Incitec Pivot Fertilisers

AGRITOPIC

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MOLYBDENUM

1. INTRODUCTION

Of all the essential micronutrients or trace elements, molybdenum (Mo) is required in the smallest amount by plants. In Australia, molybdenum deficiency in pastures was first detected by CSIRO in South Australia in 1942. Since then, molybdenum fortified superphosphate has been applied to millions of hectares of legume pastures.

2. MOLYBDENUM IN THE SOIL

The parent rocks from which soils are formed are variable in their molybdenum content. Consequently, soils are equally variable in their molybdenum status which is highlighted by differences between granitic soils in the same district. Molybdenum is the least abundant of the trace elements in soils and very little is present in forms that are available to plants. It is fortunate that plants need such minute amounts of molybdenum.

The availability of molybdenum is influenced by soil pH. For example, acid soils with a $pH_{(water)}$ less than 6.0 and the presence of iron and aluminium oxides, the availability of molybdenum is greatly reduced. Most soil molybdenum is in mineral forms, but a small portion is held in organic matter.

Molybdate is quite strongly sorbed or attached to clay particles or organic matter in soils. Therefore, it not readily leached when compared to nitrate nitrogen or chloride.

3. MOLYBDENUM IN THE PLANT

3.1 Uptake and Functions

Plant uptake of molybdenum is as the molybdate (MoO_4^{2-}) ion. Uptake may be depressed by the presence of sulfate (SO_4^{2-}) ions, which are much the same size as molybdate ions and have the same charge.

Molybdenum is mobile in plants and can move quite freely from older to younger tissue as required. Many large seeded annual plants (especially legumes) contain sufficient molybdenum to satisfy crop requirements, if the seed came from plants that were adequately supplied with molybdenum.

Molybdenum is important in nitrogen metabolism and the protein synthesis. Two important processes in which it is involved are:

- The reduction of nitrate (NO_3^-) to nitrite (NO_2^-), the first step in the synthesis of amino acids and protein.

- In root nodules in legumes, *Rhizobium* bacteria require molybdenum to fix atmospheric or molecular nitrogen (N_2).

Symbiotic bacteria require about ten times more molybdenum for nitrogen fixation than does the host plant (for protein synthesis). Hence, molybdenum deficiency commonly occurs in legumes before it does in other plants when grown in the same soil.

Non-legume plants such as cruciferous crops (particularly cabbage and cauliflower) and cucurbits have a high molybdenum demand.

Grasses are relatively tolerant of low molybdenum and deficiency in cereals only occurs in extreme conditions.

3.2 Molybdenum Deficiency in Plants

Molybdenum deficiency is important and widespread on acid (low pH) soils. It occurs in pastures and crops grown in sandy soils in the south-west of Western Australia, parts of South Australia, Victoria and Tasmania, the coast and tablelands of New South Wales and coastal areas in Queensland. It commonly occurs in plants growing on sands and on podsolic soils derived from sedimentary rocks, in legume-based pastures and in several vegetable crops. Molybdenum responses have also been reported in cereals in the Riverina, South West Slopes and Tableland areas of New South Wales, and in Western Australia.

Deficiency symptoms vary between legume and non-legume plants:

In **legumes**, a lack of molybdenum prevents proper nodulation and fixation of molecular nitrogen (N_2) by symbiotic *Rhizobium* bacteria. Symptoms of nitrogen deficiency are displayed by the plant (e.g., sub-clover). These symptoms can be relieved by applying nitrogen fertiliser (although this would not normally be the recommended treatment). Growth is stunted and nodulation is poor. The root nodules are green or colourless, not the typical healthy pink colour.

In **non-legume** plants, symptoms specific to molybdenum deficiency occur. Plants suffer essentially from a shortage of protein which is due to the failure of nitrate (NO_3^-) conversion to amino acids. Nitrates can accumulate in the plant. Specific symptoms include:

- Marginal chlorosis and eventual scorching of leaves of broad-leaved plants.
- “Whip tail” of cauliflower.
- Spotting of citrus leaves.
- In wheat, leaves are pale in colour and the plant has reduced foliage with short internodes. Young plants may even show white, necrotic areas extending back along the leaves from the tips, reduced tillering and ultimately death. In southern Australia, molybdenum deficiency may contribute to haying-off in cereals where nitrogen is applied. Patches of withered plants which are unable to cope with high soil nitrate

are symptomatic of molybdenum deficiency on red-brown earths in New South Wales, Victoria and South Australia.

In contrast to legumes, the symptoms of molybdenum deficiency in non-legume crops cannot be corrected by applying nitrogen fertiliser. It can only be corrected by adding molybdenum. In fact, the addition of extra nitrogen may make the symptoms worse.

3.3 Molybdenum Toxicity in Plants

Soils such as highly organic/ peat soils generally have high plant available levels of molybdenum which can lead to excessive molybdenum levels in plants. However, plant performance remains unaffected by these levels that pose animal nutrition problems. Most plants have a high tolerance to excess molybdenum that there are few symptoms of toxicity.

4. CRITICAL VALUES

Plant-available molybdenum in soils and the quantity taken up by plants is small, which is much less than for other nutrients. Consequently, critical levels for soil and plant tissue analysis are lower than for other nutrients. This may require the use of more sophisticated laboratory methods or equipment capable of lower levels of detection.

Incitec Pivot Limited does not analyse soils for plant-available molybdenum which is in line with many soil analysis laboratories around the world, as reliability is poor. Molybdenum is more likely to be required on soils which are acid (pH_{water} less than 6.0) and high in iron or aluminium. Sandy soils, and those which are inherently infertile (low in phosphorus) in their natural state are typically low in molybdenum.

Plant tissue analysis is a much better guide but because of the added cost of analysis, molybdenum is not routinely analysed in samples submitted to the Incitec Pivot Laboratory. Molybdenum is an optional extra and can be added easily on request.

The molybdenum content of plant material is usually low and typically less than 1 mg/kg Mo in the dry matter. It is variable and in pasture can range from 0.01 to several hundred mg/kg Mo. A molybdenum content of less than 0.1 mg/kg Mo in dried plant tissue (usually leaves) indicates molybdenum is deficient.

Molybdenum toxicity in plants is rare. Compared to other micronutrients, molybdenum can be taken up in concentrations many times that regarded as necessary for optimal plant growth without toxic effects.

Livestock grazing pastures high in molybdenum may be affected when the pasture itself it not. Where molybdenum values are about 5 mg/kg Mo or higher on a dry weight basis in pasture and forage, copper deficiency may be induced in grazing animals. Copper supplementation of livestock may be necessary. Copper deficiency can occur where molybdenum concentrations in pasture are less then 5 mg/kg Mo if dietary sulfur intake is adequate to high. This is attributable to the formation of insoluble copper sulfide in the ruminant stomach.

In the absence of a molybdenum test, plant tissue nitrate and total nitrogen (N) figures can be used to indicate if a plant may be suffering from molybdenum deficiency. High nitrate figures, coupled with low total N figures indicate that the plant is taking up adequate nitrate but not converting it to protein. While there may be other explanations e.g., sulfur deficiency, molybdenum deficiency is often the cause.

5. MOLYBDENUM FERTILISERS

Molybdenum is required in minute amounts and typical application rates of 50 g/ha Mo in legume pastures can remain effective for several years. Consequently, it needs to be applied as a dust, powder or liquid if all plants in the field are to have access to molybdenum. Accurate and uniform coverage at such low rates is not possible, so molybdenum needs to be applied with a carrier e.g., another fertiliser, water or seed.

The three most commonly used molybdenum compounds are:

- Molybdenum trioxide (MoO_3) 66% Mo
- Ammonium molybdate $(NH_4)_6Mo_7O_{24}.4H_2O$ 54% Mo
- Sodium molybdate $Na_2MoO_4.2H_2O$ 39% Mo

Molybdenum trioxide is insoluble. Commercial formulations may contain less than 66% Mo.

Ammonium molybdate and sodium molybdate are soluble in water. Sodium molybdate is the more soluble of the two.

Superphosphate is the most commonly used fertiliser on legume pasture in Australia, so adding molybdenum to it is a convenient way to apply molybdenum.

Incitec Pivot Fertilisers adds molybdenum to single superphosphate (SuPerfect) in two ways.

i) SuPerfect Mo 0.4% Concentrate is manufactured at Portland in Victoria. This is used at Distribution Centres in southern Australia, where it is back-blended with ordinary SuPerfect, and used in SuPerfect Potash Blends, to give the desired molybdenum concentration. Commonly used molybdenum (Mo) concentrations are:

  - 0.015% Mo.
  - 0.025% Mo.
  - 0.05% Mo.

ii) At Newcastle, molybdenum is added to SuPerfect by spraying a solution of sodium molybdate over a moving belt of fertiliser.

Incitec Pivot Fertilisers does not add dry molybdenum trioxide, ammonium molybdate or sodium molybdate to blends, as excessive segregation of their fine particle size would occur.

In Queensland, the only molybdenum fortified product available is SuPerfect Mo 0.025%, which is stocked at Brisbane and Cairns for use on legume pasture.

6. APPLICATION METHODS

Soil application of molybdenum can be made by topdressing Mo fortified fertilisers, spray application through a boom spray or as a seed dressing when establishing or over-sowing pasture. It can also be applied as a foliar spray.

Foliar sprays should be used in horticultural crops. They provide much more uniform coverage than can be achieved by adding molybdenum to fertilisers that are applied dry to the soil.

Molybdenum Fortified Fertilisers

The use of molybdenum fortified SuPerfect and SuPerfect Potash blends offer a convenient way of applying phosphorus, sulfur, molybdenum (and potassium) simultaneously in the one operation to legume pasture. Molybdenum does not need to be annually applied. It is typically applied once every 3 – 4 years.

Molybdenum Solutions

Ammonium and sodium molybdate can be used in the preparation of fertiliser solutions which can be sprayed onto the soil or foliage. These options provide uniform coverage. Molybdenum can be sprayed onto the soil during seedbed preparation for a new pasture or during the fallow period in crops. Repeat applications are not required for several years.

Soil sprays are less suited to established pasture, as the spray is intercepted by the foliage. In turn, the molybdenum can be ingested by grazing animals and returned/deposited unevenly to the field in dung and urine or removed if cut for hay. Molybdenum ingested by livestock while grazing may also induce nutritional disorders.

If molybdenum is to be applied through a boom spray in established pasture, time this activity when the pasture is short e.g., after grazing or cutting for hay, so that the maximum amount of the spray reaches the soil. Grazing should be delayed for at least one month to allow sufficient rainfall and significant regrowth to occur.

Lower molybdenum application rates are required for foliar sprays than for soil application. Foliar sprays only need to be applied to crops that are susceptible to molybdenum deficiency. They are not required by all crops in the rotation.

Seed Dressings

The insoluble Molybdenum trioxide should be used as the molybdenum source in seed coatings. The soluble molybdenum compounds, ammonium molybdate and sodium molybdate are not recommended as they are likely to harm the *Rhizobium* bacteria in the inoculum.

For temperate legumes, molybdenum trioxide should be thoroughly mixed with the quantity of lime required for seed coating. This pre-mix is then applied to the seed after it has been treated with inoculant and adhesive.

Lime coatings of most tropical legumes is unnecessary and may in fact be harmful. Tropical strains of Rhizobium are adapted to acid soil conditions. In this situation, coating materials such as ground rock phosphate or bauxite may be used.

Molybdenum trioxide can be coated onto non-legume seeds if necessary. Achieving a uniform mix and distribution of the molybdenum trioxide can present problems when coating seeds. Use an appropriate sticker (methyl cellulose) and seek advice on the pelleting process.

7. SOIL APPLICATION RATES

7.1 Pasture

Recommended rates for soil application of molybdenum (Mo) in pasture vary and are typically in the range of 50 to 100 g/ha Mo every 3 to 4 years. The application rate may need to be reduced where copper deficiency occurs in livestock.

In Victoria, molybdenum is recommended at 50 to 60 g/ha Mo on pasture once every 8 to 10 years. More frequent applications are required (once every 5 to 6 years) in high rainfall areas (above 1 000 mm per annum) and on high phosphorus fixing soils e.g., red clay loams. On occasions, deficiency has been recorded 2 to 3 years after the previous application.

In white or sub clover pastures in New South Wales, SuPerfect Mo 0.025 % is commonly applied at 125 kg/ha every 3 to 4 years (as an alternative to an annual application of Super). This supplies around 30 g/ha Mo. While this may be adequate in some soils and pastures, it is thought that higher rates or more frequent applications of molybdenum may be required in some circumstances.

On tropical pastures, the general rate for molybdenum is 100 g/ha Mo every 3 to 4 years. This rate is increased to 200 g/ha Mo every 3 to 4 years on glycine pastures. The frequency of application is increased to every second year for basaltic soils on the wet tropical coast of North Queensland. In drier areas and on Siratro and the Stylosanthes species, the recommended rate of molybdenum is 50 g/ha Mo every 3 to 4 years.

The application of molybdenum at high rates and/or on a too frequent basis can result in elevated concentrations of molybdenum in pasture, which in turn can be detrimental to livestock by inducing copper deficiency. While such risks are slight, care must be exercised in the application of molybdenum, particularly on light-textured sandy soils where copper is most likely to be deficient. Where copper deficiency has been diagnosed in livestock or soil copper levels are marginal, it may be necessary to reduce molybdenum application rates.

The most common way in which molybdenum is applied to legume-based pasture is as molybdenum fortified superphosphate, which is used in place of ordinary superphosphate, usually once every three to four years. Common addition rates of molybdenum to superphosphate are 0.015%, 0.025% and 0.05% Mo.

The following table shows the amount of molybdenum applied at these concentrations at various product application rates.

Amount of molybdenum (g/ha Mo) applied as molybdenum-fortified SuPerfect at various product application rates.

Molybdenum Concentration	**Product Application Rate (kg/ha)**			
	125	**250**	**375**	**500**
0.015 % Mo	-	38	56	75
0.025% Mo	31	62	94	-
0.05% Mo	62	-	-	-

SuPerfect Mo 0.015% is used where SuPerfect is applied at high rates,

and SuPerfect Mo 0.05% where SuPerfect is applied at low rates.

7.2 Legume Grain Crops

Where grain and oilseed crops are grown in rotation with legume-based pastures, molybdenum is normally applied at the start of the pasture phase. Pasture legumes have a higher requirement for molybdenum and are more responsive than non-leguminous grain crops.

Where pastures do not feature in the crop rotation and legume grain crops are to be grown, a practical way to apply molybdenum is to spray sodium molybdate onto the soil e.g., in combination with a pre-emergence herbicide provided the tank-mix is compatibility.

A typical application rate for sodium molybdate is 150 g/ha, which supplies 55 to 60 g/ha Mo. This can provide protection against molybdenum deficiency for several seasons.

8. FOLIAR SPRAYS

8.1 Horticulture

Where molybdenum deficiency occurs in vegetable crops such as cauliflower and cucurbits, it is recommended that molybdenum be foliar applied. This can be easily done with early season crop protection sprays and provides much more uniform coverage than can be achieved by incorporating molybdenum additives into basal planting fertilisers.

Molybdenum is mobile in plants and is readily translocated from old to young plant parts during the growing season, so one or two early season sprays is usually all that is required. Two sprays are recommended in crops such as cauliflower, which is very susceptible to molybdenum deficiency.

Sodium molybdate is more commonly used in spray solutions than ammonium molybdate. Typical spray concentrations for sodium molybdate are 0.04 % w/v (40 g/100L) in seedbeds i.e., before transplanting and 0.05 – 0.1 % w/v (50 – 100 g/100 L) in the field early in the life of the crop. Check compatibility before mixing with crop protectants.

Avoid late season application i.e., approaching harvest. These are usually ineffective and may result in elevated concentrations of molybdenum in farm produce. Avoid over-application.

Add Urea (500 g/100 L), plus a wetting agent at label-recommended rates. Urea helps promote the uptake of foliar applied nutrients.

Sodium Molybdate Spray Rates in Vegetables.

Situation	Rate	Comments
Seedbed	40 g/100 L (0.04 % w/v)	Apply to seedlings before transplanting.
Field	50 - 100 g/100 L (0.1 % w/v)	Apply early, in sufficient water (30 - 100 L/ha) to wet the foliage. Use the lower concentration at the higher volume. One spray is usually sufficient, except where severe deficiencies have been recorded in susceptible crops such as brassicas and cucurbits where 2 sprays 3 weeks apart are recommended. In extreme cases, a third spray may be considered.

8.2 Compatibility in Solution

Sodium and ammonium molybdate are compatible with most other fertilisers and trace elements. Do not mix with calcium fertilisers e.g., calcium nitrate or calcium chloride as insoluble calcium molybdate will be precipitated.

When preparing fertiliser solutions, fill the tank with water to near capacity, leaving space for the added fertiliser which should then be added slowly while agitating. Do not pre-mix.

Fertiliser solutions should be prepared just prior to use and not allowed to stand for extended periods, minimising sediment formation and settling in tanks.

9. WITHHOLDING PERIOD BEFORE GRAZING

Excess molybdenum in young regrowth or that ingested as fertiliser dust with pasture can induce copper deficiency in livestock. This is most likely to occur on sandy soils low in copper.

Plant levels of molybdenum can be high for up to four weeks after application. It is advisable to spell treated paddocks during this period. If rain is not received or irrigation is not applied within a month, grazing may need to be deferred for longer.

10. MOLYBDENUM IN ANIMALS

10.1 Interactions

While molybdenum is important in animal nutrition (in various enzymes), the interactions with other elements such as copper, sulfur and iron are of importance. Copper and molybdenum are mutually antagonistic i.e., one restricts the plant uptake of the other at the plant roots.

Molybdenum itself is unlikely to be toxic to livestock but an oversupply of molybdenum can induce copper deficiency in animals, particularly on light textured soils. Sulfur consumed in protein or as sulfate can also induce copper deficiency. This is due to the formation of insoluble copper sulfide in the ruminant stomach. This can occur even where there is no shortage of copper in the pasture. Sulfur applied in pasture topdressing programs may contribute to copper deficiency in livestock. On the other hand, if the diet is low in sulfur and molybdenum, copper may accumulate in the liver and other tissues, resulting in copper toxicity.

10.2 Induced Copper Deficiency in Animals

The application of molybdenum at high rates and/or with a high frequency can result in elevated concentrations of molybdenum in pasture. This can be detrimental to livestock by inducing copper deficiency. While such risks are slight, care must be exercised in the application of molybdenum, particularly on light-textured sandy soils where copper is likely to be deficient.

Where copper deficiency has been diagnosed in livestock or soil copper levels are marginal, it may be necessary to adopt or consider the following management practices:

(i) Apply molybdenum at lower rates on a more frequent basis. Molybdenum rates (per application and cumulatively) may in fact need to be reduced, particularly on sandy soils. Soil fixation of molybdenum (and other nutrients) is generally lower on light-textured soils than on heavier-textured (clay) soils. The molybdenum rate should perhaps be halved, with no more than 30 g/ha Mo being applied in a single application.

(ii) Do not treat the whole property with molybdenum at the one time. Treat part of it each year and rotate stock between paddocks.

(iii) Spell freshly fertilised paddocks for a month. If no rain is received or irrigation is applied within this time, delay grazing until after either event occurs. This helps prevent ingestion of fertiliser dust containing molybdenum which may remain on pasture. Also, young regrowth which may contain elevated levels of molybdenum.

(iv) If copper deficiency is limiting pasture growth, it too should be included in the fertiliser program.

(v) Direct copper supplementation of animals may also be required.

10.3 Induced Copper Toxicity (Toxaemic Jaundice) in Animals

The application of molybdenum can help reduce the incidence of toxaemic jaundice in areas where soil copper status is high and where establishment of legume pastures provides a diet higher in copper than do native pastures. Use of molybdenum-fortified superphosphate every 3 to 4 years in top-dressing programs helps alleviate the problem.

Seek veterinary advice to confirm the diagnosis and consult local advisers on rates and frequency of application.