Review of the Role of Molybdenum in Soils and Plants

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Plants require small amounts of molybdenum for normal growth. The element is essential in nitrogen fixation by both symbiotic and free living soil organisms and is the metal constituent of nitrate reductase in higher plants. Intervenal chlorosis, leaf cupping, and leaf malformation are symptoms of molybdenum deficiency in plants. Data from several hundred soil analyses indicate an average molybdenum content of approximately 2 p.p.m. Molybdenum deficiency in crops results when available molybdenum supply is exhausted by plants or fixed in unavailable state at low soil pH, and is corrected by application of a few ounces of molybdenum salts to the acre. Crop production has been increased on many soils throughout the world by applications of small amounts of molybdenum salts. As only preliminary surveys to determine the extent of molybdenum-deficient soils have been conducted in most agricultural areas, the element will probably assume increasing importance when more thorough surveys are completed.

MOLYBDENUM occupies a unique place among the 15 chemical elements commonly accepted as essential to the normal metabolism of higher plants. It is the latest element to be added to the essential list, the one required in smallest quantity, and the heaviest of all elements needed by plants, being the only member of the fifth period of the periodic table in the group. Whether or not this latter point is of significance remains to be determined.

Ter Meulen (*29*) was among the first to investigate the molybdenum content of soils and plants. The results of his studies, reported in 1932, indicated that the element was a common constituent of both soils and plants. Fertile soils were found to contain from 0.1 to 0.3 p.p.m., while barren sands contained but 0.005 p.p.m. of the element. Plant tissues varied in content from a mere trace to 9.0 p.p.m. on a dry weight basis. Leguminous plants contained greater amounts of the element than nonlegumes. Only traces were detected in the tissues of fruit and vegetables and in the leaves and wood of trees.

In 1930, Bortels (*7*) reported that molybdenum was of biological importance in the fixation of atmospheric nitrogen by *Azotobacter chroococcum* and, 7 years later, he obtained what is believed to be the first instance of field response to applied molybdenum salts. Growth increases were reported in several leguminous crops as a result of small applications of molybdenum salts. He also noted a significant increase in the production of seed by molybdenum-treated alfalfa plants.

Neither the presence of an element in plant tissue nor growth response of plants to applied salts of the element establishes the element as being essential to plants. It must be demonstrated that the plant will not grow normally if the element in question is withheld. Because of the minute amount of molybdenum required by plants, and the difficulties involved in removing molybdenum impurities from other nutrient salts, the essential nature of the element was not established until the work of Arnon and Stout (*3*), published in 1939.

Molybdenum Requirements of Plants

There is considerable variation in the molybdenum requirements of the various species of plants. Anderson (*1*) found that clover in a grass-legume sod responded to applied molybdenum when its molybdenum content dropped to 0.3 p.p.m. The grass did not respond even though its molybdenum content was less than 0.1 p.p.m. Vanselow and Datta (*42*) reported that deficient lemon leaves contained 0.01 p.p.m. of molybdenum, while normal leaves contained 0.024 p.p.m. of the element. From these data it would appear that the molybdenum requirement of clover is 30 times that of the lemon. Other workers have reported deficiency levels for various plants falling between these two extremes.

Plants also vary with respect to their ability to extract molybdenum from the soil. Rencher (*37*) grew 33 species of plants on a Nixon sandy loam soil and found that their molybdenum contents varied from 0.3 to 4.8 p.p.m. Orchard grass contained the higher amount, while beets, onions, and spinach had the lowest levels. Legumes, cereals, and grasses had high molybdenum contents, weeds were intermediate, and vegetable crops had the lowest contents of all.

Warrington (*44*) has pointed out that the molybdenum requirement of plants is influenced by any factor that affects the rate of growth. Reducing the supply of nitrogen resulted in delaying the appearance of deficiency symptoms of lettuce grown at a deficient molybdenum level.

Role of Molybdenum in Plant Nutrition

The importance of molybdenum in the nitrogen metabolism of certain bacteria and fungi was demonstrated before the element's essentiality to higher plants was recognized. Nitrogen fixation by a group of nonsymbiotic bacteria was found to be dependent upon the presence of small amounts of molybdenum in the culture media (*7*). The molybdenum requirement of *Aspergillus niger* was significantly increased when the fungus was supplied nitrogen in the nitrate form, indicating a possible role of molybdenum in the reduction of nitrates within the plant (*39*). Later investigations confirmed these findings and extended them to higher plants.

Molybdenum is now known to be essential in the fixation of nitrogen by the symbiotic bacteria associated with leguminous plants (*14*, *24*). Nodules from alfalfa were found to contain from 5 to 15 times as much molybdenum as is present in other root tissues (*11*, *23*). It has also been demonstrated that the element is essential for the reduction of nitrates in nonleguminous plants (*22, 31, 45*).

The role of molybdenum in nitrate reduction has received considerable study (*11, 12, 34*) and the element has been identified by Nicholas and Nason as the metal constituent of nitrate reductase (*33*).

A significant decrease of ascorbic acid in molybdenum-deficient plants has been reported (*20*). Normal content of the vitamin was restored in from 3 to 5 days after plants were injected with molybdenum salts. These investigators suggested that molybdenum was essential in ascorbic acid synthesis, or that the high nitrate accumulation resulting from molybdenum deficiency caused the destruction of ascorbic acid.

A Polish worker has reported that applications of molybdenum salts caused plant immunity of certain virus diseases. An attempt at Rutgers to repeat this work failed to produce positive results (*37*).

Plant tolerance to molybdenum applications are high when compared to those for the other micronutrients. Hewitt (*19*) has pointed out that the range between deficiency and excess of molybdenum is 50 times that of the other essential trace elements. Millikan (*30*) concluded from his work that the regulation of the physiological availability of iron within the plant was an essential function of molybdenum. The value of molybdenum in alleviating plant injury caused by excesses of manganese, zinc, copper, boron, nickel, and cobalt was demonstrated in this and other investigations.

Symptoms of Molybdenum Deficiency in Plants

Plant symptoms that are now recognized as those of molybdenum deficiency were described and studied many years before the causal factor was known. In some instances specific symptoms were encountered frequently enough to receive names. "Whiptail" of cauliflower and "yellow spot" of citrus are two examples.

Hewitt and Jones (*21, 22*) have described the symptoms of molybdenum deficiency in some 21 crop plants. These symptoms are fairly uniform for most crops and include interveinal mottling and cupping of the older leaves, followed by the appearance of necrotic spots at leaf tips and margins (*3, 14, 40*).

With alfalfa and other legumes, the initial symptoms are similar to those of nitrogen starvation (*14*). Leaves become light green in color and growth is retarded. Eventually the older leaves become scorched and are shed prematurely.

New leaves are affected first in cauliflower and some other members of the Brassica (*22*). The young leaves show

Figure 1. Molybdenum-deficient cauliflower in a New Jersey field

an abnormal twisting and the leaf tissue develops in a narrow ragged pattern along the midrib. Seriously affected plants do not produce heads (Figure 1).

Molybdenum Content of Soils

Robinson and others (*38*) analyzed 400 samples in a systematic survey for total molybdenum content of agricultural soils in the United States. They found a remarkable constancy in the results, with 95% of the samples examined containing from 0.6 to 3.5 p.p.m. of molybdenum. They also cite Russian and Argentine work, where average molybdenum contents of 2.6 and 2.0 p.p.m. were found. The molybdenum content of 18 representative New Jersey soils fell within the range of 0.8 to 3.3 p.p.m. (*13*).

Soils having higher molybdenum contents have been reported from France (4.3 to 6.9 p.p.m.) (*6*) and from Hawaii (8.9 to 73.8 p.p.m.) (*18*).

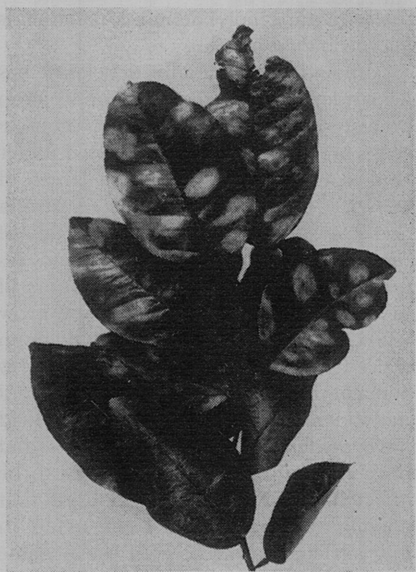
As with other plant nutrients, the total content of molybdenum in soil tells us little with respect to the amount of the element a soil will supply to plants. Working with California soils containing excessive amounts of available molybdenum, Barshad (*4*) found the element to be present in the soil mainly in three forms: soluble molybdate salts, combined with organic matter, and as an exchangeable molybdate anion held by soil colloids.

Factors Affecting Availability of Soil Molybdenum to Plants

Of the several factors that have been investigated with respect to their influence upon the availability of soil molybdenum to plants, soil pH has been found to be of greatest importance. Lewis (*27*) was among the first to recognize this relationship. While searching for ways to reduce the molybdenum content of the herbage in certain English pastures, he found that reducing the soil pH was most effective. This finding has been confirmed by numerous other investigators (*15, 17, 38*).

The importance of pH on molybdenum availability is further substantiated by the fact that molybdenum deficiency usually occurs on acid soils. It has been demonstrated that soil clays will absorb molybdate ions from acid solution and that these ions are released again to alkaline solutions (*4*).

Many investigators have shown that liming molybdenum-deficient soils will correct the deficiency. In Australia, New Zealand, and other areas where liming materials are expensive, application of from 2 to 3 ounces of sodium molybdate to the acre is almost as effective in increasing growth as an application of 2 tons of limestone, and more effective when coupled with a limestone dressing of only 224 pounds to the acre (*9*).



COURTESY FLORIDA CITRUS EXPERIMENT STATION

Figure 2. Molybdenum deficiency in Florida citrus

There are factors other than pH which apparently either affect the availability of soil molybdenum or influence plant requirement for the element. A well-limed soil may be depleted of its available molybdenum supply by crop removal or through losses by leaching. The presence of appreciable amounts of other heavy metals such as copper, manganese, nickel, and zinc in the soil solution increases plant requirement for molybdenum (*30*).

Applications of salts containing sulfate anions decrease the uptake of molybdenum from acid soils (*41*). This effect is thought to be due to the fact that the two anions, being similar in size, compete for absorption by plant roots. Sulfate does not affect molybdenum uptake on alkaline soils (*5*).

The effect of phosphate in increasing molybdenum uptake has been noted by several investigators (*2, 5, 41*).

Molybdenum Deficiency in Agricultural Soils

Although Bortels (*8*) reported response of legumes to molybdenum applications in the field in 1937, little attention was given this work until the discovery by Anderson (*1*) of molybdenum-deficient soils in Australia, some 5 years later. This finding aroused the interest of agricultural workers throughout the world, and within a few years, soils deficient in available molybdenum were found in Tasmania (*17*), France (*26*), New Zealand (*10*), England (*35*), Hawaii (*46*), Ireland (*32*), and the United States (*13, 40, 43*). A recent survey shows that molybdenum-deficient soils have been found in 11 states in this country and are suspected in four others (*36*). It is likely that such soils exist in every major agricultural area of the world and that all soils will eventually require molybdenum amendments for specific crops.

Although molybdenum deficiency has been identified in more than 40 crop plants, legumes, citrus, and vegetable crops are most commonly affected under field conditions. The largest areas of known deficient soils are in Australia and New Zealand, where hundreds of thousands of acres of pasture land require treatment with small amounts of molybdenum to enable legumes to grow (*25*). It is estimated that molybdenum is needed on from 25 to 50% of the citrus acreage in Florida. Other reports of molybdenum deficiency in the field have dealt with isolated situations and have not indicated large acreages to be affected. However, it is doubtful that adequate surveys have been made in any agricultural area, with the possible exception of Australia and New Zealand, to determine the extent of soils that will respond to applied molybdenum.

Effect of Molybdenum upon Livestock

Cattle and sheep grazing on pasture herbage of high molybdenum content are affected by a disease known as "teart" (*16*), particularly if the herbage is low in copper. Actually the high molybdenum intake induces copper deficiency in animals. The malady was described as early as 1910. Symptoms include diarrhea, graying of hair, and general debilitation. It has been reported from England, Ireland, Australia, California, and Florida. Complete and prompt recovery results from feeding affected animals small daily dosages of from 1 to 3 grams of copper sulfate (*28*).

COURTESY FLETCHER AVIATION CORP., ROSEMEAD, CALIF.

Figure 3. Airplane designed for aerial top-dressing of molybdenized superphosphate and other fertilizers in New Zealand

Ferguson (*16*) concluded that herbage containing less than 5 p.p.m. of molybdenum is safe for livestock feeding. Other investigators consider 10 p.p.m. to be the critical level, providing the copper content of the forage is normal.

Applying Molybdenum to Soils and Plants

Molybdenum salts (usually sodium molybdate dihydrate) are applied to deficient soils at rates of from 2 ounces to 4 pounds to the acre, the higher amounts being restricted to the manganiferous soils of the Hawaiian Islands. For forage crops in Australia, a rate of 2.5 ounces to the acre is used. Alfalfa, citrus, and vegetable crops require from a few ounces up to 1 pound of sodium molybdate to the acre.

Molybdenum salts are effective in correcting the deficiency when applied to either the soil or to the foilage of affected plants. Florida citrus growers find it economical to add molybdenum to their spray solutions, thereby avoiding an extra operation. In Australia and New Zealand, sodium molybdate is incorporated into superphosphate and applied to the soil with this material. Other methods of application include mixing with complete fertilizers, dissolving in water and spraying directly upon the soil, and seed treatment prior to planting of legumes.

Perennial crops may not require treatment more than once in from 2 to 6 years. From a limited amount of data it appears that annual crops will require more frequent treatment.

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SURFACTANTS IN FERTILIZERS

Effects of Surface Active Agents on Caking of Stored Mixed Fertilizer

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An investigation was undertaken to determine the effectiveness of surfactants in reducing caking tendency and curing time of mixed fertilizers. No significant reduction in caking tendency was caused by incorporating the surfactants in mixed fertilizer when the fertilizer was bagged within 1 week of manufacture and stored for over 3 weeks. The presence of an anionic surfactant did not reduce caking tendency when fertilizer was cured for 4 weeks prior to bagging. Any benefits from the use of surfactants in mixed fertilizer manufacture are dependent upon many factors, including manufacturing methods, processing equipment, and raw materials, some of which may already contain surfactants.

THE USE OF SURFACE ACTIVE AGENTS in the manufacture of mixed fertilizers has been extensively investigated by the fertilizer industry since the winter of 1952 (*1*). The initial laboratory and plant tests of the effects of surfactants in mixed fertilizers were reported in 1952 by Seymour, before the American Farm Research Association (*2*).

According to Seymour's report, the use of surfactants in fertilizer manufacture should lead to more rapid and complete ammoniation even at low moisture content because of higher initial reaction temperatures, hasten curing reactions, and ultimately improve physical condition of the fertilizer mixture by reducing its caking tendency.

This paper presents the results of a

Table I. 5-10-10 Fertilizer Formula Used in Surfactant Experiment

Material	Amount Used, Lb.
Superphosphate (19.6% available P_2O_5)	1028
Ammonium sulfate (20.5% nitrogen)	172
Potassium chloride (60.5% K_2O)	334
Vermiculite	20
Fertilizer borate	4
Sand (filler)	277
Ammoniating solution (40.3% N)	165
Surfactant	1
Total	2001

Figure 1. Design of Surfactant Experiment

(150-ton lots)