphate. The third fraction is the insoluble phosphate. The phosphate

in this fraction can be released only very slowly into the labile
pool.

    Many attempts have been undertaken to relate non-labile
phosphate to specific soil minerals. Such investigations, however,
are complicated by the fact that many soil phosphates contain
impurities, which influence their solubility and hence their
capability of exchanging phosphate ions with the soil solution.
In many soils, apatites are the most important inorganic phosphates
of non-labile pool. In addition some Fe and Al phosphates as
well as the organic soil P are also believed to exchange phosphate
ions only very slowly and thus belong to the non-labile P fraction.

5.2. Phosphorus Fixation and Release

5.2.1. Phosphorus Fixation Processes

    When a superphosphate granule is placed in the soil, water
initially moves into the granule and dissolves some of the
monocalcium phosphate into dicalcium phosphate and free phosphoric
acid. The solution coming out of the granule has a pH of 1 to 1.5.

It dissolves aluminium, iron, potassium, and magnesium compounds
in soil particles. In acid soils aluminium and iron are most
abundant and react with phosphorus to form relatively insoluble
aluminium and iron phosphates. In calcareous soils the phosphate
ions are precipitated by calcium and magnesium as relatively
insoluble compounds.

    In acid soils there is an additional fixation mechanism.
Exchangeable aluminium reacts with monocalcium phosphate and
forms compounds having the general formula $Al(OH)_2H_2PO_4$. They
resemble the crystalline form, variscite, but are more soluble.
An indirect effect of this mechanism is the precipitation of
exchangeable aluminium with phosphorus. According to the calcula-
tions of Coleman and his coworkers, I meq of exchangeable
aluminium can fix about 70 ppm P because aluminum is precipitated
in this fashion. This is often referred to as "liming with phos-
phorus".

The higher the content of iron and aluminium oxides, the larger is the phosphorus-fixing capacity of the soil. Also, the higher the exchangeable alumnum content, the larger the phosphorus-fixing capacity will be. Therefore highly acid and weathered Oxisols and Ultisols generally have high phosphorus fixation capacities, whereas less acid soils with layer **silicate** mineralogy have much lower ones. Because of the high contents of aluminum oxides, Andepts also have a very high fixing capacity.

In oxide or oxide-coated layer silicate systems, phosphorus fixation increases with increasing clay content. This is an indirect effect of the iron and aluminum oxide contents found in the clay fraction. Woodruff and Kamprath (1965) found that sandy Ultisols retained much less phosphorus than clayey Ultisols of similar mineralogy. In addition to the iron and aluminum oxide contents, the degree of crystallinity affects the magnitude of phosphorus fixation. Pratt et al. (1969) found that Brazilian Ultisols fixed more phosphorus per unit of iron oxide content than did Brazilian Oxisols. They associated this effect with the less crystalline iron oxide forms found in these Ultisols, in contrast to the more crystalline forms in the Oxisols. Because of their

larger surface area, amorphous oxides retain more phosphorus than crystalline species. However, since the iron oxide content is generally higher in Oxisols, as an order they probably fix more phosphorus than Ultisols. Among the amorphous materials Syers et al. (1971) found that amorphous aluminum compounds were more active fixers than amorphous iron oxides in Ultisols and Oxisols of southern Brazil.

The mineralogy of the soil defines the product of phosphorus fixation. In soils with oxidic mineralogy, most of the phosphorus will be fixed as iron phosphates. In kaolinitic families aluminum phosphates will be the predominant form, but with age they are transformed into iron phosphates.

The intensity of fixation according to mineralogy is as follows:

Amorphous oxides $>$ Crystalline oxides $>$ 1:1 clays $>$ 2:1 clays

(including   (gibbsite, goethite, etc.)
allophane)

5.2.2. Magnitude of phosphorus Fixation

Some idea of the maximum amounts of phosphorus that tropical soils can fix is given in Tables 5.3 and 5.4. As a group, Andepts and other soils high

Table 5.3. Amounts of Phosphorus Fixation and Amounts of Added Phosphorus Required to Give Soil Solution Concentrations to 0.1 and 0.2 ppm P in Soils from Mexico, Central America and Brazil.

Soil	Dominant Clay Mineral	Clay (%)	Fixed P (ppm)		
			Adsorption Maxima	At 0.1 ppm P Soil Solution	At 0.2 ppm P Soil Solution
Inceptisol	Montmorillonite	27	106	65	83
Ultisol	Kaolinite	38	480	285	360
Oxisol	Kaolinite	36	531	310	395
Oxisol	Kaolinite	78	-	720	900
Andept	Allophae	11	1050	500	670

Source Adapted from Rivera-House (1971) and North Carolina State University (1973).

in allophane are the highest fixers with over 1000 ppm added P. Kaolinitic soils, including Oxisols and Ultisols, follow with values ranging from 500 and 1000 ppm P except for coarse-textured ones. Soils high in montmorillonite and on the calcareous side may fix on the order of 100 ppm added P.

5.2.3. Phosphorus Release

Phosphate ions in the soil solution are what the plants actually use. The concentration of $H_2PO_4^-$ ions is on the order of a fraction of part per million. Plants accumulate in their tissue about 2000 ppm P. Therefore the soil solution must be renewed several times a day for the plants to create such a concentration gradient. Fixed phosphorus is released slowly to the soil solution as a function of the solubility of the species. Also, organic phosphorus mineralization adds $H_2PO_4^-$ ions to the soil solution, but most of them are fixed immediately.

Table 5.4. Phosphorus Fixation and Amount Needed to Maintain 0.2 ppm P in the Soil Solution on a "Weathering Transect" in Oahu, Hawaii

Soil	Annual Rainfall (mm)	Clay Minerals	pH	Fixed P (ppm) Adsorption Maxima	Fixed P (ppm) At 0.2 ppm P Soil Solution
Chromustert	500	Montmorillonite	7.6	300	85
Haplustox	600	Kaolinite	7.8	500	145
Haplustox	950	Kaolinite	6.8	525	145
Eutrorthox	1200	Kaolinite	5.1	725	235
Tropohumult	2200	Kaolinite, Gibbsite	4.4	670	335
Tropohumult	2300	Giibsite, Goethite	6.6	1320	435

Source: Fox et al. (1971).

It has been found that there is an optimum concentration of phosphorus in the soil solution associated with maximum crop growth in some species. Baldovinos and Thomas (1967) in Virginia and Fox et al . (1971, 1974) in Hawaii have shown that maximum bean and corn growth is associated with a level of 0.07 ppm P in the soil solution of clayey Ultisols, Oxisols, and Andepts. In sandy soils the optimum concentration is about 0.2 ppm P in the soil solution. This difference is probably due to the slower diffusion rate of soil solution in sandy soils because of discontinuous water films around the particles. Even at 15 bars, water films around clays can be continuous.

The relationship between the amount of inorganic phosphorus added to the soil and the equilibrium concentration of phosphorus in the soil solution is a good parameter for determining how much fertilizer phosphorus should be added to arrive at a desired level of soil solution phosphorus. These relationships, obtained in the laboratory by adding various amounts of phosphorus to the soil, shaking for 6 days, and determining how much remains in solution, are known as "phosphorus fixation isotherms" (Fox and Kamprath, 1979). Figure 5.3 shows examples of such relationships in several tropical soils. Phosphorus fixation isotherms evaluate the degree of fixation and release at one time. They are essentially intensity-capacity functions.

Figure 5.3 shows that a montmorillonitic soil fixes little added phosphorus and requires very little phosphorus in the soil to supply 0.1 ppm in solution. Clayey Oxisols and Ultisols need close to 3000 ppm added p to supply the same amount. The Andept, because of its high contents of amorphous aluminosilicates, needs about 450 ppm added P to reach that level. A very clayey Oxisol from Brazil requires over 700 ppm P to reach 0.1 ppm in the soil solution. Relatively little additional fertilizer phosphorus is required to raise the soil solution level to 0.2 ppm.

5.3. P uptake by Plants.

5.3.1. Absorption and translocation

Plant roots are capable of absorbing phosphate from solutions of very low phosphate concentrations (LONGERAGAN and ASHER 1967). Generally the phosphate content of root cells and xylem sap is about 100 to 1000 fold higher than that of the soil solution. This shows that phosphate is taken up by plant cells against a very steep concentration gradient. The uptake is active. The relationship between plant metabolism and phosphate uptake has been studied by a number of authors who have mainly observed increased rates of phosphate uptake associated with higher metabolic activity. Thus HAI and LAUDELOUT 1966 reported that an increased partial pressure of O_2 in the nutrient solution resulted in a higher phosphate uptake rate in rice roots. WEIGL 1967 also found that P uptake by Elodia canadensis was higher in
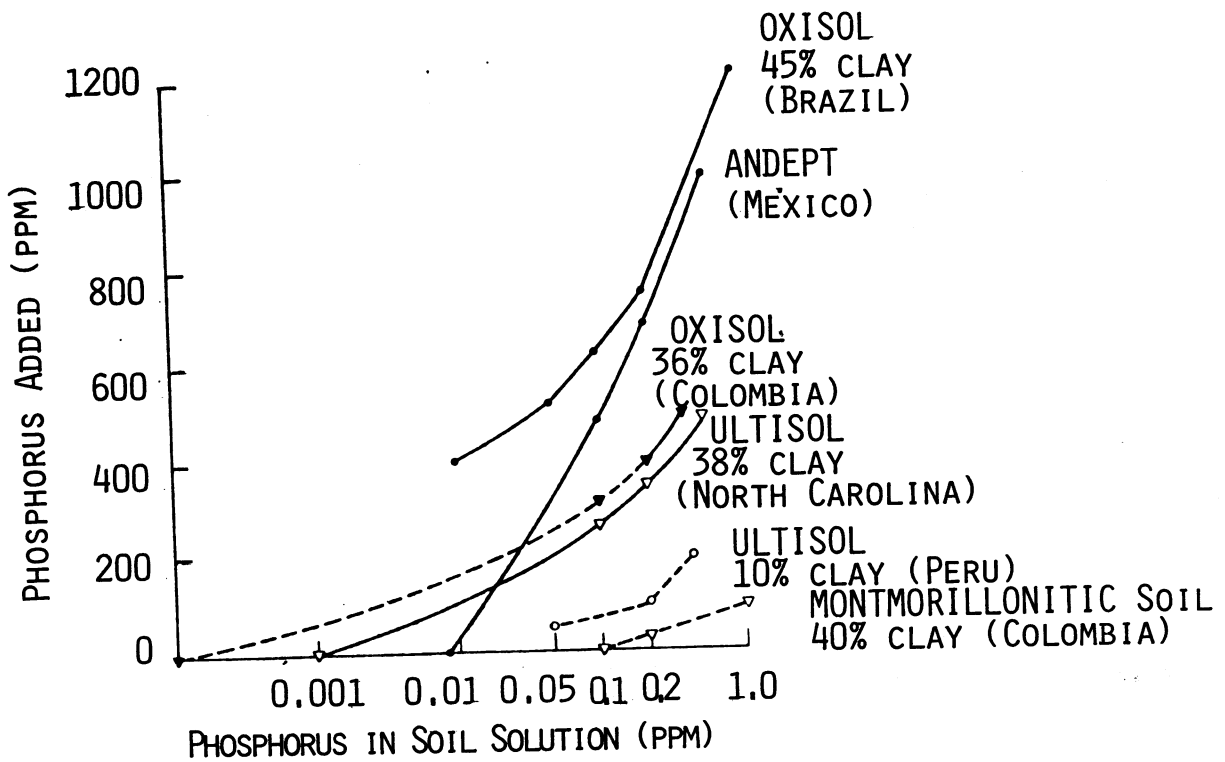
FIG. 5.3 EXAMPLES OF PHOSPHORUS FIXATION ISOTHERMS IN TROPICAL
SOILS. SOURCES: RIVERA-HOUSE (1971). NORTH CAROLINA
STATE UNIVERSITY (1973), AND FOX (1974).
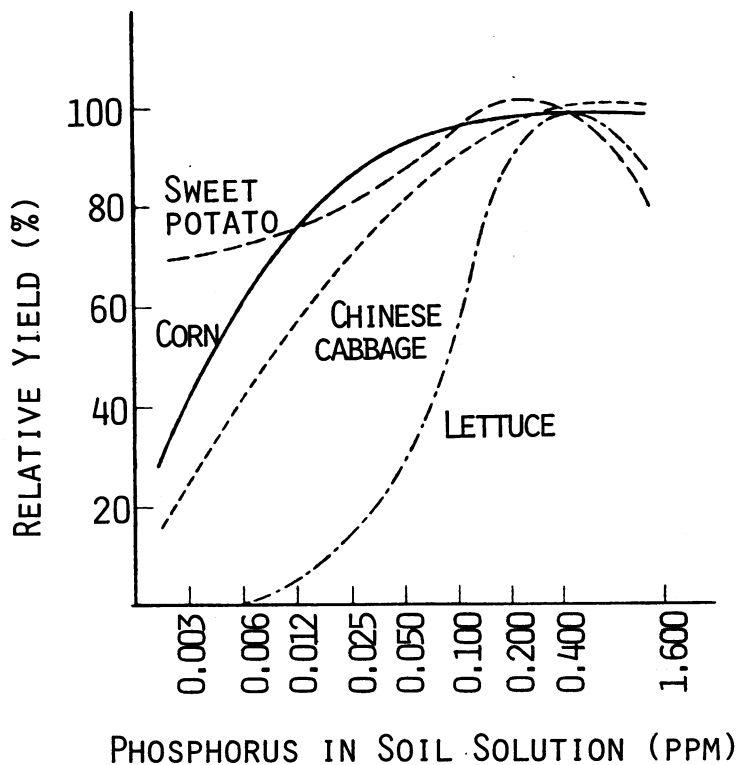
FIG. 5.4 DIFFERENTIAL PHOSPHORUS RESPONSE BETWEEN SWEET POTATO,
CORN, CHINESE CABBAGE, AND LETTUCE GROWN IN A EUTRUSTOX
OF HAWAII. SOURCE: FOX ET AL. (1974)

that respiratory carbohydrate metabolism drives the active phosphate uptake process. It is supposed that this uptake is carrier mediated. Whether one or more carrier systems are involved still remains in question. The capability for active uptake of phosphate differs between plant species and may even differ between cultivars of the same species. BARBER and THOMAS (1972) for example found considerable differences in the rate of phosphate uptake by various maize cultivars. The authors suppose that the capability of plants in take up phosphate is fixed genetically.

The rate of phosphate uptake is pH dependent. HENDRIX (1967) found that at pH4, bean plants absorbed phosphate at a 10 fold higher rate than at a pH of 8.7. Similar observations have been made by HAI and LAUDELOUT (1966) who reported a maximum uptake rate by rice roots at pH 5.6. The rate of phosphate uptake declined rapidly with increasing pH. As this decrease followed the shift in the $HPO_4^{2-}/H_2PO_4^-$ ratio in the nutrient solution, HAI and LAUDELOUT (1966), suppose that only $H_2PO_4^-$ is absorbed actively. It is doubtful whether organic P compounds are taken up by plant roots to any great extent. According to investigations by ROUX (1968) P present in polyphosphates was only taken up by young barley plants after hydrolysis to the orthophosphate form.

Phosphate absorbed by plant cells rapidly becomes involved in metabolic processes. Thus JACKSON and HAGEN (1960) reported that after a period of only 10 min, following uptake, 80% of the phosphate absorbed was incorporated into organic compounds. The organic phosphates formed in this short time consisted mainly of hexose phosphates and uridine diphosphate. Phosphate is readily mobile in the plant and can be translocated in an upward or downward direction. Thus CLARKSON et al. (1968) found that phosphate taken up by basal root segments of barley plants was translocated to the root tip as well as to the upper plant parts. Young leaves are supplied not only by phosphate taken up by the roots, but also with phosphate originating from the older leaves (BOUMA 1967).

5.3.2.   Phosphorus deficiency.

A reduction in synthesis of RNA as a result of inadequate P supply has an impact on protein synthesis. An accumulation of low molecular weight N compounds is thus often observed in P deficient tissues. In addition when protein synthesis is impaired, vegetative growth is also depressed. Thus plants suffereing from P deficiency are small with a limited root system and thin stems. In cereals tillering is affected. Fruit trees show reduced growth rates of new shoots , and frequently the development and the opening of buds is unsatisfactory. The formation of fruits and seeds is especially depressed in plants suffering from P deficiency. Thus not only low yields but also poor quality fruits and seeds are obtained from P deficient crops.

Generally the symptoms of P deficiency appear in the older leaves which are often of a darkish green colour. The stems of many annual plant species suffering from P deficiency are characterized by a reddish colouration originating from an enhanced formation of anthocyanins. The leaves of P deficient fruit trees are frequently tinged with brownish colour. Such leaves fall prematurely.

The P contents of P deficient plants are generally low with about 0.1% P or less in the dry matter. Cereals and herbage adequately supplied with phosphate have P contents of about 0.3 to 0.4%.P in the dry matter, during the vegetative growth stage. Generally the P content is higher in younger plants or plant organs. Thus the P content in mature straw of cereals is rather low (0.10 to 0.15% P in the dry matter), whereas in seeds and grains P contents in the range of 0.4 to 0.5% P in the dry matter are found. This example shows that during grain and seed formation a considerable amount of P is translocated from leaves and stems towards the seeds or grains. EATON and ERGLE (1957) reported that in mature cotton plants abour 80% of the total P of the plant is present in the seeds. The same is true for cereals.

Extremely high phosphate levels in the root medium can depress growth. In solution culture experiments for example LONERAGAN and ASHER (1967) found that very high uptake rates of phosphate were associated with reduced growth rates in some plant species (Erodium, clover, silver grass). Such effects may well be dependent on phosphate retarding the uptake and translocation of some of the micronutrients including Zn, Fe and Cu.

5.4. Phosphorus Requirements of Tropical Crops

5.4.1. Uptake

At present low yield levels of about 1 ton/ha, the phosphorus uptake of cereals and grain legumes is less than 10 kg P/ha. At high yield levels of 4 to 8 tons/ha, corn, rice and wheat remove from 14 to 35 kg P/ha.

Root crops are high extractors of phosphorus. At average yield levels of about 8 tons/ha, the phosphorus contents of cassava and potato tubers are on the order of 35 to 40 kg P/ha. When the tops are considered, and at higher yield levels, the phosphorus uptake is of course much higher. Possible exceptions are sweet potatoes and yams which have low phosphorus requirements.

Intensively managed pasture grasses and sugarcane may remove from 20 to 70 kg P/ha a year, depending on yield levels.

5.4.2. Varietal and Species Differences

Significant species differences in tolerating low available phosphorus exist. At similar yield levels, upland rice usually requires less phosphorus than corn. The general recommendation for these crops in Latin America ranges from 100 to 150 kg P_2O_5/ha for corn from 0 to 60 for upland rice (Kamprath, 1973).

The only form of phosphorus available to plants is the phosphate ions in the soil solution. A report by Fox et al. (1974) demonstrated that there is an optimum concentration of phosphorus in the soil solution correlated with good growth and that it varies with species. The results illustrated in Fig. 5.4 show that sweet potatoes (Ipomoea batatas) are more tolerant of low levels of soil solution phosphorus than is lettuce (Lactuca sativa), while corn (Zea mays) and Chinese cabbage (Brassica pekinensis) occupy intermediate positions.

If the phosphorus concentration in the soil solution that produces 95 percent of the maximum yield is considered to be the external phosphorus requirement, there are tremendous species differences. Table 5.5. indicates a tenfold difference in the external requirement between two similar vegetables, lettuce and cabbage. This table also indicates that the external requirement for a forage legume of the genus Desmodium is high during the establishment period (0.20 ppm P) but decreases to 0.01 ppm P after the second cutting. This information reflects the need for applying phosphorus to tropical legumes during the establishment period in soils low in this element.

Table 5.5 External Critical Phosphorus Levels of Several Tropical Crops

Crop	Soil Solution P Associated with 95% Maximum Yield (ppm)
Lettuce	0.40
Tomato	0.25
Cucumber	0.20
Soybean (vegetable	0.20
Desmodium aparines	
Establishment	0.20
Second cut	0.01
Sweet potato	0.10
75% maximum yield	0.003
Corn	0.60
Sorghum	0.50
Cabbage	0.04

Source: Fox et al. (1974).

The International Rice Research Institute in the Philippines is conducting a comprehensive program to select rice varieties tolerant of various soil problems, including low available soil phosphorus. Through preliminary greenhouse experiments at two rates of applied phosphorus (IRRI, 1971; Ponnamperuma and Castro, 1971), followed by field experiments at two rates of applied phosphorus (IRRI, 1972), the institute has classified a large group of varieties according to their tolerance of low soil phosphorus levels. Some examples are illustrated in Table 5.6. The classification by degree of tolerance is based on the relative response to phosphorus applications in the field.

An interesting point of this study is the possible selection of varieties not only for phosphorus tolerance but also for tolerance of other soil problems, such as iron deficiency or toxicity and the presence of toxic soil reduction products. The varieties with more ample spectra of resistance to adverse soil conditions are IR24, CAS209, and BG79. The varieties Pelita I/1 and Pelita I02 are considered genetic sources for tolerance to low phosphorus levels.

Table 5.6. Classification of Rice Varieties According to Low Phosphorus Tolerance in an Ultisol from Luisiana, Philippines

Tolerant	Moderately Tolerant	Moderately Sensitive	Sensitive
IR4-11	IR5	IR442-2-58	IR579-48-1
Bahagia	IR8	IR1008-14-1	IR747B-26-3
BG 79	IR20	IR1154-233-2	IR878B-4-220
CAS 209	IR22	Taichung (N) 1	Bala
Engkatol	IR24	TKM6	C 22
Pelita I/1	IR661-1-70		Colombia 1
Pelita I/2	IR1154-68-2		CP231xSL017
RD 1	CICA 4		ICA 10
SR 26 B	Peta		M1-48
	T442-35		M1-273
			OS 4
			SML Acorni

Source: IRRI (1972).

Pelita I02 are considered genetic sources for tolerance to low phosphorus levels.

In many acid soils it is difficult to separate the effects of high aluminium saturation from those of low phosphorus availability. Alminium tolerance has been related to the plant's ability to absorb and translocate phosphorus in the presence of aluminium. Evidence of this was supplied by Andrew and Vanden Berg (1973). Figure 5.5. shows that increasing aluminum levels in solution decreased the top growth of the two aluminum-sensitive species, Glycine wightii and alfalfa, but did not have much effect on the two tolerant genera, Stylosanthes and Desmodium. Increasing the aluminum concentration increased the phosphorus uptake of three species, but not alfalfa. The phosphorus taken up, however, was not translocated to the tops at equal rates. The translocation rate of Stylosanthes and Desmodium was about twice as fast as that of Glycine wightii and alfalfa.

5.5. Management of Phosphorus Fertilizers

5.5.1. Rates

Phosphorus responses are common in Oxisols, Ultisols, Andepts, and Vertisols. In tropical America the generally recommended rates for corn, soybeans, forages, and sugarcane are on the order of 100 to 150 kg P_2O_5/ha, usually in banded applications. The recommended rates for potatoes and wheat are on the order of 120 to 240 kg P_2O_5/ha, but for upland rice only from 0 to 60 kg P_2O_5/ha is recommended (Kamprath, 1973). In tropical Africa, where the research has been conducted at lower application rates and lower yield levels, FAO simple fertilizer trials show good crop response to rates of 20 kg P_2O_5/ha Richardson, 1968).

Phosphorus management in soils with moderate fixation capacity is usually a simple proposition. Small annual rates of superphosphate can be broadcast and incorporated into the topsoil or banded once a year.

5.5.2. Massive Initial Applications versus Moderate Banded Applications.

In soils with high phosphorus fixation capacity two strategies of phosphorus fertilization are presently in use. One is to apply moderate rates placed in bands to every crop. The other is to apply phosphorus at a rate large enough to saturate the fixation capacity of the soil at once and to count on an adequate release for many years. The high initial oost is then considered an investment that can be amortized in several years with the residual effects.

An example of this approach is illustrated by the work of Younge and Plucknett (1966) in Hawaii. They applied rates of 330 to 1320 kg P/ha to a Gibbsihumox and measured the residual effect to a grass-legume pasture for several years. After 12 years these massive applications continued to maintain forage yields, as shown in Fig. 5.6. During the first 3 years yield responses were obtained only at the lowest rate, 300 kg P/ha. With time, maximum yields were obtained at progressively higher rates, but during the first 9 years the highest yields did not vary.

In another high-fixing soil, an Ultisol from North Carolina, Kamprath (1967) studied the residual effect of massive initial applications versus small annual maintenance rates applied in bands. The corn yields obtained during the seventh year are shown in Table 5.7. The results show that small annual banded applications are superior to a high initial investment. An initial rate of 337 kg P/ha gave results similar to those obtained with an annual rate of 22 kg P/ha (as a total of 154 kg P/ha) in 7 years. This Ultisol, however, fixed less phosphorus than the Hawaiian Oxisol of Fig. 5.6. The Georgevill series of North Carolina needed 360 ppm P to provide 0.2 ppm to the soil solution, whereas the Kapaa series of Hawaii required 1000 ppm P to provide the same soil solution level.
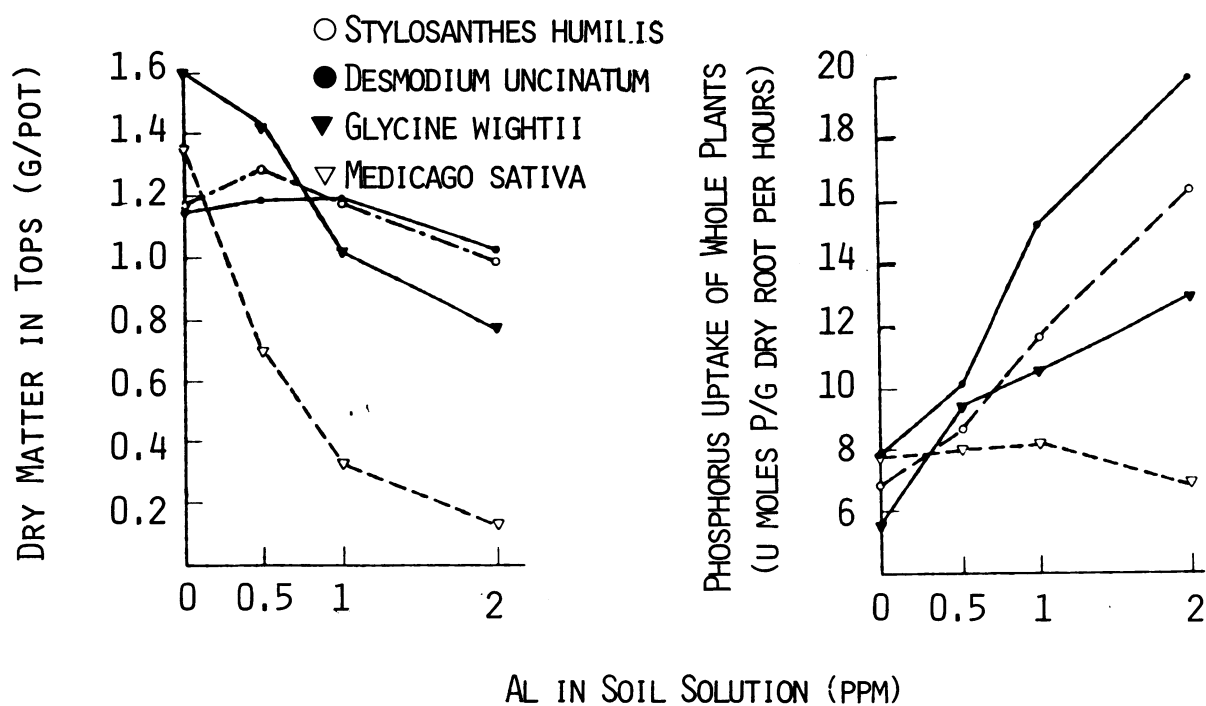
FIG. 5.5. EFFECTS OF ALUMINIUM ON GROWTH AND PHOSPHORUS UPTAKE OF FOUR PASTURE LEGUMES.

SOURCE: ADAPTED FROM ANDREW AND VANDEN BERG (1973)
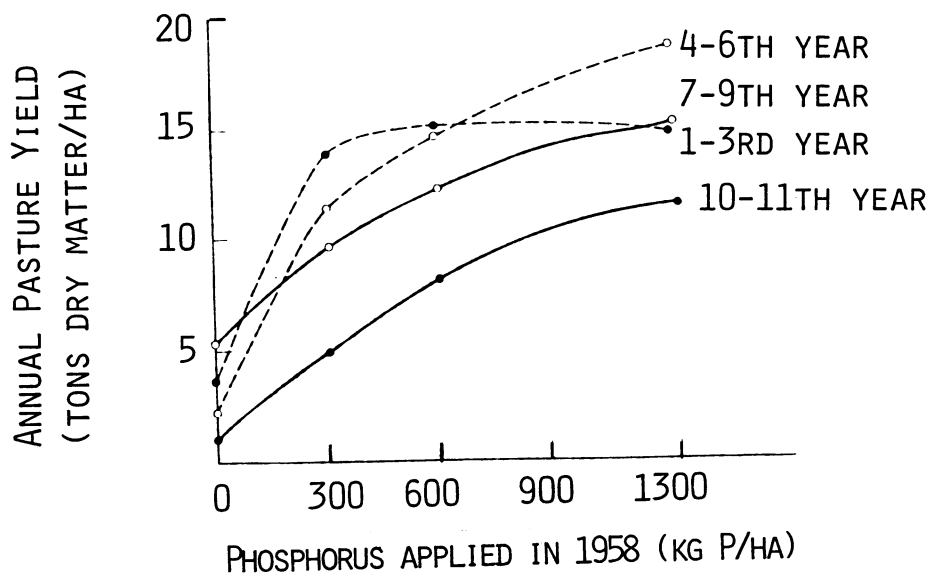
FIG. 5.6. RESIDUAL EFFECTS OF MASSIVE PHOSPHORUS APPLICATIONS TO A HAWAIIAN OXISOL ON GRASS LEGUME PASTURE YIELDS. SOURCE: ADAPTED FROM FOX ET AL. (1971).

Applying phosphorus fertilizers in bands is a simple
practice that satisfies the phosphorus fixation capacity of
a small soil volume and this makes much of the fertilizer
applied directly available to plants. The effectiveness of
banding depends on other soil factors.

Table 5.7. Effects of Massive Initial Phosphorus Application
versus Small Annual Maintenance Rates on Corn
Yields in a North Carolina Ultisol with High
Phosphorus Fixation Capacity 7 Years after the
Initial Application

| Initial Application (kg P/ha) | Yield (tons/ha) | |
| | Annual Maintenance Applications (banded) | |
	None	22 kg P/ha
0	1.7	5.7
168	3.9	6.2
337	5.5	6.8
673	7.0	7.1

Source: Kamprath (1967)

a $LSD_{0.05}$ = 1.3 tons/ha.

6.5.3. Sources of Phosphorus

Research in the temperate region indicates that phosphorus fertilizers
should have at least 40 to 50 percent P in water-soluble form
to insure an adequate supply at early growth stages (Englestad, 1972).
Ordinary and triple superphosphates and monoammonium and
diammonium phosphates meet this requirement and can be used
effectively in soils with low to moderate fixation capacities.

In acid soils that fix large quantities of phosphorus,
applications of less soluble phosphorus sources such as rock
phosphates may be more effective and economical than the highly
soluble forms. Rock phosphates are more reactive in acid soils
and usually cost one-third to one-fifth as much as superphosphate
per unit of phosphorus.
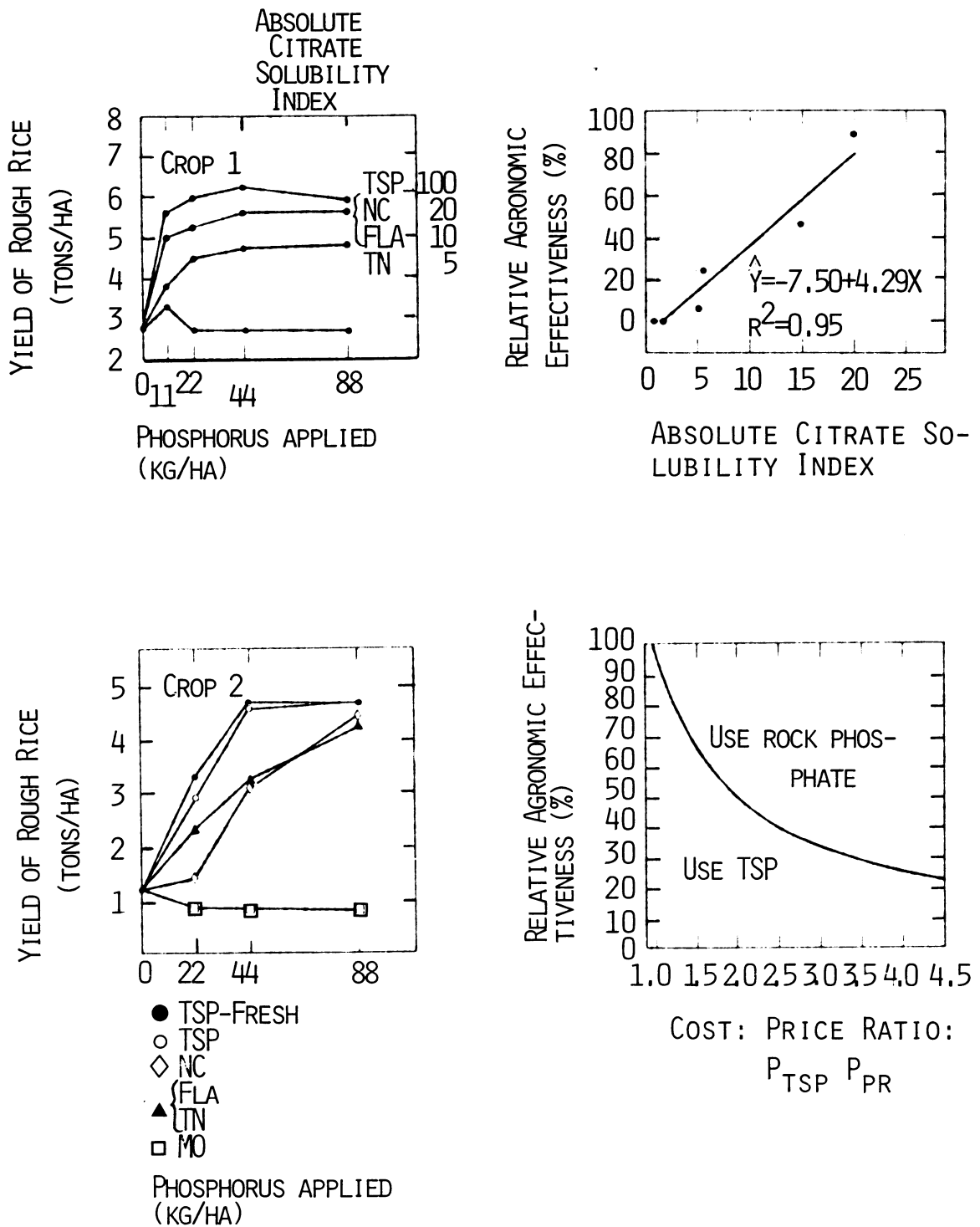
FIG. 5.7. EFFICIENCIES OF ROCK PHOSPHATE SOURCES OF DIFFERENT CITRATE SOLUBILITIES ON THE YIELD RESPONSES OF TWO FLOODED RICE CROPS IN AN ACID SULFATE SOIL OF KLONG LUANG, THAILAND, AND THE RELATIONSHIP BETWEEN ABSOLUTE CITRATE SOLUBILITY, RELATIVE AGRONOMIC EFFECTIVENESS, AND PRICE RATIO.

SOURCE: ENGLESTAD ET AL. (1974). TSP = TRIPLE SUPERPHOSPHATE. ROCK PHOSPHATES: NC = NORTH CARONILNA; FLA = FLORIDA; TN = TENNESSEE; MO = MISSOURI.

The tropical literature is full of examples that indicate the desirability of using high quality rock phosphate sources instead of superphosphates in acid soils (Motsara and Datta, 1971; Awan et al., 1971; Englestad, 1972) and the poor performance of low-citrate-solubility rock phosphate sources in acid soils (Alvarez et al. 1965; Viegas et al. 1970; Miranda et al. 1970).

The effects of rock phosphates of varying citrate solubility on flooded rice yields in an acid sulfate soil from Thailand are illustrated in Fig. 5.7. The initial and residual effects of the rock phosphates were highly dependent on their absolute citrate solubilities. The yield responses of the North Carolina and Florida rocks approximated those of triple super-phosphate. The results were then interpreted in terms of the relative agronomic effectiveness, which is the ratio of the yield response with rock phosphate divided by the yield response with triple superphosphate. The economic choice of using rock phosphate or superphosphate can be made by using the bottom right diagram of Fig. 5.7., in which the relative agronomic effectiveness is plotted against the cost: price ratios of the sources.

In the tropics high-citrate solubility deposits are limited to relatively small areas in Peru and India. The majority of the deposits in most tropical areas, including significant ones in Brazil, Columbia, Venezuela, Togo, and India, have relative solubilites lower than 40 percent. Most are unsuitable for direct applications, but their reactivity can be increased by fine grinding or by thermal alteration and fusion with silica sand, sodium, or magnesium carbonates.

An additional strategy, sometime feasible for managing soils with P fixation capacities, is to reduce their fixation through amendments that will block some of the fixing sites in the soil. This can be accomplished in some soils through liming or silicate additions.

Liming soils to pH 5.5. generally increases the availability of phosphorus. Liming precipates the exchangeable aluminum and some hydroxy aluminum as aluminum hydroxides, which fix

considerably less phosphorus. The top half of Fig. 5.8. shows
the decrease in phosphorus fixation when an Oxisol from Panama
was limed to pH 5.5. In this case less than half the phosphorus
application rate was needed in the limed·soil to approach
maximum yields in relation to the unlimed soil, as illustrated
in the bottom half of Fig. 5.8.

Silicon applications,usually as calcium silicate,
sodium silicate, or basic slag, are known to decrease phosphorus
fixation and increase phosphorus uptake by crops. For example
Roy et al. (1971) found that application of 500 ppm Si as calcium
metasilicate dramatically decreased the phosphorus fixed by
several oxidic soils (Table 5.8). The decrease was greater in
the soils that had lower phosphorus fixation capacities,
the Tropohumult and the Euthrorthox.

Table 5.8. Effects of Calcium Silicate Applications on
            Phosphorus Fixation in Hawaiian Soils (expressed as
            ppm P fixed to give 0.2 ppm P in soil solution

Soil	Si Added (ppm)		Decrease (%)
	0	500	
Tropohumult	187	100	47
Euthrorthox	425	250	41
Gibbsihumox	725	550	24
Hydrandept	1150	1050	9

Source: Roy et al. (1971).

Phosphorus management of acid tropical soils with very
high fixation capacities should include the following possibilites:
(1) a combination of banding and broadcast applications,
(2) the use of citrate-soluble rock phosphates or thermally altered
    rock phosphates with initially low citrate solubilities,
(3) decreasing the fixing capacity by liming or silicate applications
 and (4) the use of species and varieties tolerant to low levels
of available soil phosphorus. Economic considerations, such as
the relative costs of heavy initial broadcast and of banded
applications and the relative costs of the different sources of
fertilizer phosphorus, will largely dictate the best alternatives.
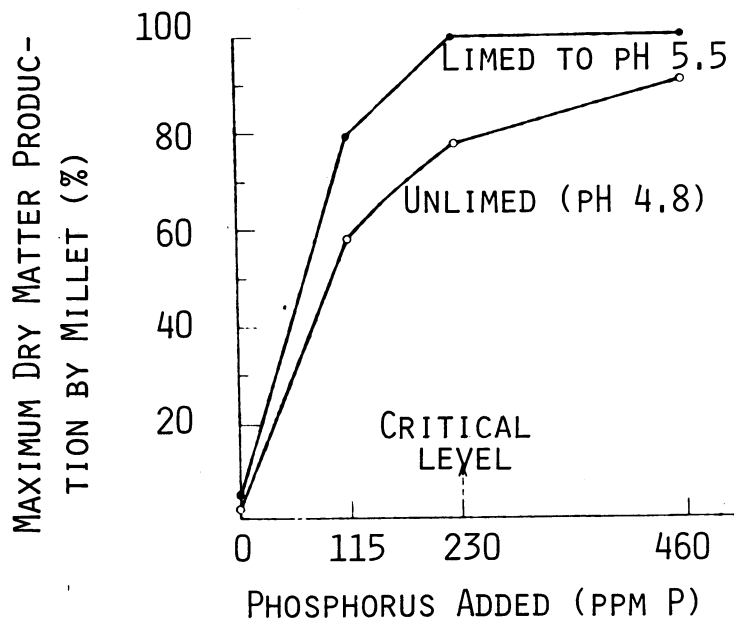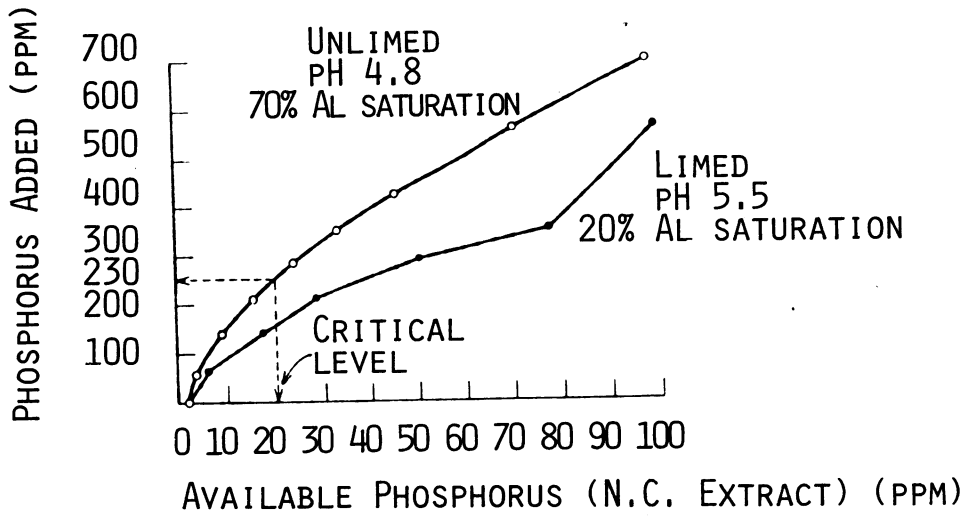
FIG. 5.8 EFFECTS OF LIMING ON PHOSPHORUS FIXATION AND
RESPONSE IN AN OXISOL FROM PANAMA.

SOURCE: ADAPTED FROM MENDEZ-LAY (1973).

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Potassium in soils and its availability to Plants.

6.1. Soil Potassium.

6.1.1. Potassium minerals and potassium release

The average K content of the earth's crust is in the order of about 2.3%. By far the greatest part of this K is bound in parimary minerals or is present in the secondary clay minerals which largely make up the clay fraction of the soil of particle size less than 2 μ . For this reason soils rich in clay are also generally rich in K (ACQUAVE et al. (1967)) and clay soils may often have in excess of 4% total K. The clay content of a soil is to some extent dependent on the soil parent material, but is also considerably affected by pedogenesis. Mature soils which have been subjected to strong weathering conditions are often low both in clay and K contents.

The main source of K for plants growing under natural conditions comes from the weahtering of K containing minerals. The most important of these minerals are listed in Table 6.1. In the potash feldspars, K is located in the interstices of the Si, Al-O framework of the crystal lattice and held tightly by covalent bonds (Rich 1968). The weathering of feldspars begins at the surface of the particle. Potassium is initially released by water and weak acids at a more rapid rate than other constituents. As weathering progresses, however, a Si-Al-O residue envelope is formed around the unweathered cored. This layer reduces the rate of loss of K from the mineral and thus protects it from further intensive degradation (RICH 1972). Minerals of the mica type and also the secondary minerals of the 2:1 layer silicates differ fundamentally in structure from the feldspars. For this reason they also differ in their properties of releasing and binding K+. The micas consist of unit layers each composed of two Si, Al-O tetrahedral sheets between which is an M-O, OH octahedral sheet where M is usually an AL^{3+}, Fe^{2+}, Fe^{3+}, or Mg^{2+}. Potassium ions occupy the approximately hexagonal spaces between the unit layers (see Figure 6.1).

Table 6.1. Potassium content of some primary and secondary clay
minerals (SCHEFFER and SCHACHTSCHABEL 1976).

	content in % K_2O
Alkali feldspars............	4-15
Ca-Na feldspars.............	0- 3
Muscovite (K mica)	7-11
Biotite (Mg mica)..........	6-10
Illite..................	4-7
Vermiculite	0-2
Chlorite	0-1
Montmorillonite...........	0-0.5

The rate of K^+ release by weathering not only depends
on the K content of a particular mineral. It is also affected
by even slight structural differences between minerals. Thus
biotite a ferromagnesian mineral although generally lower in
K content than muscovite, releases K at a faster rate because
it is weathered more rapidly. The same is true for Ca
feldspars which are degraded at a higher rate than K feldspars
(DUTHION 1966). According to RICH 1968 illite and other
2:1 minerals which contain mica like zones are the most important
sources of K in soils.

6.1.2. Potassium fixation

As the depletion of K from the interlayers of mineral
continues, the rate of release becomes progressively slower.
Interlayer sites become depleted of K^+ although they still
retain a very high K^+ selectivity with respect to divalent ions
(RAMAN and JACKSON 1964): Additions of K^+ to such minerals
results in a strong K adsorption to these positions causing a
contraction of the mineral (GRAHAM and LOPEZ 1969). This process
is called K fixation. The contraction results in a reduction in
the unit distance to about 1 nm. Zones of vermiculite structure
in weathered biotite and muscovite characterized by a 1.4 nm
layer distance thus regain the 1 nm spacing of mica when treated
with K^+ (see Figure 6.1).

The degree to which K fixation occurs depends on a number of factors including the charge density of the mineral, the extent of the wedge zone, the moisture content, the concentration of K and the nature and concentration of competing cations in the surrounding medium. Fixation tends to be high when the negative charge per unit silicate layer (= charge density) is high. When this occurs the positive K^+ ion is very strongly held by the negatively charged layers. If the wedge zone is confined to the edge of the particle only small amounts of K^+ can be fixed. However, if the zone penetrates deeply into the mineral, considerable amounts of K^+ can be withheld. Some minerals such as weathered micas, vermiculites and illites fix K^+ under both moist and dry conditions, whereas montmorillonites only fix K^+ under dry conditions. For this reason fixation is frequently high under dry than moist soil conditions (SCHROEDER 1955). As the NH_4^+ is very similar to K^+ in ionic radius, this too can be fixed by expanded 2:1 clay minerals (BARTLETT and SIMPSON 1967). Ammonium can also exchange for fixed K^+. The same holds true for H^+ (RICH and BLACK 1964). Thus both ion species, NH_4^+ and H^+, can compete with K^+ for K fixing binding sites. This means that K fixation is generally not so important in restricting K availability to plants on acid soils (pH 4.5) as on limed agricultural soils.

Potassium fixation is of considerable importance in agricultural practice. The quantities of fertilizer K rendered unavailable in this way can be very high. Generally the K fixation capacity is higher in the deeper soil layers because of the greater clay contents. Thus ARIFIN et al. (1973) found K fixation levels as high as 1000 to 2000 mg K/100 clay in the B horizon of important agricultural soils in the southern region of USA.

6.1.3. Potassium adsorption and mobility

Soil clay content is not only of important for K release and fixation, it also consideraly influences the mobility of K^+ in the soil. Potassium ions are adsorbed by clay minerals to binding sites which differ in selectivity. For the 2:1 clay minerals such as illites, vermiculites and weathered micas
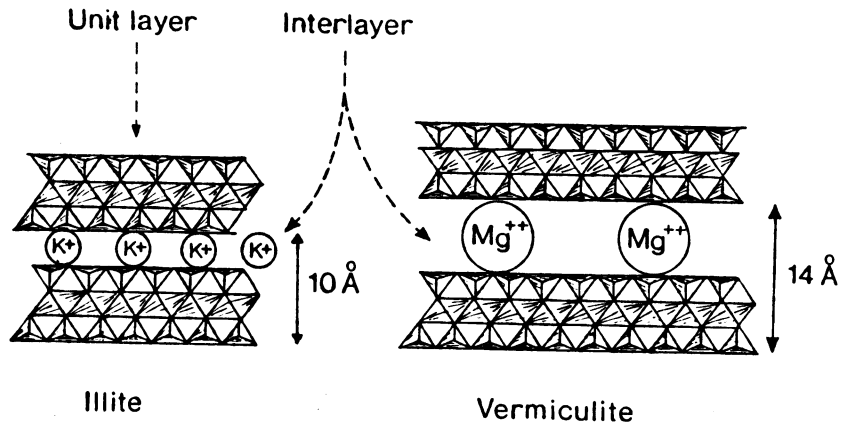
FIG. 6.1. UNIT LAYER AND INTERLAYER OF ILLITE AND VERMICULITE (Mengel and Kirkby 1982)
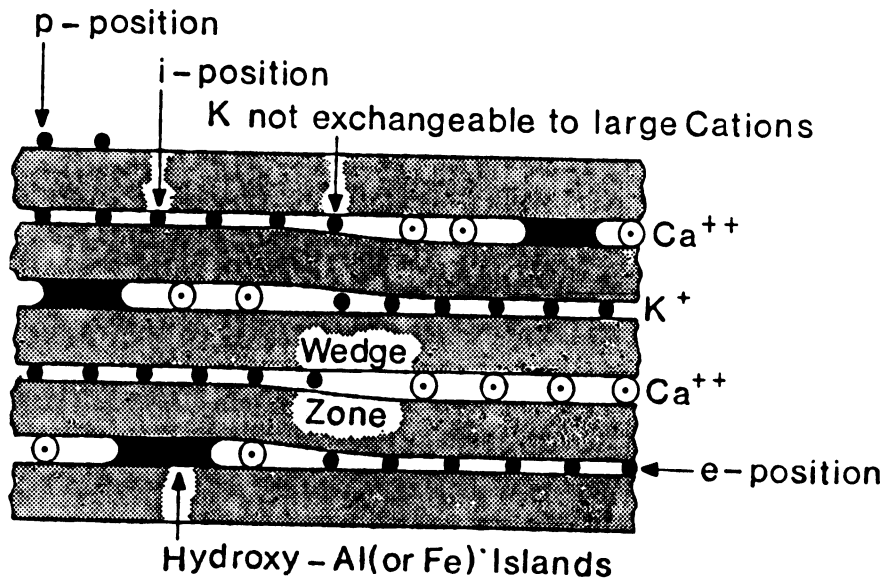
FIG. 6.2. MODEL OF AN EXPANDIBLE LAYER SILICATE WITH INTERLAYERS, WEDGE ZONE, P-, E- AND I-POSITIONS (AFTER RICH (1968))

3 different adsorption sites can be distinguished (Figure 6.2). These are as follows: sites at the planar surfaces (p-position), sites at the edges of the layers (e-position) and sites in interlayer space (i-position). The specificity of these three binding sites for K^+ differs considerably (BECKETT and NAFADY 1967).

It is clear that the behaviour of K^+ in the soil is very much dependent on the clay content and types of clay minerals present. Potassium mobility and diffusion rates are generally low in soils rich in K^+ specific binding sites. The same is true for K leaching. Under temperate climatic conditions this amounts only to about 8 kg K/ha/yr COPPENET (1969). On organic soils and sandy soils K leaching rates may be considerably higher GISKIN and MAJDAN 1969). Potassium application on these soils more prone to leaching should therefore be carried out in spring rather than in autumn, in order to prevent major K loss by winter leaching. Soils rich in clay minerals of the kaolinite type are poor in K specific binding sites. Such soils occur extensively in tropical regions. Problems associated with the inherently low K status of these soils are exacerbated by the excessive leaching resulting from the high tropical rainfall conditions.

6.1.4. Potassium fractions.

Soil potassium can be divided in 3 fractions: Potassium as a structural element in soil minerals, K adsorbed in exchangeable form to soil colloids such as clay minerals and organic matter, and K present in the soil solution. In mineral soils most K occurs in the lattices of minerals and according to SCHEFFER et al. (1960) only 1 to 3% of the total K is present in adsorbed (exchangeable) form. Potassium in the soil solution makes up only a small percentage of the exchangeable fraction. The significance of these three fractions for the availability of K to plant roots, however is in the reverse order of their amounts in the soil, the K in soil solution being by far the most important for plant supply (GRIMME et al. (1971).

The main relationships between the three fractions are shown in Figure 6.3. Potassium released by weathering of minerals is dissolved in the soil solution. It can then be taken up directly by plant roots or be adsorbed by soil colloids. An equilibrium is thus set up between adsorbed K and the free K in soil solution. The K level in the soil solution resulting from this equilibrium depends much on the selectivity of the adsorption sites. If these are specific for K^+ ions, the concentration of K^+ in the soil solution tends to be low (REZK and AMER 1969). If the binding sites are less specific for K^+, the K concentration in the soil soltuion is generally higher (NEMETH et al. (1970). The K concentration of the soil solution very largely controls the K diffusion rate towards the plant roots and therefore also the uptake of K^+ by plants (MENGEL and VON BRAUNSCHWEIG 1972). Besides the K concentration of the soil solution, the K buffer capacity of the soil is a further important factor in determining K availability. Potassium buffer capacity and its significance has been considered under intensity and quantity relationship. It need only be mentioned here that if the soil is highly buffered for K, fluctuations of the K level in the soil solution are small, whereas in soils with a low K buffer capacity, the K concentration level may decrease substantially during the growing season (NEMETH 1975).

Potassium is taken up by plants from the soil solution which in turn is mainly replenished by the exchangeable fraction (adsorbed K^+) (see Figure 6.3). In addition, some K of the so-called "non-exchangeable K fraction" is also released from minerals into the soil solution and may thus be taken up by plants (BLANCHET and BOSC (1967): The results of GRIMME (1974) show that when the relative contribution of non-exchangeable K to plant supply is high, yield levels tend to be depressed. This relationship is shown in Figure 6.4. Similar results have been reported by VON BOGULAWSKI and LACH 1971. This effect may be explained by the fact that only under conditions of low levels of K in the soil solution are substantial amounts of K released from the non-exchangeable fraction.
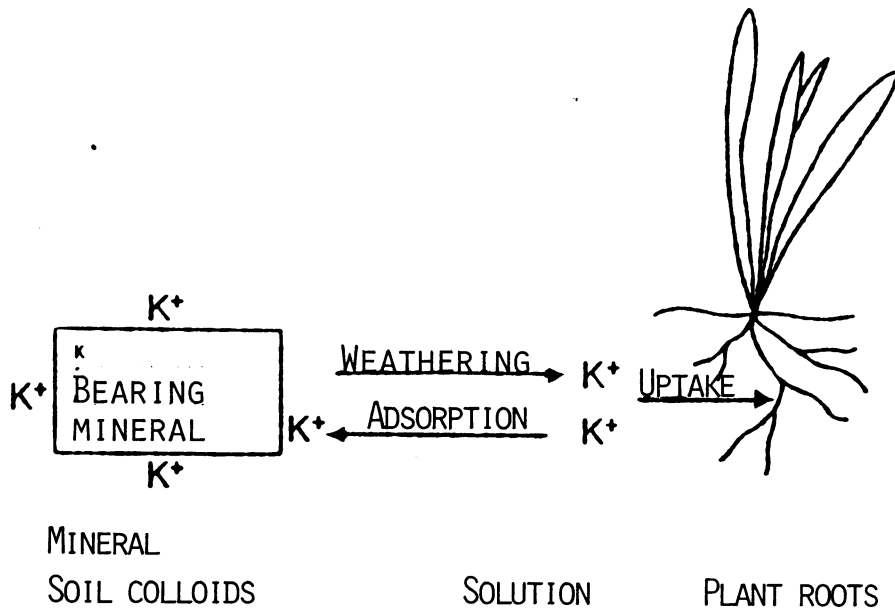
FIG. 5.3. POTASSIUM RELATIONSHIPS IN THE SOIL BET-
WEEN SOIL MINERALS AND PLANT ROOTS
(Mengel and Kirkby, 1982)

$R = -0.86$
$Y = 95 - 0.45$

UPTAKE OF NON-EXCH. K
(PER CENT OF TOTAL K-UPTAKE)
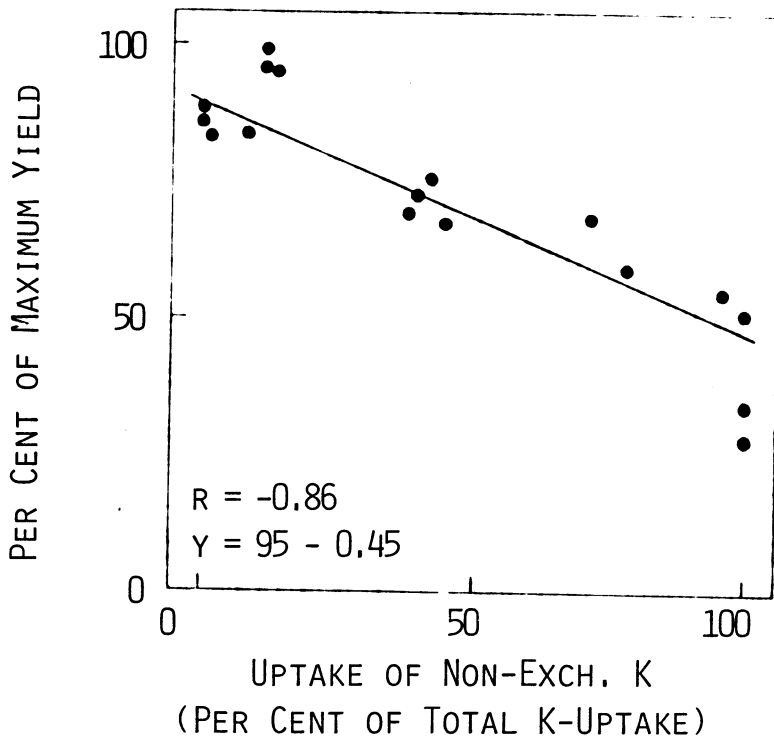
FIG. 6.4. RELATIONSHIP BETWEEN YIELD AND THE PERCENTAGE
OF K TAKEN UP FROM NON EXCHANGEABLE SOURCES
(AFTER GRIMME (1974))

6.2. Uptake and translocation

Potassium is an essential element for all living organisms. In plant physiology it is the most important cation not only in regard to its content in plant tissues but also with respect to its physiological and biochemical functions. One main feature of K^+ is the high rate at which it is taken up by plant tissues. This high uptake rate depends on an active uptake mechanism and there is evidence that of all the essential mineral cation species, K^+ is the only one which can be transported against an electrochemical gradient into plant cells. ANSARI and BOWLING (1972). Potassium in the plant is very mobile. Its main transport direction is towards the meristematic tissues. Often K^+ from older plant organs is redistributed to younger tissues.

6.3. Functions in plants.

1. The reason why K^+ is preferentially transported to young tissues is not yet known, but relationships to protein synthesis, growth rate, and supply of cytokinins have been postulated (JACOBY et al. 1973). The uptake and transport of K^+ to younger leaves is thus favoured in plants well supplied with N. PITMAN (1972) has reported that plants, in which the rate of growth is depressed, take up lower amounts of K^+ and their ability to translocate K^+ to the shoots is especially impaired. Protein synthesis and growth rate are stimulated to cytokinins, which also enhance K^+ uptake (ILAN 1971). The bulk of K^+ is mainly taken up during the vegetative growth stage. For cereals this means that in the period from tillering to ear emergence, the rate of K uptake is particularly high. Under Normal metabolic conditions hardly any net loss of K occurs from root tissue (JOHANSEN et al. 1970).

2. The high uptake rate of K into the plant results in K accumulation in cells of various tissues, even when the nutrient solution is relatively low in K^+ concentration. Potassium accumulation in the xylem depresses the osmotic potential of the zylem sap (lowers the water potential) and for

this reason it enhances both the uptake of water and root pressure (BAKER and WEATHERLEY 1969), MENGEL and PFLÜGER 1969. High K concentrations in the mesophyll cells decrease their osmotic potential in a similar way. This again has a beneficial effect on water consumption, as the lower osmotic potential improves water retention. This is apparently one reason why plants well supplied with K require relatively lower amounts of water in relation to the synthesis of organic material. (LINSER and HERWIG 1968.)

3. The lower water loss of plants well supplied with K is due to a reduction in transpiration rate (BRAG 1972) which not only depends on the osmotic potential of the mesophyll cells but is also controlled to a large extent by the opening and closing of stomata. Investigations of FISHER AND HSIAO (1968) have revealed that K plays a significant role in stomatal opening and closing. Convincing evidence for this relationship has been provided by electron probe analysis studies of Humble and Raschke (1971). They found that K content of guard cells in the open state is considerably higher than that in the guard cells from closed stomata. Potassium is therefore accumulated in the guard cells in considerable concentrations and the resulting turger causes the opening of the stomata.

4. A number of authors have shown that K^+ enhances the translocation of assimilates HAEDER and MENGEL (1972), ASHLEY and GOODSON (1972). Table 6.2. from the results of HARTT (1969) demonstrates this effect in the translocation of labelled photosynthates in sugar cane. As K^+ also promotes the rate of CO_2 assimilation COOPER et al. (1967), it may not appear that the beneficial effect of K^+ on the translocation of photosynthates is an indirect one resulting from a higher rate of CO_2 assimilartion. Under conditions where the rate of CO_2 assimilation has been controlled, however, higher levels of K nutrition have also resulted in an increased translocation rate of photosynthates, MENGEL and VIRO (1974). The effect of K^+ on the translocation of photosynthates therefore appears to be a direct one and most likely relates to photophosphorylation

When the K^+ level in the plant is high there is probably a stimulation in the production of ATP, which is needed in the loading of sieve tubes with photosynthates.

Table 6.2. Translocation of C-14 labelled photosynthates in sugar cane with a low and high K supply (total label = 100%) (HARTT (1969)

	% of total label	
	+ K	-K
Fed blade..	54.3	95.4
Sheath of fed leaf	14.2	3.9
Joint of fed leaf	9.7	0.6
Leaves and joints above fed leaf	1.9	0.1
Stalk below joint of fed leaf	20.1	0.04

5. The main function of K in biochemistry is its activation of various enzyme systems (EVANS and SORGER 1966). More than 60 different enzymes are now known which require univalent cations for activity. (EVANS AND WILDES (1971). In most cases the K^+ ion is the most efficient cation in effecting this activation. Figure 6.5 shows a typical example of an enzyme activated by univalent cations. The enzyme, a starch synthetase from sweet corn, was most strongly activated by K^+, followed by Rb^+, Cs^+, and NH_4^+. The activation by Na^+ was very poor and Li^+ had hardly any effect.

6. Potassium not only influences crop production by enhancing growth and synthetic processes. It is also highly important in raising the disease resistance of many crop species. In maize for example stalk rot and lodging are usually more severe when soil K is low in relation to other nutrients (HOOKER (1966). This beneficial effect of K in preventing lodging is also true for other cereal crops (TROLLDENIER (1969).
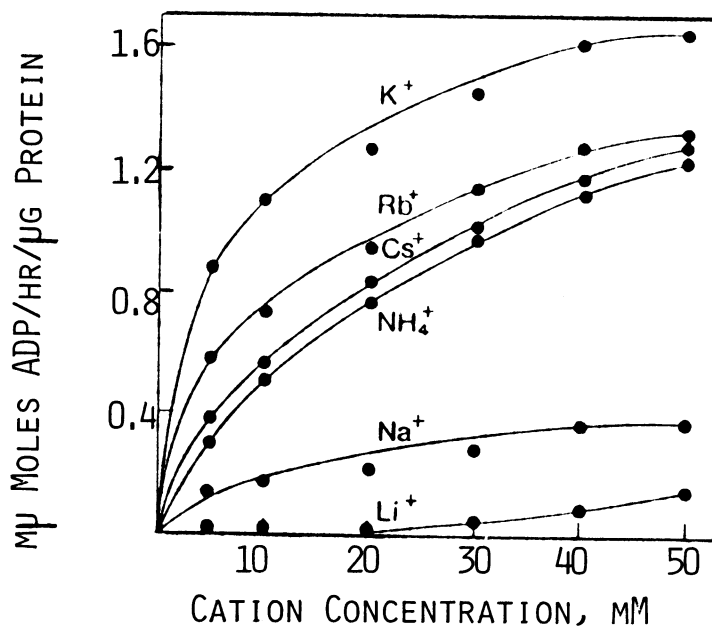
FIG. 6.5. EFFECT OF UNIVALENT CATION SPECIES
ON THE ACTIVITY OF STARCH SYNTHETASE
ISOLATED FROM SWEET CORN (AFTER NIT-
SOS AND EVANS (1969))

6.4. Potassium deficiency

Potassium deficiency does not immediately result in visible symptoms. At first there is only a reduction in growth rate (hidden hunger), and only later do chlorosis and necrosis occur. These symptoms generally begin in the older leaves, due to the fact that these leaves supply the younger ones with K^+. According to investigations of PISSAREK (1973) with rape and of MORARD (1973) with sorghum, K deficiency symptoms are first seen in the 2nd and 3rd oldest leaf and not in the oldest ones. In most plant species chlorosis and necrosis begins in the margins and tips of the leaves (maize, cereals, fruit trees), but in some species such as clover irregularly distributed necrotic spots occur on the leaves.

Plants suffering from K deficiency show a decrease in turgor, and under water stress they easily become flaccid. Resistance to drought is therefore poor (PISSAREK (1973) and the affected plants show increase susceptibility to frost damage, fungal attack and saline conditions.

Plants suffering severely from K deficiency often show an abnormal development of tissues and cell organelles. According to PISSAREK(1973) inadequate K supply resulted in a reduced growth rate of the cambium in stems of rape (Brassica napus). The formation of xylem and phloem tissue was restricted whereas the cortical tissue was affected only to a minor extent. Lignification of the vascular bundles is generally impaired by K deficiency. This effect probably makes K deficient crops more prone to lodging. K deficiency also results in a collapse of chloroplasts (PISSAREK (1973) and mitochandria (KURSANOV and VYSKREBENTZEVA (1966). Potassium deficiency symptoms of various plant species have been described in detail by ULRICH and OHKI (1966).

6.5. Crop Requirements and response.

The quantities of K removed from the soil by various crops are listed in Tables 6.3, 6.4, and 6.5. The tables give some indication of the rates at which K should be applied, the normal range being from about 40 to 250 kg K/ha/year. The quantity of K removed from a soil depends very much on the yield level and also on the rate of K leaching. The figures in Tabels, 6.3, 6.4 and 6.5 therefore provide only a rough working basis for fertilizer recommendations, as uptake is highly dependent on K availability. Where availability is poor, K uptake by the crop from the soil is also low and unsatisfactory yields are obtained. Under such conditions fertilizer recommendations based on an average total K uptake for a particular crop will not meet the needs of the crop nor raise the soil fertility status. The reverse situation occurs when soils are high in available K. Here fertilizer applications based on crop uptake can result in a higher K uptake than is needed for maximum yield and hence also in a waste of fertilizer.

One of the most important factors influencing K availability is soil texture. As already indicated, soils with heavy textures are higher in potassium bearing minerals and therefore generally contain higher reserves of available K. This is clearly shown from the data of CRABTREE (1969) presented in Table 6.6, where the K uptake was compared from a clay loam and sandy loam with the same exchangeable K. Potassium uptake by 4 successive oat crops was about 30% higher from the clay soil, due to the higher K buffer capacity. The K taken up by the crop originated from different soil K fractions. In the clay loam quite a substantial amount of K absorbed by the crop came from the non exchangeable K fraction.

Different crops respond to a varying extent to K fertilizers. Generally sugar beet, sugar cane, potatoes, tomatoes and celery have a very high demand whereas grapes, cotton and wheat take up much lower amounts of K. This is as shown in Tables 6.3 and 6.4. These values give some indication of the needs of various crops but as already

indicated it must be borne in mind that the particular cultivar, yield level, fertility status and other environmental factors including soil temperature, soil aeration and crop spacing are all important in determining K uptake by crops (NELSON 1968).

Table 6.3.   Quantities of plant nutrients removed by various Crops (calculated from data of EAKIN 1972).

Crop	Yield tonnes/ha	N	P	K	Ca	Mg	S	Cu	Mn	Zn
		kg/ha						g/ha		
Grains										
Barley (Grain).......	2.2	40	8	10	1	2	3	34	30	70
Barley (Straw).......	2.5	17	3	30	9	2	5	11	360	60
Wheat (Grain)........	2.7	56	13	14	1	7	3	33	100	160
Wheat (Straw)........	3.8	22	3	33	7	4	6	11	180	56
Oats (Grain)	2.9	55	10	14	2	3	6	34	134	56
Oats (Straw)	5.0	28	8	75	9	9	10	34	-	330
Maize (Grain)........	9.5	150	27	37	2	9	11	66	100	170
Maize (Straw)	11.0	110	19	135	29	22	16	55	1700	330
Hay										
Lucerne..............	10.0	200	20	170	125	24	21	66	500	470
Coastal Bermuda Grass.	20.0	340	35	250	66	27	40	230	-	-
Red Clover	6.0	110	13	95	77	19	8	45	600	400
Timothy..........	6.0	66	13	90	20	7	6	33	340	220
Other Crops.										
Sugarcane.......	75.0	110	27	250	31	26	26	-	-	-
Tobacco (Leaves) ...	2.2	83	8	110	83	20	15	33	600	80
Cotton (Seed and Lint).	1.7	45	11	14	2	4	3	66	120	350
Cotton (Stalks, Leaves and Burs)	2.2	39	5	33	31	9	17	-	-	-
Potatoes (Tubers)...	27.0	90	15	140	3	7	7	44	100	60
Tomatoes (Fruit).....	50.0	130	20	150	8	12	15	80	145	180
Cabbage.............	50.0	145	18	120	22	9	50	44	110	90

Table 6.4. Nutrient removal of plantation crops (COOK 1974)

	Yield per hectare equivalent to	kg/ha				
		N	P	K	Ca	Mg
Oil palm	2.5 tonnes of oil	162	30	217	36	38
Sugar cane	88 tonnes of cane	45	25	121	-	-
Coconuts	1.4 tonnes of dry copra	62	17	56	6	12
Bananas	45 tonnes of fruit	78	22	224	-	-
Rubber	1.1 tonnes of dry rubber	7	1	4	-	-
Soyabeans	3.4 tonnes of grain	210	22	60	-	-
Coffee	1 tonne of made coffee	38	8	50	-	-
Tea	1300 kg of dried leaves	60	5	30	6	3

Table 6.5. Nutrient removal by fruit crops; medium yield, normal spacing (according to JACOB and VON UEXKÜLL (1963)

	kg/ha/year		
	N	P	K
Pome fruits.....................	70	9	60
Stone fruits...................	85	9	65
Grapes..........................	110	15	110
Oranges	170	23	120
Lemons........................	180	23	115

Table 6.6. Comparison of potassium uptake by four successive oats crops from a clay loam and a sandy loam at similar levels of exchangeable potassium (CRABTREE 1969):

	Exchangeable K me/100 g soil at the beginning	K uptake me/100g soil	Origin of K in % of total uptake	
			Exch.	Non exch.
Clay loam	0.27	0.40	26	74
Sandy loam	0.27	0.30	77	23

Another example on the use of non-exchangeable K by a crop sequence of wheat-Bajra and wheat grown in a non-saline sandy loam (pH 7.5) of north India is shown by Sachdev and Khera (1980)   Taking a cropping sequence of wheat-bajra where the general mean of 210 kg K/ha for initial soil test K values dropped (by 35 kg K/ha) to about final mean of 175 kg K/ha as a consequence of intensive cropping, as much as 80 per cent of the potassium removed in the crops originated from non-exchangeable sources.   Taking the wheat-bajra-wheat cropping sequences as a whole, when the general means of initial and final soil test K values worked out to 209 and 175 kg K/ha and while using an average of 290 kg N+ 115 kg P_2O_5/ha per cropping sequence, as much as four fifths of the total potassium removal (427 kg out of 495 kg) was contributed from non-exchangeable sources.   The reason for rapid release of non-exchangeable potassium under intensive cropping is that a concentration gradient is set up from high concentration of K in unexpanded part towards the K-depleted expanded part of the clay.

Table 6.7   Utilization of soil potassium from exchangeable sources by wheat-bajra-wheat cropping sequence (1972-74)

Range of potassium removal	Relative utilization of soil potassium		Total potassium removal	Soil test potassium level		Average of the quantities of fertiliser used			Total N+P₂O₅	No. of plots
	Exchange-able	Non-exchange-able		Initial	Final	Wheat	Bajra	Wheat		
						$N+P_2O_5$	$N+P_2O_5$	$N+P_2O_5$		
kg K/ha										
230-290	57(₂₂)*	202(₇₈)	259ᵃ ± 18	214 ± 26	173 ± 18	10+20	40 ± 25	10+20	60+65	15
291-350	61(₁₉)	263(₈₁)	324ᵇ ± 18	215 ± 25	174 ± 16	35+30	50+30	35+30	120+90	21
351-410	37(₁₁)	333(₈₈)	380ᶜ ± 15	201 ± 27	170 ± 13	75 + 30	70+30	75 ⊤ 30	220 - 90	24
411-470	29(₇)	411(₉₃)	440ᵈ ± 13	194 ± 30	184 ± 18	100+35	50+40	100+35	250 ÷ 110	13
471-530	68(₁₄)	427(₈₆)	495ᵉ ± 19	220 ± 29	171 ± 15	110+40	70+35	110+40	290 + 115	8

*Figures in brackets indicate per cent contribution
't' test of 'a' with b,c,d and e was sign.ficant at 1 per cent level

Source :Sachdev and Khera (1980).

In order to evaluate K requirements of crops it is also important to consider the total length of the growing period. Tomatoes and sugar beet for example take up about the same amount of K as sugar cane, per unit area per year. In the two former crops, however, the growth period is only about 120 days whereas in sugar cane the growth period may extent over the whole year (NELSON 1968). This indicates that crops with the same total uptake may have a very different K demand (= uptake/unit time). Requirement also varies depending on the stage of growth the highest uptake rate often being in the vegetative stage. In potatoes for example 50% of the total K is absorbed in the first third of the growth period. In the cereals too, K is particularly needed during vegetative growth, and K application during the reproductive stage hardly affects grain yield (CHAPMANand KEAY 1971). This favourable influence of K in the early growth stage of cereals appears to result from increasing the number of ears per unit area (FORSTER and MENGEL 1969).

Another important factor in determining K uptake by crops is the type of rooting system and its extent. This is well demonstrated in the competition which occurs between legumes and grasses for K uptake. In the field when these species are growing together, K uptake is considerably higher by grasses, and under low level K conditions this can lead to the disappearance of legumes from the sward. This competition was studied by LAMBERT and LINCK (1964) using intact root systems of lucerne and oats supplied with K-42. When whole root systems were used 91% of the labelled K was found in oats and only 9% in the lucerne. However, when the K-42 was applied separately to intact roots segments of lucerne and oats more labelled K appeared in the lucerne than in oats. These results indicate that root morphology (root length, number of root hairs) and probably also the individual K uptake potential (K absorbing power) of crop species appear to be important factors influencing competition between plant species for K.

The response to K uptake by crops depends to a considerable extent on the level of N nutrition. Generally the better crop is supplied with N the greater the yield increase due to K HEATHCOTE(1972). On the other hand applied N is only fully utilized for crop production when K supply is adequate.

In moving from an extensive to an intensive cropping system responses to K fertilizers are frequently not observed in the first years of application (ANDERSON 1973). This is particularly true in more arid regions where little or no K losses occur by leaching. Potassium reserves accumulated in the upper soil layers are often sufficient to supply crop needs in the first few years of intensive cropping. However, as soon as these reserves are exhausted because of the higher K requirements of increased crop yields and continuous cropping, responses due to K fertilization may be expected. The data of Table 6.8 from field experiments in East Africa show such an example where in the first two-year cycle the response to K fertilizer supply was poor or even negative whereas in the second two-year cycle a beneficial effect was observed for most crops (STEPHENS 1969).

Table 6.8. Yield increases due to potassium fertilizer in the 1st and 2nd cycle of cropping (STEPHENS 1969).

	Yield increase in kg/ha	
	1st cycle	2nd cycle
Maize............	-30	138
Cotton	10	46
Sweet potatoes....	1050	1800
Beans...........	13	12
Millet and Sorghum	-84	85

6.6. Fertilizers and application

Potassium is supplied to crops as a straight fertilizer or in the form of compounds. The most widely used and cheapest potash fertilizer is potassium chloride (KCl) which is known commercially as muriate of potash. The fertilizer contains

about 50% K (60% K_2O). Besides this high grade form lower grade Cl fertilizer types (41% K and 33% K, or 58% K_2O and 40% K_2O) are also on the market. These forms contain substantial amounts of NaCl and are therefore suited to natrophilic crops (sugar beet, cabbabe, oats). When added to the soil, KCI dissolves in soil solution giving K^+ and Cl^- ions. Potassium sulphate (K_2SO_4 potash of sulphate) contains a somewhat lower K content of about 43% K (52% K_2O) and is more expensive due to higher production costs. Potassium nitrate (KNO_3) 37% K (44% K_2O, 13% N), and potassium metaphosphate (KPO_3) 33% K (40% K_2O, 27% P) are both of relatively minor importance. Another K fertilizer is potassium magnesium sulphate (K_2SO_4, $MgSO_4$). This contains 18% K (22% K_2O) and 11% Mg (18% MgO) and is useful where Mg is required in addition to K^+. Magnesium kainite ($MgSO_4$ + KCl + NaCl) is a low grade K fertilizer 10% K (12% K_2O), 3.6% Mg (6% MgO) and 18% Na (24% Na_2O). This is used mainly in Germany and the Netherlands for pasture dressing.

With the exceptions of potassium metaphosphate and potassium silicate all potash fertilizers are soluble in water. They are therefore very similar in availability so that differences between these fertilizers result from accompanying anions. In some cases the application of sulphur, magnesium, or sodium may be agronomically beneficial and an appropriate fertilizer should be chosen. Some crops are sensitive to high amounts of chloride. These chlorophobic species include tobacco, grapes, fruit trees, cotton sugar cane, potatoes, tomatoes, strawberries, cucumber and onions. It is preferential to treat these crops with potassium sulphate. For potatoes, the use of sulphate rather than chloride generally results in higher starch contents HAEDER (1975) found that chloride affects the translocation of photosynthates from the upper plant parts to the tubers. This effect is shown in Table 6.9. In the "chloride treatment" a relatively high accumulation of labelled photosynthates occurred in the stems whereas in the treatment " Cl/SO_4 " (half chloride, half sulphate) the negative effect of chloride on photosynthate translocation was alleviated to some degree.

Table 6.9. Effect of Chloride and sulphate nutrition on the relative
           distribution of labelled photosynthates in potato plants,
           total amount of labelled C = 100% (HAEDER 1975).

Plant organs	Treatment		
	Cl	Cl/SO$_4$	SO$_4$
Leaves................	37	40	34
Stems	38	29	23
Tubers................	21	27	39
Roots	4	4	4

Most field crops are not sensitive to chloride and for
this reason are generally treated with muriate of potash. Oil
palms and coconuts even appear to have chloride requirement
(VON UEXKÜLL 1972). Potassium nitrate is mainly used for
spraying on fruit trees and horticultural crops. Potassium
metaphosphate and potassium silicates are used in cases
where it is desirable that solubility should be low in order
to prevent high concentrations in the root vicinity. Because
of the high prices of these low soluble K fertilizers, they
are only used occasionally for horticultural crops.

Potassium fertilizers are usually applied broadcast
(REITH 1972) and only in soils with a low level of available
K^+ or with a high K fixation capacity is banded application
recommended. Using this technique the K fixation capacity of
a restricted soil volume can be saturated and within this
zone excess K^+ is available for uptake. In experiments with
maize WELCH et al. (1966) observed that responses to banded
K fertilizer were as much as 4 times greater than a broadcast
treatment. It is also opportune to apply K fertilizers to K
fixing soils just before sowing the crop and also later as
a top dressing in order to reduce the time of contact between
fertilizer K^+ and the K fixing minerals. The longer the time
of contact the more fertilizer K^+ is fixed.

Kim and Park (1973) found that the yield increase on the plot with top dressing split in 4 is highly significant. The application of potash at transplanting and the two instalment split application also increased yields although not significantly. The table further shows that yields increase with the number of instalments in the split dressing, that is the more splitting of top dressing the higher is the yield of rice. This might be due to the increased potash uptake by the rice plant when the potash is placed in the top layer, rich in oxygen, rather than in the sub-layer where greater amounts of ferrous iron and hydrogen sulphide are found, and which inhibit absorption particularly of potash.

Table 6.10. Effect of different methods of application of potassium on the yield of unhulled rice.(Kim & Park 1973

Treatments	Yield (kg/10a)	Index on no potassium application (%)	Index on method of potassium application (%)
No potassium	463	100	–
100% application at transplanting	498	108	100
Complete split top dressing (30-20-30-20%)	611	132[**]	123[*]
50% at transplanting +50% top dressing	533	115	107

LSD	5%	74,53
	1%	128,00
CV (%)		4,2

On fine textured soils the vertical movement of K in the soil profile is restricted. This may affect the supply of fertilizer K to the roots of some crop species. For example BUDIG (1970) found that grapes suffered from K deficiency although the upper soil layer was rich in available K. However, the deeper soil layers (40 to 60 cm), from which the grape roots mainly drew their nutrients, were depleted for K^+. For such crops deep application of fertilizer K^+ is recommended.

High K losses due to leaching occur only on sandy soils, organic soils and soils with kaolinite as the main clay mineral. These soils should be treated with fertilizer K just before the crop is sown or planted in order to avoid excessive K losses by leaching in rainy periods (winter rainfall, rainy season). For some crops split applications are even recommended under high leaching conditions.

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Sulphur in Soils and in Crop Nutrition

7.1. Sulfur Deficiency problems.

Widespread sulfur deficiencies and responses have been
reported all over the tropics. One of the first reports was
from the Cerrado of Brazil, where McClung et al. (1959) observed
responses not only in savannas but also in soils recently cleared
of virgin forests. In Central America sulfur deficiencies
are also widespread, particularly in Andepts, where their
volcanic origin would lead one to assume that such soils would
be high in this element(Fitts, 1970). In sub-Saharan Africa
sulfur is limiting in Alfisols and Oxisols with annual rainfall
greater than 600 mm and in sandy soils of central Africa,
according to a review by Bolle-Jones (1964). Sulfur deficiencies
also occur in Asia, particularly the Punjab of India and in
Malysia (Olson and Englestad, 1972). They also have been reported
in Australia and Hawaii (Williams, 1972: Fox et al. 1971).

In general sulfur-deficient soils have one or more of
the following properties. They are high in allophane or oxides.
They are also low in organic matter, and often sandy. Soils
subject to repeated annual burning are often sulfur deficient
since about 75 percent of the sulfur is volatilized by fire.
Sulfur-deficient soils occur in unpolluted, inland areas where
the atmosphere is low in sulphur.

7.2. Sulfur Contents and Forms.

7.2.1. Total Sulfur.

In the temperate region total soil is positively correlated
with organic matter content and inversely correlated with degree
of weathering. Olson and Englestad(1972) provided the following
topsoil average values for total sulphur in the temperate region:
500 ppm for Mollisols, 400 ppm for Alfisols, and 200 ppm for
Ultisols. Following this reasoning, they assumed that tropical
soils would average about 100 ppms. A summary of eastern
Australia soils by Williams and Steinbergs (1958) shows an
average content of 167 ppm S, of which only 7 ppm is inorganic
sulfur. Tropical soils high in organic matter and allophane,

however, have large quantities of total sulfur. A Eutrandept
from Hawaii had 1280 ppm S in its topsoil (Fox et al., 1971).

7.2.2. Organic Sulfur

Most of the sulfur contents of unfertilized tropical
soils are in the organic form. The C:N:S or organic matter
ratio is on the order of 126:10:1 for soils of Nigeria and
eastern Australia, according to surveys by Oke (1971) and
Williams and Steinbergs (1958).

Organic sulfur is mineralized like organic nitrogen.
There is a great similarity between nitrogen and sulfur cycles.
Sulfur mineralization rates range from 1 to 10 percent per year.
Barrow (1961) found that immobilization occurs at C:S ratios
greater than 200 and that materials containing less than 0.15
percent S are immobilized. Andepts and other soils high in
allophane are also high in organic sulfur, but plants growing
on these soils are usually very deficient in sulfur because
the mineralization rate of this element is slow when organic
matter is intimately associated with allophane. Flushes of
sulfur mineralization upon wetting previously dried soils have
also been observed by Barrow. It seems logical to assume that
the processes involved are similar to those governing nitrogen
flushes. The fate of the mineralized sulfur, however, may be
different from that of nitrates because of the sulfur fixation
capacity of many soils.

The organic S fraction of the soil is rendered available
to plants by microbial activity. In this process of mineralization
H_2S is formed which under aerobic conditions readily undergoes
autoxidation to SO_4^{2-}. In anaerobic media, however, H_2S
is oxidized to elemental S by chemotrophic sulphur bacteria
(Beggiatoa, Thiothrix). The same bacteria can also oxidize S to
H_2SO_4 under aerobic conditions. Elemental S is also oxidized
by chemotrophic bacteria of the genus Thiobacillus. The overall
process may be expressed in chemical terms as follows:

$$2H_2S + O_2 \longrightarrow 2H_2O + 2S + 122 \text{ kcal}$$

$$2S + 3O_2 + 2H_2O \longrightarrow 2H_2SO_4 + 282 \text{ kcal}$$

$$\text{net: } 2H_2S + 4O_2 \longrightarrow 2H_2SO_4 + 404 \text{ kcal}$$
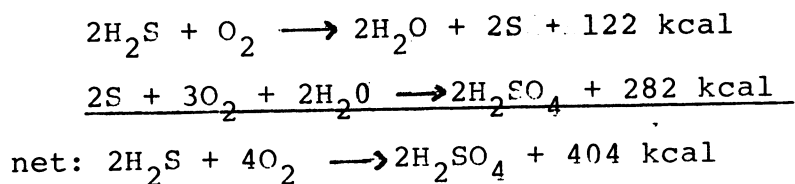
The oxidation of S thus results in the formation of H_2SO_4. A consequent increase in soil acidity thus occurs. The same process also accounts for the acidification resulting from the addition of elemental S to soils. This treatment is sometimes used to depress the pH of alkaline soils. In a similar way to the reactions described above FeS can be oxidized biologically and chemically to elemental S according to the equation:

$$FeS + H_2O + \tfrac{1}{2}O_2 \longrightarrow Fe(OH)_2 + S$$
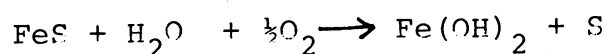
Under reducing soil conditions (waterlogged soils, paddy) H_2S is formed both by mineralization of organic matter and sulphate reduction. Under such conditions H_2S can be oxidized anaerobically to elemental S. This oxidation occurs through the agency of photosynthetic green and purple bacteria which utilize the H from the H_2S molecule as an H donor in photosynthetic electron transport. When this process is restricted H_2S may accumulate to toxic levels and this impair plant growth. To some extent, the detrimental effect of H_2S can be alleviated by the addition of ferrous salts which form the sparingly soluble FeS

The process of S conversion in soils are shown in Fig. 7.1.

7.2.3. Inorganic Sulfur

Sulfates are the main inorganic form of sulfur in aerobic soils. In tropical soils susceptible to leaching, SO_4^{2-} ions are found in small quantities, associated with Ca^{2+}, Mg^{2+}, and K^+. In addition to organic sulfur mineralization, SO_4^{2-} ions may be added to the soil through rainfall, fertilizers, pesticides, irrigation water and gases from volcanic eruptions. Rainfall
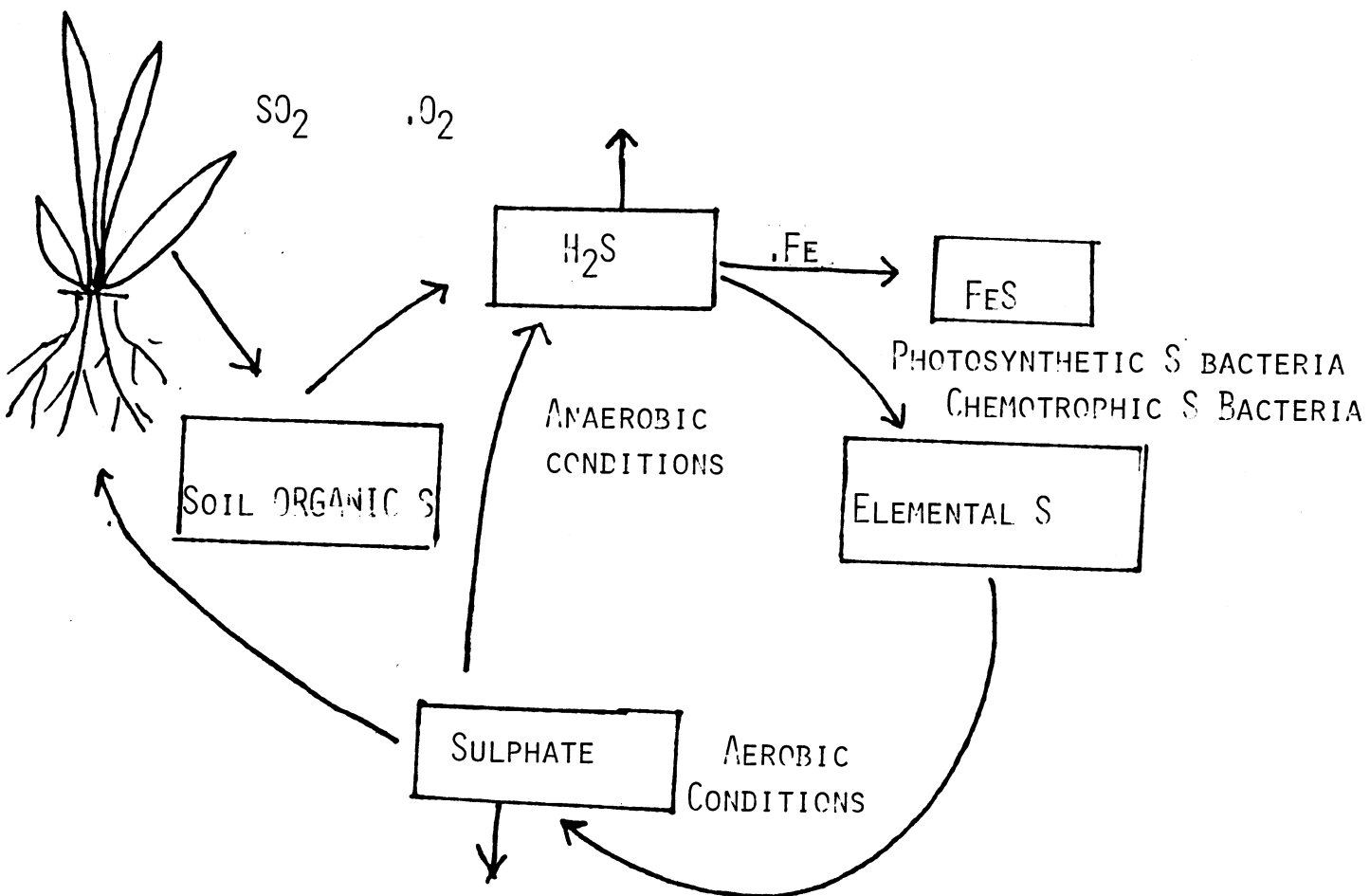
FIG. 7.1. SULPHUR CYCLE IN NAUTRE. (Mengel and Kirkby, 1982)

usually contains less than 1 ppm S: this is equivalent to about 10 kg S/ha a year, a quantity that may be sufficient to prevent sulfur deficiencies. Rainfall contributes high amounts of sulfur in polluted areas and near the oceans. The contributions of fertilizers and other farm chemicals may be considerable, particularly when ammonium sulfate and ordinary superphosphates are used. Sulfurous gases from volcanic eruptions may be adsorbed directly by plants or dissolved in the soil solution.

Soils high in iron and aluminum oxides or allophane have considerable capacity to sorb sulfate ions through anion exchange sites. This process results in an accumulation of inorganic SO_4^{2-} in many Ultisols, Oxisols, and Andepts with oxidic mineralogy. Water-soluble SO_4^{2-} and phosphate-extractable SO_4^{2-} contents are generally higher in such soils than in those with pure layer silicate systems, as Table 7.2 shows.

When soils of oxide-coated or oxide mineralogy are heavily fertilized and leaching occurs, relatively large quantities of SO_4^{2-} accumulate in the subsoils because of their sulfur sorbing capacity. In Brazilian subsoils of Table 7.1 inorganic sulfur became the dominant fraction. The same occured in a heavily fertilized Eutrorthox of Hawaii, where large quantities of SO_4^{2-} accumulated in the subsoil. Under such conditions certain crops may show sulfur deficiency symptoms at early growth stages when the root systems have not penetrated the subsoil. This deficiency gradually disappears as the roots come in contact with the SO_4^{2-} in rich subsoil.

7.2.4. Sulfur Sorption and Release

Two mechanisms are recognized as responsible for the sulfur sorption in soil. One is the exchange of SO_4^{2-} for OH- ions on iron and aluminum oxide surfaces. This reaction also occurs in anion exchange sites along the edges of kaolinite particles and positively charges organic radicals. In subsoils it may result in pH increases of 0.3 to 0.9 unit.
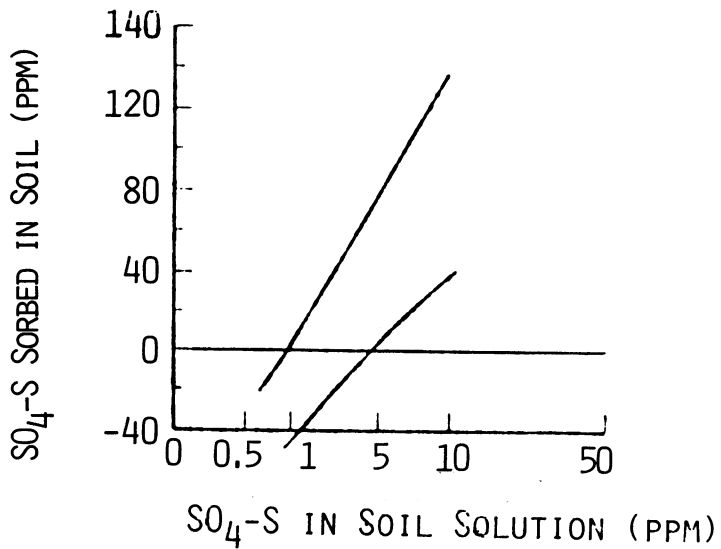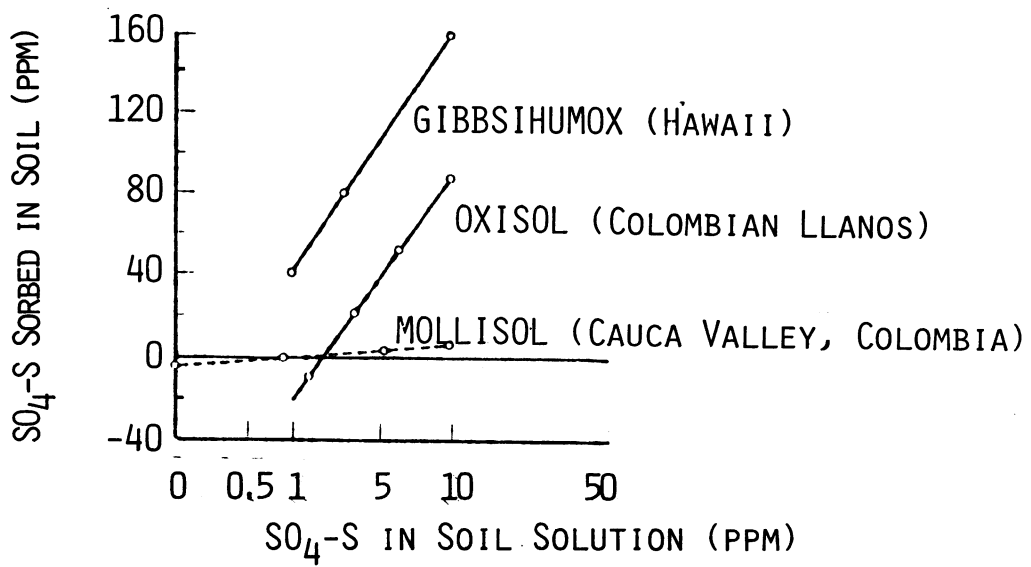
FIG. 7.2 EXAMPLES OF SULFUR SORPTION ISOTHERMS.
SOURCE: FOX ET AL. (1971) AND FOX (1974)

$$\text{Fe} \diagdown \quad \text{O} \diagup \text{OH} \\ \text{Fe} \diagup \quad \text{Fe} \diagdown \quad \text{O} \diagup \text{OH} \quad + SO_4^= \; \rightleftharpoons \; \text{Fe} = \text{O} \diagup SO_4 \quad + \; 2OH^-$$
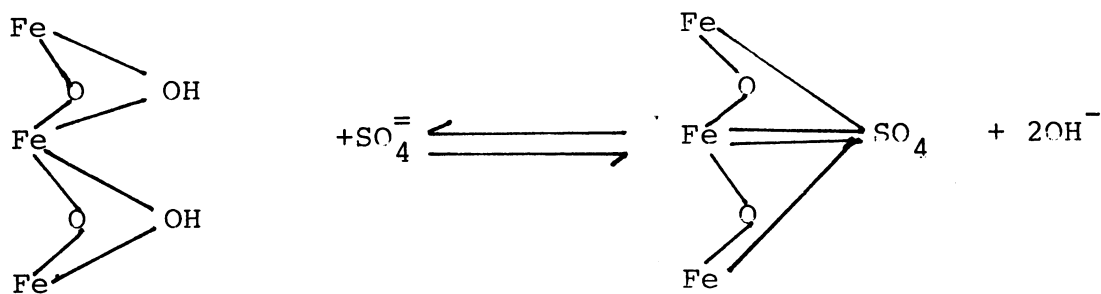
The second mechanism is the formation of complexes with hydroxy aluminum as follows:

$$Al(OH)^{2+} \quad + \quad SO_4^{2-} \longrightarrow Al(OH)SO_4$$
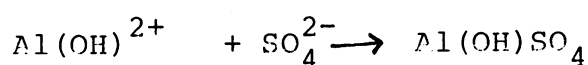
The sorption and release properties of sulfur can be characterized by adsorption isotherms in a way very similar to that used for phosphorus. Figure 7.2. shows examples of these relationships in some tropical soils. The montmorillonitic Mollisol from the Cauca Valley of Colombia does not exhibit any sulfur sorption, a finding typical also of other soils with similar mineralogy from Hawaii and Australia, according to Fox et al. (1971). Several Oxisols show strong sulfur sorption capacity, particularly in the subsoil.

In addition to mineralogy, other factors affect the intensity of sulfur sorption. In oxide systems sorption increases as pH decreases since OH^- ions tend to replace SO_4^{2-} ions at high pH values. Sulfur sorption is decreased by phosphorus sorption since the $H_2PO_4^-$ ions replaces SO_4^{2-} ions. This reaction takes place in the topsoil and may cause sulfate movement into the subsoil, where the sulfur can be sorbed.

The effect of pH on sulfate sorption is shown in Fig. 7.3. But it also applies to another anions.

Sorbed sulfur is held much less tightly by clay particles than is fixed (or sorbed) phosphorus. Therefore the availability of sorbed sulfur is generally higher than that of fixed phosphorus. The SO_4^{2-} ions have to be released in the soil solution before they can be taken up by plants. In Hawaii 8 to

Low pH

Sesquioxide
Surface

O

O — AlOH ⊕
          |
          H
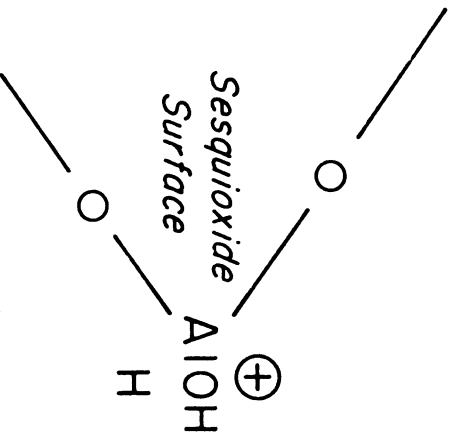
At low pH, sesquioxide surfaces adsorb H⁺ from solution and become positively charged

Zero Point of Charge

Sesquioxide
Surface

O

O — AlOH ◎
          ↑↓
          H⁺(aq)
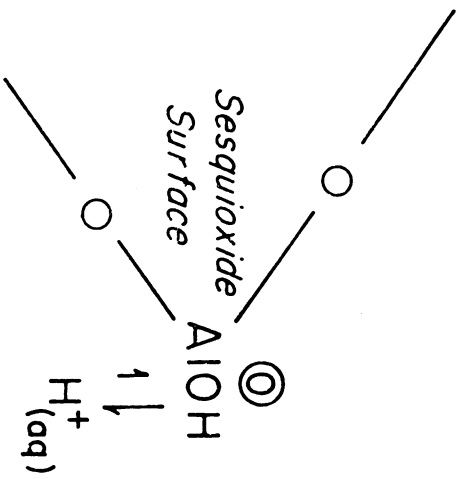
At higher pH called the Zero Point of Charge, adsorbed H⁺ dissociates into solution, leaving the surface with no net charge

High pH

Sesquioxide
Surface

O

O — AlOH ⊖
          ↑↓
          H⁺(aq)
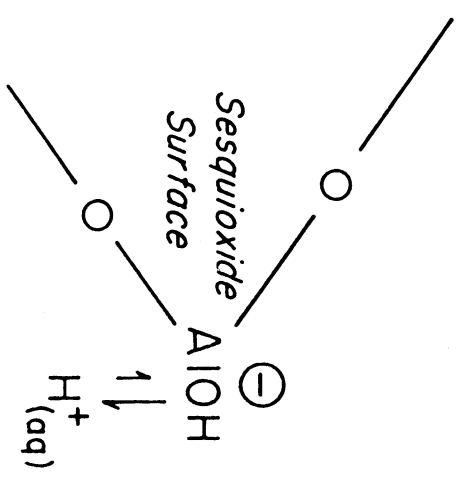
At very high pH (>9); an additional H⁺ dissociates, leaving the surface negatively charged

Figure 9.3 Schematic representation of the effect of pH on surface charge of sesquioxides

10 ppm of phosphate-extractable sulfur is considered to be
the critical level (Hasan et al., 1970). No critical levels
for water-soluble sulfur have been developed.

7.3. Uptake and translocation

Plants mainly absorb S in the form of SO_4^{2-} . In the
pH range to which roots are normally exposed, uptake is not very
pH sensitive. HENDRIX (1967) found the highest uptake rate in
bean plants at pH6.5. Other plant nutrients scarcely affect
the absorption of SO_4^{2-} by plant cells. Selenate, however, which
is closely chemically related to SO_4^{2-} , depresses SO_4^{2-} uptake
substantially. This indicates that both ion species probably
compete for the same carrier site. The actual uptake mechanism
is not fully understood. NISSEN (1971) supposes that only a single
uptake mechanism exists, the selectivity of which depends much
on the prevailing SO_4^{2-} concentration in the nutrient solution.
This still needs further elucidation. According to investigations
of ANSARI and BOWLING (1972) with sunflowers, SO_4^{2-} is absorbed
and translocated against an electrochemical gradient, which
suggests that SO_4^{2-} uptake is an active process.

Sulphate is mainly translocated in an upward (acropetal)
direction and the capability of higher plants to move S in
a downward (basipetal) direction is relatively poor. In
solution culture experiments with clover BOUMA (1967) found that
as a result of interruption of the SO_4^{2-} supply (transfer into
SO_4^{2-} free solution) S in the roots and petioles was translocated
towards the younger leaves. The S of the older leaves,however,
did not contribute to the S supply of younger tissues. This
shows that translocation against the transpiration stream did
not occur.

There is now a considerable body of evidence to show that
plants can utilize atmospheric SO_2 as part of their S supply.
Faller et al. (1970), growing various plant species in growth
chambers with defined SO_2 concentrations in the atmosphere as
the sole S source, found that growth was reduced in the treatment
where SO_2 was absent. Once SO_2 is absorbed through the stomata

TABLE 7.1. EFFECT OF 20 TO 30 YEARS OF CROPPING ON THE CONTENTS AND RESPONSES TO SULFUR IN TWO CERRADO SOILS OF BRAZIL IN POT CONDITIONS

Soil	Cropping History	Topsoils (ppm)		Subsoils (ppm)	
		Organic S	Inorganic SO_4-S	Organic S	Inorganic SO_4-S
Ultisol	Virgin	36	4.0	12	6.4
(Baurú)	Cropped	24	2.5	10	12.0
Oxisol	Virgin	247	3.7	11	3.3
(Riberão Preto)	Cropped	60	7.2	10	12.3

SOURCE: MCCLUNG ET AL. (1959)

TABLE 7.2. INORGANIC SULFUR CONTENTS EXTRACTED FROM HAWAIIAN TOPSOILS (PPM S)

Great Soil Group	H_2O-Extractable	$Ca(H_2PO_4)$-Extractable
Red Desert (Aridisol)	8	16
Dark Magnesium Clay (Vertisol)	18	11
Low Humic Latosol (Ustox)	20	55
Humic Latosol (Ultisol)	23	33
Humic Ferruginous Latosol (Humult)	22	53
Hydrosol Humic Latosol (Hydrandept)	11	134

SOURCE: FOX ET AL. (1965)

TABLE 7.3. EFFECT OF ATMOSPHERIC SO_2 CONCENTRATION ON THE GROWTH OF VARIOUS PLANT SPECIES, GROWN IN A SULPHATE FREE NUTRIENT SOLUTION (DATA FROM FALLER (1968)

	SO_2 Concentration, mg SO_2/m^3					Experimental Period in Days
	0.0	0.2	0.5	1.0	1.50	
	YIELD IN G DM/PLANT					
Sunflowers	70	103	103	113	100	15
Maize	100	110	118	111	107	13
Tabacco	31	41	43	54	46	9

it is distributed throughout the entire plant and has been
detected in various S fractions such as protein S, amino acid S
and sulphate S. The influence of the level of SO_2 nutrition on
plant growth is shown in Table 7.3. (Faller 1968).

7.4. Functions of Sulfur

Cysteine and methionine are the most important S containing
amino acids in plants, where they both occur as free acids as
building blocks of proteins. One of the main functions of S in
proteins or polypeptides is in the formation of disulphide
bonds betwen polypeptide chains. The synthesis of the dipeptide
cystine from two cysteine molecules illustrates the formation
of a disulphide bond from two SH groups.

$$
\begin{array}{c}
COOH \\
| \\
H_2N \,—\, CH \\
| \\
CH_2 - S(H \quad H)S - CH_2
\end{array}
\qquad
\begin{array}{c}
COOH \\
| \\
H_2N - CH \\
| \\
\end{array}
\qquad 2H \xrightleftharpoons{} H_2
\qquad
\begin{array}{c}
COOH \\
| \\
H_2N - CH \\
| \\
CH_2-[S-S] \quad - \quad CH_2 \\
\uparrow \\
S - S - bond
\end{array}
\qquad
\begin{array}{c}
COOH \\
| \\
H_2N - CH \\
| \\
\end{array}
$$

2 x Cysteine → Cystine + 2 H
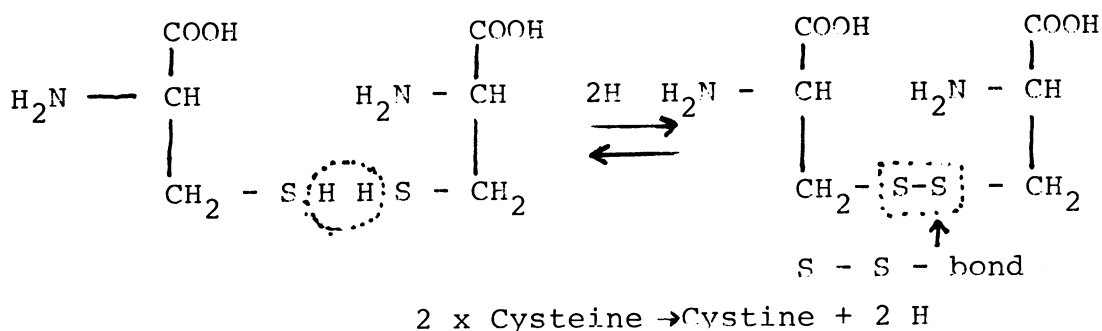
The whole reaction serves as a redox system which can take up
or release H atoms depending on prevailing metabolic conditions.
Under reducing conditions (excess of H or reduced coenzymes)
the equilibrium is shifted in favour of cysteine whereas under
oxidizing conditions cystine is formed. The system thus functions
as either an H donor or an H acceptor. The glutathione redox-
system is analogous to the cysteine/cystine system.

Sulphur is an essential element of the the thiazole ring
which is a component of the vitamin thiamine. Thiamine may occur
as the free vitamin or as thiamine pyrophosphate. In contrast
to animal tissues, plants contain thiamine very largely in the
free vitamin form. Little is known of the role of thiamine
in plants.
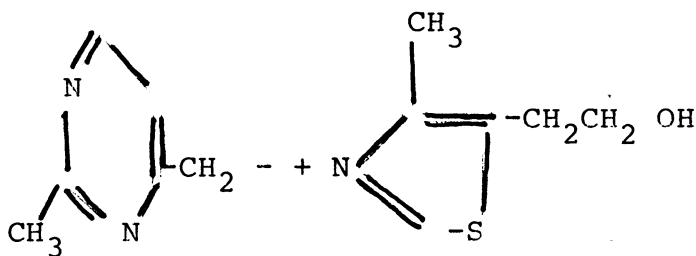
Thiamine (Vitamin B_1)

The total S content in plant tissues is the order of 0.2 to 0.5% S in the dry matter. ULRICH et al. (1967) studying S uptake and S content of lucerne (Medicago sativa) in solution culture found that in the range of inadequate S supply, raising the sulphate supply only increased the organic S content without increasing the sulphate content. As soon as the S demand of the plant was satisfied, however, the content of sulphate S increased whereas the content of organic S remained relatively constant. This relationship is shown in Figure 7.4. from the data of DELOCH (1960) for sunflowers. These results demonstrate that S taken up in excess of the demand of the plant for the synthesis of organic S compounds is stored as SO_4^- S.

7.5. Sulphur deficiency and toxicity

As S is an essential constituent of proteins, S deficiency results in an inhibition in protein synthesis. The S containing amino acids (cysteine, methionine) which are essential building blocks of protein are deficient and thus proteins cannot be synthesized. For this reason non-S containing amino acids accumulate in S deficient plant tissues. COLEMAN (1957) observed that asparagine, glutamine and argenine are mainly accumulated. This finding is consistent with the results of EPPENDORFER (1968), who found an accumulation of amides in the soluble amino fraction of barely shoots suffering from an inadequate S supply. According to the findings of RENDIG et al. (1976) the accumulation of amide N in S deficient maize plants is associated with low levels of sugars. These low sugar contents result from the poor photosynthetic activity of chlorotic S deficient plants.
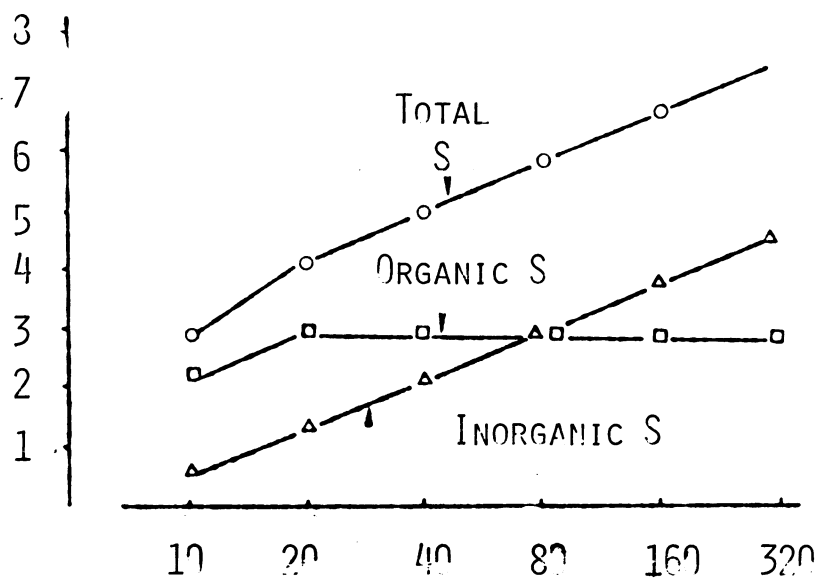
FIG. 7.4 INFLUENCE OF INCREASING LEVELS OF SO_4
NUTRITION ON THE TOTAL S, SULPHATE S AND
ORGANIC S OF SUNFLOWER LEAVES (AFTER DELOCH 1960).

In field crops sulphur deficiency and nitrogen deficiency are sometimes difficult to distinguish. In this instance leaf analysis can be invaluable. In S deficient plants the SO_4-S are very low whereas amide N and NO_3-N are accumulated. This contrasts markedly with N deficiency were soluble N levels are depressed and SO_4^{2-} levels are normal.

In plants suffering from S deficiency the rate of plant growth is reduced. Generally the growth of the shoots is more affected than root growth. Frequently the plants are rigid and brittle and the stems remain thin. In Cruciferae the lateral extension of the leaf lamina is restricted and the leaves are rather narrow. Chloroplast formation is affected and according to KYLIN (1953) decomposition of chloroplasts may even occur in severe cases. In contrast to N deficiency, chlorotic symtoms occur first in the younger, most recently formed leaves. This shows that older plant tissues cannot contribute substantially to the S supply of younger leaves, which are obviously mainly dependent on S taken up by the roots. ULRICH et al. (1967) described the S deficiency symptoms of lucerne as follows: "Sulphur deficiency symptoms appeared first at the top of the alfalfa plant. The leaves turned from a light green to a light yellow, often followed by pronounced yellowing. In time, all leaves on the plant became light-yellow to yellow in colour". This development of S chlorosis observed in lucerne also holds true for many other plant species.

Plants are comparatively insensitive to high SO_4^{2-} concentrations in the nutrient medium. Only in cases where SO_4^{2-} concentrations are in the order of 50 mM as for example in some saline soils, is plant growth adversely affected. The symptoms, a reduction in growth rate and a dark green colour of the leaves are not specific for S excess and are more typical of salt affected plants. Provided that SO_4^{2-} and Cl- are given in isoosmotic concentrations, SO_4^{2-} is often more detrimental than Cl- salinity.

The critical concentration of SO_2 in the atmosphere above which toxic effects in plants are observed is in the range of 0.5 to 0.7 mg SO_2-S/m^3. High SO_2 concentrations result in

necrotic symptoms in the leaves. The SO_2 concentration of the atmosphere is generally about 0.1 to 0.2 mg SO_2-S/m^3. In industrial areas, however, concentrations several times higher than these normal levels have been registered.

7.6   Sulfur Requirements by Tropical Crops.

Sulfur uptake values are similar to those of phosphorus in tropical crops for which data are available. Sulfur concentrations in plant tissue are also similar to phosphorus concentrations, ranging from 0.1 to 0.3 percent S. A good indication of sulfur deficiency is a decline of the N:S ratio of tissues below 17:1 because the ratio of protein nitrogen to protein sulfur is 15:1. Among species, grain and pasture legumes as well as cotton are especially sensitive to sulfur deficiencies.

A sulfur deficiency at early growth stages may disappear later when the soil comes in contact with the subsoil. In such cases small starter fertilizer applications may be needed.

Some of the atmospheric SO_2 is dissolved in rain drops and in this form penetrates the soil, where it is oxidized to SO_4^{2-} . Soils in highly industrialized areas are thus adequately supplies with S. The quantities of atmospheric S supplied to soils decreases with the distance from the sea.

7.7. Sulfur Fertilization

In general, rates on the order of 10 to 40 kg S/ha are sufficient to overcome sulfur deficiencies. Fig. 7.5. shows how such rates tripled the yield of pasture in the presence of phosphorus. Jones and Quagliato (1970) showed that 10 to 20 kg S/ha is sufficient for most tropical pasture legumes and alfalfa. For coffee an annual rate of 30 kg S/ha increased yields by 82 percent over a 10 year period in Brazil (Table 7.4). Sulfur fertilization is an established practice in this area.
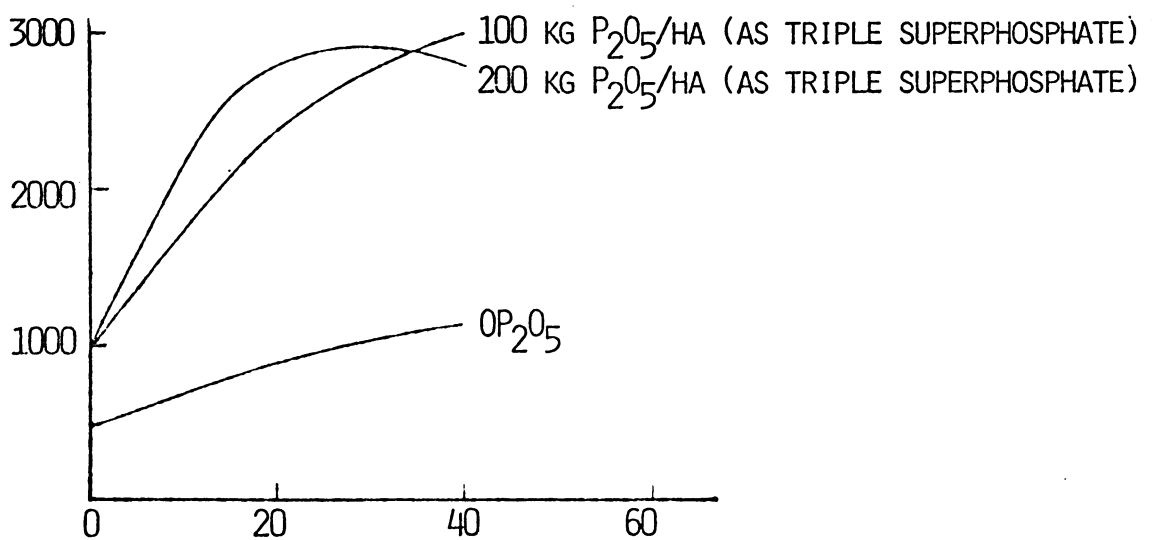
FIG. 7.5. EFFECTS OF SULFUR AND PHOSPHORUS FERTILIZATION ON THE GROWTH OF PASPALUM NOTATUM (BATATAIS GRASS) IN A BRAZILIAN ULTISOL. SOURCE: MCCLUNG AND QUINN (1959)

TABLE 7.4. EFFECT OF SULFUR FERTILIZATION ON ANNUAL COFFEE
YIELDS ON A RED-YELLOW LATOSOL (OXISOL) OF BRAZIL

ANNUAL APPLICATION (KG S/HA)	COFFEE YIELD (AVERAGE OF 10 YEARS) (KG/HA)
0	1320
16	2040
33	2341
66	2400
132	2172

SOURCE: DE FREITA ET AL. (1972)

TABLE 7.5. SULPHUR CONTENT IN GRAINS AND SEEDS OF VARIOUS CROPS
(DELOCH (1960)

GRAMINEAE		LEGUMINOSAE % S, DM		CRUCIFERAE	
BARLEY	0.18	BROAD BEANS	0.24	RAPE	1.0
OATS	0.18	BUSH BEANS	0.24	WHITE MUSTARD	1.4
WHEAT	0.17	PEAS	0.27	OIL RADISH	1.7
MAIZE	0.17	SOYA	0.32	BLACK MUSTARD	1.0

Most of these requirements are small enough for some
nitrogen and phosphorus carriers to supply them. When urea
and triple superphosphate are used, only small applications are
needed to achieve high yields.

The total S requirement of different crops depends on
plant material production and also on the crop species. Crops
with a high production of organic material such as sugar
cane, maize and Bermuda grass have a high demand for S which
is in the order of 30 to 40 kg S/ha/yr (see Table 6.3). A
high S requirement is also characteristic of protein rich crops
(lucerne, clover) and particularly of the Cruciferae. Thus the
requirement of rape is about 3 times higher than that of cereals.
Cruciferae need an appreciable amount of S for the synthesis of
mustard oils. For this reason they respond most sensitively
to an inadequate S supply. The S requirement of different
crops is also reflected in the S content of their seeds and grains
as is shown in Table 7.5. (DELOCH 1960).

The most important S containing fertilizers are gypsum,
superphosphate, ammonium sulphate, potassium sulphate, and sulphate
of potash magnesia. Sulphur coated fertilizers also contribute
to the S supply of plants. Dressings of gypsum ($CaSO_4.2H_2O$)
are often used in cases where soils are absolutely deficient
in S.

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Calcium in Soils and in Crop Nutrition.

8.1. Calcium bearing minerals and weathering.

The mean Ca content of the earth's crust amounts to
about 3.64%. It is thus higher than that of most other plant
nutrients. Calcium in the soil occurs in various primary minerals.
These include the Ca bearing Al-Si-silicates such as feldspars
and amphiboles, Ca phosphates, and Ca carbonates. The latter
are particularly important in calcareous soils and are usually
present as calcite ($CaCO_3$) or dolomite ($CaCO_3.MgCO_3$). The
various forms of apatite occuring in soil include most known
forms of Ca phosphates. The Ca content of different soil types
varies widely depending mainly on parent material and the degree
to which weathering and leaching have influenced soil development.
Soils derived from limestone or chalk, and young marsh (polder)
soils are usually rich in Ca with a high content of $CaCO_3$. The
Ca content of such soils is often in the range of 10 to 20%.
Even the surface layer of soils developed on limestone, however,
can be low in Ca where leaching is excessive. Old soils, highly
weathered and leached under humid conditions, are generally low
in Ca. Two typical examples of such soils are podzols of the
temperate zone and the laterites of the humid tropics. In more
arid conditions high Ca contents in the upper soil layer may
occur in the form of an accumulation of gypsum ($CaSO_4.2H_2O$).

Calcium bearing minerals play an important role in
pedogenesis. Thus soils derived from Ca containing parent material
such as basalt and dolerite generally contain higher amounts of
secondary clay minerals. Soils developed from calcite, dolomite
and chalk mainly belong to the rendzina group of soils.   These
shallow soils contain appreciable amounts of $CaCO_3$ and for this
reason are alkaline in reaction. A high soil pH and the presence
of Ca^{2+} favour the formation of Ca-humate complexes and account
for the dark colour of this soil type.

The weathering of the primary Ca bearing minerals depends
considerably on the formation of H^+ in the soil. Hydrogen ions
and probably also chelating agents attack the Ca of the lattice
structure of minerals and thus cause a dissolution of the mineral
and a release of Ca^{2+}. These weathering processes along with
the release of Ca^{2+} from exchange sites of soil colloids by H^+

account for the considerable amounts of Ca leached under humid climatic conditions (COPPENET (1969). The rate of leaching of Ca^{2+} increases with the annual rainfall and with the content of Ca bearing minerals in the soil. Quantities of Ca leached under temperate conditions are in the range of 200 to 300 kg Ca/ha.

The weathering of carbonates is much dependent on the production of CO_2 in the soil. Calcite ($CaCO_3$) is a rather insoluble mineral, the solubility only being in the order of 10 to 15 mg Ca per litre (about 0.3 mM). In the presence of CO_2, however, $Ca(HCO_3)_2$ is formed which is much more water soluble.

$$CaCO_3 + CO_2 + H_2O \longrightarrow Ca(HCO_3)_2$$
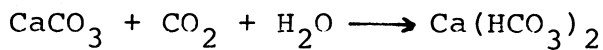
In soils containing free $CaCO_3$ the formation of $Ca(HCO_3)_2$ is thus an important means by which the leaching of Ca takes place. However, even in soils not containing $CaCO_3$, some $Ca(HCO_3)_2$ can be leached, as bicarbonate can also be produced from the dissociation of carbonic acid contained in rain water or from carbonic acid produced by the respiration of organic material in the soil. Hydrogen ions produced in the dissociation can release Ca^{2+} by weathering or by the exchange 2 H^+ for 1 Ca^{2+} from clay colloids. This explanation to some extent accounts for the reason why applications of organic material to soils increases Ca leaching. Druing organic matter decomposition there is an increase in CO_2 release and hence also in carbonic acid formation in the soil.

8.2. Calcium adsorption and soil solution.

Besides the Ca bearing minerals a substantial amount of Ca^{2+} is adsorbed to organic and inorganic soil colloids. This exchangeable Ca^{2+} is of particular importance for soil structure. Calcium promotes the coagulation of soil colloids and thus imporves soil structure and the stability of soil particles. For soils in which 2:1 clay minerals dominate, about 80% of the soil exchange capacity should be saturated with Ca^{2+} in order to maintain a satisfactory soil structure. For soils with kaolinite as the most important clay mineral a lower percentage of

Ca^{2+} saturation in the order of about 20% is recommended
(BROYER and STOUT 1959). The adsorption sites of the inorganic
soil colloids are not very selective for Ca^{2+}. As the electro-
static charge of Ca^{2+} is high due to its divalency and rather
thin hydration shell, Ca^{2+} is relatively strongly adsorbed to
a different kinds of clay minerals in the soil. The adsorption
bond of Ca^{2+} to organic colloids and especially to the humic
acids is more specific. Thus in chernozems and calcareous peat
soils, both of which soil types contain $CaCO_3$, the humic acids
are mainly present in the form of Ca humate. Calcium adsorbed
to soil colloids tends to equilibrate with the Ca^{2+} of the soil
solution. According to the investigations of NEMETH et al.
(1970) on a number of soil types, there is a fairly linear
relationship between the exchangeable Ca^{2+} and the Ca^{2+} of the
soil solution under equilibrium conditions (see Fig. 8.1.).

Most inorganic soils contain high enough levels of Ca^{2+}
in soil solution and their exchange sites are well enough
saturated with Ca^{2+}, to adequately meet crop demands. It thus
appears that liming is primarily a means of improving soil
structure and pH. On acid peat soils, however, as are frequently
used in horticulture, the natural Ca content can be so low
that plants suffer from Ca deficiency. Here the application
of Ca containing fertilizers is advisable.

8.3. Uptake and translocation

Higher plants often contain Ca in appreciable amounts and
generally in the order of about 5-30 mg Ca/g dm. These high
Ca contents, however, mainly result from the high Ca levels
in the soil solution rather than from the efficiency of the
Ca uptake mechanism of root cells. Generally the Ca^{2+} concentration
of the soil solution is about 10 times higher than that of K^+.
The uptake rate of Ca^{2+}, however, is usually lower than that of
K^+. The same is true for the uptake of other nutrient ions.
This indicates that plants have not developed such a highly
efficient uptake mechanism for Ca^{2+} as for other plant nutrients.
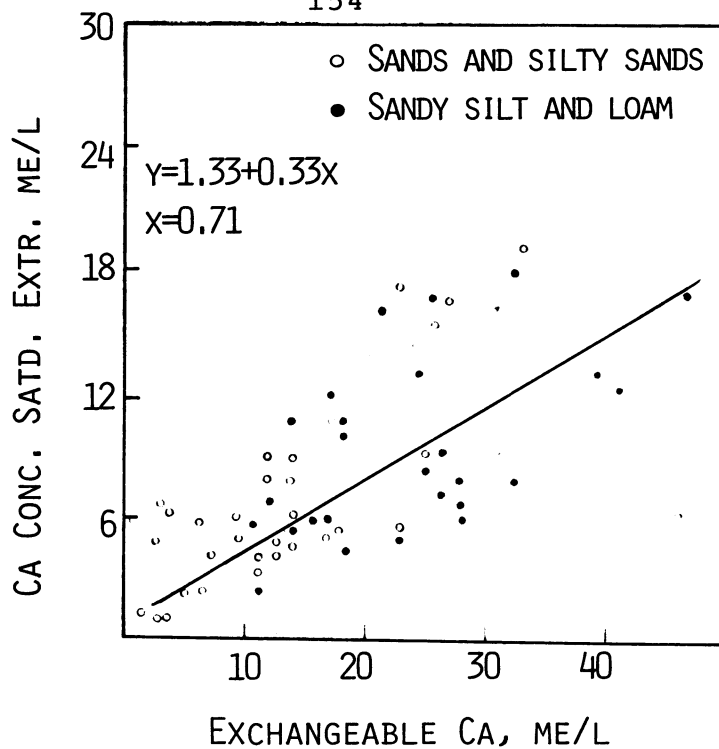
FIG. 8.1. CORRELATION BETWEEN EXCHANGEABLE CA AND SOIL SOLUTION CA CONCENTRATION FOR 72 DIFFERENT SOILS (AFTER NEMETH ET AL. (1970))
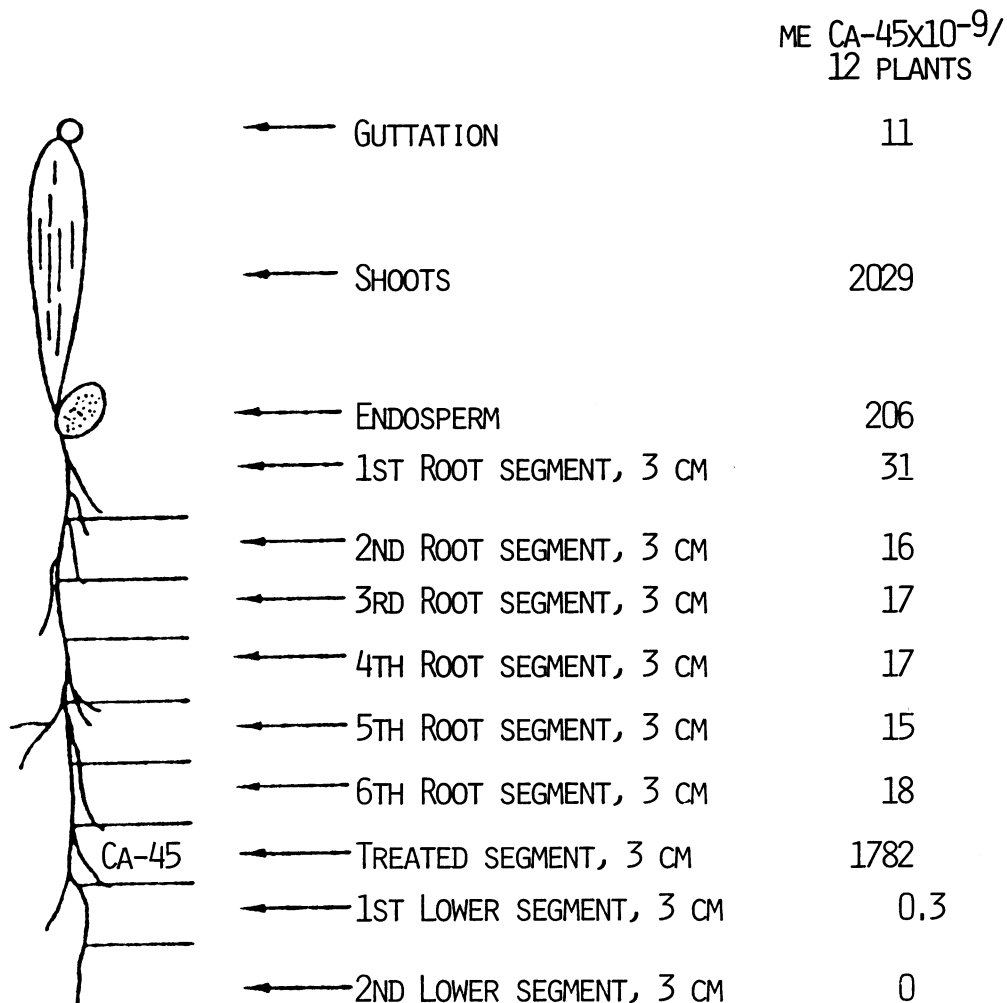
FIG. 8.2. DISTRIBUTION OF CA-45 IN A MAIZE SEEDLING FOLLOWING APPLICATION TO A SPECIFIC SECTION OF THE ROOT (AFTER MARSCHNER AND RICHTER (1974))

WALLACE et al. (1966) have shown that plants can grow satisfactorily when only very low levels of Ca are present in the nutrient medium (0.05mM) provided that other divalent ions are also maintained at low concentrations. The plants shown in these experiments were much poorer in Ca than field grown plants. Maize leaves contained only in the order of 0.1 mg Ca/g dm and tobacco leaves about 0.8 mg Ca/g dm. However, the plants were not Ca deficient and WALLACE suggests that the normally higher levels of Ca are necessary in some way to detoxify divalent metal cations.

Whether Ca^{2+} is taken up actively by plant roots as defined by transport against an electrochemical gradient through biological membranes, is still an open question. Experiments of MAAS (1969) with root segments of maize indicate that at least in the low concentration range (0.005 - 0.05 mM Ca) the uptake was metabolically controlled, whereas at higher concentrations (5-50 mM ca) diffusion was the main process responsible for Ca uptake. The rate of uptake was also dependent on the counter anion, being highest with NO_3^-. This was followed by chloride and was lowest with sulphate. CLARKSON and co-workers have carried out experiments investigating the ability of different parts of roots to absorb and translocate nutrients to the tops. The technique used has been to expose a small section of root from the intact plant to a radioactive tracer whilst supplying the rest of the plant root with the same bathing solution. Such experiments have revealed that ions differ markedly in behaviour. Potassium and phosphate are taken up and translocated to the tops almost equally well over the whole length of the root whereas the movement of Ca and Mg to the shoots is largely restricted to a region just behind the root tips. This difference in behaviour has been explained in terms of structure and particularly the development of the casparian strip.

From the above findings Ca uptake appears mainly to be a passive process. The same holds for the translocation of Ca^{2+} within the plant. Calcium in the xylem sap is translocated in upward direction with the transpiration stream. Thus to a large extent the intensity of transpiration controls the upward

translocation rate of Ca^{2+}. This has been demonstrated
in experiments of MICHAEL and MARSCHNER (1962) in which both
oat plants and white mustard plants were exposed to different
air humidities. When the air humidity was high (low transpiration
conditions) there was a decrease in translocation of Ca^{2+} to
the upper plant parts and also a depression in the rate of
Ca^{2+} uptake.

The rate of downward translocation of Ca^{2+} is very low
due to the fact that Ca^{2+} is hardly transported in the phloem.
Thus RIOS and PEARSON (1964) observed that the downward transport
of Ca in cotton plants was inadequate to support root growth
in the Ca deficient nutrient solution portion of a split root
medium. Once Ca is deposited in older leaves it cannot be
mobilized to the growing tips. This has been convincingly
shown by LONERAGAN and SNOWBALL (1969) using autoradiographs.
The plants were not able to utilize Ca from older leaves for
the growth of meristematic tissues, even when Ca deficiency
symptoms were observed in the growing tips. Another example
demonstrating poor Ca transport in the phloem has been presented
by MARSCHNER and RICHTER (1974). These workers supplied root
segments of young plants with labelled Ca^{2+}. It was found that this
Ca was translocated exclusively to the upper plant organs
and not to the root tips. Some data of this experiment are shown
in Figure 8.2.

8.4. Functions of Ca

Calcium is required for cell elongation and cell division.
The exact reactions in which Ca^{2+} is involved in these processes,
however, are not yet known. There is much evidence that Ca
plays an essential role in biological membranes. Micro electron
probe studies of ROLAND and BESSOLES (1968) have thus revealed
that Ca is located especially in the border zone between the
cytoplasm and cell walls indicating high Ca contents in the
plasmalemma.

Calcium defiency obiously impairs membrane permeability, and this also affects retention of cellular diffusible compounds (DICKONSON (1967)). Membranes thus become more leaky. As the deficiency progresses there is a general disintegration of membrane structures. In whole plants the disorder occurs first in meristematic tissues such as root tips, growing points of upper plant parts and storage tissues. Calcium also appears to play a role in the inhibition of abscission and delays leaf senescence (POOVAIAH and LEOPOLD (1973)).

In contrast to other cation species, Ca^{2+} plays a comparatively minor role in enzyme activation.

8.5. Calcium deficiency and disorders

As already outlined above Ca deficiency is characterized by a reduction in growth of meristematic tissues. The deficiency can be first observed in the growing tips and youngest leaves. These become deformed and chlorotic and at a more advanced stage necrosis occurs at the leaf margins. The affected tissues become soft due to a dissolution of the cell walls. Brown substances occur which accumulate in intracellular spaces and also in the vascular tissue where they can affect the transport mechanism (BUSSLER (1963)).

Absolute Ca deficiency as described above occurs relatively seldom as most mineral soils are rich in available Ca. Indirect Ca deficiency resulting from an undersupply of Ca to fruit and storage tissues, however, is an often observed disorder. SHEAR (1975) cites a list of 35 such Ca related disorders in fruits and vegetables. In apple the disease is called bitter pit as the whole of the surface of the apple is pitted small brown necrotic spots. In tomato the disease is known as blossom-end rot and is characterized by a cellular breakdown at the distal end of the fruit. A similar Ca deficiency disorder occurs in water melon. All these fruits are mainly supplied with Ca^{2+} by the transpiration stream which translocates Ca^{2+} directly from the soil solution. If the xylem sap is low in Ca^{2+} or the rate of transpiration of the fruits is poor as occurs under humid conditions, inadequate levels of Ca may be supplied to the fruits and deficiency symptoms may result. Calcium translocation in the xylem sap

may be depressed by NH_4-nutrition, soil water stress, soil salt concentrations. These factors have therefore been found to favour the occurrence of blossom-end rot in tomatoes.

Calcium appears only to be transported from the soil solution to the upper plant parts via root tips. Any factor which prevents the growth of new roots (poor aeration, low temperatures etc.) may therefore be expected to prevent Ca uptake and thus induce deficiency. This may account for the observation that Ca related disorders often occurs on soils adequately supplied with Ca, and that the weather appears to be a controlling factor.

The importance of maintaining an adequate level of Ca in the xylem sap is very clear from the results of CHIU and BOULD (1976). These workers observed that Ca stress during the fruiting stage of tomatoes caused serious blossom end rot of fruits thus showing that Ca absorbed by the plants before fruiting was not subsequently available for fruit development. The results provide further evidence of the immobility of Ca in the phloem. In addition they also indicate that leaf analysis for Ca is not a reliable index for predicting Ca deficiency in fruits. Crop responses to calcium fertilization will be discussed under liming of acid soils.

Magnesium in Soils and in Crop Nutrition

9.1. Soil Magnesium

The Mg content of most soils generally lies in the range of between 0.05% for sandy soils and 0.5% for clay soils, higher levels are found in clay soils because Mg is present in relatively easily weatherable ferromagnesian minerals, such as biotite, serpentine, hornblende and olivine. In addition it occurs in secondary clay minerals including chlorite, vermiculite, illite and montmorillonite. Some soils contain Mg as $MgCO_3$ or dolomite ($CaCO_3$ $MgCO_3$). In arid or semi-arid regions soils may contain large amounts of Mg as $MgSO_4$.

The distribution of Mg in soils may be considered in the same way as the distribution of K and divided into non-exchangeable, exchangeable and water soluble forms. These three forms are in equilibrium. By far the largest fraction of soil Mg is in the non exchangeable form which includes all the Mg in the primary

minerals and most of the Mg in the secondary clay minerals.
Generally this fraction has not been considered of importance in
the direct release of Mg to plants (SALMON and ARNOLD (1963)).
More recent evidence suggests, however, that in some soils non
exchangeable Mg may be more available than was previously believed.
In soils containing high contents of expandable clay minerals both
lattice and interlayer Mg may be available to plants (CHRISTENSON
and DOLL (1973)), although the release rate of this Mg is low in
comparison with crop demand. Exchangeable Mg is usually in the
order of about 5% of the total Mg and this fraction along with
the water soluble Mg is of greatest importance in the supply to
plants. Exchangeable Mg normally constitutes from 4 to 20% of
the cation exchange capacity. It is thus normally considerably
lower than Ca which is in the order of 80% and higher than K
which can be up to about 5%. Magnesium in the soil solution like
Ca^{2+} is present in fairly high concentrations and often between
2 to 5 mM, although the levels can vary considerably and values
between 0.2 to 150 mM have been reported. Some Mg occurs in soil
in association with organic matter, but this fraction is usually
small and less than 1% of the total soil Mg.

9.2. Uptake and translocation

Magnesium is generally taken up by plants in lower quantities
than Ca^{2+} or K^+. The contents of Mg in plant tissues is usually
in order of 0.5% of the dry matter. Cation competitive effects
in uptake are of particular importance for Mg^{2+} as such effects
frequently lead to Mg deficiency in the field. The competitive
effect of NH_4^+ on Mg^{2+} uptake was observed by E.G. MULDER (1956)
The mechanism of the competition between NH_4^+ and Mg^{2+} is not yet
clear. It probably depends on both the H^+ released during NH_4^+
incorporation, as well as on the direct effect of the NH_4^+ itself.
D. MULDER (1950) reported that high levels of K^+ in the soil
resulted in Mg deficiency in apple leaves. Many other authors
have observed this antagonism both in water culture and field
experiments. The level of Mg^{2+} in the nutrient medium is also
of importance in relation to Mn uptake. LÖHNIS (1960) showed in
a number of plant species that it is possible to prevent the
appearance of Mn toxicity by increasing the level of Mg supply.
These antagonistic and synergistic ionic effects in Mg uptake

appear to relate to ionic balance effects rather than to specific competitive effects for carriers.

Although high levels of K nutrition often depress total Mg uptake, increasing K supply affects the Mg content of different plant organs to a varying extent. As can be seen from Table 9.1. increasing K supply reduced the Mg content of tomato leaves and roots considerably. The Mg content in the fruits, however, was somewhat increased by the higher levels of K in the nutrient solution. This observation was obviously not accidental as it was found at all six harvests of the tomatoes (VIRO (1973). LINSER and HERWIG (1968) also reported that increased K supply resulted in higher Mg contents in the seeds of flax. It thus appears that K^+ promotes the translocation of Mg^{2+} towards fruits and storage tissues.

In some ways the transport of Mg^{2+} in the plant resembles that of Ca^{2+}. Higher levels of Mg^{2+} are usually found in the older than in younger leaves. Magnesium like Ca^{2+} too moves upwards in the transpiration stream. In contrast to Ca^{2+}, however, Mg^{2+} is mobile in the phloem.

9.3. Functions of Mg

In plant tissues a high proportion of the total Mg, often over 70%, is diffusible and associated with inorganic anions and organic acid anions such as malate and citrate. Magnesium is also associated with indiffusible anions including oxalate and pectate (KIRKBY and MENGEL (1967)). Cereal grains contain Mg as the salt of inositol hexaphosphoric acid (phytic acid). The most well known role of Mg is its occurence at the centre of the chlorophyll molecule. The fraction of the total plant Mg associated with chlorophyll, however, is relatively small and only in the order of 15 to 20%. Even in plants deficient in Mg the amount does not exceed 30%. Besides its function in the chlorophyll molecule Mg^{2+} is required in other physiological processes. One major role of Mg^{2+} is as a cofactor in almost all enzymes activating phosphorylation processes. Magnesium (Mg^{2+}) forms a bridge between the pyrophosphate structure of ATP or ADP and the enzyme molecule. The fundamental process of energy transfer occurs in

TABLE 9.1. EFFECT OF AN INCREASING K SUPPLY ON THE CATION OF VARIOUS ORGANS OF THE TOMATO PLANT (VIRO (1973))

TREATMENT MM K/L NUTRIENT SOLUTION	K	NA	CA	MG
		IN % DM		
	LEAVES			
2	0.5	0.40	4.7	0.61
10	3.3	0.19	4.2	0.27
20	4.2	0.18	3.3	0.15
	ROOTS			
2	0.2	0.36	3.9	0.33
10	2.2	0.25	3.2	0.31
20	2.4	0.13	3.3	0.26
	FRUITS			
2	1.6	0.10	0.09	0.07
10	2.5	0.07	0.08	0.08
20	2.7	0.06	0.07	0.09

TABLE 9.2. MINERAL MG FERTILIZERS

	%	MGO
MAGNESIAN LIMESTONE (MG CARBONATE)	5	20
GROUND BURNT MAGNESIAN LIME (MG OXIDE)	10	33
KIESERITE ($MgSO_4 \cdot H_2O$)	27	
EPSOM SALTS ($MgSO_4 \cdot 7\ H_2O$)	16	
SULPHATE OF POTASH MAGNESIA ($K_2SO_4 \cdot MgSO_4$)	11	
MAGNESITE ($MgCO_3$)	45	

(Mengel and Kirkby, 1982)

photosynthesis, glycolyis, the tricarboxylic acid cycle and respiration. Magnesium is therefore important throughout the metabolism. Magnesium is not the only ion able to activate phosphorylation. It can be substituted by Mn^{2+} and to a lesser extent by other cations. Quite apart from its function in the chlorophyll molecule, inadequate levels of Mg in the plant can inhibit CO_2 assimilation. Magnesium is required both in photo-phosphorylation as well as in phosphorylation reactions which limit the regeneration of ribulose diphosphate in the Calvin cycle. It is also required to activate the enzyme ribulose diphosphate carboxylase (RuDP carboxylase). NEALES (1955) reported that in barley plant with Mg contents lower than 0.12 mg Mg/g fresh weight no net assimilation could be observed. This observation is con-sistent with the lower starch contents found in Mg deficient pota-toes and a decrease in the carbohydrate content in the grain of Mg deficient oats. The beneficial effect of increasing the Mg content of the maize leaf on CO_2 assimilation is shown in Figure 9.1 (LEASLEE and MOSS (1966)).

Nitrogen metabolism is also influenced by Mg nutrition. The influence of increasing Mg supply on the protein content in roots and shoots of young oat plants is shown in Figure 9.2. Generally when plants are Mg deficient the proportion of protein N decreases and that of non-protein N increases (HAEDER and MENGEL (1969). From this it may be concluded that Mg deficiency inhibits protein synthesis.

9.4. Magnesium deficiency

Magnesium deficiency symptoms differ between plant species although some general characteristics are apparent. As already mentioned Mg^{2+} is mobile in the plant and deficiency always begins in the older and then moves to the younger leaves. Intervenial yellowing or chlorosis occurs and in extreme cases the areas become necrotic. Another characteristics particularly of plants exposed to strong sunlight is their generally withered appearance, reminiscent of K deficiency, where the water content of the plant is disturbed. Individual leaves suffering from Mg deficiency, however, are stiff and brittle and the intercostal veins are twisted. Mg deficient leaves often fall prematurely. In cereals and the monocots in
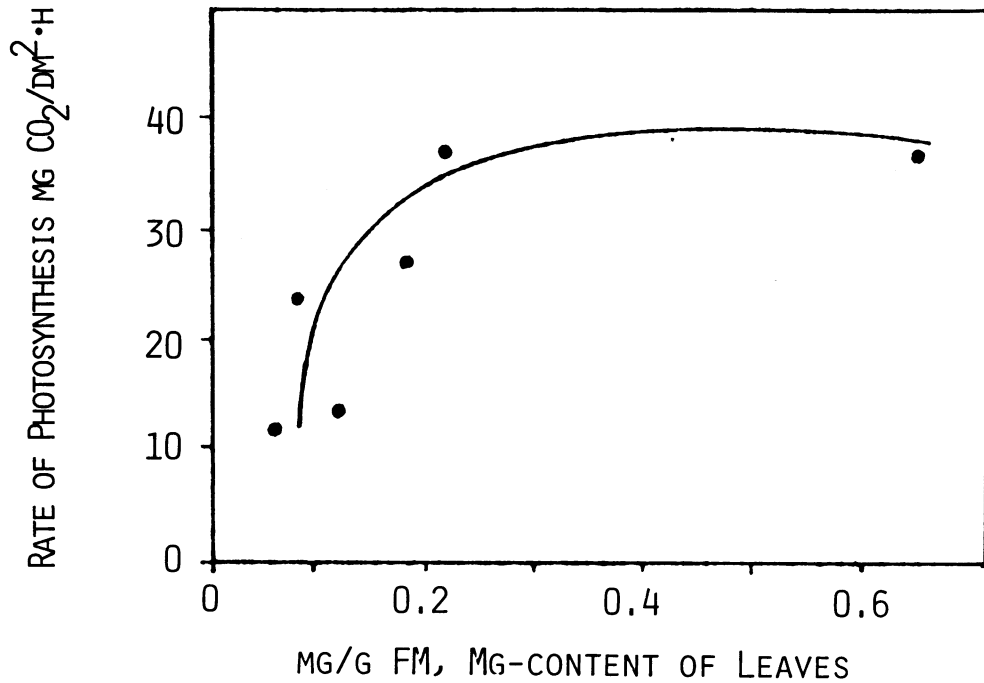
FIG. 9.1. RELATIONSHIP BETWEEN MG CONTENT OF MAIZE LEAVES AND CO_2 ASSIMILATION (AFTER PEASLEE AND MOSS (1966))
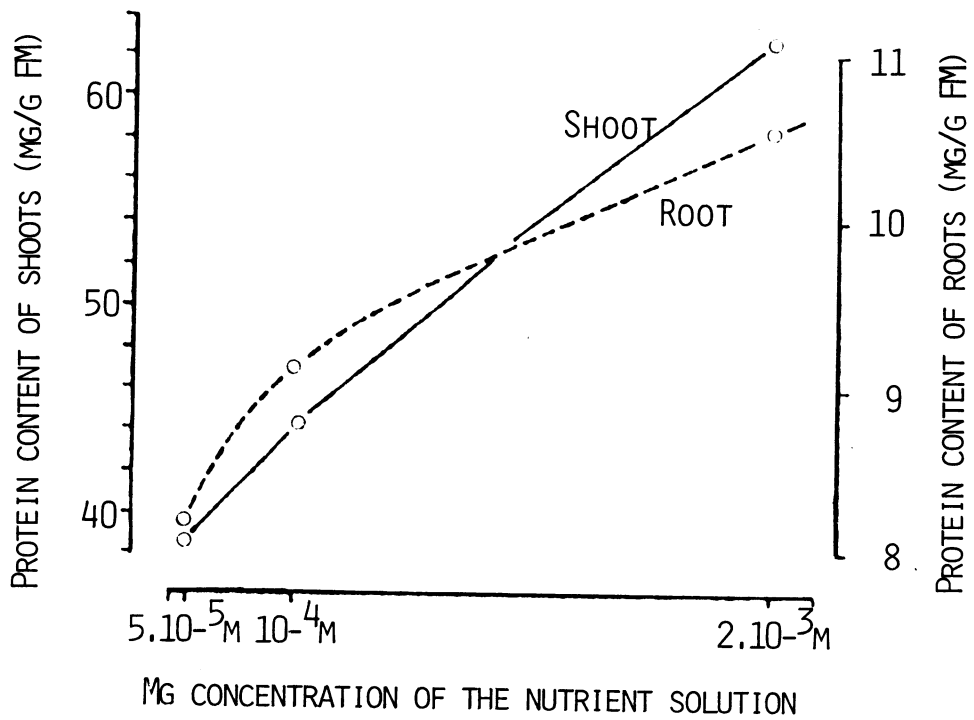
FIG. 9.2. EFFECT OF MG SUPPLY ON THE PROTEIN CONTENT IN SHOOTS AND ROOTS OF YOUNG OAT PLANTS (AFTER HEADER AND MENGEL (1969))

general the appearance of Mg deficiency is different. As in the
case of the dicots, the water and carbohydrate metabolism of the
plant is also affected and deficiency begins in the older leaves.
With the cereals, however, the base of the leaf first shows small
dark green spots of chlorophyll accumulation which are apparent
against the pale yellow background colour of the leaf. In more
advanced stages of deficiency the leaves become more chlorotic and
striped. Necrosis occurs particularly at the tips of the leaf.
The symptoms are the same for wheat, oats, rye and also for maize
in the early stages. As the plants age, however, the leaves of
maize take on a more spotted appearance.

In leaf tissue the threshold value for the occurrence of defi-
ciency symptoms is in the region of about 2 mg/g dry matter,
although this is dependent on a number of factors including
plant species. WARD and MILLER (1969) observed Mg deficiency
symptoms in tomato leaves when the Mg content dropped below
3 mg Mg/g dry matter. Plants inadequately supplied with Mg^{2+}
often show a delay of the reproductive phase. A detailed de-
sription of deficiency symptoms in many crops and the Mg levels
in different plant species under varying conditions may be ob-
tained from the data of EMBLETON (1966).

9.5. Crop requirements and critical levels

The amounts of Mg taken up by some important crop plants is shown
in Table 6.3. For arable crops the average uptake is in the
region of about 10-25 kg Mg/ha/yr and generally the uptake of root
crops is about double that of cereals. Sugar beet, potatoes, fruit
and glasshouse crops are particularly prone to Mg-deficiency.
In recent years the importance of Mg as a fertilizer has increased.
Previously Mg was applied unwittingly as an impurity along with
other fertilizers. The high purity of fertilizers used at the
present day, however, means that this source of Mg application to
the soil no longer exists. Increased crop yields resulting from
higher applications of non-Mg containing fertilizers have also
placed a greater demand on the soil for Mg. High levels of K^+
or NH_4^+ as already mentioned restrict Mg^{2+} uptake by plants.
For these reasons Mg deficiency in crop plants is becoming more
frequent and Mg applications are now common. Deficiencies occur
particularly in highly leached humus acid soils or on sandy soils

which have been given heavy dressings of lime. In some cases Mg
deficiency occurs on soils high in K. The importance of ion
antagonism in relation to Mg uptake has already been stressed.
Clearly on acid soils it is possible to have a H^+ or even possibly
an Al^{3+} competition for Mg^{2+} uptake, whereas Ca^{2+} competition may
occur on highly limed soils. Figure 9.3 from STENUIT (1959) shows
the relationship between soil pH and the intensity of Mg deficiency
in oats grown in sandy soils. At a pH of about 5 the possibility
of the occurrence of Mg deficiency is at a minimum. Lowering or
raising pH depresses Mg uptake as a result of H^+ or Ca^{2+} compe-
tition. From this discussion it is clear that the presence and
concentrations of H^+, K^+ and Ca^{2+} in the root environment can con-
siderably influence the uptake of Mg^{2+} by crops.

In experiments with sugar beet TINKER (1967) obtained responses
in soils with cation exchange capacities of 5 to 10 me/100g soil
when they contained less than 0.2 me Mg/100 g soil (2 to 4% of the
exchange capacity or 24 ppm exchangeable Mg). More recently re-
porting on the same crop from a survey of 60 field experiments
DRAYCOTT and DURRANT (1971) have suggested a limit of 35 ppm
exchangeable soil Mg^{2+} and 0.4 mg Mg/g dry matter of the leaf as
critical levels at which no further yield increases result from
Mg-fertilizer.

9.6. Magnesium fertilizers

The major Mg fertilizers used and their approximate Mg contents
are shown in Table 9.2. Magnesium is supplied in most cases
as carbonate, oxide or a sulphate. In general sulphate fertilizers
are more rapidly effective than carbonate fertilizers but are also
more expensive. Applications of dolomitic limestone are particul-
arly useful on acid soils which need regular liming. Decomposition
of the dolomite is also assisted by low soil pH. On more neutral
soils $MgSO_4$ e.g. kieserite is more appropriate particularly on
arable land where high levels of Mg are rapidly required.

The various form of $MgSO_4$ differ considerably in solubility.
Epsom salts $MgSO_4$ 7 H_2O although more expensive is more soluble
than kieserite ($MgSO_4$ H_2O). This has a practical significance,
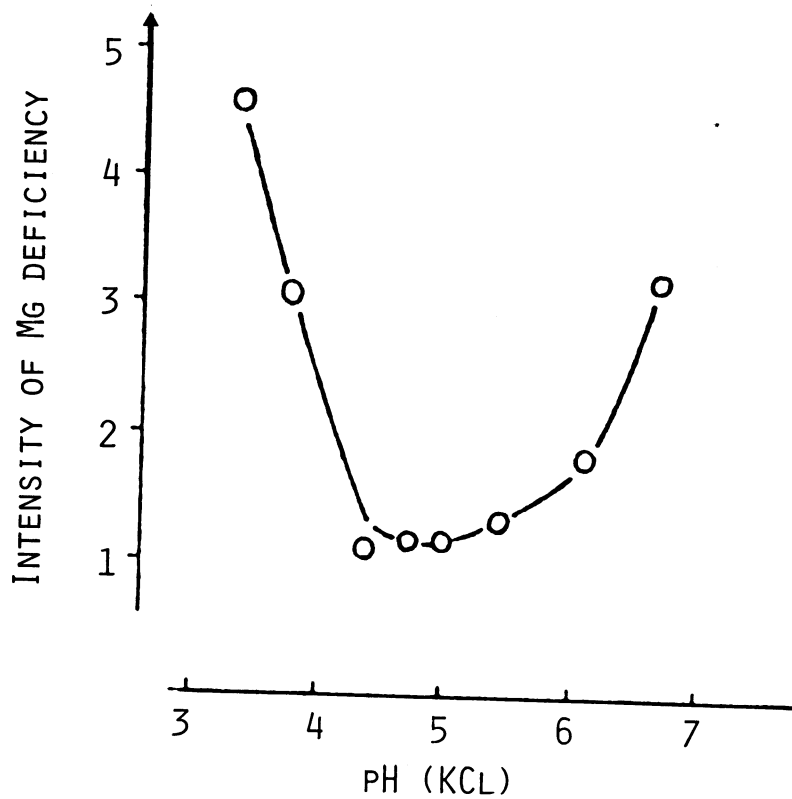
FIG. 9.3. MG DEFICIENCY SYMPTOMS IN OATS AND SOIL PH
(AFTER STENUIT (1959))

for, as has been pointed out by COOKE (1972), whilst 500 kg/ha $MgSO_4$ as kieserite applied to soil may be needed to prevent Mg deficiency in tomatoes, the trouble can be controlled by spraying 35 kg/ha of Epsom salt ($MgSO_4$ 7 H_2O) dissolved in 400 l water applied on a number of occasions over the growing season. Fertilizers containing only samller percentages of Mg such as kainite, basic slags and some PK and NPK fertilizers, are useful in maintaining the Mg level of the soil. In cases, however, where Mg deficiency is suspected higher graded Mg fertilizers are prefered. Mg problems in soils and plants are also discussed under liming of acid soils.

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ZINC IN SOILS AND IN CROP NUTRITION

10.1 Zinc Deficiency Problems

Zinc deficiency is probably the most widespread micronutrient disorder in tropical crops and particularly rice. It occurs in parts of India, Pakistan, the Philippines, and Colombia under lowland conditions (Tanaka and Yoshida, 1970; CIAT, 1971; IRRI, 1972). It also occurs throughout the Cerrado of Brazil under upland conditions (DeSouza and Hiroce, 1970).

In India, more research effects have gone into zinc fertili- sation than in all the remaining micronutrient deficiency disorders put together. For example, based upon the work done in the ICAR's Coordinated Micronutrient Scheme, Katyal, et al. (1980) concluded that out of about 55,000 soil samples analysed so far, nearly 50 per cent fell into zinc deficient category (Table 10.1), whereas the deficiency of remaining micronutrient cations was confined to less than 12 per cent of the samples.

Incidence of zinc deficiency is more on alkaline, low organic matter, light textured soils. Low temperature, removal of top soil and poor drainage aggrevate zinc deficiency.

10.2 Soil Zinc

The average Zn content of the lithosphere is about 80 ppm (Goldschmidt, 1954). In soils it is usually present in the range of 10-300 ppm occurring in a number of different mine- rals. The ionic radius of Zn^{2+} is very similar to that of Fe^{2+} and Mg^{2+}. To some extent therefore Zn^{2+} may substitute for these ions by isomorphous replacement in mineral struc- tures, in particular in the ferromagnesian minerals augite, hornblende and biotite. The occurrence of Zn in these minerals makes up the bulk of Zn in many soils. In addition Zn forms a number of salts including ZnS, sphalerite (ZnFe)S, zincite ZnO, and smithsonite $ZnCO_3$. Apart from ZnS, however, which may be present under reducing conditions, most of these salts are too soluble to persist in soils for any length of time. The two Zn-silicates $ZnSiO_3$ and Zn_2SiO_4 (willemite) also occur in some soils.

As well as in the occurrence in minerals, Zn may be found on exchange sites of clay minerals and organic matter or adsorbed on solid surfaces. The element may be adsorbed as Zn^{2+}, $ZnOH^+$ or $ZnCl^+$ and may also become nonextractable possibly by entering holes normally occupied by Al^{3+} in the octahedral layer. According to Grimme (1968) the intensity of Zn adsorption by goethite increases as the pH rises and for this reason the mobility of Zn is particularly restricted in neutral and alkaline soils. The level of Zn in soil solution is very low. Hodgson et al. (1966) reported values of between about 3×10^{-8} to 3×10^{-6} M. Zn solubility is especially low on soils of high pH and particularly when $CaCO_3$ is present.

Zn interacts with soil organic matter, and both soluble and insoluble Zn organic complexes are formed. According to Hodgson et al. (1966), on average, 60% of the soluble Zn in soil occurs in soluble Zn organic complexes.

10.3 Uptake and translocation

The levels of Zn in plant material are low and as shown in Table 10.2 are generally in the order of up to 100 ppm in the dry matter. The Zn requirement of plants is correspondingly small. The availability and uptake of Zn and other micronutrients has been considered by Loneragan (1975) in an excellent review paper.

There is considerable disagreement in the literature as to whether Zn uptake is active or passive. This has been discussed in some detail by Moore (1972). He holds the view that on balance the evidence suggests that Zn uptake is metabolically controlled.

Evidence for active uptake has been presented by Schmid et al. (1965) using barley roots, who observed a steady state uptake rate for Zn typical of metabolic uptake. Zn uptake was considerably reduced by low temperature and metabolic inhibitors. The same observation was made in sugar cane leaf. In addition both experiments showed that Cu strongly inhibits Zn uptake. It seems possible that these two ions complete for the same carrier site. Similar competitive effects of Fe and Mn on Zn uptake have been reported in rice seedlings

TABLE 10.1. DISTRIBUTION OF MICRONUTRIENT DIFICIENT SOIL
SAMPLES

ELEMENT	NO. OF SAMPLES	PER CENT DEFICIENT
ZN	55,180	47
FE	49,436	11
MN	47,203	5
CU	50,428	1

SOURCE: KATYAL ET AL. (1980)

TABLE 10.2. ZINC CONTENT OF VARIOUS CROPS PPM DM (BOEILLE AND
LINDSAY (1969))

	DEFICIENT	LOW	SUFFICIENT	HIGH
APPLE LEAVES	0-15	16-20	21- 50	51
CITRUS LEAVES	0-15	16-25	26- 80	81-200
LUCERNE TOPS	0-15	16-20	21- 70	71
MAIZE LEAVES	0-10	11-20	21- 70	71-150
SOYA BEAN TOPS	0-10	11-20	21- 70	71-150
TOMATO LEAVES	0-10	11-20	21-120	>120

TABLE 10.3. EFFECT OF ZINC APPLICATION ON THE TOTAL DRY MATTER
YIELD OF MAIZE. (SINGH & STEENBERG, 1974)

ZN RATE PPM	TOTAL DRY MATTER YIELD (G/POT)	
	3 WEEKS AFTER PLANTING	6 WEEKS AFTER PLANTING
0	4.27	15.93
0A	4.36	12.10
5A	5.77	17.51
25A	5.42	18.53
LSD	1.0	4.01

A = ACTIVITY OF ^{65}ZN (50 µC/POT)

(Giordano et al., 1974). In addition these workers showed that severe retardation of Zn absorption is brought about by various metabolic inhibitors. This is again indicative of an active process for Zn uptake.

The form in which Zn is translocated from the roots to the upper plant parts is not known. However, Zn has been detected in xylem exudates of decapitated tomato and soya bean plants in considerably higher concentrations than in the bathing solution of the roots (Tiffin, 1967). Electrophoretic evidence indicates that Zn is not bound to stable ligands as is the case with Cu^{2+}, Ni^{2+} and Fe^{3+}. In tomato exudates Tiffin (1967) observed that Zn is slightly cathodic and concluded that it is not translocated as citrate, as zinc citrate complexes are anodic. The mobility of Zn in plants is not great. Zinc accumulates in root tissues especially when Zn supply is high. In older leaves Zn can become very immobile.

10.4 Functions of Zn

In its function in some enzyme systems, Zn^{2+} resembles Mn^{2+} and Mg^{2+} in that it brings about the binding and conformation between enzyme and substrate. A number of enzymes including enolase are thus activated in more or less the same way by Mn^{2+}, Mg^{2+} or Zn^{2+}. Until relatively recently the only authenticated enzyme specifically activated by Zn^{2+} was carbonic anhydrase. This enzyme catalyses the reaction

$$H_2O + CO_2 \rightleftharpoons H^+ + HCO_3^-$$
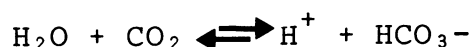
This enzyme has been shown to be localized in the chloroplasts (Jacobson et al., 1975). These workers suppose that it functions in mediating short term transient pH effects thus acting as a buffer.

Zn is closely involved in the N-metabolism of the plant. Price et al. (1972) cite a number of references indicating that the earliest possible causal event of Zn deficiency is a sharp decrease in the levels of RNA and the ribosome content of cells. This reduction in RNA synthesis leads to an inhibition

of protein formation whilst glucose, nonprotein N and DNA are relatively increased.

Zn is required in the synthesis of tryptophane (Tsui, 1948). As tryptophane is also a precursor of indole acetic acid the formation of this growth substance is also indirectly influenced by Zn.

In Zn deficient tomato plants Tsui (1948) observed low rates of stem elongation, low auxin activities and low tryptophane contents. More recently Salami and Kenefick (1970) have confirmed this work growing maize in nutrient solution. These workers found that Zn deficiency symptoms could be eliminated by additions of either Zn or tryptophane to the nutrient medium thus providing indirect evidence of the necessity of Zn for the synthesis of optimum tryptophane levels. In complete contrast to these results Takaki and Kushizaki (1970) who also worked with maize found higher levels of tryptophane in Zn deficient plants and concluded that Zn is required in the synthesis of indole acetic acid from tryptophane. As has been pointed out by Price (1970), a causal relationship between Zn, tryptophane and indole acetic acid has yet to be established.

According to Jyung et al. (1975) Zn has a possible role in plant metabolism involved in starch formation.

Zinc along with Cu has been shown to be a constituent of the enzyme superoxide dismutase. This enzyme brings about the decomposition of O_2- radicals which can be produced from molecular O_2. It thus protects aerobic organisms from attack by O_2-radicals.

10.5 Zinc deficiency

Plants suffering from Zn-deficiency often show chlorosis in the interveinal areas of the leaf. These areas are pale green, yellow, or even white. In the monocots and particularly in maize, chlorotic bands form on either side of the midrib of the leaf. In fruit trees leaf development is adversely affec-ted. Unevenly distributed clusters or rosettes of small stiff

leaves are formed at the ends of the young shoots. Frequently the shoots die off and the leaves fall prematurely. In apple trees the disease occurs in the early part of the year and is known as rosette or little-leaf. Not only is leaf development restricted. Fewer buds are formed and of those that are, many remain closed. Crop yields are consequently drastically reduced. The bark of Zn deficient trees too is characteristically affected and is rough and brittle. Zn deficiency is closely related to the inhibition of RNA synthesis.

10.6 Crop requirement and availability

Zn deficiency is one of the commonest micronutrient deficiencies and it is becoming increasingly significant in crop production. The susceptibility of crop plants to Zn deficiency varies considerably depending on species and even cultivars. The cereals such as oats, barley, wheat, and rye as well as the grasses are rather insensitive. Other crops such as potatoes, tomatoes, sugar beet, and lucerne are only moderately sensitive whilst some crops including maize, hops, flax, and field beans are highly susceptible to Zn deficiency. This final group along with fruit trees, citrus and grapes may be regarded as test crops for Zn availability.

In most soils the total Zn content by far exceeds crop requirement and availability is the important limiting factor.

As already mentioned the concentration of water soluble Zn in soil solution falls with increasing pH. Liming thus depresses Zn uptake, as has been observed in ryegrass by Cottenie and Kiekens (1974). From the practical viewpoint this is of importance as Zn deficiency occurs more usually on naturally high pH soils or on highly limed soils. Singh & Steenberg (1974) found good response of zinc in maize in a highly limed sandy soil (Table 10.3).

Calcareous soils are particularly prone to Zn-deficiency. Tanaka and Yoshida (1970) in surveying the most important rice growing areas of Asia found that Zn deficiency of rice only occurs on soils with high pH and in particular on calcareous

soils of high pH. In paddy rice Zn deficiency is often accompanied by visible symptoms of Fe toxicity.

In an analogous way to Fe the availability of Zn also depends on the content of chelating agents in the soil, which can be exuded by plant roots or result from the decomposition of organic matter (Lindsay, 1974). This is probably the reason, why many workers have established a high correlation between available Zn and soil organic matter and why Zn deficiency frequently occurs on sites where the organic surface soil has been removed. According to Lindsay (1974) various metallic ions compete for the binding sites of chelating agents. The Zn^{2+} of the Zn EDTA complex is completely replaced by Ca^{2+} at higher pH values. This replacement of Zn^{2+} by Ca^{2+} may well account for the low Zn availability on high pH calcarious soils.

A low total Zn level may be an important contributory factor but availability factors also play a role. In practice high available phosphate levels in soil are well known to reduce Zn availability. It was formerly held that this occurred because the formation of zinc phosphate $Zn_3(PO_4)_2 4H_2O$ in the soil reduced the Zn concentration in the soil solution to deficiency levels. However this was not observed in experiments testing the solubility of this compound under various conditions (Jurinak and Inouye, 1962). These workers found that even when the solubility was at a minimum it was over 100 times greater than the Zn concentration required for maximum growth as determined by Carroll and Loneragen (1969). It seems likely therefore that the physiological effects of Zn/P interactions in the plants are more important in limiting Zn availability than Zn/P soil relationships.

10.7 Zinc application

Zn uptake by crops is usually less than 0.5 kg/ha/yr. In practice Zn deficiency is easy to correct either by spraying or by soil application with Zn fertilizers. Applications are usually in the range of about 4 kg/ha of Zn and this is effective for 3 to 8 years. $ZnSO_4$ is the most commonly used fertilizer largely because of its high solubility.

While zinc sulphate is the common zinc carrier, limited
attempts have been made to find out alternative zinc sour-
ces. In such instances, comparisons have been made bet-
ween sparingly soluble salts like zinc carbonate, zinc phos-
phate and zinc oxide and soluble zinc sulphate. Whether
judged by grain yield or zinc content of straw, despite low
water solubility the performance of these carriers was more
or less equal to soluble zinc sulphate for wheat (Sinha &
Associate, 1977).

On acid sandy soils it may be preferable to spray the crop
or use a less readily available Zn source because $ZnSO_4$ is
very easily leached. The same applies to alkaline soils
which fix Zn very strongly. Under such conditions Zn che-
lates are often used.

The possibility of complexing zinc with fulvic acid obtained
from organic manures has already been established (Prasad
& Sinha, 1976). Its superiority has also been proved (Pra-
sad & Sinha, 1976). There is need to develop technology
for their manufacture.

Even continuous use of organic manures not only counteracts
the depletion of zinc and other micronutrients but has been
shown to augment the micronutrient availability from soil
also. Organic manures contain micronutrients and their addi-
tions to soil will build up their levels. This is, corrobo-
rated by data from a permanent manurial experiment in India.
Without FYM, after 10 years, the net effect was a 50 per
cent decline in available zinc while the FYM treatment boo-
sted the available zinc up by 37 per cent. Favourable effect
of manures on the available zinc is supported by the data
of Sharma and Meelu (1975), Mann et al., (1978).

With the intensification of agricultural production in tro-
pical and subtropical zones the occurrence of Zn deficiency
has increased. De (1974) found enormous grain yield increa-
ses of pearl millet by an application of $ZnSO_4$/ha on sandy
soils in India.

Singh & Singh (1976, 1978) found highly significant increase
in rice yield when zinc enriched seedlings were transplanted

TABLE 10.4. EFFECT OF ZINC SOURCES ON GRAIN YIELD OF WHEAT AND ZINC CONTENT OF WHEAT STRAW

TREATMENT	GRAIN YIELD (Q/HA)	ZINC CONTENT (PPM)
CONTROL	25	6.5
ZINC SULPHATE	32	11.8
ZINC PHOSPHATE	31	10.9
ZINC CARBONATE	30	11.6
ZINC OXIDE	31	11.7
ZINC SILICATE (FRITS)	28	7.9
C.D. (5 PER CENT)	2	1.4

ZINC SOURCES WERE ADDED EQUIVALENT TO 20 KG ZN/HA.
SOURCE: SINHA & ASSOCIATES (1977)

TABLE 10.5. EFFECT OF ZINC APPLICATION ON 3 USE ENRICHMENT OF RICE SEEDLINGS AND THEIR PERFORMANCE IN A ZINC DEFICIENT SOIL

ZN CONT.(PPM) MEANS OF Fo 2 FI			SOIL APPLICATION KG ZINC SUL./HA OF NURSERY	YIELD IN QUINTAL/HA (MEAN OF 4 REPLICATION)		
				GRAIN		
ROOTS	LEAF SHEATHS	LEAF BLADES		F_0	F_1	MEANS
61.6	56.6	48.3	0	5.12	14.50	9.81
90.0	63.6	68.2	75	19.25	28.00	23.62
125.0	63.8	98.6	150	20.00	13.50	16.75
181.2	148.2	108.3	300	15.50	17.00	16.25
269.8	191.6	150.0	600	25.25	30.50	27.87
353.2	284.9	173.2	1200	40.25	49.00	44.62
376.6	307.6	167.2	2400	43.00	52.00	47.50
			MEANS	24.50	29.91	

C.D. AT 5% = 20.77

F_0 = MO FOLIAR SPRAY F_1 = THREE FOLIAR SPRAY. SOURCE: SINGH & SINGH (1976 AND 1978)

Table 10.6. Effect of Zn application on the grain yield of
wheat (Serry et al. (1974))

Treatments	Alluvial Soil	Calcareous soil
	TONNES/HA	
NPK	4.21	1.49
NPK + Zn foliar spray	4.67	1.54
NPK + 24 kg $ZnSO_4$/ha soil appl.	4.68	1.86
NPK + 48 kg $ZnSO_4$/ha soil appl.	4.62	2.09

in a zinc deficient calcareous soil in India. The yield
increase obtained was more than 8 times (Table 10.5).

The effect of Zn application on the grain yield of wheat
on two locations in Egypt is shown in Table 10.6. On the
alluvial soil the Zn response was only modest and the fo-
liar application was as efficient as the soil application.
For the calcareous soil, the soil application of Zn re-
sulted in a very marked increase in grain yield (Serry
et al., 1974). A detailed discussion of Zn fertilizers
and their use is given by Giordano and Mortvedt (1972)
and by Lindsay (1972).

IRON IN SOILS AND IN CROP NUTRITION

11.1 Iron Deficiency Problems

Next to zinc, among the micronutrients, deficiency of iron
is the most widespread. It is most frequently encountered
in soils with high pH, high carbonates/bicarbonates, low or-
ganic matter, light texture and high phosphates. It is aggre-
vated by low temperatures. Among crops upland rice is, per-
haps, the most vulnerable to iron deficiency and dicots the
least.

Iron deficiencies are widespread in central and northern
India, the Philippines, and parts of Japan and the United
States (Tanaka and Yoshida, 1970; Ponnamperuma and Castro,
1972). In flooded soils iron deficiency is associated with
aerobic pHs higher than 7 or insufficient soil reduction.
When rice is grown on calcareous soils, iron deficiency may
occur in upland conditions but may be absent in flooded areas
because of the generally increased availability of iron under
flooding. Iron deficiency has been recorded in acid soils of
pH around 5.0 both in the Philippines (DeDatta et al., 1975)
and in Brazil (Costa and deSouza, 1972) in upland conditions
during periods of water stress. Although the solubility of
iron is high, apparently the crystallinity of the forms or
sheer water stress may induce iron deficiency. Not all cal-

careous soils produce iron deficiency in rice. No iron deficiency symptoms and prominent iron coatings have been observed in calcareous soils of pH 8.3 throughout the coast of Peru (Sanchez 1976).

11.2 Soil Iron

Iron makes up about 5% by weight of the earth's crust and is invariably present in all soils. The greatest part of soil Fe usually occurs in the crystal lattices of numerous minerals. The primary minerals in which Fe is present include the ferromagnesian silicates such as olivine, augite, hornblende and biotite. These minerals along with the biotite micas constitute the major Fe source in igneous rocks. Primary Fe oxides which occur in many soils include haematite (Fe_2O_3), ilmenite ($FeTiO_3$), and magnetite (Fe_3O_4). In sedimentary rocks Fe oxides and siderite ($FeCO_3$) are usually the most common primary Fe forms. Iron may also be present in secondary mineral lattices in soils and it is an essential element in a large group of clay minerals. As weathering proceeds, Fe originally present in the easily weatherable ferromagnesian primary minerals appears in illitic clay minerals. The high stability of primary Fe oxides means that during oxidative weathering Fe oxides accumulate as hydrous oxides in the clay fraction. Thus in soils at an advanced stage of oxidative weathering as is the case of lateritic soils, these oxides together with Al oxides and kaolinite predominate in the profile (Oades, 1963).

The content of soluble Fe in soils is extremely low in comparison with the total Fe content. Soluble inorganic forms include Fe^{3+}, $Fe(OH)_2^+$, $FeOH^{2+}$ and Fe^{2+}. In well aerated soils, however, Fe^{2+} contributes little to the total soluble inorganic Fe except under high soil pH conditions. Iron solubility is largely controlled by the solubility of the hydrous Fe(III)oxides. These give rise to Fe^{3+} and its hydrolysis species (Lindsay, 1972):

$$Fe^{3+} + 3OH^- \rightleftharpoons Fe(OH)_3 \text{ (solid)}$$
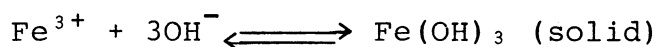
The equilibrium is very much in favour of $Fe(OH)_3$ precipitation and is highly pH dependent, the activity of Fe^{3+} falling with increasing pH. At higher pH levels Fe^{3+} activity in solution decreases 1000 fold for each pH unit rise. The soluble Fe level reaches a minimum in the pH range between 6.5-8.0 (Lindsay, 1972). Acid soils are thus relatively higher in soluble inorganic Fe than calcareous soils where levels can be extremely low. This may well contribute to Fe deficiency in crops growing on these soils.

When soils are waterlogged a reduction of Fe^{3+} to Fe^{2+} takes place accompanied by an increase in Fe solubility. Reduction is brought about by anaerobic metabolism of bacteria. This process of Fe reduction is of particular importance in paddy soils where rather high Fe^{2+} concentrations can result. This can often produce toxic effects in rice plants, known as "bronzing". The leaves are at first covered by tiny brown spots which develop into a uniform brown colour. This frequently occurs in rice leaves containing more than 300 ppm Fe (Tanaka and Yoshida, 1970).

After nitrates and manganese compounds are reduced, the solubility of iron increases because of the reduction of Fe^{3+} compounds to more soluble Fe^{2+} compounds. A peak in the concentration of exchangeable Fe^{2+} or soil solution Fe^{2+} occurs normally within the first month after flooding and is followed by a gradual decline. The magnitude and intensity of these peaks vary substantially with soil properties. Figure 11.1 shows that the most pronounced peaks occur in acid soils high in organic matter. These are usually Oxisols or Ultisols with large quantities of reducible iron. High pH soils show small increases in Fe^{2+} because of their lower contents of reducible iron. The percentage of total free iron reduced within a few weeks of flooding ranges from 5 to 50 percent. More iron is reduced when the oxidized forms are less crystalline (Ponnamperuma, 1972). The grayish color of reduced soils is attributed to FeS, although hydrated magnetite $[Fe_3(OH)_8]$, ferrous silicates, and vivianite may also be present.
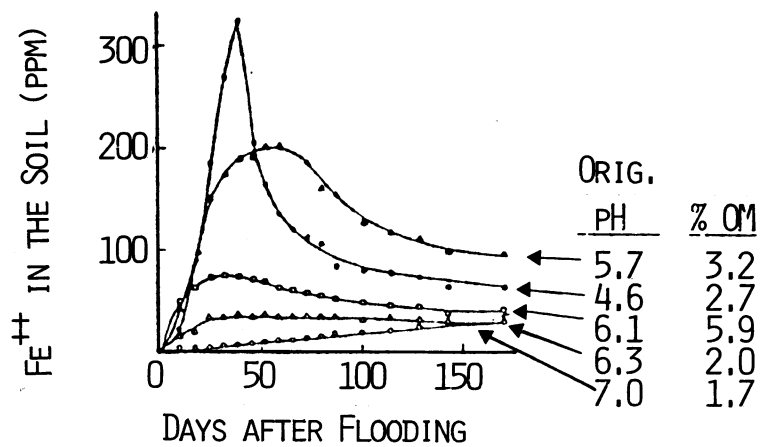
FIG. 11.1 CHANGES IN CONCENTRATION OF FE^{2+} IN THE SOIL SOLU-
TIONS OF FIVE FLOODED SOILS. SOURCE: PONNAMPERUMA
(1965)
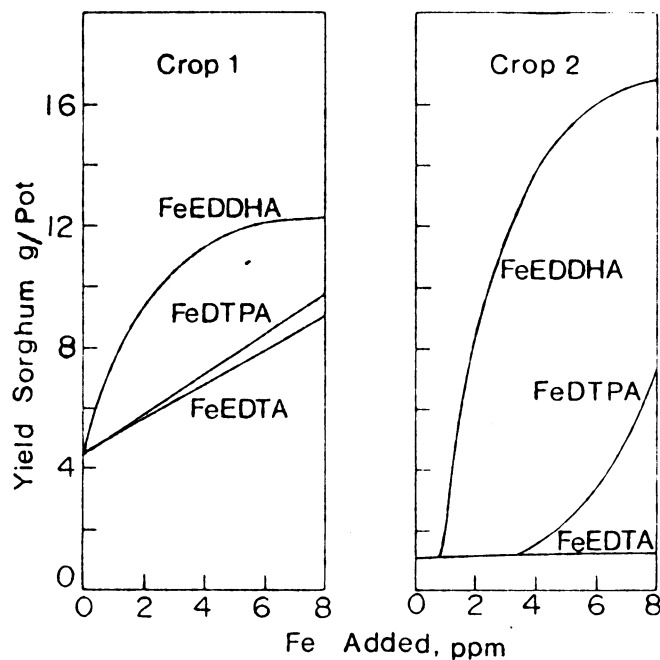
FIG. 11.2 EFFECTIVENESS OF VARIOUS FE CHELATES IN CORRECTING FE DEFICIENCY
IN A CALCARIOUS SOIL FOR TWO CROPPINGS OF SORGHUM (AFTER LINDSAY
(1974))

EDTA = ETHYLENE DIAMINE TETRAACETIC ACID
DTPA = DIETHYLENE TRIAMINE PENTAACETIC ACID
EDDHA = ETHYLENE DIAMINE (DI O-HYDROXYPHENYLACETIC ACID)

Iron reduction is considered the most important reaction
occurring in flooded soils because it raises the pH, incre-
ses the availability of phosphorus, and displaces cations
from exchange sites. The increase in Fe^{2+} concentration is
usually beneficial to rice in alkaline soils, reaching 20
ppm in the soil solution, a level that is usually sufficient
to eliminate iron deficiency.

11.3 Uptake and translocation

Iron may be supplied to plant roots as Fe^{2+}, Fe^{3+} or as Fe
chelates. Absorption appears to be dependent on the ability
of the roots to reduce Fe^{3+} to Fe^{2+}. According to Chaney
et al. (1972) the reduction is essential before Fe can be
absorbed and these authors suggest that Fe^{3+} reduction at
the outer plasmalemma is mediated by a source of electrons
from within the cell *via* a cytochrome or flavin compound.

When Fe chelates are supplied to plant roots at the normally
low Fe levels required by plants, it seems likely that there
is a separation between Fe and chelate prior to Fe absorp-
tion, Chaney et al., 1972. Only at high levels in the nutrient
medium were Jeffreys and Wallace (1968) able to detect appre-
ciable quantities of Fe chelates in plants.

There is ample evidence as reviewed by Moore (1972) that the
uptake of Fe is metabolically controlled. The results of Tiffin
(1966) for example show Fe concentrations in stem exudates
of decapitated sunflower and soya bean plants, up to 30 times
greater than in the ambient solutions. The uptake of Fe is
considerably influenced by other cations. Competitive effects
on iron uptake have been observed with Mn^{2+}, Cu^{2+}, Ca^{2+},
Mg^{2+}, K^+ and Zn^{2+} (Lingle et al., 1963). Such effects on ab-
sorption may partially account for the ability of heavy metals
to induce Fe deficiency in a number of plant species.

Iron uptake is particularly depressed by high pH, high phos-
phate and Ca^{2+} concentrations in the nutrient medium. High
pH levels as well as good aeration conditions favour the oxi-
dation of Fe^{2+} to Fe^{3+} and thus the precipitation of Fe(III)

salts. Nitrate nutrition depresses Fe uptake whereas it is enhanced by NH_4-nutrition. This finding can probably be explained by the differences in pH at the plant roots exerted by the two N forms.

Iron is not readily mobile between different plant organs. Green plants deprived of Fe soon become chlorotic in the younger plant parts whilst older tissues remain green. Younger tissues are therefore dependent on a continuous Fe supply in the xylem or by a foliar application. The major form in which Fe is translocated in the xylem appears to be as ferric citrate.

11.4 Biochemical functions

The tendency for Fe to form chelate complexes and its ability to undergo a valency change are the two important characteristics which underlie its nummerous physiological effects.

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

The most well known function of Fe is in enzyme systems in which haem or haemin function as prosthetic groups. Here Fe plays a somewhat similar role to Mg in the porphyrin structure of chlorophyll. These haem enzyme systems include catalase, peroxidase, cytochrome oxidase as well as the various cytochromes. Catalase and peroxidase catalyse the following reaction

$$\text{catalase:} \quad H_2O_2 + H_2O_2 \longrightarrow O_2 + 2H_2O$$
$$\text{peroxidase:} \quad AH_2 + H_2O_2 \longrightarrow A + 2H_2O$$
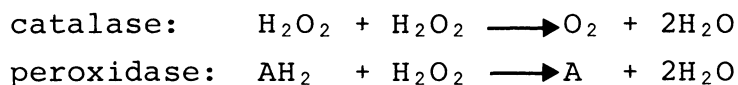
The precise role of these enzymes in plant metabolism is still not understood.

In green plants there is often a good correlation between the level of Fe supply and the chlorophyll content, plants well supplied with Fe being high in chlorophyll. More recently applying radioactive Fe-59 to tomato plants suffering from Fe chlorosis Machold and Scholz (1969) observed that the distribution of Fe-59 in the leaves corresponded exactly to the areas in which regreening occurred. There is still considerable

controversy as to whether Fe plays a direct role in chlorophyll formation. In a review of the functions of Fe in plants Price et al. (1972) suggest that Fe is not directly involved in the enzymic synthesis of porphyrins, and claims that the observed effects cited above are due to indirect causes.

The possible involvement of Fe in protein metabolism has been suspected from the findings of a number of authors who have observed that in Fe deficiency the protein fraction decreases simultaneously with an increase in the level of soluble organic N compounds (Perur et al., 1961).

11.5 Iron deficiency

The deficiencies of Fe and Mg are somewhat similar as both are characterized by a failure in chlorophyll production. Iron deficiency, however, unlike Mg deficiency always begins in the younger leaves. In most species chlorosis is interveinal and a fine reticulate pattern can often be observed in the newly formed leaves, the darker green veins contrasting markedly against a lighter green or yellow background. The youngest leaves may often be completely white and totally devoid of chlorophyll. In the leaves of cereals the deficiency is shown by alternate yellow and green stripes along the length of the leaf. As high concentrations of Fe occur in chloroplasts it is not surprising that Fe deficiency causes marked changes in their ultrastructure.

A fairly well defined pattern of chemical composition is often shown in plants suffering from Fe chlorosis. The ratio of P/Fe is frequently higher than in comparative green tissues, and the role of phosphate in inactivating Fe has been reported by a number of authors (Brown et al., 1959, Kashirad and Marschner, 1974). Total iron concentrations considered alone are of little use in chlorosis studies, and Fe levels may even be higher in chlorotic tissues. This again indicates an inactivation of Fe, and the estimation of "active" acid soluble Fe has been found to correlate better with chlorophyll contents and Fe deficiency symptoms.

11.6 Iron application

Iron deficiency is rather difficult to correct since inorganic sources of iron are, by and large, agronomically less effective as soil application. In experiments where iron chlorosis was checked successfully rate around 100 kg Fe/ha were required (Mikkelsen et al., 1965). Obviously, such high levels are impracticable.

In contrast to inorganic iron sources, the chelates of iron are able to maintain iron availability for a longer time (Dahiya & Singh, 1979) and the results thus far obtained favour their use from the point of effectiveness. High cost limits their use. Patel et al. (1977), found foliar applications to be essentially ineffective to prevent chlorosis in rice nurseries, Takkar and Nayyar (1979) have strongly advocated iron sulphate sprays to alleviate iron deficiency in transplanted rice. Randhawa and associates (1970) demonstrated that soil application excelled the foliar sprays in increasing yields of lowland rice. Despite contrasting results, once the iron chlorosis has appeared, the best remedy seems foliar application of iron sulphate. Storage of iron sulphate solution should be discouraged.

The results of Lindsay et al. (1967) showing the yield response of sorghum to various Fe chelates correcting Fe deficiency in a calcareous soil are presented in Figure 11.2 Fe EDDHA [ethylenediamine di (o hydroxyphenaylacetic acid)] the chelate which gave the highest response is stable throughout the pH range 4-10, whereas the stability of Fe DTPA (di ethyltriamine pentacetic acid) and Fe EDTA (ethylene diamine tetraacetic acid) falls above pH 7 and 6 respectively so that correspondingly lower sorghum yields were obtained.

MANGANESE IN SOILS AND IN CROP NUTRITION

12.1 Manganese Deficiency Problems

Manganese deficiency is not widespread. The soil conditions which favour iron deficiency generally cause Mn deficiency

also. On the other hand, Mn toxicity in acid and flooded soils has been observed in rice crop (Tanaka and Yoshida, 1970).

12.2 Soil Manganese

Manganese occurs in various primary rocks and particularly in ferromagnesian materials. The Mn released from these rocks by weathering forms a number of secondary minerals the most prominent being pyrolusite (MnO_2) and manganite [MnO (OH)]. Manganese and Fe oxides often occur together in nodules and iron-pans. Total Mn levels may differ considerably between soils. According to Swaine (1955) Mn contents between 200 and 3000 ppm are most common. The most important Mn soil fractions are Mn^{2+} and the Mn oxides in which Mn is present in trivalent or tetravalent form. Divalent Mn is adsorbed to clay minerals and organic matter and is also the most important Mn form in soil solution. The relationships between the Mn^{2+} and the Mn oxides are presented in Figure 12.1. This so-called Mn cycle in the soil (Dion and Mann, 1946) shows that the equilibrium between the various Mn forms is governed by oxidation - reduction processes. The most important fraction in plant nutrition is Mn^{2+}. In addition, easily-reducible Mn contributes to plant supply. These combined fractions, Mn^{2+} and easily-reducible Mn, are called "active Mn". As the level of Mn^{2+} in the soil depends on oxidation-reduction reactions, all factors influencing these processes have an impact on Mn availability. These factors include soil pH, organic matter content, microbial activity and soil moisture. Under waterlogged conditions as for example in paddy soils, reducing processes dominate and thus provide a high level of Mn availability which may even result in Mn toxicity (Tanaka and Yoshida, 1970). The effect of anaerobic soil conditions (flooding) and of liming on Mn availability as reflected in Mn content of lucerne grown on the soil is shown in Table 12.1 (Graven et al., 1965).

Manganese availability is also higher in acid soils due to the higher solubility of Mn compounds under low pH condi-
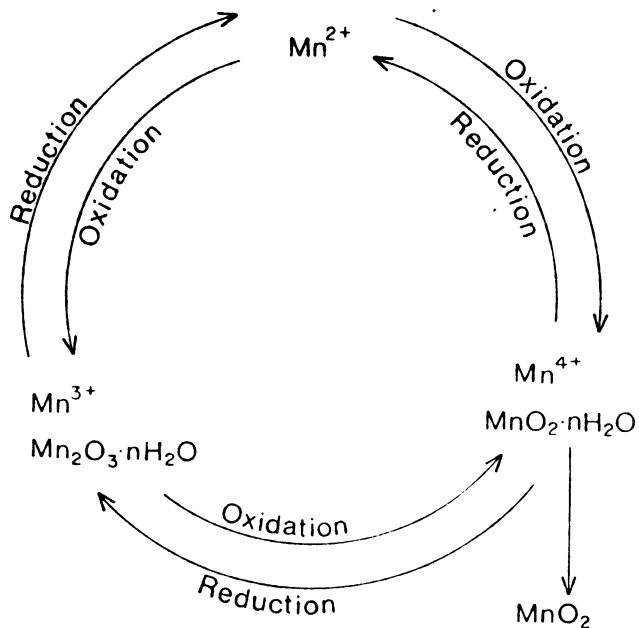
FIG. 12.1 MN OXIDATION-REDUCTION CYCLE IN THE SOIL
(AFTER DION AND MANN (1946))
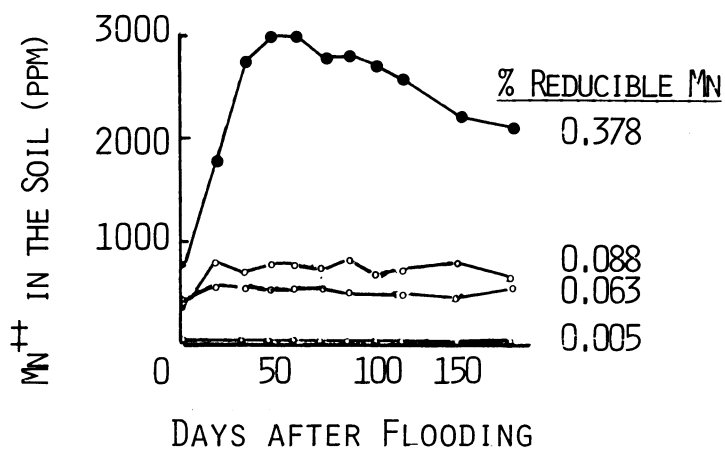
FIG. 12.2   CHANGES IN CONCENTRATION OF Mn^{2+} IN FOUR SOILS
WITH FLOODING. SOURCE: PONNAMPERUMA (1965)

tions. Lindsay (1972) stresses that the soluble Mn^{2+} decreases 100 fold for each unit increase in pH. Under high soil pH conditions Mn availability can thus be inadequate to meet plant demand.

Table 12.1. Effect of liming and a 3 day period of flooding on dry matter yield and Mn contents in lucerne (Graven et al., 1965).

Treatment g $CaCO_3$/pot	Flooding	g, DM pot	Mn content ppm Mn in DM
0	-	3.1	426
0	+	1.2	6067
20	-	5.7	99
20	+	3.0	954

According to Geering et al. (1969), the Mn^{2+} level of the soil solution of acid and neutral soils is in the range of 10^{-6} to 10^{-4} M. These workers suggest that in soil solution Mn is present largely as organic complexes. On the other hand Lindsay (1974) found that the affinity of Mn^{2+} for synthetic chelates is comparatively low and complexed Mn can easily be replaced by Zn^{2+} and Ca^{2+}. The levels of Mn in soil solution are considerably higher than those of Cu and Zn.

The solubility of manganese increases sharply upon flooding because of the reduction of Mn^{4+} compounds to the more soluble Mn^{2+}. Figure 12.2 shows that a peak concentration of Mn^{2+} in the soil occurs during the first month, followed by a gradual decrease. Ponnamperuma (1972) attributes this decrease to precipitation of Mn^{2+} as $MnCO_3$. Soils high in reducible manganese undergo the most pronounced changes in spite of original pH or organic matter levels. Acid soils high in manganese and organic matter develop peak concentrations of 90 ppm Mn^{2+} in the soil solution, followed by a decline and stabilization at about 10 ppm. Alkaline soils or soils low in manganese seldom contain more than 10 ppm Mn^{2+} in the soil solution.

12.3. Uptake and translocation

The rate of Mn uptake differs considerably between plant species. Generally, however, uptake rates are lower than for other divalent cation species (Ca^{2+}, Mg^{2+}). There is ample evidence that Mn uptake is metabolically mediated (Moore, 1972). In a similar way to other divalent cation species, Mn^{2+} participates in cation competition. Magnesium in particular depresses Mn uptake. Liming also reduces uptake not only by the direct effect of Ca^{2+} in the soil solution, but also as a result of the pH increase.

Mn is relatively immobile in the plant. It is still not clear whether it can be translocated in the phloem to any extent. Tiffin (1972) studied the translocation of a number of heavy metals in tomatoes. In electrophoretic examinations of exudates it was found that Mn migrated towards the cathode. It thus appears that Mn is mainly transported as Mn^{2+} and not as an organic complex.

Manganese is preferentially translocated to meristematic tissues. Young plant organs are thus generally rich in Mn. In solution culture experiments Williams and Vlamis (1957) found that the addition of Si improved the distribution of Mn in barley plants.

12.4. Functions of Mn

In its biochemical functions Mn^{2+} resembles Mg^{2+}. Both ion species bridge ATP with the enzyme complex (phosphokinases and phosphotransferases). According to Lehninger (1975), however, the bridge formed by Mn^{2+} differs slightly from that formed by Mg^{2+}. Decarboxylases and dehydrogenases of the TCA cycle are also activated by Mn^{2+}, although it appears that in most cases Mn^{2+} is not specific for these enzymes and can be substituted by Mg^{2+}. In other reactions there is a specific Mn requirement. Manganese brings about the oxidation of IAA by activating IAA oxidases.

Manganese is also in some way involved in the oxidation-reduction processes in the photosynthetic electron transport

system. According to Bishop (1971) Mn is essential in photo-
system II where it participates in photolysis. When Mn is
deficient, the structure of chloroplasts is markedly impaired
even when other organelles show no visible alteration. Two
separate Mn fractions were isolated by Cheniae and Martin
(1970) in chloroplasts; one was loosely and the other firmly
bound to the membrane. It appeared that the loosely bound
fraction was associated with O_2 evolution whereas the firmly
bound Mn fraction was an essential part of the as yet unknown
electron donor in photosystem II.

12.5. Deficiency and toxicity

As already pointed out, chloroplasts are the most sensitive
of all cell organelles to Mn deficiency. In whole plants
Bussler (1958) reported that tissues suffering from Mn de-
ficiency have a small cell volume, cell walls dominate and
the interepidermal tissue is shrunken. Manganese deficiency
resembles Mg deficiency, as in both cases interveinal chloro-
sis occurs in the leaves. In contrast to Mg deficiency, how-
ever, Mn deficiency symptoms are first visible in the younger
leaves, whereas in Mg deficiency the older leaves are first
affected. Manganese deficiency symptoms in the dicots are
often characterized by small yellow spots on the leaves. In
this respect this syndrome differs from that of Fe deficiency
where the whole young leaf becomes chlorotic. In monocots
and particularly in oats, Mn deficiency symptoms appear at
the basal part of the leaves as greenish grey spots and stri-
pes. Oats in particular are prone to Mn deficiency during the
tillering stage. The disease is known as "grey speck". The
turgor of the affected plants is reduced and at an advanced
stage of disease the upper part of the leaf breaks over near
the middle.

The Mn status of plants is reflected in their Mn contents.
The critical deficiency level for most plant species is in
the range of 15 to 25 ppm Mn in the dry matter of upper plant
parts.

Manganese toxicity symptoms are generally characterized by
brown spots in older plant organs and by an uneven distribution
of chlorophyll. The toxicity is often accompanied by Fe de-
ficiency symptoms.

12.6 Manganese in Crop Nutrition

Most soils contain adequate levels of available Mn so that
Mn applications are unnecessary. The total amount of Mn taken
up by arable crops is low and ranges from between 500 to 1000 g
Mn/ha. Calcareous peat soils (organic soils, high in pH) are
particularly low in available Mn and it is on these soils that
Mn deficiency often occurs in crops. Application of Mn salts
to the soils, e.g. $MnSO_4$, is usually of no use in alleviating
deficiency, because the applied Mn^{2+} is rapidly oxidized.
When such soils are treated with Mn fertilizers, banded place-
ment rather than broadcast application should be carried out.
Randall and Schulte (1971) found that 5.6 kg/ha of banded Mn
as sulphate was equivalent to 67.2 kg/ha of broadcast Mn.
Generally for soil application $MnSO_4$ is superior to Mn chelates,
although foliar application of Mn is frequently recommended
on these calcareous organic soils. Draycott and Farley (1973)
in comparing soil application of Mn silicate and Mn oxides
with Mn foliar sprays found that the soil application did not
prevent Mn deficiency in sugar beet whereas Mn foliar applica-
tion corrected the deficiency and increased sugar yields.
Spraying 1 to 5 kg Mn/ha is sufficient to offset deficiency
in most crops.

Some podzolic soils are particularly liable to be low in avai-
lable Mn. This group of soils however, differs from the orga-
nic soils already discussed, in that podzols are inherently
low in Mn. This low Mn status mainly results from high leach-
ing. Manganese deficiency on these sites is frequently aggra-
vated by liming because of the resulting pH increase. As Mn^{2+}
applied to these soils is not so rapidly oxidized as in the
calcareous organic soils, Mn soil applications are well able
to correct the deficiency. Rates of about 30 kg Mn/ha as
$MnSO_4$ are generally applied. In severe cases, however, levels

as high as 100 to 200 kg Mn/ha are recommended (Henkens, 1965). In addition to the soil types mentioned above alluvial soils and marsh soils derived from calcareous materials are also prone to Mn deficiency. The uptake of Mn by crops can be depressed by high levels of available Fe, Cu or Zn.

Soil analysis is not very reliable in diagnozing available soil Mn status in relation to crop response. According to Browman et al. (1969) who compared a number of the standard methods, NH_4-acetate extraction with a correction for pH gave the most satisfactory results. Similar observations were made by Farley and Draycott (1976). Ammonium acetate extractable Mn correlated best with Mn deficiency, plant Mn, and response to treatment. The most important results of this study are shown in Table 12.1.

Table 12.1. Sugar beet response to Mn in relation to NH_4-acetate extractable soil Mn, and Mn in the dried foliage (Farley and Draycott, 1976).

Ammonium acetate extractable soil Mn ppm	Plants with symptoms %	Mn in dried foliage ppm	Response
< 1.2	100-50	<20	large
1.2-1.8	49-25	20-30	small
> 1.8	<25	>30	none

Crops differ in their susceptibility to Mn deficiency. Two of the most well known deficiency diseases in arable crops are grey speck in oats (*Avena sativa*) and marsh spot in peas (*Pisum sativum*). Other sensitive crops are: apple, cherry, citrus, raspberry, and sugar beet.

On acid soils high in Mn availability, plants can take up considerable amounts of Mn so that levels in the order of 1000 ppm Mn in the dry matter are not uncommon. Löhnis (1960) found Mn contents in *Vaccinium myrtillus* higher than 2000 ppm in the dry matter. On such soils Mn toxicity in crops is often observed. The disease is aggravated by reducing conditions in the soil.

COPPER IN SOILS AND IN CROP NUTRITION

13.1 Copper deficiency problems .

Copper deficiencies in field crops are not widespread in the tropics. They are however, encountered in soils with high organic matter and light texture. Peat soils in general are highly susceptible to copper deficiencies. In a report from India, Katyal (1980) reported that out of 55 000 soil samles analysed for Cu, only 1% fell in the deficient range.

13.2 Soil Copper

Copper occurs in the soil almost exclusively in divalent form. The largest fraction of Cu is usually present in the crystal lattices of primary and secondary minerals. In addition Cu occurs in organic compounds, is present as an exchangeable cation on soil colloids and is a constituent of the soil solution.

The important minerals containing Cu are chalcopyrite $(CuFeS_2)$ bornite (Cu_5FeS_4), enargite (Cu_2AsS_4) chalcocite (Cu_2S) and some oxides of Cu $(Cu_2O$ or $CuO)$.

The concentration of the soil solution is usually very low being in the range of 1×10^{-8} to 60×10^{-8} M. HODGSON et al. (1966) observed that more than 98% of soil solution Cu is complexed with organic matter. Copper is, in fact, more strongly bound to organic matter than are other micronutrient cation (e.g. Zn^{2+}, Mn^{2+}), and Cu organic complexes play an important role in regulating Cu mobility and availability in the soil.

According to Lindsay (1972) the level of Cu in soil solution decreases with increasing pH due to stronger Cu adsorption. The equilibrium concentration of Cu maintained by sparingly soluble Cu salts such as carbonate and oxides is higher than the normal levels of Cu in the soil solution. The presence of carbonates or oxides in the soil therefore plays no part in restricting Cu availability. The Cu concentration in the soil solution is governed by copper adsorption to soil particles.

As Cu is strongly bound to soils, it is very immobile.
Copper added to the soil as a result of the use of Cu con-
taining sprays or fertilizers is thus largely restricted to
the upper soil horizons (Delas 1963).

As Cu deficiency occurs primarily on humus rich soils which
bind Cu^{2+} very strongly, it may be supposed that certain defined
organic forms are more readily able to render Cu unavailable.
This has been confirmed by neutron activation studies of
organically bound Cu in soil solution by Mercer and Richmond
(1970). These workers showed that Cu availability in organic
soils depended not only on the concentration in soil solution
but also on the form in which the Cu occurred. Copper com-
plexes in the soil solution of molecular weight <1000 were
much more available to plants than Cu complexes with a
molecular weight in excess of 5000.

13.3. Uptake and translocation

Copper is taken up by the plant in only very small quantities.
The Cu content of most plants is generally between 2-20 ppm
in the dry plant material. Copper uptake appears to be a
metabolically mediated process and there is evidence that
Cu strongly inhibits the uptake of Zn and vice versa (Schmid
et al. 1965 , Boven 1969). This apart, however, the uptake
of Cu is largely independent of competitive effects and re-
lates primarily to the levels of available Cu in the soil.
Coppers is not readily mobile in the plant although it can
be translocated from older to younger leaves. Results of
Loneragan (1975) show that the movement of Cu is strongly
dependent on the Cu status of the plant. In wheat plants
well supplied with Cu, movement from the leaves to the grains
can readily occur, but in deficient plants Cu is relatively
immobile. In a number of plant species Tiffen (1972) showed
that Cu is present in xylem exudates in anionic Cu complex
form.

13.4. Fractions of Cu

Many years ago it was proposed that Cu plays a part in photo-
synthesis (Arnon 1950). Investigation since then have reve-
aled that Cu is a constituent of the chloroplast protein
plastocyanin which form part of the electron transport chain
linking the two photochemical systems of photosynthesis
(Boardman 1975). Additional evidence suggests that Cu may
play a part in the synthesis or the stability of chlorophyll
and other plant pigments although the mechanism is not clear.

Several Cu containing enzymes are known that catalyze reac-
tions that reduce both atoms of molecular oxygen. These
oxidases include the cytochrome oxidase as well as a number
of other enzymes including ascorbic acid oxidase, laccase,
diamine oxidase, plastocyanin and polyphenol oxidase.

Recent experimental data suggest that the desaturation and
the hydroxylation of fatty acid is also catalyzed by Cu
containing enzymes (Wahle and Davies (1977). Thus the de-
saturation of stearic acid by $\Delta 9$-desaturase which results
in the production of oleic acid requires Cu and O_2.

It is believed that Cu mediates in these oxidation reaction
by undergoing cyclic oxidation associated with electron
transfer.
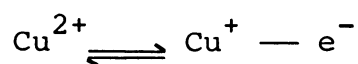
$$Cu^{2+} \rightleftharpoons Cu^+ - e^-$$

In the oxidized proteins it is supposed that the Cu atoms are
present as a $Cu^{2+}-Cu^{2+}$ pair thus enabling the transfer of
two electrons to one molecule of oxygen.

Copper appears to participate both in protein and carbo-
hydrate metabolism. In Cu deficient plants protein synthesis
is disturbed and there is a build up of soluble amino-N com-
pounds. This can be explained both by the function of Cu
as a cofactor in enzyme synthesis, as well as by the possible
effect of Cu on DNA and RNA synthesis. In young growing
organs, where protein synthesis is most active, lower levels
of DNA have been observed in Cu deficient tissues (Ozolina
and Lapina 1965).

Observations of Hallsworth et al. (1960) suggest that there
is a specific requirement for Cu in symbiotic N_2 fixation.
At low levels of Cu nutrition nodulation of *Trifolium sub-
terraneum* was considerably depressed, although as yet no
mechanism for this has been identified.

13.5. Copper deficiency and toxicity

Copper deficiency is well known in a number of different crop
plants. In cereal crops the deficiency shows first in the
leaf tips at tillering although in severe cases it may appear
even earlier. The tips become white and the leaves are narrow
and twisted. The growth of the internodes is depressed.
As growth progresses the deficiency becomes more severe and
in extreme cases ear or panicle formation is absent.
A typical feature of the deficiency in cereals is the bushy
habit of the plants with white twisted tips and a reduction
in panicle formation. When the deficiency is less pronounced
panicle formation may occur but the ears are not fully
developed and may be partially blind. In fruit trees the
deficiency particularly affects the terminal shoots. The
disease is known as "Summer dieback" as the dying off of
twigs and growing points is a common feature of the defici-
ency. Exactly as in the cereals the generative phase of
flowering and fruit formation is most affected. This charac-
teristic behaviour of Cu deficiency affecting newly devel-
oping tissues, appears to be dependent on the low mobility
of Cu in deficient plants (Loneragan 1975). A detailed
survey of symptoms of Cu deficiency in a number of crop
plants is given by Caldwell (1971).

For most plant species high amounts of Cu in the nutrient
medium are toxic to growth. The effect appears to relate in
part to the ability of Cu to displace other metal ions and
particularly Fe from physiologically important centres.
Chlorosis is thus a commonly observed symptom of Cu toxicity,
superficially resembling Fe deficiency (Daniels et al. 1972).

The inhibition of root growth is one of the most rapid
responses to toxic Cu levels. Wainwright and Woolhouse (1975)
compared the effects of increasing Cu concentrations in a

nutrient culture on the plasmalemma of the roots of a non-tolerant and a Cu-tolerant race of *Agrostis tenuis*.
Damage to the plasmalemma as measured by K^+ leakage was considerably higher in the non-tolerant race. It was con-cluded that as the effect of excess Cu was to damage membrane structure, part of the Cu tolerance behaviour operates through an exclusion mechanism in the plasmalemma. Calcium plays an essential role in maintaining membrane structure. The findings of Wallace et al. (1966) that high levels of Ca alleviate Cu toxicity thus also supports the view that excess Cu exerts a detrimental influence on membrane structure.

13.6. Crop requirement and availability

As the total Cu content of plant material is normally less than 10 ppm the Cu requirement of crop plants is corres-pondingly small. Most soils contain adequate levels of available Cu to meet this demand. Soils in which Cu defi-ciency occurs are either inherently low in Cu or more usually are poor in available Cu. The Cu inherently low group in-cludes soils which are excessively leached, such as the sandy podzolic soils and soils developed on parent material poor in copper. Included in the second category where avail-ability limits plant uptake are organic and peaty soils, calcareous soils and some soils high in clay content.
Copper deficiency is common on newly reclaimed peats and for this reason the deficiency has been called "reclamation disease".

Crop plants differ in their sensitivity to Cu deficiency.
In general, the most responsive crops to Cu fertilizers are oats, spinach, wheat, and lucerne. In the medium range are cabbage, cauliflower, sugar beet and maize, whilst beans, grass, potatoes, and soya beans show a low response.

Brown (1956) grew 19 plant species on calcareous and organic soils to test their susceptibility to Fe and Cu deficiency.
Five species developed Cu deficiency on the organic soil; six developed Fe deficiency on the calcareous soil but did not develop Cu deficiency, four showed retarded growth and

slight Fe and Cu deficiencies; and four did not develop
either Fe or Cu deficiency. The influence of Cu fertili-
zation on oats, one of the most sensitive crops, is shown in
Table 13.1. from the results of Scharrer and Schaumlöffel
(1960). These findings from a glasshouse experiment clearly
show that Cu deficiency decreases grain yield in favour of the
formation of vegetative plant material. The study of Cu
deficiency in the field is often more complex than under
glasshouse conditions. In an extensive survey of Cu defici-
ency on chalk rendzina soils Davies et al. (1971) observed
that deficiency symptoms in barley and wheat were aggravated
when these crops followed a Brassica crop. Blackening
symptoms were observed in wheat and the deficiency symptoms
were accentuated by warm wet summer conditions.

Table 13.1. Effect of Cu application on the yield of oats,
grown on a Cu deficient soil (Scharrer and
Schaumlöffel 1960).

Cu application, mg Cu/kg soil	Straw, g/pot	Grains, g/pot
None................................	72.6	29.6
1.2	57.0	56.7
8.3	58.4	57.7

Fertilizer application can also lead to the onset of Cu
deficiency, and particularly where high levels of N and P
are applied. Applications of Zn fertilizers have also been
shown to aggravate Cu deficiency in soils with marginal Cu
levels (Chaudhry and Loneragan 1970).

Copper fertilization

When it is considered that an average cereal crop removes
only about 20-30 g Cu/ha, it is clear that the amount of Cu
which is necessary to apply is small. However, as already
mentioned, Cu is strongly bound to the soil and for this
reason the amount of Cu fertilizer applied must exceed the
crop uptake considerably. Both inorganic and organic Cu

fertilizers are used to alleviate Cu deficiency (Murphy and Walsh 1972). Most frequently $CuSO_4$ is applied to the soil. A single application of about 1-10 kg Cu/ha is usually adequate on mineral soils whereas somewhat higher levels are needed for organic soils. There are, however, a number of problems associated with $CuSO_4$. When the salt is applied to the soil a large proportion of the Cu^{2+} ions are rapidly brought into solution and are immobilized by strong adsorption to exchange sites. In addition toxic residual effects can result on some soils. Where low or medium responsive vegetable or field crops are being grown, a total application not in excess of 22 kg Cu/ha has been recommended (Murphy and Walsh 1972). Some of the residual effects of soil application have been alleviated either by the use of Cu metal dusts which release Cu at a slower rate (Kühn and Shaumlöffel 1961) or more usually by the use of Cu chelates. Foliar applications of Cu are usually made using $CuSO_4$, Cu oxychloride, Cu oxide or Cu-chelates. Again the sulphate form is less satisfactory because of scorching of the foliage. Seed dressing with Cu-salts have been tried, although the results have been variable (Murphy and Walsh 1972).

If foliar applications (0.1 per cent $CuSO_4$) are made neutralization with lime (0.05 per cent) is essential. Since copper is immobile in the plant, multiple sprays will be required to obtain maximum production.

MOLYBDENUM IN SOILS AND IN CROP NUTRITION

14.1. Molybdenum Deficiency Problems

Molybdenum deficiencies have been reported throughout the
world, especially on acid soils in North America, Australia and
New Zealand (Anderson, 1956).Since Mo is essential for symbiotic
N-fixation, Mo deficiency is most often observed on legumes.
However, deficiency also has been noted on many other agronomic
and horticultural plants.

Recently, rice has been shown to respond to its application,
particularly in terms of nitrogen utilization.(Gupta and
Basuchoudhri, 1977).

14.2. Soil Molybdenum

The total Mo content of most agricultural soils lies between
0.6-3.5 ppm with an average total Mo content of 2.0 ppm and an
average available content about 0.2 ppm (Cheng and Ouellette,
1973). Values can, however, vary widely depending on the parent
material. The important minerals in soils containing Mo are
molybdenite (MoS_2) ilsemannite ($Mo_3O_8 \cdot 3H_2O$), powellite
($CaMoO_4$), and ferrimolybdite ($Fe_2(MoO_4)_3 \cdot 8H_2O$). In contrast
to the heavy metals already discussed, Mo largely occurs in the
soil as an oxycomplex (MoO_4^{2-}). This property clearly distingui-
shes Mo from the other heavy metal nutrients and molybdate more
resembles phosphate or sulphate in its behaviour in the soil.
In a similar way to these two anions, molybdate is adsorbed by
soil minerals and colloids (Barrow, 1970). This adsorption is
closely dependent on soil pH. At neutrality it is very low but
increases as the pH falls. Molybdenum availability to plants
is thus poorest on acid soils and is improved by liming,
provided the soil is not inherently deficient in Mo. This
increase in availability can be explained by the exchange of
adsorbed molybdate ions on the colloid for OH$^-$ in the soil
solution. Other anions may also exchange for molybdate provided
their exchange energy is high enough. In practical terms this

may be of significance in the beneficial effect of phosphate
application on Mo availability (Walker et al., 1955).
Hydroxyl ions, however, appear to be the most effective ions
in increasing the Mo level in soil solution and hence Mo up-
take by plants.

From the above discussion it is understàndable that the Mo
content of the soil solution may vary considerably. Concentrat-
ions in the order of a 2×10^{-8} to 8×10^{-8}M have been reported
(Lavy and Barber, 1964). The fraction of Mo in the soil solution
of the total soil Mo may also be very different between soils.
In some Californian soils for example it has been established
that 2/3 of the total Mo is water soluble whereas in Mo deficient
soils in Florida the water soluble Mo made up less than 1%
of the total Mo (Wiklander, 1958). In addition to Mo adsorbed
on soil colloids and the Mo in soil solution, the element also
occurs in nonexhangeable form in a number of mineral structures.
These include MoS_2, present in soils under reducing conditions,
Ca-molybdate, and hydrated Mo oxides. Molybdenum may also be
associated with Fe oxide minerals in adsorbed, occluded or
semicrystalline forms as is the case in the sesquioxide fraction
in acid soils (Taylor and Giles, 1970). On ironstone soils of
low pH, Mo may be so strongly fixed that Mo deficiency may occur.

A fraction of soil Mo is present in organic form. With the break-
down of organic matter this is frequently converted to a plant
available form.

14.3. Uptake and Translocation

Mo is absorbed as molydate by plants. Uptake can be reduced by
competitive effects of SO_4^{2-}. (Reisenauer, 1963). On the other
hand phosphate ions enhanced Mo uptake into the tops in short-
term experiments (Stout et al., 1951). Although there is no
direct evidence that Mo is taken up actively, the ionic interac-
tions described above are suggestive of active uptake (Moore,
1972). The form in which Mo is translocated is unknown.
Tiffin, (1972), has suggested that it may possibly move in the

xylem as MoO_4^{2-}, as Mo-S amino acid complex or as a molybdate complex with sugars or other polyhydroxy compounds. According to Hewitt and Agarwala (1952), Mo is located primarily in the phloem and vascular parenchyma. It is only moderately mobile in the plant.

14.4. Functions of Mo

Molybdenum is an essential component of two major enzymes in plants, nitrogenase and nitrate reductase, both of whose effective mechanism probably depends on the valency change.

$$Mo^{5+} \rightleftharpoons Mo^{6+} + e^-$$

Nitrogenase consists of two enzyme protein complexes the bigger of which contains Fe and Mo in a ratio of about 9:1. According to Bergersen, (1971), the basic mechanism of N_2 fixation by nitrogenase, and thus the Mo function too, is the same for free living N_2 fixing bacteria as for N_2 fixing microorganisms living in symbiosis with higher plants. The essentiality of Mo for *Actinomyces alni* of alder *(Alnus glutinosa)* was established by Becking, (1961). In the absence of Mo, alder seedlings developed N deficiency. When Mo was supplied, N uptake was enhanced and Mo accumulated in the root nodules at the site of N_2 fixation (Table 14.1.).

Nitrate reductase is the most well studied Mo containing enzyme. It was isolated from soya beans by Evans and Nason, (1953) and it catalyzes the reduction of NO_3^- to NO_2^-. The activity of the enzyme in cauliflower is enhanced by increasing levels of Mo supply (Candela et al., 1957).

Table 14.1. Mo contents in various plant parts of young
           alder (Becking, 1961).

	Leaves	Stems	Roots	Nodules
	ppm Mo in the dry matter			
No Mo application.....	0.01	0.14	0.24	2.00
Mo application........	0.27	1.89	2.62	17.3

The uptake of Mo in plants per unit of dry matter production
is greater in the presence of NO_3-N than NH_4-N (Giordano et al.,
1966). Nevertheless some reports suggest that plants supplied
with NH_4-N do appear to have a small requirement of Mo for
normal growth (Agarwala and Hewitt, 1955). From this evidence
it would seem likely, therefore, that Mo must be a component
of at least one other essential enzyme system than the two al-
ready mentioned. One such Mo containing enzyme is aldehyde
oxidase although its occurrence in plants is very restricted as
in the potato tuber.

The more recent work of Hewitt and Gundry, 1970 has cast
considerable doubt on the occurrence of essential Mo enzyme
systems in plants other than the two major functions already
discussed. These workers showed that under sterile conditions
cauliflowers grown with NH_4-N and without Mo did not develop
Mo deficiency symptoms, whereas under non sterile conditions
Mo deficiency appeared. Most experiments comparing different
forms of N in relation to Mo requirement have been conducted
under non sterile conditions. It may well be therefore that
the Mo requirement reported in earlier investigations in plants
supplied with NH_4-N may have resulted from the Mo demand for the
reduction of NO_3^- taken up after nitrification of NH_4^+ in the
nutrient medium. It will be of interest to see whether the
results of Hewitt and Gundry, 1970 are repeated in other plant
species.

14.5. Deficiency of Mo

As the most important function of Mo in plant metabolism is in NO_3^- reduction, Mo deficiency resembles N deficiency (Hagstrøm and Berger, 1965). Molybdenum deficient plants are restricted in growth, their leaves become pale and eventually whiter. Flower formation may be restricted. The similarity to N deficiency is particularly applicable to the *Leguminosae* in which Mo deficiency may restrict N nutrition by affecting both NO_3^- reduction and N_2 fixation. In clover stands Mo deficiency often occurs very unevenly giving rise to a yellow chequered appearance against a dark green background of normal plants.

Molybdenum deficiency frequently appears first in the middle and older leaves. They appear yellow to a yellowish green and the leaf margins roll in on themselves. Leaves are also often small and covered by necrotic spots. Molybdenum deficiency has probably been most frequently observed in the *Cruciferae* and in particular in cauliflower. Interveinal chlorotic markings occur on the leaves which often have a grey-green limp appearence. The middle lamella of the cell wall is not completely formed. This can be observed at a very early stage in leaf development. In extreme deficiency the leaf lamina is not formed and probably only the leaf rib is present. This appears rather like a whip and for this reason the deficiency is called "Whiptail".

14.6. Crop Requirement and Availability

The Mo content of plant material is usually low and less than 1 ppm in the dry matter. Some typical results of the contents of a number of plant species are shown in Table 14.2. Contents are normally low because of the extremely small levels of MoO_4^{2-} in the soil solution. In contrast to other micronutrients, however, Mo can be taken up in much higher amounts by plants without normally resulting in toxic effects. Agarwala and Hewitt (1954) found for example that Mo contents in plant material may vary by a factor of 100. Cotton plants supplied with excess Mo accumulated levels of up to 1500 ppm Mo in their leaves.

Table 14.2.   Mo content of different plants in ppm Mo in the
              dry matter (Johnson, 1966)

Lucerne leaves............0.34	Sugar beet tops..........0.72
Phaseolus bean tops.........0.40	Tomato leaves healthy....0.68
Spinach leaves.............1.60	Tomato leaves deficient..0.13

Most soils contain enough Mo in available form to adequately
meet the needs of crop plants.   In some areas, however, particu-
larly on acid soils (pH<5.5), Mo deficiency can arise because
of high Mo fixation in the soil.   Thus in the USA the geographic
pattern of Mo deficiency mainly follows the regions of acid
sandy soils, although the effect may be masked by the common use
of lime (Kubota and Allaway, 1972).   Highly podzolised soils
frequently show Mo deficiency as the total Mo content is low,
and the element is largely unavailable because of the low soil
pH.   Molybdenum deficiency symptoms are commonly observed on
soils derived from quartzic material, sandy pebbly alluviums,
sandy loams and on soils with high anion exchange capacities
(Cheng and Ouellette, 1973).   Soils with secondary iron oxide
accumulations such as the ironstone soils of Australia and
Holland are also often Mo deficient as they fix Mo very strongly.
Molybdenum deficiency may occasionally appear on peat soils.
This is most likely brought about by the retention of Mo by
insoluble humic acid from the peat.   Humic acid probably reduces
the MoO_4^{2-} to Mo^{5+} which becomes fixed in this cationic form
(Szalay and Szilagyi, 1968).   In some freely drained calcareous
and serpentine derived soils an absolute deficiency of Mo can
occur.   In general the critical level for Mo deficiency is about
0.1 ppm available Mo in the soil.

Individual crop plants differ considerably in their requirement
for Mo.   The *Cruciferae* and particularly cauliflower and
cabbage have a high Mo demand.   The same also applies to the
legumes because of the requirement of the root nodule bacteria.

In a survey of 21 states in the USA lucerne was found to be
the most common crop species showing Mo deficiency, followed
by cauliflower, broccoli, soya beans, clover and citrus
(Berger, 1962). In gereral the monocots are not very sensitive
to Mo deficiency. Plants which are Mo deficient usually have
Mo levels lower than 0.2 ppm in the dry matter. Thus in Mo
deficient cauliflower leaves, Mo contents of 0.1 ppm in the
dry matter were found by Massumi, 1967, whereas in the leaves
well supplied with Mo the content amounted to about 0.5 to
0.8 ppm Mo.

14.7. Mo Fertilization

Most frequently liming is enough to prevent Mo deficiency. In
some cases, however, it is only by the application of Mo salts
that it is possible to increase yields and plant Mo content
(Hagstrøm and Berger, 1965). Molybdenum application is always
preferable to liming when an increase in soil pH is not neces-
sarily desireable.

On the other hand great caution must be taken with Mo fertili-
zation as this can result in high Mo levels in fodder which are
toxic to animals.

Sodium molybdate and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ are very soluble and are
the most widely used sources of Mo. Less soluble MoO_3 has
been reported to be as effective as the more soluble sources
of Mo, but molybdenite (MoS_2), an ore, has been found unsatis-
factory (Anderson, 1956). Molybdenum frits have been as effective
as the soluble sources of Mo.

Molybdenum deficiency is corrected by soil, foliar or seed
treatment. For soil application, 50 to 100 g/ha of Mo is
generally needed for agronomic crops, and that as much as
400 g/ha may be needed for vegetable crops, (Anderson, 1956).

A few studies have been conducted comparing foliar application
with other methods of applying Mo. For example, Hagstrøm and
Berger (1965) found that foliar spray and slurry seed treatments
were equally effective when applied at a rate of 56 g/ha of Mo
on peas when the plants were 10 cm high (Table 14.2.).

Table 14.2. Effect of seed and foliar application of Mo on the yield of canning peas (Hagstrøm and Berger, 1965).

Treatment*	Yield, kg/ha	
	Vines	Peas
Check	1,070	1,520
Seed application: Slurry	2,150	2,770
Dust	1,500	1,950
Foliar spray	2,370	2,500
LSD. 05	427	410

*Molybdenum was applied as $Na_2MoO_4 \cdot 2H_2O$ at a rate of 56 g/ha.

BORON IN SOILS AND IN CROP NUTRITION

15.1 Boron Deficiency Problems

Boron deficiencies most often occur on light coloured sands and silt loam in humid regions. Kanwar and Randhawa (1974) revealed that low organic matter, light texture and high calcium carbonate favour B deficiencies. Boron deficiency is usually most pronounced on alfalfa and on certain root and cruciferous crops, such as cabbage, cauliflower, rutabagas, and turnips. More B fertilizer is used on alfalfa than any other economic crop specie.

15.2 Soil Boron

Boron occurs in the soil primarily as boric acid (H_3BO_3) or borate. This may be present in the soil solution, or adsorbed on soil particles. The most well known B containing soil mineral is the fluorine borosilicate, tourmaline although this is so resistant to weathering that it is of no significance on the soluble levels of B in the soil. Other minerals containing B are borax ($B_4O_7 \cdot 10H_2O$), colemanite ($Ca_2B_6O_{11} \cdot 5H_2O$), ludwigite ($Mg_2 Fe BO_5$). The levels of B in sedimen-

tary rocks is usually much higher than in igneous rocks.
In some shales for example levels of about 100 ppm B are
present in comparison to values for granite of about 15 ppm
(Taylor, 1964). In soils the level is generally in the range
of 7-80 ppm.

The nature of borate adsorption in soils is still not well
understood. However, it differs fundamentally from that of
other anions such as phosphate and molybdate where adsorp-
tion increases with decreasing soil pH. For borate, adsorp-
tion decreases as the soil pH is lowered. Borate availability
is thus lowest in alkaline soils. Retention is partially de-
termined by clay minerals and sesquioxides. Hence soils rich
in clay have lower water soluble B contents than light soils,
in relation to their total B levels. Maximum adsorption occurs
in the pH range 7 to 9 and it appears that greater retention
is brought about by the clay minerals than the sesquioxides,
$Al(OH)_3$ being more effective than $Fe(OH)_3$, (Sims and Bingham,
1968).

It is well known that B availability is considerably dimini-
shed by liming, which frequently can give rise to B deficiency.
This poorer availability may as already indicated be ascribed
to the increased adsorption of borate to soil particles. It
is also possible that at high soil pH levels B substitutes
for Al in complex Ca alumino-silicates.

The B content of soils in arid and semi-arid climates is in
general higher than in humid climatic zones (Kanwar and Shah
Singh, 1961). Under high leaching conditions B is easily re-
moved from soils and podzolic soils in particular are low in
B. On the other hand as the B content of sea water is quite
appreciable (4.7 ppm) soils affected by the sea may also be
very high in boron.

15.3 Uptake and translocation

Boron is probably taken up by plants as the undisocciated
boric acid although the process is not well understood.
There is still controversy as to the extent to which the

uptake process is passive or active. Tanaka (1967) reported
that part of B accumulated by sunflower roots was passively
adsorbed forming a borate complex with polysaccharides in the
free space. This suggestion was mainly based on the stoichio-
metry found between B uptake and H^+ release. Other workers
have also reported that B uptake is a non metabolic process
(Bingham et al., 1970). In an investigation into the uptake
of B by excised barley roots Bowen and Nissen (1976) have
characterized the fractions of the free space B. A high frac-
tion of the total B was found to be present in the water free
space or reversibly bound in the cell walls as borate poly-
saccharide complexes. According to these workers there is a
component of B uptake under metabolic control but this can
only be detected experimentally after B reversibly accumulated
in the free space has been removed. It would seem that the
active component is probably relatively small. Uptake thus
mainly follows water flow through the roots.

Boron is relatively immobile in plants and frequently the B
content increases from the lower to the upper plant parts.
According to the findings of Michael et al. (1969) in tobacco,
the rate of transpiration has a decisive influence on the up-
ward transport of B in this plant, which suggests that B is
mainly translocated in the xylem. This accounts for the accu-
mulation of B in leaf tips and margins. Accumulation of B
can in some circumstances lead to toxic effects and some
plant species are adapted to secrete B in guttation droplets
(Oertli, 1962). The movement of B along with the transpiration
stream also explains the fact that B deficiency always begins
at the growing points. This behaviour is similar to that of
Ca. Like Ca B too is virtually absent from the phloem sap.
The presence of borate in the phloem causes callose to be
deposited and narrows the pores in the sieve plates. Accord-
ing to Epstein (1973) the exclusion of B from sieve tubes
may be an adaptive mechanism to allow free flow in the phloem.
High concentrations of B occur in certain plant organs such as
anthers, stigma, and ovary, where levels may be twice as high
as in stems.

15.4 Functions of B

In its physiological role in the plant B differs fundamentally from other micronutrients. Unlike Mn^{2+}, Zn^{2+} or Mg^{2+} it does not bring about reactions by chelation of enzyme and substrate. It also does not depend on its effectivity for a valency change as do Fe, Mn or Mo. The borate ion much more resembles phosphate reacting with OH^- groups from sugars, alcohols, and organic acids to form esters of boric acid.

More than 40 years ago it was suggested that B forms polyhydroxy compounds with cell wall components, which raise the stability of the cell wall.

Physiologically B is regarded as an important element for tissue development. In the absence of B abnormal formation and development of tissues occurs. According to Odhnoff (1957) cell differentiation is inhibited when B is deficient. These effects on cell division and development are very rapid. In tomato root tips for example elongation halted six hours after transfer to a B free nutrient solution (Albert and Wilson, 1961).

The most well known hypothesis for the role of B in plant metabolism is that of Gauch and Dugger (1954) which claims that B facilitates sugar translocation. The hypothesis is based again on the property of boric acid complexing with polyhydroxyl compounds including alcohols and sugars.

These workers suggest that a sugar borate complex could more easily pass through cellular membranes than the highly polar sugar molecules alone. Sugar transfer across the membrane could thus take place by a reversible reaction between sugar and borate. There is some evidence in favour of a sugar borate relationship being involved in sugar translocation. For example when B nutrition is adequate, gradients in favour of sugar translocation to the growing points are found. Conversely when B is deficient, sugar translocation does not occur. Conclusive evidence that B is directly implicated in sugar translocation in plants is still lacking.

A number of metabolic roles have been suggested for B apart from that of sugar transport. One such role has been proposed by Lee and Arnoff (1967). Boron is known to complex with 6 phosphogluconate and they suggest that in healthy plants B might modulate the activity of the enzyme 6 phosphogluconate dehydrogenase by complexing with its substrate 6 phosphogluconate.

Boron is of considerable importance in the synthesis of nucleic acids. A decrease in RNA content was claimed to be the first symptom in B deficient tomato roots following a cessation in growth (Johnson and Albert, 1967). The effect of deficiency could be prevented by additions of the bases thymine, guanine and cystosine. From these findings it was concluded that B plays a role in N base utilization and hence in RNA metabolism.

The disturbing effect of B deficiency on nucleic acid metabolism and protein synthesis is demonstrated very well in the results of Hundt et al. (1970) in a study on N-metabolism of sunflowers in relation to B supply. In plants poorly supplied with B, NO_3-N accumulated in the roots, leaves and stems showing that NO_3-reduction and amino acid synthesis were inhibited. When only a low level of B was resupplied to moderately B deficient plants, there was a rapid response to P-32 uptake and incorporation into DNA or RNA, and enhanced protein synthesis (Table 15.1). The role of B and other plant nutrients in protein synthesis has been very well reviewed by Amberger (1975).

Table 15.1. Influence of B on DNA phosphate, RNA phosphate and protein of sunflower plants, suffering from moderate B deficiency (Hundt et al., 1970).

B in the nutrient solution, ppm	Leaves	Roots
DNA phosphate in % of total phosphate		
0	0.2	0.5
1	1.4	1.8
RNA phosphate in % of total phosphate		
0	1.4	3.6
1	6.4	13.0
Protein N mg/pot		
0	627	713
1	1267	1468

15.5 Boron deficiency

Boron deficiency first appears as abnormal or retarded growth
of the apical growing points. The youngest leaves are mis-
shapen, wrinkled and are often thicker and of a darkish blue-
green colour. Irregular chlorosis between the intercostal
veins may occur. The leaves and stems become brittle indicat-
ing a disturbance in transpiration. As the deficiency progres-
ses the terminal growing point dies and the whole plant is
reduced and flower and fruit formation is restricted or inhi-
bited.

Boron deficiency also affects root development, and in B free
nutrient solutions root growth is inhibited (Bussler, 1960).
Roots appear slimly and are thickened, and the tips are ne-
crotic.

The most well known B deficiency symptoms are crown and heart
rot in sugar beet. The symptoms begin with anatomical changes
at the apical growing points. The youngest leaves are curled
and stunted and turn brown or black. Eventually the inner
leaves are affected and the main growing point dies. Older
leaves are brittle and chlorotic. The crown of the beet begins
to rot and infection then sets in, and the whole plant becomes
affected. As might be expected the healthy part of the beet
is low in sugar. In turnips and swedes, B deficiency results
in glassy like roots which are hollow and cracked. The appear-
ance of cracked stems is also an indication of B deficiency in
celery. The development of scaly surfaces and the formation
of internal and external cork like material is typical of the
features associated with B deficiency in many plants including
tomatoes, cauliflower, citrus and apple.

15.6 Crop requirement

Crops differ in their sensitivity to B deficiency. The most
sensitive crops are sugar beet, mangels and celery. Various
Brassica crops such as turnips, cauliflower, cabbage and
Brussels sprouts also have a high B requirement. Of the fruit
trees, apples and pears, are known to be particularly sensi-
tive to B deficiency (Bradford, 1966). Fruit formation is

impaired and yield depressions as high as 80% may occur compared with plants adequately supplied with B.

Some legumes also have a high B requirement. Ouellette and Lachance (1954) reported that in Canada a considerable extent of the lucerne crop suffered from B deficiency. The degree of B deficiency correlated negatively with the B level in the plant, and lucerne plants with less than 15 ppm B were regarded as inadequately supplied.

In general, dicots have a higher B requirement and B content than monocots. For this reason B deficiency of cereals is less common. Syworotkin (1958) distinguishes between three plant groups with regard to B content and B requirement: Monocots, dicots and dicot species with a latex system such as dandelion, poppy and some *Euphorbiaceae* (Table 15.2).

Table 15.2. Boron content of various plant groups (Syworotkin, 1958), (B in ppm DM).

Monocots	Dicots	Dicots with a latex system
Barley 2.3	Peas 22	Dandelion 80
Wheat 3.3	Beets 49	*Euphorbia* 93
Maize 5.0	Lettuce 70	Poppy 94

15.7 Boron application

Borax and sodium tetraborate ($Na_2B_4O_7 \cdot 5H_2O$) are the most popular B fertilizers. Other Na borates, such as sodium pentaborate ($Na_2B_{10}O_{16} \cdot 10H_2O$) and Solubor, also are used. The Na borates generally are used only for soil applications, with the exception of Solubor, which can be used for both soil and foliar applications because of its greater solubility and compatibility with most spray materials. Limited use of H_3BO_3 for soil and foliar applications has been noted. Colemanite, a naturally-occuring Ca borate is often used on sandy soils

because it is considerably less soluble and less subject to leaching than Na borates.

Boron deficiency is commonly corrected by application of B fertilizer to the soil. While sprays of B compounds (H_3BO_3, Solubor) are often beneficial, soil applications remain effective longer (Burrell, 1958). Boron compounds used in foliar sprays also can be mixed with liquid fertilizers for application to the soil.

The optimum rate of soil-applied B will depend on plant species, soil cultural practices, rainfall, liming, and soil organic matter as well as other factors. In general, a rate of 1.2 to 3.2 kg/ha of B is needed for soil treatments on legumes and certain root crops, while lower rates (0.6 to 1.2 kg/ha) are needed for the other crops.

Due to their relatively high requirement for B, the legumes, especially alfalfa, have shown significant responses to B fertilizers. Powers and Jordan (1950) found B response on alfalfa from application of 2.4 kg/ha of B in a greenhouse study. In field trials on alfalfa Wear (1957) noted significant response to 1.8 kg/ha of B at eight locations in USA.

Certain root crops, such as members of the *Chenopodeaceae* family, have high B requirements for normal growth. For example, red beet yields were increased 140% when 19.2 kg/ha of B was applied to a silty clay (Powers & Jordan, 1950). Wear (1957) found significant red beet yield responses when 2.4 kg/ha of B was applied to a fine sandy loam soil.

For crops with lower B requirements, such as cotton, application of 0.6 kg/ha of B in the fertilizer band has resulted in optimum yields (Keogh & Maples, 1969). The sensitivity of sweet potatoes to applied B was demonstrated by Bryan (1945). He found maximum yield with the addition of 0.6 kg/ha of B and decreasing yields with increasing B additions and eventual B toxicity at 3.6 kg/ha of B.

In a growing crop, boron deficiency can successfully be eliminated by foliar spray. Best results are obtained if several sprays are made (Grupta & Cutcliff, 1978).

15.8 Boron toxicity

As B is toxic to many plant species at levels only slightly above that required for normal growth, toxicity effects may occasionally arise by excessive use of B fertilizers or on soils with high B contents such as those derived from marine sediments. The toxicity is, however, more usually associated with arid and semi arid regions where B levels are frequently high in the soil. The B status of irrigation water is particularly important in these regions. Reisenauer et al. (1973) cite the observations of the *University of California Agricultural Extension Service* (1969) which found that at 1 ppm in the water sensitive crops may show visible injury and at 10 ppm even the tolerant crops may be affected. According to Reisenauer et al. (1973) toxicity in crop plants is likely to occur when the level of hot water soluble B in the soil exceeds 5 ppm B, whereas soil levels of <1 ppm B are generally not high enough for optimum plant growth.

Some of the most sensitive crops to B toxicity are peach, grapes, kidney beans and figs. Semi-tolerant plants include barley, peas, maize, potato, lucerne, tobacco, and tomato whilst the most tolerant crops are turnips, sugar beet, and cotton. Toxic effects of B result in leaf tip yellowing followed by progressive necrosis. This begins at the tip and margins and finally spreads between the lateral veins towards the midrib. The leaves take on a scorched appearance and drop prematurely. These effects have been described in detail for a number of plant species (Bradford, 1966).

Solubor ($Na_2 B_4 O_7 \cdot 5H_2O$ + $Na_2 B_{10} O_{16} \cdot 10H_2O$)

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Role of fertilizers in agricultural production, fertilizer
consumption and production processes of important NPK fertilizers

16.1.   Role of fertilizers.

In many of the developing nations today, population
density has become so high that the supply of human labour has
exceeded the number that can be employed on the available
arable land with traditional method of culture. More intensive
cultivation and high productivity per unit of land become critical
in such situations in providing the essentials for life.
Substantial increase in agricultural production are acutely
needed to support rapid growing populations in most areas of
the world today. The increased production potentially available
simply from opening up new lands to cultivation is very limited
and can supply only a fraction of the requirements of today's
rapidly growing populations. The attainment of the most economical
yields and the greatest return from land and labour demands,
the addition of substantial quantities of off-farm physical inputs
such as improved seeds, fertilizers, crop protection chemicals,
irrigation and precision implements for land preparation, seeding,
fertilizer application and cultivation.

There exists a big gap between the actual crop yields
and potential yields. For example, the average global grain
production of the world is of the order of 1300 million tonnes.
But Buringh et al (1975) postulated maximum food production
potential of 49330 million tonnes and thus the postulated production
potential was about 30 times as much as the present level of
production. (Table 16.1). After estimating the area of
potential agricultural land in different parts of the world with
suitable adjustments for soil conditions and water deficiency,
they converted the climatic parameters into a single composite
measure called "gross photosyntehsis" (GP). They developed
appropriate conversion factors to transform GP values into dry
matter production and finally into grain equivalents. According
to their study, Asia has the maximum untapped production potential
followed by south America and Africa.

Table 16-1   Total production potentials of continents and the   world-

(After Buringh et al. 1975)

Continent	A	PAL	IMAP	MPDM	PIAL	IPALI	MPDMI	MPGE
S.America	1,780	616.5	333.6	25,224	17.9	340.7	25,710	11,106
Australia	860	225.6	74.2	5,297	5.3	76.1	5,462	2,358
Africa	3,030	761.2	306.5	24,162	19.7	317.5	25,115	10,845
Asia	4,390	1,083.4	433.5	24,966	314.1	581.6	33,058	14,281
N.America	2,420	628.6	320.0	15,443	37.1	337.5	16,374	7,072
Europe	1,050	398.7	233.1	8,289	75.9	247.1	9.653	4,168
Antartica	1,310	0	0	0	0	0	0	0
Total	14,840	3,714.1	1,700.9	1,03,381	470.0	1,900.5	1,15,372	49,830

A: Area of a broad soil region (10^6ha).

PAL: Potential agricultural land   (10^6ha).

IPAL: Imaginary area of PAL with potential production without irrigation (10^6ha).

MPDM: Maximum production of dry matter without irrigation (10^6tonnes/year).

PIAL: Potentially irrigable agricultural land (10^6ha)

IPALI: Imaginary area of PAL with potential production,   including irrigation (10^6ha).

MPDMI: Maximum production of dry matter including irrigation (10^6 tonnes/ year).

MPGE_: Minimum production of grain equivalents, including irrigation (10^6 tonnes/year).

This however, cannot be achieved simply by application of fertilizers and an appropriate combination of production technology is required to fulfill this gap. But fertilizer is an essential ingredient of production technology and must be available in appropriate kind, quantity and timing if needed levels of poduction are to be achieved and if the economic development is to proceed.

There is lot of data available in the literature indicating the important role of fertilizers in crop production, but only a few willbe described to illustrate the importance of fertilizers. Fig. 16.1 shows a close relationship between rice yield and fertilizers used (Shields 1970).

16.1.1. Proportion of Agricultural Production due to Mineral Fertilisation.

In "Agriculture: toward 2000" (an FAO document of November 1979), it is indicated that between 1965 and 1976 fertilisers were responsible for 56% of the yield increases in developing countries. On this basis there is a forecast of fertilizer requirements which will require, between now and the year 2000, a five-fold increase in the present comsumption of developing countries.

The enlargement of the cultivated area, 200 million ha between 1975 and 2000, the extension of the irrigated areas, and the use of genetics will play a part in the forecast of an agricultural growh rate of between 6 and 9%, according to the geographical area. But mineral fertilization has a decisive role to play in this respect. What could its true importance be?

The principal cereals, wheat, rice, maize, sorghum, have been considered, particularly in respect of countries where the production of these crops is important.
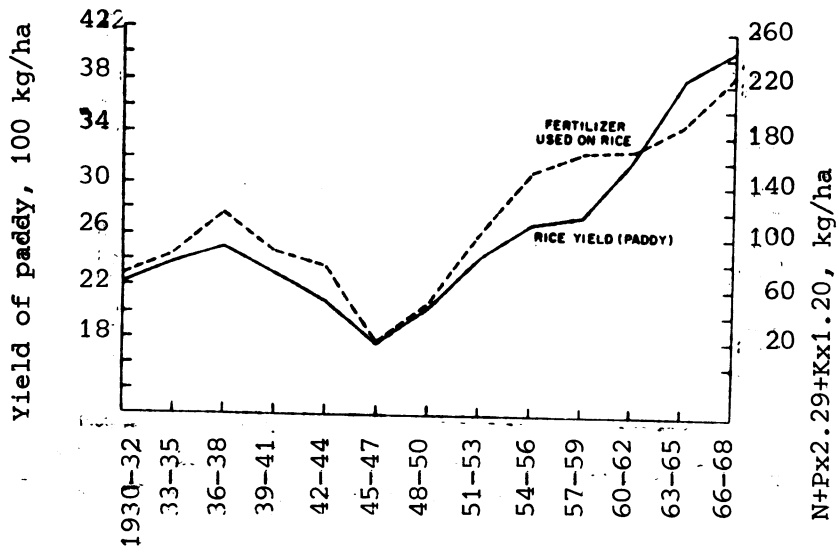
Fig. 16.1. Relationship between yield of paddy and
fertilizer used in period 1930-68 (bv
3-year averages), Taiwan
(Shields, 1970).

On the scale of large geographical areas, the average increases in production made possible by the best $N-P_2O_5-K_2O$ treatment are the following:

Table 16.2

	West Africa			South and East Africa		Latin America			Far East	
	Maize	Rice	Sorghum	Maize	Sorghum	Maize	Rice	Wheat	Rice	Wheat
Average increase in yield in kg/ha	1636	1309	1479	1709	968	1572	1164	1319	1769	1892
kg/ha-average rate										
N	92	74	45	56	65	63	37	108	129	135
P_2O_5	70	31	45	44	32	61	59	40	56	79
K_2O	32	0	45	6	17	31	31	30	26	45

Depending on the cereal and the region, the cereal yield increased by 10 to 19 dt/ha, the average approaching 15 dt/ha, which is just about equal to the present cereal yield in the developing countries. Can one deduce from this that the correct use of fertilizers would allow a doubling of current production?

The individual examination of certain countries is necessary in order to provide the reply.

1. Wheat

Wheat yield increased by 60% in Algeria by fertilizer application of 40:40:40 kg NPK/ha. In Pakistan, the short term projections show that an increase of fertilizer consumption of 14%per year would increase wheat production by 6.3%. The target of 25t/ha will be achieved with $N-P_2O_5$ level of 100-60 and that of 35 ton/ha seems obtainable with 173 kg N and 87 kg P_2O5/ha.

The result however, show (Fig. 16.2) that the efficiency of
fertilization was lower in comparison to Germany. Repeated
normal annual fertilization and a return to the soil of
crop residue will bring about a progressive improvement of the
soil fertility, with a result, a greater.efficiency of
fertilization.

In case of Ethiopia, Syria, Turkey, a possible increase
of wheat yields by 57 to 73% was obtained.

2. Rice.

The following table presents certain results of the
Fertilizer Programme on rice, in countries where this cereal is
important.

Table 16.3 -   Rice Yields in kg/ha

	1978 area in 1000 ha	1978 Yield	Control Plot	Best treatment	% increase
Brazil	5552	1304	2141	3758	76.6
Bangladesh	10000	1890	2347	4850	106.4
Indonesia	8812	2921	3530	5390	62.6
Thailand	8288	2051	2825	3955	41.6

3. Maize

Table 16.4 - Maize Yields in kg/ha

	1978 area in 1000 ha	1978 Yield	Control Plot	Best treatment	% increase
Brazil (1977)	11682	1637	2625	4693	78.5
Kenya	1490	1577	3472	5323	53.5
Nigeria	1665	871	1447	2223	52.7
Zaire	700	696	851	2025	130.6
Indonesia (1977)	2550	1188	1552	2668	72.0

Fig. 16.2. **WHEAT YIELD RESPONSES TO FERTILIZERS IN GERMANY AND PAKISTAN (PUNJAB).**

YIELD (tons/ha)

Germany [1]

Punjab 1976/77 [2]

FERTILIZER APPLICATION (Kg N/ha)
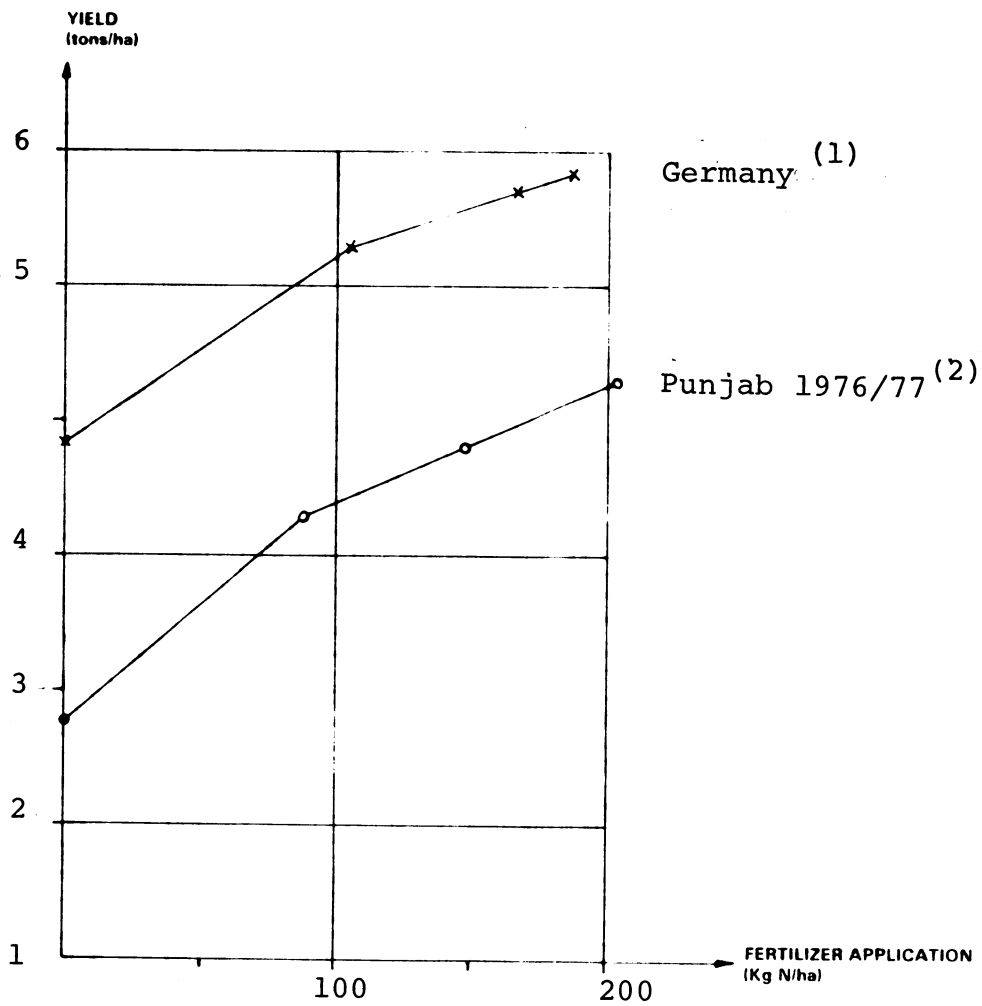
[1] 111 experiments winter wheat 1969/71.
[2] 70 experiments wheat, Punjab 1976/77.

Source: Ahmad and Bertilson op. cit.

16.1.2   Conclusion

The results available clearly indicate that a doubling of the capacity of cereal production in developing countries is possible.

Since 1953, the developed countries have already passed from 400 million tonnes of cereals to .800 and developing countries from 380 to 750, with, in the case of the latter, the effect of an increase in cultivated area which increased from 350 to 460 million hectares, while in developed countries the cereal area remained strictly stable at about 300 million ha.

In the developed countries, the scope for progress can still be up to 30 to 40%; in the developing countries, another doubling is still possible.

The role of mineral fertilisation is essentially the same in two cases, with the difference that in the one case the game is practically played whilst in the other it is just beginning (See Fig. 16.3 on fertilizer consumption and agricultural production).

GRAIN PRODUCTION AND FERTILIZER CONSUMPTION.

Fig. 16.3

Grain
Kg per inhabitant per annum)

Developed countries

Developing countries.

FERTILIZER CONSUMPTION (million tonnes nutrient)
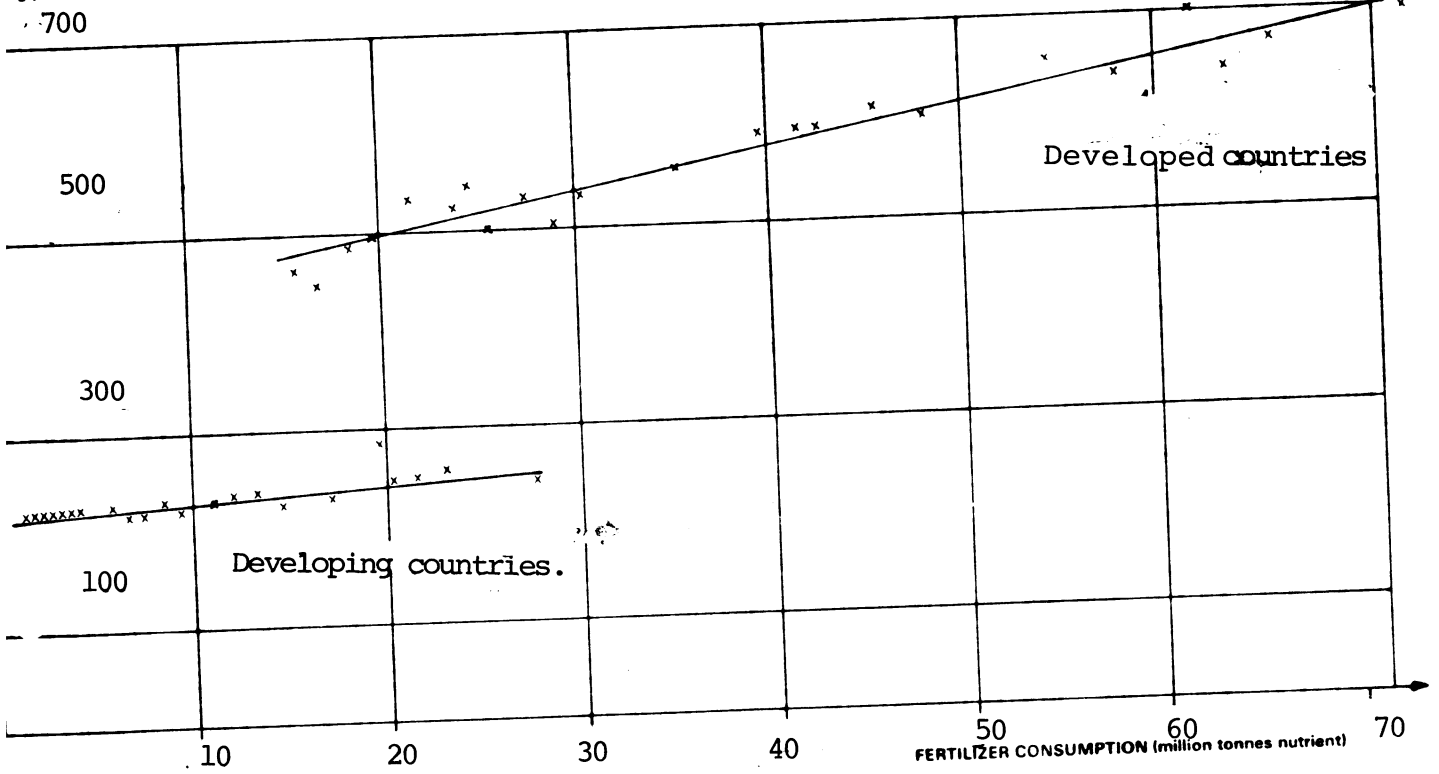
16.2 Fertilizer consumption

Fertilizer consumption data are presented in Tables 16.5 to 16.9. Table 16.5 shows the total world consumption from 1970 to 1979 whereas in Table 16.6·world consumption of fertilizers is divided into economic classes. Tables 16.7 and 16.8 show the percentage consumption of different fertilizers of N and P, respectively. In table 16.9 fertilizer consumption in kg/ha of agricultural and arable lands in economic classes as well as in some countries of these classes is presented. Table 16.10 and 16.11 shows the production estimates of K and rock phosphate.

Table 16.5

World consumption of fertilizers.

1000 MT

Years	N	P	K
1970	28691	8223	12839
1971	31767	8671	13836
1972	33348	9153	14508
1973	35677	9802	15655
1974	38721	10533	17274
1975	38596	9894	16365
1976	42908	10547	17774
1977	45039	11572	19145
1978	47800	12352	19420
1979	51435	13287	20573

Table 16.6

World consumption of fertilizers by

economic classes

1000 MT

	1969			1979		
	N	P	K	N	P	K
Dev. ed. Market Econ	14560	5155	7513	21267	6206	10440
Dev. ing. Market. Econ	4694	860	867	10155	2435	2398
Centr. Plann. Econ.	9422	1918	3894	19993	4646	7735
	1974			1979		
All.Dev. ed. count.	27527	8464	15132	33529	9912	17606
All Dev. ing. count.	11170	2092	2076	17905	3375	2967

Table 16.7

World Consumption of N in different fertilizers.

(Percent of total consumption).

1979.

	1979.
Ammonium Sulfate	6.9
Ammonium nitrate +	16.5
Cal. Amm. nitrate	7.6
Calcium nitrate	0.3
Urea	30.0
Liquid NH_3	13.9
Amm. phosphate	3.6
N P and NPK fertilizers	17.0
Others	4.2

Table 16.8

World consumption of P in different fertilizers

(percent of total consumption)

1978/79

	1978/79
Single superphosphate	12.3
Triple "	10.7
Amm. phosphate	24.4
P in NPK	37.2
P in NP	6.9
Basic slag	2.3
Rock phosphate	1.5
Others	1.7

World consumption of P 1979-80. 31.6 million tonnes.

Estimated world consumption
of P   1982-83   36.7   "   "

Table 16.9

Consumption of fertilizers in kg/ha of Agricultural (A) and arable (B) lands. (1978).

	N		P		K	
	A	B	A	B	A	B
World	11.3	36.4	2.9	9.4	4.5	14.5
Dev. ed. Markt.Econ	17.3	49.8	5.1	14.7	9.0	26.1
Centr. Plann. Econ.	17.7	51.3	4.1	11.9	6.9	19.8
Dev. ing. Markt.Eco.	6.8	24.1	1.3	4.5	1.2	4.0
W. Europe	56.2	98.2	15.8	27.6	27.1	47.4
Norway	114.1	127.4	30.5	33.8	78.0	87.1
Denmark	129.6	142.7	20.3	22.3	49.0	54.0
Sweden	68.7	85.4	16.1	20.1	28.9	35.9
Netherlands	216.0	515.8	18.6	44.3	43.8	104.6
East Germany	124.8	155.6	30.0	37.4	60.1	74.9
West Germany	102.8	168.8	30.0	49.4	74.2	121.9
France	62.1	104.7	26.7	47.2	44.0	74.2
U.S.A.	20.9	44.5	4.9	10.5	9.9	21.1
U.S.S. R	12.6	33.0	3.8	10.1	7.4	19.3
China	21.6	69.4	2.5	8.3	1.4	4.6
India	16.5	17.7	2.3	2.4	2.6	2.7
Pakistan	27.4	34.2	3.3	4.2	0.2	0.3
North Korea	204.0	207.7	45.5	46.3	63.7	64.9
Japan	131.6	146.4	61.7	68.7	109.2	121.5
Egypt	172.8	172.8	13.4	13.4	1.1	1.1
Lat. America	3.7	17.4	1.5	7.0	1.8	8.5
Oceania	0.5	5.7	1.1	12.7	0.4	4.6

Table 16.10

Estimated production of technical grade potash

In 1000 MT. /1978/79.

	K
France	93.0
German Dem. Rep.	78.9
Germany. Fed. Rep. of	125.1
Israel	5.8
Italy	5.8
Spain	8.4
USSR	311.2
Canada)	346.9
U.S.A)	
World	975.1.

Table 16.11

Production of rock phosphate (1978).

1000 MT.

World	· 124536	
Africa	32058	
Morroco		19273
Togo		2827
Tunisia		3713
South Africa		1762
N.C. America	50303	
U.S.A.		50037
S. America	1205	
Brazil		1094
Asia	11933	
China		4400
Israel		1723
Jordan		2320
Vietnam		1500
Ocenia	4154	
Christmas Islands		1455
Naluru		1999
U.S.S.R.	24800	
Developed mark. Econ.	54778	
Developing mark. Econ.	38558	
Centr. Planning Econ.	31200	
Developed All	79578	
Developing All	44958.	

16.3. Production Technology of some important fertilizers of N, P, and K.

### 16.3.1. Historical background.

The origin of commercial fertilizers goes back to the last century. The first factory for the production of fertilizers came into function in 1846 in England which was built to manufacture superphosphate. Superphosphate and guano were the first fertilizers of some economic importance. Import of guano from Peru to Europe also started in 1840's. Guano the dried excrement of sea birds and bats, though a natural product, was assorted and ground in Europe and can be called as a commercial fertilizer- In 1850's saltpeter from Chile was introduced in Europe and in 1861, the first factory to manufacture fertilizer of calcium salts began in Strassfort in Germany. Since then calcium fertilizers came into use.

Around the turn of the century, greater concern on N supply for future was focused. The first factory for production of nitrogenous fertilizer from the air began in 1902 at Niagara. In 1913, the Haber process of combining nitrogen and hydrogen directly went into commercial operation in Germany. In U.S.A., the first two successful ammonia went over to Haber-Bosch method in 1929.

16.3.2. Nitrogenous fertilizers.

Although there is a long list of N. fertilizers which are utilized in different parts of the world. In this chapter, only a few import N-fertilizers, especially used in the tropical countries, will be discussed.

The origin of all N-fertilizers is the nitrogen from the air and ammonia production is the first step in the manufacture of most N-fertilizers. A nitrogen production flow chart is shown in Fig. 16.4
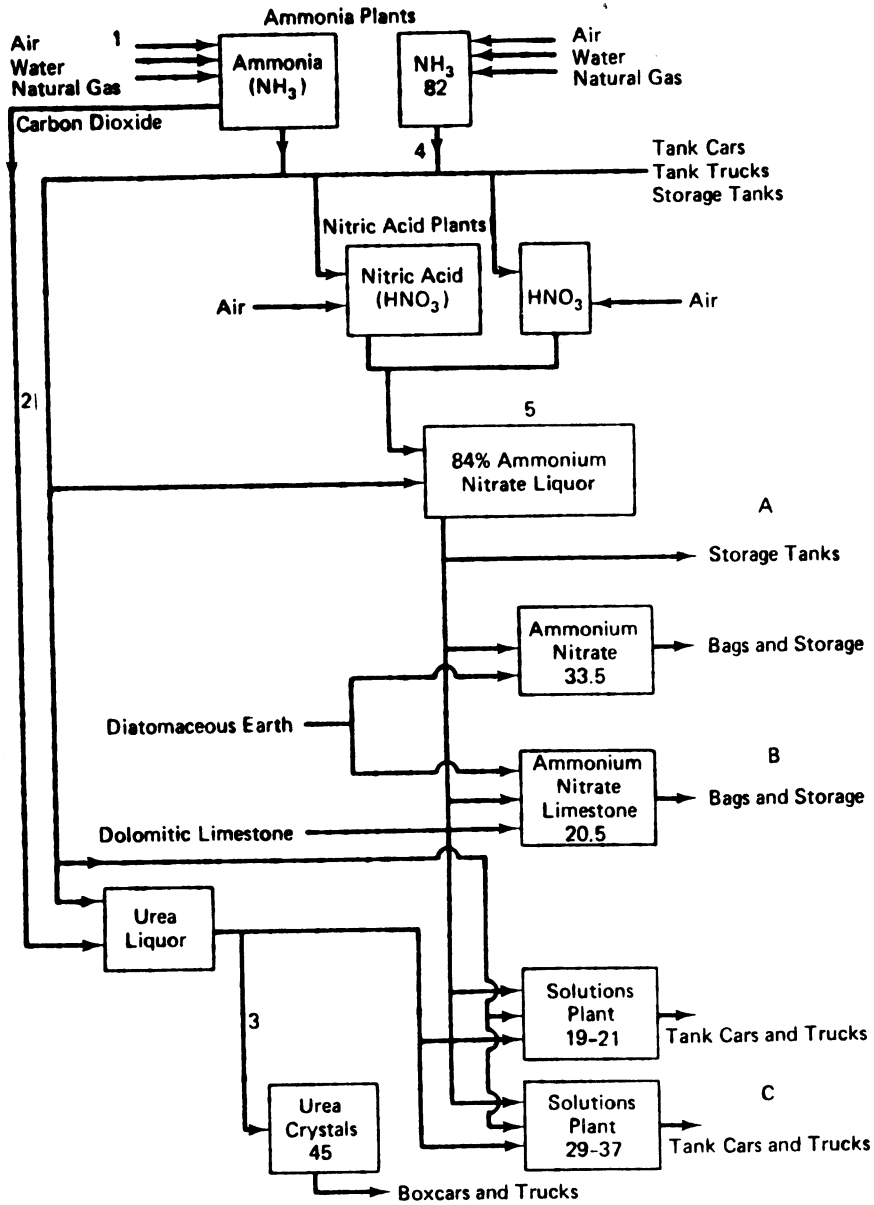
16.4

Figure .Nitrogen fertilizer production flow chart. (Jones, 1979)

A description of five steps in production is given below:

1. Air, water and natural gas are taken into ammonia plants where ammonia is produced. A by-product in the production of ammonia is CO_2.

2. The ammonia and carbon dioxide can be pumped together in a reactor at 3,000 psi (204 atm) and 365°F (185°C) to form urea liquor.

3. The urea liquor can be formed into urea crystals that are used for fertilizers and in the manufacture of glues, paints, varnishes, plastics and livestock feed.

4. The ammonia can be sent on to the nitric acid plants where additional air is mixed with it at a ratio of nine parts of air to one part of ammonia. When this mixture is passed over platnium, it gives off oxide of nitrogen. It is then scrubbed with a condensate (distilled water) that gives nitric acid.

5. The nitric acid is then combined with additional ammonia to form 84 percent ammonium nitrate liquor. The ammonium nitrate liquor is sent on to (A) storage tanks, (B) solids plants or (C) solutions plants.

Solid Plants.

1. The ammonium nitrate liquor is taken into the ammonium nitrate plant where it is pumped to the top of the prilling tower. The ammonium nitrate is then sprayed out in small droplets; it falls 56.1 m forming small prills. The prills are coated with 3 percent diatomaceous earth. This product contains 33.5 percent nitrogen.

2. Ammonium nitrate liquor is taken into the ammonium nitrate limestone plant where it is sprayed into a rotating bed of dolomitic limestone. The product then goes through a drying process and is screened, cooled, and sent to the warehouse. This material

is also coated with diatomaceous earth and contains
20.5 percent nitrogen.

Solutions Plant

The ammonium nitrate liquor is taken into the solutions
plant where it can be diluted and made into a straight ammonium
nitrate direct-application solution or combined with urea to form
an ammonium nitrate-urea solution. Ammonia can also be added to
the solutions for producing manufacturing-type solutions.


16.3.2.1. Ammonia.

Along with rock phosphate, potash salts and sulfur, ammonia
is a basic raw material of the fertilizer industry. It, or its
derivatives, is found in all nitrogen-bearing fertilizers.

<u>Method of Manufacture.</u> The synthesis of ammonia is a simple
process in contrast to the preparations of the raw materials. All
of the nitrogen used in ammonia production comes from the air. Hydro-
gen for the process is derived from water, naptha, natural gas, coal
or oil. The original Haber-Bosch process is the basis of all the
various processes. It consists of subjecting a mixture of nitrogen
and hydrogen to high pressures, in the presence of an appropriate
catalyst.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$
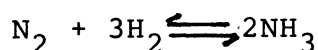
The reaction is exothermic, yielding 11.0 kcal per mole
NH_3. An iron catalyst is used to increase the yield because the
reaction rate is slow. Ammonia synthesis in most U.S. factories
is carried out at temperatures of $932^{\circ}F$ ($500^{\circ}C$) and at an operating
pressure of 2.940 to 14,700 psi (200 to 1,000 atm).

In countries where the availability of natural gas or refinery
gas is limited, water gas is an important source. It is produced by
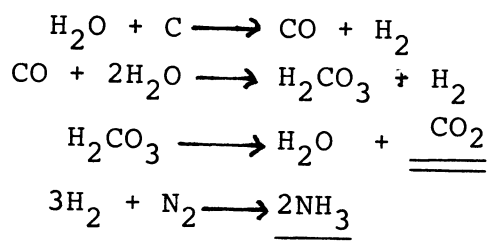passing steam over red-hot coke in a water-gas generator.

$$H_2O + C \rightarrow CO + H_2$$

$$CO + 2H_2O \rightarrow H_2CO_3 + H_2$$
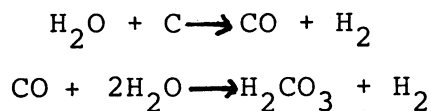
<u>Shipment and Handling</u>   The high pressures exerted by anhydrous ammonia can be dangerous,but they are no more dangerous than the pressures exerted by steam boilers that are in common use in factories and on the farm. Persons handling these gases should become familiar with the regulations. Ammonia is handled as a liquid under pressure and is released as a gas through an ammonia-resistant hose into the soil. Bronze and brass fittings react chemically with ammonia and should·not be used.

Incomplete filling of tanks is a safety measure. When the temperature of liquid ammonia in the tank is $30^{O}F$ $(-1^{O}C)$, the tank can be safely filled to 86 percent of its capacity. At $100^{O}F$ $(38^{O}C)$, the tank can be safely filled to 95 percent of its volume. If a tank **was** completely filled with liquid ammonia, a very small increase in temperature would be sufficient to raise the pressure enough to cause an explosion if the pop-off valve failed to work.

16.3.2.2 <u>Urea</u>

<u>Description</u>   Urea is a white, crystalline organic chemical that, in the pure form, contains 47 to 48 percent nitrogen. The material is used as an ingredient in the manufacture of paints, glues, plastics, paper, textiles, feeds, weed-control chemicals and (in the pelleted and conditioned form) fertilizer. The fertilizer grade contains 45 to 46 percent nitrogen. It is rapidly replacing ammonium nitrate as the world's leading solid nitrogen fertilizer because of its economy of production, higher nutrient content and fewer pollution problems during manufacture.

<u>Method of Manufacture</u>. Urea is a product that is suitable for manufacture by an ammonia plant. The needed raw materials, CO_2 and NH_3 are available in an ammonia plant as may be noted by the following basic reactions that take place in ammonia synthesis:

$$H_2O + C \longrightarrow CO + H_2$$
$$CO + 2H_2O \longrightarrow H_2CO_3 + H_2$$
$$H_2CO_3 \longrightarrow H_2O + \underline{\underline{CO_2}}$$
$$3H_2 + N_2 \longrightarrow \underline{\underline{2NH_3}}$$

Ammonium carbamate is formed by combining pure ammonia
with pure carbon dioxide gas at 5000 psi (340 atm). It loses a
molecule of water and is thus converted into urea.

$$2NH_3 + CO_2 \xrightarrow{\text{5000 psi}} NH_2COONH_4$$

$$NH_2COONH_4 \longrightarrow CO(NH_2)_2 + H_2O$$
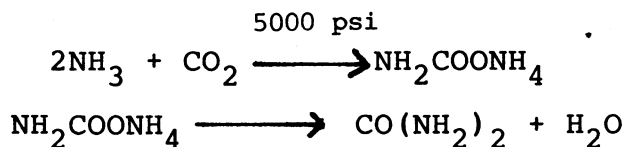
Great care must be taken in the final production stage to prevent
formation of biuret, which, if present in large enough quantities,
is damaging to growing plants. The solution of urea is concentrated
in vacuum evaporators and is finally dried by spraying into a tower
where it solidifies into pellet or prilled form.

16.3.2.3. Ammonium Sulfate

Fertilizer-grade sulfate of ammonia contains 20 to 21 percent
nitrogen and 24 percent sulfur. Today more sulfate of ammonia is
manufactured from synthesized ammonia than from coke-oven by-product
ammonia. Ammonia nitrogen is retained by the soil in an exchangeable
from until it is oxidized to nitrate by nitrifying bacteria.
It does not leach as readily as nitrogen in the nitrate form. Much
of the nitrogen in mixed fertilizers is in the form of
$(NH_4)_2SO_4$.

Because sulfate of ammonia is acid-forming, it is preferred
in areas having neutral or slightly alkaline soil. Soils of an acid
nature that are limed properly can be, and are, fertilized with sulfate
of ammonia to provide the nitrogen needs of the crop.

Description. Ammonium sulfate is a white, crystalline salt that,
in pure form, contains 21.2 percent nitrogen and 24.2 percent sulfur.
The commercial product most popular for agricultural use is a
light gray, free-flowing material made specifically for direct
application and for blending in other granular materials. It is
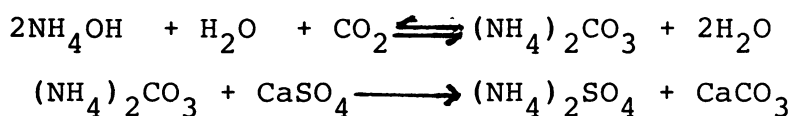sold with a guaranteed analysis of 20 percent nitrogen.

Method of Manufacture. There are two processes used for the manufacture of $(NH_4)_2SO_4$. One of them involved the use of ammonia that is produced as a by-product of the destructive distillation of coal to produce coke; "destructive distillation" is a term used where heating is accomplished with the exclusion of air. The other process utilizes ammonia produced synthetically.

Beginning about 1950, the tonnage of ammonium sulfate made from synthesized ammonia surpassed that of the coke-oven industry even though the by-product process has an economic advantage because of low ammonia cost. In each of the processes, the final reaction is closely related to the following:

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$
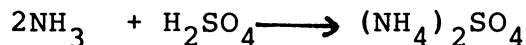
Neutralization takes place in a reactor, and the slurry is transported to a crystallizer where the sulfate of ammonia crystals are taken off the bottom and centrifuged. The mother liquor is recycled to the reactor. Crystal growth is regulated by airflow, time and temperature.

A German process, which involves the use of ammonia, gypsum and carbon dioxide at 5 atmospheres of pressure, is of interest. It is of importance in the event of a sulfur shortage.

$$2NH_4OH + H_2O + CO_2 \rightleftharpoons (NH_4)_2CO_3 + 2H_2O$$
$$(NH_4)_2CO_3 + CaSO_4 \longrightarrow (NH_4)_2SO_4 + CaCO_3$$

$CaCO_3$ precipitates and is separated from the liquor by centrifuging. The $(NH_4)_2SO_4$ is then recovered by evaporation of the water.

16.3.3. Phosphatic fertilizers

Rock phosphate is the basic raw material for all the phosphatic fertilizers. The production of rock phosphate in various parts of the world are presented in Table 16.11.

The fundamental process that are employed to make the phosphorus in phosphate rock more available are heat treatment and acid treatment. Both processes destroy the insoluble, crystalline apatite structure resulting in a product that contains phosphorus that is more soluble and more readily available to plants. Heat from gas or oil will do this, but electrical energy is required to produce elemental phosphorus. Acid treatment is effected with sulfuric, phosphoric and nitric acids.

16.3.3.1. Ordinary Superphosphate

Superphosphate is a term in reference to phosphates, the phosphorus of which is in a form readily available to plants. Ordinary or normal superphosphate refers to those that contain up and including 24 percent P_2O_5 (10.5 percent phosphorus).

Description. It is marketed as a gray, brown or almost white material in either powdered or granular form. It has an acid odour.

Method of Manufacture. Superphosphate is a product resulting from the mixing of approximately equal quantities of 60 to 70 percent sulfuric acid (93 to 98 percent acid, diluted with water) with phosphate rock ground to pass a 100-mesh (0.14 mm) sieve and containing 72 percent BPL, $Ca_3(PO_4)_2$. There are two manufacturing processes commonly used. They are the Sturtevant process and the Broadfield den continuous process. The sulfuric acid and ground phosphate rock are mixed together in a simple cone mixer that uses a swirling action for mixing. A popular manufacturing method in the fertilizer industry is the use of a TVA cone mixer and a Broadfield den that allows the continuous mixing of rock and acid, producing superphosphate at the rate of 40 to 50 tons (36 to 46 m tons) per hour. The resulting material, which is dried at a temperature exceeding $212^{\circ}F$ ($100^{\circ}C$) developed in the reaction, is later cured and ground, or granulated by using a tilted rotating drum. Another process in use is the Sturtevant process or batch mixing process. The reaction for both may be expressed as follows:

$$Ca_{10}PO_4)_6F_2 + 7H_2SO_4 + 3H_2O \rightarrow 3\ CaH_4(PO_4)_2 \cdot H_2O + 7CaSO_4 + 2HF$$
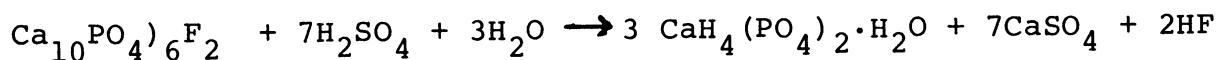
<u>Chemical Characteristics</u>   Ordinary superphosphate is two-fifths monocalcium phosphate and three-fifths gypsum by weight. It has a pH of about 3. It analyzes about 20 percent P_2O_5 (9 percent phosphorus), 19 to 22 percent calcium and about 10 to 12 percent sulfur. A representative sample of ordinary or normal superphosphate also contains traces of magnesium, iron, aluminium, copper, manganese, zinc and chlorine. Because it is of low analysis, its importance for supplying fertilizer phosphorus in many countries is declining.

16.3.3.2. Phosphoric Acid.

A very small amount of phosphoric acid is added as such to the soil via irrigation water, but for the most part it is considered as a raw material for further processing. Three kinds of phosphoric acid are in various stages of use and product development. These are classified according to the way they are made. The first two are referred to as wet-process and electricfurnace acids. The third is made from acid produced by either one or both of the first two methods but is upgraded to contain up to 76 percent P_2O_5 (33 percent phosphorus) by dehydrating very pure H_3PO_4; it is called superphosphoric acid. Some is used to produce detergents, food stuffs and many other products, but most of it is used in the production of fertilizer.

Wet-Process Phosphoric Acid.

The same ingredients that are employed in producing superphosphate are used to manufacture wet-process acid. The main difference is that an excess sulfuric acid is used. A liquid is produced when an excess of sulfuric acid is mixed with finely ground rock phosphate. The principle reaction for producing H_3PO_4 by the wet process is:

$$Ca_{10}F_2(PO_4)_6 + 10H_2SO_4 \tfrac{1}{2} 20H_2O \rightarrow 10CaSO_4 \cdot 2H_2O + 2HF + 6H_3PO_4$$
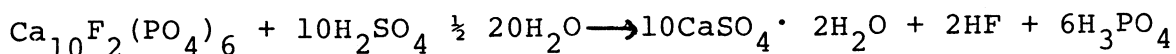
The $CaSO_4$ is removed by decantation and filtration.
It requires about 10 to 15 percent more sulfuric acid to
produce phosphoric acid by the wet methods than to produce
ordinary 20 percent superphosphate. It is usually referred
to as green acid because of impurities, primarily vanadium.
It contains 28 to 30 percent P_2O_5 (12 to 13 percent phosphorus)

16.3.3. Triple Superphosphate

Description. Triple superphosphate is marketed as a
gray, brown or almost white material. It is in either powdered
or pelletted form. It has an acid odour. The prefix
triple was first used when ordinary superphosphate contained
16 percent P_2O_5 and triple superphosphate contained three
times as much 48 percent P_2O_5.

Method of Manufacture. Much of the triple and concentrated
superphosphate is made by a process on which the Tenessee
Valley Authority holds United States patents. It is a
continuous mixer steel cone into which phosphate rock and
phosphoric acid are fed simultaneously; a slurry is
discharged from the cone onto a moving conveyor belt similar
to the Broadfield den continuous mixer used for ordinary
superphosphate. The slurry solidifies on the belt and
is further processed to powder form for use in mixed
fertilizer production or to pellet form for direct
application to the soil. The reaction between the
tricalcium phosphate in the ore and phosphoric acid may
be represented simply as follows:

$$Ca_{10}(PO_4)_6F_2 + 14H_3PO_4 + 10H_2O \longrightarrow 10CaH_4(PO_4) \cdot H_2O + 2HF$$
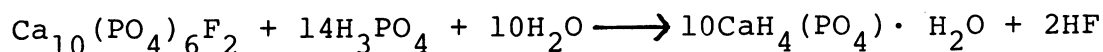
Chemical Characteristics. Triple superphosphate is
essentially ordinary superphosphate with most of the gypsum
removed. It is largely monocalcium phosphate monohydrate.
It analyses 45 to 50 percent P_2O_5 (20 to 22 percent phosphorus,
12 to 16 percent calcium and 1 to 2 percent sulfur. Most
of its phosphorus is in water soluble form. It is used in

compounding high-analysis mixed fertilizers.

16.3.3.4. Concentrated Superphosphate

Description. Tennessee Valley Authority concentrated superphosphate contains about 54 percent available P_2O_5 (24 percent phosphorus), most of which is monocalcium phosphate, $Ca(H_2PO_4)_2$. The P_2O_5 in triple superphosphate (45 to 50 percent P_2O_5) is chiefly monocalcium phosphate monohydrate, $Ca(H_2PO_4)_2 \cdot H_2O$. The loss of a molecule of water, small amounts of fluorine and volatiles in the production of concentrated superphosphate accounts for its higher analysis. The free moisture content is about 1 percent or less.

Method of Manufacture . Tennessee Valley Authority concentrated superphosphate is produced by the acidulation of phosphate rock with superphosphoric acid diluted to 73 to 74 percent P_2O_5. Continuous acidulation and partial granulation are accomplished in a rotating drum. After it is denned and cured, the superphosphate is screened to minus 6-mesh (3.3 mm).

16.3.4. Potassic Fertilizers

The most important potassic fertilizers are potassium chloride and potassium sulfate.

16.3.4.1. Potassium Chloride (Muriate of Potash)

Description. Potassium chloride (KCl) is refined red or grayish red (it may be red, pink, gray or white) salt. When the trace amount of iron in the colored salt is removed, it looks and tastes much like table salt. It is manufactured into fine, standard, coarse and granular grades. The coarser materials mix well with granular nitrogen-phosphorus compounds to form nitrogen-phosphorus-potassium-bended multinutrient fertilizers.

Method of Manufacture.

Potassium chloride (muriate of potash) is prepared through refining techniques for removing KCL from underground ores as brines. Two processes are used for the purification of KCL from potash ores; flotation and crystallization. Both processes involve a separation of NaCL from KCL. Crystals of these two chemicals are commonly found interlocked in a mineral mixture called sylvinite. The flotation process is by far the most prevalent, and the greatest proportion of the agricultural muriate of potash is produced by flotation beneficiation.

In flotation process, small quantitirs of special reagents called flotation agents are added to the KCL-NACL mixture to coat or film the KCL particles selectively. The treated mixture is then agitated in a mechanical cell in such a manner that air bubbles are introduced and a frothing condition develops. The finely divided air bubbles attach themselves to the filmed KCL particles and float them to the surface of the cell where the froth, rich in selected KCL, is skimmed off.

Figure 16.5 illustrates the floation process and the major production steps used in underground and surface operations at a potash mine and refinery.

Solid ore recovery and processing is described below and will be better understood if the sequence of numbers in Figure 16.5 is matched with the numbers in the parentheses in the description that follows. The loosened ore is loaded in shuttle cars (1). The cars shuttle 15-ton (13.7 m ton) loads to a conveyor belt that carries the ore to the base of the shaft (2). There, the ore is crushed to a maximum size of six inches (15.2 cm). Ore storage bins here and on the surface assure uninterrupted operations. Continuous-mining machines are employed in all recently constructed facilities. These machines grind the ore from the lode body, thus eliminating blasting, crushing and shuttle cars; conveyor belts move the ore to shafts for lifting above ground. At the shaft, the ore is hoisted to the surface in buckets in 20-ton (18.2 m ton) loads (3). The shaft, divided by a wall, has a second hoist for men and equipment. Fresh air is piped down one side and exhaust air up the other.
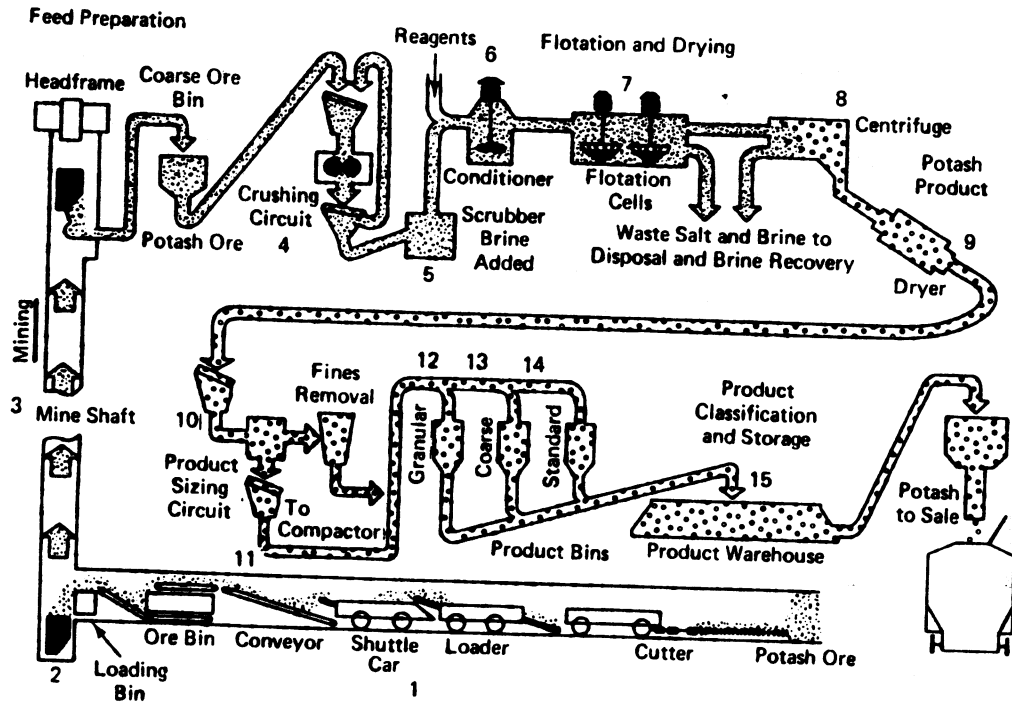
Feed Preparation

Headframe — Coarse Ore Bin

Reagents 6   Flotation and Drying

8   Centrifuge

Potash Product

Conditioner   Flotation Cells

Crushing Circuit 4

Scrubber Brine Added

Potash Ore   5

Waste Salt and Brine to Disposal and Brine Recovery

9

Dryer

Mining

3 Mine Shaft   10   Fines Removal   12 13 14   Product Classification and Storage

Granular Coarse Standard

Product Sizing Circuit   To Compactor   15   Potash to Sale

11   Product Bins   Product Warehouse

Ore Bin Conveyor Shuttle Car Loader   Cutter   Potash Ore

2   Loading Bin   1

Figure 16.5 How potash is mined and refined. (Courtesy of Texas Gulf Sulfur, New York, N.Y.)

(Jones, 1979)

Ammonium Phosphate—(11-48-0)

$$NH_3 + H_3PO_4 \rightarrow NH_4H_2PO_4 + Heat$$

Anhydrous Ammonia Storage

Neutralizing Tanks

Thickener

Evaporator

50% Phosphoric Acid

Hot Air — Dryer

Ammonium Phosphate Fertilizer

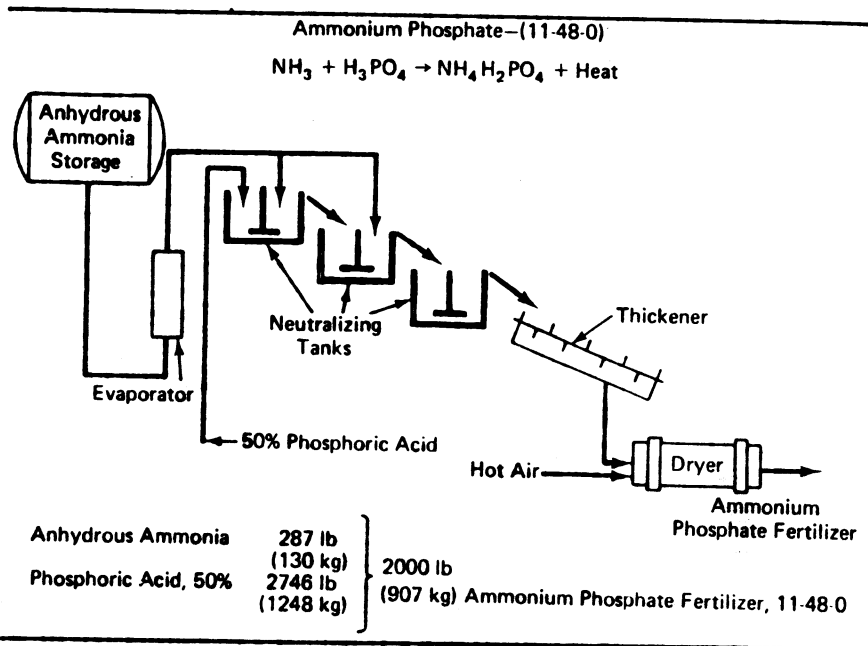| Anhydrous Ammonia | 287 lb (130 kg) | 2000 lb (907 kg) Ammonium Phosphate Fertilizer, 11-48-0 |
| Phosphoric Acid, 50% | 2746 lb (1248 kg) | |

Figure 16.6 Flow diagram of manufacture of fertilizer-grade monoammonium phosphate.   (Jones, 1979)

On the surface, the ore moves from building to building by conveyor. It first goes through the crushing circuit (4) at the mill where it is reduced to about 1/8-inch (0.32-cm) particles. In this size, the ore pieces are either KCL or NaCl. In a scrubber (5), brine is added to make a slurry. In a conditioner (6), the ore is mixed with the flotation reagent as described previously. Potash is skimmed from the surface of flotation cells (7), centrifuged to remove the brine (8),and dried in a rotary kiln dryer (9). The final processing is the product-sizing circuit (10): the product is screened, and fine particles are compacted (11). Granular (12), coarse (13) and standard (14) sizes are stored separately, first in product bins, then in huge warehouses ready for shipment.

The crystallization process employed in separating potassium chloride from sodium chloride is largely dependent on their different solubilities in hot and cold water. The solubility of potassium chloride increases rapidly with a rise in temperature whereas the solubility of sodium chloride varies only slightly. Cool bine saturated with both salts is heated to $212^{O}F$ ($100^{O}C$) and passes over the fine ground ore. The ore solution is subsequently cooled slowly; the KCl precipitates and leaves the NaCl in the cool supernatent liquid.

Secondary Processing. Increasing demand for potash products in coarse and granular forms has resulted in the development and application of techniques for transforming finely divided materials into products of large particle size. Two methods of converting fine muriate of potash into coarser particles are fusion and compaction. Compaction is the newer process and is more widely used.

Fusion Process. Finely divided KCL from flotation recovery is heated to $1391^{O}F$ ($755^{O}c$) to form a melt, which is solidified by cooling. The flakes thus formed are crushed and screened to give the desired particle size.

Compaction . This newer technique is essentially one of feeding variously sized muriate particles at temperatures ranging from 200° to $250^{O}F$ (93° to $121^{O}C$) between pressure rolls ((300 tons (273 m tons)) in order to compress it into sheets (1/8 to 1/16 inch

(0.32 to 0.16 cm thick) or briquets, which are crushed and screened to desired sizes. Brine or water may be added prior to compacting. Heat-compacting rollers will assist the process.
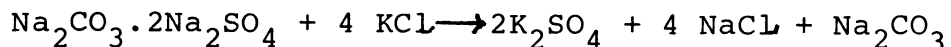
16.3.4.2. Potassium Sulfate

Description. Potassium sulfate (K_2SO_4) is refined beige- to pink-coloured salt. It is manufactured into fine, granular or semigranular grades. It may be mixed with a slurry of other materials to form compound fertilizers or used in granular blends.

Method of manufacture. Potassium sulfate is manufactured by a number of processes from a number of different raw materials. Four of them known as the Langbeinite, Trona, Mannheim and Hargreaves processes, are discussed. The Langbeinite process consists of dissolving langbeinite, a double sulfate of potassium and magnesium, in water and subsequently adding a concentrated solution of potassium chloride in accordance with the following equation:

$$K_2SO_4 \cdot 2 \, Mg \, SO_4 + 4 \, KCl \longrightarrow 3 \, K_2SO_4 + 2 \, MgCl_2$$

Potassium sulfate precipitates and is separated from solution by centrifuging. The wet cake is dried, screened and sent to storage.

In the Trone process for the manufacture of potassium sulfate, KCL is first reacted with burkeite, $Na_2CO_3 \cdot 2Na_2SO_4$, to produce a high potassium glaserite cake, $Na_2SO_4 \cdot 3K_2SO_4$. The glaserite is separated and then treated with high purity KCL brine. This converts into solid potassium sulfate, which is filtered from the NaCL brine.

$$Na_2CO_3 \cdot 2Na_2SO_4 + 4 \, KCL \longrightarrow 2K_2SO_4 + 4 \, NaCL + Na_2CO_3$$

The potassium sulfate is washed, dried and sent to fertilzer-grade K_2SO_4 bulk storage.

The reaction between potassium chloride and sulfuric acid to yield potassium sulfate proceeds in two stages. Potassium acid sulfate is formed in the first stage which is exothermic and is initiated at normal temperatures.

$$KCl + H_2SO_4 \longrightarrow KHSO_4 + HCl$$
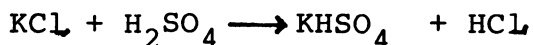
In the second stage, which is endothermic, the acid sulfate is converted into the normal sulfate by further reaction with potassium chloride under the influence of external heat.

$$KCl + KHSO_4 \longrightarrow K_2SO_4 + HCl.$$
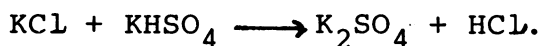
In commercial practice, both stages of the reaction are conducted in a Mannheim-type salt cake furnace. Potassium chloride and sulfuric acid in the required proportions are fed in separately and continuously from the top and near the center. The reactions proceed toward completion as the mixture gradually is moved outward through the hotter zones [1112° to 1292°F(600° to 700°C)] to the circumference and outlet by slowly rotating plows. The hot potassium sulfate product requires cooling before being bagged or sent to storage. The hydrogen chloride evolved passes out of the furnace at the top and is absorbed in water to form hydrochloric acid. The K_2SO_4 contains little free acid.

Potassium sulfate is also manufactured from kainite, $Kcl.MgSO_4.3H_2O$, in Italy, Germany and the United States by the Hargreaves process, involving the reaction of KCl with sulfur as follows:

$$2KCl + SO_3 + H_2O \longrightarrow K_2SO_4 + 2HCl$$
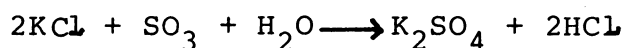
Potassium sulfate contains 52% K_2O, 16 % S and not more than 2.5% Cl.

16.3.4. Multinutrient Fertilizers.

Manufacturing Techniques. The three principal techniques used in the manufacture of most multinutrient fertilizers are acidulation, ammoniation and granulation. Acidulation is the process or technique of treating a material with an acid. The most common acidulation process is the treatment of phosphate rock with acid.

Ammoniation is the process or technique of introducing ammonia into superphosphate that forms ammoniated superphosphate. For ammoniation of ordinary superphosphate, the commerical operator works in the range of 6 to 7 pounds (2.7 to 3.2 kg) of ammonia per unit (20 pounds or 9.1 kg of P_2O_5) and 4 to 5 pounds (1.8 to 2.3 kg) per unit in concentrated superphosphate.

Granulation is the process or technique of collecting small size particles into larger granules or pellets of about 4- to 8-mesh (4.3- to 2.3- mm) size. It is a technique that has been widely adopted as a means of improving the handling and storage properties of fertilizers.

16.3.5.1. Ammonium Phosphate - Soild Fertilizer

Description. Ammonium phosphate is a pelletized white to dark gray material produced as round granules about the size of small vetch seed or number-4 birdshot.

Method of Manufacture. Phosphoric acid is first made by treating finely ground rock phosphate with an excess of sulfuric acid to produce gypsum and phosphoric acid. This is the so-called wet-process method of phosphoric acid manufacture. Spent sulfuric acid from the refining of petroleum products by the alkylation process has been found to be satisfactory for the production of wet-process phosphoric acid used in the manufacture of ammonium phosphate fertilizer.

Anhydrous ammonia is added to the liquid phosphoric acid to form technical grade monoammonium phosphate, containing 11 percent nitrogen and 21 percent phosphorus (48 percent P_2O_5) (Fig. 16.6).

$$NH_3 + H_3PO_4 \longrightarrow NH_4H_2PO_4$$
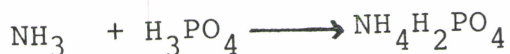
monoammonium phosphate

More ammonia may be added to wet-process acid to form technical-grade diammonium phosphate, containing 16 to 18 percent nitrogen and 20 to 21 percent phosphorus (46 to 48 percent P_2O_5).

$$2NH_3 + H_3PO_4 \longleftrightarrow (NH_4)_2HPO_4$$

diammonium phosphate

Ammonia may also be reacted with a mixture of phosphoric and sulfuric acids to form ammonium phosphate sulfate containing 13 to 16 percent nitrogen, **9** to 15 percent phosphorus (20 to 39 percent P_2O_5) and 7 to 14 percent sulfur.

$$4H_3PO_4 + xH_2SO_4 + (4 + 2x)NH_3 \longrightarrow 4NH_4H_2PO_4 \cdot x (NH_4)_2SO_4$$
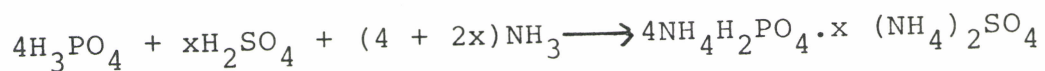
Phosphoric acid and anhydrous ammonia are introduced into a large reactor (Figure 16.6) where they combine to produce a thick viscous slurry of monoammonium phosphate. A mixture of phosphoric and sulfuric acid can be introduced in varying proportions to make 16-9-0 (16-20-0), 15-13-0 (15-30-0), 13-15-0 (13-39-0) or other grades as desired. These grades are triple salts containing more or less of ammonium sulfate, monoammonium phosphate and diammonium phosphate.

From the reactor the slurry flows to a paddle mixer, called a blunger, where small granules of fertilizer of the same analysis (previously manufactured) are coated with the slurry. Potassium salts may also be introduced here if a nitrogen-phosphorus-potassium grade is desired. It is possible to start the granulating process by "seeding" the slurry in the blunger with small pellets or granules. The blunger contains heavy intermesing paddles that roll the pellets and coat each uniformly with the product slurry. Without the previously manufactured granules, the slurry will not develop into granules. The freshly coated pellets are discharged from the blunger into an open-flame drier and emerge dry.
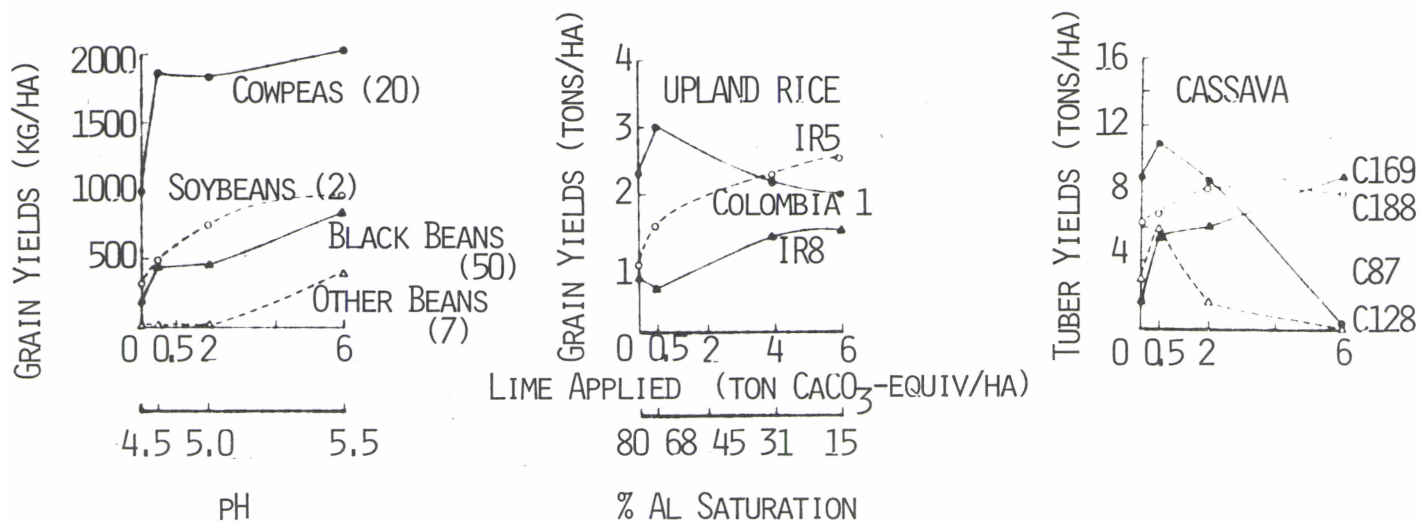
FIG. 17.3. VARIETAL AND SPECIES DIFFERENCES IN TOLERANCE TO ACID SOIL CONDI-
TIONS IN AN OXISOL FROM CARIMAGUA, COLOMBIA. NUMBERS IN PARENTHESES
REFER TO THE NUMBER OF GRAIN LEGUME VARIETIES TESTED.
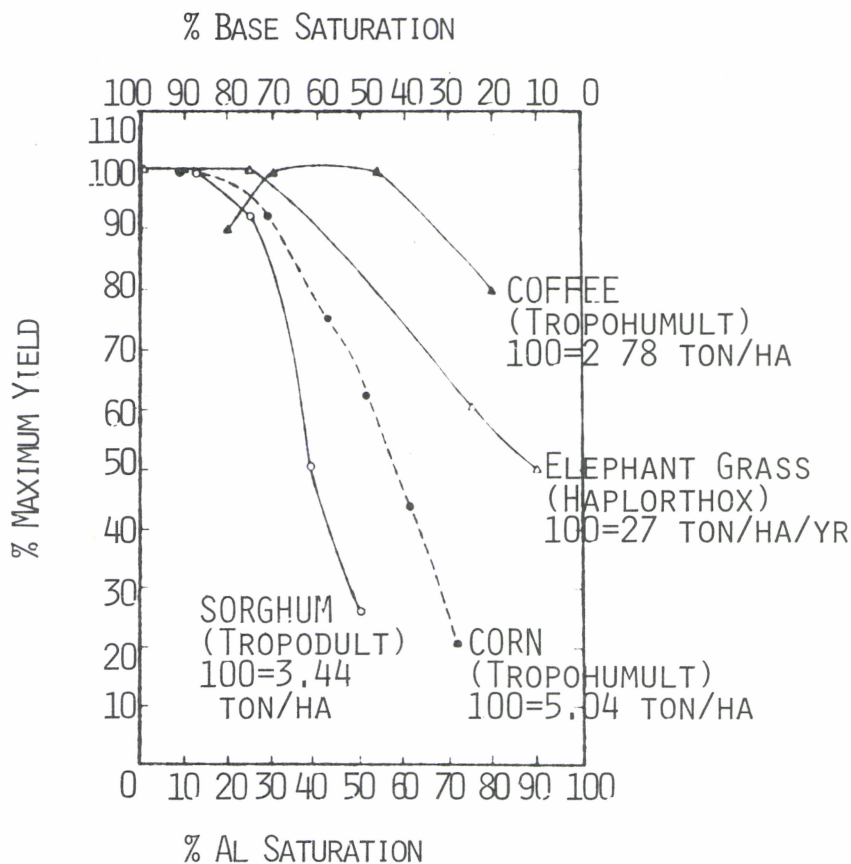SOURCE: ADAPTED FROM SPAIN ET AL. (1975).

FIG. 17.4. YIELD RESPONSES TO LIMING IN PUERTO RICAN OXISOLS AND
ULTISOLS. SOURCE: COMPILED FROM ABRUÑA ET AL. (1964,
1965, 1975).

17.3 LIMING

From the above consideration it should be obvious that the purpose
of liming is primarily to neutralize the exchangeable aluminum, and
that this is normaly accomplished by raising the pH to 5.5. When
manganese toxisity is suspected, the pH should be raised to 6.0.
The factors to be considered are (1) the amount of lime needed to
decrease the percent aluminum saturation to a level at which the
particular crop and variety will grow well, (2) the quality of lime,
and (3) the placement method.

17.3.1 DETERMINATION OF LIME REQUIREMENT

A large amount of effort has been devoted to finding the best
methodes for estimating lime needs in the tropics. Part of the
confusion was certainly caused by attempts to lime soils to neutra-
lity and the use of titratable acidity as the criterion. Kamprath
(1970) suggested that lime recommendations be based on the amount
of exchangable aluminum in the topsoil and that lime rates be cal-
culated by multiplying the milliequivalents of aluminum by 1.5.
The result is the millequivalents of calcium needed to be applied
as lime. Lime rates calculated by this method neutralize 85 to 90
percent of the exchangeable aluminum in soils containing 2 to 7
percent organic matter. The reason for 1.5 as a factor is need to
neutralize the hydrogen ions released by organic matter or iron and
aluminum hydroxides as the pH increases. In soils with higher
organic matter, the factor has to be raised to 2 or 3 because of
the presence of exchangeable hydrogen. This method has been used
successfully in Brazil and other Latin American countries since
1965. For every milliequivalent of exchangeable aluminum present,
1.5 meq of calcium or 1.65 tons/ha of $CaCO_3$-equivalent should be
applied. This procedure has been found successfulin the tropies and
eliminates the need for time- consuming neutralization tests in the
laboratory.

The application of this concept has reduced the rates of liming
substantially, prticularly in acid Oxisols and ultisoils low in effec-
tive CEC. In most cases where I to 3 meq of exchangeable aluminum
is present, lime applications are now on the order of 1.6 to 5 ton/
ha. In the past, rates on the order of 10 to 30 ton/ha were frequ-
ently recommended and applied with mixed results.

Another important component of lime requirement determination is

the level of exchangeable aluminum that specific crops or varieties
can tolerate. Crops originally developed in calcareous soils, such
as cotton sorghum, and alfalfa, are susceptible to levels of 10 to
20 percent aluminum saturation. For them, liming should be aimed
at zero aluminum saturation in order for the application to last for
a few years. Corn is sensitive to 40 to 60 percent aluminum satura-
tion. Although liming to zero aluminum saturation might be benefical, lowering
the aluminum saturation level to 20 percent could be more economical. Other crops
such as rice and cowpeas are more tolerant. Coffee,pineapple,and som pasture
species seldom respond to lime, even in soils with high aluminum
saturation.

An example of these relationships is illustrated in Fig. 17.4,
where the relative yields if sorghum corn,elephant grass (Pennisetum
purpureum), and coffee from liming trials are plotted as a function
of aluminum saturation. Sorghum yields began to drop dramatically
at about 15 percent aluminum saturation, and corn at about 40 percent
Elephant grass yields dropped sharply at about 60 percent aluminum
saturation, while coffee suffered a yield decrease only at 80 percent.

17.3.2 LIMING MATERIALS.

Table 17.3 shows the most important liming materials. The carbon-
ates are simply ground limestone or chalk. Burning Ca carbonate
at 1100^0 results in thermal dissociation:

$$CaCO_3 \rightarrow CaO + CO_2$$
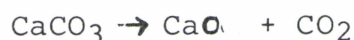
Table 17.3 Liming materials

Liming material	Formula	Neutralizing value in CaO
Calk or limestone	$CaCO_3$	50% CaO
Slaked lime	$Ca(OH)_2$	70% CaO
Burnt lime	CaO	85% CaO

"Burnt lime" is produced in this way. The Ca oxide formed (CaO)
readily reacts with water thus forming Ca hydroxide (hydrated lime
or slaked lime).

$$CaO + H_2O \rightarrow Ca(OH)_2$$
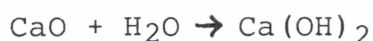
On contact with CO_2 this forms $CaCO_3$.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

Thus when hydrated lime is exposed to the atmosphere for a long period of time it is gradually converted to Ca carbonate by atmospheric CO_2.
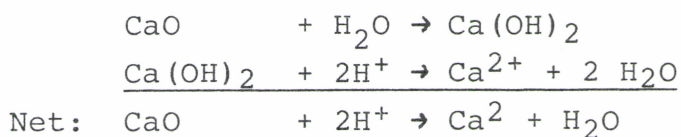
Frequently liming materials also contain substantial amounts of Mg as well as Ca. Burnt magnesium lime for example consists mainly of CaO and MgO, and contains more than 5.5% Mg. Ground magnesium limestone is a mixture of $CaCO_3$, and $MgCO_3$ with an Mg content of 3% Mg and more. These Mg containing materials are particularly used for liming Mg deficient acid soils.

The value of liming material depends on their "neutralizing value", which is expressed in terms of equivalents of CaO. 100kg of $CaCO_3$ have the same neutralizing effect as 56 kg CaO. Thus the neutralizing value of 100 kg $CaCO_3$ is 56, whereas 100 kg $Ca(OH)_2$ has a neutralizing value of 76. As the neutralizing value is realted to the quantity of carbonate or oxide present in the liming material $MgCO_3$ or MgO also contribute to the neutralizing efficiency. Generally all oxides, carbonates, and even silicates are alkaline in reaction. For this reason Ca silicates present in basic slags and sinter phosphates have a neutralizing effect and are thus of some importance in controlling soil pH. In long-term field experiments Schmitt and Brauer (1969) found, that in plots supplied regularly with basic slag, the pH was only slightly depressed whereas in plots treated with equivalent amounts of other P fertilizers the soil pH fell from 6.5 to 5.4 over a ten year period. Similar results have been obtained by Roscoe (1960).
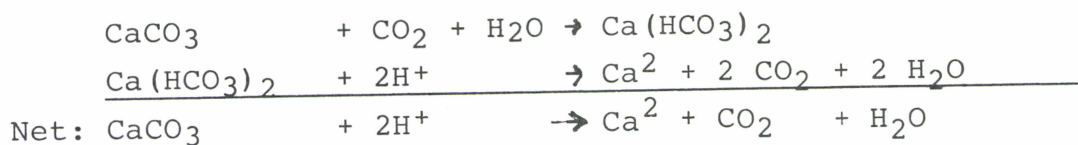
17.3.3 Reaction of lime in soil.

As already mentioned above CaO reacts readily with H_2O, to from Ca hydroxide which directly neutralizes the free H^+ of the soil solution.

$$
\begin{aligned}
CaO &+ H_2O \rightarrow Ca(OH)_2 \\
\underline{Ca(OH)_2 &+ 2H^+ \rightarrow Ca^{2+} + 2 H_2O} \\
\text{Net:} \quad CaO &+ 2H^+ \rightarrow Ca^2 + H_2O
\end{aligned}
$$

Because of the higher solubility CaO and Ca(OH)$_2$ both these com-
pounds are quick acting in comparison with CaCO$_3$. Thus when a rapid
change in soil pH is required or where soil reaction are slow, as
in cold and wet soils, the application of Ca O or slaked lime Ca(HO) is recommended.
CaCO3 reacts more slowly. Under strong acid conditions it dissolves
relatively quikly by neutralizing soil H$^+$.

$$CaCo_3 + 2H^+ \rightarrow Ca^{2+} + H_2O + Co_2$$

Under weak acid or even neutral conditions the presence of CO$_2$
favours the dissolution of CaCO3 by forming Ca bicarbonate which
in turn neutralizes soil H$^+$:

$$CaCO_3 \quad + CO_2 + H_2O \rightarrow Ca(HCO_3)_2$$
$$\underline{Ca(HCO_3)_2 \quad + 2H^+ \qquad \rightarrow Ca^2 + 2 CO_2 + 2 H_2O}$$
$$\text{Net: } CaCO_3 \qquad + 2H^+ \qquad \rightarrow Ca^2 + CO_2 \quad + H_2O$$

Ca silicates present in basic slags and sinter phosphates are even
slower in their neutralizing than CaCO$_3$.

$$CaSiO_3 + 2 H^+ \rightarrow Ca^{2+} + SiO_2 + H_2O$$

The rate of dissolution of liming materials also depends on particle
size. Finely ground material reacts more rapidly than coarse
material due to its larger surface (Barrows et al. 1968).

17.3.4 Placement.
Lime is commonly incorporated into the top 15 cm several days before
planting the crop. Although this is usually the best way, there are
instances in which plowing in is not possible and others in which
deeper incorporation is beneficial.
Liming established pastures precludes incorporation unless reseeding
is contemplated. Usually basal applications are well incorporated,
but smaller applications aimed at correcting the acidifying effect
of nitrogen fertilizers are effective when brodcast to the pasture
surface, In a Puerto Rican Oxisol, Abruna et al. (1964) observed
no differences in pasture yields between surface-applied and
incorporated lime applications.

When extremely acid Oxisols have their topsoil limed to pH 5.5,
most of the root development of corn occurs in the topsoil. The
high subsoil aluminum saturation prevents deeper root development.
When short-term droughts occur during the rainy season, plants may
suffer from water stress while the subsoil is still moist. For this
reason, Gonzalez and Kamprath (North Carolina State University,
1973) comparaed incorporating lime at two depths, 0 to 15 and 0 to
30 cm, in an Oxisol from Brasilia. This soil has a excellent
granular structure that permitted deep incorporation with a roto-
tiller. The results of the first corn crop are shown in Fig. 17.5.
Deeper applications produced higher yields. Root studies showed
that higher yields were associated with deeper root development in
the 0 to 30 cm layer, which diminished water stress during short-
term droughts. The feasibility of deep lime incorporation depends
largely on soil structural properties and available equipment.
It seems reasonable to assume that this would be possible in sandy
soils and highly aggregated Oxisols and Andepts, but doubtful in
Ulitsols with clayey argillic horizons.

17.3.5 Residual Effect oF Liming.

The residual effect if liming depends on how fast calcium and magnes-
ium are being displaced by the residual acidity of nitrogen fertil-
izers. Soils tests are an adequate tool for determining when
additional lime should be applied.
The residual effect of liming elephant grass pasture fertilized
annually with 800 kg N/ha as ammonium sulfate (Abruna et al. 1964)
is shown in Fig. 17.6. There was little response during the first
year; but as the residual acidity of the ammonium sulfate appli-
cations became effective, optimum yields were obtained with 4 ton/ha
of lime. The response curves were sharper every year because of
the decreases of the unlimed treatments.
Mahilum et al.(1970) studied the residual effect of liming on a
Hawaiian Hydrandept. They found that after 5 years a rate of 2
tons lime/ha kept the aluminum level at about 1 meq (from an original
value of 3 meq), even though most of the calcium was to lower levels.
Apparently aluminum ions did not readily reoccupy the exchange sits
even when calcium laeached below. After 5 years the residual effect
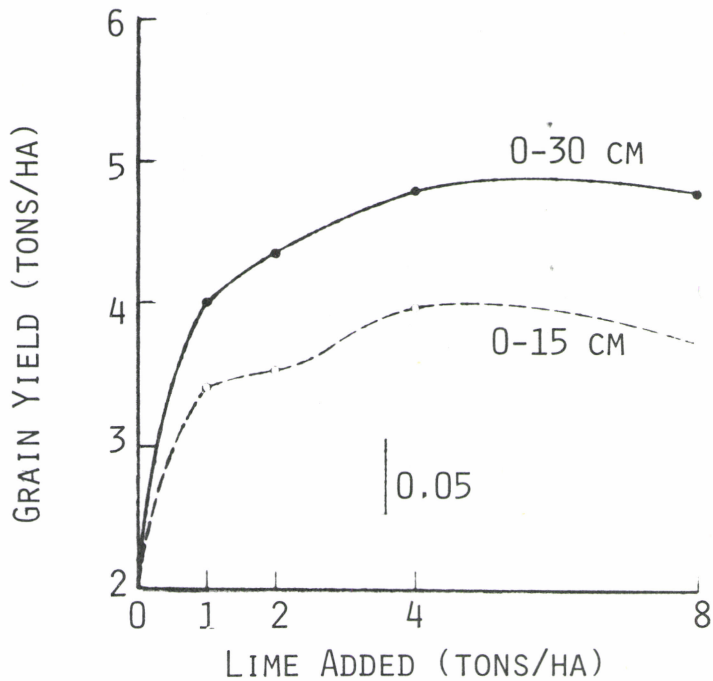of liming at the rate of 5 ton/ha completely disappeared.

FIG. 17.5. EFFECT OF LIME INCORPORATION ON CORN YIELDS IN AN OXISOL FROM BRASILIA, BRAZIL. SOURCE: E. GONZALEZ (NORTH CAROLINA STATE UNIVERSITY, 1973)
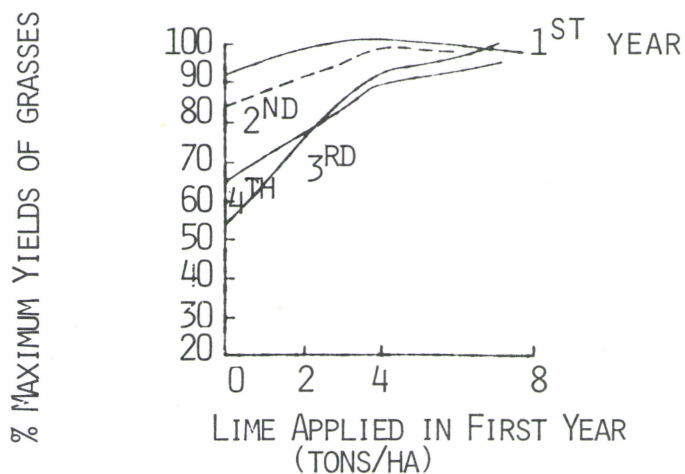

FIG. 17.6. RESIDUAL EFFECT OF LIME APPLICATIONS ON THE RELATIVE YIELDS OF PASTURE GRASSES IN PUERTO RICAN OXISOLS AND ULTISOLS. SOURCE: ABRUÑA ET AL. (1964).

In sharp contrast De Freitas and Van Raij (1975) obtained positive corn and soybean responses to lime in a sandy Oxisol of Sao Paulo, Brazil, 6 years after application. They observed increasing yield responses with time and attributed them to the dissolution of the coarser lime particles.

17.3.6   OVERLIMING

The tropical soil literature is full of reports citing the lack of response or the negative response when tropical soils are limed. This has created the generalized idea that liming does not work in the tropics (Richardson, 1951). In many cases, soils were limed to neutrality. This concept originated in the United Stats Midwest in corn legume rotations because alfalfa and clover grew best at a pH of 6.5 to 7.0 because of their high calcium requirements. This practice implied that liming to neutrality was also best for corn and small grains in rotation with alfalfa. The soils in question were Mollisols or Alfisols essentially devoid of pH-dependent charge. Kamprath (1971) reviewed the reasons for the lack of positive lime responses when highly leached soils are limed to neutrality. The consequences of overliming are yield reduction, soil structure deterioation, and decreased avaliability of phosphorus, boron, zinc, and manganese. Overliming can be defined as liming at rates higher than necessary to neutralize the exchangeable aluminum or eliminate manganese toxicity. Ghani et al. (1955) found that liming with MgO decreased infiltration rates and noncapillary porosity in an acid lateritic soil of Bangladesh, while $CaCO_3$ did not produce a consistent effect. No correlations between such changes in physical properties and crop yields have been recorded.

Overliming induces phosphorus deficiency in soil with high phosphorus fixation capacity. When a Gibbsihumox from Hawaii was limed from pH 5.3 to 6.1, the uptake of phosphorues by sorghum and Desmodium intortum increased dramatically (Fox er al. 1964). When this soil was limed to pH 7, however, phosphorus uptake decreased and severe phosphorus deficinecey was observed, apparently because of the formation of insoluble calcium phosphates.

Overliming soils high in oxide coatings greatly increaces the adsorption of boron by clays and reduces the availability of boron. Kamprath (1971) cites several examples from the southeastern United States of such problems arising when the soil pH increases beyond 6.5 in Ultisols. Lime-incduced manganese deficiencies can

also be observed at pH levels above 6.2 because manganese tends to precipitate at this pH range in the presence of iron and aluminum oxides.

Overliming may also induce zincdeficiencies. The solubility of zinc decreases rapidly at a pH of 6 to 7. In soils naturally low in zinc excessive liming does decrease the availability of zinc, as demonstrated when Cerrado Oxisols are overlimed.

The bulk of the evidence suggests that highly weathered soils should not be limed to pH values greater than 5.5. Beyond that level, yield decreases can occur. However, in many cases overliming produces no yield decreases, just a flat plateau. Detrimental effects are most commonly noted on oxidecoated layer silicate systems or oxide systems in soils low in available phosphorus, boron, and zinc and high in phosphorus fixation capacity. According to McLean (1974) overliming layer silicate systems with little pH-dependent charge causes hardly any detrimental effects.

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SOIL FERTILITY EVALUATION

Soil fertility evaluation and improvement programs are essentially organizational vehicles that function to implement the practical use of an extensive body of soils research knowledge. Such programs are concerned with (1) the summarization, organization, and evaluation of existing information on soils and crop production in particular service areas, (2) the techniques and procedures for evaluating fertility and productivity problems at specific field sites, (3) the development of correlation procedures to employ the general research information in the solution of individual site problems, and (4) the development of research, analytical, and educational services to implement the coordinated use of the information. Such programs make the best use of the accumulated knowledge when they direct its application to the solution of problems on individual field sites that include excesses as well as deficiencies. The program operations, therefore, eventually should provide techniques for making field site evaluations followed by systematic procedures to ascertain the site needs for management in the light of all relevant research information.

Several approaches are presently in use in the tropics, as well as in the rest of the world. The most widespread ones are based on soil testing, plant analysis, missing element techniques, simple fertilizer trials, and frequently a combination of these.

In the tropics, effective soil fertility evaluation methods exist in many Latin American countries and in India, but few in tropical Africa and Southeast Asia. The main reason for the limited development in these areas is probably the lack of widespread fertilizer use in Africa, and the preponderance of flooded rice culture in Southeast Asia.

18.1. Fertility Evaluation Systems Based on Soil Testing.

One of the most popular approaches in use by a large
number of tropical countries is that developed by the cooperative
International Soil Fertility.

Evaluation and Improvement Program (ISFEIP). Its
concept and scope are best described as follows:

A soil fertility evaluation program involves several
parts. Soil fertility has to do principally with plant nutrient
elements and soil conditions. Evaluation is concerned with
levels of availability and nutrient balance in the soil, including
appropriate methods for assessing these factors (soil tests,
conditions.
plant analysis, soil survey, climatic) Improvement involves
the addition to the soil of fertilizers, lime, manures, and other
amendments in such quantities, at such times in the season,
and in such ways as to provide the optimum nutritional environment
for crop production. Thus, a soil fertility evaluation and
improvement program is site-specific and situation-specific.
It is the judicious use of information for a specific field in
which consideration is given to factors that will influence yield,
the capability of the farmers, and the availability of capital
(ISFEIP, 1974).

According to Fitts (1974) such a program involves six
interrelated facets:

1. Sampling (soil and plant).
2. Laboratory analyses (soil and plant).
3. Correlation between analysis and yield response.
4. Interpretation and recommendations.
5. Putting information to use.
6. Research.

18.1.1. Soil Sampling.

Taking a representative soil sample is both the first
step and the largest source of error in the soil fertility
evaluation program. A representative soil sample is composed

of 10 to 20 subsamples from the rooting zone to a field with
no major variation in slope, drainage, color, or past fertilizer
history. Nonrepresentative areas such as fence rows and
manure piles must be avoided. Appropriate information is also
needed, including the name and address of the farmer, field number,
previous crop, and fertilizer practices. These are best
provided by printing the desired information on the soil boxes.

How deep the sample should be depends on the crop to be
grown and the depth at which amendments are likely to be
incorporated. This is almost universally the plowed layer or
the top 15 cm. In the case of deep-rooted crops such as sugarcane
and tea, a subsoil sample is often taken. For established pastures
or permanent crops where fertilizers are not likely to be
incorporated, the top 15 cm is usually taken.

Another important question is where to sample when
phosphorus has been applied in bands. The answer is between the
bands if their locations are known. A third consideration is the
time of the year. Soil samples should be taken substantially
before planting so that the results will be available when the
decision on how much fertilizer to apply is made. In ustic soil
moisture regimes, this means sampling during the dry season.
Upward ion movement during the dry season may change some of the
soil test results, principally in regard to soluble salts.

How often a field should be sampled depends primarily
on the intensity of fertilizer use and the economic value of
the crop. For average management intensity once every 3 years
is recommended by ISFEIP (1971), while for very intensively
managed areas annual sampling is necessary.

After arrival at the laboratory, the soil sample is dried,
ground either by pounding or by electric-powered grinders, passed
through a 2 mm sieve, assigned a laboratory number, and stored
until ready for analysis. In most cases the original sample box,
which has the source information and now a laboratory number,
is kept.

18.1.2. Laboratory Organization.

The soil-testing laboratory is the backbone of the fertility evaluation program (Fitts, 1974). Unlike research laboratories, service laboratories must be geared to handle large numbers of samples rapidly and accurately. A complete system of semiautomated apparatus has been developed by the ISFEIP program especially for tropical laboratories. This system has been described by ISFEIP (1973), Perur et al. (1974), and Hunter (1975) and is summarized in the following paragraph.

Soil samples are measured volumetrically, eliminating the time-consuming weighing process, and then placed in multiple-unit trays of 30, where the extracting and diluting solutions are added or transferred by specially designed diluter-dispenser. Other apparatus transfers the aliquots to spectrophotometers and pH-measuring units automatically. Shaking, stirring, and cleaning apparatus are also semiautomatic and capable of handling 30 units at a time. A single technician can run 100 soil samples a day, measuring 10 determinations per sample (Hunter, 1975). The apparatus are based on manual operation and use a minimum of electrical power. Expensive electronic equipment such as pH meters, spectrophotometers, and atomic absorption apparatus are used only in the last phases. An additional advantage is that the same units can be used for plant tissue as for soil analysis. The bulk of the work is done with two extractants; the dilute double acid or modified Olsen extractants for available P,K,Ca,Mg,Na,Fe,Mn,Zn and Cu, and the 1 N. KCl extraction for Al. Tests for N, B, S, and Mo require other methods that have not yet been adapted to the system. Soil pH measurements are also adapted to routine analysis.

18.1.2.1. Selection of Extraction Methods.

The selection of extractants for available nutrients has received major attention in soils research and is a subject of considerable discussion. According to Bray (1948), a successful soil test laboratory methods should meet three criteria:

1. It must extract all or a proportionate part of the
    available forms of nutrients in soils with widely
    different properties.

2. The procedure must be rapid and accurate.

3. The amounts extracted should be correlated with the
    growth and response of each crop to the nutrient in
    question under various conditions.

Nitrogen. Bartholomew (1972) classified soil tests for nitrogen
into three categories: (1) determination of organic nitrogen
or some chemically extracted fraction of organic nitrogen,
including organic matter as an indicator of organic nitrogen;
(2) incubation methods to evaluate mineralization rates, and
(3) direct measurement of inorganic nitrogen. Unfortunately
none of these methods meets the three criteria given above
in most cases.

Total soil nitrogen or organic matter content is
sometimes correlated with nitrogen response in soils with similar
properties and climatic conditions. In such cases the tests meet
the three criteria except the one for wide applicability, and
can be useful at the local level. Although good correlations
between total nitrogen and yield response in the greenhouse are
common (Cornforth and Walmsley, 1971), they become less frequent
under field conditions. Baynes and Walmsley (1973), for example,
correlated total soil nitrogen and nitrogen response in corn
at several locations in the West Indies. They were able to predict
the presence or absence of nitrogen response with a critical
level of 0.17 percent N in two-thirds of the cases.

Usually, total nitrogen and organic carbon are poorly
correlated with nitrogen response in the field. Because
of the lack of a better method, however, many laboratories use
these measures to provide some information to farmers.

<u>Phosphorus</u>. The situation with phosphorus is the opposite
of that with nitrogen. Several effective soil tests for
estimating available phosphorus meet all three of Bray's criteria
and are used throughout the world. A list of the main procedures
used in the tropics appears in Table 18.1. Of these the most
common are the Olsen, the Bray2, and the North Carolina (also
called the "Mehlich" or "dilute double acid") methods.

The effectiveness of each of these methods is related to
its ability to extract different forms of inorganic phosphorus.
A recent comparison on widely different soils from Bangladesh
illustrates the relative abilities of the common soil phosphorus
tests to identify different phosphorus fractions (Table 18.1).
Most acid extractants are effective in determining Ca-P. The
North Carolina Bray1, Bray 2, 0.3 N HCl, and the Na-EDTA methods
are effective in extracting both Ca-P and Al-P. The alkaline
Olsen method, however, is the only one sensitive to Fe-P.
No methods are capable of extracting reductant-soluble, occluded,
and organic forms of phosphorus. Results similar to those
presented in Table 18.1 have been obtained by a number of
other workers.

Phosphorus tests for flooded rice soils are not as
succsessful as those for aerobic crops. Reduced conditions under
rice make P more soluble and thereforeordinary soil tests for
P fail to assess P level of soils.

<u>Potassium</u> . The available forms of potassium in most soils
are exchangeable and soluble potassium. A series of extractants
is able to account for both forms in ways that satisfy Bray's
three criteria. The most commonly used method is the 1 N
ammonium acetate extraction; it is usually the best or at least
as good as others (Datta and Kalbande, 1967; Rodrigues, 1974).
Attempts to use the same extractant for estimating available
potassium as is used for phosphorus have also been successful.
The North Carolina extraction is now used for both these
elements in Brazil.

<u>Lime requirement</u>. The many recommendations for determining
the lime requirements of acid soils have been summarized by
McLean (1973). Of these only two meet Bray's soil test criteria;

Table 18.1 *Correlation between Common Phosphorus Soil Tests and Inorganic Phosphorus Fractions in Various Soils of Bangladesh*

Soil Test	Extractant	Ca-P	Al-P	Fe-P	Reductant-Soluble Fe-P	Occluded Fe-P and Al-P
Olsen	0.5 M NaHCO₃ at pH 8.5	.55	.62	.78*	.01	-.17
Truog	0.002 N H₂SO₄ at pH 3	.90*ᵃ	.59	.09	-.32	-.49
North Carolina	0.025 N H₂SO₄ + 0.05 N HCl	.88*	.65*	.06	-.39	-.62
HCl	0.3 N HCl	.95*	.70*	.23	-.38	-.61
Bray 1	0.03 N HN₄F + 0.025 N HCl	.72*	.73*	.46	-.17	-.48
Bray 2	0.3 N NH₄F + 0.025 N HCl	.78*	.74*	.38	-.24	-.50
Schofield	0.01 M CaCl₂	.06	.05	.03	-.30	-.60
Morgan	NaOAc + HOAc	.79*	.56	.18	-.47	-.60
DTA	0.02 N Na₂-EDTA	.77*	.95*	.41	-.23	.53

Source: Ahmed and Islam (1975).
Asterisks indicate statistical significance.

Table 18.2 *Soil Test Methods, Soil Factors Influencing Their Interpretation, and Typical Ranges in Critical Level for Micronutrients*

Element	Interacting Factorsᵃ Essential	Interacting Factorsᵃ Probable	Method	Range in Critical Level (ppm)
B	Texture, pH	Lime	Hot H₂O	0.1-0.7
Cu	—	O.M., Fe	NH₄C₂H₃O₂ (pH 4.8)	0.2
			0.5 M EDTA	0.75
			0.43 N HNO₃	3-4
			Biological assay	2-3
Fe	—	pH, lime	NH₄C₂H₃O₂ (pH 4.8)	2
			DTPA + CaCl₂ (pH 7.3)	2.5-4.5
Mn	pH	O.M.	0.05 N HCl + 0.025 N H₂SO₄	5-9
			0.1 N H₃PO₄ and 3 N NH₄H₂PO₄	15-20
			Hydroquinone + NH₄C₂H₃O₂	25-65
			H₂O	2
Mo	pH	Fe, P, S	(NH₄)₂C₂O₄ (pH 3.3)	0.04-0.2
Zn	pH, lime	P	0.1 N HCl	1.0-7.5
			Dithizone + NH₄C₂H₃O₂	0.3-2.3
			EDTA + (NH₄)₂CO₃	1.4-3.0
			DTPA + CaCl₂ (pH 7.3)	0.5-1.0

Source: Cox and Kamprath (1971).
ᵃ Climatic and crop factors, although highly important, are not considered here.

direct pH determination and the use of exchangeable aluminium
extracted by 1 N KCl. Liming to a desired pH may not correlate
well with crop responses because of the imperfect correlation
between pH and aluminium, overliming problems, and differences
in plant tolerance of acidity.

The exchangeable aluminium determination
is a simple soil test that has correlated well with lime
response in acid soils of the tropics (Kamprath, 1967).

Secondary nutrients. Exchangable calcium and magnesium can be
determined by atomic absorption from the same extracts as
potassium with little complication.

Soil tests for sulfur are still a problem because current
methods are cumbersome and often inaccurate. The main problem
is the turbidimetric determination of sulfate as $BaSO_4$. The
present methods and their problems are discussed by Reisenauer
et al. (1973) and others. The water and $Ca(H_2PO_4)_2$ extractions
are the most common ones. Efforts at simiplifying sulfur
determinations to the level of other soil tests are currently
under way.

Micronutrients. A variety of methods are presently in use for
determining the availability of B, Cu, Fe, Mn, Mo, and Zn in
soils. The literature on the subject has been reviewed by Cox and
Kamprath (1971). The critical levels for the various routine
soil tests and the interacting factors are shown in Table
18.2. As mentioned before, the modified Olsen extraction can now
be used for detemrining Cu, Fe, Mn, and Zn from the same
extraction as P, K, Ca and Mg (ISFEIP, 1972). Boron and
molybdenum, however, require separate extractions. In general,
micronutrient soil tests are effective when sufficient efforts
are made in regard to correlation and interpretation.

Salinity and Alkalinity. Electrical conductivity on a saturated
soil paste is almost universally accepted as the best method
for salinity determinations. Care must be taken concerning
the time and the depth of samples, as soluble salts are
extremely mobile in irrigated systems. Alkalinity is best
determined by calculating exchangeable sodium saturation.
Sodium is easily determined in the same extracting solution

as potassium, provided that the extractants are sodium free.

18.1.3. Soil Test Correlation

The most difficult aspects of the soil fertility evaluation process are the correlation, interpretation, and recommendation phases, because of the complex phenomena involved. A soil test value per se is worthless; it is an empirical number that may or may not indirectly reflect nutrient availability. Soil test values become useful only when they are correlated with crop responses. Such correlations are usually conducted at two levels: an exploratory one in the greenhouse with a large number of widely diverging soils, and a more definite one in the field with fewer, but carefully selected, soils.

The primary purpose of greenhouse correlation is to compare different extraction methods and determine tentative critical levels. The purpose of field test correlations is to establish definite critical levels for a selected extraction method. Good greenhouse correlations, however, do not prove the effectiveness of a particular soil test; this can be demonstrated only in the field. The bulk of soil-testing research in the tropics, unfortunately, stops at the greenhouse stage.

Plant growth and yields are functions of many variables beyond the single nutrient under consideration. Actual yields are functions of over a hundred variables, which can be grouped into soil, crop, climate, and management categories. Consequently when yields are correlated with one varialbe such as available phosphorus, this means that available phosphorus is a more important limiting factors than the numerous uncontrolled variables in any correlation study. Better correlations are normally obtained in greenhouse studies, where the uncontrolled variables are more uniform. Nevertheless a considerable scatter of points occurs when absolute yield, yield response, nutrient uptake, or other growth parameters are plotted as functions of soil test values. The continuum of points is commonly split into several arbitrary categories such as "low", "medium", and "high" (Fig. 18.1). Recommendation rates are based on the fertilizer needed to raise the soil test level to "high".
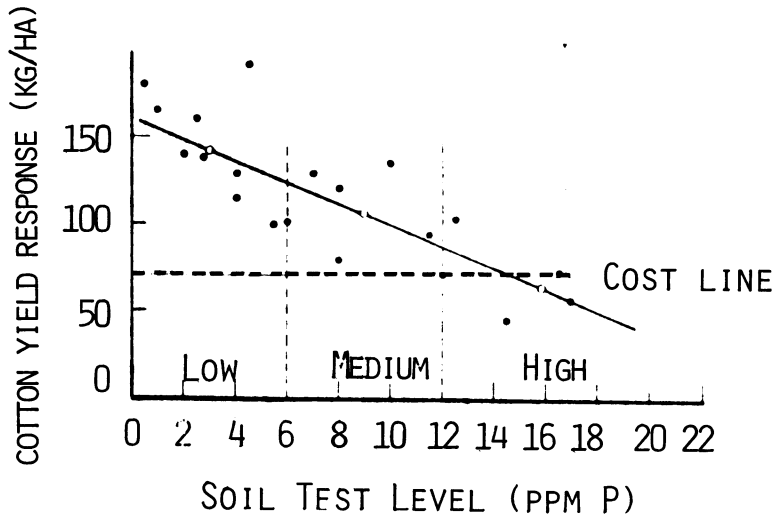
FIG. 18.1. ARBITRARY GROUPING OF SOIL TEST CATEGORIES
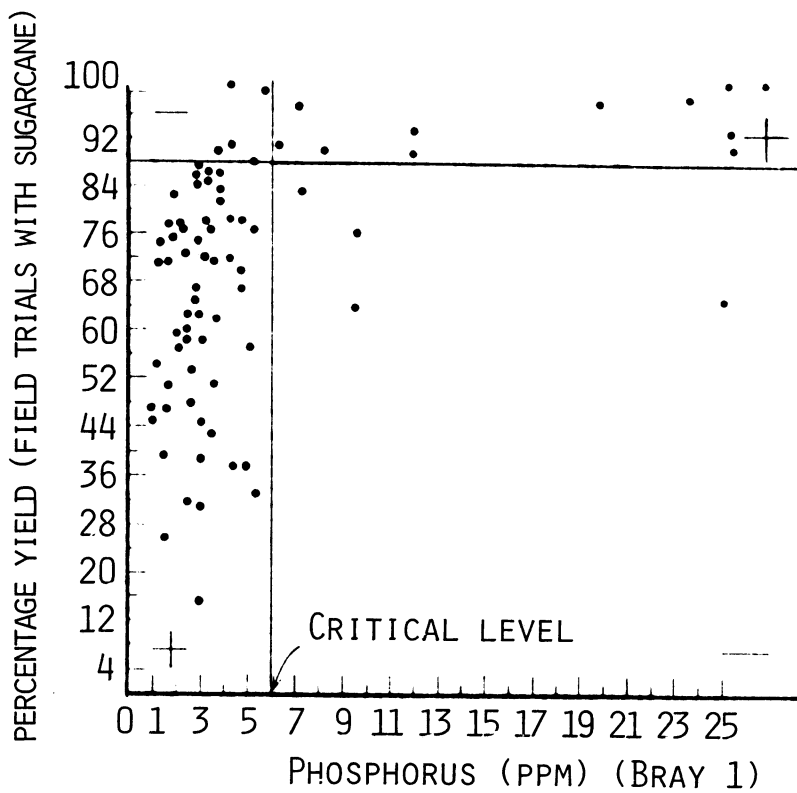
SOURCE: HAUSER (1973)

FIG. 18.2. ANALYSIS OF SUGARCANE DATA FROM PERNAMBUCO,
BRAZIL, BY THE METHOD OF CATE AND NELSON.
EACH DOT REPRESENTS A FIELD PLOT.
SOURCE: ISFEIP (1967)

When relative yields rather than absolute yields are used, the variability is considerably reduced. Relative yield calculations are of two kinds: percent yield response, in which the actual yield response is divided by the absolute yield at the zero level, and the value obtained when the yield at a certain fertility level is divided by the maximum yield attained. In both cases, relative yield values reduce the variability of results and direct soil test correlation toward its realistic goal: the prediction of soil-crop situations for which there is a likelihood of significant fertilizer response. (Waugh et al., 1973). Soil test correlations cannot predict yields or even absolute yield responses because of the many other variable involved.

A major breakthrough in soil test correlations occurred with the development of the Cate-Nelson method (Cate and Nelson 1965). The simple graphic method consists of plotting relative yields (percents of maximum) as a function of soil test values, as Fig. 18.2 illustrates. Instead of attempting to fit a continuous mathematical function through the scattered points, a plastic overlay sheet divided into quadrants by a horizontal and a vertical line is used. This sheet is superimposed on the data in such a way that the maximum number of points falls in the lower left and upper right quadrants, and the minimum number of points is left in the upper left and lower right quandrants. The point at which the vertical line intersects the x-axis is con-sidered to be at the critical level for the soil test in question. The point at which the horizontal line intersects the y-axis separates soils with high response from those with low response. The critical level, therefore, divides the data points with a likelihood of a large yield response from those with little probability of obraining a response.

In comparison with the conventional correlation techniques, the Cate-Nelson method presents some fundamental and practical advantages. By separating the data points into two populations, it follows Leibig's law of the minimum, because the critical level is the point beyond which the nutrient in question is no longer a limiting factor. In contrast, continuous regression models show no inflection points and force the groupings to be arbitrary. The main advantage of the Cate-Nelson approach is

that it recognizes the basic limitation of soil tests: they
are able only to separate the soils that are likely to respond
to the added nutrient from those unlikely to respond. Thus
the population is split into two soil-crop categories.

Another advantage is that the method identifies the soils
in which the extractant does not work well (the points lying
in the top left and bottom right 'quadrangles). They can be
subjected to further study and refinement.

The simplicity of this approach has a major practical
advantage, particularly in tropical laboratories without ready
access to digital computers. All that is needed is a piece
of transparent paper instead of complex mathematical calculations
that must be handled by computers. The statistical soundness
of the technique, however, has also been proved by fitting a
discontinuous linear regression model and comparing it with the
conventional curvilinear models (Cate and Nelson, 1971).
(Table 18.3).

The use of this technique is shown in Fig. 18.3.
The first step, a comparison of different soil test methods,
was conducted in the greenhouse. In this case all soil test
methods correlated well, and each one produced a critical level.
The results were then taken to the field, using the North
Carolina extractant. The results confirmed 10 ppm as the critical
level under field conditions (Fig. 18.3).

The critical level is specific to certain soils-crop
situations, even with the same extractants. Each laboratory,
therefore, should establish its own critical levels for its
major soils and crops. For example, two different critical
levels were found for zinc in Peru when the soil population
was split between calcareous and acid soils. This example
confirms the previously described strong influence of pH level
on available zinc, and shows how the correlations can be
refined by such groupings.

Table 18.3 *Performance of Different Mathematical Models on a Worldwide Sample of Correlations between Relative Yields and Soil Test Levels*

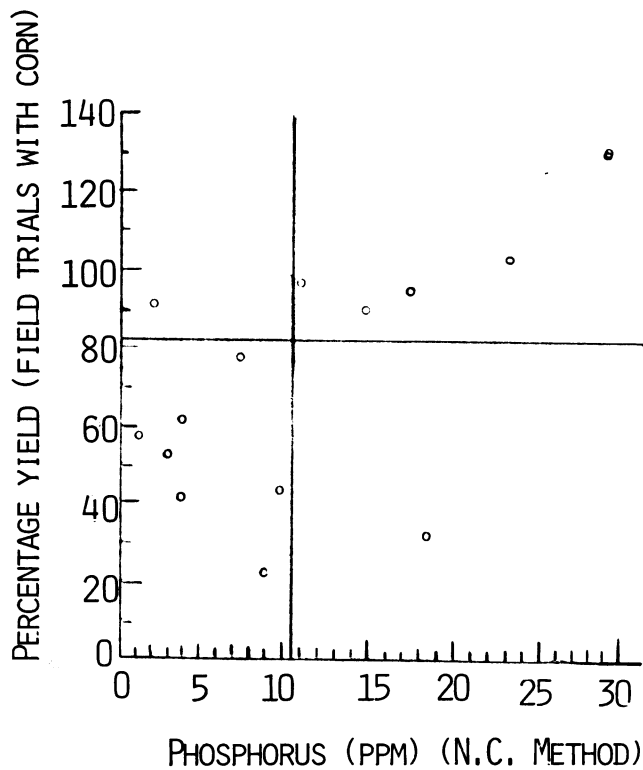| Regression Model	Equation	R^2
Quadratic	$Y = b_0 + b_1 x - b_2 x^2$	.58
Logarithmic	$Y = b_0 + b_1 (\log x)$	.59
Mitscherlich	$Y = A(1 - e^{cx})$	.66
Cate-Nelson	$Y = b_0 + b_1 x_1$	.73
	where $x = 0$ if below critical level	
	$x = 1$ if above critical level	

Source: Cate and Nelson (1971).

FIG. 18.3. CORRELATION BETWEEN THE CHOSEN SOIL TEST METHOD AND CORN RESPONSE IN THE FIELD IN RECIFE, BRAZIL,
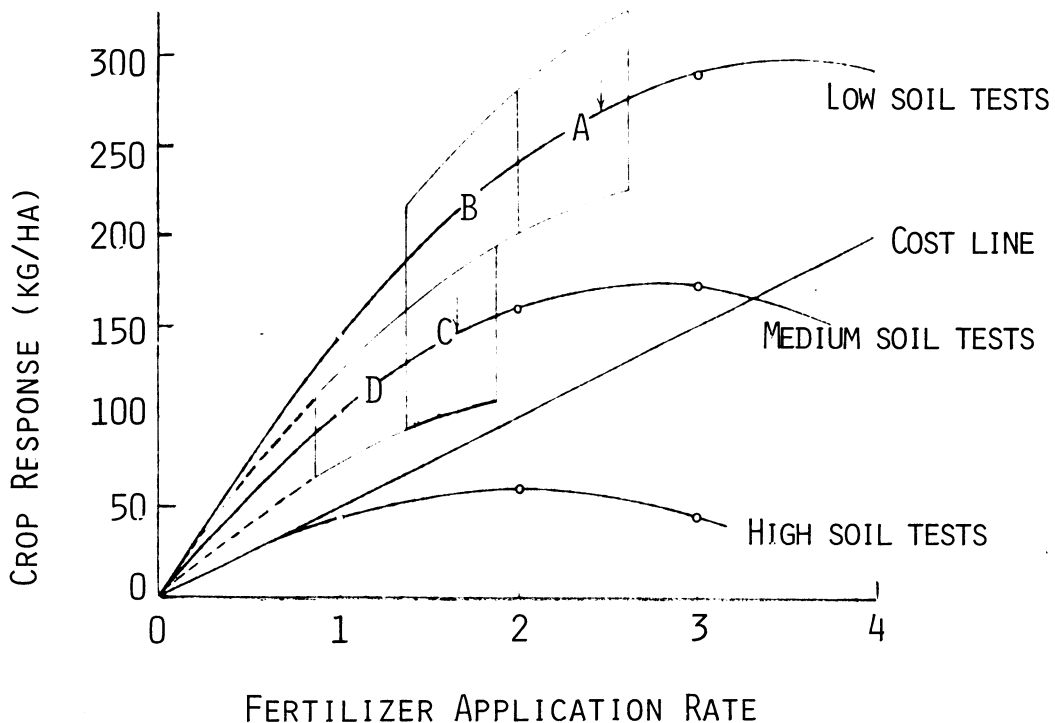
SOURCE: ISFEIP (1967)

FIG. 18.4. INTERPRETATION GRAPH, USING CONTINUOUS CURVILINEAR RESPONSE FUNCTIONS FOR THE COTTON FERTILIZATION EXPERIMENTS OF FIG. 18.1 ARROWS INDICATE OPTIMUM ECONOMIC RATES. SOURCE: ADAPTED FROM HAUSER (1973)

The Cate-Nelson method is now widely used in the tropics
(Goswami et al., 1971; Roufunnisa et al., 1971, Baynes
and Walms ley, 1973; Palencia, 1974; Perur et al., 1974).
In some laboratories, the interpretation is modified by splitting
soils into the levels "low", "medium", and "high". The critical
level usually falls between "medium" and "high" in such cases
(Hauser, 1973). The Cate-Nelson approach has not been used
in United States or Australian soil-testing programs. Soil test
correlation methods in these countries are based on multiple
regression computer programs with strong emphasis on nutrient
interactions (Cope and Rouse, 1973; Colwell, 1971).

18.1.4.   Interpretation and Recommendations.

The purpose of soil test interpretation is to establish
how much of each nutrient must be applied to bring about a
given yield response within a predictable crop-soil category .
A separate crop-soil category indicates that interpretation must
be different for soils above or below the critical level and
also for different crops.

As in the case of correlations, two main methods of
soil test interpretation are used in the tropics: the continuous
(curvilinear) and discontinuous (linear) models.

Continuous models. These classic models are based on the law
of diminishing returns, where appropriate curvilinear functions
are fitted to yield response data. The most commonly used
functions are the quadratic, square-root, logarithmic, and
Mitscherlich. Statistical techniques determine which function
fits the data best by providing the largest coefficient of
determination (R^2). The optimum fertilizer rate occurs at that
point in the curve where the marginal revenue equals the marginal
cost (i.e. the point where the price of the last yield increment
equals the cost of the last increment of fertilizer). The point
can be determined mathematically or graphically by drawing
a price: cost ratio line, expressed in the agronomic equivalents,

in the yield response diagram. The optimum yield is then
determined at the point where a tangent of the price: cost
ratio line intersects the response curve.

Separate yield response equations are prepared according
to the groupings made during the correlation process for each
crop. If the Cate-Nelson technique is used, equations for soils
testing above and below the critical level can be developed.
If the continuum is split into "very low", "low," "medium",
"high" and "very high" categories, there will be five response
functions and an optimum fertilizer recommendation for each
soil test level. An example of this second approach is shown
in Fig. 18.4 based on the correlation data presented in Fig.
18.1 . Figure 18.4. presents a helpful modification: an
optimum range rather than an optimum level is indicated.

Ranges A and C reflect recommendations for the highest
profit per hectare, while B and D are areas of lower fertilizer
cost and higher return per unit of fertilizer (Hauser, 1973).
Similar interpretations for other economic alternatives have been
presented by Heady and Ray (1971). This modification is helpful
in handling the economic uncertainties typical of developing
countries.

Such complex models are effective when there is
adequate information about the variables involved, and when
prices are stable. They usually fail in the tropics, however,
because there are insufficient data to quantify all variables.
Their use in tropical regions is limited to after-the-fact
analysis in areas with detailed information; they do not serve
successfully as predicting tools.

Discontinuous linear model. A series of studies conducted
in England by Boyd (1974) and in the United States by Bartholomew
(1972) summarized many fertilizer response functions over the
world and concluded separately that in most instances fertilizer

FIG. 18.5. LINEAR RESPONSE AND PLATEAU (LRP) MODEL, BASED ON LIEBIG'S
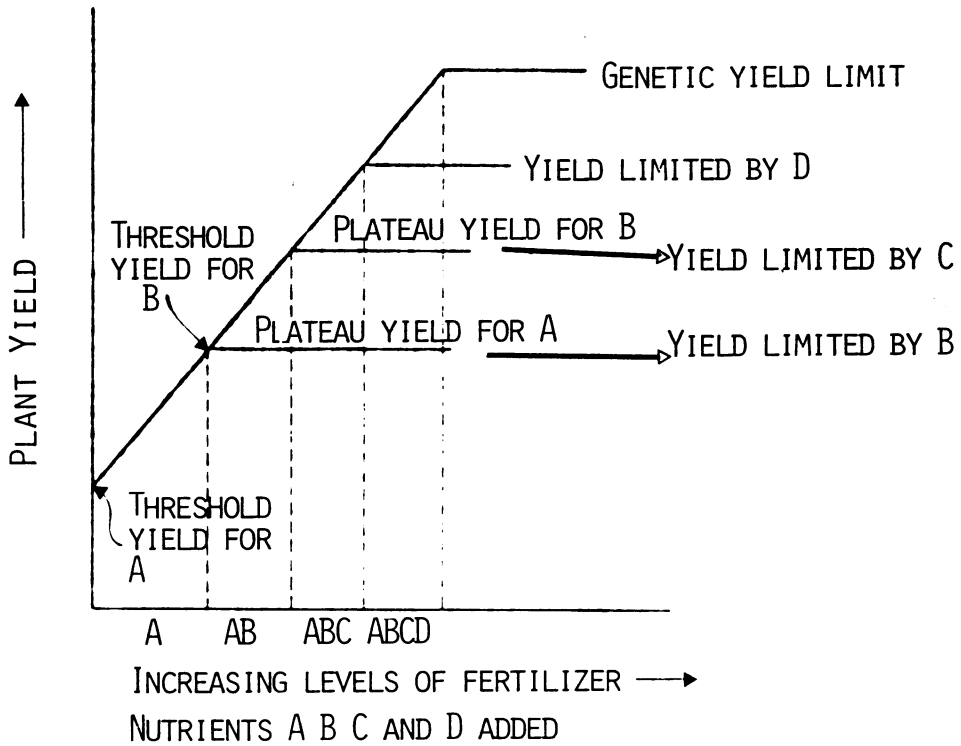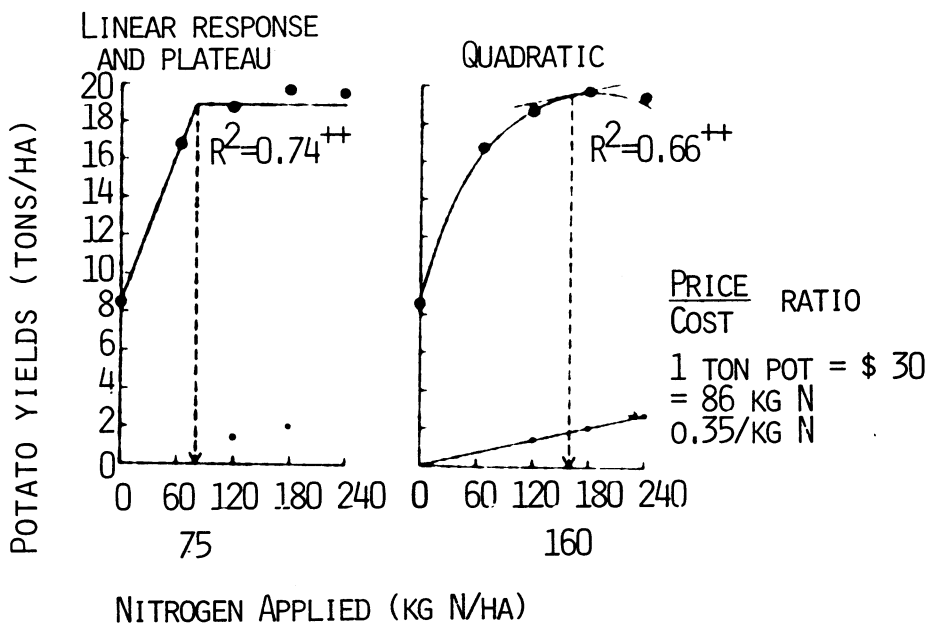LAW OF THE MINIMUM. SOURCE: WAUGH ET AL. (1973)

FIG. 18.6. DETERMINATION OF NITROGEN RECOMMENDATIONS FOR POTATOES IN A
SET OF FIELD EXPERIMENTS FROM BOLIVIA ACCORDING TO THE LINEAR
PLATEAU RESPONSE AND THE CONVENTIONAL CURVILINEAR MODELS. EACH
DOT IS THE MEAN OF SEVERAL FIELD EXPERIMENTS IN A GIVEN CROP-
SOIL CATEGORY. SOURCE: ADAPTED FROM WAUGH ET AL. (1973)

response curves can be characterized by a sharp linear increase
followed by a flat horizontal line.

Waugh, Cate, and Nelson then developed the"linear response
and plateau" model, which is also based on Leibig's law of the
minimum and is a logical extension of the Cate-Nelson correlation
model (Waugh et al. 1973, 1975). In this model fertilizer
response from a field or a group of fields is represented by two
straight lines for each individual nutrient. The first line
represents the relatively steep response of an added nutrient
until it ceases to a limiting factor. This is followed by
a flat plateau, where further additions no longer increase
yields. The fertilizer response curve so constructed consists
of three main points. The "threshold yield" is the yield
at the zero level of the nutrient in question, but not of all
nutrients. The "plateau yield" is the yield at the point where
the nutrientceases to be a limiting factor; it is not the
maximum yield because other factors may still limit yields.
The "relative yield" is simply the threshold yield divided by
the plateau yield. The fertilizer rate needed to reach the
plateau yield is the recommended rate for the particular nutrient.

As one nutrient ceases to be limiting, others may still
be so. This concept, which is the classic interpretation
of Leibig's law of the minimum, is illustrated in Fig. 18.5. The
final plateau yield is the effectof genetic limitations, solar
radiation, and other uncontrolled variables.

Regression studies indicate that there is no difference
between this model and the curvilinear ones in terms of
coefficients of determination (R^2). In fact, the linear
responee and plateau model provided the highest R^2 in 27 of
37 response functions studied by Waugh et al. (1973). Although
there is no question that the actual biological function is
curvilinear, the interpretation of it as two straight lines is
of conisderable value in simplifying soil-testing interpreations.
It also provides more realistic rate recommendations, since the
bias toward unrealistically high fertilizer recommendations
of the quadratic equation is eliminated.

The comparison between the two approaches is shown
in Fig. 18.6 for the same data set. The dotted lines indicate
how the fertilizer recommendations are arrived at. The linear
response model has only one optimum point independent of cost
and prices. The curvilinear model shows an optimum point based
on the particular price: cost ratio at the time the
experiments were conducted. It is very interesting to note the
wide differences in optimum recommended rates between the two
methods. The linear response and plateau model has a lower
recommended rate because it attempts to reach a yield plateau
of only about 19 tons/ha. This rate in effect provides
nearly maximum yields, while preserving an efficient return
per unit of fertilizer, because it is still along the increasing
slope. The quadratic model in this case almost doubles the
optimum recommendations in order to obtain a yield of 20 tons/ha.
This is in the relatively flat part of the curve, where
variability is quite high. Small changes in yields result
in large changes in recommended rates. In other comparisons,
however, the difference in recommended rates might not be as
large as in this example.

Another example is shown in Table 18.4. In this case
there were no significant differences in recommended rates
or profitability of the prediction, but both models overestimated
the rates required for the actually most profitable combination.

The decision on which model to use may vary with individual
inclinations and the availability of computers. The linear
response and plateau model is new and controversial. It has
been successfully applied in several countreis (Perur et al., 1974
Palencia, 1974) and is at least as good in predicting yield
response as the quadratic model. Moreover, the linear response
and plateau model has a very practical advantage: it does
not require a computer or complex calculations.

18.1.5. Using Soil Test Recommendations

Regardless of how fertilizer recommendations are determined, they are worthless unless farmers use them. Their effective application depends on the educational and extension aspects of the soil evaluation program, as well as on the validity of the recommendations themselves. The educational and promotional aspects are initially geared to capture the farmer's attention. Usually this effort involves field days, demonstration plots, radio programs, and audiovisual aids. After farmers are aware of the program, they will accept or reject the recommendations.

Failures in soil testing efforts are due to many factors. A principal one is the inability to obtain yield responses of such magnitude that yields can be doubled in areas with low average yields. E.W. Russell (1974) recognized this as one of the limiting factors preventing widespread fertilizer use in Africa. No rational farmer is going to adopt a practice that may increase his yield by 10 or 20 percent if his risks are higher than this. The lack of such yield responses may be due to incomplete research, such as limiting correlation studies to the greenhouse stage, or to extrapolating a few field results with one crop to widely divergent ones.

In areas where soil fertility evaluations of the type described have been put into practice, positive correlations between the number of soil tests and fertilizer consumption exist (Kanwar, 1971; ISFEIP, 1972). Although a correlation does not imply a cause effect relationship, it is clear that successful soil testing and increased fertilizer consumption go hand in hand. At the beginning of a program it is probable that soil tests increase fertilizer use; as fertilization practices become widespread, increasing fertilizer demand augments the need for additional soil analysis.

18.1.6.   Research

The last phase of a soil fertility evaluation is research to improve the quality of recommendations. This involves troubleshooting on problem samples through greenhouse research, plant analysis, refining soil-crop categories, and finding out why some soils are in the wrong quadrangle of the correlation graph. New extraction methods and improved laboratory techniques must be evaluated under local conditions. Like any other service function, soil fertility evaluation requires research to keep it up-to-date. From the advances in the past few years, this appears to be a very productive area of research and innovation.

18.2.   Fertility Evaluation Systems based on Plant Analysis

Other soil fertility evaluation systems are based on plant analysis. These are particularly widespread in areas without effective soil-testing systems and are especially popular for permanent crops. The division between fertility evaluation systems based on soil testing and those utilizing plant analysis is somewhat arbitrary because plant analysis is a component of systems based on soil testing and vice versa. Nevertheless, some evaluation systems are primarily based on plant analysis.

Plant analyses are used for three main purposes: (1) to identify nutritional problems and quantify their correction through the establishment of critical levels; (2) to compute nutrient uptake values as a key for fertilizer use; and (3) to monitor the nutrition of permanent crops, a practice called "croplogging."

18.2.1. Critical Levels.

When plant samples are taken from the same anatomical part and at the same growth stage, certain critical levels can be established above which the plant is sufficiently supplied

Table 18.4 *Comparison of Recommended Rates and Profitability as Determined by the Graphic Linear Response and Plateau Model and by a Generalized Quadratic Equation with 20 Variables: Mean of 26 Corn Experiments from Minas Gerais, Brazil*

Model Used	Recommended Rate (kg/ha)		Profitability of Recommended Rates (Cr $/ha)
	N	P_2O_5	
Actual best treatment	107	50	1460
Graphic LRP	120	85	1118
Computed quadratic	127	64	1109

Source: North Carolina State University (1973).

Table 18.5 *Examples of Critical Levels Separating Deficiency and Adequacy in Some Crops*

Element	Sugarcane[a]	Rice[b]	Corn[c]	Soybeans[d]
N (%)	1.5	2.5	3.0	4.2
P (%)	0.05	0.10	0.25	0.26
K (%)	2.25	1.0	1.90	1.71
Ca (%)	0.15	0.15	0.40	0.36
Mg (%)	0.10	0.10	0.25	0.26
S (%)	0.01	0.10		
B (ppm)	1	3.4	10	21
Cu (ppm)	5	6	5	10
Fe (ppm)	±10	70	15	51
Mn (ppm)	10 20	20	15	21
Mo (ppm)	—		0.1	1.0
Zn (ppm)	10	10	15	21
Si (%)	---	5		

[a] From Humbert (1973). Values refer to leaf blades 2, 4, 5 and 6 except for P, K, Ca, Mg, and Zn, which represent leaf sheaths 2, 4, 5, and 6.

[b] From Tanaka and Yoshida (1970). N, P, K, and Fe values are for leaf blades at tillering stage; Ca, Mg, S, B, and Cu values, for straw at harvest; Mn and Zn values, for shoots at the tillering stage.

[c] From Jones and Eck (1973). All values are for the ear leaf at tasseling except for Mo, which represents the entire plant.

[d] From Small and Ohlrogge (1973). Lower limit of sufficiency range for upper fully developed trifoliate leaf blades sampled before pod set.

with the nutrient in question and below which it is not.
A second set of critical levels is needed for nutrients that
can be present in toxic amounts, such as boron, iron, and
manganese, or in cases where an excessive amount of the nutrient
can cause yield declines. An example of the latter is
excessively high nitrogen contents in tall-statures rice varieties.
The range between these two critical levels is called the
"sufficiency range". The term "critical level" is normally
used in conjunction with the deficiency-adequacy threshold.

Plant analysis critical levels are less site- and
situation-specific than those obtained from soil tests, as long
as they are standardized with respect to plant part, age,
and in some cases varieties. Table 18.5 shows some typical
examples from standardized plant parts and growth stages.

18.2.2. Nutrient Uptake as a Predictive Tool

The general failure of soil tests for nitrogen has
encouraged a completely different approach for estimating
fertilizer rates. In a review of the world literature Bartholomew
(1972) observed a constant relationship between grain yields
of cereal crops and their total nitrogen uptake (including
roots). This relationship is shown for commercial grain yields
of corn, wheat, and rice in Fig. 18.7. The slopes of the curves
indicate that corn and rice averages from 30 to 35 kg grain/kg
N added, whereas wheat averaged only 15 to 20 kg. The lower
efficiency of wheat is thought to be the result of genereally
drier climate and the lodging susceptibility of tall-statured
varieties. If one knows the average yields without nitrogen
fertilization (threshold yields) and the plateau yields for
a specific area, the amount of nitrogen required for increasing
yields from the threshold to the plateau can be obtained from
such a graph. Bartholomew's uptake-grain yield relationships
are illustrated in the top half of Fig. 18.7. For example,
if the threshold yield of corn is 2 tons/ha and it is known
that with nitrogen fertilization and good management 6 tons/ha is
probable, the crop will need to take up 100 kg N/ha extra
(140-40) to attain 6 tons/ha, provided that nitrogen is the
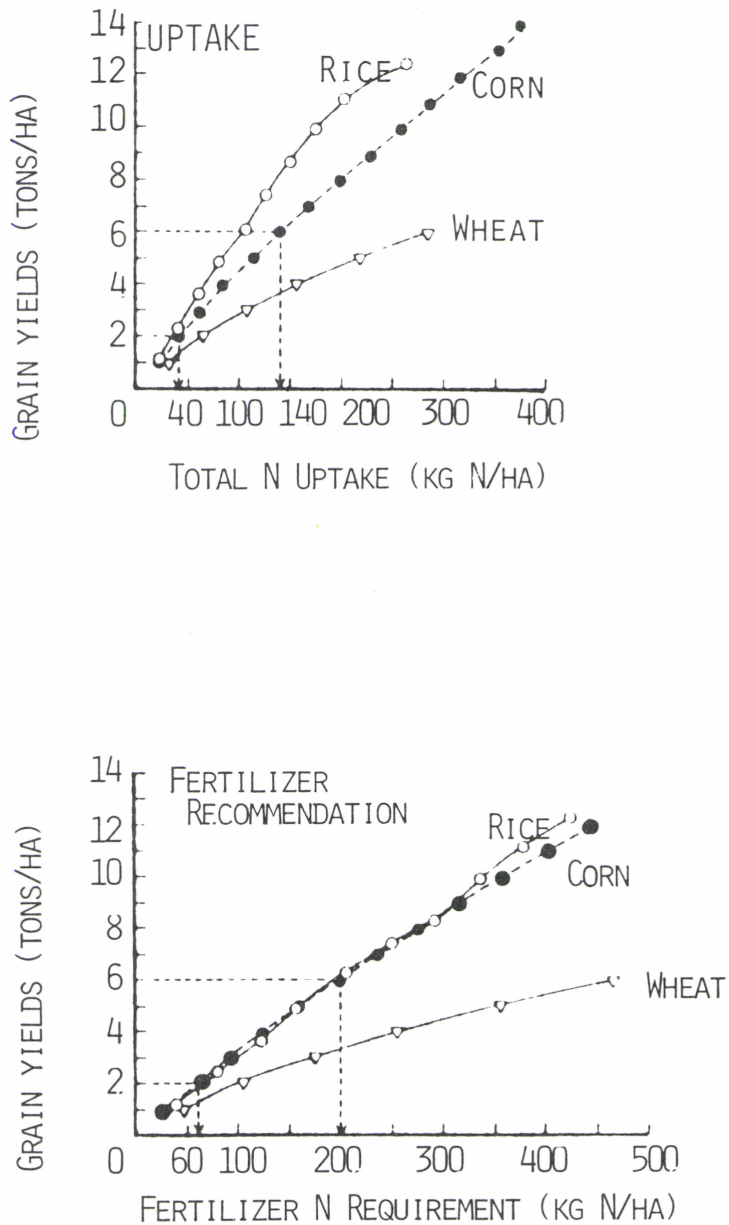main limiting factor within this yield range. Figure 18.7

FIG. 18.7. PROCEDURE FOR CALCULATING NITROGEN RATES FROM CROP UPTAKE DATA
BASED ON AVERAGE FIELD TRIALS AND AVERAGE FERTILIZER RECOVERY.
RICE EXPRESSED IN UNHULLED (PADDY) GRAIN FIELDS.
SOURCE: ADAPTED FROM DATA BY BARTHOLOMEW (1972)

also shows the differences in nitrogen requirement between the three cereals. Rice required about 17 kg N to produce an extra ton of rough rice, corn about 25 kg N, and wheat about 42 kg N. These figures shows that wheat is the least efficient user of nitrogen of these three crops.

Not all the fertilizer nitrogen will be taken up by the plant. The efficiency of fertilizer utilization varies with soil, varieties, climate and management. On the basis of a worldwide survey, Bartholomew (1972) calculated the actual fertilizer nitrogen requirements at high,medium, and low levels of fertilizer efficiency. The lower half of Fig. 18.7 is based on the average nitrogen recovery rate. The percentage rates are 36 for rice, 72 for corn, and 62 for wheat. The amounts of fertilizer nitrogen required for a given yield increase are almost identical for corn and rice. They range from 30 to 35 kg grain/kg N. The high efficiency in nitrogen uptake of rice, however, is offset by the lower efficiency of applied nitrogen under flooded conditions, as compared to corn. Wheat responds at a rate of 15 to 20 kg grain/ kg fertilizer, in-spite of the high recovery of applied fertilizer nitrogen. The nitrogen fertilizer recommendation to increase yields from 2 to 6 tons/ha of corn would be 140 kg N/ha, the difference between the points marked with the arrows on Fig. 18.7.

18.2.3. Crop Logging.

As mentioned before, plant analysis is particularly useful for permanent crops, where soil tests are less meaningful because of the high proportion of roots in the subsoil. An intensive plant-sampling system was developed by Clements (1960) to monitor the nutrient and water status of sugarcane plantations as a guide for fertilization and irrigation. This system, subsequently called "crop logging", is used in various sugar-cane growing areas but principally in Hawaii. It is described in great detail by Humbert (1963). Individual fields are sampled every 35 days during the first 6 months of growth,

and the results are plotted on running graphs. The charts show
the percentage of nitrogen in leaf blades and the percentages
of phosphorus and potassium in elongated leaf sheaths. Rainfall,
irrigation, temperature, and plant height records are also
kept, and fertilizer and irrigation practices are recorded.
When the plant analysis laboratory is capable of analyzing plant
samples quickly, crop logging gives an excellent measure of crop growth
and increases the efficiency of fertilizers and irrigation.
Crop logging has also been practiced on other permanent crops,
but not on short-term crops such as corn because there is not enough
time to make use of the analyses.

18.3.   Fertility Evaluation Systems based on Missing Element
        Techniques.

        A third major approach is based on the identification
of nutrient deficiencies by the missing element technique.
This involves growing indicator plants in the greenhouse or in
the field on a soil to which a "complete" fertilization
treatment is added, and a series of treatments in which one
element is not added.

        According to Chaminade (1972), pot experiments
with the missing element technique give three types of information:
(1) which elements are deficient, (2) the relative importance
of the deficiencies, and (3)   rate at which fertility is
depleted with successive cuttings when a pasture indicator
crop is used. The IRAT researchers consider deficiencies serious
if the dry matter production is depleted to 40 percent or less
of the complete treatment. Field trials with the appropriate
missing elements follow the pot experiments and serve as the
basis for fertilizer recommendations. The French approach places
strong emphasis on soil survey to select the soils to work with;
the rate determination experiments are supplemented by research
on rotation systems, the residual effects of fertilization,
and the quantities needed to maintain the appropriate feritlity
level. Nutrient uptake serves as a basis for those maintenance
applications.

Missing element techniques have the disadvantages that only early growth data are obtained, that nutrient deficiencies may be exaggerated because of the small volume of soil, and that the effort necessary precludes their use for large numbers of soils from farmers' fields. Their greatest value is for preliminary screening in research projects or for obtaining needed additional information on soils for which poor soil test yield response correlations are obtained.

18.4. Simple Fertilizer Trials on Farmers' Fields.

A fourth major approach used in evaluating soil fertility in the tropics consists of the simple fertilizer trials conducted under the leadership of the Food and Agricultural Organization (FAO) of the United Nations. The purpose of this program is to introduce fertilizers as a means for increasing yields in large areas of the tropics. This program has been described at its different stages by Mukerjee (1963) and Hauser 1973).

The FAO program is based on H.N. Mukerjee's "method of dispersed experiments" . Its basic assumption is that fertilizer needs are best estimated by conducting a large nubmer of unreplicated fertilizer trials in farmers' fields chosen at random without prior analysis. Individual trials dispersed over a visually uniform area or soil type are considered replicates, and the average yield of such areas is determined. The individual experiments consist of a small number of treatments, usually a 2 x 2 x 2 factoral NPK design. The rates are rather small (20 and 40 kg/ha) because the purpose is to provide maximum efficiency of fertilizer investment, which is normally attained in the initial part of the response curve. Later designs include up to 16 treatments to establish the response curve of two nutrients. The underlying philosophy of this program is that fertility response must be evaluated in farmer's fields and not under controlled conditions at experiment stations.

Hundreds of thousands of such trials have been conducted with major crops in all or large parts of 40 countries, including the Philippines, Pakistan, Bangladesh, India, Indonesia, Malaysia, Vietnam, Ceylon, Thailand, Ghana, and Brazil. The

results are published in individual country reports with limited
distribution. Whenever soil maps are available, the results
are given by soil groups; in the absence of maps, by
geographical areas thought to be uniform. Whenever soil testing
laboratories are available, correlation between yield response
and soil test levels are attempted but usually with limited
success. Mukerjee (1963) stated that the average estimate
of nutrient needs for a visually uniform area is insufficient to
provide a fertilizer recommendation to an individual farmer.
He considered soil tests necessary to attain this objective.

The overall results of the program were recently
summarized by Hauser (1974). The average yield response with
the modest fertilizer rates used was 60 percent of the
check yields. In grain crops this represented a yield increase
from 1.0 to 1.6 tons/ha and an average of $3.3 per dollar invested
in fertilizer. The overall increase in fertilizer cost in
all countries involved averaged $40 million per year during
the last 10 years.

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