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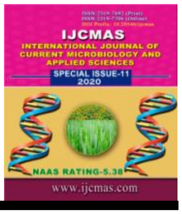

Review Article

Role of Micronutrients in Crop Production

Rihana Rahman[1*], Javid Ahmad Sofi[1], Insha Javeed[2],
Tajamul Hussain Malik[1] and Shemoo Nisar[3]

[1]Department of Soil Science, [2]Department of Vegetable Science,
[3]Department of Fruit Science; Sher-e-Kashmir University of Agricultural Sciences and
Technology of Kashmir, Shalimar, Srinagar-190025, Jammu and Kashmir, India
**Corresponding author*

ABSTRACT

Micronutrients are abundantly present in the soil but plants usually acquire them in relatively trace amounts; hence, regarded as tracer element. B, Cu, Fe, Mn, Zn, Mo and Ni are such micronutrients required in minute amounts by plants but inexorably play an eminent role in plant growth and development. Plant metabolism, nutrient regulation, reproductive growth, chlorophyll synthesis, production of carbohydrates, fruit and seed development, etc., are such effective functions performed by micronutrients. These tracer elements when present at adequate level, elevate the healthy growth in plant physiological, biochemical and metabolic characteristics while their deficiency promotes abnormal growth in plants. Prevalence of micronutrient deficiency has become more common in recent years and the rate of their reduction has further been increased by the perpetual demands of modern crop cultivars, high soil erosion, etc. (Dubey *et al.*, 2015). Indian soils are extensively deficient in micronutrients and 5.4% soils of India recorded Cu deficiency (Shukla *et al.*, 2014). Copper fertilization significantly increased the growth and yield parameters of rice crop in Cu deficient soils while the soils with adequate or high Cu status showed declining response (Silviya, 2017). Application of Zn significantly increase the plant growth parameters viz plant height, number of branches per plant and chlorophyll content of Okra (Lata *et al.*, 2018). Obaid *et al.*, 2013 reported that the application of Zn at 3% combined with Mn at 60 mg/l gave highest fruit set and significantly increased the yield. Application of one kg Mo/ha significantly increased fresh and dry weight of nodules in Cluster bean (Yadav, 2017). It was determined that foliar applications of iron showed positive effect on yield, fruit number which significantly resulted in an increase in marketable yield in Tomato (Denden *et al.*, 2016). The foliar application of Ni significantly increased the yield attributes viz., number of ear pot^{-1}, number of grains ear^{-1}, straw yield, grain yield and weight of 1000 grains of barley (Kumar *et al.*, 2018). Application of chlorine significantly increased fresh ear yield in corn (Zenda *et al.*, 2017). Application of boron during flowering increased the growth of the pollen tube at flowering stage. Boron foliar sprays to boron deficient fruit trees under dry conditions delayed bloom and increased fruit set and final fruit number per tree (Dar, 2017).

Keywords

Micronutrients, Role of micronutrients, Growth, Quality, Yield

Introduction

Micronutrients or Trace elements are essential for plant growth and development but it is needed in very small quantities in the plant system. It includes Fe, Cu, Cl, Mn, B, Ni, Zn and Mo. The accumulation of these micronutrients by plants generally follows the order of Mn>Fe>Zn>B>Cu>Mo. This order may change among plant species and growth conditions (e.g.; flooded rice). They is usually found in association with larger molecules such as cytochromes, chlorophyll and protein (usually enzymes).

Micronutrients may be minor in terms of the amounts needed by the crop, but they can be major in terms of their impact on crop growth. Whenever the supply of one or more of these elements is inadequate, yields will be reduced and the quality of crop products impaired, but crop species and cultivars vary considerably in their susceptibility to deficiencies. Micronutrients play a vital role in crop growth, crop productivity, soil fertility and human nutrition (Patel *et al.*, 2015). Arnon and Stout (1939) proposed that, Cu is an essential element for plant growth. Among the micronutrients, Cu plays an important role in the crop growth by increasing the tillering and pollen viability of the crop (Das, 2014). Copper is a component of large number of proteins and enzymes like plastocyanin, diamine oxidase and ascorbate oxidases and Cu containing enzymes play an important role in photosynthesis, respiration and in lignin formation. It acts as a structural element in regulatory proteins and involves in photosynthesis electron transport, mitochondrial respiration, stress responses, cell wall metabolism and hormone signaling. The cereal crops show white tips as Cu deficiency symptoms and the deficiency of such micronutrient has been identified as the main limiting factor for crop yield, food quality and human health (Alloway, 2008). Indian soils are extensively deficient in micronutrients and 5.4 per cent soils of India recorded Cu deficiency. The total Cu content in Indian soils ranged from 1.8 to 960 mg kg-1 and the available Cu content ranged from 0.10 to 378 mg kg-1. More than 25 per cent of Cu deficiency was recorded high in the soils of Tamil Nadu (Shukla *et al.*, 2014). Incidence of micronutrient deficiencies in crops has increased markedly in recent years due to intensive cropping, loss of top soil by erosion, losses of micronutrients through leaching, liming of acid soils, decreased proportions of farmyard manure compared with chemical fertilizers, increased purity of chemical fertilizers, and use of marginal lands for crop production. Micronutrient deficiency problems are also aggravated by high demand of modern crop cultivars (Bell, 2006). Plant acquisition of micro- nutrients is affected by numerous soils, plant, microbial, and environmental factors. Factors such as pH, redox potential, biological activity, SOM, cation exchange capacity, and clay contents are important in determining availability of micronutrients in soils.

Plant factors such as root and root hair morphology (length, density, surface area), root induced changes (secretion of H+, OH-, HCO3-), root exudation of organic acids (citric, malic, tartaric, oxalic, phenolic), sugars, and non-proteinogenic amino acids (phytosiderophores), secretion of enzymes (phosphatases), plant demand, plant species/ cultivars, and microbial associations (enhanced CO2 production, rhizobia, mycorrhizae, rhizobacteria) have profound influences on plant ability to absorb and utilize micronutrients from soil (Clark and Zeto, 2000). After decades of continuous cropping, the nutrients extracted from the soil by both crops have reduced soil fertility dramatically in some areas. It has also increased pest pressures and nutrient mining (which occurs when nutrients are mined and transported long distances and lost permanently for the sub-region).As a result, yields have stagnated or declined in many areas. Soil organic content could be improved by incorporating crop residue into the soil, but the burning of crop residue negates this approach and increases environmental pollution. Water shortages are another problem, as access to groundwater has diminished in several areas. It showed that a small amount of nutrients, particularly Zn, Fe, and Mn applied by foliar spraying increases significantly the yield of crops (Sarkar *et al.*, 2007). As people are concerned about the environment and plant leaves uptake nutrients better than soil application, foliar spraying was created (Bozorgi *et al.*, 2011).

Importance of micronutrients in crop production

Increases quality and yield because most micronutrients act as cofactors in various enzymes taking part in the various metabolic activities of the plant like protein metabolism, carbohydrate metabolism, photosynthetic rate etc. therefore there will be increase in protein content, TSS and other quality parameters which results improving the quality and other micronutrients like iron, it is important for chlorophyll formation, photosynthesis will also increase and thus increase in yield.

In legumes, it influences N_2-fixationbecause micronutrients like Fe and Mo is an important constituent of Nitrogenous enzymes which helps in leghaemoglobin formation(O_2 scavenger).

Effect of micronutrient concentrations in planting seed on the vigour of next season’s crop.

Major economic impact of micronutrient concentrations in a farming operation is through the increased efficiency of macronutrient fertilizer use.

Management tools to help with decision making

Take soil and plant tissue samples from the affected and unaffected areas within the same field for a complete comparative analysis. This service is available from most soil testing laboratories. Call the laboratory for sampling details for a complete comparative test.

Keep good field records: know which fields had previous problems with micronutrients; soil test annually; and monitor each crop for symptoms. The amount of micronutrients needed varies by crop. Geo-reference micronutrient deficient areas within a field to make site-specific management easier. Micronutrients are expensive in comparison to macronutrients, so site-specific management makes economic sense.

If all indications point to a micronutrient deficiency, then foliar apply a plant available form of the micronutrient in strips across the affected field at the appropriate crop stage to see if the micronutrient fertilizer corrects the deficiency. Alternatively, soil apply the micronutrient to a test strip across the field in question at the beginning of the next crop season, and monitor crop response over more than one season. Assess the yield of treated and untreated areas to see if the yield response is economic. As over applying micronutrients can lead to toxicity levels resulting in yield loss, caution is necessary, especially with the micronutrient B.

What should you do when your soil test shows a marginal level for a micronutrient? A marginal level for a composite sample would imply patches in a field may be deficient. A marginal level should be treated as a flag to tell you to monitor the field more closely for the micronutrient deficiency. It can be considered that marginal soil test levels do not exist, as a soil is either sufficient or deficient. A measure of need may be made by proving an economic yield response to the application of a micronutrient. The best suggestion is to apply a test strip to verify whether a micronutrient is going to give a positive yield response, and also verify whether the returns are economical.

If a producer decides to apply a micronutrient to an entire field, leaving a “no micronutrient applied” check strip will be beneficial in determining whether there was an economic response.

If a micronutrient recommendation based on a soil and/or a tissue test is made for a field that has no history of a micronutrient deficiency, then further investigation, including crop scouting and another soil and tissue test, would be advisable.

Crop symptoms occur when micronutrient deficiencies are moderate to severe.

Micronutrient deficiencies that do not display symptoms but reduce the yield of a crop are referred to as “hidden hunger.” Know the field when assessing for “hidden hunger.”

If soil tests over a number of years indicate that a micronutrient level is decreasing into the marginal range for that crop, then consider applying the micronutrient - but first in test strips to see if there is a positive yield response and if that yield response is economical. On the other hand, applying micronutrients when they are not needed may reduce yields and/or economic returns.

Causes of micronutrient deficiencies

Intensive cropping

Crops are grown intensively on a piece of land which results in depletion of micronutrients.

High demand of modern crop cultivars

Since there is need to develop new crop cultivars which have high potential yield and have high quality parameters to meet the market demand. These modern crop cultivars require more nutrients i.e. deplete the soil of micronutrients.

Losses of top soil by erosion

It is due to precipitation, heavy wind etc. thus deficiency will occur.

Losses of micronutrients through leaching

Excessive rainfall results in leaching of micronutrients in the deeper layers of soils, thus there is deficiency of micronutrients in the rhizosphere.

Use of marginal lands for crop production

Use of poor soils which have less fertility for crop production (Nayyar, 1999).

Factors affecting availability of micronutrients

Soil pH

Soil pH influences solubility, concentration in soil solution, ionic form, and mobility of micronutrients in soil, and consequently acquisition of these elements by plants. As a rule, the availability of B, Cu, Fe, Mn and Zn usually decreases, and Mo increases as soil pH increases. These nutrients are usually adsorbed onto sesquioxide soil surfaces. Boron is the only micronutrient to exist in solution as a nonionized molecule over soil pH ranges suitable for the growth of most plants.

Organic matter

Soil organic matter may be grouped into water-insoluble (humic acids or humin) and water-soluble (fulvic-acids and small molecular weight microbial products) compounds. Humic acids contain many anionic oxygen groups (phenolic hydroxyl and carboxyl, aliphatic carboxyl, alcoholic hydroxyl), which may interact with metal cations. Predominant reactions between humic acids and metals are ionic-bonding or complexation reactions. The increases in humification of organic matter increased these reactive groups and enhanced the potential for reaction with metallic cations. Metal complexation with humic substances normally forms strong metal complexes, while ionic bonding with low molecular weight organic acids (acetic acid, malic acid, citric acid) form relatively weak bonds. Both types of bonding normally result in the enhancement of metal mobility and/or plant availability, but some complexes are not readily available to plants.

Temperature

Availability of most micronutrients tends to decreases at low temperature because root activity and microbial activity gets reduced and low rates of dissolution and diffusion of nutrients. Temperature can affect mobilization /immobilization reactions to decrease /increase solubility of organically bound soil Cu and its acquisition by plants (Moraghan and Mascagni, 1991). e.g. Iron deficiency, which occurs predominantly in calcareous and alkaline soils, is commonly enhanced by low soil temperature and high water (wet) and /or poorly aerated conditions (Marschner, 1995). Low soil temperatures reduce root growth and metabolic activity and increase HCO^{3-} levels in the soil solution to increase the severity of Fe deficiency with the increased solubility of CO_2 in soil solutions. On the other hand, high soil temperature may decrease Fe acquisition by increasing the microbial decomposition of organic materials to stimulate microbial activity and CO_2 production to increase the severity of Fe deficiency (Moraghan and Mascagni, 1991)

Moisture

When moisture content decreases, colloidal particles may become immobilized as a result, micronutrient adsorption on surface of soil particles, but when moisture content increases, leaching occurs. Excess soil moisture can restrict diffusion of O_2 within soils and favor Mn reduction. At lower soil redox potentials, high levels of Fe^{2+} may also be formed which could lead to Mn-Fe antagonisms. Manganese deficiency has rarely been observed in rice grown under flooded conditions, and Mn toxicity was aggravated in alfalfa grown under hot dry conditions.

Role and deficiency symptoms of micro-nutrients

Zinc

Zinc has been the micronutrient most often needed by western crops. It is common for Citrus crops to be given foliar zinc treatments one or more times per year. Other tree crops, grapes, beans, onions, tomatoes, cotton, rice, and corn have generally required zinc fertilization.

Unlike other metal ions such as copper, iron, and manganese, zinc is a divalent cation (Zn^{++}) that does not undergo valence changes and therefore has no redox activity in plants. High concentrations of other divalent cations such as Ca^{++}inhibit zinc uptake somewhat. Zinc acts either as a metal component of enzymes or as a functional, structural, or regulatory cofactor of a large number of enzymes. More than 80 zinc-containing proteins have been reported. The rate of protein synthesis and the protein content of zinc-deficient plants are drastically reduced. The accumulation of amino acids and amides in these plants demonstrates the importance of zinc for protein synthesis. Zinc is an essential component of RNA polymerase and if the zinc is removed, the enzyme is inactivated. Zinc is also a constituent of ribosomes and is essential for their structural integrity. The decrease in protein content of zinc-deficient plants is also the result of enhanced rates of RNA degradation. Higher rates of RNase activity are a typical feature of zinc deficiency (Rehm, 2010).

Large applications of phosphorus fertilizers to soils low in available zinc may induce zinc deficiency and increase the zinc requirement of plants. Part of the induced deficiency may be due to the inhibition of uptake by other divalent cations or a dilution of plant zinc due to increased growth from the added phosphorus. Soil chemical processes may cause enhanced zinc adsorption to hydroxides and oxides of iron and aluminum and to $CaCO_3$. Several experimental results indicate that there are additional phosphorus-zinc interactions in plants, including inhibition of zinc translocation from the roots to the shoot and “physiological inactivation” of zinc within the shoots. The latter suggestion is based on the observation that symptoms of zinc deficiency are related to the phosphorus/zinc ratio rather than to the zinc concentration in the shoots. Phosphorus-zinc interactions in soil are complicated by the infection of roots with vesicular arbuscular mycorrhiza. Infected roots take up more zinc than noninfected roots. Mycorrhizal infection of roots is strongly depressed by an increase in phosphorus supply. There is some evidence that zinc may have a role in mitigating phosphorus toxicity. Experimental results with ochra showed toxic levels of phosphorus in leaves of plants grown without adequate zinc. Although the connection between zinc deficiency and phosphorus toxicity is not well understood, there is substantial evidence that zinc affects phosphorus metabolism in the roots and increases the permeability of the plasma membranes of root cells to phosphorus and to chloride. Zinc stabilizes biomembranes and may therefore have specific function in the structural orientation of macromolecules within membranes and thus in membrane integrity. Zinc deficiency is widespread among plants grown in highly weathered acid soils and in calcareous soils. In the latter case, zinc deficiency is often associated with iron deficiency. The low availability of zinc in calcareous soils of high pH results mainly from the adsorption of zinc to clay or CaCO3. In addition, zinc uptake and translocation to the shoot are strongly inhibited by high concentrations of bicarbonate (HCO_3^-). In contrast to iron deficiency, zinc deficiency can be corrected fairly easily by the soil application of zinc salts such as ZnS_O4 (Lohry, 2007).

Symptoms of zinc deficiency in plants include

Decrease in stem length and shortening of internodes, rosetting of terminal leaves.

Reduced fruit bud formation.

Mottled leaves, interveinal chlorosis. Sometimes, a red spot-like discoloration (caused by anthocyanins) on the leaves often occurs. Symptoms of chlorosis and necrosis on older leaves ofzinc-deficient plants are most likely the result of phosphorus toxicity.

Dieback of twigs after the first year.

Striping or banding on corn leaves (Jain, 2007).

There was significant increase in the plant growth parameter viz. plant height at 45 DAS and at harvest, number of branches per plant and chlorophyll content of okra with application of 7.5 kg zinc per ha but remained at par 5.0 kg zinc per ha as per table number 1. These findings clearly indicated that zinc played a significant role and enhancing the growth of okra. Improvement in plant height at 45 DAS (95.46 cm) and at harvest (118.23 cm), number of branches per plant (2.58) and chlorophyll content (1.60 mg/g) with the application of zinc might be due to supply of micro nutrients, availability and uptake nutrients from soil due to favorable conditions (Kumar and Sen., 2004).

Iron

Iron (Fe) is required for the formation of chlorophyll in plant cells. It serves as an activator for biochemical processes such as respiration, photosynthesis and symbiotic nitrogen fixation. (Reddy,2004) Iron deficiency can be induced by high levels of manganese or high lime content in soils. Iron is taken up by plants as ferrous (Fe^{2+}) or ferric (Fe^{3+}) ions. The function of iron in plants depends on the ready transitions between its two oxidation states in solution. Plants store iron as ferritin, a protein that encapsulates ferric iron. Under aerobic soil conditions, iron is largely insoluble as a constituent of oxides and hydroxides. Ferric iron tends to be tied up in organic chelates. Hence, the concentration of free iron in the soil solution is exceedingly low in many soils. Plants have mechanisms to mobilize iron and make it available for absorption by their roots. Some of these mechanisms are not specific to absorption of iron. Roots extrude protons and thereby lower the pH of the rhizosphere: the lower the pH, the higher the solubility and availability of iron. Roots also release organic acids into the soil. That has a dual effect on the availability of iron: it lowers the external pH and the acids may form soluble complexes with iron. There are two mechanisms specific to iron absorption. The first (characteristic of dicots and non-graminaceous monocots) acidifies the rhizosphere by extruding protons. Ferric iron is reduced to ferrous iron by an inducible Fe^{3+}reductase enzyme at the plasma membrane. The reduced iron is transported across the membrane by Fe^{2+} specific ion transport system. The second mechanism (characteristic of corn, barley, and oat) involves the extrusion of siderophores (Greek meaning "iron carriers") by the roots. No reduction to ferrous iron takesplace. Crops often affected by iron deficiency are corn, sorghum, certain soybean varieties, turf, and certain tree crops and ornamentals (Cannolly, 2002).

Symptoms of iron deficiency include

Interveinal chlorosis of young leaves. Veins remain green except in severe cases.

Twig dieback.

In severe cases, death of entire limbs or plants (Jain, 2007).

The yield per plant was affected by iron treatments (Table 2). Specifically, the total yield was greatest in 1000 mg^{-1} FeSO4 and then decreased as the concentration increased. The yield of small fruits was greatest in 2000 mg-1 $FeSO_4$, but was lowest in the 1000 mg.-1. The medium size fruit yield was greatest in 1000 mg.-1 $FeSO_4$, which was more than 43% of the control, and was lowest in 2000 mg.-1 $FeSO_4$. Large fruit yield was mainly observed in 1000 mg.-1 FeSO4. As a result, marketable yield in response to the 1000 mg.-1 treatment was more than 40% of the control, while the yield at 2000 mg.-1 was less than 22 % of the control. The1000 mg.-1 FeSO4 was most effective at promotion of yield, followed by the 500 mg.-1 FeSO4. However, the 1500 and 2000 mg.l-1 treatments were inhibitory and resulted in greatly reduced.

Promotional effects of iron on fruit weight have been reported in several studies. Foliar application of iron has led to significant increases in mean fruit weight in strawberry, as well as fruits number and yield per tree of lemon. Similar results were founded in pomegranate. Our results indicated that 1000ppm was the optimum level for tomato production based on the yield of medium and large fruits.

Manganese

Manganese serves as an activator for enzymes in growth processes. It assists iron in chlorophyll formation. It is part of the system where water is split and oxygen gas is liberated. The splitting of water is an oxidation, namely $2\ H_2O \rightarrow O2 + 4\ H^+ + 4\ e^-$. The other protein in which manganese is an integral constituent is the manganese-containing superoxide dismutase. This enzyme is widespread in aerobic organisms.

The function of this enzyme is to provide protection from free oxygen radicals formed when O2 receives a single electron. Superoxide dismutases convert this highly toxic free radical into hydrogen peroxide (H_2O_2) which is subsequently broken down to water (Millaleo, 2010).

High manganese concentration may induce iron deficiency. Manganese uptake is primarily in the form of Mn^{++}. Manganese is generally required with zinc in foliar spraying of citrus. Other tree crops may show deficiencies, but otherwise there is no common recognition of requirements for this element. There is a growing body of knowledge suggesting that manganese additions may enhance glyphosate resistant soybean yield.

Symptoms of manganese deficiency include

Interveinal chlorosis of young leaves. Gradation of pale green coloration with darker color next to veins. No sharp distinction between veins and Interveinal areas as with iron deficiency.

Development of gray specks (oats), interveinal white streaks (wheat), or interveinal brown spots and streaks in barley (Jain, 2007).

Data concerning the effect of treatments on fruit set (%), fruit weight (g) and yield (kg) during the two experimental seasons are listed in Table 3. The data cleared that, zinc and manganese spray significantly increased fruit set compared with the control at both seasons. Moreover, spraying zinc at 3% combined with manganese at 60 mg/L was more effective than the other treatments, which gives the highest fruit set of 49.34 and 50.69 % for both seasons, respectively This result may be due to the use micronutrient elements are needed in relatively very small quantities for adequate plant growth and fruit production. Results also indicated that, control treatment was the highest in fruit weight Perhaps due to the role of these elements in increasing the number of perfect flowers and increase fruit set, leading to increased the number of fruits and therefore increase food competition. Moreover, spraying zinc and manganese exhibited favorable effect on increasing yield (Kg) in the two experimental seasons. The highest yield value was recorded by spraying zinc at 3% combined with manganese at 60 mg/L.

Boron

Boron functions in plants in differentiation of meristem cells. The general consensus is that its major function has to do with the structure of the cell wall and the substances associated with it. It is necessary for sugar translocation and helps in pollen grain germination. It is present in soil solutions with a pH less than 8 mainly as un- disassociated boric acid ($B(OH)_3$), the principle form taken up by roots, and disassociates to $B(OH)_4^-$ only at higher pH values (Gupta, 1993).

Boron deficiency

Boron deficiency is a widespread nutritional disorder. Under high rainfall conditions boron is readily leached from soils as $B(OH)_3$. Boron availability decreases with increasing soil pH, particularly in calcareous soils and soils with high clay content. Availability also sharply decreases under drought conditions, probably because of both a decrease in boron mobility by mass flow to the roots and polymerization of boric acid. Symptoms of boron deficiency in the shoots are noticeable at the terminal buds or youngest leaves, which become discolored and may die.

Internodes are shorter, giving the plants a bushy or rosette appearance. Deficiency is found mainly in the youngest plant tissues. Interveinal chlorosis on mature leaves may occur, as might misshapen leaf blades. Drop of buds, flowers, and developing fruits is also a typical symptom of boron deficiency. With boron deficiency, cells may continue to divide, but structural components are not differentiated. Boron also apparently regulates plant metabolism of carbohydrates. Boron is non-mobile in plants, and a continuous supply is necessary at all growing points.

Dar *et al.*, 2017 observed that pre bloom foliar application of boron to apple trees (Table 4) increases fruit set as well as yield moreover soil application of boron also increases yield but to a lesser extent. Further the author explains the increase in yield through soil application of boron to be due to increase in fruit size and through increase in fruit number in case of foliar spray. Besides increasing fruit set and yield Wojcik *et al.*, (2008) reported an increase in total soluble solids as well as total acidity due to soil boron application. This can be because of transportation of higher amount of assimilates into fruit tissues.

Chlorine

Chlorine is a strange mineral nutrient. Its normal concentration in plants is more typical of a macronutrient and yet the chlorine requirement for growth is more like a micronutrient. Chlorine is ubiquitous in nature and it occurs in aqueous solutions as chloride (Cl^-).

Evidence indicates that it is highly mobile and its main higher plant functions relate to charge compensation and osmo-regulation. Because chlorine is usually supplied to plants from various sources (soil reserves, rain, fertilizer and air pollution) there is much more concern about toxic levels than about deficiency. Nonetheless, a few cases have been noted of positive responses to the application of chloride as a fertilizer for wheat.

Symptoms of chlorine deficiency include

A blue-green shiny appearance of young leaves.

Wilting, followed by chlorosis.

Excessive branching of lateral roots.

Bronzing of leaves.

Chlorosis and necrosis in tomatoes and barley (Jain, 2007).

Copper

Copper is present in plants in complexed form. Like other potentially toxic heavy metals, copper in excess is bound to phytochelatins (Greek meaning “plant claws”) and sulfur containing peptides. Copper in solution is present as cuprous (Cu^+) and cupric (Cu^{++}). Cuprous copper is readily oxidized to cupric and so cuprous copper is only found in complexed forms. Cuprous complexes are usually colorless, whereas the cupric complexes are often blue or brown. Copper is an activator of several enzyme systems in plants and functions in electron transport and energy capture by oxidative proteins and enzymes. It may play a role in vitamin A production (Rehm,2009). A deficiency interferes with protein synthesis. Native copper supply has been recognized only rarely as needing supplementation. Some tree crops grown on organic soils or sands may need supplementation. Copper can be toxic at low levels so a need should be firmly established prior to supplementation. Deficiency symptoms vary greatly among species.

Symptoms of copper deficiency include

Leaves may be chlorotic or deep blue-green with margins rolled up.

The bark of trees is often rough and blistered, and gum may exude from fissures in the bark.

Young shoots die back.

Flowering and fruiting may fail to develop in annual plants and they may die in the seedling stage.

Stunted growth.

Formation of gum pockets around central pith in orange. Silviya and Stalin 2017 studied that the yield of grain and straw was significantly increased with the application of graded Cu doses (Table 5). The fourth location which was with minimum initial soil Cu content recorded the highest yield of grain and straw (6.23 and 7.47 t ha^{-1}), respectively. The lowest yield of grain and straw was recorded in L12, where the initial soil Cu status was high. Among different treatments, the treatment with 1.50 kg ha-1of Cu (T4) registered the highest yield of 6.50 and 7.74 t ha^{-1} of grains and straw respectively, and the yield increase being 30.2 and 25.7 per cent respectively over control was noted. The lowest mean yield was recorded in the control treatment with 4.54 t ha^{-1} of grains and 5.75 t ha^{-1} of straw.

Molybdenum

Although molybdenum is a metal, it occurs in aqueous solution mainly as molybdate anion. Molybdate seems to be relatively mobile in plants and higher concentrations can be found in roots than leaves when supplies are limited. Leaf concentrations may rise as molybdenum supplies increase. The molybdenum requirement is lowest of any mineral except, in certain species, nickel. The functions of molybdenum as a plant nutrient are related to the valency changes it undergoes as a metal component of enzymes. Only a few enzymes have been found to contain molybdenum in plants. In higher plants two molybdenum containing enzymes, nitrogenase and nitrate reductase, are of vital importance in crop production. All biological systems fixing N_2 require nitrogenase. Each nitrogenase molecule contains two molybdenum atoms, which are associated with iron. Therefore, the root nodule requirement is relatively high. As would be expected, the growth of plants relying on N_2 fixation is particularly stimulated by the application of molybdenum to deficient soils. The response of root nodule activity to molybdenum is spectacular and indirectly reflects the increase in the capacity for N_2 fixation brought about by molybdenum additions(Gungula,2006). In soils with low molybdenum availability, the effect of application of molybdenum to legumes depends on the form of nitrogen supply (fixed N_2 or added inorganic N fertilizer). The yield enhancement of adequately rhizobial infected soybeans from added molybdenum will be higher when fertilizer nitrogen is not added because N_2 fixation is facilitated by molybdenum. Molybdenum serves as a cofactor for the enzyme nitrate reductase. Molybdenum deficiency reduces the nitrate reductase activity, which inhibits the plant's ability to synthesize proteins. There are conflicting reports as to whether there is any molybdenum requirement for plants supplied exclusively with reduced N such as ammonium or urea. Conventional wisdom is that plants supplied a mixed N regime thrive best (therefore establishing a molybdenum requirement) (Kaiser, 2005).

Molybdenum deficiency is widespread in legumes and certain other plant species grown in acid mineral soils with a large content of reactive iron oxide hydrates. Liming may increase molybdenum availability to the point where luxury consumption occurs. This may be dangerous to ruminant livestock, which are very sensitive to excessive concentrations of molybdenum. Plants generally have a wide range of acceptable molybdenum concentrations. High, but nontoxic, molybdenum concentration in seeds ensures proper seedling growth and higher final grain yield. There is an inverse relationship between seed molybdenum content and yield response to added molybdenum fertilizer. Uptake rate of molybdenum is extremely low in the first 4 weeks after germination. Thus, the molybdenum requirement has to be met by retranslocation from the seed.

Symptoms of molybdenum deficiency include

Interveinal chlorosis. Veins remain green producing a mottled appearance.

Stunting and lack of vigor. This is similar to nitrogen deficiency due to the key role of molybdenum in nitrogen utilization by plants.

Marginal scorching and cupping or rolling of leaves (Jain, 2007).

Yadav *et al.*, (2017) studied that the Application of 1.0 kg Mo/ha increased seed yield by 22.1 and 8.0 per cent, respectively, over control and 0.5 kg Mo/ha table 6. The results on seed and straw yields thus confirmed the trend observed in growth and yield attributing characters with application of molybdenum, Shivkumar and Kumutha (2003).

Choosing a micronutrient application

Neither the treatment nor prevention of micronutrient deficiencies is complicated or expensive. The drag on yield and waste of time and resources caused by the deficiency costs plenty. Knowing how micronutrients behave in plants and soils will help determine if you need to take remedial or preventative action. It really depends on how and when you make a diagnosis. Soil applications are nearly always more effective and economical than foliar. However, if a problem expresses itself after the crop is emerged, then foliar treatment is the logical remedy. Tissue tests offer additional evidence of a problem but may not paint a complete picture. They will augment the soil test. Unfortunately, soil tests will not provide a completely accurate representation either. Generally, micronutrient soil tests will provide an indicator of the potentially available nutrient or give the total amount found. They usually have not been subjected to the correlation and calibration effort that the macronutrients have been subjected to. This is not to say that they are wrong or totally inaccurate, but the will serve better as guidelines and verifiers of a field's capabilities. Finally, soil micronutrient concentrations have been shown to vary widely in a field. It is important to obtain representative soil samples for analysis. There are a myriad of micronutrient products available. Each may claim a stake in how available the product is but the true test is how well it works in your field. Chelates are not better because they are chelated (more on chelates to follow). An example would be chelated manganese. Manganese chelates, when applied to soils high in iron are usually ineffective because the available iron replaces the Mn in the chelate. Manganese is kicked out into the soil chemical complex and is rendered unavailable. Sometimes, an efficiency factor is applied to a chelate. Authors (including universities) will recommend using a fraction of the recommended rate. These efficiency factors are often based on economics rather than agronomics. Efficiency factors may be appropriate in certain circumstances, but don't be fooled into thinking you bought 40 pounds of nutrient in a ten-pound container. There is evidence that there are differences in plant availability of different products. Researchers in Colorado did greenhouse studies to investigate whether there was a relationship between plant available zinc and the amount of water-soluble zinc in various fertilizers.

They found that plants grown in zinc deficient soils increased yield and absorbed zinc directly in proportion to the degree of water-soluble zinc in the fertilizer material. In this case, the greenhouse study is applicable to field conditions and verifies a positive relationship. Efficiency is also related to application method. Generally, banding is more efficient than broadcast. One of the easiest ways to band fertilizer is as starter (fertilizer applied with the planter unit). Broadcasting of some micronutrients is not recommended because the use rates are so low. However, broadcasting may be the only alternative in some systems. You can expect that chelated forms (where available) are likely to move in the soil more than non-chelated. This may be especially important in no-till systems where starter is not used. This scenario is likely to be rare since the value of starter has been shown to be great in no-till systems (Epstein, 2005).

Factors associated with supply and acquisition

Sufficient concentrations and available forms of micronutrients must be at or near root surfaces to meet plant acquisition needs. Nutrient supplies to plants are governed by such factors as concentrations inside plants and in soil solution, supply and chemistry at root surfaces or in the rhizophere, and interactions of one nutrient with another At any given time, concentrations of nutrients in the solution immediately adjacent to roots appear to be one of the best measures for assessing absorbtion potential, although plant and rhizosphere factors may influence the rates of absorption (Frageria *et al.*, 1997).

Deficiencies and toxicities

Micronutrient deficiencies and toxicities are widespread and have been documented in various soils throughout world. The deficiency of essential micronutrients induces abnormal pigmentation, size and shape of plant tissues, reduces leaf photosynthetic rates, and leads to various detrimental conditions (Masoni *et al.*,; 1996) Specific deficiency symptoms appear on all plant parts but discoloration of leaves is most commonly observed.

Table.1 Effect of zinc on growth, yield and yield attributes of okra

S.No	Characters	Zinc levels (kg/ha)				
		Control	2.5kg Zn(Zn1)	5.0 kg Zn (Zn2)	7.5 kg Zn (Zn3)	CD (P= 0.05)
1	Plant height(cm) at 45 DAS	87.29	89.05	92.09	95.46	5.29
2	Plant height at harvest(cm)	102.57	105.05	113.09	118.23	6.46
3	Leaf area(cm2)	98.31	105.77	113.97	116.80	5.04
4	No. of branches	2.31	2.36	2.50	2.58	0.10
5	Chlorophyll content (mg/g)	1.40	1.48	1.53	1.60	0.09
6	Fruit length (cm)	8.15	10.05	11.13	11.70	0.42
7	No. of fruit/plant	19.35	20.91	21.90	22.33	1.23
8	Fruit yield/plant (g)	60.07	187.40	224.84	233.67	10.30
9	Fruit yield/plot (kg)	1.44	4.50	5.40	5.61	0.25
10	Fruit yield/ha (q)	33.37	104.11	124.91	129.81	5.72

Table.2 Cumulative fruit yield of tomato per plant as affected by various concentrations of $FeSO_4$

Fe SO4 (ppm)	Yield(g/plant)			
	Small (<100g)	Medium (100-200g)	Large (>200g)	Total
Control	2064	4113	1903	8080
500	1874	5962	2320	10156
1000	2385	7268	2913	11869
1500	2150	4038	1777	7965
2000	1688	3195	1472	7052

Table.3 Effect of spraying Mn and Zn on fruit set and yield of pomegranate trees

Zn (%)	Mn (mg/l)	Fruit set (%)	Yield (kg)
0	0	43.25	23.56
	20	45.19	23.63
	40	45.47	23.81
	60	46.08	23.98
1.5	0	43.87	24.59
	20	45.89	24.95
	40	47.11	25.07
	60	48.80	25.40
3	0	46.34	25.71
	20	48.00	25.97
	40	49.45	26.56
	60	50.55	26.77
CD at 5% level		2.94	2.40

Table.4 Effect of boron on fruit set, yield and quality in apple

Treatment	Fruit set(%)DAF			Yield (kg/tree)	Mean fruit weight(g)	TSS(%)	Acidity(%)
	14	28	42				
Soil application	36.2	15.3	7.2	4.3	226	13.6	0.7
Foliar application	40.2	25.3	15.2	6.8	191	12.5	0.65
Control	39.4	11.4	6.9	3.1	188	12.4	0.63

Table.5 Effect of copper on grain yield(t/ha) of rice

Cu levels (kg/ha)	L1	L2	L3	L4	L5	L6	L7	L8	L9	L10	L11	L12
Control	3.85	4.05	4.16	4.38	4.45	4.58	4.63	4.70	4.77	4.84	4.98	5.07
0.50	4.77	5.12	5.28	5.61	5.58	5.72	5.92	5.88	5.85	5.80	6.21	6.07
1.00	5.97	6.21	6.38	6.25	6.00	6.38	6.68	6.60	6.44	6.38	5.60	5.45
1.50	6.83	6.83	7.05	7.28	7.14	6.87	6.47	6.40	6.17	6.07	5.50	5.42
2.00	6.55	6.70	6.80	6.98	6.93	6.66	6.40	6.25	5.92	5.85	5.32	5.28
2.50	6.53	6.69	6.75	6.90	6.90	6.54	5.75	5.70	5.40	5.22	5.12	5.10
CD (5%)	0.08	0.16	0.11	0.15	0.10	0.14	0.13	0.53	0.09	0.12	0.09	0.09

Table.6 Effect of molybdenum application on seed yield and straw yield of cluster bean

Treatments	Seed yield (kg/ha)	Straw yield (kg/ha)
Control	1278	2938
0.5 kg/ha Mo	1444	3209
1.0 kg/ha Mo	1560	3482
1.5 kg/ha Mo	1614	3569
CV (%)	8.1	8.9

Table.7 Critical micronutrient concentration (mg kg^{-1}) in soil for some field crops

Element	Crops	Extracting solution	Critical concentration	
			Range	Mean
B	Alfalfa, sugarbeet	Hot water	0.1-2	0.8
Cl	Wheat, Barley, Oats	Water	>22	
		0.01M $Ca(No_3)_2$		
		0.05M K_2So_4		
		CaO		
Cu	Maize and small grains	NH_4HCO_3-DTPA	0.12-2.5	0.8
		Mehlich-1	0.1-10	3
Fe	Sorghum and soyabean	NH_4HCO_3-DTPA	2.5-5	4.8
	Sorghum	DTPA-TEA		4.5
Mn	Soyabean,	Mehlich-1	4-8	7
	Small grains	NH_4HCO_3-DTPA	1-2	1.4
				3
				3.9
Mo	Forages, Legumes	NH_4-oxilate	0.1-0.3	
Zn	Beans, Maize	NH_4HCO_3-DTPA	0.25-2	0.8
	Rice,Sorghum	Mehlich-1	0.5-3	1.1
	Maize	0.1M HCl	2-10	5
	Maize			0.86
	Rice			1

[Source : Cox, 1987]

Table.8 General description of mineral toxicity symptoms on plants

B	:	High B may induce some interveinal necrosis, and severe cases turn leaf margins straw color (dead) with distinct boundaries between dead and green tissue. Roots appear relatively normal.
Cl	:	High Cl results in burning leaf tips or margins, reduced lead size, sometimes yellowing, resembles K deficiency, and root tips die.
Cu	:	High Cu may induce Fe deficiency (chlorosis). Light colored leaves with red streaks along margins. Plants become stunted with reduced branching and roots are often short or barbed (like wire). Laterals may be dense and compact.
Fe	:	Excess Fe is a common problem for plants grown in flooded acidic soil. May induce P, K and Zn deficiencies. Bronze or blackish-straw colored leaves extending from margins to midrib. Roots may be dark red and slimy.
Mn	:	Excess Mn may cause leaves to be dark green with extensive reddish-purple specks before turning bronze yellow, especially interveinal tissue. Uneven distribution of chlorophyll. Margins and leaf tips turn brown and die. Sometimes Fe deficiency appears, and main roots become stunted with increased number and density of laterals.
Mo	:	Excess Mo induces symptoms similar to P deficiency (red bands along leaf margins), and roots often have no abnormal symptoms.
Zn	:	Excess Zn may enhance Fe deficiency. Leaves become light colored with uniform necrotic lesions in interveinal tissue, sometimes damping off near tips. Roots may be dense or compact and may resemble bared wire.
Ni	:	High Ni results in white interveinal banding alternating with green semichlorotic areas with irregular oblique streaking,dark green veins and brown patches. Yellowing of leaves may resemble Fe or Mn deficiency.
Co	:	Pale green leaves with pale longitudinal stripes.

[Source : Clark and Baligar, 2000]

Table.9 Crop and soil conditions under which micronutrient deficiencies may occur

Micronutrient	Soil	Crop
Boron	Sandy soils or highly weathered soilslow in organic matter	Alfalfa and clover
Copper	Acid peats or mucks with pH <5.3 and black sands	Wheat, oats, corn
Manganese	Peats and mucks with pH > 5.8, black sands and lakebed/depressional soils with pH > 6.2	Soyabeans, Wheat, Oats, Sugarbeets, Corn
Zinc	Peats, mucks and mineral soils with pH > 6.5	Corn and Soyabeans
Molybdenum	Acid prairie soils	Soyabeans

[Source : Kelling, 2005]

Table.10 Micronutrient sources commonly for correcting micronutrient deficiencies in plants

Micro-nutrients	Common fertilizer sources
B	Sodium tetraborate (14-20%B), Solubor(20%B), Liquid boron (10%B), Boric acid (17% B)
Fe	Ferrous ammonium sulfate(14%Fe),Ferrous ammonium phosphate (29%Fe)
Zn	Zinc sulfate (23-36%Zn), Zinc ammonium complex (10%Zn), Zinc oxide (50-80%Zn), Zinc chelate(9-14%Zn)
Cu	Copper sulfate(13-35%Cu),Copper oxides (75-89%Cu)
Cl	Potassium chloride (47%Cl), Sodium chloride (60% Cl), Ammonium chloride (66%Cl), Calcium chloride (64%Cl), Magnesium chloride (74%Cl)
Mn	Manganese sulfate (23-25%Mn), Manganese oxide (41-68%Mn)
Mo	Ammonium molybdate (54%Mo), Sodium molybdate (39%Mo), Molybdenum trioxide (66%Mo), Molybdic acid(53%Mo)
Ni	Nickle chloride (25%Ni), Nickle nitrate (20%Ni), Nickle oxide (79%Ni)

[Source : Singh, 2004]

Table.11 Methods of correcting micronutrient deficiencies

Micro-nutrients	Soil application	Foliar application
B	0.75-7 kg Borax/ha	0.1-0.25%B solution
Cl	20-50kgKCl/ha	Unknown
Cu	1-20kg $CuSO_4$/ha(every 5-10 years)	0.1-0.2% solution $CuSO_4.5H_2O$ or 0.1-4kg Cu/ha as $CuCl_2.2H_2O$, $CuSO_4.5H_2O$ or CuO
Fe	30-100kg $FeSO_4$ or FeEDDHA/ha (need annual treatment of 0-10 kg/ha)	2% $FeSO_4.7H_2O$ or 0.02-0.05%FeEDTA solution (several sprays needed)
Mn	5-50kg $MnSO_4$/ha	0.1% $MnSO_4$ H_2O solution or 3-6kgMn/ha
Mo	0.01-1kg ammonium molybdate or lime to pH 6.5	0.07-0.1% Na or ammonium molybdate (100gMo/ha)
Zn	0.5-35kg $ZnSO_4$ orZnEDTA/ha	0.1-0.5% $ZnSO_4 7H_2O$ solution (0.17-1.5 kg/ha)

[Source : Baligar and Jones, 1997]

Deficiency and toxicity symptoms may be confused with drought, disease, insect and other damage so correct diagnosis may be difficult without experience. Critical concentration ranges of micronutrients in soil for important field crops (Table 7). Some description of deficiency (already discussed in previous) and toxicity symptoms associated with many crop plants in Table 8 has been provided.

Supply and uptake

Micronutrient uptake by roots depends on nutrient concentrations at root surfaces, root absorption capacity, and plant demand.

Micronutrient acquisition includes dynamic processes in which mineral nutrients must be continuously replenished in soil solution from the soil solid phase and transported to roots as uptake proceeds. Mineral nutrient transport to roots, absorption by roots and translocation from roots to shoots occur simultaneously, which means that rate changes of one process will ultimately influence other processes involved in uptake (Frageria, 1997). In soil systems mineral nutrients move to plant roots by mass flow, diffusion, and root interception.

Oxidation and reduction

Oxidation –Reduction reactions occur when electrons are transferred from a donor to an acceptor. The donor loses electrons to increase in oxidation number, and the acceptor gains electrons to decrease in oxidation number.

Redox reactions with various forms of Mn(Mn^{2+} and Mn^{4+}), Fe ($Fe^{2+}$and Fe^{3+}), and Cu (Cu^{+} and Cu^{2+})are common in soils (Lindsay,1979). Redox reactions in soils can also be influenced by organic metabolites produced by roots and microorganisms.

Rhizosphere

The rhizosphere is defined as the zone of soil immediately adjacent to plant roots in which the kinds, numbers, and/or activities of microorganisms differ from those of the bulk soil.

This zone usually contains fungi, bacteria, root and microorganism secretions, sloughed off or dead materials from microorganisms and roots, and chemical properties that are markedly different from the bulk soil.

The chemistry of the rhizosphere has pronounced effects on the availability of micronutrients. An example of rhizosphere activity is mycorrhizae. Mycorrhizae associated with crop plants are primarily arbuscular mycorrhizal fungi (AMF).

Interactions with other elements

The understanding of micronutrient interactions between and among the various mineral nutrients is important for balancing nutrient supplies to plants, improving growth and yields of plants, and eliminating deficiencies and toxicities imposed on plants. Mineral interactions are generally measured in term s of growth responses and changes in mineral nutrient concentrations in plants.

Method of application

The best method of micronutrient application depends on the element and when the deficiency is being addressed.

Soil application

For deficiencies known at the start of the season, soil application is preferred to foliar application for most nutrients. Micronutrients banded with starter fertilizers at planting time usually are more effective over a longer period than foliar-applied micronutrients. This method also gets the nutrient to the plant at the earliest opportunity. Soil-applied micronutrients also may be **broadcast,** but a concentrated band near the plant allows lower use rates of sometimes expensive materials. Manganese should only be banded, because of the ability of most soils to strongly “fix” this element. However, boron should not be banded as high concentrations near the seed can be toxic.

Foliar application

Foliar application is especially useful for some elements that are not used efficiently when applied to the soil, such as iron. This method also is useful for quick uptake in emergency situations when deficiencies are noted or in cases where other materials are being sprayed. Like banding, foliar applications generally have lower use rates, but more than one application may be needed. However, because the crop partially develops prior to foliar application, irreversible damage may have occurred before the needed nutrient is supplied.

Broad-spectrum micronutrient applications are not recommended to treat a single micronutrient deficiency, as this approach is expensive and potentially harmful to the crop. The harm can occur because of potential toxicities, or because the presence of additional nutrients may interfere with the uptake of the needed nutrient. Achieving a uniform spread pattern is important to correct deficiencies, regardless of whether the material is liquid or solid, banded or broadcast, or preplant or foliar applied.

Selecting micronutrient sources

There are three main classes of micronutrient fertilizers: inorganic, synthetic chelates and natural organic complexes.

Inorganic sources consist of oxides, carbonates and metallic salts such as sulfates, chlorides and nitrates. Sulfates are the most common metallic salts used in the fertilizer industry because of their high water solubility and plant availability. Less soluble oxides must be ground finely or partially acidulated with sulfuric acid to form oxysulfates in order to increase their effectiveness. Metal-ammonia complexes such as ammoniated Zn sulfate decompose readily in soils and provide good agronomic effectiveness. Chelates are fertilizers in which the micronutrient is combined with an organic molecule to increase its stability and effectiveness in the soil. Chelates such as Zn-EDTA are more stable and more effective in correcting Zn deficiency than other forms of applied Zn. These synthetic chelates are more effective and less variable than natural organic complexes such as lignosulfates, phenols and polyflavonoids (Stevens, 2002).

Future Strategies of Research

Screening and/or breeding of micronutrient efficient crops and their cultivars should be done on a priority basis, and more importantly, nutrient efficient crop rotations should be recommended to farmers of the State, particularly those on deficient soils. Systematic studies to monitor micronutrient deficiencies in different crop rotations and soils should be carried out using GIS. The entire state may be covered once in 2 to 3 years and repeat survey should be done after 4 to 5 years to monitor the trends. In addition, critical limits for main crops of the State should be refined for different soils. Limited information is available on emerging deficiencies of B and Cu in the State and on the response of different crops to application of Cu and B in deficient soils. More field experiments should be initiated to generate information on response, critical limits and their efficient management under field conditions (Sadana *et al.*, 2010)

Micronutrients are required in very small quantities by the plant for their function. Since they are involved in various enzymatic activities, their deficiencies causes malfunctioning of the plant activities. To manage these micronutrient deficiencies spraying of suitable chemicals at recommended levels by foliar application will alleviate the deficiency. Increases in crop yields from application of micronutrients have been reported in many parts of the world. Factors such as pH, redox potential, biological activity, SOM, cation –exchange capacity, and clay contents are important in determining the availability of micronutrients in soils, Further, roots –induced changes in the rhizosphere affect the availability of micronutrients to plants. Major root induced changes in the rhizosphere are pH, reducing capacity, redox potentials, and root exudates that mobilize sparingly soluble mineral nutrients. Root exudates may make elements like Fe more available, but they may also produce water –soluble metal chelating agents which reduce metal activity with roots. Micronutrient application rates range from 0.2-100kg/ha, depending on the micronutrient, crop requirement and method of application. Higher rates are required for broadcast than for banded applications on soil or as foliar sprays. The development micronutrient-efficient and/or tolerant-resistant genotypes appear promising for improving future crop production.

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