

ZINC IN SOILS AND CROP NUTRITION

Brian J. Alloway



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FOREWORD

Zinc (Zn) is an essential micronutrient and has particular physiological functions in all living systems, such as the maintenance of structural and functional integrity of biological membranes and facilitation of protein synthesis and gene expression. Among all metals, Zn is needed by the largest number of proteins. Zinc-binding proteins make up nearly 10 % of the proteomes in eukaryotic cells, and 36% of the eukaryotic Zn-proteins are involved in gene expression (*Andreini et al., 2006, J. Proteome Res. 5: 3173-3178*). Tolerance to environmental stress conditions has a high requirement for Zn to regulate and maintain the expression of genes needed to protect cells from the detrimental effects of stress (*Cakmak, 2000, New Phytol. 146:185-205*).

Zinc deficiency appears to be the most widespread and frequent micronutrient deficiency problem in crop and pasture plants worldwide, resulting in severe losses in yield and nutritional quality. This is particularly the case in areas of cereal production. It is estimated that nearly half the soils on which cereals are grown have levels of available Zn low enough to cause Zn deficiency. Since cereal grains have inherently low Zn concentrations, growing them on these potentially Zn-deficient soils further decreases grain Zn concentration. It is, therefore, not surprising that the well-documented Zn deficiency problem in humans occurs predominantly in the countries/regions such as India, China, Pakistan and Turkey where soils are low in available Zn, and cereals are the major source of calorie intake.

Zinc deficiency in humans is a critical nutritional and health problem in the world. It affects, on average, one-third of the world's population, ranging from 4 to 73 % in different countries (*Hotz and Brown, 2004, Food Nutr Bull 25: 94-204*). The recent analyses made under the Copenhagen Consensus in 2008 (www.copenhagenconsensus.com) identified Zn deficiency, together with vitamin A deficiency, as the top priority global issue, and concluded that elimination of the Zn deficiency problem will result in immediate high impacts and high returns for humanity in the developing world.

It is, therefore, highly important to develop cost-effective and quick solutions to the Zn deficiency problem. Low Zn in plant tissues is a reflection of both genetic- and soil-related factors. A basic knowledge of the dynamics of Zn in soils, understanding of the uptake and transport of Zn in plant systems and characterizing the response of plants to Zn deficiency are essential steps in achieving sustainable solutions to the problem of Zn deficiency in plants and humans.

This book "*Zinc in Soils and Crop Nutrition*" by Brian Alloway contributes significantly to our better understanding of the complexities of Zn dynamics in soil and plant systems. It contains very valuable basic and practical information for a wide audience, including students, agronomists and scientists who are involved in research, extension or education in soil science, plant mineral nutrition, plant physiology and also human nutrition. Detailed information on the prevalence and diagnosis of Zn deficiency problems for a number of countries and crop plants is an excellent feature of this book.

This book has been available electronically since 2004. It has now been decided to publish this updated version in a print format. This is a great idea that will further contribute to a wide distribution of the useful information contained in the book.

I would like to congratulate Prof Brian Alloway on this excellent achievement, and thank the International Zinc Association (IZA) and the International Fertilizer Industry Association (IFA) for their support which has made the publication of such a valuable book possible.

Ismail Cakmak

Sabanci University
July 2008, Istanbul

ABBREVIATIONS AND GLOSSARY

AAS	atomic absorption spectrophotometry (analytical method for trace elements)
AB-DTPA	ammonium bicarbonate with DTPA, soil test reagent
Acrisols	red-yellow coloured soils typical of humid tropical, sub-tropical and warm temperate areas, often found associated with Ferralsols (FAO-UNESCO Soil Classification).
Adsorption	retention of ions on the surface of the soil solid phase
Aerobic rice	rice grown without continuous flooding under aerobic soil conditions (also called upland rice)
Aerosols	particles < 30 µm in diameter suspended in air
Alfisols	moist mineral soils with medium to high base status which contain a horizon of clay accumulation. Occur in cool-hot humid areas and also semi-arid areas
AM	arbuscular mycorrhizae (fungi which colonise the root and assist in the absorption of soil ions from the soil solution) - also called vesicular arbuscular mycorrhizae (VAM)
Anion	negatively charged ion (e.g. hydroxyl ion OH ⁻)
Arenosols	sandy textured soils (sand particles 0.05-2 mm in diameter) whose properties are dominated by the high sand content (e.g. low clay contents and low available water capacities)
ASNS	alternate submerged, non-submerged rice growing system (an alternative to continuously flooded paddy rice (see also GCRPS))
Auxin	compound regulating plant growth (e.g. IAA-indole acetic acid)
Biofortification	process of increasing the content ('density') of micronutrients, such as zinc, in food crops, especially cereals. There are two types: agronomic biofortification involves using fertilisers to increase the density of zinc in cereal grains; genetic biofortification uses specially-bred crops which have been selected on the basis of their ability to concentrate zinc and other micronutrients in their edible parts, such as grains.
Biosolids	another name for sewage sludge – the insoluble residue from waste water treatment
Bread wheat	used for baking bread (in contrast to durum wheat)
C ₃ plants	plants with a basic photosynthesis mechanism which fixes carbon dioxide in only one stage
C ₄ plants	plants which fix carbon dioxide in two stages and can raise its concentration in their leaves above ambient levels
Ca	calcium
CaCO ₃	calcium carbonate
Calcisols	soils in which there is a substantial accumulation of calcium carbonate (calcareous soils), characterized by a 'calcic' horizon (>15% CaCO ₃ equivalent)
Calcite	calcium carbonate (CaCO ₃)
Cation	positively charged ion (e.g. zinc occurs as divalent cation Zn ²⁺)
Cation Exchange Capacity (CEC)	the sum of exchangeable cations that can be adsorbed by a soil, soil constituent or other material at a particular pH
Cd	cadmium
CGIAR	Consultative Group on International Agricultural Research (co-sponsored by FAO, International Bank for Reconstruction and Development (World Bank), the UN Development Programme and the UN Environment Programme)

Chlorophyll	green pigment in plants involved in photosynthesis
Chlorosis	lack of chlorophyll formation resulting in yellow stripes and patches on leaves (major symptom of zinc deficiency)
CIMMYT	International Maize and Wheat Improvement Centre
Clay minerals	aluminium silicate minerals with a large surface area, clay particles < 2 µm in diameter. Clay minerals give soils part of their adsorptive capacity, cohesiveness and water retention
Co	cobalt
Co-precipitation	occlusion of metal ions in precipitates of iron, manganese and aluminium oxides
CSIRO	Commonwealth Scientific and Industrial Research Organisation (Australia)
Cultivar (cv)	cultivated variety of a plant species with distinctive characters (often vary considerably in zinc efficiency/tolerance to deficiency)
Cu	copper
Cut soils	soils in which the topsoil has been removed during levelling of fields for irrigation
DAP	diammonium phosphate (high analysis phosphatic fertiliser, 21% N 23% P) usually with very low contents of metal impurities
dS m ⁻¹	deciSiemens per metre (measure of electrical conductivity [EC] in the soil solution – used in the assessment of salinity in soils)
Diagenesis	the process by which sediments derived from the weathering of rocks are converted into sedimentary rocks and may eventually undergo weathering and form the parent material of sandy soils (Arenosols etc)
DTPA	diethyl triamine penta-acetic acid, soil test reagent
Durum wheat	used for making pastas and semolina, not good for baking (unlike bread wheat)
EDTA	ethylene diamine tetra-acetic acid, a chelating agent used for soil tests and for soluble micronutrient fertilisers
Enzyme	an organic compound (often containing a metal, such as zinc) which catalyses a specific reaction within a cell
FAO	Food and Agriculture Organisation of the United Nations
FAO-UNESCO	sponsors of the soil map of the world (and soil classification) 1974
Fe	iron
Ferralsols	deep red-yellow soils of the humid tropics which have undergone severe weathering, are strongly acid and normally have low total contents of most micronutrients (called Oxisols in the USDA Soil Taxonomy classification).
Ferromagnesian minerals	rock-forming minerals containing relatively high concentrations of iron and magnesium (e.g. augite, olivine)
Fertigation	supplying fertiliser nutrients in irrigation water
Galvanised	steel coated with a corrosion-resistant layer of zinc
GCRPS	ground cover rice production system (alternative to continuously flooded paddy rice) genotypes plants with different genetic makeup (e.g. species and cultivars)
Gleysols	soils which are either permanently or intermittently wet with reducing conditions at shallow depth
GM	genetically modified (i.e., crop cultivar)
Gypsiferous soils	soils in semi-arid/arid regions with a high content of gypsum often forming a gypsic horizon
Gypsum	calcium sulphate (CaSO ₄) which has a neutral reaction, unlike calcium carbonate which is alkaline.
ha	hectare: unit of land area (10,000 m ² , 2.47 acres)
HarvestPlus	a Global Challenge Program of the Consultative Group on International Agricultural Research (CGIAR) dedicated to reducing micronutrient malnutrition through the biofortification of staple food crops.

HC ₅₀	hazardous concentration for 50% of species
Hydrozincite	zinc hydroxycarbonate (Zn ₅ (OH) ₆ (CO ₃) ₂) (solid)
ICP-AES	inductively-coupled plasma atomic emission spectrometry (analytical technique for trace element ions in solution)
Igneous rocks	rocks which have crystallized from molten magma (e.g. basalts, granites)
ILZRO	International Lead Zinc Research Organisation
Interveinal	between the leaf veins (e.g. interveinal chlorosis symptoms)
IPNI	International Plant Nutrition Institute
IRRI	International Rice Research Institute
K	potassium
kg ha ⁻¹	kilogrammes per hectare (application rates for zinc fertilisers)
Latent deficiency	deficiency of an essential nutrient (e.g. zinc) in plants without the appearance of obvious symptoms (also called sub-clinical or hidden deficiency)
Ligand	organic group which, combined with a metal ion, forms a complex molecule
LOEC	lowest observed effect concentration (toxicology)
Loess	wind-blown (aeolian) silt particles (can form soil parent material)
MAP	monoammounium phosphate (high analysis phosphatic fertiliser, 11% N, 21% P) usually with very low contents of metal impurities
Metalloproteins	proteins containing metal ions in their structure (includes metallo-enzymes)
Mg	magnesium
mg kg ⁻¹	milligrammes per kilogramme (equivalent to ppm or µg g ⁻¹)
Micronutrient	element required in small but critical concentrations for normal healthy growth of plants and/or animals (e.g. zinc) also called 'essential trace element'
Mn	manganese
N	nitrogen
Necrosis	abnormal death of part of leaf or other plant tissue (necrotic spots)
NH ₄ Ac	ammonium acetate, soil test reagent
Nitisols	deep, red, clay-rich soils, formed on base-rich parent materials; not so severely weathered and leached as Ferralsols and are some of the most fertile tropical soils (FAO-UNESCO Soil Classification).
NKP fertilisers	nitrogen, phosphorus and potassium (macronutrients) fertilisers
O	oxygen
Okra	vegetable
OsZIP	<i>Oryza sativa</i> zinc-iron regulated-protein-a transporter protein involved in the Translocation of zinc from the root to the developing grain
Oxisols	deep red soils of humid tropical regions (USDA Soil Classification-see Ferralsols FAO-UNESCO)
P	phosphorus
Paddy	the flooded field in which lowland rice is grown (c.f. upland rice)
Pb	lead
PEC	predicted environmental concentration-background concentration
pH	measure of acidity or alkalinity of a solution (scale 0-14, 0-7 is acid, 7 is neutral, and 7-14 is alkaline)
Phytate	phosphorus-containing compound (inositol hexaphosphate) found in cereals which can bind zinc and reduce its availability to monogastric animals, such as humans
Phytosiderophore	substance secreted from the roots of certain plant species which mobilizes iron and other cations from soil in the vicinity of the root

PNEC	predicted no effect concentration (toxicology)
Poaceae	the gramineae family (grasses and cereals – the most important plant family with regard to human nutrition)
Proteoid roots	clusters of dense root branchlets (5-10 mm long) supporting a high density of root hairs which significantly increases the root absorbing area
PZC	pH at which a variable charge soil constituent (e.g. iron oxide) is neutral (neither positively nor negatively charged)
Rhizosphere	thin layer (approx 2 mm thick) around plant roots which is a zone of intense microbial activity due to root secretions etc
S	sulphur
Sedimentary rocks	rocks which have formed from sediments which are the products of weathering of pre-existing rocks (e.g. sandstones, mudstones, limestones, clays)
SOD	superoxide dismutase (enzyme)
Soil Taxonomy	USDA soil classification system
Solonchak	soils with high concentrations of salts at some time of the year in the topsoil (salts are mainly sodium chloride and sodium sulphate)
Solonetz	salt-affected soils developed under the influence of salts such as sodium bicarbonate, sodium carbonate, sodium silicate and magnesium carbonate
Sub-clinical deficiency	deficiency of an essential nutrient (e.g. zinc) in plant or animal without the appearance of obvious symptoms
Superphosphate (ordinary)	phosphatic fertiliser (7-9% P) usually with significant concentrations of metal impurities (e.g. zinc)
Tarai soils	shallow water table soils found in the foothills of mountain ranges (term used in India and adjacent countries)
t ha ⁻¹	tonnes per hectare (equivalent to 1.1 tons per acre)
Trace element	elements which occur in relatively low concentrations in plant and animal tissues (<100 mg kg ⁻¹) and in rocks all trace elements together comprise <1% of total elemental composition
Triple - superphosphate	phosphatic fertiliser (18-22% P) with lower contents of metal impurities than ordinary superphosphate
USDA	United States Department of Agriculture
UNESCO	United Nations Educational, Social and Cultural Organisation
VAM	vesicular arbuscular mycorrhizae (fungi which colonise the root and assist in the absorption of soil ions from the soil solution)
Vertisols	deep clayey soils (>30% clay) dominated by clay minerals that expand on wetting and shrink on drying, forming cracks to at least 50 cm when dry. Topsoil falls down these cracks and, in time, the soil profile becomes inverted
YEB	youngest emerged leaf blade, for plant tissue analysis
YFEL	youngest fully emerged leaf (used in plant analysis)
YOB	youngest open blade, for plant tissue analysis
yr ⁻¹	per year
Zinc efficiency	the extent to which a plant cultivar is able to grow and develop in soils with low available supply capacities for zinc
Zn	zinc
ZnO	zinc oxide
ZnSO ₄	zinc sulphate

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In addition to a large number of scientific papers, he has edited two books: "Micronutrient Deficiencies in Global Crop Production" (2008; Springer) and "Heavy Metals in Soils" (1990, 1995; Blackie Academic and Professional). He was also a member of the editorial board of "Essentials of Medical Geology" (Editor-in-Chief O. Selinus; 2005; Elsevier) and is co-author, with D.C. Ayres, of the textbook "Chemical Principles of Environmental Pollution" (1993, 1997; Blackie Academic and Professional).

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EXECUTIVE SUMMARY

Zinc is essential for the normal healthy growth and reproduction of plants, animals and humans and when the supply of plant-available zinc is inadequate, crop yields are reduced and the quality of crop products is frequently impaired.

In plants, zinc plays a key role as a structural constituent or regulatory co-factor of a wide range of different enzymes and proteins in many important biochemical pathways and these are mainly concerned with:

- ❖ carbohydrate metabolism, both in photosynthesis and in the conversion of sugars to starch,
- ❖ protein metabolism,
- ❖ auxin (growth regulator) metabolism,
- ❖ pollen formation,
- ❖ the maintenance of the integrity of biological membranes,
- ❖ the resistance to infection by certain pathogens.

When the supply of zinc to the plant is inadequate, one or more of the many important physiological functions of zinc is unable to operate normally and plant growth is adversely affected. The changes in plant physiological mechanisms brought about by a deficiency of zinc can result in the plant developing visible symptoms of stress which might include one or more of the following: stunting (reduced height), interveinal chlorosis (yellowing of the leaves between the veins), bronzing of chlorotic leaves, small and abnormally shaped leaves and/or stunting and rosetting of leaves (where the leaves form a whorl on shortened stems). These different types of symptoms vary with plant species and are usually only clearly displayed in severely deficient plants. In cases of marginal deficiency, plant yields can often be reduced by 20% or more without obvious visible symptoms. This is called 'hidden', 'latent' or 'subclinical' deficiency. Zinc-deficient soils causing hidden deficiency may remain undetected for many years unless soil or plant diagnostic tests are carried out, because there are no

obvious signs of stress in the crops growing on them. However, a change to growing less zinc deficiency-tolerant crop species or cultivars, or the adoption of more intensive farming methods may lead to the development of a more severe deficiency in the crop accompanied by visible symptoms which will bring the problem to the notice of the farmer.

Losses of yield of 20% or more as a result of hidden zinc deficiency can have an economic impact on the farmer. In more intensive types of arable farming where expensive inputs of seed, fertilisers, agricultural chemicals and possibly irrigation water are involved, the failure of crops to realize their potential yield is a major loss of income to the farmer. In developing countries, the cost to the nation from significant shortfalls in food production is also considerable because increased imports of grain will often be required to make up this shortfall.

With the world population continuing to expand and the problems of producing extra food to provide an adequate standard of nutrition for this growing population, it is very important that any losses in production from a cause so easily corrected as zinc deficiency are prevented. This necessitates identifying the main areas of zinc-deficient soils and crops and treating them with zinc fertilisers to correct the shortage in the supply of zinc to the crops, or growing more zinc-efficient crops which can tolerate lower available concentrations of zinc.

Zinc deficient soils can be identified by soil testing, or the analysis of the crop plants (usually leaves) growing on them. The results obtained from soil and/or plant analysis can be compared against the lower critical values for zinc in local soil types for specific crops and a decision made on whether or not zinc fertiliser applications to the soil or crops are required. Unless the plants are very young, or it is a perennial crop, plant analysis tends to be mainly of value for the following crop because it is often difficult to rectify a

deficiency in a growing annual crop to prevent a loss of yield. However, foliar applications of zinc fertilisers can be made to salvage as much yield as possible.

Many plant species are affected by zinc deficiency on a wide range of soil types in most agricultural regions of the world. The major staple cereal crops: rice, wheat and maize are all affected by zinc deficiency, together with many different fruit, vegetable and other types of crops including cotton and flax. Maize is the crop species which is most susceptible to zinc deficiency and, in many countries, it receives the highest proportion of zinc fertiliser applications. Rice is also highly susceptible to zinc deficiency, especially that grown in lowland (paddy) production systems, because the chemical conditions in the waterlogged soils are conducive to zinc deficiency. After nitrogen, phosphorus and potassium are equal second and zinc and sulphur are equal third in importance in the nutrition of rice. As a result of the increasing scarcity of water for irrigation in Asia and other regions, alternative systems of rice cultivation are being developed which will significantly reduce the water requirement. From the experience in some areas with calcareous and alkaline soils, it appears that rice crops in these new systems will often require more zinc fertilisation than traditional paddy crops. If these new cultivation systems are widely adopted, much larger amounts of zinc fertilisers are likely to be required for rice cultivation.

Although wheat is more tolerant of zinc deficiency than either maize or rice, zinc deficiency problems do occur in large areas of wheat-growing soils especially in West Asian countries with a Mediterranean-type climate, such as Turkey. The calcareous soils in these countries have very low concentrations of plant-available zinc and cause widespread zinc deficiency in this crop. These deficiencies only occurred when new high-yielding varieties of wheat were introduced. These varieties were less tolerant of the low available-zinc status than the indigenous ('landrace') varieties which were well adapted to local conditions, but did not give such high yields. Individual varieties of most crop species vary widely in their susceptibility to zinc deficiency.

An alternative approach to the problem of treating zinc deficiency is to select and/or breed crops which are 'zinc-efficient' and able to tolerate low available concentrations of zinc in the soil. This approach is one of matching the plant to the soil, rather than modifying the soil to suit the plant. There are zinc-efficient cultivars of rice and wheat which are grown quite widely in areas of soils with a low zinc status. However, continued cropping of soils with marginal levels of available zinc with zinc-efficient crops will deplete the zinc supply to levels below which even these tolerant varieties can cope with and zinc fertilisers will eventually be needed to replenish the zinc taken off in the crops.

The soil conditions which most commonly give rise to deficiencies of zinc in crops can include one or more of the following:

- ❖ low total zinc concentrations (such as sandy soils),
- ❖ low pH, highly weathered parent materials with low total zinc contents (e.g. tropical soils),
- ❖ high calcium carbonate content (calcareous soils),
- ❖ neutral or alkaline pH (as in heavily limed soils or calcareous soils),
- ❖ high salt concentrations (saline soils),
- ❖ peat and muck (organic soils),
- ❖ high phosphate status,
- ❖ prolonged waterlogging or flooding (paddy rice soils),
- ❖ high magnesium and/or bicarbonate concentrations in soils or irrigation water.

Soils with one or more of these properties can be found in many areas of the world. Countries with particularly widespread zinc deficiency problems include: Afghanistan, Australia, Bangladesh, Brazil, China, India, Iran, Iraq, Pakistan, Philippines, Sudan, Syria, Turkey, many states in the USA and parts of Africa and Europe.

Once identified, zinc-deficient soils can be easily treated with zinc fertilisers to provide an adequate supply of zinc to crops. Several different zinc compounds are utilised as fertilisers but zinc sulphate is by far the most widely used. Zinc sulphate is most frequently broadcast (or sprayed as a solution) evenly

over the seedbed and incorporated into the topsoil by cultivation before sowing the seed. One application of between 20-30 kg ha⁻¹ of zinc sulphate will often have an improving effect on the zinc status of the soil which will last for around five years before another application is required. However, this will vary in different areas; in some of the most deficient soils, such as those with a high content of calcium carbonate, zinc fertiliser applications may have to be larger and more frequent.

Placement of the zinc fertiliser below and to one side of the seed at sowing is also frequently used in more intensive crop production systems. In this case, lower application rates are used because of the close proximity of the fertiliser band to the developing roots. Foliar sprays of zinc sulphate, zinc nitrate or chelated forms of zinc are mainly used on fruit trees and plantation crops, but they can also be used to salvage annual field crops and reduce yield loss.

In all cases of treating zinc-deficient soils, regular soil or plant testing is recommended to determine when additional applications of zinc fertilisers are required and to ensure that zinc does not accumulate in the soil to undesirably high levels.

An adequate supply of zinc is essential for obtaining cost effective yields of crops all over the world. The cost to the farmer of lost production is high but the expense of applying zinc fertiliser when crop symptoms, soil tests or plant analysis show that they are required is relatively low. No farmer in areas where soils have been shown to be deficient can afford not to maintain an adequate zinc status in his soils.

Around 30% of the world's human population has diets deficient in zinc. Zinc deficiency in humans affects physical growth, the functioning of the immune system, reproductive health and neurobehavioural development. Therefore the zinc content of staple foods, such as rice and wheat, is of major importance. There is a rapidly developing field of research on the biofortification of plant foods with zinc. This involves both the breeding of new varieties of crops with the genetic potential to accumulate a high density of zinc

in cereal grains (genetic biofortification) and the use of zinc fertilisers to increase zinc density (agronomic biofortification). Although the plant breeding route is likely to be the most cost-efficient approach in the long run, for the time being, the use of fertilisers is necessary to improve the zinc density in diets while the plant breeding programmes are being carried out. Hence, in addition to ensuring that crop yields are not restricted by deficiency, zinc fertilisers will also be used, where necessary, to increase the zinc density of staple foods. However, it will be necessary to monitor both the zinc concentrations in the cereal grains and also the soil to ensure that the enrichment of the grains occurs without the accumulation of zinc in soils to possibly harmful levels.

INTRODUCTION



Zinc is a trace element found in varying concentrations in all soils, plants and animals and it is essential for the normal healthy growth of higher plants, animals and humans. Zinc is needed in small but critical concentrations and if the amount available is not adequate, plants and/or animals will suffer from physiological stress brought about by the dysfunction of several enzyme systems and other metabolic functions in which zinc plays a part.

The essentiality of zinc for plants was only scientifically established about 70 years ago and in some parts of the world the existence of deficiencies has only been recognised during the last 20 or 30 years. The relatively recent discovery of widespread zinc deficiency problems in rice and wheat is linked to the intensification of farming in many developing countries. This has involved a change from traditional agriculture, with locally-adapted crop genotypes and low inputs of nutrients, to growing modern, high-yielding plant varieties with relatively large amounts of macronutrient fertilisers and agrochemicals. Many of the new crop varieties are much more susceptible to zinc deficiency than the traditional crops and the increased use of macronutrient fertilisers, especially phosphorus, can render a deficiency of zinc more likely. A whole new type of farming, involving the sequential cropping of rice and wheat on the same land in South and East Asia has been made possible by new crop varieties and agronomic expertise.

In developing and more advanced countries including: Bangladesh, China, India, Pakistan and the Philippines, the need to maximize food production is very great and

so increased productivity of the land is essential. Therefore, any factors, such as zinc deficiency, which can prevent crops from attaining their potential yield need to be addressed. In addition to food staples, such as rice and wheat, the productivity of many other crops can be significantly reduced by zinc deficiency. These crops include: tea, coffee and cocoa, fruit trees, grapes and many vegetables. Fibre crops such as cotton and flax are also widely affected. Fortunately, the causes and occurrence of zinc deficiency in many crops growing on diverse types of soil in most agricultural regions of the world are reasonably well understood. The tools are available to diagnose crop problems revealed by visible symptoms and to identify soils of marginal or deficient zinc supply capacity. Therefore, the problem of widespread zinc deficiencies can be solved if farmers and agronomists are made aware of the condition and how to treat it.

However, zinc deficiency is not just a problem in developing countries, it occurs in most of the states in the USA, in Australia, in parts of Europe and many other technologically advanced countries. The main difference between the situation in these countries and in the developing countries is the existence of an extension agronomy service and rapid access to analytical facilities to minimize time loss before unsuspected conditions can be diagnosed and treated, thus helping to reduce yield losses.

Apart from large areas of certain types of soils recognised as being prone to zinc deficiency, such as sandy, calcareous, saline and wetland rice soils and highly

weathered and leached tropical soils, smaller patches of land with some of these types of soils can be affected in almost any country. The problem of zinc deficiency is therefore a global one and, of all the trace elements essential for plants (zinc, copper, boron, manganese, iron, chlorine, molybdenum, and nickel), zinc deficiency is the most commonly encountered and widespread deficiency problem of all.

This book deals with the more fundamental aspects of the soil-plant relationships of zinc, from the origins and forms of zinc in soils and the factors controlling its availability, to the physiological functions of the metal and the effects which an inadequate supply can have on plants. Zinc concentrations in staple foods are discussed in relation to the problem of zinc deficiency in humans and of ways in which the zinc density of cereal grains might be increased through biofortification. The book then proceeds to cover the types of visible symptoms of deficiency which may be observed in different species of crop plants and discusses their use as a means of diagnosing deficiencies. Soil testing and plant analysis are then reviewed along with the lower critical concentrations of zinc in soil test extractions and plant tissue samples which are used in their interpretation. Having dealt with the soil chemical and plant physiological aspects of zinc deficiencies and the various means available to identify deficient soils and crops, the report then goes on to cover the types of zinc compounds which are used as fertilisers and the application rates commonly used for different crops in many parts of the world.

The countries and/or regions of the world which are reported in the literature to be affected by zinc deficiency in crops are dealt with (using the IFA Regions and Countries Statistical Classification) to put the problem into a geographical and agronomic context. This chapter is then followed by a more detailed discussion of the importance of zinc deficiency in maize, rice and wheat, the world's three most important cereal crops. Large areas, amounting to millions of hectares of these crops, are affected by zinc deficiency causing lost yield and low zinc concentrations in foodstuffs, which is both an economic and human health problem. This consideration of maize, rice and wheat complements earlier sections on soil types prone to deficiency and the countries and regions affected by the problem and serves as a case study to illustrate just how important the zinc status of soils is in the agronomy of world crop production. The book is rounded-off by a discussion and conclusions chapter, some suggestions for further research and a checklist for zinc deficiency in crops.



FUNDAMENTAL ASPECTS OF ZINC IN SOILS AND PLANTS

2.1 Origin and Behaviour of Zinc in Soils

2.1.1 Introduction

Zinc is one of the eight trace elements which are essential for the normal healthy growth and reproduction of crop plants; the other elements are: boron, chlorine, copper, iron, manganese, molybdenum, and nickel. These elements are referred to as 'essential trace elements' or micronutrients, because they are only required in relatively small concentrations in the plant tissues (5-100 mg kg⁻¹). Some of these elements, namely: copper, iron, manganese and zinc, with, in addition, cobalt, chromium, iodine, and selenium, are also essential for animals. Apart from the eight trace elements, nine major elements (present in much higher concentrations, >0.1%) are also essential for plants and these are: carbon, hydrogen, oxygen, nitrogen, potassium, calcium, magnesium, phosphorus and sulphur.

All soils contain measurable concentrations of the essential trace elements, as well as other trace elements which are not essential for plants and/or animals (non-essential elements), but the concentrations can vary considerably; in some cases they can be very low. Trace elements in soils are derived from the geochemical weathering of the rock fragments on which the soil has formed (the soil parent material), together with inputs from atmospheric deposition (as dust and aerosol-sized particles in dry deposition or rainfall) and inputs from agricultural activities such as livestock manures, fertilisers and agrichemical sprays. Soils on river floodplains will also have received trace elements from floodwaters and sediments. All of these sources and inputs can vary greatly in magnitude and result in soils having a wide range of total trace element concentrations. The extent to which the total concentration of a trace element, such as zinc, in a soil is available for uptake by plants or movement down the soil profile depends on a range of soil properties.

2.1.2 Total Zinc Concentrations in Soils

The range of total zinc concentrations in soils reported in the literature tends to show an overall mean total concentration of around 55 mg Zn kg⁻¹. Kiekens ⁽¹⁾ reported a typical range of zinc in soils of 10-300 mg kg⁻¹ with a mean of 50 mg Zn kg⁻¹.

In Australia, which has very old soils developed on heavily weathered rocks, the range of total zinc concentrations is < 2-180 with a mean zinc concentration of 34 mg kg⁻¹ ⁽²⁾. More recently, Bertrand *et al.* ⁽³⁾ identified a range of total zinc concentrations of 4-41 mg kg⁻¹ in alkaline, non-calcareous (< 2% CaCO₃) arable soils in South Australia and Victoria, and 5-36 mg kg⁻¹ in calcareous soils (>2% CaCO₃) in the same regions.

In the USA, Holmgren *et al.* ⁽⁴⁾ reported a mean zinc concentration of 56.5 mg kg⁻¹ for 3045 soils from "uncontaminated" agricultural sites. The median (50 percentile) concentration was 53.0 mg kg⁻¹. Angelone and Bin ⁽⁵⁾ reported an overall mean zinc concentration of 68 mg Zn kg⁻¹ for soils in most European countries.

A survey of soils in England and Wales, involving 5692 sample sites on a 5 km grid, showed a mean zinc content of 97 mg kg⁻¹ (median 82 mg kg⁻¹) but this included soils contaminated from various sources such as metalliferous mining and heavy applications of sewage sludge (full range 5-3548 mg Zn kg⁻¹) ⁽⁶⁾. When divided into textural classes, the following median zinc concentrations were found: sandy soils 35 mg kg⁻¹, coarse loamy soils 65 mg kg⁻¹, fine silty soils 90 mg kg⁻¹, and clayey soils 106 mg kg⁻¹.

In France, Baize ⁽⁷⁾ reported the median zinc contents of soils of different textural classes: sandy soils 17 mg kg⁻¹, silty soils (< 20% clay) 40 mg kg⁻¹, loams (20-30% clay) 63.5 mg kg⁻¹, clayey soils (30-50% clay) 98 mg kg⁻¹, and very clayey soils (> 50% clay) 132 mg kg⁻¹.

For Poland, Kabata-Pendias *et al.* ⁽⁸⁾ reported the following means and ranges for soils of different textural classes:

sandy soils 37 mg kg⁻¹ (3-762), loess soils 60 mg kg⁻¹ (28-116) and loams 75 mg kg⁻¹ (37-725).

For German soils, Gorny *et al.* (9) reported the following median zinc concentrations: sandy soils 27.3 mg kg⁻¹, loam/silt soils 59.2 mg kg⁻¹, and clay soils 76.4 mg kg⁻¹.

These examples show a clear trend of low concentrations in sandy soils and higher zinc concentrations in soils with larger clay contents. This is a consequence of both the higher zinc concentrations in clay and shale parent materials and also the greater ability of clay-rich soils to adsorb and retain zinc and other elements relative to soils with lower percentages of clay and higher percentages of sand. Sandy soils all over the world are often found to have low, or deficient, zinc concentrations for crops. It is important to stress that in many parts of the world, soils tend to be very heterogeneous in their

distribution, especially in areas affected by glacial and periglacial processes with a wide range of soils developed on drift deposits. Patches of sandy soil of low zinc and other nutrient element status can often be found amongst more clay-rich soils with adequate levels of available micronutrients.

The values given in Table 2.1 show similar mean values and ranges for zinc in the soils of these Asian countries as are found in European and north American soils. However, total contents do not provide a good indication of the concentrations available to plants except that soils with very low total concentrations are more likely to be deficient than those with higher concentrations.

Table 2.1

**Means and Ranges of Total Zinc Concentrations
in Soils from Tropical Asia**

from Katyal and Vlek (10)

Country	Soil Type/Climatic zone	Mean Zn (mg Zn kg ⁻¹)	Range of Zn
India	Arid/semi-arid	59	20-89
India	Humid/sub-humid tropics	52	22-74
India	Vertisols	-	69-76
India	Oxisols (coarse textured)	-	24-30
Philippines	Rice soils	-	63-135
Vietnam	Ferrallitic soils	102	40-485
Sri Lanka	Patana soils (wet with high organic matter)	75	35-102
Indonesia	Sulawesi and Sumatra	-	33-174
Thailand		45	5-158

2.1.3 Factors Controlling the Total Zinc Content of Soils

2.1.3.1. Composition of the Soil Parent Material

The total zinc content of a soil is largely dependent upon the geochemical composition of the weathering rock parent material on which the soil has developed. However, in some cases, environmental pollution or the agricultural application of zinc-rich materials can mask the parent material's contribution.

The average zinc content of rocks in the Earth's crust is 78 mg Zn kg⁻¹ and the average concentrations of zinc in the various types of rock which make up the Earth's crust are given in Table 2.2.

In Table 2.2, the higher concentrations of zinc shown for the basic igneous rocks, such as basalts are due to zinc occurring in ferromagnesian minerals including augite, hornblende and biotite, where it has been isomorphously substituted for Fe²⁺ or Mg²⁺ which are the principal components of the crystal lattice, along with silicon, aluminium and oxygen.

More silica-rich igneous rocks, such as granites and metamorphic rocks including gneiss, have much lower total zinc contents and their residual weathering product is usually quartz sand which gives rise to either sandy soils or sandy sediments which undergo diagenesis and form sandstone sedimentary rocks with low concentrations of zinc and other essential micronutrients.

In addition to the commonly occurring types of rocks in the Earth's Crust, high concentrations of zinc are found in relatively isolated locations in 'ore minerals' which are mined as economic sources of the metal. The most ubiquitous zinc ore mineral is sphalerite (ZnS); other less common predominantly zinc-containing minerals include: smithsonite (ZnCO₃), zincite (ZnO), zinkosite ZnSO₄, franklinite (ZnFe₂O₄) and hopeite (Zn₃(PO₄)₂ · 4H₂O). Generally, these ore mineral deposits are unlikely to have much influence on the zinc content of most agricultural soils apart from those in areas underlain by unexploited mineralisation, or soils on land in the vicinity of mines

Table 2.2

Average Concentrations of Zinc in the Major Types of Rock Which Make Up the Earth's Crust (mg Zn kg⁻¹, or ppm)

From Krauskopf⁽¹¹⁾ and Wedepohl⁽¹²⁾

Igneous Rocks

Ultramafic (e.g. dunite, peridotite and serpentinite)	58
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Basalt and Gabbro	100
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Diorite and Andesite	70
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Granite	48
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Sedimentary Rocks

Limestone	20
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Sandstone	30
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Clays and Shales	120
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Bituminous shales	200
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which have become contaminated from the mining and/or smelting operations.

Sedimentary rocks have been formed (by diagenesis) from the products of the weathering of igneous rocks. These have been transported, deposited by sedimentation and formed into new types of rocks. Sedimentary rocks form around 75% of the solid rocks at the earth's surface but these are, in turn, covered by drift deposits in many places. These drift deposits will have been largely derived from the weathering and transport of sedimentary rocks and examples include: boulder clays, fluvio-glacial sands and gravels, wind-blown silt/sand particles (loess), alluvium and slope deposits. In some parts of the world, certain drift deposits form the parent materials of the soils in large agriculturally important areas, such as the loess deposits in China and the alluvial soils of the Indo-Gangetic Plain and the Nile Valley. In humid tropical regions, many of the soils will have been very heavily weathered so that all of the primary minerals from igneous and sedimentary rocks, which contained zinc and other

essential nutrient elements, will have been chemically decomposed, leaving acid soils with very low concentrations of both major or trace plant nutrient elements. These acid, highly weathered soils are often found to be deficient in zinc and other micronutrients and occur in large areas in South America and parts of Africa.

From the values given in Table 2.2, it can be seen that soils formed on limestones and sandstones or on drift containing large proportions of these rock materials, will tend to have lower total zinc concentrations than soils developed on clays and shales or mafic igneous rocks. It is also found that many zinc deficiency problems around the world are associated with sandy soils (Arenosols) and calcium carbonate-rich soils (Calcisols). (See Section 2.2)

2.1.3.2 Inputs from Atmospheric Deposition

Apart from small wind-blown particles of soil and rock and sea spray, soils receive significant inputs of zinc and other elements (and organic pollutants) from the atmosphere. Emissions to the atmosphere from the burning of coal and oil (e.g. electricity generation), waste incineration, industrial processes (including non-ferrous metal smelting) and general urban/industrial emissions can result in variable amounts of zinc reaching soils. This mainly affects agricultural land in, or near to, areas of industrial activity and high urban populations. Long-range transboundary transportation of atmospheric pollutants can, however, result in aerosol-sized particles containing zinc, other elements and acidic compounds, such as sulphates, being carried by winds for possibly hundreds or thousands of kilometres. Examples include contamination of soils in southern Norway from sources, such as electricity generating stations, in the UK and other parts of Northern Europe, deposition in Canada from sources in the North Eastern USA and deposition of soil particles in Northern Canada from sources in China.

Recent values given for the deposition of zinc in 10 European countries give an average deposition of $217 \text{ g ha}^{-1} \text{ yr}^{-1}$ ⁽¹³⁾. This value is based on the average values for each of the 10 countries which have zinc deposition ranging from low values of $20 \text{ g ha}^{-1} \text{ yr}^{-1}$ in Finland and $68 \text{ g ha}^{-1} \text{ yr}^{-1}$ in Norway to high values of

$540 \text{ g ha}^{-1} \text{ yr}^{-1}$ in both Germany and Poland. The mean deposition of zinc onto agricultural land in England and Wales, based on 42 months of monitoring at 34 sites, was $221 \text{ g ha}^{-1} \text{ yr}^{-1}$ ⁽¹³⁾. Zinc showed the highest amount of deposition of any of the trace elements monitored (arsenic, cadmium, chromium, copper, mercury, nickel, lead and zinc)⁽¹³⁾. For the 10 European countries considered, the second highest deposition was lead ($34 \text{ g ha}^{-1} \text{ yr}^{-1}$) and for England and Wales lead deposition was $54 \text{ g ha}^{-1} \text{ yr}^{-1}$. In New Zealand, Gray *et al.*⁽¹⁴⁾ reported an average deposition of zinc of $1025 \text{ g ha}^{-1} \text{ yr}^{-1}$ which is much higher than any other country and the reason for this was not obvious.

The levels of zinc deposition from the atmosphere in many technologically developed countries were probably higher in the past when there were larger amounts of pollution from heavy industry in many parts of the world. The introduction of strict emissions limits has also brought about a reduction in amounts of pollutants emitted to the atmosphere. However, the relatively small amounts of zinc deposited on the soil are unlikely to provide enough zinc to overcome deficiency problems in soils and will not have a very marked effect on total zinc concentrations in the top 15 cm of soil. If the deposition of zinc is very high, such as in locations near to emissions from heavy industries, such as foundries, it could affect the zinc status of both soils and crops and could possibly even cause toxicity problems in sensitive plants after several years.

2.1.3.3 Agricultural Inputs

2.1.3.3.1 Livestock Manures

Anywhere in the world where livestock are housed or kept in yards, the manure (faeces and urine plus, possibly, some bedding material such as straw) is usually used as a fertiliser (mainly nitrogen, phosphorus and potassium) and soil conditioner, except in some developing countries where it is dried and burnt for fuel. All manures contain zinc derived from the original animal diet (e.g. grass, hay, cereals etc), but additional amounts of zinc may have been intentionally added to livestock diets. In areas with intensive livestock production, zinc (together with copper) is often fed to the animals for health and welfare reasons, or as growth promoters. For example, zinc is used in the

diet of young pigs to control post-weaning diarrhoea problems, and is also fed to poultry for nutritional reasons (zinc is an enzyme co-factor).

In England and Wales, Nicholson *et al.* ⁽¹³⁾ have estimated that 2000 t of zinc is spread onto agricultural land from animal manures each year. Most comes from cattle manures because cattle form the largest livestock component (54 Mt of manure dry matter). Over the total agricultural area of England and Wales, livestock manures were responsible for around 40% of the total inputs of zinc. However, at individual sites, other richer sources of zinc, such as sewage sludge could have added greater amounts of zinc ⁽¹³⁾.

2.1.3.3.2 Fertilisers

Some compounds used as fertilisers can contain significant amounts of zinc. Superphosphate is the fertiliser which has been found to contain the highest concentrations of zinc (< 600 mg Zn kg⁻¹), but its use is declining due to its replacement by higher purity compounds such as monoammonium phosphate (MAP) and diammonium phosphate (DAP).

In England and Wales, fertilisers of all types were found to contribute a total input of 90 g ha⁻¹ yr⁻¹ and phosphatic fertilisers contributed about one third of this. In South Australia, during the 1980's and 1990's, the declining use of superphosphate with a significant zinc impurity was identified as a major reason for the widespread increase in zinc deficiency occurring in crops and pastures ⁽¹⁵⁾. In many areas around the world where zinc deficiency has been identified as a major problem, zinc fertilisers (such as zinc sulphate) will have been applied regularly and will have resulted in significant increases in the total and available zinc concentrations of the soils.

2.1.3.3.3 Sewage Sludge

Sewage sludges (also called 'biosolids') are widely recognised as being important sources of trace elements in soils. However, the concentrations of zinc and all other trace elements can vary widely between different sewage treatment plants, due to differences in the amounts of industrial and domestic discharges, and also differ over time at any individual sewage treatment plant.

Zinc concentrations in sewage sludges reported in the literature range from 91- 49000 mg kg⁻¹ ⁽¹⁶⁾. However, in more technologically advanced countries, there has been a trend for zinc concentrations in sewage sludges to decrease over the last two decades due to the imposition of stricter discharge limits and changes in the structure of industries. For example, the median zinc concentrations of sewage sludges used on agricultural land in the United Kingdom decreased from 643 mg Zn kg⁻¹ dry solids in 1982/83 to 454 mg Zn kg⁻¹ in 1990/91. This trend has continued over subsequent years. However, with applications of sewage sludge of around 8 t ha⁻¹ (dry solids) in alternate years, or less frequently (amount limited by maximum permissible nitrogen application of 250 kg N ha⁻¹) the amount of zinc applied at a particular site can be significant, but it would take many years for the total concentrations to reach the statutory limits in many countries (See Section 2.5). The amount of land receiving sewage sludge in any country as a percentage of the total area of agricultural land is likely to be relatively small (<1% in the UK).

Sewage sludges provide beneficial inputs of macro-nutrients (especially nitrogen and phosphorus) and micronutrients. In some developing countries, sewage and waste waters from metal-based industries are used for crop irrigation and there is sometimes a risk that excess levels of metals may accumulate in the soils and crops.

2.1.3.3.4 Industrial Waste Products

Various industrial waste products are sometimes applied to soils both as potentially useful soil amendments and also as a means of disposal. These materials can include, food processing wastes, slaughterhouse wastes, sludges from paper manufacture and recycling and metallurgical materials such as foundry sands and steelworks slags. It is difficult to generalize about the contribution of these sources to zinc inputs to soils. They are likely to make a relatively low contribution to zinc inputs overall, but may be important at individual sites. In addition to potentially valuable inputs of micronutrients such as zinc, some waste materials may also contain significant amounts of non-essential trace elements, such as arsenic and cadmium, which need to be minimized in order to avoid possible crop toxicity or quality problems in the long-term.

Although not a waste product, run-off water from galvanized (zinc-plated) metal roofing and rainfall drips from barbed wire fencing can be a significant source of zinc for soil in the immediate vicinity in some parts of the world. However, this will only have a very localised effect, but should be borne in mind when fields are being sampled for soil testing, because it could result in misleadingly elevated zinc concentrations in some areas.

2.1.3.3.5 Agrochemicals

Apart from fertilisers and manures, several other materials applied to either crops or soils on a regular basis can contain significant amounts of zinc. Perhaps the most important of these are the zinc-containing fungicides. Disinfectant footbaths containing zinc sulphate solution are used on dairy farms in some countries and can cause significantly elevated concentrations of zinc in fields near the footbaths.

Perhaps the most significant use of zinc as an agricultural pharmaceutical is in the control of facial eczema in both cattle and sheep in New Zealand. This condition is caused by a toxin secreted by a fungal pathogen *Pithomyces chartarum*, which grows on dead pasture plant species in warm moist conditions. Zinc oxide is used and is either administered directly to the livestock (and subsequently excreted on to pastures) or sprayed on to the pasture herbage. It has been estimated that sheep and cattle production in the Waikato District of North Island, New Zealand can load up to $6.72 \text{ kg Zn ha}^{-1}\text{yr}^{-1}$ to the soils (17).

2.1.4 Forms of Zinc in Soils

The total amount of zinc in soils is distributed over 5 fractions (or pools). These comprise:

- i) The water soluble pool: present in the soil solution,
- ii) Exchangeable pool: ions bound to soil particles by electrical charges,
- iii) Organically bound pool: ions adsorbed, chelated or complexed with organic ligands,

- iv) Pool of zinc sorbed non-exchangeably onto clay minerals and insoluble metallic oxides,
- v) Pool of weathering primary minerals.

It is only the zinc in the soluble fractions and those from which ions can be easily desorbed which is available to plants and which is also potentially leachable in water percolating down through the soil profile.

Zinc in soils occurs in the following forms (1):

- i) Free ions (Zn^{2+} and ZnOH^+) and organically complexed zinc in solution,
- ii) Adsorbed and exchangeable zinc held on surfaces of the colloidal fraction in the soil, comprising: clay particles, humic compounds and iron and aluminium hydrated oxides,
- iii) Secondary minerals and insoluble complexes in the solid phase of the soil.

The distribution of zinc between these forms is governed by the equilibrium constants of the corresponding reactions in which zinc is involved (1).

These reactions include:

- i) precipitation and dissolution,
- ii) complexation and decomplexation,
- iii) adsorption and desorption (1).

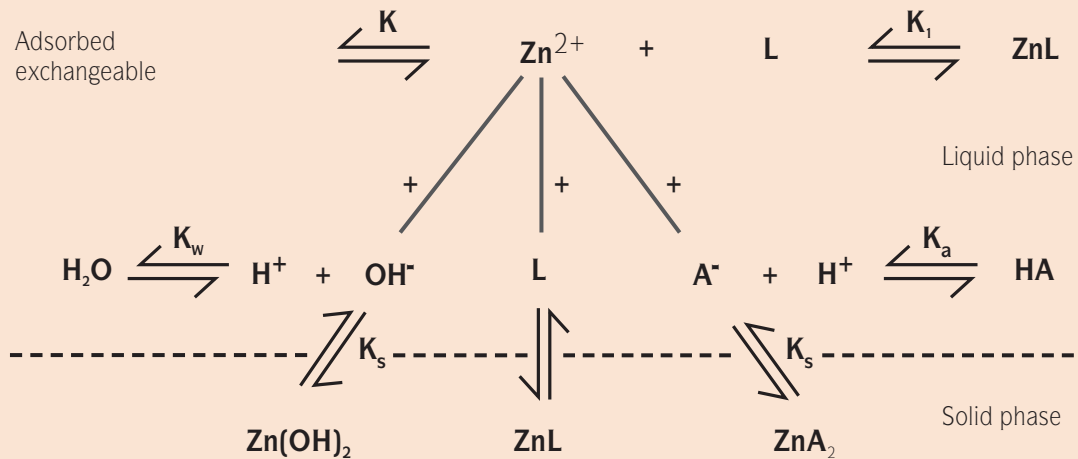
Figure 2.1 from Kiekens (1) illustrates the chemical equilibria between zinc and the main soil components, where A is an anion, L is an organic ligand and HA is humic acid.

The main parameters controlling the interactions of zinc are:

- i) the concentration of Zn^{2+} and other ions in the soil solution,
- ii) the type and amount of adsorption sites associated with the solid phase of the soil,
- iii) the concentration of all ligands capable of forming organo-zinc complexes,
- iv) pH and redox potential of the soil.

Figure 2.1

Chemical Equilibria between Zinc and Soil Components (from Kiekens ⁽¹⁾)



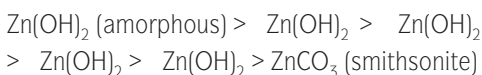
2.1.4.1 Zinc in the Soil Solution

A very small proportion of the total zinc content of a soil is present in the soil solution. Kabata-Pendias and Pendias⁽⁸⁾ reported, from values in the literature, that the concentration of soluble zinc in soils ranged from 4-270 $\mu\text{g L}^{-1}$ (ppb) which is very low compared with average total concentrations of around 50-80 mg kg^{-1} (ppm). However, in very acid soils, soluble concentrations of 7137 $\mu\text{g L}^{-1}$ have been found, indicating that solubility is strongly, but inversely linked to soil pH.

According to Kiekens ⁽¹⁾, the reaction $\text{Soil-Zn} + 2\text{H}^+ \rightleftharpoons \text{Zn}^{2+}$ $\log K^0 = 5.80$ can be expressed as $\log \text{Zn}^{2+} = 5.8 - 2\text{pH}$, or $\text{pZn} = 2\text{pH} - 5.8$.

This equation shows that the activity of Zn^{2+} in soils is directly proportional to the square of the proton activity. Therefore, the solubility of zinc will increase with decreasing values of soil pH.

The solubility of several zinc minerals decreases in the following order:



> ZnO (zincite) > $\text{Zn(PO}_4)_2 \cdot 4\text{H}_2\text{O}$ (willemite) > soil Zn
 > ZnFe_2O_4 (franklinite).

All of the Zn(OH)_2 minerals, ZnO and ZnCO_3 are about 10^5 times more soluble than soil zinc (adsorbed to solid surfaces) and would therefore make highly suitable fertiliser sources of zinc.

Soil pH governs the speciation of zinc in solution. At pH values below 7.7, Zn^{2+} predominates, but above pH 7.7, ZnOH^+ is the main species, and above pH 9.11 the neutral species Zn(OH)_2 is dominant. At pH 5 the activity of Zn^{2+} is 10^{-4} M (6.5 mg/L^{-1}) but at pH 8 it decreases to 10^{-10} M (0.007 $\mu\text{g/L}^{-1}$)⁽¹⁾.

Zinc forms soluble complexes with chloride, phosphate, nitrate and sulphate ions, but the neutral sulphate (ZnSO_4^0) and phosphate (ZnHPO_4^0) species are the most important and contribute to the total concentration of zinc in solution. The ZnSO_4^0 complex may increase the solubility of Zn^{2+} in soils and accounts for the increased availability of zinc when acidifying fertilisers, such as ammonium sulphate ($\text{NH}_4(\text{SO}_4)_2$) are used.

Low molecular weight organic acids also form soluble complexes with zinc and contribute to the total soluble concentration in a soil. The often observed improvement

in the available zinc status of some deficient soils after heavy applications of manure is probably the result of an increase in soluble, organically-complexed forms of zinc. Barrow (18) reported work which showed that organic ligands reduced the amounts of zinc adsorbed onto an oxisol soil and that the effect was most pronounced with those ligands, including humic acids, that complexed zinc most strongly. Soluble forms of organically-complexed zinc can result in zinc becoming increasingly mobile and plant available in soils. In many cases, complexation of organic zinc with organic ligands will result in decreased adsorption onto mineral surfaces (19).

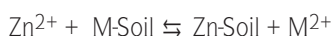
Kiekens and Cammerlynck (20) showed that zinc in soils was evenly distributed between organically-complexed forms and inorganic or Zn^{2+} in solution. Stevenson (21) showed the general order of preference for the formation of organic complexes in soils (both solid state and soluble forms) is: $Fe^{3+} > Cu^{2+} > Co^{2+} > Zn^{2+} > Fe^{2+} > Mn^{2+}$.

2.1.4.2 Adsorption of Zinc by Soil Constituents

Available space does not permit a comprehensive coverage of this important aspect of soil chemistry and readers seeking more details are referred to standard soil chemistry texts, such as those by Brady (22), White (23) and Sposito (24).

Adsorption mechanisms play a very important role in the soil-plant relationships of zinc. These mechanisms control the concentrations of zinc in the soil solution, and hence that which is immediately available to plant roots, and also the amounts of zinc in labile forms which can be desorbed and become available to plants.

Exchangeable adsorption of zinc (and any other) cations in soils can be expressed in its simplest form as:



where M is any other divalent cation. The mechanisms involved in the adsorption of ions on solid surfaces (of clay minerals, hydrous oxides of iron and manganese, and humic organic matter) include: cation exchange, specific adsorption, binding to organic matter, chemisorption and precipitation.

Cation exchange is the non-specific, reversible adsorption of positively charged ions on negatively charged sites on mineral and/or organic colloid surfaces. The negative charges on soil solids can be of two types; permanent, as in the case of clay minerals where the charges are due to isomorphous substitution in the crystal lattice and a charge imbalance, and variable (pH-dependent) charges, such as on hydrous oxides and organic matter. With variable charges, at low pH the surfaces have a positive charge, but above the point of zero charge (PZC) pH the sites are negatively charged. Hence, the cation exchange capacity of a soil usually shows an increase with pH due to more of the variable charge sites being negatively charged. When soils become acidified there is a reduction in the cation exchange capacity (due to fewer negatively charged sites) and more cations are present in the soil solution.

There is an order of preference or selectivity for the cations that are attracted to negatively charged solid surfaces and this can vary for the different types of adsorbents (clay minerals, hydrous oxides, and humic substances). An example of the order of preference on the iron oxide goethite is: $Cu > Pb > Zn > Co > Cd$; for peat the order is: $Pb > Cu > Cd = Zn > Ca$, and for the clay mineral illite, the order is: $Pb > Cu > Zn > Ca > Cd > Mg$ (16). These examples indicate that zinc tends to be less preferentially adsorbed than copper and lead. Cations adsorbed by cation exchange are held in the soil against leaching but can be readily replaced to become available for uptake by plant roots.

There is some evidence to show that phosphate ions can increase the retention of zinc ions on hydrous oxide surfaces. This could be due to the phosphate reducing the point of zero charge (PZC) and therefore increasing its negative charge, which results in more zinc cations being adsorbed, or to the phosphate providing more negatively charged sites or complexation sites (19).

Kiekens (25) stated that there appeared to be two different mechanisms involved in the adsorption of zinc by clays and organic matter. One mechanism operates mainly in acid conditions and is closely related to cation exchange, and the other mechanism operates in alkaline conditions and mainly involves chemisorption and complexation by organic ligands.

Apart from reversible adsorption by cation exchange, zinc can also be sorbed irreversibly by lattice penetration in clay minerals. The latter mechanism fixes amounts of zinc in excess of the cation exchange capacity and may be due to sorption of zinc in a hydrolysed form and precipitation of $\text{Zn}(\text{OH})_2$. This 'fixation' of zinc tends to increase over time and can affect the long-term availability of zinc fertilisers.

The formation of carbonates can occur as part of chemisorption. Papadopoulos and Rowell (26) found that chemisorption of zinc on calcium carbonate formed a solid-solution of $\text{Zn}_x\text{Ca}_{1-x}\text{CO}_3$. However, the continuity from surface adsorption to precipitation was broken by the precipitation of zinc hydroxycarbonate (or 'hydrozincite') ($\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$ (solid)) which has a higher stability than zinc carbonate (ZnCO_3). However, the calcium carbonate appeared to constrain the adsorbed zinc to conform to a carbonate structure despite its lower stability than the hydroxycarbonate.

Kiekens (25) also studied the adsorption of zinc on a calcareous soil and found that the reaction was not reversible due to some of the zinc being irreversibly fixed by the soil. These findings on the fixation/sorption of zinc on calcium carbonate have some important implications for the behaviour of zinc in calcareous soils. Some of the worst zinc deficiency problems in crops occur on calcareous soils in arid and semi-arid regions of the world (See Section 2.2).

Uygun and Rimmer (27) have pointed out that calcareous soils tend to have pH values of 8 or above and that under these pH conditions, iron oxides readily precipitate out and form coatings on the carbonate minerals. They showed that an increase in pH from 8 to 8.3 can double the strength of bonding of zinc to calcite but with 0.05% of iron oxide on the calcite the bonding increases 7-fold between pH 8 and 8.3. They found that with a coating of iron oxide on the calcite, the sorption of zinc was greater than it is with pure calcite and the extent to which zinc is immobilized is greater and it is less readily desorbed than it is from pure calcite. Therefore, the occurrence in calcareous soils in semi-arid and arid regions of calcite with thin coatings of iron oxide results in zinc being even less available to plants than with pure calcite, and a higher risk of zinc deficiency in crops.

Zinc is co-precipitated with both iron and manganese oxides and franklinite (ZnFe_2O_4), which contains both Fe^{3+} and Fe^{2+} , could be the mineral form which partly controls the activity of zinc in soils in addition to the other adsorption mechanisms mentioned in this section (28).

Lindsay (26) showed that there are no phosphate compounds of zinc which are sufficiently insoluble to account for the observed correlation of zinc deficiency problems in crops which have received heavy applications of phosphatic fertilisers through the formation of an insoluble zinc phosphate mineral. In fact, the zinc phosphate mineral which would be most likely formed ($\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$) is sufficiently soluble to be useful as a combined zinc and phosphorus fertiliser.

2.1.4.3 Secondary Minerals

As stated above, franklinite (ZnFe_2O_4) is probably the main zinc-containing secondary mineral which at least partly controls the availability of zinc in soils, apart from adsorption/desorption mechanisms (28). The occurrence of insoluble zinc sulphide (ZnS) in strongly gleyed soils, such as some paddy soils with pronounced reducing conditions, may also be partly responsible for the low availability of zinc in these soils.

2.1.5 Factors Affecting the Availability of Zinc in Soils to Plants

The zinc which is available to plants is that present in the soil solution, or is adsorbed in a labile (easily desorbed) form. The soil factors affecting the availability of zinc to plants are those which control the amount of zinc in the soil solution and its sorption-desorption from/into the soil solution. These factors include: the total zinc content, pH, organic matter content, clay content, calcium carbonate content, redox conditions, microbial activity in the rhizosphere, soil moisture status, concentrations of other trace elements, concentrations of macro-nutrients, especially phosphorus and climate.

Some of these factors are briefly summarised here in a practical crop production context:

- ❖ Sandy soils and acid highly leached soils with low total and plant-available zinc concentrations are highly prone to zinc deficiency.
- ❖ Availability of zinc decreases with increasing soil pH due to increased adsorptive capacity, the formation of hydrolysed forms of zinc, possible chemisorption on calcium carbonate and co-precipitation in iron oxides. Alkaline, calcareous and heavily limed soils tend to be more prone to zinc deficiency than neutral or slightly acid soils.
- ❖ When rapidly decomposable organic matter, such as manure, is added to soils, zinc may become more available due to the formation of soluble organic zinc complexes which are mobile and also probably capable of absorption into plant roots.
- ❖ Available zinc concentrations in soils with high organic matter contents (peat and muck soils) may be low due to either an inherently low total concentration in these organic materials and/or due to the formation of stable organic complexes with the solid-state organic matter.
- ❖ High levels of phosphorus may decrease the availability of zinc or the onset of zinc deficiency associated with phosphorus fertilisation may be due to plant physiological factors.
- ❖ Some forms of phosphatic fertilisers, such as superphosphate, contain significant amounts of zinc as impurities and also have an acidifying effect on soils. When these are replaced with "high analysis" forms of phosphatic fertilisers, such as mono-ammonium phosphate (MAP) and diammonium phosphate (DAP) the incidence of zinc deficiency has often been found to increase.
- ❖ Higher concentrations of copper in the soil solution, relative to zinc, can reduce the availability of zinc to a plant (and *vice versa*) due to competition for the same sites for absorption into the plant root. This could occur after the application of a copper fertiliser.
- ❖ In waterlogged soils, such as paddy rice soils, reducing conditions result in a rise in pH, high

concentrations of bicarbonate ions, sometimes elevated concentrations of magnesium ions and the formation of insoluble zinc sulphide (ZnS) under strongly reducing conditions. The reducing conditions in periodically waterlogged soils also give rise to increased concentrations of divalent ferrous (Fe^{2+}) and manganese (Mn^{2+}) ions, from the dissolution of their hydrous oxides, and these could compete with zinc ions for uptake into roots.

- ❖ Nitrogen fertilisers, such as ammonium nitrate and sulphate of ammonia, can have a combined beneficial effect on the nutrition of crop plants by both supplying nitrogen, which is often the principal yield-limiting nutrient, and also an increase in zinc availability through the acidification of the soil resulting in desorption of zinc, and through improved root growth (and hence an increased volume of soil explored by roots) in the more vigorously growing plant.
- ❖ Where topsoil has been removed, often as a result of levelling fields for irrigation, crops grown on the subsoil can be highly prone to zinc deficiency, especially in calcareous soils. The topsoil contains the most organic matter and when removed there are shortages of macronutrients as well as micronutrients. However, N,P,K fertilisers usually address the macronutrient requirements but the zinc status of these "cut" soils also needs to be considered.

2.2 Soil Types Associated with Widespread Zinc Deficiency in Crops

Although it is recognised that zinc deficiencies in crops can be found on very many types of soils in the different bio-climatic zones of the world, there are a relatively small number of widely occurring types of soil which are more frequently associated with zinc deficiency than any other. These are:

1. Calcareous soils,
2. Sandy soils,
3. Strongly weathered deep tropical soils
4. Saline and Sodic (salt-affected) soils,
5. Vertisols,
6. Gleysols (poorly drained/waterlogged soils).

2.2.1 Calcareous Soils (Calcisols)

The Food and Agriculture Organisation of the United Nations (FAO) recognise calcareous soils as having major problems for agriculture (not just zinc deficiency). The FAO defines calcareous soils as being soils in which a high amount of calcium carbonate dominates the problems related to agricultural land use. They are characterized by the presence of calcium carbonate in the parent material and by a calcic horizon, which is a layer of secondary accumulation of carbonates (usually of calcium or magnesium) in excess of 15% calcium carbonate equivalent and at least 5% more carbonate than an underlying layer. In the World Reference Base Soil Classification System, calcareous soils mainly occur in the reference group of Calcisols ⁽²⁹⁾.

Calcareous soils are typical soils of semi-arid and arid climates with a sparse natural vegetation of xerophytic shrubs and ephemeral grasses. Owing to the arid conditions, Calcisols must normally be irrigated to be productive. The availability of water for irrigation is often a constraint on development as is also the composition of this water (especially its salt content). Calcisols tend to be low in organic matter and available nitrogen. The high pH and calcium carbonate content render phosphate unavailable due to the formation of the insoluble calcium phosphate (apatite). Zinc and iron deficiencies (lime-

induced chlorosis) are a problem in many areas where intensive cereal production is carried out on Calcisols. Potassium and magnesium nutrition may also be affected by antagonisms with the high concentrations of calcium.

The total global extent of Calcisols is estimated to be 800 Mha, mainly concentrated in arid or Mediterranean-type climatic zones. The total area is difficult to estimate because many Calcisols occur together with salt-affected soils (Solonchaks) that are actually salinized Calcisols. The global distribution of Calcisols is shown in Figure 2.2 (see next page).

Under the FAO-UNESCO system of soil classification, these calcareous soils can be classed as Fluvisols, Rendzinas, Yermosols, Xerosols, Kastanozems or Cambisols. However, in the World Reference Base for Soil Resources, the Rendzina, Yermosol and Xerosol groups have been merged with others and are no longer used on maps ⁽²⁹⁾. In the USDA Soil Taxonomy classification, these soils are: Xerochrepts (Inceptisols), Argids or Orthids (Aridisols), Rendolls or Xerolls (Mollisols), Xeralfs (Alfisols).

In West Asia (also known as the Near East) seven broad types of calcareous soils can be distinguished:

2.2.1.1 Soils with a Calcic Horizon

(Calciorthids, USDA; Calcic Xerosols and Calcic Yermosols, FAO-UNESCO). These soils are found developed on Pleistocene (recent) alluvial deposits and are extensive in: Syria, Jordan, Iraq, Iran and Egypt.

2.2.1.2 Soils with a Petrocalcic Horizon

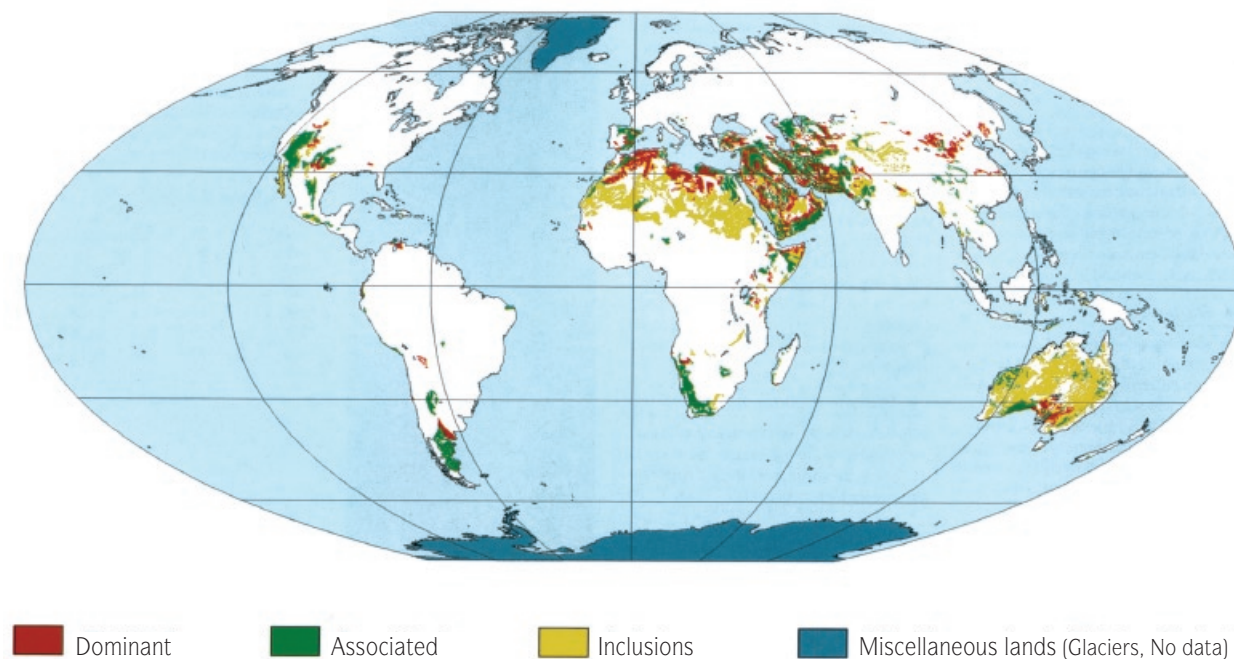
(Durorthids, USDA; Calcic Xerosols and Calcic Yermosols, FAO-UNESCO). These soils are similar to those in 2.2.1.1, except the calcic horizon has a cemented hard lime pan (called "caliche"). They are found in extensive areas in Saudi Arabia and in northern Syria.

2.2.1.3 Soils with a Gypsic Horizon

(Calciorthids, USDA; Calcic Xerosols and Calcic Yermosols FAO-UNESCO). These are calcareous soils with a horizon of gypsum accumulation in the subsoil and are not usually suitable for irrigation. They occur extensively in northern Iraq and eastern Syria.

Figure 2.2

Global Distribution of Calcareous Soils (Calcisols)



World Reference Base for Soil Resources. Bridges, Batjes & Nachtergaele (1998)

2.2.1.4 Shallow Soils over Limestone or Marl

(Lithic Camborthids and Lithic Haplorthids, USDA; Lithic Cambisols, Lithic Xerosols and Lithic Yermosols, FAO-UNESCO). These slope soils have a shallow root zone underlain by partially weathered rock and only shallow rooted crops which can tolerate the high CaCO_3 content can be grown. These soils occur extensively in: Afghanistan, southern Lebanon, western Egypt, Iran, Pakistan and most other countries in West Asia.

2.2.1.5 Calcareous Soils Formed in Alluvium or Loess without a Calcic Horizon

(Camborthids, Xerorthents and Torriorthents, USDA; Yermosols, Xerosols, Fluvisols and Regosols, FAO-UNESCO). These soils have $>15\%$ CaCO_3 mostly in the silt size fraction. There is no strong zone of lime accumulation so the rooting zone is quite deep. They occur in arid alluvial plains and arid mountain valleys and are very extensive in Afghanistan, Iraq, Iran, Pakistan, central Saudi Arabia and Yemen. In many areas these soils are strongly saline or saline-alkaline as well, e.g. the soils of the Mesopotamian Plain.

2.2.1.6 Slightly or Moderately Calcareous Soils

(Camborthids, USDA; Xerosols FAO-UNESCO). These soils occur in semi-arid zones, usually on Pleistocene alluvial, or loess deposits. They have a fairly good structure and a significant amount of organic matter in the sub-soil. They present the least problems among the calcareous soils but are still prone to zinc deficiency. They are found in the semi-arid parts of Iraq, Iran, Jordan, Lebanon, Syria, Pakistan, Yemen and possibly other countries.

2.2.1.7 Calcareous Very Clayey Soils

(Xererts and Usterts, USDA; Chronic and Haplic Vertisols, FAO-UNESCO) (see also Section 2.2.3). Although not true calcisols because they do not have a calcic horizon, these soils are often included with the calcareous soils because of their relatively high concentrations of calcium and magnesium. They have a very high content of expanding and cracking clays (montmorillonite). Problems concerned with CaCO_3 are minor although important for some crops, such as the low availability of zinc. These soils are extensive in Sudan but also occur in small areas in Lebanon, Syria, Iraq and Pakistan.

2.2.1.8 Calcareous Soils in Australia

(Calcarosols, CSIRO). In Australia, calcareous soils are classified as 'Calcarosols' and these soils are one of the most widespread and important groups of soils in southern Australia (30). Calcarosols are generally calcareous throughout the profile and do not have a distinct, or abrupt textural B horizon. In South Australia, there are more than 1 Mha of highly calcareous soils containing more than 10% CaCO₃. On the Eyre Peninsula, which produces around 40% of the state of South Australia's wheat, one of the major arable soils is a grey sandy loam containing < 90% CaCO₃. The most serious crop nutritional problem on this highly calcareous soil is phosphorus deficiency due to low availability, but both zinc and manganese deficiency are also common in these soils (15).

2.2.1.9 Response of Crops on Calcareous Soils to Fertilisation

Calcareous soils tend to be low in organic matter and available nitrogen. The high soil pH results in phosphorus being unavailable and, frequently, zinc and iron can be deficient. Zinc deficiency problems on calcareous soils have often been exacerbated by the removal of topsoil during land levelling for improved surface irrigation. Yields on these 'cut' soils are often reduced due to lack of available nitrogen, phosphorus, zinc and, sometimes, iron and also, in many cases, by soil compaction. Although these deficiencies can be corrected by applying relatively large quantities of fertilisers, heavy applications of livestock manure worked into the soil can often overcome the problem. However, supplies of manure are often not available and so it is beneficial to stockpile the 0-15 or 20 cm layer of topsoil during levelling and redistribute it over the new land surface.

Interestingly, experiments in the Lebanon with the fertilisation of maize in two calcareous soils showed that plants grown on the more calcareous of two soils (33% CaCO₃) had a higher concentration of zinc and manganese in the tops than the less calcareous soil (14% CaCO₃). This can be explained by the finding that less phosphorus was translocated to the plant tops, indicating that it had probably been tied up with the higher calcium content in the roots of the plants on the more calcareous soil. The phosphorus in the less calcareous soil was more active in the plant and held the zinc and manganese in less mobile forms in the roots, preventing their translocation to the leaves (31).

Other experiments in the Lebanon have shown a positive interaction of zinc, boron and plant population in giving the highest yields of maize grain. Very high levels of zinc and boron were used (up to 90 kg Zn ha⁻¹) and these could give rise to problems on many other soils. Experiments with maize on non-calcareous soils in New Mexico have shown a positive interaction between nitrogen, zinc and boron, but the amounts of zinc used were an order of magnitude lower than on calcareous soils (6 kg Zn ha⁻¹). However, it can be concluded that maize has high requirements for both zinc and boron as plant populations and yield levels are raised (31).

On calcareous soils in South Australia, zinc uptake in wheat has been significantly increased by applying zinc sulphate in solution with a fluid nitrogen-phosphorus fertiliser placed below sowing depth, compared with granular application of nitrogen-phosphorus fertilisers containing zinc (15).

2.2.2 Sandy Soils (Arenosols)

In the context of agricultural problem soils, sandy soils are soils in which a coarse texture dominates the problems related to agricultural use. Sandy soils have at least 65% sand-sized grains (0.06-2 mm diameter) and less than 18% clay-sized particles (< 0.002 mm diameter) and more than 65% sand in the top 100 cm of the soil profile. In the World Reference Resource Base Soil Classification system, sandy soils occur in the following soil groups: Arenosols, Regosols, Leptosols, and Fluvisols (32).

Regions of sandy soils can be divided into two broad categories: residual sands formed by the weathering of old, usually quartz-rich parent material, and shifting, or recently deposited sands in deserts and beach areas where sand has accumulated after transport by wind, water or ice. Sandy soils can occur all over the world from extremely cold climates to extremely hot and dry climates. Arenosols, the most characteristic sandy soils, cover around 900 Mha, mainly in the arid zone which includes the southern Sahara, Southwest Africa, and Western Australia. Several million hectares of highly leached arenosols are found in the perhumid tropics, notably in South America and parts of Southeast Asia. The global distribution of arenosols is shown in Figure 2.3. Small areas of young Arenosols occur in all parts of the world. In previously glaciated areas, sandy patches of drift deposits are frequently found, sometimes even within a

field and giving rise to localised nutritional, available water and even erosion problems (32).

Although most sandy soils are unused wastelands, in some areas arable cropping is possible with irrigation. In temperate areas, mixed arable cropping is practiced but supplemental irrigation by a sprinkler system is often required during dry weather. In the perhumid tropics, sandy soils are depleted of nutrients and need very careful management.

Quartz grains do not contain traces of zinc and are not able to adsorb cations and so the adsorptive capacity of a sandy soil is dependant on its low concentration of clay or silt-sized material and its organic matter content. As a result of their high infiltration rates, sandy soils are very prone to leaching (32).

The low clay content of sands can result in them having a low pH buffering capacity and so sandy soils will often be acid in humid environments where precipitation exceeds evaporation. However, calcareous sandy soils and sandy drift material containing limestone fragments can have neutral and alkaline pH values.

The smaller sand grains are very susceptible to wind erosion and so cultivated sandy soils are susceptible to erosion unless precautions are taken. Loss of the more organic and nutrient-rich topsoil can exacerbate deficiencies.

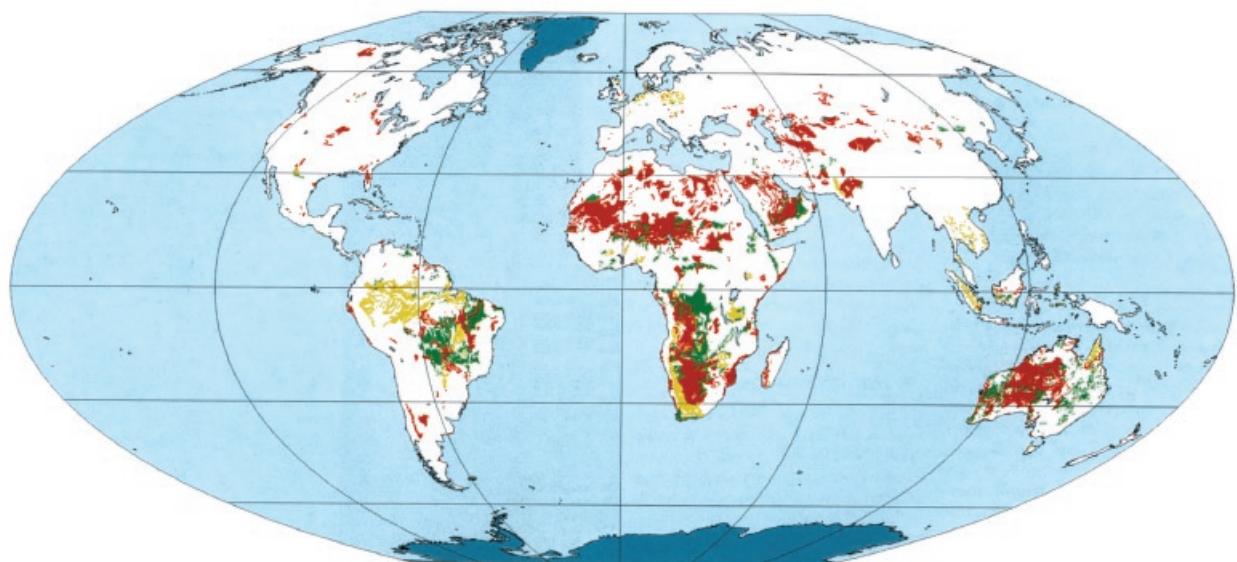
2.2.3 Ferralsols: Strongly Weathered Deep Tropical Soils

These soils are estimated to cover an area of around 750 Mha and are characteristic of the humid tropics on the continental shields of South America (Brazil) and Africa (Democratic Republic of Congo, Central African Republic, western Angola, Guinea and eastern Madagascar). They also occur in areas of easily weatherable rock with hot humid climates, as in parts of Southeast Asia and some Pacific islands (29).

Ferralsols are generally red to yellowish in colour, depending on the rock on which they developed. They have been heavily weathered and leached and so the content of zinc and other micronutrients is very low. They are generally very acid, with a pH of around 5 and need to

Figure 2.3

Global Distribution of Sandy Soils (Arenosols)



■ Dominant ■ Associated ■ Inclusions ■ Miscellaneous lands (Glaciers, No data)

World Reference Base for Soil Resources. Bridges, Batjes & Nachtergaele (1998)

be limed to pH 6.5 or 7 to grow high-yielding crops. This increase in pH renders zinc and other micronutrients, such as iron and boron less available. Ferralsols generally have a high phosphate fixation capacity and thus require relatively heavy applications of phosphatic fertilisers for arable crops. Both the raised pH and the high phosphate applications increase the risk of zinc deficiency.

Under both the FAO-UNESCO and World Reference Base for Soil Resources system of soil classification, these soils are classed as Ferralsols; associated soils include Acrisols (1000 Mha in Southeast Asia, southeast USA, southern fringes of Amazon Basin and both East and West Africa), Nitisols (mainly on high plateaux in eastern Africa and also in smaller areas at lower altitudes in India, the Philippines, Java, Central America and Brazil) and Plinthosols (mainly in West Africa, South America, and Western Australia) (29).

2.2.4 Vertisols

Vertisols are dark, montmorillonite-rich clay soils with characteristic shrinking and swelling properties. These soils have a high clay content (> 30% to at least 50 cm depth from the surface) and when dry have cracks which

are at least 1 cm wide and reach a depth of 50 cm or more. They are also often called 'heavy cracking clay soils' or 'swell-shrink soils'. They have high calcium and magnesium contents and are sometimes also included with calcareous soils although they do not have a calcic horizon (33).

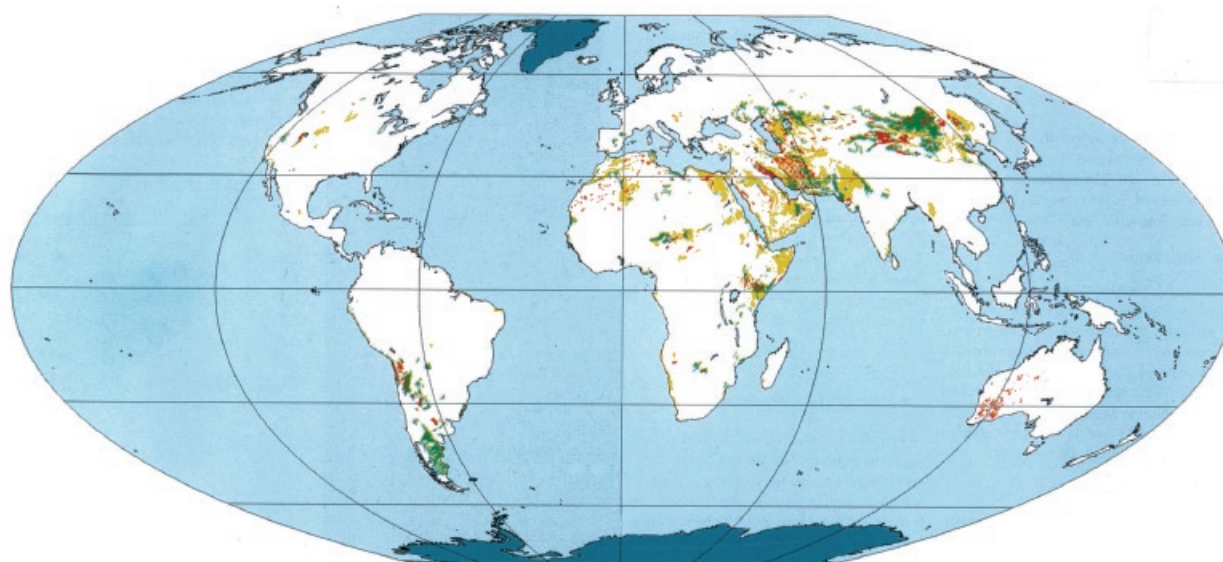
As a result of the expansion and contraction in these soils with wetting and drying, large amounts of topsoil fall down the cracks in dry periods and in due course some of the underlying material heaves up to the surface. The name Vertisol is actually taken from "inverted soil" because of the underlying material being cycled through the profile.

Vertisols occur in hot environments with marked wet and dry seasons. They are generally found in sedimentary plains, both on level ground and in depressions. The natural climax vegetation is savannah grassland and/or woodland. Vertisols cover a total area of about 340 Mha and most occur in the semi-arid tropics in Africa (the Gezira and other parts of central Sudan, South Africa, Ethiopia, and Tanzania), in South Asia (the Deccan Plateau in India) and in Australia (33).

The contents of calcium and magnesium are high in vertisols and the pH is usually above 7. Phosphate fixation

Figure 2.4

Global Distribution of Solonchaks (Saline Soil)



Dominant
 Associated
 Inclusions
 Miscellaneous lands (Glaciers, No data)

World Reference Base for Soil Resources. Bridges, Batjes & Nachtergaele (1998)

can be a problem and micronutrients, especially zinc and iron, are often deficient.

Katyal and Vlek⁽¹⁰⁾ reviewed various papers reporting zinc deficiency in rice, wheat, maize, sorghum, cotton and groundnuts on vertisols in India.

2.2.5 Saline and Sodic (Salt-Affected) Soils

Salt-affected soils contain considerable amounts of soluble salts. They occur in arid and semi-arid regions where evapotranspiration greatly exceeds precipitation.

Saline soils are soils in which a high salt content dominates the problems related to agricultural use. They are characterized by an electrical conductivity of more than 15 dS m^{-1} (in a saturated paste extract)⁽³³⁾. The Solonchaks are the most characteristic saline soil in the World Reference Base system. Solonchaks cover an area of between 260 Mha and 340 Mha and have a widespread, but scattered, distribution in Saharan Africa, East Africa, Namibia, Central Asia, Australia and South

America, where they are often associated with Sodic soils⁽³⁵⁾. The global distribution of Solonchaks is shown in Figure 2.4.

Sodic soils are soils in which a high content of sodium dominates the problems related to agricultural use. They are characterized by a Natric horizon associated with humus-rich surface horizons and saline subsoils. The Solonetz is the most characteristic soil group of the Sodic soils in the World Reference Base system. Solonetz soils cover around 135 Mha but their distribution is very scattered and individual areas are often too small to map at a world scale. Sodic soils are important in: the Ukraine, Kazakhstan, Hungary, Bulgaria, Romania, China, USA, Canada, South Africa and Australia⁽³⁶⁾.

The high pH conditions and high calcium concentrations in most saline soils are responsible for the low availability of zinc and the occurrence of zinc deficiency in crops on these soils. In sodic soils, the domination of exchange sites by sodium ions causes zinc ions to be lost by leaching especially under irrigation with water containing a high concentration of sodium.

Figure 2.5

Combined Global Distribution of the Main Types of Soils Associated with Zinc Deficiency Derived from the World Reference Base for Soil Resources Atlas by Bridges, Batjes and Nachtergaele (1998)



Note: Not all the areas of soil shown on this map have conditions suitable for crop production (e.g. desert areas)

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2.2.6 Gleysols

Gleysols are soils which are either permanently, or temporarily wet (waterlogged) with reducing conditions at depth. Those soils which are permanently reduced generally have grey or blue-green colours, but soils with alternating reducing and oxidising conditions can have reddish brown colours (usually present in mottles) when they dry out and are oxidized. Unlike waterlogged subunits of other soil types, Gleysols have a permanent groundwater table and are found in valleys ⁽³⁷⁾.

In the tropics and sub-tropics, Gleysols are widely used for rice growing, but in more temperate bioclimatic zones they are more generally used for grazing, or crop production where the water table can be lowered by drainage to allow an adequate freely-drained rooting depth. In many places where drainage is impractical they are often associated with peats (classified as Histosols) and still have swamp vegetation. These are not the only types of soil used for rice growing in the tropics and sub-tropics but are ideally suited to this crop ⁽³⁷⁾. It is mainly the areas of gleysols in the tropics and sub-tropics which are most important with regard to zinc deficiency problems because rice, a crop which is highly susceptible to zinc deficiency, is grown in these (and other) soils in these regions.

2.2.7 Global Distribution of the Main Soil Types Associated with Zinc Deficiency

Figure 2.5 shows the combined areas of these five main types of soils which are most frequently associated with zinc deficiency. However, this cannot be considered to be the total area of zinc-deficient soils. Although it does not include small localised areas in many parts of the world, it is likely to be an over-estimation of the area of deficient soils. This is because some of the area shown in Figure 2.5 will not be suitable for growing crops due to either adverse climate and/or shortage of available supplies of water for irrigation (e.g. desert areas). In some places indigenous varieties of crop species, which are well adapted to local soil conditions, will be tolerant to zinc deficiency (but have poorer yields than new varieties), and considerable areas

will have been treated with zinc fertilisers. Nevertheless, it is useful to see the location of the main areas of potential zinc deficiency problems.

2.3 Zinc in Plant Nutrition

2.3.1 Physiological Aspects of Zinc in Plants

This topic was extensively reviewed by Brown *et al.* ⁽³⁸⁾ and the following section is mainly based on their review and individual papers which they used have not been referred to in this brief coverage of the subject. Readers seeking more details are recommended to the chapter by Brown *et al.* in 'Zinc in soils and plants' edited by A.D. Robson (1993) ⁽³⁸⁾, the review by Welch (1995) 'Micronutrient Nutrition of Plants' ⁽³⁹⁾, or the second edition (1995) of Marchner's book 'Mineral Nutrition of Higher Plants' ⁽⁴⁰⁾.

A biological requirement for zinc was first identified by Raulin in 1869 when the common bread mould (*Aspergillus niger*) was found not to be able to grow in the absence of zinc. However, its essentiality was not established until 1926 and it was only in 1932 that zinc deficiency was first identified under field conditions (in Californian apple orchards and South Australian citrus trees). In the time since 1932, zinc has been found to be a vitally important micronutrient in crop production and deficiencies of this element have been shown to be more widespread throughout the world than those of any other micronutrient ⁽³⁸⁾.

Graham *et al.* ⁽⁴¹⁾ comment that it would appear that there is a critical level required for zinc in the soil before roots will either grow into it or function effectively. According to Marschner ⁽⁴⁰⁾, the metabolic functions of zinc are based on its strong tendency to form tetrahedral complexes with N-, O- and particularly S- ligands and it thereby plays both a functional (catalytic) and a structural role in enzyme reactions. Although more than 70 metalloenzymes containing zinc have been identified, these only account for a relatively small proportion of the total zinc in a plant ⁽³⁸⁾.

In plants, zinc does not undergo valency changes and its predominant forms are: low molecular weight complexes, storage metalloproteins, free ions and insoluble forms associated with the cell walls. Zinc can become inactivated within cells by the formation of complexes with organic ligands or by complexation with phosphorus. Depending on the plant species, between 58% and 91% of the zinc in a plant can be in a water-soluble form (low molecular weight complexes and free ions). This water-soluble fraction is widely considered to be the most physiologically active and is regarded as a better indicator of plant zinc status than total zinc contents. The low molecular weight complexes are normally the most abundant soluble form of zinc and are probably the most active form of the metal ⁽³⁸⁾.

2.3.1.1 Low Molecular Weight Complexes of Zinc

In plant leaves, soluble zinc occurs mainly as an anionic compound possibly associated with amino acids. In lettuce, the soluble zinc fraction has been found to have a molecular weight of 1259 Daltons and to contain sulphur, reducing sugars and amino acids and the sum of these fractions represented 58% of the total zinc in the leaf. In seeds, 62-70% of the total zinc has been found to be soluble. Free zinc ions only form a small proportion of the total soluble content (5.8% in tomato and 6.5% in alfalfa) ⁽³⁸⁾.

The low molecular weight complexed forms of zinc are probably physiologically active because they can be degraded and may also be involved in homeostatic mechanisms where they may act as a buffer system to bind excess free zinc ions. An example of this is the group of phytochelatins, which have been identified in a wide range of species and are synthesized in response to exposure to excess concentrations of cadmium, zinc and mercury ⁽³⁸⁾.

2.3.1.2 Zinc in Proteins

In plants, zinc acts as a functional, structural or regulatory co-factor of a large number of enzymes. More than 70 metallo-enzymes containing zinc have been identified and these occur in all of the six classes of enzymes:

oxidoreductases, transferases, hydrolases, lyases, isomerases and ligases ⁽⁴²⁾. The zinc atom is usually tightly bound to the apoenzyme and can only be removed with severe chemical treatment. It forms strong complexes with radicals of polar groups containing oxygen, nitrogen and sulphur ⁽³⁸⁾.

In enzymes that require zinc for activity, zinc is mostly bound through imadazole and cysteine. X-ray analysis shows that catalytic zinc is bound with three protein ligands and a water molecule, whereas in enzymes where zinc plays a structural or regulatory role, it is fully coordinated with four protein ligands. The presence of a water molecule, indicating an open coordination site is considered essential for the catalytic function of zinc ⁽³⁸⁾.

According to Srivastava and Gupta ⁽⁴³⁾, zinc plays a vital role in many important enzyme systems including:

- ❖ Carbonic anhydrase (transport of CO₂ in photosynthesis),
- ❖ Several dehydrogenases: alcohol dehydrogenase, glutamic dehydrogenase, L-lactic dehydrogenase, malic dehydrogenase, D-glyceraldehyde-3-phosphate dehydrogenase, and D-lactate dehydrogenase,
- ❖ Aldolase,
- ❖ Carboxypeptidase,
- ❖ Alkaline phosphatase,
- ❖ Superoxide dismutase (converting superoxide radicals to hydrogen peroxide and water),
- ❖ RNA polymerase (protein synthesis),
- ❖ Ribulose bi-phosphate carboxylase (important role in starch formation),
- ❖ Phospholipase.

2.3.1.3 Physiological Functions of Zinc

2.3.1.3.1 Carbohydrate Metabolism

Zinc exerts an effect on carbohydrate metabolism through its effects on photosynthesis and sugar transformations. In general, zinc does not affect respiration in plants.

a) Photosynthesis - A deficiency of zinc can cause a reduction in net photosynthesis by 50%-70% depending on the plant species and the severity of deficiency. This reduced efficiency of photosynthesis could be due, at least in part, to a reduction in the activity of the enzyme carbonic anhydrase. Zinc is a constituent of carbonic anhydrase, but the carbonic anhydrase in dicotyledons is a larger molecule and contains more zinc than carbonic anhydrase in monocotyledons (such as the cereals). A sharp decline in carbonic anhydrase activity occurs when plants suffer a zinc stress and this has effects on the carbon dioxide assimilation pathway. There appears to be some uncertainty whether carbonic anhydrase is involved in photosynthesis in C_3 plants, but it is generally considered to be involved in photosynthesis in C_4 plants.

C_3 plants have the most basic photosynthesis mechanism and fix carbon dioxide once using the Calvin-Benson cycle only. Most C_3 plant species tend to have originated in relatively cool (< 25°C) and humid climates. Examples of C_3 plants include: wheat, rice and soya beans.

In contrast, the C_4 plants fix carbon dioxide twice and have a mechanism by which they are able to increase the carbon dioxide concentration in their leaves several times higher than ambient levels. They use a four carbon pathway and then the Calvin-Benson cycle and are found naturally in warmer and water-limited environments. Examples of C_4 plants include: maize, sugarcane and sorghum.

In general, in C_3 plants there is no direct relationship between carbonic anhydrase activity and photosynthetic carbon dioxide assimilation or growth of plants with different zinc nutritional status⁽⁴¹⁾. Carbonic anhydrase activity is closely related to zinc content but only has an effect on photosynthesis and dry matter

production when the activity is very low. With extreme zinc deficiency, carbonic anhydrase activity is absent.

However, with C_4 plants, the situation is different and a high carbonic anhydrase activity is required in the mesophyll chloroplasts to shift the equilibrium in favour of HCO_3^- , the substrate for phosphoenol pyruvate (PEP) carboxylase which forms C_3 compounds. Carbonic anhydrase activity may have a more key role in preventing the formation of HCO_3^- from limiting photosynthesis. Hence, zinc deficiency may have a more dramatic effect on the rate of photosynthesis in C_4 compared with C_3 plants⁽⁴⁰⁾. C_4 plants such as maize and sorghum are highly sensitive to zinc deficiency.

Zinc is a constituent of other enzymes involved in photosynthesis, including ribulose 1,5-biphosphate carboxylase (RuBPC) which has been found to catalyse the initial step of carbon dioxide fixation in photosynthesis and has been found in navy beans, barley, rice and pearl millet⁽³⁸⁾. The reduction of photosynthesis observed in zinc deficient plants can also be due, in part, to a major decrease in chlorophyll content and the abnormal structure of chloroplasts.

b) Sucrose and Starch Formation - Enzymes involved in the formation of sucrose, such as aldolase, are adversely affected by zinc deficiency. A decline in the level of sucrose in sugar beet and maize are due to lower activity of sucrose synthetase activity. Zinc may play a role in the metabolism of starch because the starch content, activity of the enzyme starch synthetase, and the number of starch grains are all depressed in zinc deficient plants. However, on the other hand, zinc deficiency has been shown to increase the concentrations of sugars and starches in the leaves of cabbage, but in the roots of beans carbohydrate concentrations were decreased. These findings suggest that zinc deficiency impairs the translocation of sucrose from the source leaves to the roots. However, experiments have shown that treatment of the deficient plants with zinc restored the phloem loading of sucrose. The reason for this impaired sucrose transport is not fully understood, but could be due to the role of zinc in the integrity of biomembranes⁽³⁸⁾.

2.3.1.3.2 Protein Metabolism

In general, the amount of protein in zinc-deficient plants is greatly reduced but the composition remains almost unchanged. In zinc-deficient bean leaves the concentration of free amino acids was 6.5 times greater than in controls but these decreased and the protein content increased after administration of zinc for 48 or 72 hours.

The mechanism by which zinc deficiency affects protein synthesis is considered to be due to a reduction in RNA and the deformation and reduction of ribosomes. In the meristem of rice seedlings, it has been found that the level of RNA and the number of free ribosomes was dramatically reduced by zinc deficiency (38).

Zinc is necessary for the activity of the enzyme RNA polymerase and it protects the ribosomal RNA from attack by the enzyme ribonuclease. High levels of ribonuclease activity are a typical feature of zinc deficiency in higher plants. As a consequence of this, the earliest causal effect of zinc deficiency is a sharp decrease in the level of RNA. However, the reduction in RNA can occur before the increase in ribonuclease activity. The importance of zinc in protein synthesis suggests that relatively high zinc concentrations are required by meristematic tissue where cell division as well as synthesis of nucleic acid and protein is actively taking place (38).

The most fundamental effect of zinc on protein metabolism is through its involvement in the stability and function of genetic material.

2.3.1.3.3 Membrane Integrity

In animals and plants, zinc is considered to play a critical physiological role in the structure and function of biomembranes. In plants this has been demonstrated indirectly. Welch *et al.* (44) used root exudates as an indicator of root plasma membrane integrity and found greater leakage of the ³²P phosphorus isotope out of roots of zinc-deficient wheat than from zinc-sufficient roots. Other workers have observed an increased net flux out of roots of potassium (K⁺), amino acids, sugars and phenolics by a factor of 2.5. When zinc was resupplied to the plant for at least 12 hours, the leakage decreased.

The role of zinc in maintaining the integrity of cellular membranes may involve the structural orientation of macromolecules and the maintenance of ion transport systems.

Zinc is also known to be required for the maintenance of membranes through the interaction with phospholipids and sulphhydryl groups of membrane proteins. The loss of membrane integrity is considered by some to be the earliest biochemical change caused by zinc deficiency. Apart from its role as a structural component in membranes, similar to that of calcium, zinc also plays a key role in controlling the generation and detoxification of free oxygen radicals (O₂[•]), which can damage membrane lipids and sulphhydryl groups. Zinc exerts an inhibitory action on membrane damage catalysed by free oxygen radicals. In general, it would appear that the major role of zinc in membranes is to protect membrane lipids and proteins from peroxidation caused by the free oxygen radicals.

Enhancement of chlorosis and necrosis in leaves by high light fluxes was considered to be due to the photo-oxidation of thylakoid constituents by activated oxygen species, such as peroxide, hydroxyl radicals and singlet oxygen. (1O₂[•]). Zinc may help to limit photooxidation since it is a protective and stabilizing component of biomembranes against activated oxygen species (38).

Zinc-deficient cotton, bean and tomato root cells have been shown by Cakmak and Marschner (45,46) to have a reduced level of superoxide dismutase (SOD) activity and an increased NADH-dependent free oxygen radical production. Catalase is another enzyme which is able to detoxify hydrogen peroxide and this tends to follow SOD in having lower levels in zinc-deficient plants.

Welch *et al.* (44) observed that zinc played a fundamental role in the stability of plant cell membranes and that unlike the case with calcium, the effect of destabilizing membranes by zinc deficiency was not easily reversed. Other elements, in addition to zinc, are also required to maintain the integrity of cell membranes and these include: calcium, phosphorus, boron, and manganese (41). In experiments with culture solutions containing no zinc, phosphorus accumulated to toxic levels in the oldest

leaves, but plants supplied with a small amount of zinc actually accumulated more phosphorus than those without zinc even though the latter were displaying symptoms of phosphorus toxicity. This is due to the zinc-deficient plants 'leaking' more phosphorus than those with zinc due to the impaired functioning of the cell membranes.

This led to the hypothesis that the zinc-deficient root cells, having impaired membrane integrity, could allow non-selective entry of boron and phosphorus into the roots which could then accumulate in the actively transpiring older leaves ⁽⁴⁷⁾. Further evidence to support this hypothesis was provided by Marschner ⁽⁴⁸⁾, who found that the roots of zinc-deficient cotton plants excreted 3.3 times more amino acids and 2.6 times more carbohydrates than zinc-sufficient control plants and the electrical conductivity of the root exudates solution also increased 3-fold. Cakmak and Marschner ⁽⁴⁹⁾ also reported that potassium leakage was significantly higher from the roots of zinc-deficient cotton, wheat and tomato plants, but this leakage could be mitigated by supplying zinc for 12 hours. Early workers in this research area had reported that the bark of fruit trees with 'little leaf' (not then recognized as a symptom of zinc deficiency) contained only about 10% of the normal potassium content ⁽⁵⁰⁾.

Cakmak and Marschner ⁽⁵¹⁾ observed that nitrate and amino acids leaked from zinc-deficient cotton plants and zinc-deficient apple trees leaked sugars and phenols. The loss of potassium is particularly important because it is a constituent of the cell sap and, if this leaks, it indicates that the integrity of the cell membrane has been impaired. Cakmak and Marschner ⁽⁴⁹⁾ considered that the principal role of zinc in preserving the integrity of cell membranes lay in its ability to protect membrane proteins and lipids from the destructive effects of superoxide radicals and their derivatives produced by redox reactions within the cell. Zinc is a constituent, together with copper, of the enzyme superoxide dismutase (SOD), which can scavenge free radicals.

2.3.1.3.4 Auxin Metabolism

Zinc is required for the synthesis of auxin (a growth regulating compound-indole acetic acid, IAA). Stunted

growth and 'little leaf' are the most distinct visible symptoms of zinc deficiency and are the result of disturbances in the metabolism of auxins, especially IAA. Low levels of IAA may be the result of inhibited synthesis, or enhanced degradation of IAA. Tryptophan is the most likely precursor for the biosynthesis of IAA. There is some evidence that zinc is required for the synthesis of tryptophan. This includes an observed increase in the tryptophan content in rice grains after zinc fertilisation of plants growing on a calcareous soil ⁽³⁸⁾.

2.3.1.3.5 Reproduction

Flowering and seed production are severely depressed in zinc-deficient plants. In subterranean clover it was shown that treatment of deficient plants with zinc had a greater effect on the number of inflorescences and seed yield than on dry matter production or the size of seed. Reduced seed production in zinc-deficient plants may be due to: (a) increased formation of abscissic acid causing premature loss of leaves and flower buds, and (b) disruption of the development and physiology of anthers and pollen grains. Zinc-deficient wheat has been reported to have developed small anthers and abnormal pollen grains ⁽³⁸⁾. Sharma *et al.* ⁽⁵²⁾ showed that zinc deficiency in maize severely retarded the development of tassels, anthers and pollen grains. They stated that the decrease in pollen production by the anthers and in the pollen fertility of low-zinc plants indicated that zinc deficiency suppressed male sexuality in maize. Subnormal zinc at any stage of anther development prior to microsporogenesis induced male sterility.

2.3.2 Mechanisms of Zinc Uptake by Plants

Zinc appears to be absorbed by roots primarily as Zn^{2+} from the soil solution and its uptake is mediated by a protein with a strong affinity for zinc. Kochian ⁽⁵³⁾ proposed that the transport of zinc across the plasma membrane was towards a large negative electrical potential so that the process is thermodynamically passive. This negative electrical potential of the plasma membrane is the driving force for zinc by means of a

divalent cation channel in dicotyledons and monocotyledons other than the Poaceae. In the Poaceae, Kochian proposed that non-protein amino acids called 'phytosiderophores' or 'phytometallophores' form a complex with zinc and transport it to the outer face of the root-cell plasma membrane. These phytosiderophores are released from the roots as a result of iron or zinc deficiency. This complex is then transported to the cell via a transport protein.

The mugineic acid (MA) family of phytosiderophores was investigated by Suzuki *et al.* (54) who showed that their secretion was increased by zinc deficiency in barley. They found that the expression of all genes involved in MA synthesis was increased in zinc-deficient barley but this did not occur in zinc-deficient rice.

Hoffland *et al.* (55) showed that the tolerance of rice plants to low zinc availability is related to the capacity of the plant to exude LMWOA (Low Molecular Weight Organic Anion) compounds. They found that both zinc and phosphorus deficiency induced significant increases in the exudation of LMWOAs which enhanced the uptake of these elements. They found that among the LMWOAs detected, oxalate was the most abundant, but citrate was considered to be more effective in mobilizing zinc. Citrate exudation rates correlated with tolerance to low available zinc concentrations. Similarly, Degryse *et al.* (56) have shown that aqueous metal complexes increase zinc and copper uptake by plants and these arise from the plant playing an active role in mediating the uptake flux through root secretions and acidification of the rhizosphere. When present, aqueous complexes can increase metal uptake because plant uptake is rate-limited by diffusion of the free-ion to the root or cell surface. The free-ion activity in chelator-buffered solutions depends in the type and concentration of the ligands present.

Nambiar (57) showed that plants could take up zinc from dry soil (matrix potential < -1.5 MPa) via excreted mucilage but this uptake was only 40% as effective as uptake from wet soil.

Zinc is taken up by plant roots as Zn^{2+} or as $Zn(OH)_2$ at high pH. As a result of low concentrations of zinc in the soil solution, uptake is mainly by direct root contact and is

metabolically controlled. Extensive interactions take place between the uptake of zinc and other micronutrients, e.g. zinc-copper, which mutually inhibit each other indicating that both are absorbed through the same mechanism or carrier sites. Zinc-deficient rice shows increased uptake of cadmium, but zinc is translocated to aerial parts to a greater extent than cadmium. Zinc addition to waterlogged soils has been found to increase DTPA extractable manganese, but decrease the uptake and translocation of copper, iron and phosphorus (58).

It has generally been recognized that zinc is transported in the plant either as Zn^{2+} or bound to organic acids. Zinc accumulates in root tissues but is translocated to the shoot when needed. Zinc is partially translocated from old leaves to developing organs. In rice seedlings, translocation of zinc from roots increases with manganese application. However, more recent research has shown the existence of transport proteins in some plant species.

Ishimaru *et al.* (59) have shown in rice that transporter proteins are responsible for zinc translocation within rice plants. These proteins are known as ZIPs (Zinc-regulated, Iron regulated Protein) and those in rice (*Oryza sativa*, 'Os') are known as OsZIPs. Their investigations showed that OsZIP-4 was highly expressed under conditions of zinc deficiency in shoots and roots especially in phloem cells. Transcripts of these proteins were also detected in the meristems of zinc-deficient roots and shoots. Although other OsZIP proteins were found, OsZIP-4 appeared to be the main protein involved in zinc translocation.

Chaudry and Loneragan (60) reported that alkaline earth cations inhibited Zn^{2+} absorption by plants non-competitively, in the order: $Mg^{2+} > Ba^{2+} > Sr^{2+} = Ca^{2+}$.

2.3.3 Relative Sensitivity of Crops to Zinc Deficiency

Although zinc deficiency is known to affect a wide range of crops in many parts of the world, genotypic differences between species render some crops more susceptible to deficiency than others. Apart from inter-specific differences, there are also important intra-specific

Table 2.3**Relative Sensitivity of Crops to Zinc Deficiency**

High	Medium	Low
Bean	Barley	Alfalfa
Citrus	Cotton	Asparagus
Flax	Lettuce	Carrot
Fruit trees (deciduous)	Potato	Clover
Grapes	Soybean	Grass
Hops	Sudan grass	Oat
Maize (corn)	Sugar beet	Pea
Onions	Table beet	Rye
Pecan nuts	Tomato	Wheat
Rice		
Sorghum		
Sweetcorn		

(Based mainly on Martens and Westerman⁽⁶¹⁾ and ILZRO⁽⁶²⁾)

differences which can in some cases be greater than differences between species. In the case of wheat, Durum wheat (*Triticum durum* Desf.) is more susceptible to zinc deficiency than bread wheat (*Triticum aestivum* L.). However, there are considerable varietal differences in both types of wheat.

The varieties (or cultivars) of crops, such as wheat and rice, which are recognised as being more tolerant of zinc deficiency have been described as 'zinc-efficient' varieties (see sections 2.3.3.1 and 2.3.3.2).

From Table 2.3, it can be seen that crops such as maize, rice and beans are highly sensitive to zinc deficiency and that wheat has only a low sensitivity. However, wheat crops in many parts of the world are still badly affected by zinc deficiency even though it has a relatively low sensitivity to deficiency compared with crops such as maize. Zinc deficiency can be a major problem in wheat, often with yields reduced by 50% as found in parts of Turkey. If maize or beans were grown on the same soils as wheat, they would probably be even more severely affected. Therefore, although the ranking of crops in

Table 2.3 is useful for comparing sensitivity to deficiency and response to zinc fertilisers, it does not indicate the extent to which these crops are affected by zinc deficiency in various parts of the world.

Brown and Jones⁽⁶³⁾ stated that plant response to a micronutrient stress is a genetically controlled adaptation. The mechanisms involved can include the ability to absorb nutrients at sub-optimal concentrations, secretion of root exudates to mobilize elements in the soil and enhance their absorption into roots, and the ability to retranslocate absorbed nutrients within the plant⁽⁶⁴⁾.

Graham *et al.*⁽⁶⁵⁾ reported that significant variations in zinc-efficiency can be found in wheat, barley and oats. This zinc efficiency character appeared to be poorly linked to efficiency for other micronutrients, such as manganese, which suggests an independent mechanism and genetic control for zinc efficiency. Working with soils of different types in South Australia, they found that zinc efficiency traits for nutrient-poor sandy and nutrient-rich clayey soils were genetically different. Zinc-efficient genotypes absorb more zinc from deficient soils, produce more dry matter and more grain yield, but do not necessarily have the highest zinc concentrations in leaves or grain. High grain zinc contents appear to be under genetic control, but this trait is not directly linked to zinc efficiency. A high grain zinc content contributes to seedling vigour and is beneficial for cereal-based human diets (Section 2.6).

In addition to cereal species, variation in zinc efficiency has also been demonstrated in the Medicago species of legumes⁽⁶⁶⁾.

Rengel⁽⁶⁷⁾ summarised the different possible mechanisms of zinc efficiency as:

1. a greater proportion of longer, fine roots (< 0.2 mm in diameter),
2. differential changes in rhizosphere chemistry and biology, including the greater release of zinc-chelating phyto siderophores,
3. an increased uptake rate resulting in a net increase in zinc accumulation,
4. more efficient utilization and compartmentalization of zinc within cells, tissues and organs, including a greater activity of carbonic anhydrase, and antioxidative

enzymes, maintaining sulphhydryl groups in the root-cell plasma membranes in a reduced state and a differential pattern of biosynthesis.

2.3.3.1 Zinc Deficiency Tolerance Mechanisms in Wheat

Cakmak ⁽⁶⁸⁾ reported that the screening of wheat varieties for zinc efficiency (tolerance to zinc deficiency) on zinc-deficient calcareous soils in Central Anatolia, Turkey, had shown a wide range of variation in tolerance, especially among bread wheats. The most zinc-efficient cultivars were those which had been developed from crosses with local landraces. Anatolian bread wheat landraces are very tolerant to zinc deficiency.

Experiments to compare the susceptibility of different cereal species to zinc deficiency showed that rye was very tolerant (low susceptibility to deficiency) and durum wheat was highly susceptible. The order of declining tolerance to deficiency was: rye > triticale (a rye/wheat cross) > barley > bread wheat > oat > durum wheat ⁽⁶⁸⁾.

All wild, primitive and modern hexaploid wheats are very susceptible to zinc deficiency, whereas primitive and modern diploid wheats and the most primitive hexaploid wheats had a higher tolerance to deficiency. These results suggest that AA and DD genomes possibly have genes responsible for the expression of high zinc efficiency in wheat ⁽⁶⁸⁾.

The physiological bases of zinc efficiency are not completely understood, but it would appear that efficient utilization of zinc at the cellular level is a major factor in it, together with an enhanced uptake of zinc by roots to maintain high growth rates at low tissue zinc concentrations.

Recently reported work by Hacasalihoglu *et al.* ⁽⁶⁹⁾ showed that, in wheat, zinc efficiency (ZE) was correlated with enhanced expression and activity of zinc-requiring enzymes including Cu/Zn superoxide dismutase and carbonic anhydrase. Zinc-efficient genotypes may be able to maintain the functioning of these and other zinc-requiring enzymes under conditions of low zinc supply. They did not find any link between zinc efficiency and root

uptake of zinc nor with the translocation of zinc from the root to the shoot.

In wheat, maize, sorghum, rice and oats, variations in reaction to zinc deficiency may be related to different capacities of the plant species and cultivars to release zinc-mobilizing phytosiderophores (phytometallophores) from roots. Cakmak *et al.* ⁽⁷⁰⁾ demonstrated that phytosiderophores released from roots under conditions of zinc deficiency enhanced the solubility and mobility of zinc by chelation from sparingly soluble zinc compounds in calcareous soils.

Holloway ⁽⁴⁷⁾ reported that root architecture does not appear to be a determining factor in zinc efficiency in wheat. Some zinc-inefficient wheat cultivars such as 'Gatcher' have more extensive root systems than 'Excalibur' which is more zinc-efficient.

2.3.3.2 Zinc Deficiency Tolerance Mechanisms in Rice

Neue *et al.* ⁽⁵⁸⁾ reported that differences in the tolerance of rice cultivars to zinc deficiency have been recognized for many years and the International Rice Research Institute (IRRI), at Los Baños in the Philippines had been selecting for zinc-efficiency since 1971. Differential responses to zinc deficiency have been attributed either to greater physiological efficiency, or to selective higher absorption from a zinc deficient medium. Rice cultivars differ in their zinc requirements. For example, cultivar M101 thrived in a zinc-deficient culture solution whereas IR26 readily developed zinc deficiency symptoms. Affinity for zinc was twice as high in the roots of M101 than in those of IR26.

Early maturing cultivars are generally more susceptible to zinc deficiency because of their high demand for zinc early in their development (i.e. before root development is sufficient to accumulate adequate amounts of zinc from the soil). Tolerance to zinc deficiency in rice has been attributed to a high tolerance of the plant to high concentrations of bicarbonate in solution which appear to affect root absorption. Less tolerant cultivars may be sensitive to lower bicarbonate concentrations than tolerant ones.

The tolerance of rice cultivar IR34 to zinc deficiency was considered by Cayton *et al.*⁽⁷¹⁾ to be associated with a lower zinc requirement, i.e. more efficient translocation of zinc, and the ability to maintain lower iron/zinc, copper/zinc, magnesium/zinc and phosphorus/zinc ratios in the shoot. Translocation of iron, magnesium, and phosphorus to shoots and absorption of copper decreased in IR34 when zinc became deficient.

Zinc deficiency tolerance and iron toxicity tolerance in rice are significantly correlated under conditions of high solar radiation. Iron increases the internal zinc requirement of susceptible cultivars of rice and inhibits zinc absorption. Iron may also disrupt the translocation of zinc by displacing zinc from the citrate carrier substance.

Kirk and Bajita⁽⁷²⁾ have shown that root-induced changes in the rhizosphere solubilised zinc and increased its uptake by rice. The solubilisation involves either root-induced acidification from H⁺ generated from the oxidation of Fe²⁺, or the intake of an excess of cations, such as NH₄⁺, relative to anions and the concomitant release of H⁺ from the roots. Most of the zinc in flooded soils is expected to be in an acid-soluble form such as sorbed on ferrous carbonates and hydroxides. The concentration of plant available zinc is very low and the plants depend on plant-induced solubilisation for the bulk of their supplies of zinc.

Neue *et al.*⁽⁵⁸⁾ reported that workers have shown that tolerance to zinc deficiency in rice cultivars appears to be a polygenic trait involving three genes. Since 1971, IRRI has screened 23,000 rice cultivars for zinc deficiency tolerance. However, all IRRI breeding lines are subject to a certain amount of selection pressure for this trait because the soils on the IRRI research farm are moderately zinc deficient. An average yield advantage of 3 t ha⁻¹ was found for zinc-efficient cultivars from 46 tests of 411 rice breeding lines at eleven zinc deficient sites in the Philippines. The yields of zinc-efficient cultivars were observed to decrease when zinc was applied and this was found to be due to a zinc-induced nutrient imbalance.

2.3.3.3 Interactions between Zinc and other Plant Nutrients

2.3.3.3.1 Zinc-Phosphorus Interactions

This topic has been extensively reviewed by Loneragan and Webb⁽⁷³⁾ and much of this section has been based on their review. In some cases, it has not been possible to quote the authors of all the papers on which this summary is based. Readers wishing to find more details are referred to the chapter by Loneragan and Webb in "Zinc in Soils and Plants" edited by A.D. Robson (1993)⁽⁷³⁾ or to "Mineral Nutrition of Higher Plants (second edition)" by H. Marschner (1995)⁽⁴⁰⁾.

High soil phosphate levels are one of the most common causes of zinc deficiency in crops encountered around the world. However, although this interaction with phosphate has been recognized for many years, the actual mechanisms responsible are still not completely understood.

Marschner⁽⁷⁴⁾ commented that, in general, plant uptake of zinc decreases sharply, often beyond a level which can be attributed to dilution effects due to growth enhancement, with an increase in the soil content or supply of fertiliser phosphorus. However, extractable zinc in soils is either not at all, or only slightly decreased by a high phosphorus supply. In acid tropical soils, the risk of phosphorus-induced zinc deficiency increases when phosphorus application is accompanied by liming. Liming will overcome aluminium toxicity and thereby increase root growth but the sharp decrease in zinc concentrations in the soil solution combined with higher zinc requirements due to enhanced shoot growth requires the additional supply of zinc to prevent a reduction in growth with high phosphorus and lime supply⁽⁷⁴⁾.

Loneragan and Webb⁽⁶⁶⁾ distinguish two different types of zinc-phosphorus interactions:

- 1) Those in which increasing phosphorus applications decrease concentrations of zinc in the shoot.
- 2) Those in which increasing phosphorus applications do not decrease zinc concentrations in the shoot.

The most common type of zinc-phosphorus interaction is the type 1, where phosphate salts bring about a decrease in zinc concentrations and this usually occurs where the supply capacity of the soil for both zinc and phosphorus are marginal, so the addition of phosphatic fertiliser promotes growth sufficiently to cause the dilution of zinc concentrations in plant tissues to levels which induce or enhance zinc deficiency.

However, there are other situations in which zinc deficiency has been induced by phosphorus without the dilution of zinc concentrations in plant shoots. It is likely that phosphorus must have either depressed zinc absorption by roots or the translocation of zinc from roots to the shoots.

There are four possible mechanisms by which phosphorus can reduce the absorption of zinc from soils:

- i) Arbuscular mycorrhizae (AM) infection of roots is suppressed by high concentrations of phosphorus.
- ii) Cations added with phosphate salts can inhibit zinc absorption from solution.
- iii) H⁺ ions generated by phosphate salts inhibit zinc absorption from solution.
- iv) Phosphorus enhances the adsorption of zinc onto soil constituents.

The role of arbuscular mycorrhizae (AM) in the uptake of phosphorus by plants is well known. The mycorrhizae effectively increase the area of the root absorbing surface in the soil and this affects the absorption of all elements, not just phosphorus. So when the concentrations of phosphorus are relatively high the suppression of the development of mycorrhizae will have the effect of reducing the uptake of other ions such as Zn²⁺. Most plants can be mycorrhizal (83% of dicotyledonous species and 79% of monocotyledonous species) but neither the Chenopodiaceae (spinach, beets and Swiss Chard) nor the Cruciferae (*Brassica oleracea* "the cabbage family", and turnips) are mycorrhizal. However, even in the other species, mycorrhizae will not tend to develop in either highly nutrient-rich environments, or where soils are very dry, saline, waterlogged or severely disturbed (38).

Brassica species do not host AM fungi, so crops following Brassica crops are likely to have low levels of AM colonization/infection and this could result in phosphorus and zinc deficiency in crops on soils of marginal zinc and phosphorus status.

Plants with finely branched root systems, such as cereals and grasses generally do not rely heavily on AM for the absorption of nutrients. However, plants with relatively coarse, poorly branched root systems and few root hairs, such as many of the legumes, may acquire a substantial proportion of their nutrients through AM fungi.

In the northern wheat belt of Australia, crops such as linseed are highly dependent on AM for their supplies of zinc and phosphorus. A reduction in AM inoculum following bare fallows of greater than 12 months has been implicated in poor phosphorus and zinc nutrition and retarded growth of following crops ('Long Fallow Disorder'). Low AM colonization can also result from severe drought or high rates of soluble phosphatic fertilisers.

Mechanisms (ii) and (iii) are not relevant to soil conditions, but apply to solution culture. The final mechanism (iv) has several possible ways in which zinc could be adsorbed and these include hydrous oxides of iron and aluminium and changing soil pH.

The situations in which phosphorus directly inhibits zinc absorption are difficult to substantiate. Loneragan and Webb (73) considered the evidence of several authors to be unacceptable due to poor design of experiments. Once in the plant there are several possible mechanisms by which phosphorus can affect the mobility and availability of zinc. These include:

- ❖ Inhibition of translocation of zinc from roots to shoots,
- ❖ Reduction in the amount of soluble zinc,
- ❖ Binding of zinc by phosphorus-containing phytate,
- ❖ Leakage of phosphorus from membranes.

The theory that the translocation of zinc from roots to shoots is inhibited by excess phosphorus is considered by Loneragan and Webb (73) not to be supported by experimental evidence. However, it has been shown for

many different crop types that, under conditions of high zinc supply, phosphorus may immobilize zinc in the roots through the formation of zinc phytate, but this is probably not relevant to zinc deficiency.

In situations where phosphorus induces the symptoms of zinc deficiency without bringing about a decrease in zinc concentrations, it is considered that the increasing phosphorus concentrations within the plant increase the plant's internal zinc requirement (a "phosphorus-enhanced zinc requirement").

In some circumstances, applications of phosphatic fertilisers can bring about an increase in zinc concentrations in plants. These can be explained by an increase in acidity in the root environment (and enhanced uptake of zinc) or to zinc impurities in the phosphatic fertiliser. Commercial fertilisers, such as superphosphate can contain appreciable amounts of zinc (and cadmium) and also acidify the soil due to their high sulphate (SO_4^{2-}) content.

Many workers have used phosphorus/zinc (P/Zn) ratios for the diagnosis of zinc deficiency, but in general, they have not been widely applicable. These ratios can vary for species and experimental conditions. Marschner and Schropp (75) found critical P/Zn ratios to be around 150 for grape leaves in soil, but the critical ratio in solution culture was in excess of 1000 for the same plant varieties.

It is widely recognized that zinc deficiency can enhance phosphorus toxicity in plant shoots. This has been reported in subterranean clover, potato, okra (*Abelmoschus esculentus*), cotton and wheat (73). In these cases, it was the phosphorus concentration in leaves which was correlated with the symptoms, but not always the zinc content.

The accumulation of high concentrations of phosphorus at low levels of zinc is considered to be responsible for the "phosphorus-enhanced zinc requirement syndrome". In some crops such as potato, okra and cotton, low zinc combined with high phosphorus supplies induced phosphorus toxicity by enhancing phosphate uptake into the plant, causing phosphate to accumulate preferentially in the leaves, probably by reducing the translocation of phosphorus out of the leaves. However, in wheat, the main effects seem to be the accumulation of phosphorus in older leaves by inhibiting phosphorus export (73).

In wetland rice, Neue and Marmaril (76) reported that phosphate application depressed the availability of zinc more with regard to native zinc in the soil than to newly applied fertiliser zinc and considered that organic metal-phosphate complexes were formed.

2.3.3.3.2 Inactivation of Plant Zinc by High Phosphorus

Loneragan and Webb (73) considered that there was compelling evidence for the precipitation of zinc by high phosphorus in plants to be the primary mechanism responsible for the syndrome of zinc deficiency leading to the formation of phosphorus toxicity.

In cotton, increased phosphorus supply enhanced the symptoms of zinc deficiency in leaves but had no effect on their total zinc concentrations. However, the fraction of zinc extracted by water from the plant tissues was reduced (51). At all levels of zinc supply, increasing the supply of phosphorus decreased the proportion of zinc extracted from the roots, stems and leaves from around 60% to nearly 30%. The concentration of water soluble zinc in leaves was closely correlated with visual zinc deficiency symptoms and the levels of chlorophyll, superoxide dismutase (SOD) and membrane permeability.

Loneragan and Webb (73) considered that the "phosphorus-enhanced zinc requirement" syndrome has only been reported from experiments with sand and solution culture where high levels of phosphate were used and has not been reported with the much lower solution concentrations of phosphorus found in soils. Likewise, the very high phosphorus concentrations in experimental plants associated with zinc deficiency are seldom encountered in crop plants. They therefore considered that 'phosphorus-enhanced zinc requirements' are merely an artifact of glasshouse experimentation and of little relevance to crop production.

Work by Huang *et al.* (77) has revealed another explanation for the apparent association between high concentrations of phosphorus in plants and zinc deficiency. It would appear that zinc plays a key role in the signal transduction pathway responsible for the regulation of phosphorus uptake. Huang *et al.* (77) showed that the expression of the genes that encode phosphorus-transporter proteins is tightly controlled but dependent upon the phosphorus

and zinc status of the plant. Under conditions of zinc deficiency the control of the expression of the high-affinity phosphorus transporter proteins breaks down and causes the accumulation of very high concentrations of phosphorus in the plant.

2.3.3.3.3 Zinc-Nitrogen Interactions

Nitrogen appears to affect the zinc status of crops by both promoting plant growth and by changing the pH of the root environment. In many soils, nitrogen is the chief factor limiting growth and yield and therefore, not surprisingly, improvements in yield have been found through positive interactions by applying nitrogen and zinc fertilisers. For example, crops often respond to zinc and nitrogen together but not to zinc alone. The application of nitrogen in the absence of zinc can lead to zinc deficiency through a dilution effect brought about by an increase in growth due to the nitrogen. However, this can also result in a negative interaction if other micronutrients, such as copper are also of marginal status in the soil. Nitrogen promoted growth can cause a dilution in copper concentration which is then exacerbated by applied zinc. This problem is really a zinc-copper interaction exacerbated by nitrogen (72).

Nitrogen fertilisers such as ammonium sulphate ($(\text{NH}_4)_2\text{SO}_4$) can have a marked acidifying effect on soils and so lead to an increase in the availability of zinc to crops in soils of relatively high pH status. Conversely, nitro-chalk ($\text{Ca}(\text{NO}_3)_2$) can increase the soil pH and reduce zinc availability.

2.3.3.3.4 Interactions of Zinc with other Macronutrients

Several macronutrient elements, including calcium, magnesium, potassium and sodium are known to inhibit the absorption of zinc by plant roots in solution culture experiments, but in soils their main effect seems to be through their influence on soil pH. For example, applications of gypsum (CaSO_4) which decreased the soil pH from 5.8 to 4.6 increased the zinc content of plants, but the equivalent amount of calcium applied as calcium carbonate (CaCO_3), which increased the pH from 5.7 to 6.6, decreased the zinc content of plants.

Potassium and magnesium have been shown to inhibit zinc absorption in solutions with low levels of calcium, but once the calcium concentration was increased, the effects disappeared. In the dry season, rice in the Philippines has been found to respond to zinc combined with potassium at some sites, but only responses to potassium were found in the wet season.

On clay-rich, calcareous alluvial soils in France, maize was found to respond to applications of both zinc and potassium with a significant response to zinc at all levels of potassium (78). It is possible that an interaction between zinc and potassium may involve leaky plasma membranes in the roots of potassium-deficient plants.

2.3.3.3.5 Interactions of Zinc with other Micronutrients

Zinc is known to interact with copper, iron, manganese and boron.

- a) Zinc-copper interactions can occur through:
- Competitive inhibition of absorption (due to copper and zinc sharing a common site for root absorption),
 - Copper nutrition affects the redistribution of zinc within plants.

Where soils are marginal or deficient in either element, application of the other will exacerbate the deficiency in the plant.

In copper deficient plants, the senescence of the oldest leaves and the export from them of nitrogen, copper and zinc was delayed compared with plants with adequate copper.

- b) Iron-zinc interactions appear to be just as complex as those between zinc and phosphorus, but they have not attracted so much attention. Increasing zinc supplies to plants have been observed to increase the iron status, to decrease it, and to have no effect on it (73).

In experiments, low concentrations of iron in solution (10 μM Fe) had no effect on zinc absorption by wheat seedlings. Where high concentrations of iron in solution (100 μM Fe) were used (such as would be found in rice

paddy soils), iron completely suppressed zinc absorption by rice seedlings from solutions of 0.05 μM ZnCl_2 and no calcium.

Under conditions of iron deficiency, zinc absorption into plants and zinc concentrations in shoots can be considerably increased. In dicotyledons, the mechanism involved is probably that of acidification of the rhizosphere resulting from a Strategy I reaction to iron deficiency. In cereals, phytosiderophores released in the Strategy II reaction to iron deficiency have been found to enhance the mobilisation of zinc from a calcareous soil. However, these phytosiderophores did not enhance zinc absorption into the root in the same way as they did for iron. The effects of these mechanisms on zinc absorption would be additional to any effect iron might have in directly inhibiting zinc absorption.

Zinc deficiency increases iron concentrations in the shoots of both Strategy I (sugar beet and navy beans) and Strategy II (maize) plants, possibly due to mechanisms involving acidification of the rhizosphere and release of reductants and phytosiderophores.

In both zinc and iron deficiency, nutrient solutions containing nitrate-N became acidified and this could be due to the increased release of reducing agents and other exudates from the roots.

Brown (79) showed that in navy beans, reduction of Fe^{3+} to Fe^{2+} was enhanced by zinc deficiency and that the effect was greater in a zinc-inefficient variety (cv Sanilac) than in a zinc-efficient variety (cv Saginaw). Later work confirmed that the zinc-inefficient variety secreted more reductant than the efficient variety under conditions of zinc deficiency stress.

Root exudates from zinc deficient plants have been shown to be capable of mobilizing more iron from Fe^{2+} hydroxides than the exudates from zinc adequate plants.

Experiments with watercress have shown that high levels of zinc have resulted in the retention of iron in stems and roots, probably due to a competitive inhibition at the site of unloading from the xylem. High manganese in combination with high iron may inhibit the absorption of zinc by rice in flooded soils and enhance zinc deficiency in rice.

Zinc-deficient plants can absorb high concentrations of boron in a similar way to zinc deficiency enhancing phosphorus toxicity in crops and this is probably due to impaired membrane function in the root.

2.3.3.4 The Role of the Rhizosphere in the Supply of Zinc to Plants

Much of this section is based on a review (unpublished) by Holloway (47). The rhizosphere is the zone around the plant root surface which is characterized by a high concentration of plant exudates and lysates and intense microbial activity.

Metal ions, such as zinc, reach the rhizosphere by both mass flow and diffusion. Zinc concentrations in soil solutions are generally too low to supply the plant's requirements and so diffusion within the rhizosphere is likely to be the main mechanism for supplying the plant with zinc. The concentrations of zinc found in soil solution are in the order 3×10^{-8} to 5×10^{-7} M and are highly dependent on soil pH. However, concentrations in the rooting depth have been found to vary with season; for example one report showed the zinc in solution increasing from 5×10^{-8} M in spring to 2×10^{-7} M in summer (78). Concentrations of zinc in the soil solution are likely to be at their lowest in calcareous soils.

Marschner (74) estimated that about 2 mg of zinc would be supplied by mass flow from a soil with a bulk solution zinc concentration of 10^{-7} M, but with a plant requiring 10-30 mg Zn kg^{-1} (dry weight), much more zinc was going to be obtained by diffusion. In soils with particularly low zinc concentrations, such as calcareous soils where the bulk solution concentration of zinc is about 10^{-8} M, diffusion is going to be even more important in supplying an adequate amount of zinc. Marschner (74) considered that about 10% of the soil in the rooting zone could be expected to supply zinc to the roots by diffusion where the average root densities were 2-4 cm cm^{-3} .

However, diffusion of metal ions can be affected by sorption reactions and increasing pH has been shown to reduce the diffusion coefficient for zinc due to a lower concentration of zinc in solution. Diffusion coefficients for zinc in calcareous soils can be around 50 times lower than in acid soils. However, increasing soil organic matter contents can result in increased diffusion coefficients

due to desorption of zinc from solid surfaces by organic complexation ⁽⁴⁷⁾.

The soil in the vicinity of the plant roots (rhizosphere) is the major source of zinc for plant growth and therefore any changes in the chemistry of this zone are likely to have a marked effect on the availability of zinc (and other ions) to plants. Perhaps most important of these changes is the pH status of the rhizosphere. The pH of the rhizosphere will change according to the plant's response to an imbalance of cation or anion uptake ratios due to the secretion of H⁺ or OH⁻ or HCO₃⁻ to maintain neutrality of charge at the root surface. For example, nitrogen absorbed as NO₃⁻ will give rise to a secretion of HCO₃⁻ and the pH will rise, whereas when absorbed as NH₄⁺ the pH will decrease due to the excretion of H⁺. Marschner ⁽⁸⁰⁾ found a pH decrease from 6.8 to 5.4 in the rhizosphere of beans growing on a Luvisol with NH₄⁺ and an increase from pH 6.8 to 7.4 with NO₃⁻. Zinc concentrations in the shoots of the NO₃⁻ plants were 34 mg Zn kg⁻¹ and 49 mg Zn kg⁻¹ in those with NH₄⁺ supplied nitrogen.

Riley and Barber ⁽⁸¹⁾ showed that the rhizosphere pH could vary by as much as 2 pH units from that of the bulk soil. The ability of plant roots to modify the rhizosphere pH can vary between plant species and varieties and is also affected by the buffering capacity of the soil.

Some plants are able to mobilize zinc from zinc-deficient sandy soil (e.g. *Brassica juncea* 'Indian Mustard') but this does not benefit a following wheat crop. However, wheat grown after a crop of peas (*Pisum sativum*) had access to more available zinc than crops grown after *Medicago truncatula* ⁽⁴⁷⁾.

2.3.3.4.1 Proteoid Roots

Holloway ⁽⁴⁵⁾ considered that the formation of proteoid roots in response to phosphorus deficiency in some species could be important in zinc nutrition. Proteoid roots comprise clusters of dense root branchlets about 5-10 mm long supporting a profusion of root hairs and thus providing a much increased root area. These proteoid roots appear to be related to the excretion of relatively large amounts of citric acid, which has a significant effect on acidifying the rhizosphere. It has been observed that the proteoid rhizosphere of White Lupin (*Lupinus alba*)

showed a pH of 4.8 in a soil with a pH of 7.8 and 20% free CaCO₃.

A six-fold increase in DTPA-extractable zinc was found in the rhizosphere of proteoid roots by Dinkerlaker *et al.* ⁽⁸²⁾ and this is probably mainly due to the lowered pH.

2.3.3.4.2 Responses of the Rhizosphere to Iron and Zinc Deficiency

Some plant species, especially those of the Poaceae Family (the grasses) respond to iron deficiency by releasing non-protein amino acids called phytosiderophores. The exudates, which are capable of chelating Fe³⁺, include: avenic acid from oats, 2"-deoxymugineic acid from wheat, and mugineic acid from rye and barley. Rice does not appear to secrete mugineic acid and only appears to be able to absorb iron above pH 6. Takagi *et al.* ⁽⁸³⁾ showed that the addition of synthetic chelates such as EDTA and DTPA and organic acids including malic and citric acids do not appear to affect the uptake of iron by rice. However, the addition of mugineic acid was able to reverse the effects of iron deficiency.

There appears to be some uncertainty about whether the phytosiderophore molecules are specific for iron or whether they can mobilize and transport other divalent cations, including zinc. Kochian ⁽⁵³⁾ proposed that zinc may be absorbed across root cell plasma membranes as Zn²⁺, or as a Zn-phyto-siderophore complex transported into the cell by a transport protein. Phytosiderophores are able to complex zinc, copper and manganese, and for zinc they appear to be as effective as DTPA in mobilizing zinc from a calcareous soil with 15% CaCO₃. Because of the ability of phytosiderophores to complex metals other than iron, it has been suggested that they should be more correctly referred to as 'phytometallophores'.

Treeby *et al.* ⁽⁸⁴⁾ showed that phytosiderophores (from iron deficient barley plants) and DTPA (both at concentrations of 10⁻⁵ M) extracted similar amounts of zinc from a calcareous soil. However, these phytosiderophores extracted around twice as much iron, but only about a third as much copper as the DTPA.

In view of the importance of the rhizosphere in supplying the plant's zinc requirements, any changes in the physico-chemical conditions in the rhizosphere are likely to be

important. Therefore the effect of cation/anion imbalances can lead to changes in pH and the release of organic acids can lead to acidification. These pH effects as well as the loss of membrane integrity in zinc deficient plants and associated leakage of ions from roots can all have important effects.

2.3.3.4.3 Effect of the Zinc Status of Plants on their Susceptibility to Disease

In 1983, Graham reviewed the evidence for linkages between zinc nutrient stress and plant disease ⁽⁸⁵⁾. In general terms, he concluded the role of zinc in defence mechanisms of higher plants against disease organisms was far from clear. There were several reports of zinc mitigating the symptoms of viral infections without eliminating the viral particles from the plant. In some cases, added zinc appeared to be helping the plant overcome a virus-induced zinc deficiency ⁽⁸⁵⁾.

However, later work by members of Graham's research group has shown more significant links between the zinc status of certain cereal and legume species and their susceptibility to certain diseases.

Grewal *et al.* ⁽⁸⁶⁾ showed that zinc-efficient wheat genotypes were less susceptible to crown rot disease in wheat caused by *Fusarium graminearum* in soils with low zinc concentrations. They suggested that growing zinc-efficient genotypes and the judicious use of zinc fertiliser was a feasible way of sustaining wheat production in areas where crown rot was a problem.

It has also been found that the concentration of zinc in the shoots of *Medicago truncatula* was inversely related to the severity of root-rot disease caused by *Rhizoctonia solani* ⁽⁵⁶⁾. In wheat also, *Rhizoctonia* root rot was found to be lower in wheat plants with higher zinc contents ⁽⁸⁷⁾.

2.4 Causes of Zinc Deficiency in Crops

Lindsay ⁽²⁸⁾ listed nine major factors affecting zinc availability (and hence likely to be related to deficiency) which included:

1) Soils of Low Zinc Content: Sandy soils, peat and muck soils with low total zinc contents (10-30 mg Zn kg⁻¹) are highly likely to cause zinc deficiency in crops. Sillanpää ⁽⁸⁸⁾ referred to deficiencies from this cause as 'primary deficiencies'.

2) Soil with Restricted Root Zones: Restrictions to root penetration, such as those due to compaction by tractor wheels, plough pans and high water tables.

3) Calcareous Soils: Calcareous soils, generally with a pH > 7.4 have relatively low available zinc concentrations because the solubility of zinc decreases with increasing pH. Very often the total zinc content of calcareous soils is similar to those in soils of other types, or even higher, but the availability is low. Adsorption of zinc onto the CaCO₃ is also a contributory factor. Sillanpää ⁽⁸⁸⁾ uses the term 'secondary deficiency' for situations resulting in the low availability of zinc; these are sometimes also called 'induced deficiencies' by others.

4) Soils Low in Organic Matter: These soils are unable to retain very much zinc and hence tend to be more prone to deficiencies. In the USA one of the most frequent locations of zinc deficiency problems in crops is where surface soil has been removed as part of levelling of fields. The underlying soil has a lower organic matter content than the topsoil and, in many cases, the subsoil also has a higher pH. Several workers have shown a positive correlation between extractable zinc and organic matter content. Both the DTPA extractable zinc and organic matter content decrease with depth in the soil profile. In cases where soil has been disturbed and subsoil brought up to the surface, such as in drainage operations, zinc deficiency is also more likely to occur.

5) Microbially Inactivated Zinc: It has been found that zinc-sensitive crops, such as maize can show increased deficiency problems when following certain crops, such as sugar beet (*Beta vulgaris*). This appears to be due to the incorporation of sugar beet leaves into the soil bringing about a reduction in the available zinc concentration. However, this has not been found by all workers and alternative explanations, such as the high phosphate applications normally used with sugar beet could also apply.

6) Cool Soil Temperatures: Zinc deficiencies are often worse during the early growing season due to low temperatures. In Colorado, zinc deficiency problems are often severe during cool wet springs and disappear by mid-July. The explanation for the effects of low temperatures are that they are due to poorly developed root systems and reduced microbial decomposition of organic matter which would release zinc to the new crop. There have been reports of phosphorus-induced zinc deficiency being more severe at low temperatures than at high temperatures. Growth can often be normal in young plants until a cool and wet period when new growth appears chlorotic and sometimes shows an abrupt colour contrast between green and yellow colouration of the leaves.

7) Plant Species and Varieties: Plants differ markedly in their sensitivity/tolerance to zinc deficiency. Intra-specific variations are sometimes as great as inter-specific variations. Several workers have demonstrated that wheat varieties can display a wide range of efficiency of zinc utilization. The most 'zinc-efficient' varieties were able to produce more dry matter and grain under conditions of low available zinc supply than zinc-inefficient varieties.

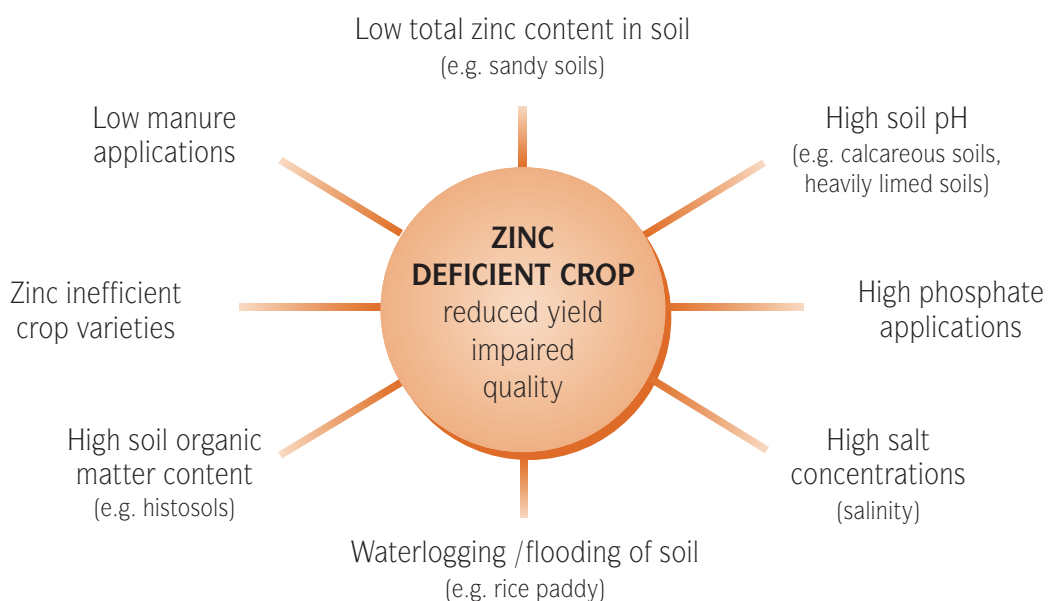
8) High Levels of Available Phosphorus: The mechanism responsible for this antagonism is not fully understood. Phosphorus could affect either the uptake of zinc through the roots and/or the translocation of zinc within the plant. An excess of phosphorus can interfere with the metabolic functions of zinc. High levels of phosphorus can also lead to a reduction in vesicular arbuscular mycorrhizal infection and this could reduce the absorbing area of the roots.

9) Effect of Nitrogen: Nitrogen can affect zinc availability in two possible ways. Firstly, increased protein formation following nitrogen fertiliser additions can lead to zinc being retained in the root as a zinc-protein complex and not translocated around the plant. Secondly, acidifying nitrogen fertilisers, such as ammonium nitrate and ammonium sulphate can lead to a decrease in soil pH and an increase in zinc availability.

As a 'rule of thumb', the soils most commonly associated with zinc deficiency problems frequently have one or more of the following characteristics:

Figure 2.6

Schematic Diagram of the Causes of Zinc Deficiency in Crops



Alloway 2008

- ❖ Neutral to alkaline in reaction (especially pH > 7.4, but can occur at pH > 6.5),
- ❖ High phosphate status,
- ❖ Sandy (coarse texture) with low organic matter content,
- ❖ Acid soil of low total zinc status developed on highly weathered parent material,
- ❖ Calcareous, or calcareous subsoils exposed by levelling/topsoil removal,
- ❖ Peat and mucks (with low total zinc contents),
- ❖ Permanently wet (waterlogged) under paddy rice,
- ❖ High bicarbonate and/or magnesium in soil or in irrigation water.

Figure 2.6 summarises the causes of zinc deficiency in crops.

2.5 Zinc Toxicity

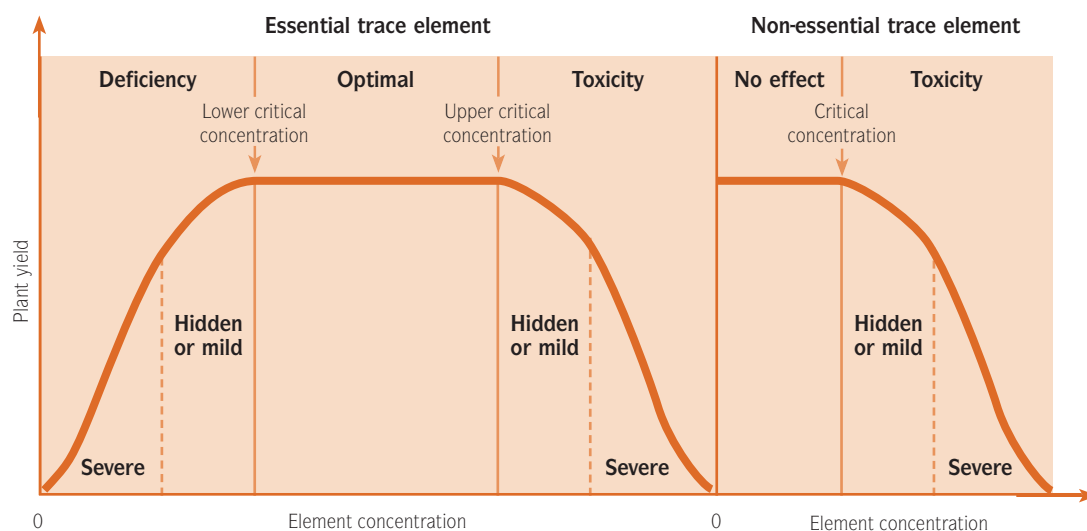
Zinc, in common with the other plant micronutrients, can limit growth when it is present both in low concentrations and also in excessive concentrations, due to deficiency and toxicity, respectively. A typical dose-response curve for micronutrients is shown in Figure 2.7.

High concentrations of available zinc in soils usually arise from various sources of pollution, including: atmospheric deposition from a nearby industrial source, such as a smelting works, flooding of alluvial soils with zinc-polluted river water and sediments, excessive applications of zinc-rich materials, including pig and poultry manures from animals fed additional zinc, and high zinc sewage sludges, or industrial waste waters. However, the accumulation of zinc to potentially toxic levels is unlikely in most agricultural systems.

Although excess zinc can be toxic to plants, just as in the case of zinc deficiency, plants vary widely in their tolerance to zinc toxicity. In general, plants tend to have

Figure 2.7

Typical Dose-Response Curves for Essential and Non-Essential Trace Elements in Crops



Alloway 1995

more advanced homeostatic mechanisms for enabling them to tolerate elevated levels of zinc than soil fauna and microorganisms. The general order of increasing sensitivity to metal toxicity is plants >> soil fauna > microorganisms.

Kabata-Pendias ⁽⁸⁹⁾ listed threshold total zinc values from the literature for zinc in sensitive plant species as 150-200 mg Zn kg⁻¹ and 100-500 mg Zn kg⁻¹ as the range of zinc contents at which the yield of many crops might be reduced by 25% due to toxicity.

With regard to soil fauna, Effroymsen *et al.* ⁽⁹⁰⁾ gave the toxicity threshold for earthworms as 200 mg Zn kg⁻¹. Lock and Janssen ⁽⁹¹⁾ found that the threshold limit value to protect an earthworm species (*Enchytraeus albidus*) could be increased from 169 mg Zn kg⁻¹ to 530 mg Zn kg⁻¹ when the pH of the soil was raised from 4 to 7 by liming.

Soil microorganisms are generally the most sensitive to toxicity of zinc and other metal ions. Saviozzi *et al.* ⁽⁹²⁾ advocated the concept of 'metal equivalents' in which the relative toxicity of several metals to microbial respiration was weighted to that of the least toxic metal, which was manganese (Mn). The Mn equivalent = Mn + 1.9Pb + 2.1Ni + 2.5Zn + 6.7Cd + 6.7Cu. This shows that zinc is much less toxic to microorganisms than either cadmium (Cd) or copper (Cu).

Perhaps one of the most sensitive microorganisms to zinc toxicity is the nitrogen-fixing bacterium *Rhizobium leguminosarum* which forms nodules in the roots of clover and its activity directly affects the growth of clover. Experiments at Rothamsted Experimental Station in England and at a research station at Braunschweig in Germany have shown a toxic response to zinc in the *Rhizobium* strain in the roots of white clover (*Rhizobium leguminosarum*, bv. *trifolii*). This toxicity occurred in soils which had received heavy applications of sewage sludge with high concentrations of zinc and had total concentrations of 250 mg Zn kg⁻¹, with a soil pH of 6-7. It was shown that the LOEC (Lowest Observed Effect

Concentration) for *R. leguminosarum* was 90 mg Zn kg⁻¹ and the median toxicity (HC₅₀ value) was 230 mg Zn kg⁻¹ ^(93,94). This microbial susceptibility to zinc toxicity is important because in pasture soils with elevated zinc levels the herbage is not likely to be affected by zinc toxicity, but it is more likely to be affected by nitrogen deficiency due to the failure of nitrogen-fixing rhizobia. Although this can be overcome by the use of nitrogen fertilisers, it is important to ensure that zinc levels in agricultural soils do not accumulate to relatively high levels. Therefore, soils receiving pig and poultry manures should be monitored in addition to the statutory monitoring of soils used for the recycling of sewage sludge. In the light of this and other evidence from soil microbiology, it was recommended that the maximum permissible zinc concentration in soils receiving sewage sludge in the UK should be reduced from 300 mg Zn kg⁻¹, the European Commission limit (86/278/EEC), to 200 mg Zn kg⁻¹ ⁽⁹⁵⁾.

A predicted non-effect concentration (PNEC) of 90 mg Zn kg⁻¹ was used in a recent environmental risk assessment of zinc and zinc products for the European Commission ⁽⁹⁶⁾. This was based on an added PNEC of 26 mg Zn kg⁻¹ derived from the statistical extrapolation of a large amount of toxicological data with an in-built conservative 'assessment factor', plus the background zinc concentration (Predicted Environmental Concentration-PEC) of 64 mg Zn kg⁻¹. The PNEC value of 90 mg Zn kg⁻¹ derived for European countries is quite close to the threshold value of 100 mg Zn kg⁻¹ given for soil microbes and microbial processes in the USA by Effroymsen *et al.* ⁽⁹⁰⁾.

The maximum zinc concentrations permitted in sewage sludge amended soils (pH 6-7) for various European countries are:

UK	200 mg Zn kg ⁻¹ ,
Denmark	100 mg Zn kg ⁻¹ ,
Germany	200 mg Zn kg ⁻¹ ,
France	300 mg Zn kg ⁻¹ ,
Italy	300 mg Zn kg ⁻¹ ,
Spain	150 mg Zn kg ⁻¹ ⁽⁹⁷⁾ .

In the USA, the USEPA Part 503 regulations gave a maximum zinc concentration in sludge-amended soils of 1400 mg Zn kg⁻¹ (97). This US figure was based on quantified risk assessment, whereas the European values are based mainly on the precautionary principle.

For other situations, apart from soils amended with sewage sludge, various indicative and guideline values have been given for a maximum zinc concentration in soils, above which zinc toxicity problems could be expected. These include: 100-400 mg Zn kg⁻¹ (7) and 100-900 mg Zn kg⁻¹ for a 10% reduction in growth (98). In the Netherlands, a Target Value for zinc in soils was given as 140 mg Zn kg⁻¹, but the intervention level at which a soil must be cleaned-up was 3000 mg Zn kg⁻¹ (99). The Netherlands' values are mainly directed at the redevelopment (clean-up) of contaminated land and not normal agricultural land which would be unlikely to have such high zinc concentrations.

In general, very high concentrations of zinc, such as > 500 mg Zn kg⁻¹ could cause some problems with yields, but it is unlikely that agricultural crops would be grown on significant areas of soils with such high concentrations. Elevated concentrations of zinc in crops probably do not constitute a toxicity hazard to humans or livestock consuming them but, it is often found that soils contaminated with zinc are also contaminated with non-essential trace elements including, cadmium and lead. High concentrations of cadmium and other non-essential elements in plant foodstuffs could pose a possible health risk to regular consumers. However, it is sometimes found that zinc and cadmium are antagonistic to each other and that a relatively high concentration of zinc in soil could help to reduce the cadmium content in crops. This is illustrated by experiments carried out in Manitoba, Canada, by Choudhary *et al.* (100) with two cultivars of durum wheat (*Triticum durum* Desf.) known to accumulate relatively larger amounts of cadmium than bread wheat (*Triticum aestivum* L.). It was found that soil-applied zinc decreased cadmium concentrations in durum wheat grain, leaf, stem and root. The foliar application increased the zinc content of leaves and stems but had little effect on plant

cadmium concentration. Nitrogen and phosphorus fertilisers increased tissue cadmium concentrations and reduced zinc contents to near deficiency levels. When zinc was applied with nitrogen and phosphorus fertilisers, the zinc tissue contents increased to a sufficiency level and cadmium concentrations decreased.

The EC risk assessment quoted data from a study by the Alterra Research Institute (Netherlands) on the average periods of time for soils to reach the critical limits for zinc. These ranged from 275 years in loess soils, to 641 years in clay soils in grassland and 550 years for sandy arable soils and up to 1205 years for clay arable soils (96). It was concluded that in the light of the model predictions, there was no need to implement risk reduction measures beyond those that were already in place in Europe and that there were therefore no existing risks from zinc and zinc compounds in agricultural soils in Europe (96).

Although zinc toxicity in crops and soil organisms is possible, it is not likely to be important in most agricultural land anywhere in the world. Apart from areas polluted by industry and fields receiving excessive applications of zinc-rich sludges and manures, or zinc-containing veterinary pharmaceuticals, most soils will mainly have zinc concentrations either within the normal background range or deficient levels of zinc. Nevertheless, it is important to ensure that deficient soils are not over-fertilised with zinc compounds and become possible toxicity problems. The normal rates of application of zinc to deficient soils are in the range 5-34 kg Zn ha⁻¹ with several years between applications and these have been found from long experience to be safe (See Chapter 5, Zinc Fertilisers).

2.6 Zinc in Crop Products and Human Nutrition

Zinc is an essential trace element for animals and humans as well as plants and therefore an adequate zinc intake is essential for their normal healthy growth and reproduction ^(101,102) (See table 2.4).

Zinc is known to bind to 925 different proteins in humans ⁽¹⁰³⁾ and there are more than 300 enzymes involved in key metabolic processes in humans which contain zinc. As a result of this very wide involvement of zinc in human metabolism, zinc deficiency can have many different effects on human health and development. These include: physical growth, the functioning of the immune system, reproductive health, neurobehavioural

development and many others which may not always be recognised as being associated with zinc deficiency. In fact Graham ⁽¹⁰³⁾ considers zinc deficiency in humans to be the ultimate hidden hunger. The International Zinc Nutrition Consultative Group (IZiNCG) has estimated that zinc deficiency affects as many as one third of the world's population, with incidence varying between 4% and 73% in different countries ⁽¹⁰²⁾. In order to treat and prevent zinc deficiency in humans, five different intervention strategies can be used. These include: supplementation using zinc compounds as medicines, food fortification through the incorporation of zinc additives in prepared foods, dietary modification and the enrichment of crop products, such as grains with zinc in various ways (biofortification) ⁽¹⁰²⁾.

Table 2.4

Revised Recommended Dietary Allowances (RDAs) for zinc by life stage, and diet type as suggested by IZiNCG ⁽¹⁰²⁾

Revisions suggested by IZiNCG for RDA for zinc (mg day⁻¹)

Age	Sex	Reference body Weight (kg)	Mixed or refined Vegetarian diets	Unrefined cereal-based diets
6-11 months	M + F	9	4	5
1-3 years	M + F	12	3	3
4-8 years	M + F	21	4	5
9-13 years	M + F	38	6	9
14-18 years	M	64	10	14
14-18 years	F	56	9	11
Pregnancy	F	-	11	15
Lactation	F	-	10	11
> 19 years	M	65	13	19
> 19 years	F	55	8	9
Pregnancy	F	-	10	13
Lactation	F	-	9	10

M = male, F = female

Many food products are derived directly from plants, including staples such as rice, wheat, maize and sorghum, but the zinc content of animal food products can also be affected by the soil-plant relationships of zinc. Zinc-deficient plants generally have low tissue zinc concentrations and therefore, in addition to reduced crop yields, the crop products from these deficient plants make a lower contribution to the zinc content of the human diet. This can be vitally important in subsistence rural economies where there is often insufficient diversity in the diet to enable low concentrations of zinc in one component of the diet to be compensated for by a higher zinc content in another. For example, lean meat, whole grain cereals and pulses generally contain the highest concentrations of zinc (20-50 mg Zn kg⁻¹ fresh weight) (See Table 2.5) ⁽¹⁰²⁾.

However, taking meat as an example, many people in developing countries either do not have access to a sufficient supply of meat, or their social and religious customs do not permit them to eat it, so this significant source of zinc in the diet is often not available to many people.

Cereal-based diets are the major source of energy and nutrients for the majority of the world's population and therefore both the zinc content of the cereal grains and its bioavailability to consumers are of fundamental importance. All cereal grains and pulses contain phytate (inositol hexaphosphate) which combines with zinc and reduces its absorption from the gastrointestinal tract of humans and other monogastric animals. Phytate, containing large amounts of phosphate, is present in

Table 2.5

**Availability of Zinc from Different Types of Diets
(from FAO/WHO/IAEA, 2002) ⁽¹⁰¹⁾**

Availability of Zinc	Type of Diet
High	Refined diets low in fibre, low in phytate (phytate:zinc molar ratio < 5), adequate protein mainly from non-vegetable sources.
Moderate	Mixed diets containing animal or fish protein, lacto-ovo, ovovegetarian diets not based primarily on unrefined cereal grains or high extraction flours. Phytate: zinc molar ratios 5-15 or not exceeding 10 if more than 50% of energy is from unfermented, unrefined cereal grains and flours. Availability of zinc improves when the diet contains animal protein sources or milk.
Low	Diets high in unrefined, unfermented, and ungerminated cereal grain, especially when fortified with calcium salts and intake of animal protein is negligible. Phytate:zinc molar ratio is >15. Diets in which 50% of the energy is in high phytate foods including: high extraction rate flours of wheat, rice, maize, grain and flours, oatmeal and millet, chapatti flours and tanok, sorghum, cowpeas, pigeon peas, grams, kidney beans, blackeye beans, and groundnut flours, and high intakes of inorganic calcium salts.

higher concentrations in cereal grains that have been grown on soils with a relatively high phosphorus status ⁽¹⁰¹⁾. The use of increased amounts of phosphatic fertilisers on crops of modern, high yielding varieties of rice and wheat can increase yields when the zinc supply is adequate, but produce grain which may have a lower percentage of available zinc due to the higher phytate content. However, where the zinc status of the soil is marginal or inadequate, the increased phosphorus supply can induce zinc deficiency in the crop and, if not corrected, result in a reduced yield of grain with a lower total zinc content as well as an elevated phytate content and hence there will be proportionally less zinc available to the consumer. Phytate contents are highest in wheat bran (3011 mg/ 100g), whole grain cereals (800 mg/100g) and lowest in rice (125 mg/100g in white rice, 262 mg/100g in brown rice). Maize also has relatively low contents of phytate (263 mg/100g in maize bran) ⁽¹⁰²⁾. Reduced availability of zinc from this cause is likely to be a greater problem with diets containing a high proportion of wheat.

Phytate will significantly reduce the availability of zinc where the phytate:zinc molar ratio is greater than 15. Alternatively, calcium x phytate:zinc ratios are also used and where this ratio is greater than 150 nmol per 1000 kcal, zinc in the diet will be highly unavailable. The latter value takes account of the antagonistic effect of calcium as well as phytate on the availability of zinc in food products ⁽¹⁰¹⁾. This is also very important because calcareous soils are widely used for growing wheat in some developing countries, especially those with Mediterranean-type climates, such as West Asia (also called the Near East). These calcareous, high pH soils (as discussed in section 2.2.1) are also an important cause of zinc deficiency in crops. Both the high calcium and low zinc contents in the grain contribute to the low availability of zinc to consumers. Calcareous soils are also a problem with low availability of phosphorus and so require relatively high applications of phosphatic fertilisers, which exacerbate the low dietary availability problem due to both increased phytate concentrations in grains but also increased zinc deficiency, if not corrected. The effect of phytate is modified by proteins in the diet and animal proteins can improve the absorption of zinc from the diet. This, again, demonstrates the merit of mixed diets with regard to zinc availability, but many people in developing

countries are unable to have a mixed diet containing both cereals and animal proteins.

Phosphorus is a vitally important macronutrient for plants and modern varieties of rice and wheat require an adequate supply of this element in order to realize their potential yield. The adverse effects of high phosphorus in the soil on zinc availability to the plant can be overcome by zinc fertilisation, but the problem of low dietary availability of the zinc is more difficult to overcome. If the concentration of zinc in staple foods, such as cereals can be increased, this will have a major beneficial effect on human dietary zinc intakes.

2.6.1 Biofortification of Cereal Grains and Pulses with Zinc

Biofortification (enrichment of grains and pulses) can be achieved in two different ways; either by plant breeding (genetic biofortification), or by applying zinc fertilisers to seeds, soil and/or foliage, at rates greater than those required for maximum yield, to increase the uptake of zinc into the plants and its translocation into seeds (agronomic biofortification) ⁽¹⁰⁴⁾. Historically, most interventions have involved people taking zinc supplements directly, or the addition of zinc to foods ('food fortification'). However, these approaches are expensive, difficult to administer and, in many cases, they have not been sustainable and have failed to reach all the people at risk of zinc deficiency. In contrast, if the crops themselves are enriched with zinc, the grains and pulses would enter the food chain normally (and either be consumed, or processed etc) and the whole population would benefit. From an agronomic viewpoint, apart from improving dietary intake, zinc-enriched grains generally result in seedlings with increased vigour and greater stress tolerance. Thus, with seedlings having a greater chance of survival and growing to maturity, it is possible to reduce seed rates and, consequently, reduce the cost of cereal production ⁽¹⁰⁴⁾.

2.6.1.1 Genetic Biofortification

Genetic biofortification is being promoted by 'HarvestPlus', which is a global alliance of institutions and scientists seeking to breed new varieties of staple crops which have

increased densities of zinc and other essential human nutrients in their seeds (www.harvestplus.org). In the long run, genetic biofortification, by either crossing strains of crops with the genetic propensity to accumulate zinc in the seed, or genetic modification, to develop new cultivars, appears to be the most sustainable and, ultimately, cost-effective strategy for increasing the zinc intake of people at risk of deficiency.

Welch ⁽¹⁰⁵⁾ stated that wheat genotypes are known to vary widely in zinc contents of the grains they produce (<143 mg Zn kg⁻¹). This, together with the fact that genotypes also differ considerably in the extent to which the zinc in grain is bioavailable to humans (and other monogastric animals, including experimental rats), suggests that it should be possible to select for both zinc density and bioavailability in plant breeding programmes. He briefly reported an experiment involving 28 lines of wheat in which the zinc had been labelled with the radioisotope ⁶⁵Zn and fed to rats. This showed a range of bioavailability from 50% to 210% relative to the reference genotype (cv Grandin) ⁽¹⁰⁶⁾.

According to Cakmak ⁽¹⁰⁴⁾ some wild and primitive wheat genotypes show the capacity to accumulate far higher zinc contents (< 190 mg Zn kg⁻¹) than most of the currently grown wheat varieties. Seeds of wild emmer wheats have been found to have high concentrations of both zinc and iron, as well as high protein contents and the plants are also relatively tolerant to drought stress, which makes them very suitable for inclusion in breeding programmes. Synthetic wheats derived from *Aegilops tauschii* have also been found to have potential for accumulating relatively high zinc concentrations in grain. In addition to the genetic aspects, Cakmak also stresses that any newly developed genotypes would need to be able to take up sufficient zinc from potentially zinc-deficient soils and accumulate this metal in the grain at concentrations of between 40 and 60 mg Zn kg⁻¹. This could possibly limit the usefulness of these new cultivars unless the zinc supply is improved. Cakmak also points out that growing an increasing percentage of high zinc-concentrating cultivars would probably exacerbate the depletion of available zinc in soils of marginal zinc status. It would therefore appear that genetic biofortification will need to be used hand in hand with agronomic biofortification ⁽¹⁰⁵⁾.

2.6.1.2 Agronomic Biofortification

Rengel *et al.* ⁽¹⁰⁷⁾ showed in a greenhouse experiment with one cultivar (cv Excalibur) that concentrations of up to 145 mg Zn kg⁻¹ could be obtained by zinc fertilisation beyond the amount required to give an optimal yield of grain. There is a considerable amount of evidence from Cakmak and others that zinc fertilisation in areas with zinc deficient soils both increases yields and the zinc content of cereal grains in currently available genotypes. However, even if newly bred zinc-enriched varieties are developed, as stated above, in many cases it will be necessary to supply zinc fertilisers in order that these varieties can express their full genetic potential for accumulating zinc in their seeds. Zinc fertilisers and their application are discussed in detail in Chapter 5.

Jiang *et al.* ⁽¹⁰⁸⁾ investigated the uptake and distribution of root and foliar-applied radiolabelled zinc (⁶⁵Zn) in aerobic rice after flowering. They found that in rice plants grown under sufficient or surplus zinc, most of the zinc accumulated in the grains originated from uptake by the roots after flowering and not from remobilisation from the leaves. This suggests that root-applied zinc fertilisers are likely to be more effective for the biofortification of rice grains than foliar sprays.

In a study of five rice genotypes that were known to have either high or low zinc concentrations in grain, Wissuwa *et al.* ⁽¹⁰⁹⁾ reported that native soil zinc status was the dominant factor determining grain zinc concentrations followed by genotype and fertiliser. A single genotype was found to have grain zinc concentrations varying between 8 mg Zn kg⁻¹ and 47 mg Zn kg⁻¹, depending on the zinc status of the soil. Importantly, they found that it was not possible to simply compensate for low available levels of zinc in soils by applying fertiliser. Increases in the total zinc content of the plant of between 50 and 200% were found in response to zinc fertilisers. In zinc deficient soils, this fertiliser zinc improved straw and grain yields, but did not have a significant effect on zinc concentrations in the grain. Genotypic differences in grain zinc concentrations were significant in all except a severely zinc-deficient soil. With genotypic means of 11 to 24 mg Zn kg⁻¹ in the deficient soil and 34-46 mg Zn kg⁻¹ in an upland soil with a relatively high zinc content. They concluded that it was feasible to

develop high zinc cultivars through conventional plant breeding but they thought that it was likely to be more of a challenge to develop cultivars that gave increases in zinc concentrations in grain in response to zinc fertiliser application.

In view of the greater sensitivity of soil microorganisms to zinc toxicity (discussed in Section 2.5) compared with plants and the relatively low PNEC values used to protect these organisms, continued use of zinc fertilisers for agronomic biofortification will have to be monitored carefully. This is because the soil ecosystem is likely to be adversely affected by zinc accumulation long before crop plants such as wheat and rice. Nevertheless, it is fortunate that the treatment of zinc-deficient soils can have the combined effect of increasing yields of cereals and also improving the nutritional quality of the grain.

Cakmak ⁽¹⁰⁴⁾ considers that seed plus foliar application of zinc is most appropriate for agronomic biofortification giving up to four-fold increases in zinc concentrations in grain. The timing of foliar applications is critically important, with applications after the growth stage of 'milk' (Zadoks 70) being more effective for loading zinc into grain. Field experiments with foliar applications of zinc sulphate before and after anthesis showed increased concentrations of zinc in grain of up to 60 mg kg⁻¹. Various forms of zinc are available for foliar application (See Chapter 5) but urea fertiliser containing zinc (zincated urea) was considered to be a good combined nitrogen and zinc fertiliser for foliar application. Rengel ⁽¹⁰⁷⁾ stressed that biofortification of crops with zinc would need to be accompanied by changes in milling practices to maximize its benefits in terms of dietary availability.

Cakmak ⁽¹⁰⁴⁾ states that, in addition to increasing the zinc concentration in seeds, fertilising with zinc also reduces the phytate content of the seed and hence reduces the phytate:zinc ratio. Thus, it not only increases the amount of zinc in the seed, but also makes it more bioavailable to the consumer.

It would appear that either foliar application alone, or a combination of foliar plus soil fertiliser application can have the desired effect of increasing zinc density in wheat grain. However, rice does not appear to show the same

response in grain zinc to soil-applied fertiliser and this will need further investigation. There appears to be encouraging evidence that genotypes of both rice and wheat which accumulate higher concentrations of zinc in grain can be selected for use in plant breeding so genetic biofortification appears to have considerable potential in the long-run and agronomic biofortification appears to be more promising for wheat so far. Cakmak ⁽¹⁰⁴⁾ does not consider that the build-up of zinc to potentially toxic concentrations is likely to be a significant problem under normal agricultural conditions, but he does see the need to monitor the available-zinc status of soils.

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SYMPTOMS OF ZINC DEFICIENCY IN AGRICULTURAL AND HORTICULTURAL CROPS

3.1 Introduction

There are a relatively small number of different types of symptoms which are found to occur in crops suffering from zinc deficiency. These may occur at varying degrees of severity and in various combinations in different plant species. However, the symptoms exhibited by plants suffering deficiencies of certain other essential nutrient elements are, in some cases, similar to those of zinc deficiency and may be confused with those of zinc or be seen together with the zinc deficiency symptoms where multiple micronutrient deficiencies occur.

3.2 Types of Deficiency Symptoms

The main types of visible deficiency symptoms are:

- a) **Chlorosis** - which is the change of leaf colour from the normal green chlorophyll colour to pale green and yellow, or even white, due to the reduced amount, or absence, of chlorophyll. In many cases in zinc-deficient plants, the chlorosis appears between the ribs in monocotyledons (grains and grasses) and between the veins of dicotyledon (broad leaf) plants and this is referred to as interveinal chlorosis.
- b) **Necrotic Spots on Leaves** - these can occur in areas of chlorosis due to the death of the leaf tissue in small concentrated areas but the necrotic spots can grow in size as the plant ages if the deficiency is not treated.
- c) **Bronzing of Leaves** - this symptom is also related to chlorosis and the yellow areas tend to turn bronze coloured.
- d) **Rosetting of Leaves** - occurs when the internodes on the stems of dicotyledon crops fail to elongate normally and so the leaves form close together in a cluster instead of being spread out between nodes in a healthy plant.

This is a very characteristic symptom of zinc deficiency in dicotyledon (broad leaf) crops, including bushes and trees.

e) **Stunting of Plants** - is a consequence of reduced dry matter production giving a smaller plant and/or reduced internode elongation of stems of developing crops.

f) **Dwarf Leaves** (also called "little leaf") - are also fairly characteristic of zinc deficiency and these leaves may also show chlorosis, necrotic spots or bronzing.

g) **Malformed Leaves** - occur, often either narrower, or with wavy edges, instead of straight edges and the leaves may also be distinctly smaller (dwarfed).

In comparison with other macro and micronutrients, the leaf symptoms of zinc deficiency are found on both old and new leaves, whereas symptoms of copper, iron, manganese and sulphur deficiency are found only on new leaves. In contrast, nitrogen, phosphorus, potassium, magnesium and molybdenum deficiency symptoms are found only on old leaves ⁽¹⁾.

3.3 Biochemical and Histological Changes in Zinc-deficient Plants

Zinc deficiency can give rise to both biochemical and histological changes in plants in addition to visible symptoms:

- a) **Biochemical Changes** : Zinc deficiency leads to the accumulation of a large number of free amino acids, amides and ureides owing to impaired protein synthesis. However, impaired protein synthesis can also occur when copper is deficient, so it is not a definitive effect of zinc deficiency. Zinc-deficient plants have increased levels of peroxidase activity, but decreased levels of auxin production. Lipids, tannins and oxalic acid have been found to accumulate in the roots of zinc-deficient maize

and tomatoes, but starch contents in the roots are reduced. Woody plants have shown an accumulation of phenolic compounds under zinc-deficient conditions (2). Semi-quantitative assays for zinc containing enzymes such as carbonic anhydrase, have been suggested as an in-field method for the diagnosis of zinc deficiency, but have not been widely adopted.

b) **Histological Changes:** Zinc-deficient tomato plants show enlarged root tips and crooked root hairs, poorly differentiated meristematic cells due to inhibited cell division; nuclei contain unknown spherical bodies, and organelles including mitochondria and chloroplasts can be deformed. Zinc-deficient cabbages have been shown to have accumulated a yellow viscous substance in the xylem tissue in the roots and this can restrict water transport (2).

3.4 Factors to be Considered When Using Visible Symptoms for Diagnosis

In view of the risk of confusing the symptoms of zinc deficiency with those of deficiencies or even toxicities of other elements, in some circumstances it would be advisable to have plant tissue analysis and/or soil testing carried out to confirm the diagnosis. Some of the factors giving rise to zinc deficiency, such as high soil pH and sandy soils can also cause deficiencies of iron and manganese and these may lead to a mistaken diagnosis, or the plant may be suffering from a deficiency of several elements simultaneously. However, in many areas where zinc deficiency is relatively common or endemic, plant tissue analysis or soil testing may not always be necessary for diagnosis. However, it should be used routinely after the problem has been diagnosed and treated in order to determine when repeat soil or foliar applications of zinc fertilisers are required.

The symptom of chlorosis is relatively common in plants under stress from a number of factors in addition to nutrient deficiencies. It can also be an indicator of phytotoxicity caused by an excess of either an essential element (including zinc and copper), or of a non-essential element (such as cadmium). In most cases the location and history of the site will help to indicate whether a

toxicity situation is likely, but only soil or plant tissue analysis can confirm the diagnosis.

The absence of obvious visible symptoms in crops which fail to produce expected yields cannot be taken as confirmation that zinc deficiency is not the cause of the problem. Sub-clinical (or hidden) deficiency of zinc can reduce the yields of some crops by up to 20% and impair quality without the appearance of distinct symptoms. Farmers sometimes have reluctantly accepted that certain crops do not grow well on certain fields or parts of their land and have not investigated the problem further. However, poor growth could be due to plant disease, poor rooting conditions, low pH and/or nutrient imbalances including zinc deficiency. Soil testing, which can be done at any time, can show the ability of the soil to supply an adequate amount of zinc (and other micronutrients) and is an important aid to managing deficient soils which are treated periodically with zinc fertilisers. The soil analysis data will reveal when an additional soil application of zinc is required. However, in some soils, such as highly calcareous soils in Australia, currently available soil tests are not considered to be a reliable indicator of plant available zinc status (R. Holloway, pers comm.).

In the following section, in addition to the common and botanical names of the crops, an indicative annual yield value is given, based mainly on data for tropical/ sub-tropical areas by Landon (3). These yield values are for commercial farms with near optimum conditions and crop husbandry practices. Subsistence farmers and smallholders in many developing regions are likely to obtain yields which are much lower than this.

Warning - the treatments reported in this chapter are included as a general indication. Treatments will vary for different crops, soils, levels of intensity of farming and environmental conditions. Changes will also be made to recommendations from time to time in the light of new research findings. Readers should therefore consult their local extension agronomists before treating a zinc deficiency problem. Frequent reference is made to 'Zinc in Crop Nutrition', published by ILZRO (4), which gives extensive details of zinc treatment practices in the USA but some of these may have changed in recent years. It is also important to note that both kg Zn and kg of

ZnSO₄ (or other fertiliser compound) are used in the following section and it is important not to confuse the two (ZnSO₄ normally contains about 26% zinc). The subject of zinc fertilisers and their application is dealt with in detail in Chapter 5. The mention of any proprietary products in this section does not imply endorsement of their use.

3.5 Zinc Deficiency Symptoms in Selected Crops

It is interesting to note that there are at least 350,000 botanical species, but less than 30 are used as crops for food and fibre. A selection of both major (widely grown) crops and those grown on a more limited scale are covered in the following section:

3.5.1 Cereal Crops (Food Staples)

3.5.1.1. Rice (*Oryza sativa* L)

(Indicative Annual Yield = 6-8 t ha⁻¹) (see also Chapter 7)

Visible symptoms of zinc deficiency in rice include: wilting due to loss of turgidity in the leaves, basal chlorosis of the leaves, delayed development of the plants, "bronzing" of the leaves and, in some cases, death of the rice seedlings⁽⁵⁾. Neue *et al.*⁽⁶⁾ stated that the common symptoms of zinc deficiency in rice are: the midrib at the base of the youngest leaf of zinc deficient rice becomes



Typical symptoms of interveinal chlorosis in zinc deficient rice plants

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chlorotic 2-4 weeks after sowing or transplanting. Then brown spots appear on older leaves. The spots enlarge, coalesce and give the leaves a brown colour. Zinc-deficient plants show stunted growth and reduced tillering. If the deficiency is not too severe the plants may recover after 4-6 weeks but maturity is delayed and yields of susceptible cultivars are reduced⁽⁶⁾.

In California, it is reported that symptoms of zinc deficiency in rice are usually observed after a flood is established. The most noticeable symptom is the plant's loss of turgidity, where the plant falls over and floats on the surface of the water. The basal leaves become pale green and after 3-7 days the leaves become chlorotic. However, although the symptoms of zinc deficiency in rice are most noticeable after flooding, more subtle symptoms can be observed before flooding. The symptoms do not normally appear in seedling rice until around 10 days after emergence but may possibly take several weeks to appear. These include: basal leaf chlorosis (beginning in the youngest leaf), loss of turgidity in the leaves and floating on the surface, bronzing (red-brown splotches on the surfaces of the oldest leaves, bronzed leaf tissue may eventually turn brown) and stacking of leaf sheaths or joints (leaf collars do not open out)⁽⁷⁾.

It is important to note that visual symptoms of zinc deficiency in rice vary, to a certain extent, with: soil type, cultivar and growth stage. Symptoms can be mistaken for those of deficiencies of nitrogen, magnesium, manganese or iron, or a virus disease called 'tungro'. Sulphur deficiency is often combined with zinc deficiency and it is difficult to distinguish between the symptoms of the two and so plant analysis is required for confirmation.

Treatment: Several alternatives are currently practiced: In the Philippines, it is the normal practice to dip seedlings in 2% zinc oxide solution (2 g ZnO/100 ml water) before transplanting, or broadcast 10-20 kg ZnSO₄ ha⁻¹ into the flooded field after the first irrigation⁽⁸⁾.

In Arkansas the usual treatment is 11.2 kg Zn ha⁻¹ as zinc sulphate or 1.12 kg Zn ha⁻¹ as a Zn-chelate.

In California, farmers are advised to make pre-flood applications of 0.9-7.2 kg Zn ha⁻¹ (2-16 lbs Zn) from whatever the source (usually ZnSO₄·7H₂O). For maximum effectiveness either zinc sulphate, zinc oxide or zinc



Fig. 3.2

Chlorosis and necrotic spots on the leaves of zinc deficient wheat.

Yara-Phosyn

chelate is broadcast or sprayed on the soil surface after the last seedbed tillage. For rice, the zinc treatment should never be incorporated into the soil (9).

Mikkelsen and Brandon (10) recommended broadcasting 9 kg Zn ha⁻¹ as either zinc sulphate or oxide before flooding. In Missouri, when rice growing soils contain less than 1 mg kg⁻¹ DTPA-extractable Zn, 5.6 kg Zn ha⁻¹ is applied. However, experiments have shown that soaking rice in a proprietary zinc compound could be used for water seeded rice production (5). In India, 25 kg ZnSO₄ ha⁻¹ is generally applied at puddling (where the previous crop was shown to exhibit symptoms of deficiency) followed by the same amount again to the current crop if symptoms of zinc deficiency appear again. If the symptoms of zinc deficiency appear even after the application of the recommended dose of zinc sulphate, as in the case of sodic and flood plain soils, 25 kg ZnSO₄ should be applied mixed with an equal amount of dry soil (as a diluent) to the affected area.

3.5.1.2 Wheat (*Triticum aestivum* L - bread wheat, *Triticum durum* Desf - durum wheat)
(Indicative Annual Yield in tropics = 4-6 t ha⁻¹)
(see also Chapter 7)

Durum wheats tend to be more sensitive to zinc deficiency than bread wheats but varieties of both types differ

considerably in their ability to tolerate low levels of available zinc (zinc efficiency).

Zinc deficiency in wheat reduces grain yield and nutritional quality. Symptoms appear first on young leaves as zinc is relatively immobile under conditions of deficiency. Light green to white chlorotic and necrotic streaks developed on either side of the leaf mid-rib are characteristic of mild deficiency in wheat. Where the deficiency is more severe, the lower leaves tend to be totally chlorotic and short, but of normal width. Sometimes they have an oil soaked appearance. As the necrosis proceeds the leaves often collapse in the middle (4). Leaf mid-ribs and margins tend to remain green but, in some cases, leaf edges appear to be tinted red or brown.

The leaves remain small, cup upward and develop interveinal chlorosis. On the upper leaf surface necrotic spots appear which later join each other to form brown necrotic and brittle patches. The necrosis is often more noticeable on middle-aged leaves which eventually wilt, bend and collapse. Zinc deficiency in fields is typically patchy and the symptoms can develop rapidly but depend on the degree of stress.

Treatment of deficiencies with zinc fertilisers or foliar sprays can increase yields and also improve the plant's resistance to 'foot rot' fungus (*F. graminearum*) (12).

Treatment: Application rates of zinc fertilisers vary in different parts of the world. In Australia, wheat and other cereals are normally treated with 0.6-2.4 kg Zn ha⁻¹ on light soils and 1.8-3.9 kg Zn ha⁻¹ on heavier soils (13).



Fig. 3.3

Interveinal chlorosis and necrotic patches on leaves of wheat.

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Various authors recommend applications of zinc sulphate in the range 2.2-11.2 kg Zn ha⁻¹ depending on the soil conditions, crop variety and local agronomic factors.

Recent recommendations for the treatment of zinc deficiency in wheat in India are 50 kg ha⁻¹ zinc sulphate for acute cases and 25 kg ha⁻¹ for moderate deficiencies ⁽¹¹⁾.

3.5.1.3 Maize (*Zea mays* L.) (also called 'Corn')
(Indicative Annual Yield = 6-9 t ha⁻¹)
(see also Chapter 7)

Maize can be grown on a wide variety of soils over a pH range of 5.0-8.0 but pH 6-7 is optimal. Maize has medium salinity tolerance ⁽³⁾.

Symptoms of zinc deficiency in maize appear as a yellow striping of the leaves.

Maize is highly susceptible to zinc deficiency. Areas of leaf near the stalk may develop a general white to yellow chlorosis ('whitebud'). In cases of severe deficiency, the plants are stunted due to shortened internodes and the lower leaves show a reddish or yellowish streak about one third of the way from the leaf margin. Plants growing in dark sandy or organic soils usually show brown or purple nodal tissues when the stalk is split. This is particularly noticeable in the lower nodes ⁽¹⁴⁾.

Treatment:

In India, if symptoms of zinc deficiency were noticed in the preceding maize crop, or where a soil test indicates zinc deficiency, 25 kg ZnSO₄ ha⁻¹ is usually broadcast at sowing. As with rice, if ZnSO₄ is to be applied to a current crop after the appearance of deficiency symptoms, 25 kg ha⁻¹ of zinc sulphate should be applied, mixed with an equal quantity of dry soil as a diluent, along the rows and hoed in before irrigating the field. When the symptoms are observed late in the growing season and inter-row cultivation is not possible, a spray application of neutralized 0.5% ZnSO₄ solution is recommended ⁽¹¹⁾.

In the USA and other areas with more intensive agriculture, zinc treatments for maize range from 2.2 to 34 kg Zn ha⁻¹ broadcast (as zinc sulphate) and 1.1-4.5 kg Zn ha⁻¹ banded (as zinc sulphate) or 0.6-3.3 kg Zn ha⁻¹ banded (as ZnEDTA)⁽¹⁵⁾.

Fig. 3.4



Maize plants showing interveinal chlorosis and "white bud" symptoms.

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3.5.1.4 Barley (*Hordeum vulgare* L.)

With zinc deficiency, the leaves show uniform chlorosis, dry-up and tip growth decreases ⁽⁴⁾.

Treatment: The same as for wheat crops.

3.5.1.5 Sorghum (*Sorghum bicolor* L.)
(Indicative Annual Yield = 3-5 t grain ha⁻¹)

Sorghum, like maize, is highly susceptible to zinc deficiency and the symptoms in grain sorghum are similar to those in maize, but less pronounced. Although not quite so susceptible as maize, zinc deficiency retards development and maturation of the seed heads in sorghum ⁽⁴⁾.

Treatment: Widespread deficiencies of zinc in sorghum growing on cut soils (topsoil removed) in Kansas (USA) have been treated with zinc sulphate at the rate of 11.2-16.8 kg Zn ha⁻¹ (10-15 lb Zn /acre) broadcast over the field. On calcareous soils in Texas and Western Australia, the deficiency in sorghum was treated with 0.7-2.24 kg

Zn ha⁻¹ (0.6-2 lb Zn /acre) as either zinc sulphate or zinc oxide. In Colorado and Nebraska soil application of zinc sulphate at 5.6-22.4 kg Zn ha⁻¹ (5-20 lb Zn/acre) or using a zinc chelate at 0.56-1.12 kg Zn ha⁻¹ (0.5 lb Zn/acre) is used. In Texas, 11.2-33.6 kg ZnSO₄ ha⁻¹ or 2.24-6.7 kg ha⁻¹ (2-6 lb/acre) of zinc chelate is recommended⁽⁴⁾.

3.5.1.6 Oats (*Avena sativa* L.)

The leaves become pale green; older leaves show collapsed areas at the margins and tips are greyish in colour. Necrosis extends down the leaf and the remainder of the leaf is grey to bronze-green ⁽⁴⁾.

Treatment: Deficiencies in oats have been widespread in Western Australia and were treated with zinc oxide applications to the soil: 0.7-2.7 kg ha⁻¹ (0.6-2.4 lb/acre) zinc oxide on lateritic sandy soils, 1.34 kg ha⁻¹ zinc oxide (1.2 lb/acre) on non-calcareous sandy loams, and 3.36 kg ha⁻¹ zinc oxide (3 lb/acre) on calcareous soils ⁽⁴⁾.

3.5.2 Pasture Grasses, Legumes and Forage Crops

3.5.2.1 Alfalfa (*Medicago sativa* L.) (also called Lucerne) (Indicative Annual Yield = 30-40 t ha⁻¹ rainfed, 80-100 t ha⁻¹ irrigated)

Although not very common, zinc deficiencies in both alfalfa and clover have been found to be responsible for reduced seed production. Deficiencies first appear as bronze-coloured specks around the margins of the upper leaves. As the deficiency progresses, the bronze spots become white and the leaves die. Under severe zinc deficiency conditions, the bronze spots will appear across the whole surface of the leaflets.

In Australia, deficiencies of zinc have been found in alfalfa and subterranean clover in New South Wales and Victoria.

3.5.2.2 Pasture Grasses and Clovers (various species)

In general, the zinc requirement of pasture herbage plants is lower than that of the more zinc-sensitive crops such as maize, beans and other field crops and so it is rare for pastures to show marked symptoms of zinc deficiency.

However, the zinc content of the herbage may be low enough to possibly give rise to zinc deficiency in grazing livestock in severe cases.

The topic of zinc deficiency in pastures has been most thoroughly studied in Australia and New Zealand and widespread deficiencies have been found in clover-grass pastures over millions of hectares in Western and South Australia on both calcareous and quartz sands and loams. However, the deficient soils occur throughout the area interspersed with soils which have adequate contents of available zinc. Zinc deficiencies occur in Tasmania on both calcareous soils and strongly acidic soils in coastal areas and on offshore islands.

The Ninety Mile Desert on the borders of Victoria and South Australia provides a very striking example of zinc deficiency in pastures. For many years this area was regarded as being very unproductive being only able to carry about one wether (castrated ram) per 20 acres (8 ha⁻¹). After the discovery of plant nutritional deficiencies and the application of zinc sulphate, copper sulphate and superphosphate, the productivity of the pastures increased to such an extent that it was able to carry 2 ewes (breeding female sheep) per acre (0.4 ha⁻¹); a more than 40 fold increase in stock carrying capacity ⁽⁴⁾.

The principal symptom of zinc deficiency in most pasture species is normally just reduced yield and no distinct chlorosis or other symptoms are evident.

Sudangrass (*Sorghum sudanese* Piper Stapf), Deficient plant leaves have broad yellow stripes between the midrib and the margin.

Subterranean Clover (*Trifolium subterranean* L.), Deficient plants have a bronze colouration on the upper surface around the midribs at the base of the laminae of the older leaves. Rosetting and dwarfing of the leaves may develop later.

Treatment: In Australia, soil application of 7.8 kg Zn ha⁻¹ (7 lb/acre) as zinc sulphate (or zinc oxide) every three to ten years depending on conditions. In Florida, the recommended annual application rate for pasture grasses, clovers and other forage crops was (in 1975) 3.4 kg Zn ha⁻¹ (3 lb/acre) on mineral soils and 4.5 kg Zn ha⁻¹ (4 lb/acre) as either zinc sulphate or oxide.

3.5.3 Other Field Crops

3.5.3.1 Cassava (*Manihot esculenta* Crantz)

(Indicative Annual Yield = 15-20 t ha⁻¹ rainfed, 25-35 t ha⁻¹ irrigated)

There are reports of zinc deficiency in cassava crops in Tamil Nadu, India and in Thailand.

3.5.3.2 Chickpea (*Cicer arietinum* L.)

(World average yield 1990-94 = 0.7 t ha⁻¹)

Although acute zinc deficiency is not very commonly seen, the symptoms are: yellowing, then bronzing and necrosis of lower and middle leaves. Foliar sprays with 0.5% zinc sulphate mixed with 0.25% calcium hydroxide are often used to treat the deficiency ⁽¹⁶⁾.

3.5.3.3 Beans (*Phaseolus vulgaris* L.)

(also referred to as Dry Edible Beans)

(Indicative Annual Yield = 6-8 t ha⁻¹)

Beans are recognised as being highly susceptible to zinc deficiency. In some areas of the USA, zinc is applied to the soil on a regular basis before sowing beans unless the soil test results indicate that levels of available zinc are adequate.

Symptoms of zinc deficiency usually appear on the second set of trifoliolate leaves. The leaves become light green and mottled. As the deficiency progresses, the area between the leaf veins becomes pale green and then yellow near the tips and outer edges. In cases of severe deficiency, the older leaves may turn grey or brown and die. In the early

stages of deficiency the leaves are often deformed, dwarfed and crumpled. On zinc deficient plants, the terminal blossoms set pods that drop off, delaying maturity. In general, zinc deficiency delays the maturity of the bean crop and decreases yields ⁽¹⁷⁾.

It has been found that crops of beans following sugar beet can be deficient in zinc due to the large quantities of phosphatic fertiliser applied to the sugar beet crop. In Michigan (USA) a reduction in phosphorus use on sugar beet and the long-term use of zinc fertilisers have reduced the incidence of zinc deficiencies in beans ⁽¹⁸⁾.

Treatment: 5.6-11 kg Zn ha⁻¹ broadcast (as zinc sulphate).

3.5.3.4 Oil Seed Rape (*Brassica napus*)

(also called 'Canola') (Average yields in temperate regions = 2.9-4.5 t ha⁻¹ – various sources)

This crop is sometimes found to suffer from zinc deficiency on severely eroded soils which have low values of available zinc revealed by soil tests (< 0.6 mg kg⁻¹ DTPA Zn). The deficiency has been reported in this crop in both India and Australia.

The symptoms include: general stunting and poor growth, flowering completely suppressed, interveinal chlorosis of leaves, starting at the margin and extending inwards. The leaves are small, slightly thickened, chlorotic and, in extreme cases, can be completely bleached ⁽¹⁹⁾.

In Australia, oil seed rape is often grown on soils with infertile subsoils and low zinc supplies in the immediate



Fig. 3.5

Oil seed rape plant showing small thickened leaves with chlorotic (bleached) patches.

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Fig. 3.6

Zinc deficient flax plant showing shortened internodes giving a rosette appearance.

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root environment can significantly reduce seed yield. Differences have been found between varieties of soil seed rape in their tolerance of zinc deficiency ⁽²⁰⁾.

3.5.3.5 Flax and Linseed

(*Linum usitatissimum* L.) (Average yields in temperate regions = 2-4.5 t ha⁻¹ – various sources)

This crop plant has cultivars which are grown for fibre to make linen (flax) and others which are grown to produce oil from their seeds (Linseed). Flax requires fairly high amounts of available zinc for healthy growth and good yields. Zinc deficiency in this crop has been reported in the western USA, Texas, Australia and France.

In zinc-deficient plants, greyish-brown collapsed spots appear on the younger leaves; the spots dry and change colour to brown or white. Shortened internodes give a rosette appearance. Later the top of the main stem becomes necrotic. Deficient plants are stunted and have yellow (chlorotic) leaves particularly in the lower area. The growing point of the main stem may die back. The 'greyish' symptom followed by reduction in growth is fairly characteristic of zinc deficiency in flax.

Treatment: In the western USA, soil application of 11.2 kg Zn ha⁻¹ (10 lb Zn/acre) is usually recommended. In growing crops, a foliar spray is required (e.g. 2.27 kg zinc sulphate in 227 litres of water [or 5 lb in 50 gallons]). In Texas, 11.2-33.6 kg ZnSO₄ ha⁻¹ (10-30 lbs/acre) or 2.24-6.7 kg ZnEDTA ha⁻¹ (2-6 lb/acre) are recommended ⁽⁴⁾. In France, post emergence treatment is

advised before the plant reaches 2-4 cm high, using a spray of 4 kg ZnSO₄ ha⁻¹ in 400 L ha⁻¹ of water ⁽²¹⁾.

3.5.3.6 Cotton (*Gossypium hirsutum* L.)

(Indicative Annual Yield = 4-5 t ha⁻¹)

Cotton is regarded as being a particularly zinc-sensitive crop. Deficiencies in cotton have been reported on calcareous soils in California, Louisiana, Arizona, and Texas in the USA and in New South Wales in Australia.

The optimum soil pH for cotton is 5.2-6.0, so the problem of high pH limiting zinc availability is not likely to be so common, but the crop will tolerate pH conditions of up to 7.5.

Zinc deficiency is often observed in newly developed fields where the topsoil has been cut away during leveling ('cut' soils). The main symptoms are a general bronzing in the first true leaves. The leaves become thick and brittle and their margins turn upward. Elongation practically ceases and shortened internodes give the plant a small bushy appearance. Growth and fruiting are delayed.

Treatment: ha⁻¹ as ZnO or ZnSO₄.7H₂O during soil preparation prior to sowing. Foliar applications of 200 g Zn ha⁻¹ as ZnSO₄.7H₂O will also mitigate the problem within the growing season. In India, 25 kg ZnSO₄ ha⁻¹ is applied to the soil ⁽¹¹⁾.

3.5.3.7 Groundnuts (*Arachis hypogea* L.)

(also called 'Peanuts')

(Indicative Annual Yield = 2-3 t ha⁻¹)



Fig. 3.7 Cotton leaves showing large areas of interveinal chlorosis.

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Fig. 3.8 Zinc deficient soya bean plants showing interveinal chlorosis and bronzing of the lower leaves.

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Zinc deficiency in groundnuts is often associated with high soil pH, high soil calcium contents and high soil phosphorus concentrations. The main symptoms of zinc deficiency are decreased internode length and restricted development of new leaves. Deficient plants accumulate reddish pigment in stems, petioles and leaf veins (22).

ILZRO (4) reports that deficiency causes reduced pegging (pods turning into the soil), but no distinct leaf symptoms.

Treatment: Foliar application is considered the most effective treatment but soil applications can also be used. In Florida, 5.6-11.2 kg Zn ha⁻¹ is recommended if the Mehlich 1 (M1) soil test gives < 0.5 mg Zn kg⁻¹ (pH 5.5-6.5) or < 1.0 mg Zn kg⁻¹ at pH 6.5-7.0. ILZRO (4) states that in Texas, 11.2-33.6 kg ZnSO₄ ha⁻¹ (10-30 lb/acre) of zinc sulphate or 2.24-6.7 kg ha⁻¹ (2-6 lb/acre) of zinc chelate is recommended.

In India, for groundnut-wheat rotations, it is recommended that 62.5 kg ZnSO₄ ha⁻¹ is applied at sowing (11).

3.5.3.8 Soya Bean (*Glycine max* L.)

(also called 'Soybean')

(Indicative Annual Yield = 1.5-2.5 t ha⁻¹ rainfed, or 2.5-3.5 t ha⁻¹ irrigated)

After maize (corn), soya beans and castor beans (*Ricinus communis*) are the crops most seriously affected by zinc deficiency in the USA. The deficiency most frequently occurs on calcareous soils which have had the topsoil displaced during the course of levelling, drainage, or other purposes ('cut' soils). Soya beans grown on sandy soils of low organic matter content, low adsorptive capacity, or high phosphorus and/or lime content can also suffer from zinc deficiency.

The main symptoms are stunted plants with light green to yellow leaves (interveinal chlorosis). The lower leaves may turn bronzed, deval (23).

Treatment: On 'cut land' (topsoil removed) in Washington, 11.2 kg Zn ha⁻¹ (10 lb/acre) as zinc sulphate is recommended. In Iowa, 11.2-22.4 kg Zn ha⁻¹ as zinc sulphate is broadcast or banded. In the sandy soils of low adsorptive capacity in New Jersey, 5.6-6.7 kg Zn ha⁻¹ of zinc sulphate is recommended (4).



Fig. 3.9 Soya bean leaf showing chlorosis and brown necrotic spots along the veins.

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3.5.3.9 Sugar Cane (*Saccharum officinarum* L.)

(Indicative Annual Yield = 70-100 t ha⁻¹ rainfed, 110-150 t ha⁻¹ irrigated)

Sugarcane can grow successfully in both tropical and sub-tropical climates. The optimum pH is 6.5 but it is grown on soils with a pH range of 4.5-8.5. Although zinc deficiency is not very common in this crop, it most frequently occurs on high pH, sandy soils. Deficiencies of zinc in sugarcane can also be enhanced by high applications of banded phosphorus and potassium, over-liming and/or high pH.



Fig. 3.10 Sugar cane plant showing distinctive interveinal chlorosis on the leaves.

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The main symptoms of deficiency are: young leaves show light-green stripes that are in the leaf veins (not between the veins as in manganese deficient leaf). The leaves are also small and non-symmetrical. Necrosis of the leaf tips may occur when the zinc deficiency is severe. A zinc deficient plant has reduced tillering and ratooning ability.

In addition, Landon ⁽³⁾ states that interveinal areas of the leaves become progressively pale with increasing deficiency. In severe cases, leaves are completely chlorotic with necrosis spreading down from the tip.

Treatment: For sugar cane in Florida on organic-rich soils (i.e. mucks and sandy mucks), 2.24 kg Zn ha⁻¹ (2 lb Zn/acre) is recommended where deficiency occurs and 1.12 kg Zn ha⁻¹ (1 lb Zn/acre) on sandy soils with less organic matter (mucky sands and sands). The zinc application should be made directly into the furrow at planting. No recommendations are made for ratoon cane (i.e. new tillers that grow up from the root after the previous cane has been harvested) ⁽²⁴⁾.

3.5.3.10 Lentils (*Lens esculenta* Moench.)

Lentils are normally grown on neutral to alkaline soils (pH 6.5-9.0) and will grow well on soils with a wide range of textures from loamy sand to heavy clay and will tolerate moderate to low soil fertility. However, they will not tolerate acid soils, waterlogging or saline conditions.

Since lentils are a legume, nitrogen fertiliser is not required, but they will respond to phosphorus and zinc fertilisers where the available contents of these elements in the soil are low.



Fig. 3.11

Close-up of interveinal chlorosis on leaves of zinc deficient sugar cane.

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Symptoms of zinc deficiency are generally localized on the older leaves. The interveinal tissue develops yellowing (interveinal chlorosis) and necrosis in small patches on the leaflets which quickly enlarge.

The size of the leaflet and internodal length are considerably reduced, so that plants have a rosette appearance in the field. Under low temperature conditions, the deficient plants may develop conspicuous purplish colouration on the leaflets.

Treatment: Foliar application of 4-5 kg ZnSO₄ ha⁻¹ zinc sulphate with 2-2.5 kg ha⁻¹ lime, or use of a proprietary zinc-containing foliar fertiliser formulation. Alternatively, preventive action can be taken on deficient soils by applying zinc sulphate at 15-25 kg ha⁻¹.

3.5.3.11 Tobacco (*Nicotiana tabacum* L.)

Tobacco is relatively highly tolerant to zinc deficiency, but when grown on severely deficient soils, plants develop 'little leaf' and rosetting symptoms.

3.5.4 Fruit Crops (Tree, Bush and other Fruits)

3.5.4.1 Avocado (*Persea americana* Mill.)

The earliest symptoms of zinc deficiency are mottled leaves developing on a few of the terminals. The areas between the veins are light green to pale yellow. As the



Fig. 3.12

Zinc deficiency in an avocado tree showing stunted leaves with marginal burn (chlorosis) and smaller, more rounded fruits.

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deficiency progresses, the yellow areas get larger and the new leaves produced are smaller. In advanced stages of deficiency, a marginal burn develops on these stunted leaves, twig die-back occurs and the distance between the leaves on the stem is shortened giving a crowded 'feather duster' appearance. Yield is reduced and some of the fruit may be smaller and rounder than is normal for the variety. The use of copper-based fungicides on avocado trees can exacerbate zinc deficiency.

Small rounded fruits are often the main symptom but can also occur combined with small leaves which also have interveinal chlorosis. These symptoms are easily confused with those of iron and manganese deficiencies and, in the case of small leaves, with 'root rot' disease.

Treatment: 3.4 kg (7.5 lbs) of $ZnSO_4$ / tree, either as an annual soil application or in quarterly irrigation. Problems have been experienced with foliar applications because the Zn remains on the leaf surface and does not appear to be absorbed (25). However, foliar spray recommendations which have been used (in 1978) were: for young trees 1364-1818 L ha⁻¹ (300-400 gallons/acre) of either 0.45 kg $ZnSO_4$ (36% Zn) in 455 L water (1 lb in 100 gallons) or 0.91 kg ZnO in 455 L of water. For mature groves of large trees 2728-3637 L ha⁻¹ (600-800 gallons/acre) (26).

3.5.4.2 Citrus Trees (*Citrus limon* L. lemon; *Citrus sinensis* L. orange; *Citrus paradisi* MacF., grapefruit; *Citrus reticulata*, mandarin)
(Indicative Annual Yield = 25-60 t ha⁻¹)

Citrus trees are particularly susceptible to zinc deficiency, which appears in the early stages as small blotches of yellow between green veins on the leaf (sometimes called 'mottle-leaf'). With severe deficiency, leaves may become increasingly yellow except for the green veinal areas. The leaves will also be small with narrow pointed tips on terminal growth. Narrow yellow leaves and delayed maturity are often considered characteristic of this deficiency in citrus.

Since zinc deficiency can be caused by high soil pH, which can also induce deficiencies of manganese and iron, it is relatively common for the symptoms of deficiencies of all three micronutrients to occur together. These are: (a) for manganese deficiency: dark green bands along the midrib



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and the main veins surrounded by light green areas giving a mottled appearance; with increasing severity light green changes to yellow-bronze; incipient Mn deficiency can disappear as the season progresses; (b) for iron deficiency: leaf veins are darker green than interveinal areas appearing on the first foliage; with increasing severity, the interveinal area becomes increasingly yellow with the entire area eventually becoming ivory in colour; trees may become partially defoliated with eventual twig die-back.

Treatment: Foliar fertiliser application of zinc. It is important to note that trees with the pathogenic disease "citrus blight" will also show similar leaf symptoms to those caused by zinc deficiency (27). Citrus trees obviously need careful investigation before treatment owing to the similarity in symptoms with manganese and iron deficiency and 'citrus blight'.

3.5.4.3 Pome Fruits (Apple-*Malus domestica*; Pear-*Pyrus communis* L.)

Zinc deficiency in both types of tree is manifested, in the spring, by small, stiff and sometimes mottled leaves developing in whorls (rosettes) near the tips of the previous season's growth. Except for these rosettes, the twigs are bare for some time. Later branches may arise below the twigs and produce leaves that at first are almost normal but later become mottled and misshapen. The formation of fruits is reduced and many of the apples that develop are small and malformed. Twigs may die back after the first year ('blind wood') (4).

Fig. 3.14



Zinc deficient apple tree showing rosetting due to reduced internodal growth and interveinal chlorosis.

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Treatment: Foliar sprays of chelated forms of zinc at manufacturer's recommended rates and timing are preferred. Zinc sulphate may be used with equal amounts of hydrated lime in the first two cover sprays. Soil applications of zinc in high pH soils give inconsistent responses. Zinc-containing fungicides (Dithane M-45 and Zineb) are also effective sources of zinc if applied at times and rates specified on the labels ⁽²⁸⁾.

3.5.4.4 Apricot, Peach and Cherry

(Apricot, *Prunus armenica* L.; Peach, *Amygdalus persica* Stokes, Cherry, *Prunus avium* L.)

These stone fruits can all be affected by zinc deficiency, which is most common on sandy and calcareous soils of neutral or alkaline reaction. In regions such as South Australia, apricot trees suffer from zinc deficiency, especially on sandy soils. Peaches and nectarines can also be affected by zinc deficiency, but tend not to need a spray application of zinc during the dormant period except at sites with a history of recurrent zinc deficiency problems. Normally, an adequate amount of zinc can be supplied by adding zinc oxide to two of the foliar sprays applied from late spring to early summer.

Zinc deficiency causes waving, crinkling and chlorosis in the leaves at the terminals of twigs and shoots. In severe cases, considerable defoliation occurs and rosettes of small leaves form at the terminals. The leaves in these rosettes sometimes do not have leaf stalks and are small and rigid; defoliation progresses upward. Formation of fruit buds is drastically curtailed and the few peaches

formed are misshapen and worthless. Symptoms of zinc deficiency in cherries resemble those of peaches.

Treatment: Foliar sprays are applied during the winter dormant period (July in Australia).

3.5.4.5 Grapes (*Vitis vinifera* L. wine grape; *Vitis rotundifolia* Michx. Muscadine grape)
(Indicative Annual Yield = 15-30 t ha⁻¹ in sub-tropics)

Zinc deficiency is a common problem in grapes in some areas and may be more widespread than recognized due to the occurrence of hidden deficiency in some locations.

Zinc deficiency can cause poor fruit set, stunted shoots and small misshapen leaves with interveinal chlorosis. Generally, deficiencies tend to occur in localised areas and not uniformly over a whole vineyard. The deficiencies are generally associated with sandy soils and soils with high pH, or high phosphorus levels. Clay soils with a high magnesium content can also have low concentrations of available zinc ⁽²⁹⁾.

In Iran, multi-micronutrient treatments including zinc, copper, iron and manganese were found to be effective in improving yields and quality of grapes.

Grape petiole analysis is widely used for the diagnosis of zinc and other nutrient problems. A satisfactory range of zinc in petioles is 35-50 mg Zn kg⁻¹ dry matter. If the zinc concentration is less than 35 mg Zn kg⁻¹ then treatment will be necessary ⁽³⁰⁾.

Treatment: Foliar application of zinc is the most effective treatment. Neutral zinc products (50-52% Zn) or zinc oxide (75-80% Zn) are both suitable. Foliar sprays are most effective in improving fruit set when applied two weeks prior to bloom, up to full bloom. If the foliar deficiency symptoms persist, a second foliar treatment may be required ⁽²⁹⁾.

3.5.4.6 Bananas (*Musa x paradisiaca* L.)
(Indicative Annual Yield = 40-60 t ha⁻¹)

Bananas have an optimum pH of 6.5 but tolerate pH 5.5-7.5. Zinc deficiency has been associated with high levels of available phosphate, alkalinity (pH > 6.0) and sandy or gravelly soils. Zinc deficiency symptoms are a 'bunchy' top effect.

3.5.4.7 Pineapple (*Ananas comosus* L.)

Zinc deficiency is common in pineapple plantations in Hawaii, French Guiana and Queensland, Australia. The disease often occurs simultaneously with copper deficiency which causes a characteristic symptom of 'crookneck' (pale green leaves which curve downwards and grow along the ground).

The first symptoms of zinc deficiency in pineapples appear at the end of the dry season. Transparent spots appear on the young leaves. These spots eventually turn yellow, spread and unite in the central region of the leaf blade. In advanced stages, larger areas become yellow and brown specks appear at the centre and form shallow cavities.

Treatment: Where zinc and copper deficiencies occur together, as in Queensland, the disorders are treated by incorporating 10 kg (12 lb) of zinc sulphate and 10 kg copper sulphate into each tonne of fertiliser used on the crop.

In Hawaii, zinc sulphate or chelates are used in fertiliser mixtures or nutritional sprays at 22.4 kg Zn ha⁻¹ (20 lb/acre). In French Guiana, sprays containing 1% zinc are applied at the end of the rainy season and these should supply 20.2 kg Zn ha⁻¹ (18 lb/acre) (4).

3.5.4.8 Guava (*Psidium guajava* L.)

This is an important crop in South Asian countries, Hawaii, Cuba, Brazil, India and Pakistan. In Pakistan alone, it is grown on an area of 58,500 ha. It is a crop which is able to adapt to a wide range of climate and soil conditions. It can grow in soils with pH values ranging from 4.5-9.4 and it is moderately resistant to salinity. Guava trees can suffer from zinc deficiency (and also iron deficiency) especially under high pH conditions.

Treatment: Foliar sprays with 7g ZnSO₄ L⁻¹ are used in Pakistan (31).

3.5.4.9 Strawberry (*Fragaria ananassa*)

Deficiencies have been observed in strawberries in Oregon, Louisiana and Washington, USA. The young leaves are chlorotic, except for the longer veins and narrow border at the margins, which remain greener. The leaf blade is relatively narrow and concave. Both leaf

Fig. 3.15



Zinc deficient coffee bush showing rosetting of leaves which are narrow and chlorotic.

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blades and petioles grow slowly, or not at all and many stunted leaves are visible on older plants (4).

Treatment: Either foliar sprays or soil applications of zinc compounds can be used. In Louisiana, strawberry fields high in phosphate are top-dressed with a zinc chelate.

3.5.4.10 Berry Crops (General)

Zinc deficiency symptoms include short internodes (stunting), small, narrow leaves, and interveinal chlorosis with shoot and branch die-back. In advanced stages, small, narrow terminal leaves are arranged in whorls or 'rosettes' (32).

3.5.5 Nut, Seed and Leaf Tree/Bush Crops

3.5.5.1 Cocoa (*Theobroma cacao*) (also called 'Cacao') (Indicative Annual Yield = 0.6-2.0 t ha⁻¹)

The ideal soil pH is 6.5 but pH values of 5.5-7.5 are tolerated. Deficiencies of zinc may be induced by high pH or soil compaction causing lack of root aeration. The main symptoms are narrow and malformed leaves which are elongated and often furled in a sickle shape and very marked aberrant veining (33).

3.5.5.2 Coffee (*Coffea arabica* L.) (Indicative Annual Yield = 1-2 t ha⁻¹)

Ideally, coffee should be grown on slightly acid soils (optimum pH 6.0-6.5), but it is often grown on more strongly acid soils and hence should be less prone to secondary zinc deficiency. The main zinc deficiency symptoms are shortened internodes giving a rosette appearance and the leaves not expanding properly. The leaves are small, deformed and narrow (often strap-shaped) with the veins visible against a yellow-green background.

3.5.5.3 Tea (*Camellia* spp) (Indicative Annual Yield = 1.7 t ha⁻¹ mature bushes)

There are two distinct varieties of tea, the small-leaved China tea (*C. sinensis*), and the large-leaved Assam tea (*C. assamica*). Tea is grown in many parts of the world where there is a warm moist climate and acidic soils (pH 4-6), which are low in calcium and generally rich in iron and manganese. The ideal soil is a well-drained deep loam or a forest soil rich in organic matter.

Zinc deficiency is a limiting factor in tea production in most production areas. In India, deficiencies are common in clonal nurseries and mature tea plants also have deficiency symptoms on a moderate to severe scale in all tea growing areas in South India.

Symptoms of deficiency include general chlorosis and characteristic malformation, dwarfing and brittleness of leaves and shortening of internodes to give a stunted appearance. In some cases, the leaves become sickle shaped, margins become wavy and the shoots present a bunched appearance.

Treatment: Foliar application of 11 kg ZnSO₄ ha⁻¹ in alternate years.

3.5.5.4 Pecan (*Carya olivaeformis* Wagh.)

Zinc deficiency symptoms include: small leaves, light-coloured leaves, wrinkled leaf edges, brown patches between leaf veins, curve-shaped leaves, shoots growing in tight bunches, numerous small shoots at the base of leaves up and down current season shoots, and, most important of all, dead shoots in the tops of trees. Pecan

trees may be adversely affected by hidden zinc deficiency before any of these symptoms have appeared.

Treatment: Foliar spray of zinc compound (either powdered or liquid zinc sulphate) 0.91 kg of zinc in 450 L (2 lbs/100 gallons) onto newly opening buds, young shoots and young leaves about every 2 weeks between April and August ⁽³⁴⁾.

3.5.6 Vegetable Crops

3.5.6.1 Carrot (*Daucus carota* L.)

Carrots grown on calcareous sands and organic soils are particularly prone to zinc deficiency and the problem is widespread in California.

Treatment: In California, a soil application of 11.2-22.4 kg Zn ha⁻¹ as zinc sulphate is recommended ⁽⁴⁾.

3.5.6.2 Onion (*Allium cepa* L.) (Indicative Annual Yield = 35-45 t ha⁻¹)

In the USA, deficiency in onions is common in California, Michigan, Oregon and some mid-western states. The optimum pH for this crop is 6-7 and it has medium salinity tolerance.

Zinc deficiency in onions shows up as stunting, with marked twisting and bending of yellow-striped tops.



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(3-4 lb/acre) as zinc sulphate or foliar application at 1.1 kg Zn ha⁻¹ with a solution of 0.5% strength (4).

3.5.6.3 Potato (*Solanum tuberosum* L.)

(Target yield = 32 t ha⁻¹) (35).

Zinc deficiency gives rise to stunted plants with chlorotic young leaves which are narrow and upwardly cupped ('fern leaf'). Other leaf symptoms are green veins, irregular spotting with grey or brown coloured dead tissue on older leaves and an erect appearance and grey or brown irregular spots appear on older leaves. The early symptoms are similar to leaf roll. The plants are more rigid than normal with smaller leaves and shorter upper internodes. In severe cases, the plants may die within two weeks.

Treatment: 11.2-22.4 kg Zn ha⁻¹ as zinc sulphate is the most common strategy for preventing zinc deficiency in future crops. The zinc sulphate can be broadcast and tilled into the seedbed or applied in a band near the seed (to the side and below the seed). Chelated forms of zinc are mainly used as a rescue treatment for a current deficient crop. They do not have much residual value for following crops. Foliar applications are normally in the range of 0.25-1.12 kg Zn ha⁻¹. Several foliar applications would be required to have the same beneficial effect as 11.2 kg Zn ha⁻¹ applied to the soil before planting.

3.5.6.4 Tomato (*Lycopersicon esculentum* Mill)

(Indicative Annual Yield = 45-65 t ha⁻¹, commercial, 10-20 t ha⁻¹ average farmer, rainfed)

In the USA, zinc deficiency in tomatoes occurs in the west, especially in California. In Texas, the disease occurs after prolonged periods of cold weather. Symptoms include: slow early growth with the leaves becoming thick and developing a faint interveinal chlorotic.

These leaves also have a tendency to curl downwards. In transplants, there is extreme relaxing (wilting) of the leaflets followed by downward curling of the petioles and, in severe cases, the petioles curl like a cork screw. This stage is followed by brownish-orange chlorosis of the older leaves which often show necrotic spots.

Treatment: Deficiencies can be corrected both by soil treatment and foliar sprays. Rates of soil application are



Fig. 3.17 Zinc deficient tomato plant with leaves showing downward curling and faint interveinal chlorosis.

Yara-Phosyn

11.2-22.4 kg Zn ha⁻¹ as zinc sulphate, but in sandy soils in Washington only 3.4-5.6 kg Zn ha⁻¹ is recommended. Foliar spraying 1.36-1.81 kg zinc sulphate in 455 L (3-4 lb in 100 gal) is recommended for seedling plants. Watering at setting out of transplants with a solution of 0.2% Zn with about 2273 L t ha⁻¹ (500 gals/acre) will also rectify the deficiency.

3.5.6.5 Lettuce (*Lactuca Sativa* L.)

Zinc deficiency in lettuces occurs in California on sandy and clay loam soils and has been reported in Wisconsin. Zinc deficiency can occur without showing obvious visual symptoms and causes stunted growth, slow maturity and reduced weight of heads.

Treatment: Deficient soils are treated with 11.2-38 kg Zn ha⁻¹ (10-34 lbs/acre) as zinc sulphate.

3.5.7 Other Economically important Crops

3.5.7.1 Rubber (*Hevea brasiliensis*)

(Indicative Annual Yield = 1-2 t ha⁻¹)

A deep rooting crop (3-4 m) with lateral roots spreading to 20 m, rubber will grow on soils pH 3.6-8.0 but the optimum pH is 4.4-5.2 (moderately acid). These conditions will favour the availability of zinc, but concentrations may be low due to low total contents in the soil parent material ('primary deficiency').

Zinc deficiency causes the leaf lamina to become narrower and twisted and to show general chlorosis with the midrib and main veins remaining dark in colour⁽³⁾.

3.5.7.2 Oil Palm (*Elaeis guineensis* Jacq.)

The typical symptom of zinc deficiency in oil palm is known as 'peat yellows'. It is characterised by a yellowish-orange discolouration of the lower fronds. In cases of more severe deficiency, the younger fronds also become pale and chlorotic, while the older fronds progressively dry out.

Treatment: Deficiency can be prevented by applying 15g zinc sulphate to the planting hole and further applications of zinc during the first two years of 100-200g per palm per year. Foliar sprays of 100-200 mg kg⁻¹ zinc sulphate can also be used for the rapid correction of deficiency⁽³⁶⁾.

3.5.7.3 Tung-Oil Tree (*Aleurites fordii* Hemsl.)

Tung trees with zinc deficiency show a characteristic bronzing of the foliage. Trees may become stunted and die within 2 or 3 years, if not treated, and lose their ability to resist the effects of cold temperatures.

Treatment:

Either: foliar spray of 1.36 kg zinc sulphate and 0.45 kg hydrated lime in 450 L, or application of chelated zinc to the soil.

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DIAGNOSIS OF ZINC DEFICIENCY IN SOILS AND CROPS

4.1 Introduction

Field observation of visible symptoms can be a quick and convenient diagnostic tool for cases of severe zinc deficiency in many crops, but requires local expert knowledge. However, in some cases there is a risk of confusing the symptoms. Perhaps most important of all is the fact that mild or even moderate cases of deficiency often do not give rise to clear diagnostic symptoms. If a crop is failing to grow or yield well, the lack of clear visible symptoms cannot be taken as an indication that the problem is not being caused by zinc deficiency (or a deficiency of another micronutrient). Sub-clinical, or 'hidden' deficiencies of zinc can sometimes cause yield reductions of 20% or more without obvious symptoms.

It is advisable to conduct confirmatory soil and/or plant analysis in cases of suspected deficiency. This also enables the zinc-supply status of the soil to be predicted for future crops so that preventative action can be taken before sowing, thus avoiding yield loss and quality impairment from a deficiency. After the use of zinc fertilisers, there is normally a period of several years while the residual effect of the applied zinc which has been adsorbed in the soil is still providing an adequate supply to successive crops. However, periodic soil or plant analysis needs to be conducted to ensure the zinc supply levels have not declined to below the critical values. On the other hand, in areas where zinc is supplied routinely to crops, soil analysis is necessary to save the expense of unnecessary zinc applications and to ensure that the element does not accumulate to undesirably high concentrations.

4.2 Soil Sampling and Analysis

Soil testing has the advantage over plant tissue analysis in that it can be carried out at any time. Owing to the spatial heterogeneity of soil properties in the field on most agricultural land, it is necessary to take an adequate number of subsamples over the area being investigated to ensure a representative sample. Spatial variation in the zinc status of soils is a particular problem in fields where soils show distinct differences in texture and other

properties and also in fields where zinc has been banded or placed for crops and not spread evenly over the surface by broadcasting. A typical field sampling protocol is to collect 25 subsamples, as cores of topsoil (0-15 cm), over an area of around 5 ha⁻¹, or less, in a W-pattern, with a soil auger or other sampling tool ⁽¹⁾. These subsamples should be placed in a clean plastic bucket and when all 25 have been collected (into the same bucket), the bulk sample needs to be thoroughly mixed and then placed on a clean sheet of plastic on a bench, or on the ground, to take a representative small subsample of around 250 g for sending off to the laboratory for analysis. This can be done by repeated quartering of the pile of mixed soil and taking small samples from each quarter, or by collecting small samples from all over the pile. The small subsample to be analysed should be placed in a clean, non-metallic container for posting/transport to the soil testing laboratory, complete with details of the sample field. It is essential to avoid contamination of soil or plant samples with zinc during sample collection and processing. Galvanised steel or brass implements or equipment should therefore not be used in either the collection or processing of samples.

For rice fields 0.1-1 ha⁻¹ in size, the procedure recommended by IRRI and others is to take 0-20 cm samples from deep rice-growing soils and 0-15 cm samples from shallower soils where deep ploughing is not practiced. The sampling protocol is to roughly divide the area of the field into 10-15 squares or rectangles of equal size and then to take one auger sample from the top 15 or 20 cm as appropriate, from a spot chosen at random within each square/rectangle. The auger cores are thoroughly mixed, visible plant debris removed and all clods and aggregates broken down. These samples are then taken to the laboratory, air dried, crushed, sieved and then reduced to size by quartering ready for testing and analysis ⁽²⁾. Johnson-Beebout *et al.* ⁽³⁾ have shown that soil extractions for flooded rice should be conducted on soils in the reduced (waterlogged) state in order to obtain a meaningful assessment of the available-zinc status of soils under flooded conditions.

On reception at the testing laboratory, the soil sample will be air dried or dried in a cool, forced-draught oven (< 30° C), lightly disaggregated and sieved ready for

chemical extraction. The chemical extraction procedure will be standard for each soil test method and must be followed without variation to ensure reliable values are obtained. Extractions are usually carried out using either an end-over-end, or a reciprocating shaker for a fixed time under specified constant temperature conditions. Analysis of centrifuged/filtered soil extracts is by either Atomic Absorption Spectrophotometry (AAS) for single elements, or inductively coupled plasma-atomic emission spectrometry (ICP-AES) for multiple elements. The latter (ICP-AES) technique has the advantage of enabling several micronutrients to be determined simultaneously and thus deficiencies of other elements, and/or possible micronutrient imbalances can be detected at the same time. The main problem is that ICP-AES instruments are much more expensive than AAS instruments and also require more specialized laboratory facilities. Appropriate analytical quality assurance procedures should be employed for all routine methods to ensure reliability of the results.

In all the stages of soil sampling and analysis, it is essential that any contamination of soil samples or analytical solutions with zinc is avoided. Galvanized (zinc-plated) buckets and other utensils, brass implements and rubber bungs and tubing should all be avoided because they contain large amounts of zinc. A small amount of contamination could be enough to give a spuriously elevated extractable zinc value, which would indicate an adequate zinc supply status when, in actual fact, the soil is deficient in the element.

The ideal soil test procedure should be one which is rapid, reproducible and correlates reliably with responses in plant yield, plant zinc concentration or zinc uptake⁽⁴⁾. The principle of the soil test is that a chemical reagent extracts an amount of zinc which can be instantly checked against critical values (based on the same extraction procedure) derived from responses of specified crops to zinc in field experiments on relevant soil types. Concentrations below the lower critical concentration will indicate a potential deficiency and the need for remedial action (such as the use of zinc fertilisers or foliar sprays). Values between the lower and upper critical concentrations will indicate an adequate zinc status and no need for corrective action, whilst extractable concentrations above the upper critical value will indicate a high zinc status where no further zinc applications should be made. Very high extractable concentrations indicate the possibility of toxicity problems in susceptible crops. In some soil tests other parameters,

such as soil pH and organic matter content are also used in conjunction with the extractable zinc concentration to make an effective diagnosis of the zinc status of the soil.

A relatively wide range of chemical reagents have been used in soil tests for zinc and these include^{(4) (7)} :

Salt solutions:

potassium chloride (1 M KCl),
magnesium chloride (0.25 M MgCl₂)
magnesium nitrate (1 M Mg(NO₃)₂)
ammonium acetate (1 M NH₄OAc) (pH 7)
sodium acetate (1 N NaOAc) (pH 4.8)

Dilute acids:

acetic acid (2.5% HAC)
hydrochloric acid (1 M HCl),
nitric acid (1 M HNO₃)
hydrochloric acid and sulphuric acid (0.05 M HCl + 0.0125 M H₂SO₄) (the 'Mehlic-1' test)

Chelating agents:

ethylenediaminetetraacetic acid (0.5 M EDTA)
diethyltriaminepentaacetic acid with calcium chloride and triethanolamine (0.005 M DTPA + 0.01 M CaCl₂ + 0.01 M TEA)

Mixtures of a chelating agent and a salt:

ammonium carbonate and EDTA
(0.05 M (NH₄)₂CO₃ + 0.01 M EDTA)
acid ammonium acetate and EDTA
(0.5 M NH₄Ac + 0.05 NHAc + 0.02 M Na₂EDTA)
ammonium bicarbonate and DTPA
(the 'AB-DTPA' test)
ammonium acetate and dithizone
(2 M NH₄Ac + 0.1% dithizone)

There has been a general trend towards the use of one, or a few, soil test procedures which can be used for several micronutrients and also potentially toxic elements in one extraction. On a global scale, DTPA is now the most widely used soil extractant, but EDTA, hydrochloric acid, ammonium bicarbonate-DTPA and the Mehlic 1 test are also still relatively popular. The critical concentrations used for interpreting soil analyses by these tests are given in Table 4.1.

The critical concentrations for the interpretation of soil tests are often highly specific to certain types of soil and crops. It is therefore important for local expert advice to

Table 4.1**Critical Concentrations for Widely Used Soil Test Extractants with Different Crops**

Soil Extractant	Lower Critical Concentration and Crop (mg Zn kg ⁻¹ dry soil)	Ref
DTPA	0.1-1.0 (range for all crops)	4
Mehlic 1	1.1 (average all crops)	4
0.05 M HCl	1.0 (rice)	5
0.1 M HCl	1.0-5.0 (range all crops)	4
0.1 M HCl	1-7.5 (several crops)	7
0.1 M HCl	2.0 (rice)	9
AB-DTPA	0.9 (sensitive crops e.g. maize)	6
NH ₄ Ac+dithizone	1.18 (rice)	7
NH ₄ Ac (1M, pH 4.8)	0.6 (rice)	5
(NH ₄) ₂ CO ₃ + EDTA	1.18-3.0 (several crops)	7
DTPA (0.005 M, pH 7.3)	0.13 (subterranean clover-sandy soil)	4
DTPA	0.55 (subterranean clover-clay soil)	4
DTPA	0.48 (chickpea)	7
DTPA	0.60 (maize)	7
DTPA	0.65 (pearl millet)	7
DTPA	0.65 (wheat, rice)	7
DTPA	0.76-1.24 (rice)	7
DTPA	0.5 (rice)	8
DTPA	0.8 (rice)	9
EDTA	1.5 (rice)	9
DTPA	0.5-2.0 (rice)	10
Mehlic 1	0.5-3.0 (rice)	10

be sought in the interpretation of soil test results and the most appropriate method of treatment, if this is required. Quite often soil pH, clay and organic matter contents will also be taken into consideration. The advantage of soil tests over plant analysis is that they enable possible deficiencies to be predicted in advance of growing the crop so that appropriate fertilisation or other treatments can be made to prevent the yield and/or quality of the future crop being impaired by zinc deficiency.

It must be noted that appropriate soil tests are not yet available for all types of agricultural soils around the world. In Australia, currently used soil tests are not considered to provide a reliable indicator of the plant-available zinc status of highly calcareous soils (R. Holloway, pers comm).

In India, it has been found that critical concentrations of DTPA-extractable zinc show a five-fold variation for different crops on a wide range of soil types in different climatic zones within the country. The range of critical concentrations was from 0.38-2.0 mg Zn kg⁻¹. For rice, DTPA-extractable concentrations ranged from 0.45 mg Zn kg⁻¹ on alluvial and sandy loam to clay Orthent and Fluvent type soils (USDA Soil Taxonomy Classification), in Madhya Pradesh state, to 2.0 mg Zn kg⁻¹ in Haplustalfs, Chromusterts and Pellustert soils in Tamil Nadu (in Tanjavur and Coimbatore regions). For wheat, critical concentrations ranged from 0.45 mg Zn kg⁻¹ on Ultisols, Rhodustalfs and Ochraqults in Bihar and also on Ochrepts, Orthents and Usterts in the Ranchi, Madhubani and Samastipur regions of Madhya Pradesh, to 0.67 mg Zn kg⁻¹ on Ustrochrepts and Ultipsamments in Haryana state.

For maize, critical concentrations ranged from 0.38 mg Zn kg⁻¹ on Inceptisols, Entisols and Aridisols in the Mehsana, Banaskantha and Sebakantha regions of Gujarat, to 1.4 mg Zn kg⁻¹ on Haplustalfs and Calcifluvents in the Patan, Nalanda, Bhojpur and Rohtas regions of Bihar state. For sorghum, critical DTPA-extractable zinc concentrations ranged from 0.5 mg Zn kg⁻¹ on Ustalfs and Ochrepts in Tikamgarh region of Andhra Pradesh to 1.2 mg Zn kg⁻¹ on various types of soils in Tamil Nadu ⁽¹¹⁾. Most of the critical values are 1.0 mg Zn kg⁻¹ or lower and the few cases where values were above 1.0 mg Zn kg⁻¹ were for calcareous and other soils where the availability of zinc is particularly low.

4.3 Plant Analysis

Plant analysis has the advantage of determining the zinc and other nutrient status of the plant at the time of sampling. All the soil and plant factors affecting the availability of zinc to the plant and its uptake and translocation within the plant will have interacted and the result will be revealed by the analysis.

As with soil analysis, a well-equipped analytical laboratory is required and a means of rapid transport of the samples to it.

Plant analysis needs to be related to specific plant tissues and stages of growth which have been found by experiment to show the strongest relationship with yield and plant quality. Critical deficiency concentrations (CDCs) are often used for the interpretation of plant analysis results. The Critical Deficiency Concentration is defined as the concentration in the specified tissue where there is a 10% reduction in the yield of the plant. These CDCs are usually determined by greenhouse experiments, but also need to be confirmed in the field because there is often a greater amount of uptake of trace elements from soils in greenhouse pot experiments than there is with the same plant varieties and the same soils out in the field ⁽⁴⁾.

The plant tissue chosen for analysis should be easy to identify and collect and be related to the movement of zinc within the plant. This latter point is very important because the mobility of zinc varies with the adequacy of its supply, being less mobile in deficient plants than those with adequate zinc.

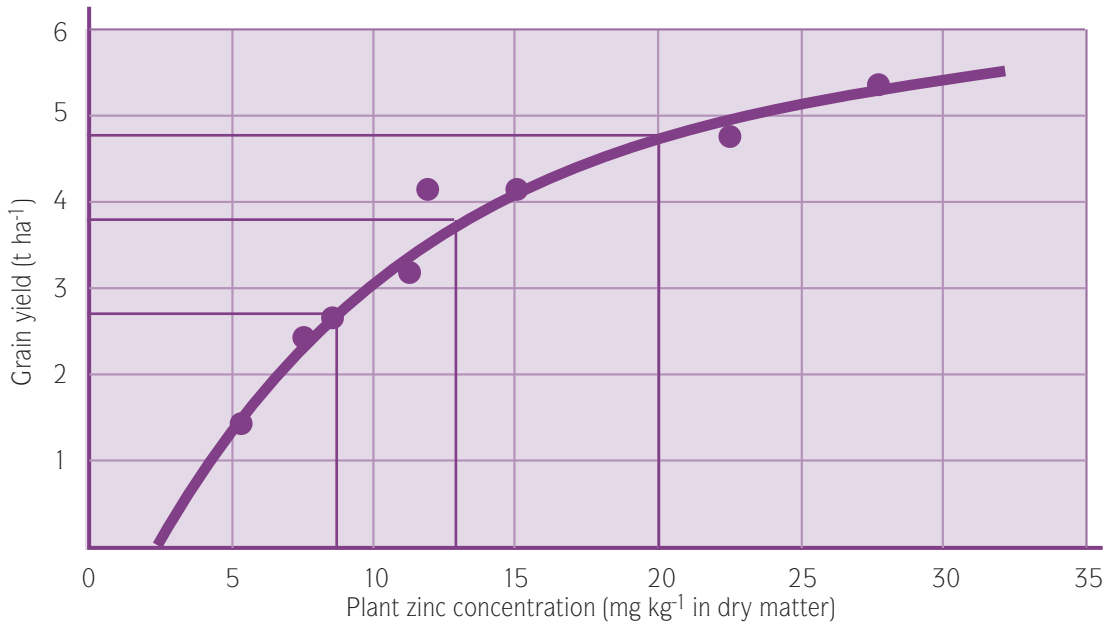
Tissues chosen for analysis include whole shoots, young leaves and, in some cases, grain or fruit. There are problems with sampling the whole shoot because concentrations differ with age. The critical concentrations of zinc decrease with increasing age of the plant. This is partly due to stems, which tend to have lower concentrations of zinc, forming a higher proportion of the shoot sample as it increases in age. There is also a problem of the C-shaped relationship between zinc concentration in the whole shoot yield. The lower portions of the growth response curve can show an increase in growth with a decline in zinc concentration. This is known as the Piper-Steenbjerg Effect and can cause problems in the interpretation of plant analyses ⁽⁴⁾. Some authors have suggested that problems with the C-shaped response curve can be minimized by analyzing whole shoot samples when the symptoms first appear, but others still consider whole shoots to be unsuitable. Nevertheless, in many parts of the world, when farmers collect the samples for plant analysis, it is often the whole shoots of young plants which are sampled.

Young leaves enable some of the problems experienced with the analysis of whole shoots to be avoided. The youngest emerged leaf blade (YEB) of cereals and the youngest open blade (YOB) of subterranean clover are often used for defining the zinc status of these crops ⁽⁴⁾. Young, recently matured tissue such as YEB or YOB has been used for plant analysis of: sugar beet, cotton, soybeans, pine trees, apples, peanuts, subterranean clover and wheat.

Figure 4.1 (see next page) is taken from work done in India and published in 1978. It shows the relationship between concentrations of zinc in young whole plants and subsequent wheat grain yield. From this graph, it can be seen that concentrations of below 30 mg Zn kg⁻¹ will result in yields not attaining their maximum potential for the site ⁽¹²⁾. The value of 20 mg Zn kg⁻¹ zinc is the lower critical concentration. Young leaves are particularly suitable for determining the zinc status of plants because symptoms of zinc deficiency usually develop in young leaves, and secondly, the zinc content of the youngest leaves is usually more stable than those of older leaves. However, as stated in Section 3.2, leaf symptoms of zinc deficiency are found on both old and new leaves.

Figure 4.1

Plant Zinc Concentrations and the Grain Yield of Wheat



From Takkar (12)

The concentration of zinc in grain can also be used as a retrospective indication of the zinc status of the previous crop and in identifying areas where future grain crops could suffer from deficiency. A critical value of 15 mg Zn kg⁻¹ has been suggested as a general value for the interpretation of grain analyses, but recent work has shown 10 mg Zn kg⁻¹ in wheat and 43 mg Zn kg⁻¹ in soybean to be more reliable (4). However, as discussed in Section 2.6, there is increasing interest in the zinc concentration (density) in grains used for human consumption. The aim will be to increase the zinc concentration in grain to 40-60 mg Zn kg⁻¹ which is much higher than the concentration indicating possible yield losses due to zinc deficiency. However, there is a need to ensure that soils are not over-fertilised with zinc during agronomic biofortification.

The leaf samples for analysis should be collected from a large number of plants. In some cases, patches of crop showing poor growth will be compared with areas of good growth, but all samples should be based on several plants of each type. On reception at the analytical laboratory, the leaves will be washed in ultra-pure water to remove any contaminating particles on the surface, mopped dry and then oven dried at 110° C, ground in a mill, taking

care to avoid any possible contamination from zinc, and then digested in hot concentrated acids (often by microwave heating). The plant tissue digest solutions are then analysed by AAS or ICP-AES (as described for soil analysis).

As a rule of thumb, concentrations of < 20 mg Zn kg⁻¹ are generally considered to indicate a deficiency in whole young plant tissue. However, the data provided in Table 4.2 (next page) show a range of critical concentrations from 7 to 32 mg Zn kg⁻¹ for different plant species and different types of leaf sample.

Table 4.2**Critical Concentrations of Zinc used in the Interpretation of Plant Tissue Analysis**

Crop	Tissue	Critical Concentration (mg Zn kg⁻¹ dry matter)	Ref
Rice	whole seedling	22	8
Maize	upper 3rd leaf (6 weeks)	16	7
Maize	upper 3rd leaf (8-10")	15	7
Maize	early leaf initial silk	20	7
Maize	whole plant (India)	22	7
Pearl millet	-	18	7
Rice	whole plant	15	7
Rice	plant top, pre-flowering	17.4	7
Rice	3rd leaf from top	16-23.5	7
Rice	whole plant (India)	15-22	5
Rice	whole shoot	Deficient < 10	9
Rice	whole shoot	Deficiency very likely 10-15	9
Rice	whole shoot	Deficiency likely 15-20	9
Rice	whole shoot	Sufficient > 20	9
Alfalfa	top 15 cm at 1/10 bloom	20	7
Cotton	upper recently matured leaves, early bloom	20	7
Soybean	upper recent matured leaves, early pod set	20	7
Soybean	3rd leaf blade at 41 days	14	7
Sugarcane	top visible dewlap leaf	15	7
Peanut	leaf	25	7
Peanut	blades of YFEL early pegging/pod fill	8-10	7
Peanut	whole plant (India)	15-22	7
Peanut	42 days after seeding	20	4
Peanut	YFEL early pegging	8-10	4
Wheat	shoot	24.5	7
Wheat	plant top, pre-flowering	14.5	7
Wheat	youngest leaf	7-16	7
Wheat	whole plant (India)	20-25	8
Wheat	tillering YEB	11	4
Wheat	post anthesis YEB	7	4
Wheat	YFEL	14	13
Wheat (spring)	shoot	32	14
Wheat (durum)	YFEL	20	14
Wheat (durum)	shoot	25	14
Canola	YFEL	15	14
Canola	shoot	23	14

Cont. next page

Crop	Tissue	Critical Concentration (mg Zn kg ⁻¹ dry matter)	Ref
Albus lupin	YFEL	16	14
Albus lupin	shoot	22	14
Cluster bean	whole plant	15	5
Soya bean	whole plant	16	5
Sorghum	YFEL	8-10	4
Sorghum	blade 1	10	4
Sorghum	blade 5	25	4
Sorghum	whole plant (India)	8	5
Cotton	37 days after seeding YMB	11	4
Cassava	YMB 63 days after seeding	30	4
Sub'Clover*	21-55 days after emergence YOL	12-14	4
Chickpea	whole plant (India)	25	5
Mustard	whole plant (India)	18	5

* Sub' clover = Subterranean Clover

YFEL = youngest fully emerged leaf, YEB = youngest emerged blade,

YMB = youngest mature blade, YOL = youngest open leaf

Table 4.3

Normal Range of Zinc Concentrations in Leaves or Petioles of Fruit Crops
(mg Zn kg⁻¹ in dry matter)

Apples	20-40
Grapes (petiole)	30-60
Cherries	15-40
Strawberry	20-50
Peaches,	20-50
Raspberry, plums and apricots	20-50

From Hanson (15)

Takkar⁽⁵⁾ has shown how the critical leaf concentration of zinc can vary between cultivars of the same crop species in different regions. After 30 days growth in soils in Madhya Pradesh, India, the critical zinc concentration in the whole plant of the rice cultivar Jaya was 16 mg Zn kg⁻¹ and that of Patel-85 was 21 mg Zn kg⁻¹. For whole plants of wheat cultivars HD 1553 and RR-21 in Madhya Pradesh, the critical concentration was 29 mg Zn kg⁻¹ but that of cultivar HD 1209 in Bihar was 24.5 mg Zn kg⁻¹.

4.4 Biochemical Tests of the Zinc Status of Plants

Assays of the activity of several zinc-containing enzymes have been shown to be a relatively reliable indicator of zinc status in certain crops, but they have not been adopted on a wide scale. Three enzymes have been used for these assays: ribonuclease in rice and maize, carbonic anhydrase in citrus and wheat, and aldolase in onions⁽⁴⁾. The main potential advantage of biochemical tests is that they can be adapted to be used in the field to give an instant indication of the zinc status of a crop. This would save the cost and time delay in sending leaf and/or soil samples to a laboratory.

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ZINC FERTILISERS

5.1 Types of Zinc Fertiliser

Three different types of compounds are used as zinc fertilisers and these vary considerably in their zinc content, price and effectiveness for crops on different types of soils. These sources of zinc include: (i) inorganic compounds, (ii) synthetic chelates, and (iii) natural organic complexes.

i) Inorganic sources include: zinc oxide (ZnO), zinc carbonate (ZnCO₃), zinc sulphate (ZnSO₄), zinc nitrate (Zn(NO₃)₂) and zinc chloride (ZnCl₂). Zinc sulphate is the most commonly used source around the world and is available in both the crystalline monohydrate and heptahydrate form. Zinc oxysulphate (xZnOxZnSO₄) is manufactured by partially acidulating zinc oxide with sulphuric acid and both the zinc content and the water soluble fraction can be controlled by the degree of acidulation. Ammoniated zinc sulphate solution is a source of nitrogen, zinc and sulphur (10-15% N, 10% Zn and 5% S) and is often combined with ammonium polyphosphate as a starter fertiliser ⁽¹⁾. Zincated urea, consisting of urea (nitrogen) fertiliser granules coated with zinc sulphate (42% N and 2% or 1% Zn) is used in India and some other places for rice on alkaline soils ⁽²⁾. Concentrated liquid suspensions of zinc oxide (ZnO) are used for foliar application but their performance is strongly determined by the size range specification of the ZnO particles present in the formulation ⁽³⁾. A liquid formulation containing urea, ammonium nitrate and zinc nitrate (15% N and 5% Zn), patented as NZN[®], is considered to be particularly effective as a foliar fertiliser, especially for horticultural tree crops ⁽⁴⁾.

ii) Synthetic chelates are special types of complexed micronutrients generally formed by combining a chelating agent such as Ethylene Diamine Tetra-acetic Acid (EDTA) with a metal ion and the stability of the metal-chelate complex determines the availability of the metal to plants. The di-sodium salt of Zn-EDTA (Na₂Zn-EDTA) is the most commonly used chelated source of zinc and is more stable than Ca-EDTA so the zinc is not likely to be replaced by calcium in the chelate in the soil or in concentrated hydroponic/fertigation solutions. Other chelates such as zinc

citrate are also used. Synthetic chelates, such as Zn-EDTA, are regarded as being 2 to 5 times more available than zinc sulphate when applied to soil, but they are also about 5 to 10 times more expensive ⁽¹⁾. Other synthetic chelate ligands used with zinc are Diethylene Triamine Penta-acetic Acid (DTPA) and Hydroxy-EDTA (HEDTA), although EDTA is by far the most widely used. With their high stability, synthetic chelates are eminently suitable for mixing with concentrated fertiliser solutions for soil, fertigation and hydroponic applications. They can also be used for foliar sprays but their relatively low zinc content means that repeat applications may be required for moderate to severe zinc deficiency situations.

iii) Natural organic complexes include those which are manufactured by reacting zinc salts with citrates or with organic by-products from paper pulp manufacture such as lignosulphonates, phenols and polyflavonoids. They are generally less expensive than synthetic chelates such as Zn-EDTA, but are generally much less effective ⁽¹⁾. This is because of the lower stability of the complex bonds with the micronutrient ion and they are therefore unsuitable for mixing with concentrated fertiliser solutions. Other types of natural organic complexes can be formed by complexing zinc with amino-acids. However, smaller amounts of these amino acid complexes are in agricultural and horticultural use compared with the paper pulp by-products.

In addition to specific zinc fertilisers, some macronutrient fertilisers can contain sufficient zinc to act as a significant source of the micronutrient when used regularly at relatively high application rates. Perhaps the best known of these is single superphosphate which has been widely used as a phosphatic fertiliser in some parts of the world for more than one hundred years. Depending on the source of the phosphate rock used in its manufacture, single superphosphate can contain concentrations of up to 600 mg Zn kg⁻¹. However, owing to concerns about over-fertilising with phosphorus after long-term use of superphosphate in some developed countries, smaller amounts of this, or other phosphatic fertilisers, are now being used. A consequence of this will be that specific zinc fertilisers will be required on soils prone to zinc deficiency. There is also a general trend towards replacing single

superphosphate with more concentrated (high analysis) phosphate fertilisers, such as monoammonium phosphate (MAP) and diammonium phosphate (DAP), which have much lower zinc contents. So again, on zinc-deficient soils, these fertilisers need to be used in association with specific zinc fertilisers ⁽⁵⁾. A phosphate and potassium fertiliser based on the ash residue from poultry manure, burnt to generate electricity, also contains a significant amount of zinc (0.2%) plus smaller amounts of copper and boron.

The full range of materials used as zinc fertilisers and their zinc contents are given in Table 5.1.

Several zinc-containing materials which can also supply zinc to soils and crops include pig and poultry manures, biosolids (sewage sludge), composts made from urban solid wastes, and certain industrial waste products. Although these materials can contain high concentrations of zinc, they frequently also have relatively high contents of other micronutrients, such as copper and/or nickel and

non-essential, potentially toxic elements, such as cadmium and lead ⁽⁶⁾ (See Section 2.1.3.3). Some biosolids can also contain significant concentrations of persistent organic pollutants. Use of these materials as zinc sources should be carefully controlled and based on broad-spectrum chemical analysis of the material. The zinc contained in pig or poultry manure results mainly from intentional additions to the animal feed as dietary supplements and hence their zinc contributions are more predictable and more straightforward to control.

5.2 Zinc Fertiliser Applications

The history of the use of zinc fertilisers goes back to 1934 when zinc sulphate was used to treat “white bud” (leaf chlorosis) in maize in Florida. Zinc deficiencies which can result in serious yield and quality loss are normally corrected by soil applications of zinc compounds. Foliar sprays are more usually used on higher value fruit trees,

Table 5.1

Commonly Used Zinc Fertiliser Materials

Compound	Formula	Zinc Content (%)
Inorganic compounds		
Zinc sulphate monohydrate	ZnSO ₄ .H ₂ O	36
Zinc sulphate heptahydrate	ZnSO ₄ .7H ₂ O	22
Zinc oxysulphate	xZnSO ₄ .xZnO	20-50
Basic zinc sulphate	ZnSO ₄ .4Zn(OH) ₂	55
Zinc oxide	ZnO	50-80
Zinc carbonate	ZnCO ₃	50-56
Zinc chloride	ZnCl ₂	50
Zinc nitrate	Zn(NO ₃) ₂ .3H ₂ O	23
Zinc phosphate	Zn ₃ (PO ₄) ₂	50
Zinc frits	Fritted glass	10-30
Ammoniated zinc sulphate solution	Zn(NH ₃) ₄ SO ₄	10
Organic Compounds		
Disodium zinc EDTA	Na ₂ ZnEDTA	8-14
Sodium zinc HEDTA	NaZnHEDTA	6-10
Sodium zinc EDTA	NaZnEDTA	9-13
Zinc polyflavonoid	-	5-10
Zinc lignosulphonate	-	5-8

Based on Mortvedt and Gilkes ⁽¹⁾, Martens and Westermann ⁽⁷⁾, and Srivastava and Gupta ⁽⁸⁾.

grape vines and for treating annual field crops to prevent serious loss of yield. Other methods include seed treatments and root-dipping of transplant seedlings (e.g. in rice production).

Soil applications are typically in the range 4.5-34 kg Zn ha⁻¹, usually in the form of zinc sulphate broadcast or sprayed (in aqueous solution) onto the seedbed, but other compounds listed in Table 5.1 are also commonly used. Higher applications are often used for crops which are particularly sensitive to zinc deficiency, such as maize, and these are determined by whether the crop is grown on alkaline and/or calcareous soils, compared to non-calcareous soils (7).

For some crops, such as maize, banded soil applications are more effective than broadcasting and can reduce the amount of zinc fertiliser required. Banding usually involves placement of the fertiliser 5 cm to one side and 5 cm below the row-planted seed. In Colorado, the recommended rate of zinc sulphate is five times lower for banding than broadcasting (9). Martens and Westerman (7) account for the greater efficiency of banded compared to broadcast zinc sulphate by the lower amount of soil-Zn contact and hence slower adsorption of the zinc in unavailable forms. Nevertheless, higher rates of banded zinc sulphate are required for severely zinc-deficient soils. Band application of zinc fertiliser at rates of 0.34-1.34 kg Zn ha⁻¹ was found to produce grain yields equal to those with 26.9 kg Zn ha⁻¹ broadcast and incorporated into the seedbed (10). However for some crops, such as soya beans, broadcasting of most fertilisers, including zinc, is more effective than banding.

It is generally recognized that the effectiveness of inorganic zinc fertilisers in soils, at least in the short term, is determined by their water solubility. Various authors have concluded that at least a 40% or 50% water soluble source of zinc is required. This is one of the reasons why highly soluble zinc sulphate is so widely used for treating deficiencies (as well as its relatively low cost and generally wide availability). Westfall *et al.* (11) reported that zinc sulphate (98% soluble), zinc lignosulphonate (91% soluble) and ZnEDTA (100% soluble) were all very efficient at supplying zinc to plants. However, ZnEDTA was two to five times more effective than either zinc sulphate or zinc lignosulphonate. Several authorities recommend using soil applications of synthetic zinc chelates at one third of the recommended rate for zinc sulphate, although chelate manufacturer's recommended application rates should normally be followed for best results. Obrador *et al.* (12) compared the mobility and bioavailability to maize plants

of zinc complexed with an amino acid with that complexed by a mixture of three synthetic zinc chelates, (EDTA, DTPA and HEDTA) in a calcareous soil. They found that the synthetic chelate complexed-zinc was more mobile and more likely to reach the roots of maize in calcareous soils than the amino-acid form. However, where precipitation from rainfall or irrigation was high, the zinc in the synthetic chelate complex was more likely to be leached down the profile.

Martens and Westerman (7) quote the work of Schulte and Walsh (13) which showed that soil applications of zinc frits (boro-silicate glass), zinc oxide and zinc sulphate were all equally effective in correcting deficiency in several crops, either banded or broadcast, but twice as much was required for broadcast application (note earlier comparisons in this chapter). This appears to differ from the orthodox view, at least in relation to sandy soils, that sparingly soluble compounds such as zinc oxide are less effective in the first year after application.

In the Central Anatolian region of Turkey, where about 45% of the country's wheat is produced, Cakmak *et al.* (14) obtained increases in yield of up to, and more than, 500% in durum and bread wheats grown on calcareous soils using fertiliser treatments of 23 kg Zn ha⁻¹ (as ZnSO₄·7H₂O) which were found to be effective for between three and seven years. The zinc sulphate was applied to the seedbed in solution and incorporated into the soil by a disc plough (14). However, the most common practice is now to supply zinc blended into macronutrient compound fertilisers. Following the work of Cakmak *et al.* (14) several domestic fertiliser companies in Turkey began manufacturing compound NP and NPK fertilisers with 1% w/w of zinc blended into them. Production started in 1994 and by 2006 the amount of zinc-blended compound fertilisers used in Turkey was more than 300,000 t yr⁻¹ (14). In addition to these zinc-blended compound fertilisers, increased amounts of zinc sulphate, zinc oxide and zinc-containing foliar fertilisers are now being applied. The economic benefits associated with application of zinc fertilisers has now been estimated, by the Ministry of Agriculture in Turkey, to be worth around US\$ 100 M annually (14).

In China, zinc sulphate and zinc oxide are the most widely used zinc fertilisers for soil applications, foliar sprays and seed coatings, but zinc chloride and synthetic zinc chelates are also becoming more widely used. Soil applications are used mainly on field crops, including maize, wheat and rice, with foliar sprays on higher value fruit and vegetable crops, although fertigation using

mainly synthetic zinc chelates are now on the ascendancy too in many areas. Soil application of zinc sulphate at a rate of 16.5 kg Zn ha⁻¹ has proved particularly effective for wheat (15).

Soil applications of 9-22 kg Zn ha⁻¹ on calcareous soils in South Australia have been found to have a beneficial residual effect for about ten years. More recent practices have been to spray zinc sulphate onto seedbeds at a rate of 1 kg Zn ha⁻¹ and cultivate it into the topsoil or as a foliar spray mixed with a compatible cereal fungicide at a rate of 0.2 kg Zn ha⁻¹. The inclusion of urea in foliar sprays of zinc sulphate increases leaf penetration and addition of a sticker can reduce wash-off (16). In addition, the phosphatic fertilisers, mono- or diammonium phosphate (MAP, DAP) can also be obtained with added zinc (5). In India, zinc-enriched DAP and nitro-phosphorus fertilisers have also been found to be effective in rectifying zinc deficiency in rice (17).

The residual value of zinc fertilisers decreases with increasing time. Using an experimental field on a highly zinc-deficient soil in Western Australia, Brennan (5) found that the effectiveness of a single zinc fertiliser treatment for wheat had decreased by 50% over a period of thirteen years. In Turkey on highly zinc-deficient calcareous soils, Cakmak *et al.* (14) found that an application of 28 kg Zn ha⁻¹ as zinc sulphate was sufficient to correct zinc deficiency in wheat for four to six years.

In South Australia, calcareous soils used for cereal growing have highly alkaline subsoils with low available zinc contents, which are becoming lower due to the use of high analysis macronutrient fertilisers. Fertilisers applied to the topsoil tend to remain in this zone and not move down the soil profile to the deeper roots. Holloway (16) investigated the feasibility of injecting a zinc-containing liquid fertiliser at 40cm depth and thoroughly mixing it with the subsoil. He found that this subsoil zinc was available to wheat roots even when the surface soil had dried out and considered this approach to be beneficial for alkaline sandy soils in low-rainfall regions such as western and northern parts of South Australia (16).

In South America, zinc sulphate (23% w/w Zn) is the most widely used zinc fertiliser due to its high water solubility, ready availability and relatively low price, at application rates of 30-50 kg ha⁻¹ as a top dressing on both upland and lowland rice and maize (18).

In India, where around half of the agricultural soils are deficient in zinc, much work has been done on evaluating

the most effective methods of applying zinc fertilisers. For soil and foliar applications, zinc sulphate is the most commonly used, but sparingly soluble zinc oxide (67-80% w/w Zn), zinc carbonate (56% w/w Zn), zinc phosphate (50% w/w Zn), zinc frits (4-16% w/w Zn) and zinc chelates (12-14% w/w Zn) are widely used. For seed treatment, a slurry of the proprietary product Teprosyn-Zn® (55 % w/w Zn) is also widely used. The chelate, Zn-EDTA has been found to be as effective as ZnSO₄ on some calcareous soils, but better than ZnSO₄ for rice in the loamy sand soils of the Punjab. In freely draining, coarse textured soils, ZnSO₄ is more effective than the less soluble forms of zinc, such as zinc carbonate, zinc oxide and zinc frits, but they were all comparable in fine-textured, zinc-retaining soils (19). Zincated urea was as effective as zinc sulphate for rice on calcareous soils when equivalent amounts of zinc were applied (2,19).

Application rates of zinc fertilisers generally used in India are; 11 kg Zn ha⁻¹ for wheat and rice; 5.5 kg Zn ha⁻¹ for maize, soybean and sugarcane; and 2.5 kg Zn ha⁻¹ for peanuts, soya bean, gram (*Phaseolus aureus* Roxb.), raya (*Brassica campestris* L.) and finger millet (*Eleusine coracana* L.). Zinc applied to soil through broadcasting and mixing into the topsoil proved to be more effective than top dressing, side-dressing, band placement, or foliar application of 0.5 to 2% ZnSO₄ solution. Although foliar applications are normally only used to recover yields in crops developing pronounced zinc deficiency during the growing season, they are widely used on higher value horticultural and plantation crops. Pre-soaking, or coating of seeds, or seedlings with a slurry of zinc oxide or the proprietary product Teprosyn-Zn®, may be a more cost effective option for crops with large seeds like maize, soya bean, wheat, groundnut, potato and gram. For rice, dipping the roots of seedlings in a suspension of 2-4% ZnO before transplanting has proved as effective as broadcasting 11 kg Zn ha⁻¹ as ZnSO₄.7H₂O. However, this has not proved effective for some other crops such as sugar cane sets. Seed treatment of potatoes with zinc sulphate was as effective as either soil or foliar application of zinc. The residual value of soil zinc applications varies considerably, but applications are often required following three to five crops of rice (19). In India, it has been found that the efficiency of zinc fertiliser use can be greatly improved when it is applied to soil mixed with livestock manure. In a field experiment, zinc sulphate at a rate of 2.5 kg Zn ha⁻¹ was mixed with 200-500 kg of fresh cow dung and following moist incubation for about one month this mixture proved to be as effective as 5 kg Zn ha⁻¹ applied as a straight inorganic salt (19).

In France and the USA, zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) is widely used as an alternative to zinc sulphate for treating deficiencies with 5.1 kg ha^{-1} zinc nitrate being effective on maize grown on clayey, calcareous alluvial soils (20).

Zinc deficiency is commonly found in coffee and citrus plantations on acidic soils in Brazil where foliar zinc applications are normally used to correct it. Rosolem and Sacramento (21) reported experiments to compare the efficiency of inorganic, synthetic chelated and natural complexes of zinc. They found that although zinc from inorganic salts was absorbed in larger proportions than from synthetic chelated zinc, the zinc from the chelated forms was more readily translocated within the plant. Zinc was applied at rates up to $4.9 \text{ kg Zn ha}^{-1}$ in coffee, up to $4.6 \text{ kg Zn ha}^{-1}$ in lemons and up to $4.6 \text{ kg Zn ha}^{-1}$ in oranges as ZnSO_4 , ZnEDTA and $\text{Zn-lignosulphonate}$. All of the treatments were effective in maintaining the zinc concentrations above threshold levels in the leaves and above the controls during most of the growing season. However, in two out of four experiments it was found that it would be possible to reduce the synthetic chelate applications to one third of the ZnSO_4 rate and in one experiment ZnSO_4 was more effective at maintaining zinc levels above threshold. Nevertheless, it was also found that zinc was translocated to new growth in the trees irrespective of the zinc source (21).

Field experiments comparing ploughed down and disked-in zinc sulphate treatments with maize on a zinc-deficient fine sandy loam soil in Virginia, USA by Hawkins *et al.* (22), showed that both treatments were equally effective in correcting zinc deficiency where the amount of zinc applied was $6.72 \text{ kg Zn ha}^{-1}$ (6lb/acre).

In transplanted, flooded rice production systems in Pakistan, Rashid *et al.* (23) reported that seed enrichment by applying 20 kg Zn ha^{-1} to the nursery bed gave a greater yield increase in the rice crop in zinc-deficient soils compared to broadcasting 10 kg Zn ha^{-1} on the whole field in a variety of soils differing in zinc status. Experiments in India by Mandal *et al.* (24) indicated that zinc fertilisers could be utilized more effectively where rice followed maize and where rice was grown after pre-flooding soils. In the USA during 2000, there was a rapid increase in the sowing of zinc-treated rice seed on high pH silt and sandy loam soils in Arkansas, which occupy about 25% of the rice-growing area (25). Recommendations in Arkansas are for seed treatment with between 2.2 and 4.4 kg Zn per tonne of seed (0.25-0.5 lb Zn/cwt seed) or foliar zinc applications at pre-flooding, or granular zinc (11 kg ha^{-1}) at pre-planting.

Johnson-Beebout *et al.* (26) found that zinc fertiliser applied to paddy rice-growing soils may become unavailable after flooding. They suggest that the optimum time for fertiliser application may be at the seeding stage. However, for loading grain with zinc (agronomic biofertilisation) it is necessary to apply zinc fertiliser at the grain filling stage of growth. Clearly, there are likely to be changes in fertiliser practice as biofortification becomes more widely adopted (See Section 2.6).

In Table 5.2 (next page), the relative sensitivity of crops to deficiencies of five micronutrients are shown on the basis of their response to fertilisers containing the respective elements. It should be noted that intra-specific differences between varieties of the same crop species can be very marked due to variations in the efficiency with which they acquire and utilise the respective micronutrients. Thus, even though a species, such as wheat is generally considered to be relatively tolerant to zinc deficiency, some varieties are more sensitive. Durum wheat (*Triticum durum* Desf.) is generally more sensitive to zinc deficiency than bread wheat (*T. aestivum* L.). However, even crops and/or varieties with a relatively low response to zinc fertilisers, such as wheat, can still be affected by deficiency on soils with very low available zinc contents (as found in Turkey). Nevertheless, highly susceptible crops grown on the same soils would be more severely affected, possibly even resulting in crop failure.

Brennan and Bolland (30) compared the effectiveness of soil-applied zinc for four crops on two alkaline soils from Western Australia in greenhouse experiments. The crops albus lupin (*Lupinus albus* L.), oil seed rape, or canola (*Brassica napus* L.), durum wheat and spring (bread) wheat were grown under three regimes: no added zinc ("indigenous zinc"), zinc sulphate applied at the time of sowing ("current zinc") and zinc sulphate incubated in the soil for fifty days before sowing ("incubated zinc"). They found that the albus lupin used the indigenous, current and incubated zinc more effectively than oil seed rape, followed, in decreasing order, by spring wheat, and durum wheat, respectively. Albus lupin and oil seed rape were about 30-40% more effective in using the "current zinc" than spring wheat and durum wheat was about 20% less effective than spring wheat. Relative to "current zinc", the "incubated zinc" was about 60% less effective for both spring and durum wheat and 50% less effective for both oil seed rape and albus lupin.

Tanner and Grant (31) conducted greenhouse experiments on the effectiveness of zinc sulphate and zinc oxide for maize when coated or incorporated into macronutrient

Table 5.2**Response of Crops to Treatment with Micronutrient Fertilisers**

	Zinc	Copper	Boron	Manganese	Iron
Alfalfa	Low	High	High	Med/Low	Medium
Apple	High	Medium	High	High	-
Barley	Medium	Medium	Low	Medium	High/Med
Oil Seed Rape*	Medium	Low	High	Medium	-
Clover	Medium	Medium	Medium	Medium	-
Grass	Low	Low	Low	Medium	High
Maize (Corn)	High	Medium	Low/Med	Medium	Medium
Oats	Low	High	Low	High	Medium
Pea	Low	Low	Low	High	Medium
Potato	Medium	Low	Low	High	-
Rice	High	Low	Low	Medium	Med/Low
Rye	Low	Low	Low	Low	Low
Spinach	Medium	High	Medium	High	High
Sorghum	High	Medium	Low	High/Med	High
Sugar beet	Medium	Medium	High	High	High
Vine (Grapes)	Low	Medium	High	High	High
Wheat	Med/Low	High	Low	High	Low

* also called Canola

Source: Martens and Chesterman (6), Loué (27), Prasad and Power (28), Follet et al. (29).

fertilisers with different acidity characteristics. They found that although zinc compounds thoroughly mixed throughout the soil gave the highest uptake of zinc, zinc oxide which was fully incorporated into acid (pH <4) fertiliser granules still gave an adequate amount of zinc for good crop growth. The uptake of zinc from these acid fertilisers increased with declining pH to a maximum at 3.7. With less acid fertilisers (pH >4), the effectiveness of the compounds, either coated on the granules or incorporated was: zinc oxide coated > zinc sulphate incorporated > zinc oxide incorporated. Application of zinc compounds with macronutrient fertilisers was more effective than a zinc oxide coating on the maize seed.

With regard to the actual methods used for the application of zinc fertilisers, Graham (32) discussed the problem of delivering relatively small amounts of micronutrient fertilisers evenly over the “target area” (field or parcel of land). He concluded that this can be done by mixing the micronutrient compounds with the macronutrient fertilisers

which act as the carrier through the larger quantities applied per hectare. However, problems arise as a consequence of the different granular sizes and density which result in their separating out, either before or during spreading. This leads to a highly uneven distribution over the “target area”. However coating the micronutrient compounds onto the macronutrient fertiliser granules is more reliable as it ensures a homogeneous distribution of the zinc within the carrier fertiliser which results in a very uniform distribution when spread over the “target area”. If acidifying nitrogen fertilisers are used they can increase the efficiency of the micronutrients in alkaline soils by creating acidic zones around the fertiliser granules which helps to keep micronutrients in a soluble form for longer. Fluid fertilisers have several advantages over solid forms, although specialised machinery is usually required for their effective application.

Applying both micro and macronutrient fertilisers together in irrigation water is another alternative approach in semi-

arid to arid areas, where intensively grown crops are irrigated for at least part of the growing season. This is called 'fertigation' and has several advantages over the use of granular fertilisers in these conditions, including more uniform nutrient distribution onto the "target area", greater availability of nutrients when the crop needs them and reduced risk of damage to plants and their roots with the generally lower concentrations of nutrients present at any time compared with relatively large applications of granular fertilisers. However, fertigation is generally best suited to sites with permeable sandy soils with good drainage and as the investment and maintenance of the delivery equipment and control systems required is relatively expensive, it is usually only employed for intensively produced high-value crops.

An alternative to applying either granular fertilisers or 'fertigation' is to spray aqueous fertiliser solutions or suspensions directly onto the soil surface. Ideally, this should be done before cultivation so that the applied zinc becomes mixed into the topsoil of the future seed-bed (32). This approach also enables relatively larger quantities of zinc, particularly zinc sulphate, to be applied as it avoids the risk of phytotoxicity by direct contact with emerging plants. The available concentrations of zinc in soils treated with solid forms of zinc fertilisers are often found to reach their highest value in the second or third growing season after several ploughing and/or other cultivations have thoroughly mixed the topsoil. Therefore it is sometimes recommended, on moderate to severely zinc-deficient sites, that an additional zinc foliar spray is applied to the crop in the first growing season after applying a zinc fertiliser to compensate for this lower availability due to uneven distribution through the rooting zone. Spraying an aqueous solution of a zinc (or other micronutrient) fertiliser uniformly over the whole surface area of soil and subsequently mixing it into the topsoil overcomes the problem of uneven distribution of fertilisers with a residual effect lasting several years (32).

It is important to recognise that at some sites multiple deficiencies of other micronutrients, apart from zinc, may also be contributing to reduced yields and inferior crop quality. Where two or more elements are deficient, supplying them together may give an overall response which is greater than the sum of the individual responses (i.e. synergism) (32). Examples of elements which can be found to be deficient along with zinc include boron, iron and manganese in calcareous soils and copper and boron in sandy soils. Since zinc and copper compete for the same absorption sites on root surfaces, if the amounts applied

of these two micronutrients are unbalanced, there is a danger that the element in excess will exacerbate or induce a deficiency of the other. An important example of multiple micronutrient deficiencies can be found in the predominantly alkaline, alluvial soils (Fluvisols) of the Indo-Gangetic Plains in South Asia. Multiple deficiencies involving zinc, manganese, copper, boron and molybdenum in various combinations are becoming increasingly common in these soils (33). This is very significant regarding the use of micronutrient fertilisers because rice-wheat cultivation systems occupy 13.5 Mha of the Indo-Gangetic Plains producing cereal staples for a high proportion of the regional population. (See Section 7.4).

In a global context, many areas affected by zinc deficiency, especially those in developing countries, have low-input arable farming systems with very little mechanisation and small fields/land parcels. In most cases, zinc fertilisers will probably be applied "manually" to soil or to seed, or in more developed areas by a simple tractor-mounted fertiliser spreader, or by foliar treatment probably using a knap-sack sprayer. Therefore, the majority of these cases of zinc deficiency are likely to be treated with inexpensive, readily available and quite low-tech zinc fertilisers, such as zinc sulphate. In contrast, fertiliser manufacturers and/or distributors in more technologically-advanced countries are able to manufacture specialist blended compound macronutrient and specific micronutrient fertilisers containing zinc and possibly other micronutrients. In intensive farming and horticultural systems, where higher value crops are grown (e.g., fruit, edible nut, vegetable and certain arable crops), a vast array of micronutrient product types (3) are applied as foliar sprays tank-mixed with agrochemicals to reduce the number of field operations. Foliar sprays of micronutrients do not give a significant residual effect in following years, so they need to be applied to each susceptible crop, and sometimes more than one application may be required. Nevertheless, micronutrients are eminently suitable for foliar application because of the relatively small amounts required by crops. Applications can be timed to when they are most needed and they by-pass the complex inter-actions in the soil which can reduce their availability (3). There is also less risk of foliar-applied micronutrients accumulating to levels which exceed maximum safe and permissible concentrations. This is particularly important when fertilisers are applied to load cereal grains with zinc (agronomic biofortification), to increase their dietary value and contribution to human and animal nutrition. (See Section 2.6).

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AREAS OF THE WORLD WITH ZINC DEFICIENCY PROBLEMS IN CROPS

Zinc deficiency in crops is found in many countries and regions around the world. This brief survey is based on reports in the international literature and it is therefore likely that some important cases of deficiency, especially those in areas with low-input agriculture which are only known locally, may have been overlooked.

6.1 FAO Global Study of the Micronutrient Status of Soils

A study of the nutrient status of soils in thirty countries was carried out for the Food and Agriculture Organization of the United Nations (FAO) between 1974 and 1982 under the direction of Professor M. Sillanpää. This study, funded by the Government of Finland, focused mainly on developing countries which were representative of their region and types of soil and agriculture but also included six highly developed countries in Europe and Oceania for comparative purposes. During this study, a selection of agricultural soils were collected from representative sites within each participating country. In Brazil and India, soils were only sampled in part of the country and were therefore not representative of the whole of these countries. An indicator crop of spring wheat (*Triticum aestivum* cv Apu) was grown on samples of all the soils in greenhouses at the Finnish Institute of Soil Science, where the project was administered and where all the analysis of soils and plants was conducted ⁽¹⁾.

The samples of soil and their associated wheat plants were analysed for a range of macro- and micronutrients and key soil properties were measured. From the analytical results, the products of soil concentration x plant concentration were calculated for each nutrient (from hereon called "concentration products"). The lowest 5% of these concentration products were allocated to Zone I and the next lowest 5% to Zone II. The middle 80% of the concentration products were allocated to Zone III, the top 90%-95% of concentration products to Zone IV and the uppermost 95%-100% of the concentration product values were put in Zone V. This implies that concentration product values in Zones I and II represent

low available concentrations of nutrient elements and those in Zones IV and V high available concentrations. Therefore those soil samples with a high probability of severe deficiencies, would be in Zone I and less severe (possibly 'hidden' or 'latent') deficiencies in Zone II. The soils with the greatest risk of crops accumulating high, possibly even toxic, concentrations of some of the nutrient elements monitored would be found in Zone V. The results for zinc are given in Table 6.1.

From Table 6.1 (next page) it can be seen that out of the twenty nine countries included in this global study (it was not possible to get the full results for one country, Ecuador), ten countries (34.5% of the countries surveyed) had soils and crops of particularly low zinc status. Those countries with a total of more than 10% in Zones I and II (i.e. those with the soils of lowest zinc status and their associated crops) include: India, Pakistan, Iraq, Lebanon, Syria and Turkey.

These countries, or the part of the country sampled, in the case of India, all had semi-arid conditions and predominantly alkaline soils. Neighbouring countries and areas of the world with a similar climate (Mediterranean type), soils and cropping systems are also likely to have similar zinc deficiency problems. In general, the most zinc deficient soils tend to be calcareous soils (Calcisols) with a high pH and a semi-arid climate. Of the world soil groups in the FAO-UNESCO classification included in the survey of thirty countries, those with the lowest available zinc contents were: Halosols, Yermosols, Xerosols, Vertisols, Kastanozems, Lithosols and Histosols.

However, many of the countries that were found to have percentages of soil-plant concentration products between 1 and 9% in Zones I and II are also likely have some areas with zinc deficiency problems; these include: Hungary, Mexico, Nepal, Philippines Thailand, Egypt, Ethiopia, Ghana, Malawi, Nigeria, Tanzania and Zambia, and comprise 40% of the countries in the study ⁽¹⁾.

Although the twenty nine countries in Sillanpää's study are not fully representative of the full global range of soils,

Table 6.1**Percentage of Soil x Plant Zinc Contents Falling in each Concentration Zone* for 29 Countries in the Global Study of Micronutrients**(Adapted from Sillanpää , 1982⁽¹⁾)

Country	Number of Soil & Plant Samples	Zinc Percentage of Samples					% Low Zinc	
		I*	II*	III*	IV*	V*	I* + II*	
Whole Study	3538	5	5	80	5	5	10	
Belgium	36	-	-	17	31	53	-	
Finland	90	-	-	71	18	11	-	
Hungary	201	-	-	96	2	1	-	
Italy	170	3	4	82	5	6	7	
Malta	25	-	-	20	36	44	-	
New Zealand	35	-	-	60	34	6	-	
Argentina	208	-	-	92	5	3	-	
Brazil	58	-	-	84	7	9	-	
Mexico	242	2	5	86	2	4	7	
Peru	68	-	-	87	4	9	-	
India	258	11	7	81	0	1	18	
Korea (Rep)	90	-	-	78	9	13	-	
Nepal	35	3	3	91	-	3	6	
Pakistan	237	8	12	91	-	1	20	
Philippines	194	1	-	80	11	8	1	
Sri Lanka	18	-	-	83	11	6	-	
Thailand	150	1	2	87	5	4	3	
Egypt	198	-	2	95	1	2	2	
Iraq	150	34	23	43	1	-	57	
Lebanon	16	6	6	88	-	-	12	
Syria	38	5	11	76	3	5	16	
Turkey	298	17	18	64	1	1	35	
Ethiopia	125	-	1	65	15	19	1	
Ghana	93	-	2	95	2	1	2	
Malawi	97	1	1	89	9	-	2	
Nigeria	153	-	1	87	5	8	1	
Sierra Leone	48	-	-	88	4	8	-	
Tanzania	163	3	2	85	5	5	5	
Zambia	44	-	2	95	-	2	2	

* Zones = percentage of the product of Soil DTPA Zn x Plant Zn growing on the respective soil: Lower 5% limit between Zones I and II (Zn DTPA x Plant Zn = 2.0), Lower 10% limit, between Zones II and III (Zn DTPA x Plant Zn = 2.8), Higher 10% limit between Zones III and IV (Zn DTPA x Plant Zn = 86), and Higher 5% limit between Zones IV and V (Zn DTPA x Plant Zn = 183).

climate and cropping, they do give a valuable indication of the widespread occurrence of potential zinc deficiency problems. A follow-up project was also conducted by Sillanpää (1990) ⁽²⁾, which involved a series of 190 field trials in a total of fifteen countries. These were: the Democratic Republic of Congo (formerly Zaire), Ethiopia, Finland, Iraq, Malawi, Mexico, Nepal, Pakistan, Philippines, Sierra Leone, Sri Lanka, Tanzania, Thailand, Turkey, and Zambia. With one exception, the Democratic Republic of Congo, these countries were also surveyed in the earlier 1982 FAO study. The results from the field experiments helped to confirm the prediction from the concentration products in the earlier survey, that zinc deficiency was the most ubiquitous micronutrient problem of all in this group of countries. The percentage of field experiments where deficiencies of the six micronutrients tested were shown to be significant, decreased in the order: Zn (49%) > B (31%) > Mo (15%) > Cu (14%) > Mn (10%) > Fe (3%). The frequency of zinc deficiency in field experiments was highest in Iraq and Pakistan, followed by Nepal, Turkey, and Thailand and lowest in Tanzania.

In the field experiment project as a whole (Sillanpää, 1990) ⁽²⁾, zinc was the only micronutrient to show an almost equal occurrence of acute and hidden (or 'latent') deficiencies (25% acute, 24% latent). Boron (B), copper (Cu), iron (Fe), manganese (Mn) and molybdenum (Mo) all had a greater incidence of hidden than acute forms of deficiency. These field experiment sites provide a very important indication of the relative importance of the different micronutrient deficiency problems, especially zinc, in the countries included in the study and also of the relatively high proportion of cases of hidden deficiency. Since hidden deficiency is not accompanied by obvious symptoms, it can often remain undiagnosed without soil or plant analysis, or controlled field experiments, such as those conducted by Sillanpää.

Zinc deficiency problems in regions and individual countries (grouped together according to the IFA Regions and Countries Statistical Classification) are considered in more detail below.

6.2 Individual Countries or Regions with Zinc deficiency Problems in Crops

6.2.1 Sub-Saharan Africa

The African countries for which there is information in the literature on the occurrence of zinc deficiency in crops include: Congo, Cote d'Ivoire, the Democratic Republic of Congo, Ghana, Guinea, Madagascar, Malawi, Mali, Nigeria, Sierra Leone, South Africa, Sudan, Swaziland, Togo, Zaire and Zimbabwe. The list of crops reported to be affected by zinc deficiency in African countries includes: avocados, bananas, cocoa, citrus, dry beans, maize, oil palm, peas, pecan nuts, rice, sugar cane and wheat.

In their recent review of micronutrient deficiency problems in Africa, van der Waals and Laker ⁽³⁾ state that there is little published information about micronutrient problems in low-input agriculture in Africa, but more information is available for the commercial crop production sector in several countries. In South Africa, widespread zinc deficiency is found in maize on sandy soils and also in sugar cane, dry beans, wheat, peas, citrus fruits, avocados, pecan nuts and bananas. Sandstone-derived soils in the High Veld and calcareous soils in the north-western Free State (an important maize growing area) are particularly prone to deficiency. In most cases, the problems were solved by the use of zinc-containing fertilisers or, in the case of fruit trees, by foliar sprays ⁽³⁾.

Kang and Osiname ⁽⁴⁾ reported cases of zinc deficiency in humid and tropical regions of Africa. These included: deficiency in maize on ferrallitic soils derived from gneiss in Madagascar, in oil palms in sandy soil at Entoumbi in the Congo, and in cocoa in Ghana and western Nigeria. Liming soils from pH 4.5 to above 6.5 in Guinea and the Cote d'Ivoire caused zinc deficiency in bananas. Zinc deficiency in rice was reported on flooded soils in Sierra Leone. Sandy soils in the sub-humid zone of south-western Nigeria showed zinc deficiency in maize (where extractable zinc levels were < 1 mg Zn kg⁻¹). Zinc deficiency is also common in rice grown on Vertisols in northeast Nigeria (Chad Basin). Zinc deficiency is also found on maize grown on sandy soils in Zimbabwe. Grain yield increases of 33% were obtained in maize with low rates of applied zinc on sandy soils in the subhumid zone of south-western Nigeria.

Zinc deficiency is also common in rice grown on Vertisols in the northeast of Nigeria and in crops grown on Vertisols in the Gezira region of Sudan. They also referred to zinc deficiency occurring in crops in the Democratic Republic of Congo, Ghana, Madagascar and Togo.

Kang and Osiname ⁽⁴⁾ reported that zinc deficiency was a major problem in crop production in the Gezira region of the Sudan. Coating seed with zinc compounds is not sufficient to correct zinc deficiency on these soils and so soil-applied zinc fertilisers must be used.

Most soils in Somalia are calcareous, but agricultural soils do not have such high CaCO₃ contents: 30% of agricultural soils have <10% CaCO₃, 31% have 10-20% CaCO₃ and 39% have 20-30% CaCO₃. Soil pH values are between 7.2-8.2, with pHs of around 8 being predominant ⁽⁵⁾. These calcareous soils and high pH conditions are highly conducive to zinc deficiency.

Joffre ⁽⁶⁾ reported that zinc deficiency in maize is widespread in Malawi and a survey of soils showed 49% of soils with less than the critical soil test concentration of zinc. The percentages of deficient soils in individual Agricultural Development Districts in Malawi ranged between 3 and 87%. The earlier survey by Sillanpää ⁽¹⁾ showed no indications of severely deficient soils in Malawi, but there were many in which marginal zinc deficiencies could occur. However, zinc deficiency was found at some, but not all, of the fourteen experimental sites in the follow-up field experiments in Malawi ⁽²⁾.

Buri *et al.* ⁽⁷⁾ reported that 66% of lowland soils in West Africa had available zinc levels below the critical level of 0.83 mg kg⁻¹ necessary for rice production. In Mali, low zinc contents in crops and fodder grown on sandy soils of the Sahel were considered by Jacks *et al.* ⁽⁸⁾ to pose a risk of zinc deficiency in the local population, especially in mothers and children.

No severe deficiencies of zinc were indicated by the soil x plant concentration products for the samples from Ethiopia, but Sillanpää ⁽¹⁾ considered that hidden deficiencies could still occur at many locations. In subsequent field experiments (Sillanpää, 1990) ⁽²⁾, zinc deficiency was found at several sites and even where yields did not appear to be affected, low zinc concentrations were sometimes found. The lowest zinc

values for the soil samples from Ghana were all from the Ashanti region, but although severe deficiencies do not appear likely, responses to zinc may still be found at some locations in this region ⁽¹⁾. Both very high and very low zinc values were found in the soil samples from Nigeria. The low zinc concentrations were more typical of sites in the Northern States. Although severe deficiencies were unlikely, responses to zinc fertilisers would be expected at many locations in this region. In Sierra Leone, the analytical survey showed that some sites would be likely to respond to zinc, although most soils had adequate levels of zinc. In the follow-on field experiment project, Sillanpää ⁽²⁾ found indications of zinc deficiencies at most of the seven field sites in Sierra Leone. Samples from Tanzania showed a wide variation in zinc concentrations, but deficiencies were likely at many locations. In Zambia, the average soil and plant concentration products of zinc were in the 'normal' zone (Zone III) but many showed a low enough value to indicate that zinc deficiency could occur ⁽¹⁾. However, little or no evidence of zinc deficiency was found in the field trials in Tanzania and Zambia, and only two out of four sites in the Democratic Republic of Congo showed possible problems due to marginal zinc ⁽²⁾.

6.2.2 South Asia

The South Asian countries with reported zinc deficiency problems in crops include: Bangladesh, India, Nepal and Pakistan. However, it is likely that the problem also affects some other countries in this region.

6.2.2.1 Bangladesh

Zinc deficiency, together with sulphur deficiency, are recognised as limiting factors in crop production in Bangladesh. About 1.75 Mha of intensively cropped land are estimated to be affected by zinc deficiency, which mainly affects rice and wheat ⁽⁹⁾. Gopalan ⁽¹⁰⁾ stated that zinc deficiency in soil and plants has emerged as a major potential problem in the wake of the intensification of agriculture, especially in rice crops grown on alkaline and waterlogged soils. He reported that studies in Bangladesh had revealed the possibility of low concentrations of zinc in a wide range of foods and feed: fruits, vegetables, legumes, grains, grasses and fodder crops. He was particularly concerned about the impact of these low zinc contents on human nutrition and wellbeing ⁽¹⁰⁾.

Two recently released wheat varieties in Bangladesh (Sourav cv. and Shatabdi cv.) and the first rice variety introduced specifically for rice-wheat systems (BR32) have been shown to be susceptible to zinc deficiency. The latter variety tends not to show obvious symptoms but zinc deficiency reduces yield.

6.2.2.2 India

In India, zinc is now considered the fourth most important yield-limiting nutrient after, nitrogen, phosphorus and potassium, respectively (13). Analysis of 256,000 soil and 25,000 plant samples from all over India showed that 48.5% of the soils and 44% of the plant samples were potentially zinc-deficient and that this was the most common micronutrient problem affecting crop yields in India (14). In comparison, 33% of soil samples were potentially deficient for boron, 13% for molybdenum, 12% for iron, 5% for manganese and 2.5% for copper. Beneficial responses to zinc fertilisation were found in 63% of 5,807 field trials conducted in farmer's fields throughout India (14). Other authors have stated that more than 50% of the agricultural soils in India are zinc-deficient which amounts to around 80 Mha (15). Around 2.5 Mha of alkaline soils on the Indo-Gangetic alluvial plains give rise to severe zinc deficiency in crops (16). Zinc fertilisation is also required on a regular basis on many alluvial soils and soils of the wheat belt in India, and also on the high-yielding tea-growing areas in the south of the country.

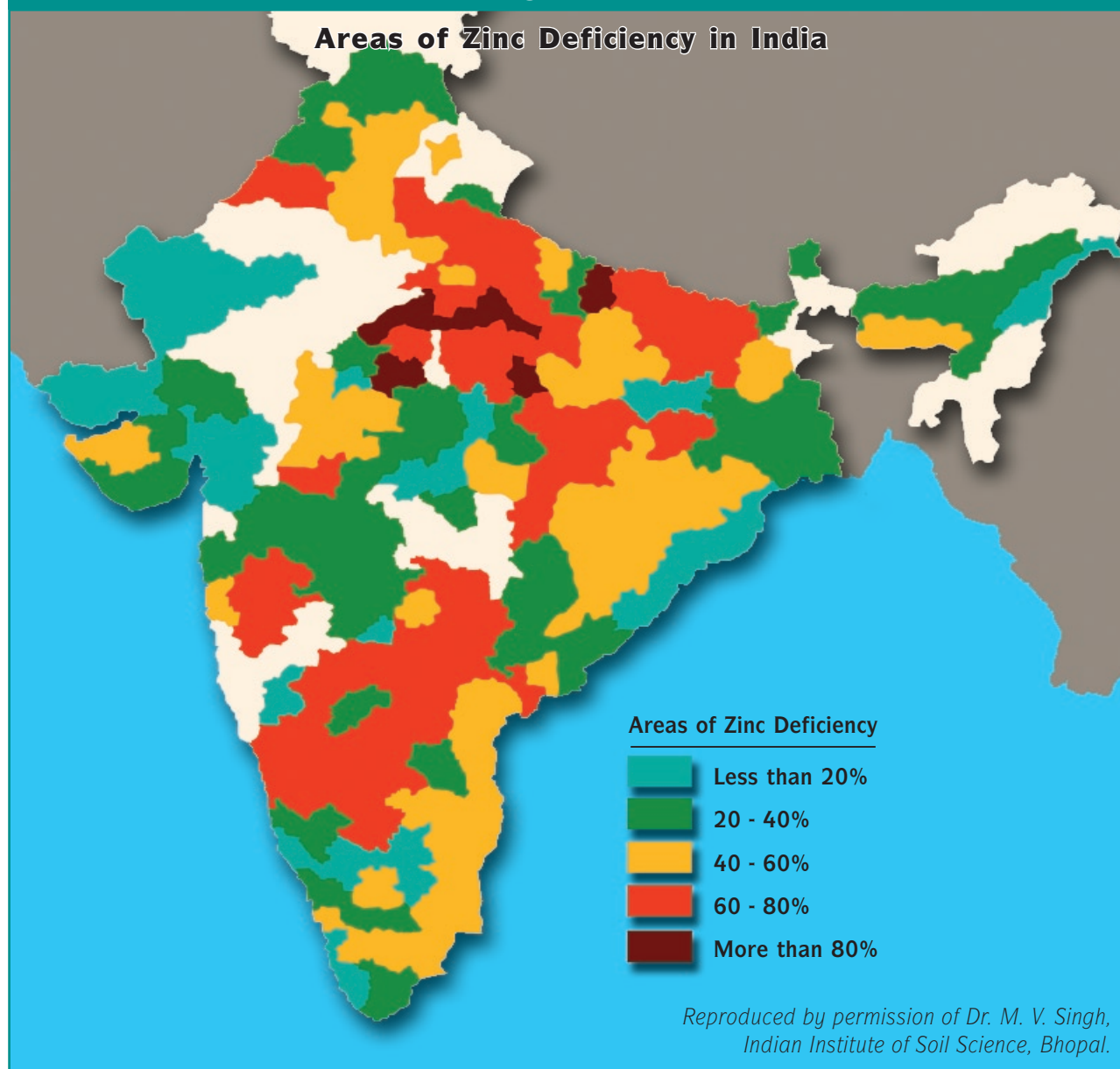
Sillanpää (1) reported that out of the thirty countries in the FAO study, India occupied one of the lowest positions in graphs of available soil and plant zinc concentrations; 18% of the DTPA extractable zinc concentration products fell in the two lowest zones (Zones I and II) and most of the rest of the values are comparatively low (mean DTPA extractable Zn = 0.90 mg kg⁻¹). The frequency of low zinc values was highest in the soil samples from Bihar, but low samples also occur in the states of Haryana, Punjab and Madhya Pradesh. Zinc deficiency was found more frequently in the soils of the arid and semi-arid regions of India than those in the humid and sub-humid zones. In Gujarat, neutral to alkaline red loamy soils (Alfisols) and low-lying alluvial rice soils were more prone to zinc deficiency than acid soils. In Andhra Pradesh, 74% of the rice growing soils, which were mainly Vertisols and Alfisols, were found to be zinc deficient (11).

Zinc deficiency is considered to be the predominant constraint for crop production on coarse textured, flood plain, alkaline, and calcareous soils which had a relatively high soil pH, a high calcium carbonate content, and low organic matter contents. Agricultural productivity is significantly affected by zinc deficiency in eleven states. It is very prevalent in the soils of the arid and semi-arid regions of: Haryana (61% of samples), Punjab (47%) and Uttar Pradesh (45%). It is also widespread (34-53%) in the black and red alluvial soils of Madhya Pradesh, Tamil Nadu and Andhra Pradesh, the leached soils of Meghalaya and West Bengal and the laterite (Ferralsol) soils of Orissa (12). A study carried out in 1959 showed that 85% of Punjab soils were deficient in zinc. In 2002, zinc deficiency problems in the Punjab were particularly serious and also on the tarai areas of Uttar Pradesh, some parts of Haryana, western Uttar Pradesh, and Delhi. Where zinc deficiency problems are acute, an application of 50 kg ZnSO₄ ha⁻¹ is recommended. In cases of moderate deficiency, 25 kg ZnSO₄ ha⁻¹ is sufficient (13).

Lowland (paddy) rice-producing soils all over India are affected by zinc deficiency in many places. Applications of zinc to correct deficiencies in rice range between 2.5 to 22 kg Zn ha⁻¹ giving a maximum yield increase of 4.8 t ha⁻¹. Zinc sulphate is the most widely used source of zinc, but zinc-enriched diammonium phosphate and nitrophosphates have also proved effective (14). Crops grown on the Indo-Gangetic Plain, including paddy rice, wheat and sugar cane are particularly prone to zinc deficiency. This region of India comprising: Rajasthan, Haryana, Punjab, Uttar Pradesh, Madhya Pradesh and Andhra Pradesh have a total irrigated area of 11.3 Mha of rice, 18.1 Mha of wheat and 2.5 Mha of sugar cane. Application of 25kg ZnSO₄ ha⁻¹ will help to increase wheat and rice yields by 500 to 1000 kg ha⁻¹. In addition to the above regions, zinc deficiency has recently become recognized as a major problem in groundnut, wheat, rice and sugar cane in Maharashtra, Gujarat and Bihar. Apart from the application of ZnSO₄, zinc deficiency can also be avoided if large applications of manures are used, but this is not possible for all fields (14).

According to Katyal and Vlek (11), zinc deficiency occurs in the Nilgiri Hills area of Tamil Nadu where the organic matter content of the soil is above 5%. Sunflower seed production in Tamil Nadu is also affected by zinc deficiency. Where soils are deficient, either

Figure 6.1



25 kg ZnSO₄ ha⁻¹ is applied as a basal treatment or applied as a 0.5% ZnSO₄ spray on the 30th, 40th and 50th day after sowing ⁽¹³⁾.

Pearl Millet (*Pennisetum typhoideum*), known locally as bajra, is grown on about 12 Mha in India (30% of world area of pearl millet production and 11% of aggregate cereal production in India). It is grown in most parts of India except the north east and is most suited to light (sandy) soils. It can be grown as either a pure stand, or as a mixed crop with other species such as cotton, sorghum, niger (*Guizotia abyssinica*), wheat, pulses and oilseeds.

Yields of 2-3.5 t ha⁻¹ are normal, but with adequate soil moisture or irrigation 3-4 t ha⁻¹ can be obtained. It is susceptible to zinc deficiency when grown on sandy soils and 2 kg ZnSO₄ ha⁻¹ are needed to rectify the deficiency.

Marwaha ⁽¹⁵⁾ reported that in Rajasthan, trials in farmer's fields on soils which had been shown by soil tests to contain sufficient available zinc, still showed responses (6-19%) to zinc fertilisers in a range of crops, including rice and wheat. He argued that the critical values used for diagnosing potential deficiencies needed to be revised and to be made more location-specific. Mean available Zn

status declined in the order: Alfisols > Mollisols > Inceptisols > Entisols.

Cereal crops are generally the most susceptible to zinc deficiency and show a high response to zinc fertilisation. On several types of soils, the available zinc status of the soil will determine whether a crop will grow or completely fail. In the case of acute deficiency, crop responses to zinc application tend to be very marked with yield increases of 92% (rice), 78% (wheat), 79% (maize), 48% (barley), and 88% in oats compared with controls which only receive NPK fertiliser (16). Results from 15,000 on-station field experiments all over India showed, that crop responses to zinc fertilisation ranged from 15.7-23 % in cereals except pearl millet, 13.4-41.2 % in pearl millet, 7.3-28.2 % in pulses, 11.4-40 % in oilseeds, 5-34 % in fodder crops and 24.4-53.8 % in cash crops such as sugar cane and cotton (16).

Increased awareness of the widespread problem of zinc deficiency has resulted in an increase in the use of zinc sulphate in agriculture of between 2,000-2,500 t yr⁻¹ in different states in India. This has resulted in an improvement in the zinc status of many soils and so zinc deficiency has decreased by 15-45% over a period of 15-20 years. However, as a result of an increase in intensive cropping, more soils are showing multi-micronutrient deficiencies. Until 1990, less than 2% of soil samples (out of a total of 63,575 soil samples from six states) showed deficiencies of more than one micronutrient, but the percentage of soils indicating multiple micronutrient deficiencies is now increasing in some areas (16).

With the population of India predicted to rise to 1.5 billion (1.5 x 10⁹) by the year 2050, the country needs to increase its current annual food production by 5 Mt yr⁻¹ compared to the 3.1 Mt yr⁻¹ achieved over the past four decades. There is very little scope for expanding the area under cultivation, so the additional food and primary products required in the future for the larger population will have to be met through increasing agricultural productivity. This is likely to further accentuate the deficiencies of zinc and other micronutrients in crops and may pose a threat to the nutritional security of the country. Therefore, maintaining adequate levels of available zinc in soils is of great importance (17). The distribution of zinc deficiency in India is shown in Figure 6.1.

6.2.2.3 Nepal

Sillanpää (2) (1990) found indications of zinc deficiency in the majority of the eighteen field experiments conducted in Nepal. Andersen (18) suggested that 30-50% of all Nepalese soils were deficient in zinc (and 85-90% deficient in boron). Jensen (19) reported that "khet" lowland terraces, where vegetables and flooded rice are grown, are most prone to deficiency and found 29% of the soils studied to have low available-zinc concentrations.

6.2.2.4 Pakistan

Hamid and Ahmad reported that (in 2001) 70% of agricultural areas in Pakistan were deficient in zinc and that nitrogen, phosphorus, zinc and potassium (deficient in that order) are the four main essential ingredients of balanced fertilisation programmes (20).

Kausar *et al.* (21) reported that although there had been a 32% increase in fertiliser use in Pakistan in the previous decade, the corresponding increase in yield was only 15%. This was ascribed to imbalanced use of fertilisers and micronutrient deficiencies, especially of zinc and boron. Qayyum *et al.* (22) reported field experiments in an area in which 47% of the soils had been diagnosed as being zinc deficient. Treatments involving NPK and micronutrients (boron, copper, iron, manganese and zinc) showed a 27.8% yield depression in maize when zinc was omitted from the treatments.

According to Rashid and Ryan (23), cases of zinc deficiency in the following crops are known to occur in Pakistan: chickpea, citrus, cotton, deciduous fruits, maize, mustard, potato, rapeseed, rice, sorghum, sugar beet and wheat. Zinc deficiency in rice was the first micronutrient deficiency disorder to be recognised in Pakistan. The symptoms of this disorder had been called 'Hadda' disease, but its cause was identified by Yoshida and Tanaka of IRRI as being due to zinc deficiency in 1969. Rashid (24) refers to an estimated fertiliser requirement of 5,730 t Zn for Pakistan, but the actual amounts used are much less than this, even in the case of rice, where the need for regular zinc fertilisation is widely understood. Average yield increases resulting from the use of zinc fertilisers in Pakistan were: 22% in potato and sunflower, 18% in maize, 13% in wheat, 12% in rice, 11% in soya bean and 8% in both cotton and sugarcane (24).

Sillanpää ⁽²⁾ conducted field trials in Pakistan and found that all nine field sites in different parts of the country were deficient in zinc. These deficiencies ranged from hidden (or latent) to severe.

In Pakistan, strongly calcareous soils with a pH of 8.2 in inter-montane valleys give rise to zinc deficiency in newly planted fruit trees (and also deficiencies of iron and manganese). Heavy applications of livestock manure on fruit trees and vegetables help to prevent deficiencies of phosphorus and micronutrients. Symptoms of deficiency in newly planted trees disappear after a few years of heavy manure applications.

6.2.2.5 Sri Lanka

Severe zinc deficiency in rice on slightly acid soils is reported to occur in a region of around 10,000 ha near Matale ⁽¹¹⁾. Sillanpää ⁽²⁾ found indications of latent zinc deficiency in most of the ten field trials in Sri Lanka.

6.2.3 East Asia

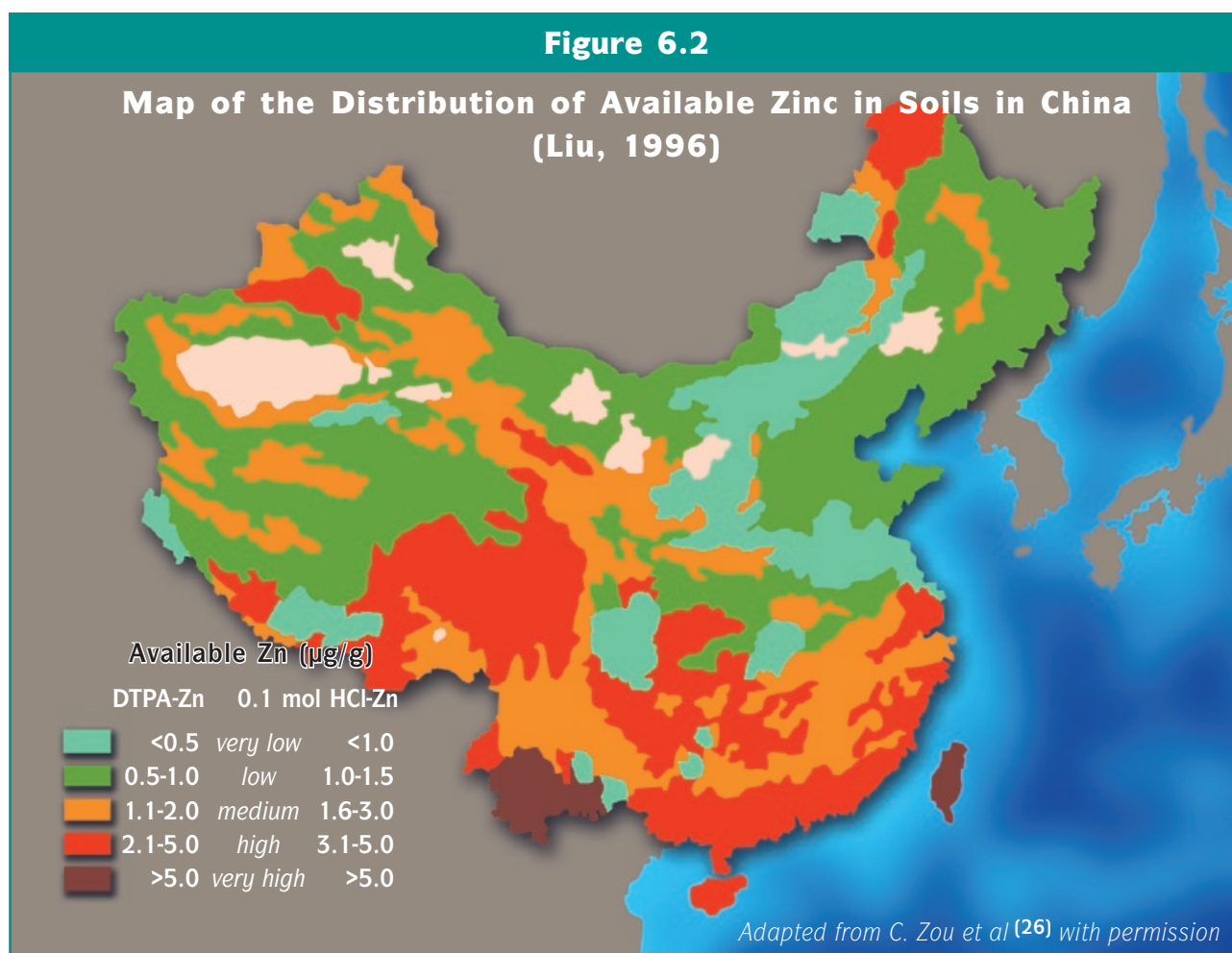
The countries in this region with reported cases of zinc deficiency include China, Philippines, Sri Lanka, Taiwan Province of China and Thailand

6.2.3.1 China

From a survey of soils in China, it is estimated that 48.6 Mha (51.1% of farmland) is potentially zinc-deficient ⁽²⁵⁾. Available-zinc contents in acid soils of southern China are much higher than those in calcareous soils of northern China ⁽²⁶⁾. (See Figure 6.2). Available zinc levels in China are assessed in soil tests using 0.5M HCl for acid soils and 0.05 M DTPA for alkaline soils. This is in accordance with the distribution of Zn deficiency problems in crops on the calcareous soils. The most widely affected crops in China are maize and rice, which respectively receive the largest amounts of zinc fertilisers. Rice production on alkaline paddy fields is widely affected by zinc deficiency and recently introduced water-saving methods of production,

Figure 6.2

Map of the Distribution of Available Zinc in Soils in China (Liu, 1996)



such as the growing of aerobic rice are also prone to zinc deficiency ⁽²⁶⁾. In addition to correcting deficiencies to maximize crop yields, there is now a move to increase the zinc density of the edible portions of staple crops. This can be by the use of zinc fertilisers and also by exploiting the genetic potential of plants to accumulate higher concentrations of zinc in their edible parts. A study of zinc contents in 115 varieties of rice, showed an eleven-fold variation, which indicates the potential for selecting genotypes with enhanced zinc accumulation characters ⁽²⁶⁾.

Rice-wheat cropping systems now occupy 13 Mha in China. Zinc deficiency can occur with this type of farming system in either, or both the rice or wheat crops ⁽²⁷⁾ (see Section 7.5).

6.2.3.2 Indonesia

On the basis of soil analysis, many upland soils, including alluvial soils, Regosols, Lithosols and Aridisols in Indonesia are considered to be zinc deficient ⁽¹¹⁾. In West Java, 29% of the soils were classed as being zinc-deficient as a result of a survey of 162 soil samples from an area of 2.5 Mha.

6.2.3.3 Japan

Zinc deficiency was identified in rice in Japan following its discovery in India in 1966. Zinc deficiency was found to be associated with the 'Akagare Type II' disorder in rice which gives rise to red, withering leaves ⁽²⁸⁾.

6.2.3.4 Philippines

Around 500,000 ha of irrigated rice in the Philippines has been reported to be zinc-deficient ⁽²⁹⁾.

Katyal and Vlek ⁽¹¹⁾ reported a zinc deficiency in rice on Hydrosols (Gleysols) in the Philippines, which was so severe that no yield was obtained without zinc treatment. Deficiencies in rice on a calcareous soil in the Philippines which gave a yield response to zinc of 4.8t ha⁻¹, were also reported. Sillanpää ⁽²⁾ found indications of zinc deficiency in half of the thirteen field trials carried out in the Philippines.

6.2.3.5 Taiwan Province of China

Although not widespread, zinc deficiency does occur in rice in the Taiwan Province of China. Responses to zinc are

recognized in sugar cane. Increases in cane yield and sugar quality of 10% were obtained with zinc fertilisers.

6.2.3.6 Thailand

Paddy rice soils in the semi-arid north east of Thailand are the most susceptible to zinc deficiency ⁽¹¹⁾. Sillanpää ⁽²⁾ found either acute or latent zinc deficiencies in all of the fifteen field experiment sites in Thailand.

6.2.4 West Asia

The hot, semi-arid (Mediterranean) climate in much of this region has resulted in many of the soils of being calcareous (Calcisols) with a high pH and low organic matter contents. These soil conditions are highly conducive to zinc deficiency ⁽²³⁾.

Zinc deficiency in wheat is a widespread problem in several countries of the West Asia (much of which is also referred to as the Near East), including: Afghanistan, Egypt, Iran, Iraq, Syria and Turkey ⁽³⁰⁾.

6.2.4.1 Afghanistan

In 2000, zinc deficiency was reported to be a major problem in wheat in Afghanistan ⁽³⁰⁾. Afghanistan has 14 Mha of cultivable land with 2.3 Mha in irrigated wheat. The country has a semi-arid climate and calcareous soils with a high pH (of the soils tested >50% pH 8-8.5, 35% pH 8.5-9.0 and 10% pH 9-9.5). All soils tested had >10% CaCO₃ and, in some cases, >40% and there is a high probability that zinc deficiency problems are already restricting crop yield and almost certainly will when phosphatic fertiliser use increases and higher yielding crop varieties are grown ⁽⁵⁾.

6.2.4.2 Cyprus

In Cyprus, 47% of the land area is in arable production and 25% in forests. The soils are of the Mediterranean type with high pH values, high CaCO₃ contents and low organic matter contents. The predominant soil types are Calcareous Lithosols and Xerosols.

Zinc deficiency is the most prevalent micronutrient disorder, especially in tree crops, but iron and manganese deficiencies also occur ⁽⁵⁾.

6.2.4.3 Iran

More than 80% of arable soils in Iran are zinc-deficient with an average yield depression of around 50%. Most of the cereal growing area and fruit tree production (citrus, apple, pear and peach) area is affected by zinc deficiency. The main causes of zinc deficiency in Iran are:

- i) calcareous soils with high pH values (mainly >30% CaCO_3 with an actual range of 16-58% CaCO_3 and pH 7.9-8.5),
- ii) high applications of phosphatic fertilisers,
- iii) high concentrations of bicarbonate (HCO_3^-) in irrigation water,
- iv) lack of zinc fertilisers.

The average application rate of zinc sulphate fertiliser to wheat crops is 1 kg ha^{-1} which gives up to $43 \text{ kg extra grain per hectare}$ ⁽³¹⁾. More than 80% of arable soils in Iran have $<1 \text{ mg k}^{-1}$ DTPA-extractable zinc and the lower critical value is $0.7\text{-}1.0 \text{ mg Zn kg}^{-1}$ ⁽³¹⁾.

Wheat grown on zinc-deficient soils produces poor yields of grain with a low micronutrient content. Wheat is the most important crop in Iran and supplies more than 45% of the protein and 55% of the calorie requirements of the people. In 2003, Iran produced around 12.9 Mt of wheat on 6.5 M ha with an average yield of 1.98 t ha^{-1} ⁽³²⁾. In 2001, it was reported that 40% of the wheat land was affected by severe zinc deficiency (37% by iron deficiency, 25% by manganese deficiency and 24% by copper deficiency). These ubiquitous zinc-deficient soils result in low zinc concentrations in plant foods and the widespread occurrence of zinc deficiency in animals and humans ⁽³¹⁾.

Maize, wheat, rice, soya bean, pea, sorghum, citrus and grape vines (very sensitive) are all affected by zinc deficiency in Iran. Citrus trees in the south and north of Iran are more prone to zinc deficiency than other fruit trees (apple, pear and peach). Crops grown in Iran that are most tolerant to zinc deficiency are vegetables and barley.

Experiments at 25 sites with treatments involving: zinc, iron, manganese, and copper showed that zinc treatments significantly increased the grain yield (by 15%), 1000 grain weight, number of seeds per spikelet, and the zinc and protein content of grain. The critical DTPA-extractable zinc concentration was shown to be $0.9 \text{ mg Zn kg}^{-1}$ soil. Regression analysis also showed that the combination of high soil pH, high content of CaCO_3 and clay, and low

annual precipitation were the major factors associated with the deficiencies of zinc and the other micronutrients. The responses to zinc were greater than those for other micronutrients; the second highest increase in grain yield was with the manganese treatment (12.3%) ⁽³³⁾.

6.2.4.4 Iraq

Widespread zinc deficiency in wheat is found in Iraq. In his global micronutrient study, Sillanpää ⁽¹⁾ found that the available zinc concentrations in the soils of Iraq were the lowest of the 30 countries studied and that zinc deficiency would seem to be a major problem. The mean DTPA - extractable Zn was 0.27 mg kg^{-1} . The soil samples were from widely scattered areas and no area could be distinguished as being more or less deficient than the rest. Two thirds of the soils collected from Iraq for the FAO study were from the Mesopotamian Plains where irrigated agriculture has been practiced for around 6000 years. The remaining samples were collected from northern Iraq where crops are grown under rainfed conditions. However, irrigation seems to have no effect on zinc levels, but boron showed a marked accumulation in the irrigated soils, probably due to inputs from irrigation water.

Sillanpää ⁽²⁾ conducted 18 field experiments in the nine provinces of Iraq and all showed some degree of zinc deficiency. In the most acute case of zinc deficiency in a field experiment in Iraq, the yield of rice was more than trebled as a result of the application of 12 kg Zn ha^{-1} .

6.2.4.5 Israel

Zinc deficiency is recognized, but rarely treated, in avocados in Israel ⁽³⁴⁾. Pecan trees on calcareous soils are also affected.

6.2.4.6 Jordan

In Jordan, steppe soils developed from soft limestones occur over 80% of the country. These soils have 20-70% CaCO_3 and are also salt-affected. Owing to the low rainfall, irrigation with groundwater is required for optimum yields but this gives rise to salinity/sodicity problems.

Alluvial soils with 15-60% CaCO_3 cover 50,000 ha of which 15,000ha is under intensive irrigation and is planted with off-season vegetables, citrus and banana. These soils

tend to have a high potassium status but are low in phosphorus. Chlorosis problems, involving iron, and possibly zinc deficiencies are common (5).

Red Mediterranean soils also occur in Jordan. These soils have <70% CaCO₃, a high potassium and low phosphorus status and narrow C:N ratios

6.2.4.7 Lebanon

The soils in Lebanon are predominantly calcareous with 10% to more than 30% CaCO₃, and the soil pH is always > 7.0. Zinc deficiency is recognized in citrus trees (23), but it is highly likely that other crops are also affected (5).

Calcareous soils on the Bekaa Plain have been shown to be zinc deficient, but the distribution of soils responding to zinc fertilisation is very erratic and so soil testing is important to avoid losing yield (see section 2.2.1).

6.2.4.8 Saudi Arabia

About 0.1% of the land area is under cultivation (225,000 ha). Barley is the main crop grown. The soils are calcareous and gypsiferous, saline soils. Irrigation waters provide adequate potassium, but phosphorus fertilisation is required. The soil conditions are highly conducive to zinc deficiency (5).

6.2.4.9 Syria

Syria is recognised as having widespread zinc deficiency problems in wheat (30). These are due to the high soil alkalinity which is the main cause of the low available zinc status.

Sillanpää (1) found that, in general, the zinc status of the soils sampled in Syria was quite low (mean DTPA-extractable zinc 1.21 mg kg⁻¹), but none of the soil extraction values indicated very severe deficiency. However, he considered it possible that crops would respond to zinc treatments at several locations.

According to Rashid and Ryan (23), zinc deficiency has been reported in both Medic and forage legumes in Syria.

6.2.4.10 Turkey

Zinc deficiency is the predominant micronutrient deficiency problem in crops in Turkey, especially over Central Anatolia, the country's major wheat growing area. Out of the thirty countries included in the global study of micronutrients in soils for FAO, Sillanpää (1) found that the samples from soil types which represented about 80% of Turkey's arable area (87% non-irrigated, 13% irrigated) indicated that the Zn status of soils in this country were among some of the lowest (mean DTPA extractable Zn 0.62 mg kg⁻¹). The main areas with very low available zinc content soils were Central and Eastern Anatolia, but about 20% of the samples from the Black Sea, Marmara and Aegean regions were also low.

On the basis of a survey of 1511 samples of cultivated soil from all over Turkey, it was found that 49.8% of these were potentially zinc deficient (35). There was a history of poor yields in the new, high-yielding varieties of wheat being grown in Central Anatolia. The crops also showed visible symptoms of stress, comprising mainly chlorotic and necrotic patches on the leaves. Field experiments carried out in 1991/92 showed that the main constraint on wheat growth and yields on the high pH calcareous soils in Central Anatolia was zinc deficiency. It was also found that durum wheat (*T. durum* Desf.) was more severely affected than bread wheat (*T. aestivum* L.). Tolerance to zinc deficiency decreased in the order: rye > triticale > barley > oat > bread wheat > durum wheat (36).

Zinc deficient areas of Turkey as a whole cover 14 Mha of cultivated land, which is equivalent to 50% of the cultivated area. Wheats grown in Central Anatolia, where the soils are mostly highly calcareous, were found to be highly responsive to zinc fertilisation. Relative increases in wheat grain yield with zinc fertilisation ranged between 5-550% with a mean of 43%. The greatest yield responses (>100%) were found where the DTPA-extractable zinc concentrations in the soils were < 0.12 mg kg⁻¹. Wheat grown in these soils without zinc generally gives very poor grain yields (< 550 kg ha⁻¹). However, soils with DTPA-extractable zinc concentrations of < 0.3-0.4 mg Zn kg⁻¹ responded to zinc fertilisers, particularly in the case of Durum wheats. Zinc applications of up to 10 kg Zn ha⁻¹ were generally found to be sufficient to supply adequate zinc on the zinc-deficient calcareous soils (37). Twelve years after the discovery that wheat crops in Central Anatolia were mostly deficient in zinc, sales of zinc-containing

fertilisers had exceeded 400,000 t. In most cases these are NPK fertilisers with 1% zinc added ⁽³⁶⁾.

Wheat is the main source of dietary calories providing on average 45% of the daily calorie intake, but probably up to 75% in some rural areas. By using zinc fertilisers to increase grain yields, the zinc content of the grains was also increased, along with a decrease in phytate content which resulted in a lower phytate:zinc molar ratio and made the zinc more available to human consumers. This has resulted in an increase in zinc intake by the population in the region most affected by zinc deficiency in wheat and has had marked beneficial effects on human health ⁽³⁶⁾.

Yakan *et al.* ⁽³⁸⁾ reported that the incidence of zinc deficiency in rice in Turkey has increased in recent years owing to the replacement of traditional rice varieties by modern varieties that are less tolerant to zinc deficiency and which also remove large amounts of zinc through higher yields, continuous cropping, and high rates of phosphatic fertiliser use. After nitrogen and phosphorus, zinc deficiency is the next most important nutritional factor limiting rice yields in Turkey and is most prevalent under conditions of high pH, calcareous, light and sandy soils, high phosphorus levels and wet soils.

Zinc deficiency in rice was first recognized in rice in Turkey in 1980 in the western part of the Black Sea region where the soils are calcareous and rice was continuously cropped without rotation and high levels of phosphorus fertiliser are used. A disorder, which was later found to be zinc deficiency, was first observed in rice in the Thrace-Marmara region of Turkey in the early 1990s but only confirmed as zinc deficiency by field experiment in 1997. Subsequent experiments indicated that 15 kg Zn ha⁻¹ was sufficient to rectify zinc deficiency in rice in this region.

6.2.5 Western and Central Europe

Zinc deficiency has been reported in areas of calcareous soils in Bulgaria, France, Greece, Hungary and Spain, and on sandy and other textured soils in England, France, Ireland, Netherlands, Poland, Sweden and Switzerland. In several cases, low total concentrations have been exacerbated by high pH, such as on calcareous soils, and/or high phosphorus levels.

In France, zinc deficiency in maize was first reported in 1961. By 1970, it was reported that 500,000 ha of land in the Pyrénées-Atlantiques and Les Landes were affected, together with 100,000 ha in the Charente and Charente-Maritime. The soils affected were mainly calcareous and some sandy-silty soils ⁽³⁹⁾.

In general, zinc deficiency is not widely recognized in much of Europe, at least in north-western parts where many of the soils are relatively young, having developed in the 8-10,000 years since the last ice age. Many of these soils are rich in clays, or have minerals which are still being weathered and releasing some zinc in plant-available forms. However, coarse textured sandy and gravelly soils with low total zinc contents have the potential to cause zinc deficiency in sensitive crops, especially when limed and treated with high rates of phosphatic fertilisers. This has been found in barley crops on sandy soils in Ireland (F. MacNaidhe, 1987, pers comm.). In addition to the pedogenic source of zinc, much of Europe receives significant inputs of zinc from agriculture (livestock manures, fertilisers and pesticides), sewage sludge recycling and/or atmospheric-deposition. Some of the atmospherically deposited zinc can either be absorbed directly through the foliage by plants, or enters the soil and is incorporated in the soil-plant system (See Sections 2.1.3.1 to 2.1.3.4).

6.2.6 Eastern Europe and Central Asia

There is little information in the international literature about this region, except for reports of zinc deficiency in wheat in Kyrgyzstan ⁽³⁰⁾.

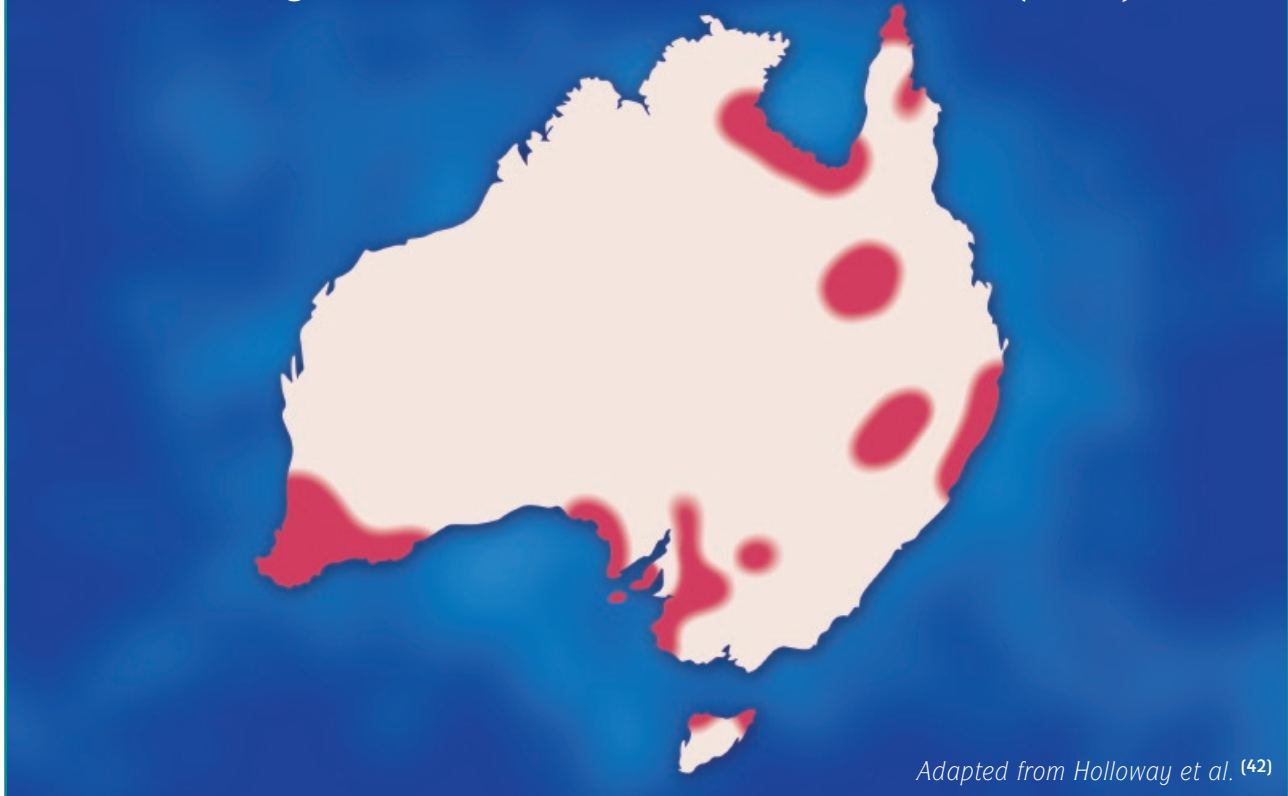
6.2.7 Oceania

6.2.7.1 Australia

Zinc deficiencies in Australia have been reported in crops on the following groups of soils: calcareous sands (Victoria), grey, brown and red clays (Queensland), Black Earths (Vertisols) (Queensland), Rendzinas and Terra Rosas (Queensland and South Australia), Solodised Solonetz and Solodic soils (Queensland), Solonized Brown Soils (South Australia), Red Brown Earths (Queensland and

Figure 6.3

**Map of Australia
Showing the Main Areas of Zinc-Deficient soils (in red)**



Adapted from Holloway et al. (42)

South Australia), Grey-Brown and Brown Podzolic soils (Western Australia), and Lateritic Podzolic soils (Western Australia and Queensland) (40).

Widespread zinc deficiency is found in the Ninety Mile Desert on the borders of Victoria and South Australia. In the south west of Western Australia there is an area of 8 Mha of zinc-deficient land. Besides the Ninety Mile Desert, zinc deficiency also occurs on acid to neutral red brown earths and a range of alkaline soils including: calcareous sands, shallow red and grey calcareous soils, heavy grey and black clays and ground water Rendzinas. Zinc deficiency in crops and pastures declined with regular use of single superphosphate, which contained up to 600 mg Zn kg⁻¹ as an impurity and was therefore a rich source of zinc as well as phosphorus. The introduction of high analysis fertilisers (such as monoammonium phosphate (MAP) and diammonium phosphate (DAP), with low contents of zinc impurities has led to a resurgence of zinc deficiency in South Australia. Zinc supplementation through addition to NP fertilisers or as

soil applications or foliar treatments is now commonplace throughout the cereal growing and horticultural areas (41).

Zinc deficiency in crops was originally encountered on infertile acid sands of the south east of South Australia, western Victoria and Western Australia and on sand over clay duplex soils. Low availability of zinc on alkaline soils has also led to zinc deficiency occurring on a wide range of alkaline soil types (42).

In many agricultural areas of Australia, lentils respond to zinc fertilisers. Zinc deficiency in citrus was first recorded on podzolic soils in Western Australia, but also occurs in widely in South Australia (42).

Clover, alfalfa and other pasture species, oats, citrus and, to a lesser extent, wheat, barley, fruits and grapes are affected by zinc deficiency in South Australia and Western Australia. Citrus and apples are severely affected and vines, horticultural crops, wheat and pastures are affected to a lesser extent in Victoria. In Tasmania, clover, apples

and pears suffer from zinc deficiency. In New South Wales the deficiency occurs in citrus, apple and stone fruit, maize, linseed, sorghum, cotton, soybeans, wheat oats and alfalfa ⁽⁴²⁾.

Zinc deficiency in wheat is a widespread problem in South Australia where zinc availability is generally low in calcareous, highly alkaline soils ⁽³⁰⁾. Zinc deficiency is becoming an increasing problem as cropping frequency increases depletion of reserves of available zinc and high analysis fertilisers are used. However, where fertilisers are applied to correct zinc deficiency, the added zinc is likely to remain near the surface even in sandy textured soils ⁽⁴¹⁾.

In the semi-arid areas, applying nitrogen, phosphatic and zinc fertilisers in liquid form to the subsoil (up to 40 cm deep) can have significant advantages in grain yield in wheat, water use efficiency and zinc uptake by crops rather than applying granular fertilisers to the surface. However, the cost is relatively high in areas with extensive production ⁽⁴¹⁾. Boron toxicity can be exacerbated in zinc-deficient soils.

The main areas of zinc-deficient soils in Australia are shown in Figure 6.3, which is adapted from a map by Holloway *et al.* ⁽⁴²⁾.

6.2.7.2 New Zealand

Sillanpää ⁽¹⁾ considered that some soils on South Island could be marginally zinc-deficient; but most of the relatively small number of soil samples collected from New Zealand showed medium to high concentration products. Zinc deficiency has been reported on the Island of Niue, a dependency of New Zealand in the South Pacific. The shallow lateritic (Ferralsol) soils have developed from the weathering of calcite and dolomite and have low available zinc contents which are responsible for the poor growth of forage and other crops ⁽⁴³⁾.

6.2.8 North America

6.2.8.1 Canada

In British Columbia and Ontario, zinc deficiency occurs in apples, pears, cherries, peaches, apricots, prunes and grapes ⁽⁴³⁾.

In Alberta, zinc deficiency occurs in irrigated field beans, wheat, barley, flax and maize on calcareous, high pH soils that have been machine levelled, or on sandy soils, or where soils have high phosphorus levels. In western Canada, flax is more sensitive to low levels of available zinc and iron than most other crops.

6.2.8.2 United States of America

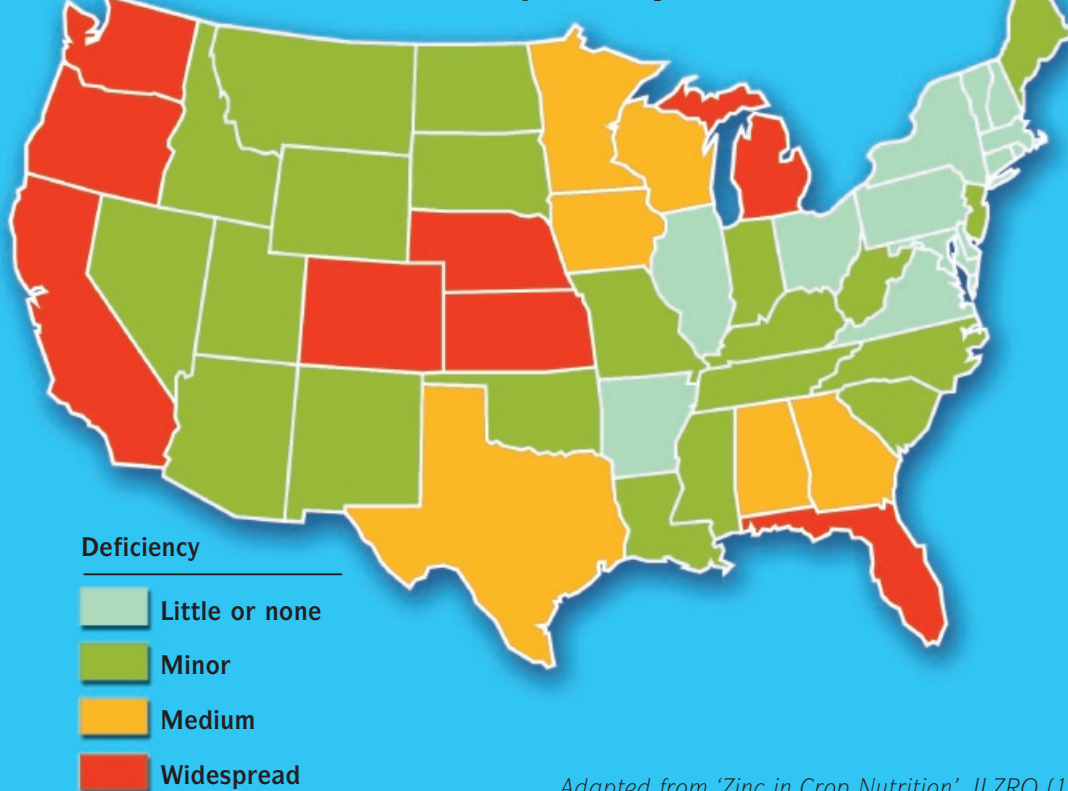
Zinc deficiencies have been observed in many parts of the USA. Even in 1937, zinc deficiencies were reported in an area which extended for 650 km (North-South) in California. Zinc deficiency caused many pecan orchards in Arizona to be abandoned. In 1956, surveys showed scattered zinc-deficient areas in eight states and by 1965, the deficiency problem was recognised in 40 states. Zinc deficiency was widespread in maize in the mid-west and in calcareous, cut, or heavily irrigated sandy soils of the west coast and the poor sandy soils of Florida. Most of these areas no longer have zinc deficiency problems because the soils or crops are regularly treated with zinc fertilisers and monitored. Deficiencies in the USA are generally assessed on the basis of plant analysis ⁽⁴³⁾.

According to Brown ⁽⁴⁴⁾, by far the greatest percentage of zinc fertiliser use in the USA, is on maize (corn) and soya bean in the West North Central States of Minnesota, Iowa, Missouri, North Dakota, South Dakota, Nebraska and Kansas. Although the areas of these crops are similar to those in the states in the East North Central region, zinc deficiency (and also that of boron, copper and manganese) is more prevalent in the West North Central region because the soils are generally more alkaline. With the higher financial returns from growing genetically modified (GM) varieties of soya beans and maize, it has become more cost-effective to use zinc and other micronutrient fertilisers. The amounts applied have greatly increased in recent years in Illinois, Indiana and Ohio, which are the primary states for growing these crops. This trend is likely to increase as larger areas of these GM varieties are grown ⁽⁴⁴⁾. It has been found that the increased use of the herbicide glyphosate in intensive arable production, including with "glyphosate-tolerant" GM crops, can have an effect on the availability of micro-nutrients such as zinc, manganese and others to crops and may therefore necessitate increased applications of zinc fertilisers to overcome this problem ^(44, 45).

Although, zinc deficiency is recognised in crops in 40 states, California and Hawaii have the largest numbers of

Figure 6.4

The Extent of Zinc Deficiency in Crops in the United States



Adapted from 'Zinc in Crop Nutrition', ILZRO (1975) (27)

different crops affected ⁽⁴⁶⁾. The number of states with zinc deficiency problems in different types of crops were given in 1975 by ILZRO ⁽⁴⁶⁾ as: maize 30, other grains 10, citrus 5, other fruits 15, nuts and coffee 15, beans 10, potatoes 6 and other vegetables 7 (states). The following list of zinc deficient crops and states in which they are found (* denotes a widespread problem) was taken from ILZRO ⁽⁴⁶⁾ (See Figure 6.4).

Alabama: maize, pecan*

Arizona: lettuce, pecan, citrus, cherry

California: maize*, beans*, lettuce*, carrots*, potatoes*, onions, tomatoes, peppers*, almond, walnut, citrus*, apple, cherry, grape*, avocado

Colorado: maize, sorghum, beans, potatoes*, apple, cherry

Delaware: maize

Florida: maize, beans*, pecan, citrus*, avocado, soybean

Georgia: maize*, chestnut

Hawaii: maize, cucumbers, tropical vegetables, potatoes, peppers, coffee, pineapple, citrus, cherry

Idaho: maize, beans*, cherry

Indiana: maize

Iowa: maize, soybean

Kansas: maize*, sorghum, beans*

Kentucky: maize

Louisiana: maize, rice, citrus*, strawberry*

Maine: maize*, apple*

Michigan: maize, beans*, onions

Minnesota: maize, soybean

Mississippi: maize, pecan, tung

Missouri: maize

Montana: apple, cherry

Nebraska: maize*, sorghum, beans, cherry, soybean, castor bean

Nevada: maize, apple, cherry

New Jersey: maize, apple, castor bean*

New Mexico: sorghum, pecan, apple, cherry

New York: potatoes

North Carolina: maize, pecan

North Dakota: maize*

Oklahoma: maize, pecan*

Oregon: maize, barley, beans, potatoes, onions, apple, cherry, strawberry*

South Carolina: maize, pecan
South Dakota: maize, sorghum
Tennessee: maize*, pecan
Texas: maize, sorghum, lettuce, carrots, tomatoes, peas
Utah: apple*, cherry
Vermont: maize
Washington: maize*, wheat, sorghum, beans*, peas*, potatoes*, onions, cherry, castor bean*
West Virginia: cauliflowers
Wisconsin: maize, beans, peas, castor bean
Wyoming: maize

N.B.: Cherry also includes other fruit crops

6.2.9 Latin America and the Caribbean

It is widely considered that zinc deficiency could limit crop production over much of the region. Brazil has widespread deficiency of zinc in citrus, coffee and maize and coffee crops are also affected in Colombia and Costa Rica (46).

In tropical America, Sanchez and Cochrane (47) reported that zinc deficiency could be limiting yields over much of the region. The deficiency is widespread in the highly weathered soils (Oxisols, Ultisols, and Latosols) in the Campo Cerrado region of the central plateau of Brazil, in the Llanos Orientales of Columbia and Venezuela as well as in Costa Rica, Guatemala, Mexico and Peru. Zinc deficiency in pineapples has caused major problems in French Guyana and Puerto Rico. Zinc deficiencies are the most striking problems and are associated with low total concentrations of zinc in the soil parent materials.

Leon *et al.* (48) report that zinc deficiency has been confirmed in highly diverse locations of tropical America for the following crops: maize, rice, sorghum, lettuce, soybeans, cotton, cassava and perennial soya beans. Using the Mehlich-1 soil test (0.05 M hydrochloric acid + 0.0125 M sulphuric acid) with a critical concentration of 1 mg Zn kg⁻¹, 95% of the 518 topsoil samples from the Cerrado region of Brazil were shown to have extractable zinc concentrations below this concentration and were therefore probably zinc-deficient. On the humid Atlantic coast of Brazil, zinc and boron deficiency have been observed in coffee. The full range of crops found to be

affected by zinc deficiency in the tropical region of Brazil is: coffee, oranges, rice, sugarcane, maize, sorghum, cassava and rubber. Field experiments in Ecuador have indicated zinc and manganese deficiencies in maize, coffee, beans, and guyana grass.

Sillanpää (1) reported that none of the samples from Brazil in the FAO Micronutrient Study had very low zinc values, but a response to zinc was possible at several sites. In the samples from Brazil, although about 6% had high zinc values, low zinc contents were more common. For Mexico, it was concluded that although there were no very low zinc values, a shortage of zinc was likely in many soils. The areas sampled in this study which were most likely to have zinc deficiency were in Queretaro, Sonora and Sinaloa. Several of the soil samples from Peru showed quite low levels of zinc in both soils and plants indicating the possibility that some areas may be at least marginally deficient in zinc (1).

Fageria and Stone (49) stated that zinc deficiency is found widely in South America and is associated with low total zinc contents in the highly weathered, deep tropical soils (Ferralsols/Oxisols and Ultisols). Zinc deficiency in crops on these acid soils in South America is made worse by liming them to raise the pH, which normally occurs with intensification.

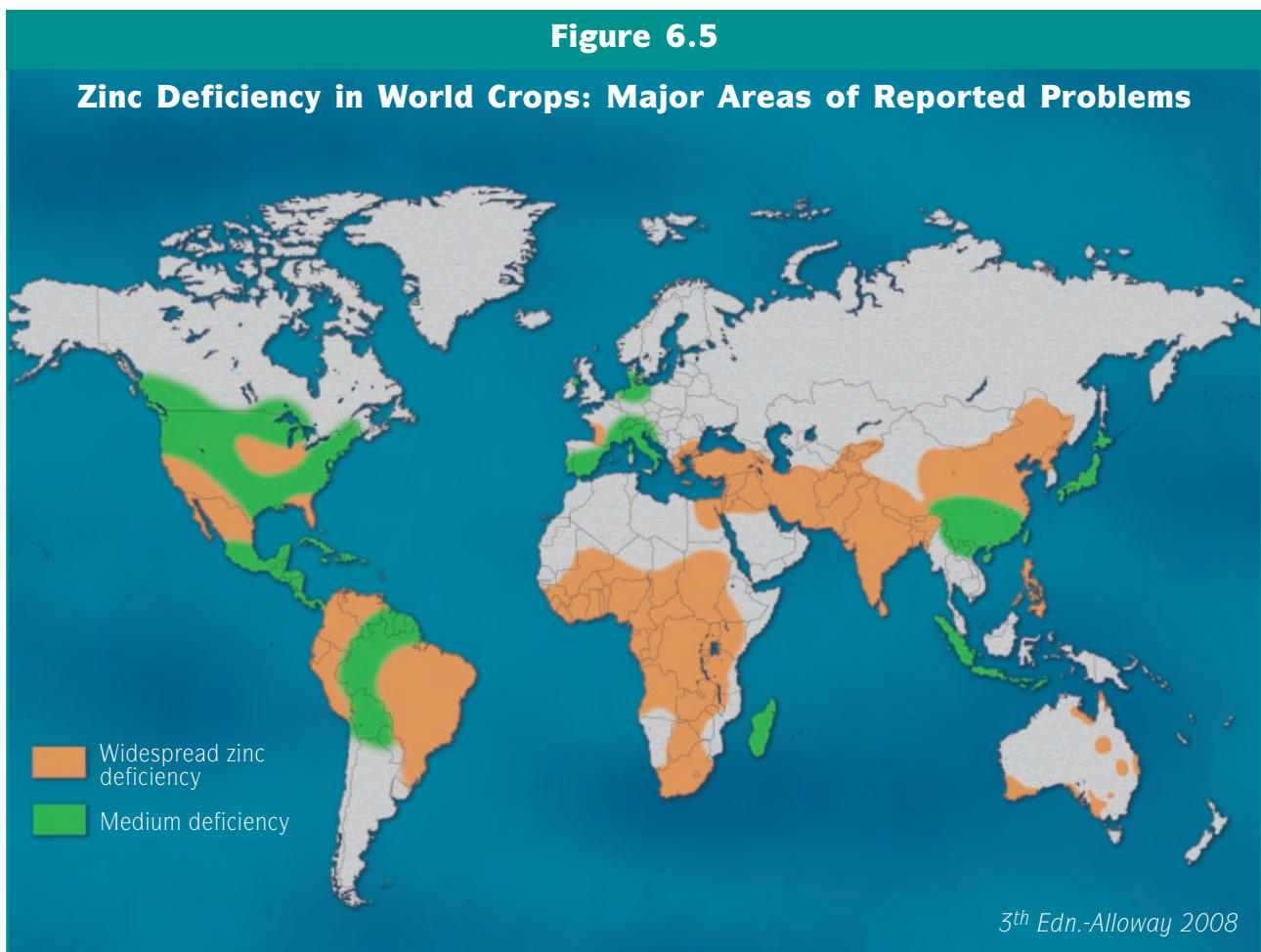
6.3 GENERAL STATEMENT

This selection of countries does not include all areas affected by zinc deficiency in crops because the information is difficult to find for some countries and regions. Nevertheless, it has been shown that zinc deficiency in crops is very widespread and economically very important on a global scale. As discussed throughout this report, the countries and regions where the deficiency is a particularly important problem tend to be those with either lowland rice production, semi-arid areas with calcareous and/or alkaline soils, or where crops are grown on highly weathered and leached soils, such as tropical red soils and Podzols, or other types of soil on sandy parent materials.

Fig. 6.5 shows the approximate global distribution of the main areas where zinc deficiency in crops has been reported. In contrast, Fig 2.5 (page 29) shows the combined distribution of the main types of soil associated with zinc deficiency. The differences in the areas highlighted in the two different maps are largely due to Figure 2.5 being based on the approximate areas covered by sandy, calcareous, saline and Vertisol soils, irrespective of whether the climatic conditions are suitable for growing crops. Hence almost the whole of Australia is shown to have soils likely to be zinc deficient. Now although zinc deficiency is a problem in Australia, only the areas around the western, southern and eastern coasts are suitable for cropping (see Fig 6.3), most of the rest is desert. Likewise, much of the desert areas in Africa and Asia are also shown in Figure 2.5 and not in Figure 6.5. Another reason for differences between the two maps is that Figure 6.5 is based on areas with zinc deficiency problems which have

been reported in the international literature. It is highly likely that some locally recognised deficient areas may not have been reported in the literature, especially where low intensity, subsistence cropping is practiced. In addition, many areas with hidden zinc deficiency may not yet have been discovered.

Owing to the importance of maize, rice and wheat as the world's major staple food crops and the zinc deficiency problems which are found in them, Chapter 7 gives a detailed consideration of these crops in the context of their zinc nutrition.



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ZINC IN THE NUTRITION OF THE MAJOR CEREAL CROPS

7.1 Introduction

Rice, wheat and maize are the world's three most important cereal crops both in terms of area harvested and in tonnages of grain produced. Direct human consumption accounts for 85% of total rice production, 72% of wheat and around 21% of maize. The cereals not directly consumed by people are mainly used for feeding livestock, although other non-food uses, such as production of alcohol for bio-fuels, are becoming increasingly important.

Wheat and rice together provide 45% of the digestible energy and 30% of the total protein in the human diet ⁽¹⁾. On the other hand, maize tends to be more widely used for feeding livestock and for producing chemicals such as ethanol than for direct human consumption, especially in the more developed countries.

Table 7.1 gives the harvested areas, total production and average yields of maize, rice and wheat for the world as a whole. The total area of arable land in the world in 2003 was 1,402.3 Mha, of which 11% was used for rice production, 14% for wheat and 10% for maize ⁽¹⁾. Rice is the principal food staple in around twenty five countries, mostly in Asia, but these include many of the world's most populous nations and it is therefore the staple food for the largest number of people in the world. Ninety one percent of rice is grown and consumed in Asia ⁽¹⁾. Wheat is the dominant staple in forty five countries, including those of Europe, North America, West Asia (the Middle East) and Oceania. Maize dominates the diets of people in Latin America and southern Africa. Sorghum and millet are also important cereals in some African countries. Apart from cereal crops, cassava or yams are the principal food staple in many tropical countries. In some Central American countries, plantains and bananas provide more digestible energy than any other food.

Table 7.1

World Harvested Areas, Total Production and World Average Yields of Maize, Rice and Wheat in 2003 (FAO, 2004) ⁽²⁾

	MAIZE	RICE	WHEAT
Total Harvested area (Mha) ⁽¹⁾	142.3	153.3	204.6
Percentage of Total Arable Land Area	10.02	10.79	14.40
Total Production (Mt) ⁽¹⁾	673.4	588.6	637.4
World Average Yield (t ha ⁻¹)	3.41	3.37	2.75

7.2 Yields of Cereals and Removal of Zinc from Soil

The average yields for the three cereal crops in selected countries around the world are presented in Table 7.2. These show a wide range, which is a reflection of differences in the intensity of the crop management (crop cultivars, fertiliser, pesticide use and irrigation) and related soil and climatic factors. However, the importance and areas of individual crops vary widely in different countries. China is the largest producer of rice, with 28% of total global production, followed by India with 22% of total production. China and India are also the two largest

producers of wheat with 16 % and 12% of the global output, respectively. However, as shown in Table 7.2, average yields of both rice and wheat are higher in China than they are in India, with rice showing the greater difference. The other major wheat producing countries are the USA (9% of global production), the Russian Federation (8%) and France (6%). The highest national average yield of wheat was 9.12 t ha⁻¹ in the Netherlands, which has a temperate climate and very intensive crop production. The largest producer of maize in the world is the USA with 40% of production, followed by China (18%), Brazil (5%) and Argentina and Mexico, each with 3%. The average maize yield in the USA (8.92 t ha⁻¹) was almost twice as high as that in China (4.85 t ha⁻¹) (2).

Table 7.2

Average National Yields for Maize, Rice and Wheat in 2003 for Selected Countries (t ha⁻¹)

	MAIZE	RICE	WHEAT
Argentina	6.47	5.40	2.06
Australia	8.23	10.29	2.00
Brazil	3.7	3.24	2.37
Canada	7.82	-	2.25
China	4.85	6.07	3.91
Egypt	7.71	9.43	6.15
France	7.14	5.61	6.23
India	2.11	2.62	3.00
Indonesia	3.25	4.54	-
Iran	8.57	5.89	1.98
Mexico	2.53	3.79	4.79
Myanmar	2.50	3.71	1.11
Pakistan	1.46	3.05	2.38
Russian Fed.	3.26	2.97	3.17
South Africa	2.90	-	1.78
Syria	4.00	-	2.74
Tanzania	1.54	1.96	1.18
Turkey	4.87	5.31	2.02
USA	8.92	7.45	2.97
Vietnam	3.22	4.63	-
World	3.41 (0.54-23.26)*	3.37 (0.7-10.29)	2.75 (0.24-9.12)

* lowest and highest average national yields of all countries listed by FAO (FAO, 2004 (2))

Maize and rice are both highly susceptible to zinc deficiency and many of the countries growing these crops, including China and India, have large areas of zinc-deficient soils which require regular applications of zinc fertilisers in order to prevent yield loss. Although, on a comparative basis, wheat is less sensitive to zinc deficiency than both maize and rice, the productivity of wheat crops in some countries, especially those with calcareous soils, such as Turkey and Iran, can be severely limited by zinc deficiency. All three of these cereal species show wide variations in zinc efficiency amongst cultivars and hence in their susceptibility to deficiency.

It is widely recognised that zinc deficiency becomes more prevalent with increasing intensity of cropping. This is both a result of changes in soil properties, such as pH, available water (irrigation) and phosphate status, and also the increased removal of readily available zinc from the soil by higher yielding crop varieties. In addition, these higher yielding crop varieties are often zinc-inefficient in comparison with the previously grown locally-adapted varieties. From Table 7.2, it can be seen that national average yields for maize, rice and wheat vary by factors of 43, 15 and 38, respectively; therefore zinc removal in cereal grains will also vary very widely. This can be very important in countries where a soil nutrient maintenance approach is used for micronutrients. Basically, this approach aims to replace micronutrients removed by crops and therefore it is important to use realistic values for the offtake of zinc by different crops.

There are many data in the literature for the uptake/ offtake of zinc in cereal grains. These tend to show a range between 60 and 300 g Zn ha⁻¹ per crop, but larger amounts have been found for high yielding crops. An interesting contrast is shown between crops managed in different ways on the same soil and under the same climatic conditions. For example, in Queensland, Australia, zinc removal in grain was 200 g Zn ha⁻¹ in irrigated wheat crops, but only 60 g Zn ha⁻¹ in dryland wheat. Similarly, 150 g ha⁻¹ was removed in the grain of irrigated maize compared to 70 g ha⁻¹ in dryland maize ⁽⁵⁾. A maize crop yielding 9.5 t ha⁻¹ of grain, grown in North America, could be expected to remove 380 g Zn ha⁻¹ in the grain and stover ⁽⁴⁾. Under subtropical conditions in India, a wheat crop producing 4.6 t ha⁻¹ of grain and 6.9 t ha⁻¹ of straw, absorbed 500 g Zn ha⁻¹ ⁽⁵⁾.

For rice, Doberman and Fairhurst ⁽⁶⁾ gave zinc removal rates of 40-60 g Zn per tonne of grain yield (average 50 g t⁻¹) with 60% of zinc remaining in the straw at maturity. Zinc fertilisation increased zinc concentrations in both grain and straw. If only the grain is removed and the straw returned to the field, zinc offtake is only around 20 g Zn t⁻¹ of grain yield. Gupta and Mehla ⁽⁷⁾ reported uptake of 120 g Zn ha⁻¹ in rice (6.5 t ha⁻¹ yield) and 70 g Zn ha⁻¹ in wheat (4.1 t ha⁻¹ yield) without NPK fertiliser. However, with a relatively high NPK fertiliser treatment (180 kg N ha⁻¹, 90 kg P₂O₅ ha⁻¹, 90 kg K₂O ha⁻¹), zinc uptake was 300 g Zn ha⁻¹ for rice (14.5 t ha⁻¹ yield) and 200 g Zn ha⁻¹ for wheat (12.4 t ha⁻¹ yield). Although these levels of NPK use are higher than used by many farmers, they clearly show how uptake (and hence offtake) of zinc increases with rising yields brought about by the use of higher NPK applications.

From the human health viewpoint, increased uptake of zinc into cereal grains is a very desirable outcome and, as discussed in Section 2.6, there is increasing interest in using zinc fertilisers to increase the zinc density of grains (agronomic biofortification) in addition to optimising yields. When modern, high yielding varieties of cereals are introduced into areas where previously low-input farming was practised, there is often a risk of these more intensively grown crops being affected by zinc deficiency. Shivay *et al.* ⁽⁸⁾ reported zinc uptake of up to 268 g Zn ha⁻¹ in rice grain treated with urea coated with 2% zinc sulphate. This was more than twice the uptake in the control plots receiving urea alone (no added zinc). The rice straw took up 575 g Zn ha⁻¹ in the nil zinc, and 1078 g Zn ha⁻¹ with the 2% zinc sulphate-coated urea.

In tropical regions, such as in Bangladesh, where several crops are harvested in one year, the annual removal of zinc has been found to range from 1040 g Zn ha⁻¹ in a summer rice-fallow-rice sequence, to 1340 g Zn ha⁻¹ for a mustard-rice-rice sequence ⁽⁹⁾. Heckman *et al.* ⁽¹⁰⁾ reported that for maize crops with grain yields ranging from 4.9 t ha⁻¹ to 16.7 t ha⁻¹ (mean 10.3 t ha⁻¹) the zinc content of grain ranged from 15 to 34.5 mg Zn kg⁻¹ (mean 26.8 mg Zn kg⁻¹) giving an average removal of 276 g Zn ha⁻¹ per crop. Experiments in India showed that, as a result of increased crop offtake, available concentrations of zinc in soil decreased by between 19 and 31% when macronutrient fertilisers and manures were used without the application of zinc ⁽¹¹⁾.

7.3 Rice

Rice (*Oryza sativa* L.) is cultivated in more than a hundred countries, but 91% of the world's rice is grown in Asia ⁽¹²⁾. The warm and moist climatic conditions in much of Asia are very well suited to rice production. Rice provides 35-80% of the calories consumed by 3.3 billion people in Asia and 8% of the calories for 1 billion people in Sub-Saharan Africa, Latin America and the Caribbean. On a global scale, rice provides 21% of *per capita* energy and 15% of *per capita* protein for humans ⁽¹³⁾. It has been predicted that sufficient rice will be needed to feed four billion people by 2015 and this will require a 50 % increase in rice production to maintain present nutritional standards (which are still not adequate for many people). To provide an adequate level of nutrition for all of these people, an increase in rice production of 70 % would be necessary. According to Doberman and Witt ⁽¹²⁾, it will be necessary for rice yields in Asia to increase by about 14 % *per annum* between 2000 and 2010 and then by 25% from 2010 to 2020. In addition to Asian countries, demand for rice has been increasing in much of Africa and in parts of Latin America.

The area of land cropped with rice in 2003 was around 153.8 Mha, with 132 Mha in Asia. This included around 42.5 Mha in India, 32.13 Mha in China, 11.02 Mha in Indonesia, 10.7 Mha in Bangladesh, 9.6 Mha in Thailand, 6.4 Mha in Viet Nam, 6.3 Mha in Myanmar and 3.6 Mha in the Philippines ⁽²⁾. In Africa, 9 Mha of land are used for growing rice. The total global production of rice in 2003 was 599.6 Mt of grain. The top ten rice producing countries are (in decreasing order): China (166 Mt), India (132 Mt), Indonesia (52 Mt), Bangladesh (38 Mt), Viet Nam (35 Mt), Thailand (27 Mt), Myanmar (25 Mt), Philippines (14 Mt), Brazil (10 Mt) and Japan (10 Mt) ⁽²⁾.

There was a 120 Mt increase in rice production in eight Asian countries between 1965 and 1980; and of this, about 25 Mt were the result of improved fertiliser use, 20 Mt due to growing modern varieties, 30 Mt to the removal of drought stress (the "irrigation effect") and about 20 Mt to "other causes" ⁽¹⁴⁾. However, interactions between these factors are important and it is difficult to ascribe yield increases to single factors.

The 'Green Revolution' (High Yielding Varieties Program) provided new varieties of rice which enabled rice production to meet the demands of a rapidly rising population. Average yields in most countries were increasing at up to 2.8% *per annum* up until the end of the 1980s. However, since 1990, rice production has increased at a slower rate (1.1%) than the population and is causing concerns for world food security. There is a 'yield gap' for rice in many countries. This is the difference between the 'potential yield', determined by variety and climate (measured at research stations) and the yield achieved in farmer's fields. The current average potential rice yield in Asia across the seasons is 8.5 t ha⁻¹. Farmers would aim for yield targets of not more than 80% of the potential yield to achieve profitable high yields and efficient input use while reducing the risk of crop failure (e.g., due to lodging and pests). There are many factors which could be responsible for farmers not obtaining higher yields, but ensuring that the crop has an adequate supply of both macro and micronutrients is likely to be one of the most important (Witt, 2003, personal communication). Deficiencies of zinc are relatively easy to correct and so, where zinc fertilisation is necessary, it could be removed from the list of possible factors which could be contributing in the failure to obtain target yields.

Modern rice varieties, such as IRRI-bred cultivars, account for at least 55% of harvested rice in Bangladesh, 66% in India, 91% in Sri Lanka and 42% in Pakistan. The average cropping density for irrigated soils in South Asia is 120%. New short-duration varieties are common in irrigated systems and cover 74% of the harvested area ⁽¹⁵⁾ (see Section 7.5 Rice-Wheat Cropping Systems).

Rice production systems:

Irrigated lowland:

75% paddy produced on 55% of global rice area.
(20% tropical Asia, 30% subtropical Asia,
1% Africa, 1% Latin America, 3% others)

Rainfed lowland:

25% of global rice area.
(20% tropical Asia, 3% subtropical Asia,
1% Africa, <1% Latin America)

Upland (dry land):

13% of global rice area
(7% tropical Asia, 1% subtropical Asia, 2% Africa,
3% Latin America)

Upland (paddy):

8% of global rice area,
(7% tropical Asia, 1% subtropical Asia, <1% Africa,
<1% Latin America)

(IRRI Rice Almanac, 1997)⁽¹⁵⁾

It is widely accepted that rice yields under flooded or lowland (paddy) conditions are generally higher than those under non-flooded conditions, due to lack of water stress, easier weed control and greater availability of certain nutrients, particularly phosphorus, and a pH of around 7.0 ⁽¹⁶⁾. The highest rice yields (6-7 t ha⁻¹) in rain-fed (non-irrigated) environments can only be achieved on soils with high water tables and sufficient rainfall to prevent water stress ⁽¹⁵⁾.

In certain soils, namely Oxisols, Ultisols and Inceptisols, flooding eliminates aluminium and manganese toxicity (through an increase in pH) and increases phosphorus availability. Flooding saline soils also decreases electrical conductivity and promotes the leaching of salts. In calcareous soils, waterlogging increases iron availability which often results in marked yield increases. In soils such as Entisols, Inceptisols, Alfisols, Vertisols and Mollisols with pH values of 6-7 (when aerated), flooding has little effect on nutrient availability. On the other hand, in iron-rich soils, such as Oxisols (Ferralsols in the FAO-UNESCO classification), there can be some deleterious effects of flooding, including the formation of toxic concentrations of the ferrous ions (Fe²⁺). In sandy soils with high organic matter and low iron contents, concentrations of organic acids and hydrogen sulphide (H₂S) may reach toxic levels and insoluble zinc sulphide could also be precipitated. Where this occurs, the only remedy is to drain the soil for short periods and restore oxidizing conditions. However, these soils are only of limited importance for rice production.

Lowland (paddy) rice production in Asia requires large volumes of water to keep it continuously submerged. With increasing problems of water scarcity throughout the region, alternative production systems requiring lower inputs of water are being developed. The shortage of

water is particularly pronounced in northern China and several new approaches have emerged. These include: a) the Aerobic Rice System which uses specially bred varieties and supplementary irrigation and fertilisation; b) the Continuous Ground Cover Rice Production System (CGCRPS) using a thin film of plastic over the soil before rice is planted and supplementary irrigation, and c) the Alternately Submerged and Non-Submerged System (ASNS). In general, significant water savings of up to 60% or more have been achieved, with yields which are similar, or only slightly lower, than in continuously submerged rice. However, the yields are still higher than obtained with traditional upland rice varieties ⁽¹⁷⁾. Apart from China, water-saving methods of rice production are also being investigated in the Philippines, Indonesia, India and Madagascar ⁽¹⁸⁾.

7.3.1 Zinc Deficiency in Rice

Zinc deficiency is the most widespread micronutrient disorder in tropical rice, occurring in parts of China, Japan, India, Pakistan, Bangladesh, Nepal, Sri Lanka, the Philippines, the USA and Colombia under lowland (paddy) conditions, and throughout the Cerrado of Brazil in upland rice. Severe zinc deficiency in rice causes chlorosis, a decrease in, or complete lack of, tillering, a slower rate of crop maturity, and increased spikelet sterility. In lowland rice producing areas, zinc deficiency is associated with calcareous soils and is accentuated by prolonged flooding. Zinc deficiency symptoms are more pronounced at early growth stages and the rice plants can sometimes recover by later growth stages.

Some authorities consider zinc deficiency to be the second most important factor limiting rice yields, after nitrogen supply. However, an IRRI survey of on-farm experiments in six countries showed that, after nitrogen, phosphorus and potassium were equal second in importance, and zinc and sulphur were equal third in importance (C. Witt 2003, personal communication.).

Working in the 1980s, Scharpenseel *et al.* ⁽¹⁹⁾ estimated that about 50% of all paddy rice soils were affected by zinc deficiency, at least to the extent that the rice crop responded favourably to zinc application (hidden



Fig. 7.1
Young rice plants showing chlorosis, a typical symptom of zinc deficiency

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deficiency). This suggests that up to 35 Mha of paddy rice could be affected. However, even if improved knowledge of the soils in rice-growing areas has rendered this an over-estimate, it is highly probable that there are still several million hectares of paddy rice which could benefit from zinc fertilisation. In contrast to the estimate of Scharpenseel *et al.*, Karim ⁽²⁰⁾ stated that, zinc deficiency is a major yield limiting factor for wetland rice on only about 2 Mha in Asia. This disparity in areas affected could possibly be due, in part, to the emphasis on “major limiting factors” and that smaller yield benefits of zinc fertilisers on a much larger area of land may not have been included. Johnson-Beeboot *et al.* ⁽²¹⁾ have found that the diagnosis of zinc deficiency on the basis of responses to additions of zinc-fertilisers can be very unreliable due to zinc sulphate fertiliser becoming rapidly unavailable under reduced (waterlogged) conditions. Farmers do not see any response to the zinc treatment and may therefore fail to detect a significant zinc deficiency in their soil. Another reason for the unreliability of fertiliser addition trials is uncertainty about the zinc content of the fertiliser used. In some countries, zinc sulphate fertilisers are often adulterated with ammonium sulphate which reduces the zinc content, so that farmers and research workers cannot be sure of the amounts of zinc applied (Johnson-Beeboot, pers comm. 2007).

Unbalanced fertiliser use at higher yield levels is one of the major factors contributing to nutrient mining in

intensive rice production in Asia, because of increased nutrient removal in grain and straw (as discussed in Section 7.2). The increase in macronutrient fertiliser (NPK) use between 1984 and 1994 was 6.8% yr⁻¹ in Bangladesh, 7.5% yr⁻¹ in India, 8.2% yr⁻¹ in Nepal and 4.7% yr⁻¹ in Pakistan. However, the increase in fertiliser nitrogen use was relatively greater than that of phosphorus, potassium, sulphur and zinc in many countries, so that yields have been stagnating in the last decade despite further increases in fertiliser consumption.

Zinc deficiency in rice was originally called “alkali disease” because it is common in high pH, sodic soils. It is also prevalent in areas where the topsoil has been removed by land levelling, or where the irrigation water is high in bicarbonate (> 4 meq L⁻¹) ⁽²²⁾. Flooding and submergence bring about a decline in available zinc due to pH changes and the formation of insoluble zinc compounds ⁽²¹⁾. The soil pH rises with the onset of reducing (gleying) conditions and zinc solubility decreases 100-fold for each unit increase in pH. The insoluble zinc compounds formed are likely to be with manganese and iron hydroxides from the breakdown of oxides, and adsorption onto carbonates, especially magnesium carbonate. In the Philippines, most soils have a low calcium to magnesium ratio, indicating that magnesium carbonates are a common constituent. Under very strongly reducing conditions, insoluble zinc sulphide (ZnS) may also be formed ⁽²³⁾.

Field reconnaissance has shown that most fields with strong zinc deficiency are perennially wet and the soil profiles have a uniform greyish colour (with no brown mottles in the top 100 cm) due to gleying (Gleysols and gleyed variants of other soil groups). Fields without zinc deficiency are usually dry for part of the year and the soil profile contains obvious rusty brown mottles indicating periodic oxidising conditions. The perennially waterlogged sites occur on slopes where upwelling water reaches the surface from shallow artesian aquifers, or are due to surface flooding from artesian wells dug by the farmers. In these poorly drained soils, both organic matter and magnesium contents are usually high and are likely to play a role in aggravating zinc deficiency. Undrained peats can also give rise to zinc deficiency in rice ⁽²⁴⁾.

Sharpenseel *et al.* ⁽¹⁹⁾ found, in experiments with ⁶⁵Zn radioisotope tracer, that zinc was most mobile (and

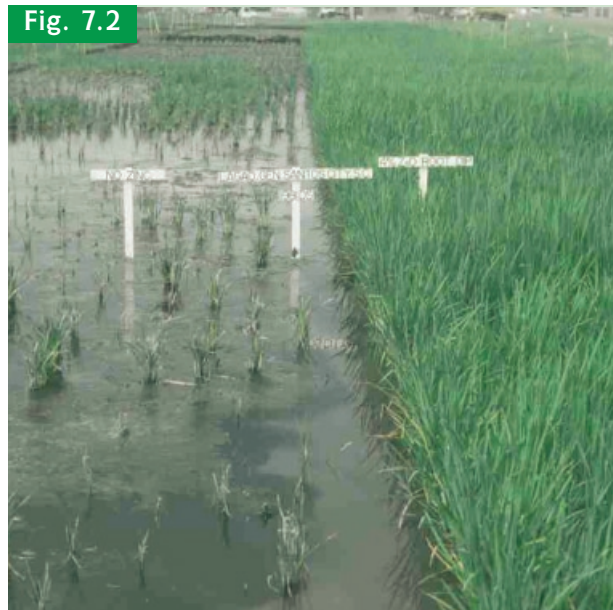
bioavailable) in freely drained soils. When waterlogged soils were air-dried and replanted with rice, the zinc deficiency was much less severe than in the waterlogged field soil. Neue *et al.* (25) investigated the reactions of zinc in flooded soils. In acid soils, zinc availability decreases after flooding owing to an increase in pH and the precipitation of zinc hydroxide ($Zn(OH)_2$). In sodic and calcareous soils, the decrease in zinc availability can be explained by the precipitation of zinc sulphide with the development of reducing conditions in flooded soils. If carbonates control the solubility, precipitation of zinc sulphide requires even more extreme reducing conditions. In addition, zinc may be strongly adsorbed on calcium and magnesium carbonates ($CaCO_3$ and $MgCO_3$) and on oxides of iron and manganese. The formation of $ZnFe_2O_4$ (franklinite, see Section 2.1.4.1) may also contribute to rendering zinc unavailable. The increased availability of calcium, magnesium, copper, iron, manganese and phosphorus with prolonged submergence depresses zinc availability and uptake by rice plants.

The soil conditions most frequently associated with zinc deficiency in rice are:

- low total zinc contents,
- low extractable zinc concentrations (0.05N HCl extractable $Zn < 1 \text{ mg kg}^{-1}$),
- $pH > 7$, such as on calcareous soils and heavily limed soils,
- high organic matter contents ($> 3\%$)
- perennial wetness due to low relief position, artesian water condition, or interflow, or upwelling of water,
- high bicarbonate concentrations,
- high magnesium content relative to calcium, such as in serpentine soils ($Mg:Ca > 1.0$),
- high available phosphorus content, use of high levels of phosphatic fertilisers,
- intensive cropping (without zinc fertilisation)
- growing high yielding varieties of rice,
- irrigation with alkaline water,
- Gleysols and gleyed variants of other soil groups
- sodic, saline-sodic, coastal saline soils,
- sandy peat soils,
- increased availability of other micronutrients and phosphorus after flooding,
- zinc sulphide precipitation when pH decreases in alkaline soil after flooding,

(Ponnamperuma (22), Dobermann and Fairhurst (6))

Fig. 7.2



An experiment with rice in a paddy field, showing severe zinc deficiency and crop failure in the plot on the left and normal growth in the zinc treated plot on the right.

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In neutral and alkaline rice soils there is a strong negative correlation between soil pH and rice grain yield when no zinc fertiliser is applied. However, the DTPA-extractable zinc concentration in paddy soils only declines slightly over the pH range 6.5-8.0, so the reason for the decrease in zinc uptake in plants without zinc fertiliser must be due to other factors apart from a decrease in zinc availability. The main factor likely to be responsible for the inhibition of zinc uptake by the rice plants and its transport from the roots to the shoots is the high concentration (15-40 mM) of bicarbonate ions (HCO_3^-) (26). Even bicarbonate concentrations of 5-10 mM inhibit root growth of zinc-inefficient cultivars, but slightly stimulate root growth in efficient cultivars. Close positive correlations exist between the accumulation of organic acids in the roots and inhibition of root growth by high bicarbonate concentrations (6). The association of zinc deficiency symptoms in rice with early growth is considered to be due to the high bicarbonate concentrations which occur during periods when reducing conditions (gleying) in the soil are at their peak (27).

As with wheat and other crops, rice cultivars also differ considerably in their sensitivity to zinc deficiency,

especially when growing on soils of high pH (28). It has been suggested that differences in the susceptibility to bicarbonate is the factor responsible for this. Zinc-inefficient cultivars grown in high bicarbonate concentrations, as well as low root zone temperature, show lower concentrations of iron and manganese as well as zinc, compared to zinc-efficient cultivars and/or high root zone temperatures. Hajiboland *et al.* (29) have shown that high bicarbonate concentrations in the soil solution increased the growth of fine roots in zinc-efficient lowland-rice genotypes but inhibited their growth in zinc-inefficient genotypes. This could at least partly explain why high bicarbonate concentrations exacerbate or cause zinc deficiency in lowland rice.

The decomposition of soil organic matter by microorganisms can give rise to chelating molecules which also modify the availability of zinc. At low pH, the lower limits of metal-organic complex stability render zinc more available (30).

Neue *et al.* (31) considered that increasing the phosphorus supply to rice reduces the uptake and translocation of zinc from the root to the shoot, especially if zinc availability is low to moderate. In maize, high phosphorus supplies reduce translocation of zinc from the root to the shoot, but do not reduce the absorption of zinc through the roots.

When nitrogen fertiliser levels are increased in rice crops, potassium applications also need to be increased. However, there have been some contradictory reports about potassium-zinc interactions in wetland rice crops. In experiments with the variety IR36 in the Philippines, at one site it was found that there was a response to zinc in the dry season, but the highest yields were obtained with potassium (200 kg K ha⁻¹) and zinc (40 kg Zn ha⁻¹) combined. However, in the wet season, there were no responses to zinc (but responses to potassium were still obtained). Responses to zinc occurred where the levels of DTPA extractable zinc were low (<1.0 mg kg⁻¹) and where either concentrations of magnesium were high, or where the Ca + Mg/K values were high (32).

Verma and Neue (33) investigated the effects of salinity and zinc application on the yield and composition of two cultivars of rice, one (IR10198-66-2) was tolerant of

salinity and the other (IR28) sensitive to salinity. The application of zinc to give concentrations of up to 10mg Zn kg⁻¹ in the soil increased the height and improved the yield-contributing characters and the root, shoot and grain yields of the salinity sensitive cultivar (IR28) but had no effect on the salinity tolerant cultivar. Zinc concentrations of 10 mg kg⁻¹ reduced the sodium content and increased the potassium content of IR28 but had no effect on the concentrations of either element in IR10198-66-2. In both varieties, zinc applications reduced the concentrations of phosphorus, calcium, magnesium and iron and increased those of zinc and manganese, but IR10198-66-2 had lower concentrations of sodium, calcium, manganese, iron, copper and zinc than IR 28.

On calcareous soils in northern China, the aerobic rice cultivation system being developed to economise on water use has been found to be more prone to zinc deficiency than continuously submerged lowland rice (14). It is not yet clear whether the decreased availability of zinc and its uptake by plants are due to changes in soil properties or plant factors. It is therefore important to note that wide-scale adoption of aerobic rice cultivation, and possibly other more water-efficient production systems, in many parts of Asia will probably require increased use of zinc fertilisers. In the future, it is possible that more zinc-efficient rice varieties may be bred for use in these systems and thus reduce the zinc fertiliser requirement.

In Brazil, on acid Ferralsols (highly weathered tropical soils rich in iron oxide), zinc deficiency is widespread in upland rice. Although zinc is more available at lower pHs, these soils have very low total zinc contents and so deficiencies occur in spite of the relatively high solubility of zinc (34).

7.3.2 Prevention of Zinc Deficiency in Rice

Doberman and Fairhurst (6) recommend the following strategies to prevent zinc deficiency in rice:

- Grow zinc-efficient varieties which can tolerate high bicarbonate and low plant-available zinc concentrations,
- Broadcast zinc sulphate onto the nursery seedbed,
- Dip seedlings, or pre-soak seeds, in a 2-4% zinc oxide suspension,

- Use acidifying fertilisers in alkaline soils (e.g., replace some urea with ammonium sulphate),
- Allow permanently flooded fields to drain and dry out periodically

7.3.3 Correction of Zinc Deficiency in Rice Crops

(See also Chapter 5, Section 5.2)

In general, it can be stated that in most soils, rice crops need nitrogen, phosphorus and zinc fertilisers, plus, in many cases, potassium as well. Rates of these elements have been quoted as: < 192 kg N ha⁻¹, 16 kg P ha⁻¹, and 5 kg Zn ha⁻¹.

Where rice seedlings are transplanted into the field from nursery beds, it was found that applying zinc sulphate to the nursery bed at a rate of 11 kg Zn ha⁻¹ was more effective in providing the transplant seedlings with zinc for the rest of their period of growth than dipping the seedlings into a suspension of zinc oxide before transplanting. Agronomists in Pakistan have shown that 'seed enrichment' with zinc involving 20 kg Zn ha⁻¹ applied as ZnSO₄ to the nursery bed was an effective treatment for zinc deficiency in transplanted rice (35).

According to Neue and Marmaril (36), the amount of zinc required to be applied to a wetland rice soil depends on: a) soil characteristics, b) the source of zinc, c) severity of zinc deficiency, and d) variety of rice to be grown. Generally, 10 kg Zn ha⁻¹ as zinc sulphate, or root dipping in a 2% zinc oxide suspension is adequate for most situations. Application of zinc to the floodwater or to the surface has been found to be more efficient than incorporation into the wetland soil.

Johnson-Beebout *et al.* (37) have recently shown that incorporation of zinc sulphate fertiliser into the soil before flooding may not be the best strategy for treating zinc deficiency in lowland rice. The availability of the zinc in this fertiliser tends to decrease when reducing conditions develop after flooding. Although foliar application would avoid this soil redox process, it would be more expensive.

Where symptoms of zinc deficiency are observed in a growing crop of rice in the field, Doberman and

Fairhurst (6) recommend that 11-25 kg zinc sulphate heptahydrate (2.2-5.5 kg Zn ha⁻¹) is applied immediately. This should be broadcast (mixed with sand) over the soil surface rather than incorporated into the soil. Alternatively, 0.5-1.5 kg Zn ha⁻¹ can be applied as a foliar spray (0.5 % ZnSO₄ solution in about 200 L water ha⁻¹) to growing plants. Starting at tillering, two or three applications at 10 to 14 day intervals may be necessary.

Applications of 5-15 kg Zn ha⁻¹ as zinc sulphate or zinc oxide, incorporated into the ground before seeding or transplanting, are usually adequate. Other alternatives include, dipping seedlings in a 1% zinc oxide suspension, or a slurry of the proprietary product Teprosyn-Zn® before transplanting, and mixing zinc oxide with pre-soaked rice seeds before direct seeding (See also Chapter 5: Zinc Fertilisers).

In experiments on marginally zinc-deficient soils, zinc-efficient rice varieties, tolerant to zinc deficiency, gave either no response to zinc fertiliser applications or even showed a negative response. Varietal tolerance to zinc deficiency in rice was found to be related to lower zinc requirements and the ability to maintain lower iron-zinc, copper-zinc, magnesium-zinc, and phosphorus-zinc ratios in the shoot. Zinc is involved in the root-to-shoot translocation mechanisms for these elements and applying additional zinc creates imbalances of these elements and hence inhibits yields in tolerant varieties. These imbalances are also exacerbated by alkaline flood waters. Organic amendments such as manures can cause or aggravate zinc deficiencies by enhancing changes in redox and increasing bicarbonate formation (31). Varietal differences in the tolerance of low zinc supplies are important. Local Colombian varieties are very tolerant whereas most IRRRI ones are not (16).

7.4 Wheat

Wheat (*Triticum aestivum* L) is the most widely grown cereal grain in the world, occupying around 205 Mha in 2003, which is about 14.4 % of the world's cultivated land area. In 1999, wheat was being grown on around 105 Mha in the developing world, on 57 Mha in Eastern Europe and the former Soviet Union (Russian Federation) and 65 Mha

in higher-income countries ⁽²⁾. The status of wheat as a staple is second only to rice. It is the staple food crop for 35 % of the world's population and provides more calories and protein in total than any other crop. Around 66 % of wheat grown is used for human consumption and around 17% for livestock feed. The remaining 17% of wheat produced includes various non-food uses and post harvest losses.

Global production of wheat is now around 637 Mt with an overall average yield of 2.75 t ha⁻¹. The average yields in selected countries are given in Table 7.2. Wheat is Asia's second most important staple and its consumption has been increasing much faster than that of rice. It now makes up 19.2% of the total calorie supply in Asia. In 1992-94, Asia accounted for 67% of the developing world's wheat production, with 39% in China, 19% in West Asia-north Africa, 7% in Latin America and the Caribbean and less than 1% in sub-Saharan Africa.

Wheat is the main staple crop in West Asia and North Africa (44.3% of the region's total food supply). Durum wheat (*Triticum durum* Desf.) accounts for 5% of wheat production in developing countries with about 80% of it being grown in West Asia and North Africa. In Iran, Iraq and Turkey the proportion of arable land used for growing wheat is 77, 72 and 67%, respectively. India has the largest area of land planted to wheat (24.9 Mha) followed by China (22.0 Mha), USA (21.4 Mha) and the Russian Federation (20.0 Mha) ⁽²⁾. Although India has a larger area of land planted to wheat than China, total production (65 Mt) is considerably lower than in China (86 Mt) ⁽²⁾.

The average wheat yield in developing countries is around 2.5 t ha⁻¹, but in marginal environments, yields may be less than 1 t ha⁻¹. However, growing modern varieties, which are more efficient in the use of macronutrients and water, could increase production considerably. In rice-wheat systems, it is estimated that the potential yield for wheat should be around 7 t ha⁻¹ ⁽¹⁾.

Turkey, together with Syria, Kazakhstan and Algeria has the highest *per capita* consumption of wheat in the world (210 kg yr⁻¹) compared to world average *per-capita* wheat consumption of 100 kg yr⁻¹. Some of these countries also have major zinc deficiency problems. Ninety percent of wheat produced in Central and West Asia and North

Africa is consumed directly as food. Turkey is among the ten largest wheat producers in the world. Intensification, including growing new high yielding varieties has enabled Turkey to produce an extra 10 Mt of wheat grain *per annum* on the same total land area since the 1970s. If traditional production methods and wheat varieties had continued to be used, it would have needed an extra 7 Mha of land to produce this extra 10 Mt of wheat grain ⁽³⁸⁾.

Around one-third of wheat produced in the developing world is grown in environments which are considered to be marginal for wheat production on account of drought, high temperatures and soil problems. However, the need to improve the productivity of these marginal areas is becoming increasingly important with regard to world food security ⁽³⁸⁾. Around 10% of world wheat production comes from areas with a Mediterranean-type climate (dry season for 1-8 months each year and an average rainfall of around 500 mm). Heat stress is a major problem in Turkey, Egypt, Sudan, India and Bangladesh. Acid soils and their associated aluminium toxicity are a major problem in Brazil. It is recognised by the main wheat breeding research organisation, CIMMYT, that there is a need to combine tolerance to drought with tolerance to heat stress, nutrient deficiencies (especially boron and zinc), salinity and other soil-borne stresses.

It is estimated that by 2020 wheat consumption will increase by 40% relative to that in 2000. In order to satisfy this requirement, production will have to increase by 2.5% *per annum* up to 2020. Unfortunately, the overall rate of increase in wheat yields in developing countries for the period 1986-95 was only 1.8%, which was lower than in the previous two decades ⁽³⁸⁾.

7.4.1 Bread Wheat

(*Triticum aestivum* L.)

Bread wheats are by far the most widely grown type of wheat and occupy about 92.5% of the world land area used for wheat production (approximately 190 Mha). The hard wheat varieties used for making bread have a high protein content (10-17%) and yield a flour rich in gluten which make it particularly suitable for yeast breads. The low protein (6-10%), softer wheats are more suitable

for biscuits and pastries. The most important developing world producers of bread wheat are: China, India and Turkey. Forty percent of wheat in developing countries is grown with irrigation. In South Asia, wheat is produced in the irrigated rice-wheat rotation system, covering 26 Mha, but it is also grown in dry land areas on residual moisture from the monsoon rains.

Cultivars of bread wheat (both spring and autumn-sown types) have been found to vary widely in zinc efficiency. Kaylayci *et al.* (39) found zinc efficiency to range between 57% and 92% in a selection of thirty seven bread wheat and three durum wheat cultivars. When these cultivars were grown on a zinc-deficient soil in a field experiment, yield increases of between 8% and 76% were found with zinc fertilisation, with an overall average yield increase of around 30%. Zinc-efficient wheat cultivars take up more zinc than inefficient cultivars from soils with low available concentrations of zinc and produce more crop dry matter, but they do not always produce seed with higher zinc concentrations (39). From a review of the literature, Rengel *et al.* (40) found that concentrations of zinc in the grain of bread wheats ranged between 4.5 and 46 mg kg⁻¹. They concluded that fertilisation of the soil with zinc sulphate could result in an increase in grain yield and a higher grain zinc content, which would be of importance to human health (biofortification). Cakmak *et al.* (41) reported that, in the Anatolia region of Turkey, where soils are predominantly calcareous and zinc-deficient, the zinc present in the grain had a very low bio-availability. This was due to the grain having very high phytate:zinc ratios (95-216). As discussed in Chapter 2 (Section 2.6), phytate:zinc molar ratios of above 15 are considered to indicate low zinc bio-availability. This low bioavailability in cereal-based diets was found to be reflected in the shorter stature and low levels of zinc in the hair of school children in South East Anatolia (41).

7.4.2 Durum Wheat

(*Triticum durum* Desf.)

Although high in gluten, durum wheat is not suitable for baking and so is often ground into semolina which is used for making pastas. Durum wheat is grown on 17 Mha worldwide with about half of the area being in developing countries. Production is centred mainly in Central India

Fig. 7.3



Zinc-inefficient wheat (cv Gatcher) grown in a calcareous soil, zinc was added to pot on the left but omitted in pot on the right.

R. Holloway

and the Mediterranean-climate regions of West Asia and North Africa where 80 % of the durum area (in developing countries) is found. Other countries producing durum wheat include Argentina, Australia, Canada, Chile, Ethiopia, France, Italy, Kazakhstan, Mexico, Russia, Spain and the USA. In 2007, both Canada and Syria were in the news for not exporting as much durum wheat as previously and causing the price of pasta to rise in Europe. In general, durum wheat varieties are more sensitive to zinc deficiency than bread wheats and many of the areas in which durum wheat is grown have zinc-deficient soils. However, individual durum wheat cultivars can vary considerably in the efficiency with which they utilize available zinc in soils and hence they also differ in their susceptibility to deficiency.

In developing countries, yields of durum wheat are generally low because this type of wheat is usually grown with low levels of inputs in semi-arid regions and other marginal areas characterized by sharp annual fluctuations in cropping conditions and also zinc-deficient soils. With irrigation, where moisture and other inputs are not limiting, high yields can be obtained but this only accounts for a relatively small proportion (28.2 %) of the durum wheat growing area.

7.4.3 Zinc Deficiency in Wheats

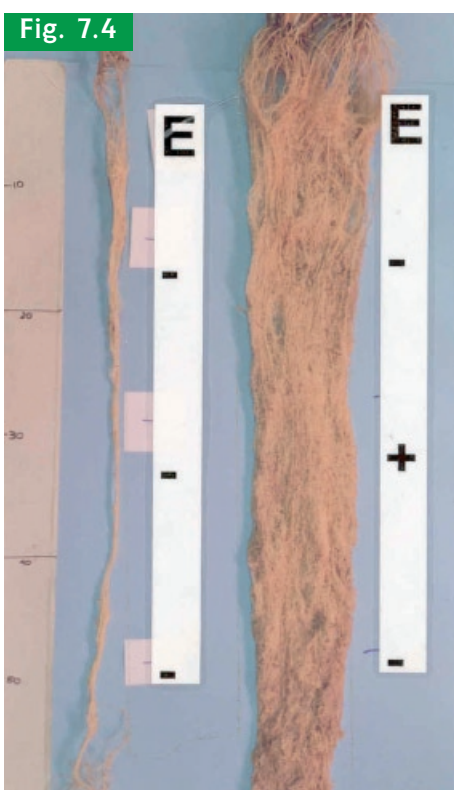
As discussed in Section 2.3.3.1, in comparison with several other major crops, including maize, wheat is considered to have a relatively low sensitivity to zinc deficiency, although cultivars can vary considerably in susceptibility. Nevertheless, on a global scale, zinc deficiency is the most widespread micronutrient deficiency problem in cereals, especially West Asia the Middle East and other countries with a Mediterranean-type climate. In Turkey, 50% of arable soils are zinc deficient (41).

Zinc deficient soils in Central Anatolia, Turkey pose a serious problem both with regard to wheat yields and also to the zinc concentrations in the wheat grain. Zinc deficiency in children and adults is linked to the consumption of food with a low bioavailable zinc content (41). (See also Chapter 6: Areas of the World with Zinc Deficiency Problems in Crops).

Most soils in Iran are highly calcareous with a pH of 7.7-8.2 and low organic matter contents (< 1%) and are prone to drought due to low annual precipitation. These factors all serve to exacerbate zinc deficiency in crops such as wheat. From the analysis of 50,000 soil samples, it is estimated that 80% of cultivated soils in Iran are potentially zinc-deficient. Zinc deficiency in crops has only been recognised in wheat and other crops in Iran since the early 1990s. Since then, the condition has been treated mainly by the application zinc sulphate to soil and by soaking seeds in zinc sulphate solution. Yields and quality of cereals have been improved as a result of zinc fertilisation and oil seed crops, beans, vegetables and orchard fruits have also benefited from treatment with zinc. Around 30,000 t of zinc-containing fertilisers are used annually in Iran (43).

7.4.4 Correction of Zinc Deficiency in Wheat

As with most crops, the normal way of correcting zinc deficiency in soils is to broadcast a zinc compound, such as zinc sulphate, on to the seedbed and incorporate it into the topsoil at rates equivalent to between 5 and 20 kg Zn ha⁻¹. However, if the zinc fertiliser is to be banded (placed to one side and below the seed in the row) then a



Roots of wheat (cv Excalibur) grown in zinc-deficient sand; plant on right received zinc applied to the 0.2-0.4 m zone of the subsoil, plant on left did not receive zinc.

R. Holloway

lower rate of 3-5 kg Zn ha⁻¹ is used. Soil applications of zinc fertilisers generally have a significant residual effect which can last from five to ten or more years. For foliar applications (usually of a chelated form of zinc such as Zn-EDTA) an even lower rate of 0.015-0.25 kg Zn ha⁻¹ is used. These foliar treatments are usually only applied to salvage an existing deficient crop and have very little residual value in the soil for following crops (39). (See Section 5.2).

In comparison with lowland (paddy) rice, the correction of zinc deficiency in wheat (and also in maize) is more straightforward. In the case of soil applications, the efficacy of zinc fertilisers tends to improve in the years following application when the zinc has been more thoroughly mixed into the topsoil through cultivation. The more soluble the source of zinc, such as zinc sulphate, the more rapidly it becomes plant-available after mixing in to the soil.

7.5 Rice-Wheat Cropping Systems

About 20% of the world's population depends on the rice-wheat cropping system for its staple food. This cropping system is a product of the Green Revolution whereby new varieties of both wheat and rice have been bred which allow a rotation of the two crops on the same land. It has involved a change from rice and wheat monocultures with low-yielding indigenous crop varieties, to an intensive rotation with short duration, higher yielding varieties of rice and wheat, grown in sequence ⁽¹⁾.

The rice-wheat system is mainly practiced over 26 Mha in South and East Asia, within sub-tropical to warm-temperate climates with cool dry winters and warm wet summers. Approximately 85% of rice-wheat farming in South Asia takes place in the Indo-Gangetic Plain. This includes large parts of India (10 Mha), Pakistan (2.2 Mha), Nepal (0.5 Mha) and Bangladesh (0.8 Mha). In China, rice-wheat farming is practiced widely in provinces along the Yangtze River Basin. The system is also found in much smaller areas in Bhutan, Iran, Japan, Korea, Myanmar, Mexico and in Egypt. Wheat is also being grown after rice in some tropical areas of the Philippines, Thailand, Indonesia, Vietnam and Sri Lanka ⁽¹⁾. India and China have the largest areas of rice-wheat farming with 10 Mha and 13 Mha, respectively.

Although it is estimated that potential yields of 7 t ha⁻¹ should be attainable for each crop, the actual yields have not yet reached this value. The average yields for four South Asian countries are 2.7 t ha⁻¹ for rice and 2.1 t ha⁻¹ for wheat. It is generally considered that these relatively poor yields are due to poor nutrition and inappropriate water management ⁽¹⁾.

In 1985, Singh and Abrol ⁽⁴⁴⁾ found from experiments with sequential rice and wheat on an alkaline soil that a single application of 4.5 kg Zn ha⁻¹ to rice alone was sufficient for both that and the following wheat crop, or 2.25 kg Zn ha⁻¹ could be applied to each crop. These applications would be adequate to meet the annual zinc requirements of the crops without any reduction in yield or the available zinc status of the soil.

Wheat is the crop grown in the cooler part of the year in the sub-tropics, but temperatures during the growth

cycle are still often above the optimum for the crop. Waterlogging, in addition to heat stress and drought, can reduce yields of wheat, and so the conditions in rice-wheat farming, where wheat follows rice, are often sub-optimal for wheat. Care must be taken to avoid waterlogging and plant breeders are working on the development of wheat varieties which are more tolerant of this. As mentioned earlier, plant breeders are also selecting for zinc efficiency. These zinc-efficient cultivars would be able to grow on soils with relatively low levels of available zinc without the need for zinc fertilisation. However, these crops will deplete the available zinc concentration in the soil and fertilisers would need to be used in due course.

Within the last thirty years or so, rice-wheat cropping systems have triggered and, with time, aggravated soil micronutrient deficiencies in the Indo-Gangetic Plain. Zinc deficiency is recognised as a widespread problem, but the extensive use of zinc sulphate fertiliser has enabled this to be corrected in many areas. Unfortunately, deficiencies of iron, manganese and boron are now becoming an increasingly serious problem and copper and molybdenum deficiencies are also occurring in some localities ^(45,46,47). It appears that a single micronutrient deficiency (zinc) has now been superseded by multiple-micronutrient deficiency problems.

The sequential changes in soil redox conditions, from aerobic under wheat to anaerobic under rice, give rise to marked changes in soil chemistry which can affect the availability of micronutrients. Zinc is less available in anaerobic, paddy (rice) soils than in aerobic (wheat) soils. As a result of many of the alluvial soils in the Indo-Gangetic Plain being calcareous with a high pH, zinc will have a low availability over much of the area. It has been found that after ten years of rice-wheat cropping, DTPA-extractable zinc concentrations in soils have declined ⁽⁴⁵⁾.

7.6 Maize

Maize (*Zea mays* L.) (also called 'corn', especially in North America) is grown widely throughout tropical regions of the world and also as a summer crop in many temperate countries. The largest producers of maize are the USA and China with 39% and 19% respectively of total maize production ⁽²⁾. More than 90% of maize produced in

industrialised countries is grown under temperate conditions, but in the developing world only 25% is grown in temperate conditions (mainly within China and Argentina). There are seventy countries with 100,000 ha, or more, of land under maize. Around 69% (96 Mha) of the area of maize production is in developing countries with China (26 Mha), Brazil (12 Mha), Mexico (7.5 Mha) and India (6 Mha) being the largest producers. However, only 46% of the world's total maize production of 600 Mt is grown there. In developing countries, average maize yields are generally less than 3 t ha⁻¹, while in developed countries they are around 8 t ha⁻¹. These marked differences in average yields are mainly due to differences in climate, crop nutrition and farming technology (48). The exceptionally high national average maize grain yield of 23.62 t ha⁻¹, given as the maximum average yield value in Table 7.2, relates to Jordan which only grew 460 ha of maize in 2003. In contrast, Chile, which had 97,000 ha of maize, had a national average yield of 12.27 t ha⁻¹ which is the highest for countries growing more than 50,000 ha of the crop (2).

A high proportion of the total production of maize is fed to livestock (64% globally, 72% in developing countries). It can be fed to livestock either as grain, as a cake made from the residue from oil extraction, as distiller's grain, a by-product of ethanol extraction, or as silage. This silage is made by chopping-up and partially fermenting the whole above-ground part of the maize plant (stems, leaves and seed cobs) and is fed to cattle. In areas on the fringes of the tolerable range of climatic conditions for growing maize, silage maize tends to predominate because when the whole crop is going to be harvested, it is less important to have the ideal climatic conditions for grain production. The world-wide demand for maize grain is increasing due to the growth in the demand for meat and poultry in many developing countries. Global demand is expected to increase by 50% from 558 Mt in 1995 to 837 Mt in 2020. The greatest growth in demand is in South Asia where it will increase by 92% by 2020 (34).

Maize is used for human food as grain from the ear (cob), from the germ, starch from the grain, and bran. Grain for human consumption is normally milled to a flour and used to prepare tortillas, and many other items including corn meal, bread, flour and baby food. In addition to its use as cereal grain for direct consumption by either humans or livestock, maize can be utilised in more ways than any

other cereal, including being made into alcohol for use as a bio-fuel, and is also used in various industrial processes. There are many varieties of maize grown around the world. These can be divided into five main types: dents, flints, floury, pop and sweet corn. These all have distinct properties which affect their utilisation. Dent is the most important type, producing grain that is used for livestock feed, starch, syrup, corn oil and alcohol (49). Perhaps the most distinct type of maize is sweet corn which has translucent kernels that contain a gene which prevents or inhibits the conversion of sugar to starch and thus gives them a distinctly sweet taste. A range of hybrid sweet corn cultivars is grown in different parts of the world. In the USA, they account for around 2% of the area of land used for growing maize.

Maize can be found growing around the world between latitudes 42° South to 50° North. The optimum conditions are well-drained, fertile soils with temperatures in the range 18-21°C and 1,200-1,500 mm rainfall (or irrigation). It has a very high degree of genetic variability which enables it to grow under a wide range of climatic conditions, including temperature and rainfall, but the crop cannot tolerate either frosts or flooding. It is grown year-round throughout the tropical regions and as a summer crop in many temperate regions.

The world average grain yield for maize is 3.4 t ha⁻¹ but average yields for different countries range from 0.5 t ha⁻¹ to 23.3 t ha⁻¹ (2). In the USA, the largest producer, average yields tend to be around 8 t ha⁻¹ (127 bushels/acre) with higher yields of around 12.3 t ha⁻¹ (195 bushels/acre) (50).

7.6.1 Zinc Deficiency in Maize

Maize is highly susceptible to zinc deficiency and zinc fertilisers have to be used routinely in many parts of the world where the crop is grown. In most countries where it is grown, maize receives the largest tonnages of zinc fertilisers of any crop, for example, in the USA (51). Individual varieties also vary widely in their sensitivity. Growing new, zinc-inefficient varieties and/or increased use of macronutrients, especially phosphate, often leads to the appearance of the symptoms of deficiency or to disappointing yields due to either acute, or hidden forms of zinc deficiency.

Apart from stunting and chlorosis in acute deficiency, zinc deficiency also causes decreased pollen viability in maize and male sterility. Research has shown that subnormal zinc supplies to maize plants at any stage of anther development, prior to microsporogenesis, induced male sterility, even though the vegetative growth may appear normal (52). This is a classic example of hidden zinc deficiency

The factors giving rise to zinc deficiency in this crop are similar to those for all other crops, except lowland (paddy) rice, where the effect of flooding is important. Zinc deficiency in maize is most widely encountered in soils with:

- A high pH (> 7.0), especially on calcareous and/or heavily limed soils,
- High soil phosphorus fertility (maize and sorghum are particularly prone to this cause of zinc deficiency)
- Saline soils
- Sandy texture and strongly leached soils (including ferruginous tropical soils: Ferralsols)
- Large expanses of exposed subsoil (with low organic matter and high calcium carbonate contents) as a result of levelling land for irrigation.

7.6.2 Treatment of Zinc Deficiency in Maize

The treatment of zinc-deficient soils for growing both maize (and also wheat) is reasonably straightforward and relies on increasing the plant-available zinc concentrations in soils by the use of zinc fertiliser compounds. Zinc sulphate is the compound most widely-used for treating deficiencies around the world because it is relatively inexpensive, easily obtained and highly soluble. This high solubility results in the added zinc being dispersed more rapidly in the soil than less soluble compounds such as zinc oxide.

Broadcast applications both of zinc fertiliser alone, or when mixed with macronutrient fertilisers, for maize (and other cereals) can be in the range of 4-22 kg Zn ha⁻¹ (< 20 lb Zn acre⁻¹ in USA), but are most frequently in the range 4-9 kg Zn ha⁻¹. If chelated sources of zinc (such as ZnEDTA) are applied to the soil, rates are usually in the range 0.5-2.2 kg Zn ha⁻¹ (53).

Foliar sprays can be used on maize but often require several applications which can be expensive. Nevertheless, they are often used in emergencies to prevent major yield losses when a deficiency is observed early in the growing season. Zinc sulphate is applied at a rate of 11 kg ha⁻¹ in 1,100 L water (10 lb ZnSO₄ acre⁻¹ in 100 gallons of water in the USA). Leaf toxicity is less likely when the zinc sulphate is mixed with hard water. If the water is 'soft' (with a low calcium content), a suspension of calcium hydroxide is often used together with the zinc sulphate to increase the hardness of the water and reduce the risk of scorch due to localised toxicity on the leaves (53).

7.7 Concluding Comments on Zinc Deficiency in Cereals

The graminaceous cereals are the most important group of crop species for supplying most of the world population's nutritional needs. As more intensive methods of crop production are introduced, to increase production on a more or less static, or shrinking arable area, the risk of zinc deficiency will increase in areas with marginal to low concentrations of available zinc in the soil. This is due to a combination of soil, crop nutrition and plant genotypic factors. The yields of all the major cereal species, especially the new high yielding varieties, respond very positively to higher inputs of nitrogen, phosphorus and potassium providing there is an adequate supply of all other nutrients and no major physical stresses, such as drought. However, if zinc becomes the limiting factor, the investment in the higher levels of macronutrients applied will not be rewarded by increased yields or improved quality. This is a very serious problem for farmers in low-input systems who are attempting to increase their productivity and profit.

All of the major species of cereals are affected by zinc deficiency and therefore both the supply and the nutritional quality of cereal grains for human consumption are dependent on an adequate level of zinc nutrition in the crops. Maize and rice are generally more sensitive to zinc deficiency than wheat, but many wheat-growing regions of the world also have zinc deficiency problems. Varieties of all the cereal species, except rye, show a high degree of variability in zinc-efficiency. There is therefore scope for breeding cultivars which are more able to utilize marginally

low available supplies of zinc and still produce grain of acceptable yield and quality. Although, as discussed in Chapter 5, there are several different forms of zinc which can be used as a fertiliser, zinc sulphate is the most widely adopted.

Basically, zinc deficiency is more straightforward, in both its causes and its remediation, in maize and wheat (with or without irrigation), than it is in lowland (paddy) rice. Low total zinc concentrations and factors promoting its adsorption in unavailable forms in the soil affect all cereal crops. However, the unique physico-chemical environment created by flooding the soil for wetland rice results in changes in redox and pH conditions and concentrations of bicarbonate, phosphate and other trace elements, which can play a role in reducing the availability of zinc to rice plants and/or its mobility within the plants. With the development of new, more water-efficient rice-growing techniques the zinc-efficiency of the newly bred cultivars, such as those of aerobic rice, need to be investigated so that the risk of zinc deficiency can be assessed.

As discussed in Section 2.6, the zinc density in cereal grains is likely to be of increasing importance, at least in developing countries where large numbers of resource-poor people have diets with inadequate amounts of bioavailable zinc. Agronomic biofortification will necessitate the modification of zinc fertiliser regimes both with regard to amounts and timing of applications. However, where biofortification with fertilisers is practiced, it is important that available zinc concentrations in soils are monitored regularly in order to ensure that excessive accumulation of zinc does not occur. Soil microbes and fauna may be adversely affected long before phytotoxicity is detected in the cereal crops.

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DISCUSSION AND CONCLUSIONS

This book has covered the reasons for the variations in plant-available concentrations of zinc in soils and the numerous soil and plant factors which can cause zinc deficiency in crops. This, together with a review of the essential physiological roles of zinc in plants, has explained why zinc deficiency is such an economically important agronomic problem in many parts of the world.

Large areas of arable land in different parts of the world have soils with characteristics which are known to cause zinc deficiency. These range from low total concentrations of zinc, such as are found in sandy or heavily weathered tropical soils, to low availability of zinc in calcareous, alkaline and flooded/wet soils. The use of increased amounts of high purity phosphatic fertilisers with modern, high yielding varieties of rice, wheat and other crops, often causes or exacerbates zinc deficiency where the plant-available levels of zinc in soils are marginal.

Maize, rice and wheat, the world's three most important cereal crops, are all affected by zinc deficiency. In the case of rice, at least 70% of the crop is currently produced in flooded soils in the paddy system. This has many advantages for the production of rice, but is relatively inefficient in its use of water and alternative rice-growing systems which are more water-efficient are being developed in some countries. With regard to the behaviour of zinc, flooding the soil reduces its availability to the crop and increases the concentrations of soluble phosphorus and bicarbonate ions which can exacerbate zinc deficiency problems. It has been estimated that possibly up to 50% of paddy rice soils are affected by zinc deficiency. This could involve up to 35 Mha in Asia alone.

Although the area of land under lowland (paddy) rice production may decrease as a result of its replacement by more water-efficient production systems, it appears that these new production systems are also prone to zinc deficiency. For example, in China, it has been found that the new aerobic rice genotypes are susceptible to zinc deficiency and therefore require the application of zinc fertilisers.

Maize is the crop species which is most susceptible to zinc deficiency and generally accounts for the highest use of zinc fertiliser per hectare than any other crop. With the

increase in demand for maize for both livestock feed in developing countries and for ethanol production in more developed countries, the mitigation of zinc deficiency in this crop is going to remain an important crop nutrition priority.

Wheat is less sensitive to zinc deficiency than rice and maize, but it is still severely affected by zinc deficiency in many parts of the world. Low available zinc concentrations in calcareous soils with a relatively high phosphorus status tend to be the most widely found cause of zinc deficiency in wheat. Wheat is grown on large areas of alkaline, calcareous soils in West and East Asia, Australia and North America. In Turkey, where wheat is the predominant cereal crop, 14 Mha of arable soils are estimated to be affected by zinc deficiency and around 12 Mha are affected in Iran.

In South and East Asia, rice tends to be the crop most affected by zinc deficiency due to the effect of flooding on zinc availability. The Indo-Gangetic Plain, which includes parts of Pakistan, and six Indian states, has large areas of zinc-deficient alluvial soils and sequential rice-wheat cropping is carried out on a large scale. It has been estimated from advisory soil test samples that, on average, 49% of soils from all the main agricultural areas in India are deficient in zinc. If it is assumed that these are representative of the country as a whole, India, with a cultivated land area of 160 Mha, could possibly have up to 78 Mha of zinc-deficient soils.

China currently has the largest population in the world, but only one third of the world average *per capita* area of cultivable land. With land being so scarce, it is essential that crop productivity is not lost through zinc deficiency. Around 48.6 Mha of farmland in China (51% of total) is zinc-deficient and requires zinc fertilisation, mainly for maize and rice. In the Philippines, 8 Mha of wetland rice are estimated to be zinc-deficient.

In Australia, in one area alone, the Ninety Mile Desert, on the borders of South Australia and Victoria, there are 8 Mha of zinc-deficient land. There are also extensive areas of zinc-deficient soils in other parts of the country, especially Western Australia and South Australia.

Apart from these widespread occurrences of deficient soils, often in hot and dry, or humid tropical climatic zones, smaller areas of zinc-deficient soils occur in many other parts of the world, including humid temperate zones, such as in North Western Europe. These areas of soils may sometimes be so small that they only affect a few fields, or even parts of fields with patches of sandy or calcareous soils. However, these are still of importance to individual farmers whose costs of production are high and who therefore cannot afford to lose valuable yield through a nutrient imbalance problem like zinc deficiency.

Once zinc-deficient soils have been identified, the problem is easily (and cost-effectively) rectified by the application of zinc fertilisers to the seedbed, banded with the seed, or by foliar sprays directly onto the crop.

From these relatively few examples, it can easily be seen that zinc deficiency is very important on a global scale. Many cases of deficiency occur in developing countries, where there is an urgent need to increase food production in order to feed their population without relying on food imports. Growing modern, high yielding varieties of crops with appropriate use of macronutrient fertilisers, agrochemicals and irrigation is a major development in food self-sufficiency. However, the sensitivity of new crop hybrids to zinc deficiency, the adverse effects of high phosphorus levels and of flooding soils for rice production on zinc availability, can all result in a failure to realize the potentially high yields expected due to an increase in the incidence in zinc deficiency.

Although zinc deficiency causes characteristic visible symptoms in plants, this often only occurs in cases of relatively severe deficiency. Where the deficiency is more marginal, yields may be reduced and quality impaired without the appearance of obvious symptoms in the crop. This hidden deficiency may be of greater economic importance than cases of severe deficiency accompanied by clear symptoms. Where there are symptoms of severe deficiency, farmers will be aware that something is wrong and either seek advice, and/or carry out a corrective treatment. However, hidden deficiencies may go undetected for several growing seasons without farmers realizing that their disappointing yields are due to zinc deficiency. The cost of this lost production can be considerable when the farmer will have had the expense of all the other inputs necessary for achieving high yields. On a national and global basis, with the need to produce larger tonnages of staple foods, it is not acceptable for

large areas of land to be producing poor crop yields as a result of a deficiency of a micronutrient like zinc, which could be so easily and cost-effectively rectified.

The zinc status of soils and crops are, in most cases, easily assessed by soil or plant analysis and it is important that farmers should investigate land where poor yields are obtained without other obvious explanations such as drought or disease, especially in areas with highly susceptible soils. Likewise, crops displaying visible symptoms of stress including those most characteristic of zinc deficiency, such as interveinal chlorosis, stunting due to reduced internode elongation, little leaf and resetting, should also be investigated to confirm the deficiency. In some cases, other micronutrients, such as manganese and iron may also be deficient and require correction.

Where farmers are applying zinc fertilisers, either to the soil or as foliar sprays on a regular basis, regular soil or plant analysis should be carried out to determine whether sufficient residues of zinc have accumulated in the soil to enable applications to be discontinued for one or more years. This saves the farmer the expense of the zinc fertiliser application and helps to ensure that zinc does not accumulate to undesirably high levels. Local expert advice should be sought on all aspects of the management of the zinc status of soils.

Zinc, in common with the other essential trace elements, can limit plant growth when present at either very low concentrations or at very high concentrations. Excess levels of zinc in soils are unlikely to occur from normal agricultural use of zinc fertilisers, but potentially harmful concentrations can occur from repeated applications of zinc-rich livestock manures, agricultural pharmaceuticals, sewage sludges or industrial by-products to land. Environmental pollution of land from nearby industrial sources, such as metalliferous mines and smelters, normally only affects relatively small areas and these are usually recognised by both farmers and local environmental regulators. However, in these situations, soil and plant analysis will be required in order to avoid possible pollution problems. In acid soils, adverse effects of slight excesses of zinc can be rectified by liming to raise the soil pH and reduce the availability of zinc.

When zinc fertilisers are applied to soils, the balance of other micronutrients could also be affected, so farmers must be on the look out for any signs of stress following zinc treatment. As with macronutrients, balanced

fertilisation with micronutrients should be practiced whenever possible.

With the growing awareness of the large numbers of people in different parts of the world suffering from zinc deficiency, it is now realized that the zinc nutritional status of staple crops needs to be considered in addition to ensuring that these crops have sufficient zinc for optimum yields. Methods of biofortification are currently being researched. So far, it has been found that rectifying zinc deficiency in cereals has often been accompanied by an increase in the zinc density of the grains and this has had a beneficial effect on the health of people consuming these crops, especially mothers and children. HarvestPlus is coordinating research into biofortification with special emphasis on breeding new varieties with high zinc densities in their grain, but there is also a key role to be played by the use of zinc fertilisers (agronomic biofortification) and research is also being focused on this.

Zinc is important for high yielding and high quality crops (within the constraints of local growing conditions) and it is therefore important that farmers, agronomists and extension workers should ensure that the zinc status of their soils and crops are adequate to satisfy both the yield and quality criteria.

RECOMMENDATIONS FOR FUTURE RESEARCH PRIORITIES

- Collaborative multidisciplinary research involving soil scientists, agronomists, plant breeders, human nutritionists and food technologists on the biofortification of staple foods with zinc in a form which is bioavailable to consumers.
- Screening of crop varieties to identify those which have the potential to accumulate high densities of zinc in their grains. These could then be used in breeding programmes to develop new genotypes for growing in areas where people are affected by zinc deficiency.
- Screening of cultivars of major crop species for zinc-efficient strains to be used in plant breeding. This would enable crop genotypes to be matched to soils and reduce the requirement for zinc fertilisers. Lists of crop varieties which are highly susceptible to zinc deficiency would also be useful for farmers and extension workers so that they can be extra vigilant with those most at risk of deficiency.
- Feasibility study of developing fertilising techniques for subsoils in dry regions (such as Australia).
- Investigate the suitability of field-based biochemical test kits for assessing the zinc status of crops without relying on analytical laboratories.

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