**4. CALCIUM (Ca):**

* Ca is a secondary macro nutrient, which is essential secondary macronutrient abundantly present in soil therefore it is not be needed to apply as fertilizer.
* It is at 4th position after N, P and K.
* Significant concentration in plant tissue 5-30 mg g‑1 of plant dry weight.

**Soil Cahas 3-forms:**

1. Soluble form of Ca2+, which form complexes with soil colloidal complex.
2. Exchangeable form is relatively soluble form, which is adsorbed with soil particles.
3. In the form of minerals **i.e.** feldspar and calcium phosphate.

These minerals are original source of soluble and exchangeable form of Ca++.

**Factor affecting the availability of Ca:**

1. **pH:**

At high soil pH, high Ca concentration is available. At high soil pH >7.2, P-availability is reduced because of high Ca-phosphate because soluble Ca++ increases.

pH$ ∝ $Ca

1. **Cation exchange capacity(CEC):**

In soil with high CEC, Caavailability is high and vice versa.

CEC$ ∝ $Ca

1. **Ca interaction with other nutrients:**

If there is a very high concentration of Na, K, Mg, NH4+, Al3+, Fe3+ and Fe2+, availability of Ca2+ is reduced. These all nutrients have antagonistic effect with Ca2+.

* If there is a high Na concentration it will replace Ca2+ at soil binding sites and Ca2+ availability is reduced because of poor soil structure.
* P-availability is reduced due to high Ca2+ concentration due to the formation of Ca-phosphate in alkaline soil condition.
* At low pH in acidic condition Fe and Al become soluble that combine with Ca2+, thus Ca availability is also reduced.
* If Ca2+ is applied, boron toxicity is reduced because Ca reduces B uptake and utilization.
* Ca++ is immobile in both plant and soil.

**A) Ca2+ uptake:**

* Uptake occurs through facilitative diffusion by Ca2+ channels through roots.
* On the plasma membrane and tonoplast there is active uptake of calcium by Ca2+-ATPase or by Ca2+/H+ antiport.
* 11 different Ca2+-ATP pumps have been identified in plants.

**Functions or Roles of Ca:**

1. **Cell division:** It is required in mitotic spindle formation, therefore needed for meristematic regions (tip of shoot, it is actively cell division part).
2. Nitrate uptake and metabolism.
3. Enzyme activation (in ATP hydrolysis and phosphate metabolism).
4. Osmotic adjustment and opening and closing of stomata.
5. Cell membrane integrity by bridging phosphor-lipids at un-esterified phospho-lipids.
6. Acts as a cross link in pectic chains of cell wall. Also play role in cell wall development by pectic polysaccharide bridges. High calcium results in high pectate formation resulting in disease reduction due to cell wall integrity.
7. **Stability of fruits:** Ca acts as singling molecule [inositol triphosphate (IP3)] and secondary messenger (Ca-Calmodulin protein).
8. Blossoming (initiation of flower) is reduced by low Ca concentration in plants e.g. blossom end rot of tomato, bitter pit of apple and tip turning brown is due to Ca deficiency.
9. **Interaction with plant growth regulators (PGR):**
* Synergistic affect with cytokinins thus senescence is delayed.
* At high Auxin Concentration Catransport is increase.
* If ABA accumulation increases under stress conditions, Ca2+ in cytoplasm also increases.
1. **Ca in fruit ripening:** Caincreases ethylene concentration thus fruits ripening is enhanced.

**5. MAGNESIUM (Mg):**

* Mg is the 10th most abundant element that constitutes about 2% of earth crust.
* 3rd most plentiful element dissolved in sea water.
* The Mg concentration averages between 0.1 to 0.5% in plants.
* Component of several primary and secondary minerals in soil as insoluble forms.

**Mg in soil occurs in 3 forms:**

1. Non-exchangeable (fixed).
2. Exchangeable (Adsorbed to soil colloidal complex).
3. Soluble in soil solution.

**A) Uptake of Mg2+:**

* It is available and adsorbed in ionic form as divalent cation (Mg2+) by the crops from soil colloidal complex & soil solution.
* Its uptake occurs through facilitative diffusion by specific Mg channels and carriers.

**Interaction with other elements:**

* Mn2+, Ca2+, K+ and NH4+, Fe2+ and Al3+ compete with Mg2+.
* Highly available Mn2+ influences reduces Mg2+ uptake.
* Across plasma membrane, the Mg2+ transport occurs through Mg2+ channels whereas across tonoplast, the Zn and Mn antiport occurs along with proton.

**B) Redistribution:**

* Very mobile in plants.
* Redistribution occurs through phloem.
* Mg++ is stored in vacuole when it is in excess.
* Deficiency symptoms appear on older leaves.

**C) Metabolic roles / Functions:**

**1. Its biggest function is that it is an integral part of chlorophyll a, b and c**: 6-35% of Mg is bound to chloroplasts in plants. Mgis the Fe of the plans and it is at central position in plant’s chlorophyll as Fe is at central position in animal’s blood haemoglobin.

**2. Chloroplast thylakoid stacking is also stabilized by Mg2+:** So important for efficiency of photosynthesis.

**3. Rubisco activation:**

RUBISCO ACTIVATION

RUBISCO H+ RUBISCO RUBISCO RUBISCO

 CO2 H+ Mg+

LYSINE LYSINE LYSINE LYSINE

 H+ CO2 Mg+

NH3 NH2 NH NH

 H+

 COO- COO

 INACTIVE Mg2+

 ACTIVE

RUBISCO INACTIVATION

**4. Role in energy transfer:**

**i.** ATPase act on Mg-ATP complex rather than ATP alone during transfer of terminal phosphate of ATP. Energy transfer within the plant is by de-phosphorylation i.e.

ATP ADP AMP

**ii.** Mostly activates the enzymes used in energy transfer.

**iii.** It provides stability to ATP.

MgADP +Pi MgADP……Pi MgATP

**5. Role of nitrogenase ATP during BNF:** ATP acts as MgATP instead of ATP alone during nitrogenase action in BNF.

**6. Mgand nucleotides:**

It maintains DNA structure integrity by playing role twisting of DNA.

**7. Mg role in protein synthesis:**

* Mg++ is required for synthesis and maintenance of DNA and RNA & hence indirect role in protein synthesis.
* Helps in ribosome assembly and endoplasmic reticulum.
* Acts as co-factor of peptidases enzyme.

**8. Mgrole in Enzyme activation:** It is an activator of:

* Starch synthetase.
* RNA polymerase
* Glutathione synthase – an antioxidant.
* PEPcase & Rubisco.

**9. Mg role in Calvin cycle:**

* ATPs are required in Calvin cycle at least at four different steps and these are Mg-ATPs.
* Activator of Rubisco.
* Also activates fructose-1,6-bisphosphase.

**D) Deficiency symptoms of Mg:**

1. Pale green yellow older leaves by gradual chlorosis due to lack of chlorophyll.
2. Interveinal chlorosis.
3. In some crops, upward curling of leaves.
4. Weak stalk & long branched roots.
5. Pre-harvest leaf drop.
6. Mg toxicity does not occur if toxicity occurs the photosynthetic rate is reduced.

**6. SULPHUR (S):**

S is a secondary macro nutrient.

**A) Uptake:**

From soil: SO3-, SO42- (this form is usually up-taken)

From air: SO2, S2O3 (thiosulfate), H2S [though stomata]

Active uptake occurs through SO42-/ 2H+ symport just like NO3-.

**B) Assimilation / Metabolism (S-reduction):**

After uptake, reduction of S will take place within the plant just like N. The system that operates is called **Adenosine phosphosulphate system.**

“The system which works for Sulphur metabolism or reduction within the plant after its uptake is known as adenosine phosphosulphate system (APS)’’ (Figure 6)

Sulfate is loaded into xylem for translocation to shoots. In the chloroplast, its reduction takes place into organic acid such as cysteine & the excess sulfate is loaded into vacuole and successively transported to cytoplasm.

**Redistribution:**

It is immobile in plant therefore deficiency symptoms occur on younger parts. But recent study has shown that it is partially immobile. Its redistribution takes place to those plants which have highly protein **e.g.** Brassica oils are rich in sulphur compounds.

**Biological Roles:**

1. In *Allium cepa* (onion),alliins are produced which are rich in Sulphur.
2. S containing amino acids **e.g**. Cysteine (acts as precursor of other amino acids), cysteine and methionine (most abundant in plants).
3. Glutathione is S-containing antioxidant and precursor for phytochelatins (chelating compounds of plants).
4. Vitamin thiamin: act as Co-enzyme A (In respiration, Acetyl Co-enzyme A at first step of Kreb’s cycle).
5. Di-Sulphide bridges in proteins.
6. Part of Ureas Co-enzyme A.
7. Sulfoquinovosyl diacylglycerol is S-containing lipid.

**Deficiency symptoms:** Just like N, chlorosis and necrosis occur in younger leaves.