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ADVANCED MICRONUTRIENT FERTILIZERS FOR PLANT NUTRITION

1. **Mandira Barman**
ICAR-Indian Agricultural Research Institute, New Delhi-110012, India
E-mail: mandira.iari@gmail.com
2. **Debarup Das**
ICAR-Indian Agricultural Research Institute, New Delhi-110012, India
3. **Indu Chopra**
ICAR-Indian Agricultural Research Institute, New Delhi-110012, India
4. **Vinod Kumar Sharma**
ICAR-Indian Agricultural Research Institute, New Delhi-110012, India
5. **Debasis Golui**
ICAR-Indian Agricultural Research Institute, New Delhi-110012, India
6. **Debrup Ghosh**
ICAR-Indian Agricultural Research Institute, New Delhi-110012, India
7. **Naresh Kumar**
ICAR-Indian Agricultural Research Institute, New Delhi-110012, India

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Introduction

Micronutrients, crucial for plant, animal, and human growth, suffer widespread soil deficiency globally, impacting crop yield and human health. Zinc (Zn), copper (Cu), Iron (Fe), manganese (Mn), nickel (Ni), boron (B), molybdenum (Mo), and chlorine (Cl) are the essential micronutrients for plants and also known as 'trace elements'. The most used micronutrient fertilizers are sulphate salts of Zn, Cu, Fe and Mn. After application, these elements react rapidly with various soil components via oxidation and/or precipitation or may react with clay-colloids and various mineral-complexes, making them unavailable to the crops. Also, there is no synchronization of nutrient release with crop demand. Current micronutrient fertilization methods exhibit low (<5%) crop use efficiency due to fixation and loss issues. Use of water- soluble micronutrient fertilizer further worsens the situation. Slow-release fertilizers offer some improvement, but nanotechnology presents promising solutions.

Functions of micronutrients in plant nutrition

Micronutrients are indispensable for plant growth and development as they play crucial physiological roles in plant as follows:

- Iron is vital for enzymes like cytochrome oxidase, catalase, and peroxidase.
- Manganese aids photosystem II and functions in photolysis, participating in TCA cycle enzymes.
- Zinc is linked with carbonic anhydrase, dehydrogenases, and hormone synthesis, crucial for plant reproduction and growth.
- Copper supports enzymes like cytochrome oxidase, polyphenol oxidase, and ascorbic acid oxidase.

- Molybdenum is essential for nitrogen metabolism via nitrate-reductase and nitrogenase.
- Cobalt is necessary for symbiotic N fixation and cobalamin coenzyme formation.
- Nickel is vital in urease enzyme and N metabolism.
- Boron is key in phenol metabolism, membrane integrity, and sugar translocation, crucial for water absorption and pollen tube growth.

Common micronutrient fertilizers

The most used fertilizer for Zn, Cu, Fe and Mn in India are water-soluble sulphate salts *i.e.* $ZnSO_4.7H_2O$, $CuSO_4.5H_2O$, $FeSO_4.7H_2O$ and $MnSO_4.H_2O$, respectively. Besides inorganic salts, water soluble chelated micronutrient fertilizers like, Fe-EDTA and Zn-EDTA are also being used in India. However, as these chelated fertilizers are costlier than sulphate salts, farmers still prefer to use sulphate salts. Both $Na_2B_4O_7.10H_2O$ and H_3BO_3 are used as fertilizer for B. Molybdenum is usually applied as $(NH_4)_6Mo_7O_{24}$which is water soluble. Use of micronutrient fortified fertilizers like, zincated-urea, boronated single-super-phosphate are also being used in limited scale.

Advanced micronutrient fertilizers

Conventional micronutrient fertilizers release nutrients too quickly, leading to wastage and environmental problems. Slow-release and controlled-release fertilizers, like SRF and CRF, offer a solution by releasing nutrients gradually, matching plant needs. These advanced fertilizers ensure optimal plant growth with fewer applications and minimize environmental impact. Various types of CRF are discussed below:

1. Less soluble micronutrient fertilizers

Chandra et al. (2009) proposed that an ideal SRF will be an insoluble micronutrient fertilizer, but capable of being solubilized by plant roots through processes such as ion-exchange or organic acid secretion, and subsequently absorbed through chelation. Examples include metal-ammonium phosphates and polyphosphates forming chelates, enhancing micronutrient concentration in soil. Arslanoglu (2019) discusses controlled-diameter struvite particles for Cu(II) adsorption. Hydrolyzed fertilizers like metaphosphates show promise; Bandyopadhyay et al. (2008, 2014) synthesized crystalline-polyphosphate SRFs, enhancing yields in rice and potato crops. Abat et al. (2015) synthesized slow-release B-containing mono-ammonium phosphate, safe for crops. Chandra et al. (2009) synthesized water-insoluble polymeric phosphates containing iron and magnesium, increasing paddy yield by 46.9% in greenhouse experiments at low iron application rates.

2. Encapsulated micronutrient fertilizers

Encapsulation with natural or synthetic polymer films shields nutrients, slowing their release into soil. This enhances micronutrient fertilizer efficiency by creating a barrier against nutrient transport. Polymer properties, such as those of ethyl cellulose or chitosan, regulate micronutrient release (Abedi-Koupai et al., 2012; Monreal et al., 2016). Cost-effective, biodegradable coatings with non-toxic degradation products are preferred. Although lab studies show promise, field testing of these polymer-coated fertilizers is limited. Additionally, aluminosilicates serve as carriers for Cu (Huo et al., 2014).

3. Nanotechnology based micronutrient fertilizers

Nano-fertilizers (NFs) aim to enhance Micronutrient Use Efficiency (MUE) by reducing nutrient loss and increasing plant uptake. Nano-composite polymers slowly release bound nutrients, potentially surpassing current controlled-release fertilizers. Nano-biosensors, embedded in biopolymer coatings, respond to soil microbe signals, releasing nutrients accordingly, though evaluation is nascent. Physically or biologically synthesized nano-sized chemical fertilizers are commonly used. Mandal et al. (2019) synthesized and tested a nanoclay polymer composite (NCPC) based Zn fertilizer with promising results in greenhouse trials. NCPCs act as superabsorbents, regulating nutrient release through clay content. However, synthesis and evaluation of nano-fertilizers are still at preliminary stages. Few examples of crop responses towards nanotechnology enabled micronutrient fertilizers are given below:

Iron

Rui et al. (2016) tested Fe_2O_3-NPs on peanut plants in a greenhouse, and observed improved growth and Fe content. The Fe_2O_3-NPs also regulated phytohormones and antioxidant enzymes. Ghafariyan et al. (2013) found that low concentrations of Fe-NPs increased soybean leaf chlorophyll in a solution culture. Delfani et al. (2014) noted enhanced black-eyed pea growth, chlorophyll, and Fe content with Fe-NP foliar spray, surpassing conventional Fe salts.

Manganese

Dimpka et al. (2018) compared the effect of soil and foliar applications of nano-Mn (Mn_2O_3) with bulk-Mn and ionic-Mn (6 mg/kg/plant) on wheat yield and nutrient uptake. Soil application reduced shoot Mn in all treatments but increased grain Mn translocation efficiency (nano-Mn: 22%, bulk-Mn: 21%, salt-Mn: 20%, control: 16%). Foliar nano-Mn enhanced grain (12%) and shoot (37%) Mn content, indicating better crop response. Pradhan et al. (2013) found metallic Mn-NPs improved mung bean growth and photosynthesis compared to $MnSO_4$ salt, showing significant increases in root/shoot length, biomass, and rootlets.

Zinc

Zn-NPs' impact on plant growth is widely studied. Mahajan et al. (2011) observed enhanced growth in mung bean and chickpea at low ZnO-NP concentrations. Zhao et al. (2013) found soil-applied ZnO-NPs (400, 800 mg kg^{-1}) improved cucumber growth, while foliar sprays enhanced phytase and phosphatase activities in cluster bean (Raliya and Tarafdar, 2013). Venkatachalam et al. (2016) noted cotton growth improvement with ZnO-NPs and P supplements. Biologically synthesized Zn nano-fertilizer enhanced pearl millet growth and chlorophyll content (Tarafdar et al., 2014). Lin and Xing (2007) reported root elongation improvements with ZnO-NP exposure in radish and rape. However, high Zn-NP concentrations may be inhibitory or phytotoxic (Zhao et al., 2014), with levels above 10 mg L^{-1} showing adverse effects on ryegrass growth (Lin and Xing, 2008).

Copper

Shah and Belozerova (2009) found Cu-NP application at 130 and 600 mg kg^{-1} boosted lettuce-seedling growth by 40% and 91%. However, higher concentrations (200-1000 mg L^{-1}) were phytotoxic to mung bean, wheat, and yellow squash seedlings (Lee et al., 2008; Musante and White, 2012). Nekrasova et al. (2011) noted that waterweed supplied with 0.25 mg Cu L^{-1} through Cu-NPs increased photosynthesis by 35% over control in a three-day study. Stampoulis et al. (2009) found zucchini biomass decreased by 90% with 1000 mg Cu L^{-1} Cu-NPs over 14 days, suggesting optimal growth at 0.02 mg Cu L^{-1}, with toxicity at higher concentrations.

Molybdenum

Taran et al. (2014) studied Mo-NPs' impact on chickpea growth with four treatments: water, Mo-NPs, nitrogen-fixing bacteria, and microbes plus Mo-NPs. Chickpea seeds were treated with these for 1–2 hours before planting in loamy soil. Rhizosphere soil analysis showed a significant increase in microorganism development under the fourth treatment, proving it optimal for chickpea root nutrition. Roots and nodule mass per plant were also higher under the fourth treatment.

Conclusions

Precision techniques are crucial to minimize micronutrient loss in soil to improve the use efficiency of applied fertilizers. Researchers are actively working in the development of controlled-release fertilizers and nanotechnology-enabled fertilizers. However, their field-scale application is still in early stages, requiring further research on dosage, timing, and cultural practices. The effects of encapsulated and nano-fertilizers on crop yield and quality remain unclear, but hold promising potential, particularly in nanotechnology.

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