9 COPPER

9.1 Role in citrus production

Copper is involved as a catalyst in many enzymatic reactions including the reduction of molecular oxygen. Copper is also involved in the metabolism of protein and carbohydrates where it fulfils the roll of a co-factor in enzyme synthesis. Without enough copper certain enzymes will not be manufactured.

About 70% of the total copper in the plant is present in the chloroplast. It is part of the chloroplast protein and therefore involved in photochemical systems of photosynthesis.

Copper is only slightly mobile in the plant and the relocation rate from old to new tissue can cause a temporary deficiency in fast growing shoots and leaves. The copper status also influences the rate of relocation. The lower the Cu status the lower the relocation rate. Copper moves in the plant as an organic copper complex.

The absorption rate of copper depends on the concentration of copper in the soil, which in turn depends also on the pH.

Copper deficiency

Copper deficiency is quite common country wide and needs to be supplemented from time to time. The reduction in the application of copper compounds to control fungi, puts more emphasis on foliar sprays to maintain an adequate Cu status in the trees. Acute Cu deficiency results in gumming on shoots and in the albedo of the skin. However, gumming in and on shoots is also an indicator of other forms of stress. Another well know symptom which is very specific for copper deficiency, is the abnormal large and dark green leaves. The large leaves frequently appear on fast growing shoots where a single growth flush exceeds 40cm in length. Another specific symptom of a copper deficiency is shoots that are bending sideways in an S-shape

When a single growth flush exceeds 40cm the mass of copper required at the tip exceeds the supply rate from the roots. The leaves typically contain less than 3mg Cu per kg. However, six weeks later, the supply had caught up with the requirement and the concentration of copper in the leaves increase to optimal levels of >5 mg per kg. This phenomenon is frequently found in young trees.

In practise it is quite difficult to prove the importance of micro nutrient elements because of the many sources of contamination. However under controlled conditions, deficiencies of any of the micro nutrients have an impact on the number, quality and size of the fruit.

Excess copper

In the past copper was used extensively to control diseases and caused accumulation of copper in the soil. Copper toxicity can develop especially in neutral and acid soils. When the pH of the soil decreases for some or other reason, the toxicity will be aggravated. The most recognisable symptom of copper excess is damage to the roots. The roots show symptoms resembling aluminium toxicities where the roots form multiple branching which do not developed.

When products like copper oxychloride and copper hydroxide are applied as foliar sprays, the copper concentrations reported by leaf analysis might be excessively high. Most of the detected Cu is trapped in the waxy layer on the surface of the leaves. Washing according to the standard program will remove only some of the copper and the rest will be added to the copper in the leaf. The “outside” copper does not form part of the bio-active copper and high concentrations need not be harmful. When the waxy layer is removed the copper concentrations are within acceptable and safe levels.

Excessive soluble copper in the soil can be reduced by liming.

Sources of copper

Copper oxychloride is one of the oldest sources and is still an effective method to correct copper deficiencies by foliar sprays. It is also used in disease control and when it forms part of the pest control program, can be omitted in the nutritional program.

Copper hydroxide is used in the same manner and for the same purpose as -oxychloride with similar effects.

Other formulation of copper includes copper carbonate, copper sulphate and organic copper complexes.

Copper chelates can be used as foliar applications.

9.2 Fertilisation with copper

Soil applications
Any reaction that will acidify the soil will increase the concentration of soluble copper. For this reason, applications of copper to the soil are risky. Precipitated copper (at high pH levels) can accumulate and cause damage whenever the pH drops. That is why stem applications of copper oxychloride increase the concentration of Cu in the leaves of trees on acid soils but not on alkaline soils. Copper applied to the stems will wash down to the soil. If the pH is low enough is will dissolve and be absorbed by the trees. Stem application is only successful in raising the copper status if the soil has a pH of <6,00, contains less than 20% clay and less than 1% organic carbon. Organic materials fix Cu easily and in peat rich soils could induce a copper deficiency.

Stem applications are not recommended to supply nutrient Cu because of the risk of accumulation and subsequent toxicity when the pH drops.

Fertigation with microjets
Applications of copper products through microjets are not recommended for the same reasons as stem applications.

Fertigation with drippers
Low concentrations of soluble copper are required in the nutrient solution. Concentrations of >0,1 mg Cu per litre water can reduce root growth. Accumulation of copper on the perimeter of the wetted volume has the potential to intoxicate the roots when the pH drops. With drippers this is a real threat because the pH can drop substantially over a short period.

Sampling and analyses of the perimeter is therefore a good idea to monitor the development of copper accumulation. More than 30mg Cu/kg soil extracted with 3N acid is potentially dangerous. The copper content of soils should not exceed 2,00 mg/kg when extracted with 0,1N acid.

Damage or symptoms caused by excess Cu is seldom visible in the top growth because the damage is done to the roots.

Foliar sprays
As from 2006, the European Union limits the application of copper to 6000g Cu per ha per annum. At a rate of 2500 litres per ha and 150g copper oxychloride per 100 litre water, 1875g Cu per ha will be applied.

Foliar sprays containing > 200mg Cu per litre water are potentially dangerous and could be toxic, causing leaf burn and leaf drop. However on crops other than citrus, copper sulphate is successfully applied as a foliar spray at a rate of 100g per 100 litres water (250mg Cu per litre). A fairly safe application rate of copper sulphate is 90-100g $CuSO_4$ (25% Cu) per 100 litre (225 to 250mg Cu/litre). Copper Count N, a fungicide is applied safely at a rate of 500ml per 100 litre (400mg Cu/litre) water.

Cu, Zn and B in combination give better results than single sprays.

Any copper product can darken blemishes on the skin of fruit. The process that gives rise to the darkened blemish is the reaction of the cell sap with the copper to give a dark brown to black organic copper complex. When a small fruit is injured the blemish will be darkened by any copper product and grow larger with the fruit and will be more visible. When copper is sprayed on mature fruit, only sap from a fresh injury will react with the copper. At this stage an injury will be a culling factor with or without the copper. Copper will not react with old injuries. It needs the sap from the cells to form a dark complex. With the suspensions, copper oxychloride and copper hydroxide, much more copper in total is applied to the trees than with the soluble and chelated products. The potential danger of darkening blemishes is therefore much higher with the suspensions. With copper oxychloride 1875g and with copper sulphate 625g Cu per ha are applied.

For these reasons copper products should be applied prior to blossom even on mature fruit.

Copper sprays do not damage the fruit but will accentuate any fresh blemish.

Copper oxychloride contains 50% total copper of which < 2% is soluble in water. However, if the suspension is acidified by buffers or for instance zinc or magnesium nitrate, more copper will dissolve and toxicities are eminent. This will not happen to the soluble products like copper sulphate which is completely soluble and an increase in the concentration on acidification is not possible.