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RECENT WORK ON MOLYBDENUM AND SOME MICRO-NUTRIENT INTERACTIONS

By

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INTRODUCTION

Since 1941-42, when the effect of various incidental constituents of Chilean nitrate were being studied, micro-nutrient investigations in the Botany Department at Rothamsted have been largely concerned with molybdenum. This element is the most recent to be shown essential for higher plants, and not until 1939 did Arnon and Stout prove it essential for tomato. Piper (1940), Hoagland (1941) and Warington (1946) followed with oats, plum and lettuce respectively, and proof has now been extended to a number of other crops. It was from field experiments in Southern Australia and Tasmania, however, that the practical importance of the element first came to be appreciated, Anderson (1942) and Fricke (1943) demonstrating that failure of subterranean clover on certain ironstone soils was due to molybdenum deficiency. The discovery in New Zealand (Davies, 1945, and Mitchell, 1945) that whiptail disease of cauliflower was caused by molybdenum deficiency soon followed, confirmation of the field symptoms being obtained in sand culture by Hewitt and Jones (1947).

MOLYBDENUM DEFICIENCY

Among the points established during the course of the earlier field trials was the greater availability of molybdenum under alkaline conditions (Stephens and Oertel, 1943) a fact to which Fricke (1944) attributed the benefit he obtained from the addition of lime only on soils responding to molybdenum dressings. These results fall into lire with those of Ferguson, Lewis and Watson at Jealott's Hill (1940), who had {ound that liability to " teartness " in cattle, caused by excess molybdenum in the herbage of pastures in Somerset, was increased by a rise in soil pH.

The notable response of legumes to molybdenum and the observation that molybdenum-deficient clover was invariably pale, led to enquiries regarding the effect of this element on nitrogen fixation by the nodule organism. Bortels (1930) had already shown that molybdenum was needed for normal growth of Azotobacter in culture media lacking nitrogen, and Steinberg (1936) that it was required for nitrate reduction by Aspergillus. Jensen and Betty (1943) recorded increased nitrogen content in the roots of molybdenumtreated luceme and white clover, and high concentrations of the element in their nodules, while in 1946 Anderson and Thomas followed with proof that molybdenum was essential for symbiotic nitrogen fixation. Mulder (1948) confirmed Steinberg's results and showed in addition that molybdenum was required tor nitrate reduction in higher plants of a non-leguminous type and also for denitrification. Hewitt, Agarwala and Jones (1950) further found that ascorbic acid production was much diminished by a lack of molybdenum.

Since the beneficial effect of liming suggested that response to molybdenum might be influenced by the calcium supply or the pH of the substrate, and one function of the element at least seemed to be connected with nitrogen nutrition, the next series of solution cultures at Rothamsted were designed to study the efiect of these three factors (Warington, 1950). Here the amount of calcium supplied was found to have a marked effect on growth of both lettuce and red clover, more being required as acidity increased, but the level provided had no influence on the response of either plant to molybdenum. Variation in initial pH value $(4.2-8.2)$, with calcium at a uniform standard rate, also affected growth very noticeably, in spite of a rapid levelling up in the reaction of the solutions, but with the possible exception of the most alkaline medium, visual molybdenum deficiency symptoms were invariably obtained unless molybdenum was provided. Response to molybdenum occurred with both species at all levels of nitrogen tried, and in both inoculated and uninoculated clover, the number of nodules formed in the latter set being greater when molybdenum was lacking, as described by Anderson and Thomas (1946). Nitrate-nitrogen accumulated in the shoots of the molybdenum-deficient lettuce and clover shoots confirming the results of Mulder (1948) and Hewitt, Jones and Williams (1949). There was also some indication that lettuce was more liable to damage {rom excess molybdenum when the nitrate supply was raised, an effect in keeping with the results of subsequent pot experiments (Brenchley, 1948).

MOLYBDENUM EXCESS

(a) Microscopic effects

Prior to the discovery that molybdenum was essential in plant nutrition, Sheffield (1934), working at Rothamsted, had found that addition of salts of molybdic acid induced changes in cell contents of solanaceous plants, inclusion bodies similar to those resulting from virus infection being formed. The nature of the compound, however, was not determined. Later microchemical tests, carried out on tissue from potato tubers arld tomato shoots of plants grown with toxic quantities of molybdenum, showed that the characteristic golden colour developed under these conditions was caused by globular yellow bodies of a tannin-molybdenum complex (Warington, 1937). In the tomato, blue granular compounds of molybdenum with anthocyanin were also detected. A form of leaf mottling appeared on the leaves of tomatoes suffering from excess molybdenum, simulating virus symptoms, but subsequent inoculation tests showed that the plants were free from disease.

(b) Macroscopic efects

Most plants show high tolerance to molybdenum, and herbage containing amounts sufficient to cause " teart " disease of cattle remains undamaged itself. The species comprising the pastures, however, vary widely in their capacity to absorb the element, clovers and Yorkshire fog in particular showing much higher contents than the other grasses or weeds growing on the same soil

(Ferguson, Lewis and Watson, 1950). Tolerance to molybdenum also depends on the nature of the soil as well as the crop, Brenchley (1948) finding that dressings harmless to tomatoes grown on loam or allotment soil were very toxic on sandy Woburn soil. Further, Solanum nodiflorum was uninjured on allotment soil by a dressing which proved lethal to it on a cucumber soil rich in nitrogen, and while flax suffered considerable damage on this latter soil, tomato treated with the same rate of molvbdenum on it remained unharmed. Other soil properties as well as nitrogen content and pH value would, therefore, seem to be factors determining uptake of molybdenum. HCl-soluble iron may also be of importance, for of thirteen Australian soils tested, Williams and Moore (1952) found least molybdenum absorbed by oats when the soil was rich in iron the differences reaching significance independent of pH value.

INTERACTIoNS BETWEEN MoLYBDENUM AND oTHER ELEMENTS

It is generally recognized that interaction between the various major and minor elements are of paramount importance, and much recent work with molybdenum has dealt with this aspect. From pot and field experiments (1948, 1949a), Millikan concluded that manganese and molybdenum were antagonistic, and showed later (1951) that addition of high concentrations of molybdenum to flax grown witl excess manganese reduced the manganese content and altered its distribution, while Anderson and Spencer (1950) found that manganese accentuated molybdenum deficiency in clover and lowered its uptake.

Earlier Millikan (1947) had shown that molybdenum, if presented in sufficiently high concentrations, could counteract chlorosis induced in flax by a number of heavy metals given in toxic amounts. Hewitt (1949), on the other hand, found molybdenum enhanced the chlorotic symptoms of metal excess in sugar beet. He considered that some aspect of nitrogen nutrition was probably involved whichever way the interaction worked, and Bennett (1945) had already put forward the view that chlorosis was a disturbance of nitrogen as well as of iron metabolism.

The possibility that vanadium might give similar results to molybdenum seemed worth investigating, for Horner et al. (1942) had shown that the two elements could replace each other in Azotobacter nutrition, though Vanselow and Datta (1949) found no evidence for this in citrus. Comparison was, therefore, made of the effects of high concentrations of molybdenum or vanadium in the presence of manganese excess (Warington, l95I). Flax and soybean were grown in nutrient solutions containing manganese at toxic (10-25 p.p.m.) and non-toxic (1 p.p.m.) levels, each combined with a range of concentrations of molybdenum or vanadium. Relatively high rates were required before any interaction with manganese was obtained, and the effects of the two elements were contrasting. Molybdenum (20 p-p.m. and to a less extent l0 p.p.m.) intensifled the chlorosis induced by high mangarese as Hewitt (1949) found with sugar beet, but both rates of molybdenum proved harmless in the presence of only I p.p.m. manganese.

Vanadium (equivalent to 1.0 or 5 or l0 p.p.m. Mo), on the other hand, counteracted some of the symptoms of manganese toxicity, suppressing at least temporarily the apical chlorosis of both crops and reducing the leaf curling in soybean, though eventually the higher levels of vanadium induced apical chlorosis on their own account. Vanadium equivalent to only 0.1 p.p.m. Mo, however, failed to exert any noticeable effect at all. Thus, under this set of experimental conditions, high vanadium gave results similar to those obtained by Millikan for high molybdenum (1947) and later by him for aluminium also $(1949b)$.

INTERACTIONS BETWEEN VARIOUS METALS AND IRON

(a) Visual effects

That metal toxicity causes disturbances in iron nutrition is no new discovery, for in 1919 Johnson cured pineapples suffering from excess manganese by spraying with iron. Similar antidoting effects of iron on other metals in excess have been found by various authors using either additions of iron to the nutrient medium or external applications to the leaves. Counteraction of metal toxicity by elements other than iron has, however, only recently been claimed. Since vanadium was one of the elements possessing this property, information regarding its efiect on plants sufiering from- a direct (as distinct from metal-induced) shortage of iron seemed desirable. Ferric citrate was used as a source of iron, the standard amount selected as control depending on the crop grown. Within the concentrations tried (0.05-5 p.p.m. V) vanadium failed to relieve iron-deficiency chlorosis in soybean or flax, 2.5 or 5 p.p.m. \- in fact proving more toxic if the iron content of the solution was reduced to one-half or one-third of the control (10 p.p.m. Fe) (Warington, 1954). Increasing the iron to 20 p.p.m., on the other hand, almost removed the symptoms of vanadium excess in peas in both root and shoot, and similar, though less-pronounced, effects were obtained with flax. Injury from manganese and molybdenum excess was similarly reduced by an increase in the iron provided, but if two or more of these elements were presented together the same quantity of iron was less eficient in counteracting their toxicity. This suggested that their effects towards iron were additive. The method of supplying the iron was important, for the same total amount given gradually proved less capable of offsetting the damage from vanadium and molybdenum than when supplied in a single initial dose. This, however, did not hold for manganese. Identical changes in the level of iron supplied had little or no effect in the presence of low concentrations of these elements, though there were indications, confirmed later, that there was a limit to the amount of iron that could be given without causing injury. Damage to citrus from excess iron has been described by Smith and Specht (1953), who, moreover, found it could be offset by application of high copper, zinc or manganese. A similar compensating efiect of high molybdenum on excess iron has been found in flax (Warington, unpublished).

(b) Effects on plant composition

Attempts to interpret these interactions between manganese, molybdenum, vanadium and iron necessarily include a study of the changes in plant content of the elements concerned, though visual

differences may occur without any corresponding change in plant composition. Chlorosis, for example, is not always accompanied by a reduction in iron content of the shoot. McGeorge (1949) found a correlation between chlorosis and the soluble fraction of iron only, though Smith, Reuter and Specht (1950) showed that it held for total iron if the material was washed with a detergent. Absence of any correlation was interpreted by Millikan (1949a) as indicating a lack of utilization of iron within the plant rather than to a reduction in uptake. Analyses of soybean shoots (Warington, 1954) showed that the total iron content was scarcely affected by the quantity of iron supplied (5-20 p.p.m. Fe) provided manganese, molybdenum and vanadium were present at a low rate, but it was much reduced bv high concentrations of all three elements. On the other hand, there was little change in the iron found in the shoots of flax grown with high vanadium. Berger and Gerlofi (1947) and Sideris (1950) also record a drop in iron content of shoots of potato and pineapple respectively on the addition of high manganese. Sideris attributed this to interference with translocation and immobilization of iron in the root, as there was no indication of external precipitation, a view supported by Epstein and Stout's results (1951). Smith and Specht (1953) have described similar inhibitory effects on movement of iron within the plant following the addition of high copper or zinc.

The manganese and vanadium contents of the soybean shoots, already referred to, fell sharply as the iron supply was increased, in agreement with the results of Twyman (1951) and Morris and Pierre (1947) for manganese. Reduction in molybdenum content, however, was less clearly shown, in spite of the fact that visual toxic symptoms had been counteracted by the additional iron. The method whereby the iron offsets metal toxicity thus appears at first sight to be a reduction in the amount of injurious metal in the shoot. This does not explain the recovery of colour following the application of iron paints or sprays, and it seems more likely that some interaction between the heavy metal and iron takes place in the root, resulting in changes in translocation of both iron and metal. Further analytical work will be needed before any definite conclusions can be drawn.

OTHER FACTORS AFFECTING METAL TOXICITY

The degree of injury caused by molybdenum, manganese and other elements also depends on the nature of the nitrogen supply. Millikan (1950) found manganese more toxic with nitrogen supplied as nitrate than as ammonia; the reverse was true for molybdenum. Further, ammonium molybdate proved more toxic than the sodium salt in the presence of nitrate, though both were equally damaging if the nitrogen was given in the form of ammonia or urea. Response to iron was also influenced by the form in which the molybdenum was provided, ammonium molybdate proving more efficient in overcoming iron deficiency than the sodium salt (Millikan, 1950) overcoming from deficiency than the soutunt saft (Millixan, 1990)
Warington, unpublished). That the incidence of chorosis is affected by many other factors such as potash supply, light, temperature, age of plant, etc., only adds to the complexity of the problem.

CONCLUSIONS

The ultimate aim of all investigations with micro-nutrients is to determine their function in plant nutrition. Information on this point is at present scanty. Approached from the point of view of deficiency, manganese, molybdenum, copper and zinc each appear to be associated with specific plant processes. If given in excess, these four elements may either cause disturbances in iron nutrition similar to each other and to those induced by metals not yet considered essential, (e.9., varadium, nickel and cobalt) or exhibit antagonistic properties according to circumstances. The health of the plant seems to depend as much on a correct balance between the nutritive elements as on the presence of each, and precise statements regarding demand or tolerance for any particular micro-nutrient are, in consequence, of limited value only. Much further work will be needed before these metal interrelationships are fully understood.

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