Secondary and micronutrient fertilizers

(A) Secondary fertilizers [Ca, Mg and S]

1. Calcium Fertilizers:

Nearly all multi nutrient liquid fertilizer formulations and more than 50 per cent multi nutrient solid fertilizers are almost devoid of calcium .Multi nutrient fertilizers use, warrants the use of calcium. The source of calcium with basic chemical formula, its content and solubility are mentioned in the following table.

Basic chemical data of various calcium sources:

S.No.	Source	Formula	Ca (%)	Water solubility g/100 g at 25 ^{0}C
1	Burnt lime	CaO	70	0.12
2	Hydrated lime	$Ca(OH)_2$	50	0.16
3	Calcite lime	$CaCO_3$	36	0.01
4	Dolamitic lime	$CaCO_3$ $Mg CO_3$	17	>0.1
5	Basic slag	$[CaO]_5$ P_2O_5 SiO_2	29	>0.1
6	Gypsum	$CaSO_4$ $2H_2O$	22	0.24
7	Calcium nitrate	$Ca(NO_3)_2 2H_2O$	20	100
8	SSP	$Ca(H_2PO_4)_2$ $CaSO_4$	20	1.0
9	TSP	$Ca(H_3PO_4)_2$	13	1.80
10	Rock phosphate	$Ca_5(PO_4)_3F$	33	0.002
11	Calcium chloride	$CaCl_2$	36	100.00

Global reserves of Ca are considerably large since whole mountain ranges consist of lime stone. Calcium nick named as root developer, which is slightly mobile in plants. Calcium deficiency in plants is rarely caused by shortage of available reserves in the soil, except in acidic soils.

2. Magnesium Fertilizers:

In multi nutrient fertilizers, finely ground dolamitic limestone is used as filler and it is a incidental supplier of Mg.

S.No.	Source	Formula	Mg (%)	Water solubility g/100 grams at 25 ^{0}C
1	Magnesium oxide	MgO	45	6.2 x10 $^{-5}$
2	Dolamite	$CaCO_3$ $MgCO_3$	12	0.032
3	Kiserite	$MgSO_4$ H_2O	18.2	68.40
4	Langbeinite	K_2SO_4 $2MgSO_4$	11.2	100.0
5	Magnesium sulphate	$MgSO_4$ $7H_2O$	10.5	91.10

3. SULPHUR FERTILIZERS:

1. Plants take sulphur in the form of sulphate [SO_4^{2-}] ion. Sulphur fertilizers predominantely contain sulphate, some of which are easily soluble and some are slightly soluble
2. Gypsum [$CaSO_4$ $2H_2O$] is a calcium sulphate because its slight solubility in water which is slow acting
3. Elemental sulphur is also an important sulphur fertilizer with strong acidifying action. It can be used either directly or as an additive to other solid fertilizers eg sulphur coated urea. The following table gives the basic chemical data of sulphur sources

S.No.	Source	Formula	S (%)
1	Ammonium sulphate	$(NH4)_2$ SO_4	23
2	Potassium sulphate	K_2SO_4	18
3	Magnesium sulphate	$MgSO_4$	13
4	Super phosphate	$Ca(H_2PO_4)_2$ $CaSO_4$	12
5	Gypsum	$CaSO_4$ $2H_2O$	18
6	Aluminium sulphate	$Al_2(SO_4)_3 18H_2O$	14

The sulphur requirements of plants are approximately 2/3 of their phosphorus requirements and are provided from various sources such as air, rain water, soil and fertilizer. Fields near Industrial zones are supplied with 10-30 kg ha $^{-1}$ per year from SO_2 waste gases.

MICRONUTRIENT FERTILIZERS

Higher green plants are known to require seven micronutrients viz.,Fe,Mn Cu, B Mo ,Cl etc., . But this number may have to be increased in future.

Sources of micronutrients:

S.No.	**Micronutrients**	**Formula**	**Content (%)**
A	**IRON**		
	1.Ferrous sulphate	$FeSO_4$ $7H_2O$	20
	2.Fe-chelate	Fe-EDTA	5
	3.Fe-Chelate	FeEDHA	6
B	**MANGANESE**		
	1. Manganous sulphate	Mn SO_4 4 H_2 O	24
	2.Manganous sulphate (Monohydrate)	Mn SO_4 H_2 O	32
	3. Mn –chelate	Mn-EDTA	13
C	**ZINC**		
	1.Zinc sulphate	$ZnSO_4$ $7H_2O$	23
	2.Zinc sulphate (Monohydrate)	$ZnSO_4$ H_2O	36
	3.Zn-chelate	Zn-EDTA	14
D	**COPPER**		
	1.Copper sulphate	Cu SO_4 $5H_2O$	25

	2.Copper sulphate (Monohydrate)	$Cu\ SO_4\ H_2O$	36
E	**BORON**		
	1. Borax (Na-tetra borate)	$Na_2B_4O_7\ 10H_2O$	11
	2.Borax anhydrous	$Na_2\ B_4O_7$	22
	3.Boric acid	H_3BO_3	18
F	**MOLYBDENUM**		
	1 Sodium molybdate	$Na2MoO_4\ 2H_2O$	40
	2.Ammonium molybdate	$(NH4)_6MoO_{24}$	54
	3Molydenum trioxide	MoO_3	66
	4.Calcium molybdate	$CaMoO_4$	48

The need for the micronutrient fertilization has been increasing due to the following causes:

1. Change in the plants:

Change in the plant varieties from traditional to high yielding varieties (HYV). HYV have a capacity to remove more nutrients both major and minor. HYV have low mobilizing capacity of micro nutrients from the soils hence they are to be applied through external application.

2. **Change in soil**:

Change in soil condition from acid to alkaline (Increased soil reaction) and aeration cause greater immobilization of most micronutrients except molybdenum (Fe, Zn, Cu and Mn). High acidic nature of the soil induces both calcium and magnesium deficiency.

3. Changes in fertilization: Using high doses of NPK in the form of complex fertilizers, induces deficiencies of secondary and micro nutrients.

1. Antagonistic action due in part to excessive fertilization with NPK Eg. Higher K content in soils effects the uptake of Fe, Mn, and B.
2. Excess P leads to deficiencies of Zn, Fe, Cu and increases Mo availability.
3. More the sulphate present in the soils, lesser the availability of Mo.
4. Lesser or least micronutrient constituents in multinutrient fertilizers.

4. Changes in overall growth conditions.

1. Intensive cultivation: Intensive cultivation leads to micro nutrient deficiencies
2. Non availability and application of organic manure.
3. Under/ over limed condition.
4. Parent material: Most of the micronutrients originates from parent material and influences the availability or deficiency of micronutrients to plants
5. Land levelling and shaping: Most of the micronutrients are concentrated on the surface soil except Molybdenum. Levelling of land and deep tillage operations leads to deficiencies.
6. Low Si/Mg ratio: Leads to fixation of Zn in soil.
7. Calcium carbonate: More the $CaCO_3$ in soils lesser the availability of Fe, Cu, Mn, Zn.
8. Soil texture: Boron availability is more in coarse textured soils and in finer textured soils it gets fixed, unavailable to plants.
9. Secondary clay minerals: Montmorillonite clay adsorb more of Zn, Cu and leads to deficiency or unavailability to plants.
10. Soil moisture: Dry conditions of soil fix more of Boran and is released under wet conditions. Presence of more moisture reduces the availability of Mn.
11. Interaction with macronutrients: Heavy nitrogen interferes with availability of Cu, Mn, Zn and leads to deficiencies in plant.
12. Liming reduces the availability of Mn, Zn, Fe, Cu.
13. Seasonal variation: Nutrient deficiencies are more during cold season.
    - Out break of B deficiency is common in dry seasons
    - Summer drought aggravate Fe chlorosis.
    - High and low soil temperatures induces Zn deficiency in soils having low Zn.

PRINCIPLES INVOLVED IN MICRONUTRIENT FERTILIZATION

1. Iron Fertilization:

Majority of Fe-fertilizers are water soluble .Salts or organic complexes (chelates). They are predominantly applied as foliar sprays, however this requires repeated application. In addition to supplying iron to deficit soils, it is necessary to mobilize iron in the soil itself through acid –N – fertilization. Fe removal amounts to a few kg/ha /year

2. Manganese Fertilization:

Manganese sulphate is the best known water soluble fertilizer and is suitable for leaf fertilization .It can also be used as a soil dressing, but is easily fixed in deficit soils when the pH is more soil Mn supplies can be improved by

1. Using acid forming fertilizers
2. Compacting loose soils
3. Preventing excessive drying
4. Supply of easily decomposed organic matter ,which on conversion creates reducing conditions and thus Mn released .It is a practical means of Mn supply than to add Mn fertilizer. About ½ to 1.0 kg of Mn /ha/year is removed by crops in general.

3. Copper Fertilization:

Copper sulphate [Blue Vitriol] is the oldest water soluble Cu-fertilizer .It can be applied as soil dressing or foliar nutrient .However; its acidic side effects are likely to cause leaf scorch on foliar application.

1. Hence less caustic agents like green copper $Cu_2Cl(OH)_3$ or Cu-chelates are safe to use.
2. Copper removal by crops in general varies 30-100 g/ha /year.
3. Copper is highly immobile in soil and as such needs thorough mixing with top soil.

4. Zinc Fertilization:

Zinc sulphate is the simplest form of water soluble fertilizer

1. It is acidic in reaction and causes leaf scorch on foliar application unless free acidity in neutralized with lime**.**
2. Improvement of natural zinc sulphate (Soil zinc) can be done by the application of acid forming N-fertilizers to combat Zn-deficiency. Crop removal of Zn varies from 100-400 g /ha /year

5. Boron Fertilization:

Borax **(**Na –tetra borate) is historically famous water soluble boron fertilizer.

1. The effectiveness of chile –salt peter was attributed to the presence of borax as natural admixture**.**
2. It can be applied to soil or foliage
3. Boron removal by crops is about 50 g / ha /year

6. Molybdenum Fertilization:

Sodium molybdate and ammonium molybdate are the important Mo fertilizers suitable for soil or foliar application and also for seed treatment.

1. Molybdenum removal by crops varies from 5 to 20 g/ha /year

Classification of micronutrient fertilizers

Micronutrient fertilizers are classified into two broad categories:

1. Inorganic salts
2. Chelates

1. Inorganic salts:

Supplying micronutrients are salts like ZnSO4, CuSO4, MnSO4, Fe SO4 etc., All these are readily soluble in water and can be used both for soil application and foliar spray.

2. Chelates:

This is next important category of micronutrient fertilizers. Chelates are metallic molecules of varying sizes and shapes in which the organic part binds the nutrient in a ring like structure. For the chelation of nutrient cation the common chelating agents used in chelating micronutrients as follows.

1. EDTA : Ethylene Diamine Tetra Acetic Acid
2. HEDTA : Hydroxy Ethylene Diamine Tetra Acetic Acid
3. EDDHA : Ethylene Diamine Dihyroxy Acetic Acid
4. NTA : Nitrilo Tri Acetic Acid
5. DTPA : Diethylene Triamine Penta Acetic Acid