MOLYBDENUM RESEARCH IN NEW ZEALAND

By E. B. DAVIES, Senior Chemist, Rukuhia Soil Research Station, Hamilton.

Molybdenum is a silvery-white metal falling in the same group as chromium and tungsten. Molybdenite, the only ore of commercial importance, is world-wide in distribution, but the chief sources are from Colorado and New Mexico, U.S.A., and Chile. A very small amount was mined at Mt. Radiant, Karamea, about 1917. In 1941 world production was 17,000 tons a year, of which 15,000 tons came from U.S.A. Present annual production approaches 20,000' tons. The main consumption is in heat-resistant steel alloys, such as are used in high-speed cutting tools, rifle barrels, and so on. Molybdenum is used for the filament supports in electric light bulbs on account of its high melting point (2550 degrees C.). The metal is in short supply at present and rationed.

A connection with biological processes was first shown by H. Bortels in 1930, who found that molybdenum was essential for the fixation of nitrogen by the bacterium *Azotobacter* chroococcum. It later became evident that the molybdenum had a further function, Steinberg (1937) finding that it was necessary to the mould *Aspergillus niger* for utilisation of nitrate nitrogen. Ter Meulen in 1932 found that a fertile soil contained more molybdenum than moor or a sandy waste. (The biological effects of molybdenum will be discussed more fully by Mr Adams in the fourth paper of this symposium). After the early work with micro-organisms the essentiality of molybdenum for the healthy growth of a variety of higher plants was demonstrated, largely by use of water cultures. In 1942 in investigating a response of subterranean clover to wood ashes in South Australia, A. J. Anderson found that the critical element was molybdenum, and demonstrated marked increases in yield brought. about by additions of sodium molybdate.

EARLY WORK IN NEW ZEALAND

The first evidence of molybdenum deficiency in New Zealand was obtained as the outcome of intensive investigation of the disease "whiptail" of cauliflowers. This malformation had been reported in other parts of the world as controllable by heavy liming. Eventually Davies, in 1944, working on an affected Brooklyn soil in garden plots and in the glasshouse, was able to demonstrate characteristic symptoms in all treatments lacking the element molybdenum (E. B. Davies, 1945). The symptoms were very similar to those of molybdenum deficiency in tomatoes as described by Arnon and Stout, in California, and were curable in a matter of days by molybdate applications. Treated plants in the garden, though showing remarkable growth superiority, nevertheless developed whiptail-like symptoms. K. J. Mitchell (1945), however, working in a Services Vegetable Production area at Papatoetoe, was successful in controlling whiptail with applications of ammonium molybdate as low as llb. per acre.

In view of the response of clovers, a much more important crop, in South Australia; attention here was turned to permanent pasture. Small observational plots were, laid down on a variety of soils in the Waikato, but without any visible effect. A replicated yield trial of Davies and Arnold on an ironstone soil in North Auckland, Okaihau gravelly clay loam, was more successful. The trial was laid down on October 17, 1945, on existing pasture and speedily showed a visible response, all molybdate-treated plots being obvious a month after the application. Pasture was denser, greener, and contained more suckling clover *(Trifolium dubium)*. The pasture was cut on 22nd November, 1945. Yields of dry, matter and molybdenum contents are shown in the table.

Treatment	Yield D.M. grams/plot	Mo content p.p.m.
1. Control	460	0.7
2. Sodium molybdate 2½lb. per acre	550	13.6
3. Carbonate of lime 2 tons per acre	506	1.1
4. Sodium molybdate and carbonate of lime	615	14.1

The plots were small (5 links square) and one control gave a lush growth of grass, obviously the result of unsuspected urine contamination. The yield concerned was therefore discarded and the "missing plot technique" applied for statistical analysis.

The effect of molybdenum was significant at the 1 per cent level and of the order of 20 per cent increase in yield. The effect of carbonate of lime was significant at the 5 -per cent level. Observational trials subsequently laid down on the time soil type by E. H. Arnold have also, shown molybdenum responses.

An interesting feature of the experiment was that the soil was higher in total molybdenum content than any other New Zealand soil at' that time examined, exceeding 5 parts per million. It was evident that the matter of availability was involved and work was put in hand toward finding a suitable test for available molybdenum. For trial purposes six soils of known molybdenum response supplied by Dr. Piper of the 'Waite Institute, Adelaide, were used. This work has 'been completed and the selected method applied extensively, particularly in the last 2 years (Grigg 1952).

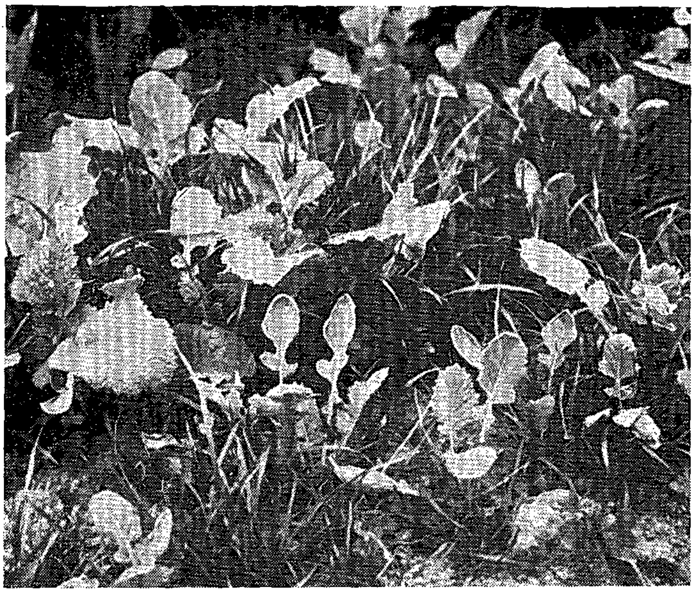
A response to molybdenum, particularly in conjunction with boron, on Te Kopuru sand, another North Auckland soil, was demonstrated- in pot experiments by officers of the Soil Bureau in 1946. The Department of Agriculture followed up the result with field trials, but without success, climatic and other conditions proving unfavourable.

OTAGO. AND SOUTHLAND INVESTIGATIONS

In 1946 W. R. Lobb laid down a pasture trial with molybdenum on the high tussock country north of Outram, but with negative results. Small "sighter" trials in the same area with cauliflowers likewise gave no response. In Outram, however, cauliflowers did 'respond.

There were a number of indications that molybdenum deficiency might be a limiting 'factor in the South.

1. The heavy rates of liming customary in Otago and Southland, far above requirement as judged by soil analyses, could become explicable if needed to make soil molybdenum more available, (as happened in the early control of whiptail).
2. An extremely low-grade Southland limestone reputed locally to have special merit was found on analysis to have a molybdenum content of 5.54 p.p.m. as 'against 0.11 to 0.68 p.p.m. in five other. Southland stones examined. The amount would correspond to 0.2oz. Mo per ton.



A mixed crop of rape and soft turnips growing on molybdenum-deficient soil. The rape is showing typical symptoms of molybdenum deficiency in its stunted growth and deeply-cupped leaves.

This photograph was taken in the same paddock as the preceding one, but the crop here has received a dressing of sodium molybdate.

3. Certain soils were analysed and the available molybdenum found to be comparable with that in molybdenum deficient Australian soils.

4. W. R. Lobb pointed out that Mr J. 0. H. Tripp in Outram had obtained responses in experimental strips treated with 2cwt. and 4cwt. of basic slag, but none from even 1 ton of superphosphate. Slag contains traces of molybdenum as well as vanadium, manganese and tungsten above the level found in superphosphate. Later analyses showed the content in various samples to range from 7.5 to 9.2 p.p.m. No sample of the actual slag involved was available.

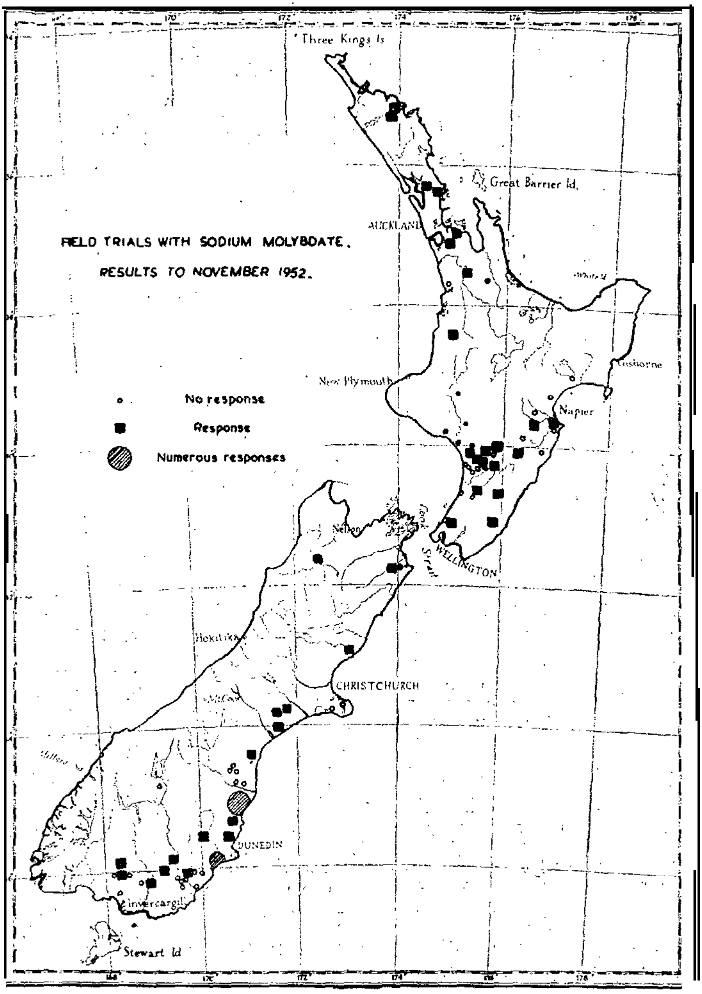
A number of observational molybdenum trials on existing pasture were therefore proposed and laid down by the field staff of the Extension Division:-Winton (5/12/49), Waimumu (16/12/49), Stoney Creek Otapiri, Benmore, South Hill-end (13/4/50), Outram (24/4/50), and Pukerau (13/12/50). Many of these were on heavily limed areas and such, it was found later, do not respond to molybdenum even though the soil test is low. A replicated yield trial was planned. for an unlimed area in South Hill-end and eventually laid down on 13th August, 1950. Responses were slow in forthcoming. In September 1950 the Director of the Extension Division in consultation with the Rukuhia Soil Research Station recommended inclusion of molybdenum treatments in a rates of liming trial proposed by Mr G. A. Holmes at Invermay. The suggestion was carried out with results which Mr Holmes will present. Later the South Hill-end trial also gave responses as did that on Mr Tripp's farm at Outram. 'This latter was followed up by a replicated yield trial, giving highly significant responses.

TABLE 1.

MOLYBDENUM TRIAL—OUTRAM

Relative Yields Dry Matter (Superphosphate = 100)

cut	Superphosphate 3cwt.	Superphosphate and sodium Molybdate ½oz./acre	Superphosphate and sodium Molybdate 2½oz./acre	Slag 3cwt.
10/12/51 . .	100	161	175	121
14/1/52 . .	100	1'76	145	99.5
10/3/52 . .	100	106	92	86
Totals . .	100	145	129	98



OTHER MOLYBDENUM RESPONSIVE AREAS

Meanwhile, in the autumn of 1948, at the instance of G. H. Harris, who had been impressed by molybdenum responses in Australia, a pilot trial had been conducted at Motunau, North Canterbury, by the Soil Conservator, Christchurch. Superphosphate with 2 tons of lime and superphosphate with 7ozs .of sodium molybdate gave equally marked increases above superphosphate alone. A further and very striking response -was obtained on a' Departmental trial at Te Hana, North Auckland, laid down in August 1950. It became evident that molybdenum deficency was likely to be widespread and *a* network of simple observational trials was laid down by field officers of the Extension Division. At the Director's instance, special attention was paid to the areas bordering the Taieri Plains.. Soil samples from all sites were examined for available molybdenum. It is early yet to survey results, but a general idea of the spread of responses is given in, the' map. Negative results indicated should be regarded as provisional. Many are on soils low in molybdenum, but with high pH figures.

Some 625 soil samples for molybdenum determination have been received from field officers, 5'7 per cent being found to be low in available molybdenum (0.12 p.p.m. MO or under). .The samples were from areas suspected of molybdenum deficiency and are far from a random selection. Several Instructorates are represented by a very few samples or even unrepresented, and- no broad statement of the extent of likely deficiencies is possible. Highly leached soils are low in molybdenum, notably those of the West Coast; samples from Central Otago, a region of sparse rainfall, have on the whole been well provided. Taranaki is a high rainfall area, yet has shown little evidence of molybdenum deficiency. The reason probably lies in the andesitic ash from which much of the soil is derived. Considerable numbers of low molybdenum samples have been received from Warkworth, Auckland, Palmerston North, Blenheim, Greymouth, Ashburton, Waimate, Oamaru, Dunedin, Balclutha and Invercargill.

FACTORS CONCERNED IN MOLYBDENUM RESPONSE

1. In the first observational, trial on Mr Tripp's farm no response to molybdenum was forthcoming until the plot. had been treated with super-phosphate. Neither was there any response to superphosphate without molybdenum. It has been shown (P. R. Stout et al, 1951) that phosphate greatly increases uptake of molybdenum and also that a phosphate deficiency hinders the transfer of molybdenum. from the root zone to the foliage. It is likely that phosphate

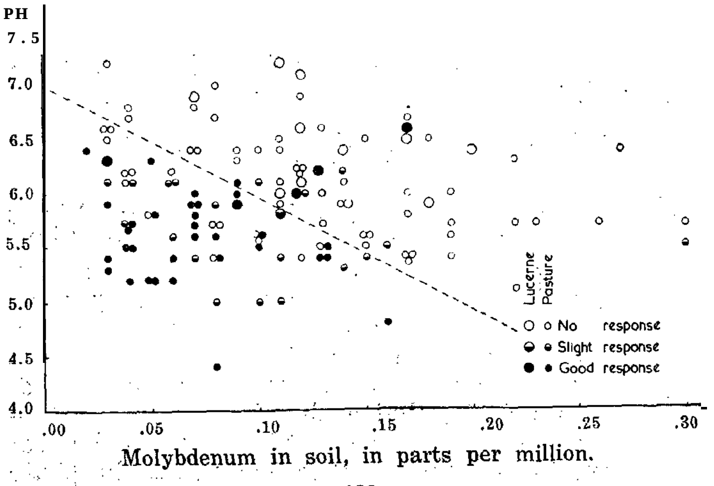
deficiencies must be made good if any benefit is to derive from.molybdenum application.

2. Though there have been indications of a grazing response before development of the clover constituent of the sward, the most striking evidence of the effect of molybdenum has been in the dark colour and vigorous growth of the legumes. The main effect on grasses is through the nitrogen build-up. It follows that for a rapid benefit clovers must be present. Even when stunted clovers are present effects in several trials have not been observed for 15 to 20 months. The delay may be due to the slow development of the necessary population of nodule bacteria in the soil and clover roots.

3. Calcium as well as molybdenum is essential for nitrogen fixation. Highly leached soils need lime as well as molybdenum.

4. In a comparison of field observations and laboratory results a relationship between soil acidity, molybdenum supply, and response has become evident. At high pH levels nearing neutrality a low molybdenum figure seems adequate. In strongly acid soils a higher level is demanded.

MOLYBDENUM RESPONSE AS A FUNCTION OF SOIL MOLYBDENUM AND SOIL ACIDITY.



It is suggested that the available molybdenum figure determined is really a 'measure 'of the potentially available store, the rate of release depending on the soil reaction. Rapid release from a small reserve is equivalent to slow release from a greater amount. The relationship is evident from the diagram.

The three marked responses above the response line are of lucerne, which may demand more molybdenum than clover.

Rapid release from a small reserve suggests the possibility of an absolute deficiency developing.' The total molybdenum, content of most soils is, however, far above the amount determined in the soil test. The rate at which it may become accessible is not known, though liming. again may have an effect.

Insoluble molybdenum	→	potentially available molybdenum	pH →	available molybdenum

RETENTION OF MOLYBDATE APPLICATIONS

Added molybdate seems to be held in the soil in much the same way as phosphate, but so far there is little evidence of repeated applications proving necessary. In the Invermay trial the "available" molybdenum in successive ½in. soil samplings taken 9 months after laying down was determined in the control, heavily limed, and molybdate-treated plots.

Results showed little downward movement of molybdenum, the greater amount being retained in the surface inch. (Grigg, 1952).

RESPONSES OF NON-LEGUMES

In legumes and non-legumes molybdenum is essential for the reduction of nitrate as a step toward protein synthesis. In the former case the amount required is much less than that needed for nitrogen fixation by the nodule bacteria. In cauliflowers "whiptail" soils often have an available molybdenum content far above the clover response level. A condition very similar. to whiptail is brought about by high levels of active manganese in the soil, such as are associated with highly acid conditions. In linen flax a manganese molybdenum antagonism has been shown to operate, the manganese inhibiting uptake of molybdenum (Millikan, 1950). This action of manganese, which can be countered by liming, may supply the reason for the relatively large applications of molybdenum seemingly found necessary in whiptail control in some cases. Other brassica crops, for example rape, show molybdenum deficiency symptoms similar to cauliflowers. Young plants are stunted, the leaves light green and mottled between the veins and the leaf edges frequently bent in or cupped as in the illustration. In older plants the leaf blades assume a ragged distorted appearance, sometimes with a pronounced quilting effect.

I cannot too strongly emphasise that molybdenum is not a magic cure-all that obviates the need for other essential, plant nutrients or for liming. In molybdenum-deficient areas it can remove the need for heavy liming. The element is in short supply and should be used only where field trials or soil analyses indicate a response is likely. Moreover, and this point has been made repeatedly in the Journal of Agriculture (Sept. 1950, p 268; Oct. 1951, p 247-250) and elsewhere, unnecessarily high applications can lead to stock trouble. The maximum recommended, rate is 2½ozs sodium molybdate per acre, and this should not be exceeded nor need it be repeated for some years. This is particularly so on peat, where Cunningham and Hogan (1949) have shown molybdate applications to produce a dangerously high molybdenum level in pasture, particularly when associated with copper deficiency. Aerial topdressing with. molybdenised superphosphate should be a real aid in development of molybdenum-deficient hill country where heavy liming is not practicable.

Acknowledgements:

Stationed in Hamilton, remote from affected areas we are dependent for any field trial work on officers. of the Extension Division. I would like to thank those who have assisted in this respect. In particular I would commend the good work of Mr Stockdill, who is not represented in this symposium. I should also like to mention Mr J. L. Grigg on the Rukuhia Soil. Research Station staff. who has carried out all the. Extension Division molybdenum analyses, developed the soil test and devised the rapid analytical procedure.

Collaboration from the Soil Bureau in the provision of soil type samples and in other ways is gratefully acknowledged.

The prompt results. achieved by Mr Holmes and staff in the present investigation make clear the advantages of a research station on the spot with staff free to devote time and attention to detail in trial management.

REFERENCES

Anderson, A. J. (1942) J. Austr. Inst. Agr. Sci. 8, 73.

Arnon, D. I. and Stout, P. R. (1939) Plant Phys. 14, 599-602.

Bortels, H. (1930) C.A. 26, 2481, 1932.

Cunningham, I. J. and Hogan, K. G. (1949) N.Z.J. Sci. Tech. 31a, (1), 39-41

Davies; E. B. (1945) Nature, 156, 392.

Grigg, J. L. (1952) In press.

ter Meulen, H. (1932) Nature,. 130, 966;

Millikan, C. R. (1950) Austr. J. Sci.. Res. 3, 450-473.

Mitchell, K. J. (1945) N.Z.J. Sci. Tech. 27, 285.

Steinberg, R. A. (1937) J. Agric. Res. 55, 891.

Stout, P. R., Meagher,. W. R., Pearson, G.. A., and Johnson,, C. M. (1951) Plant and Soil 3, 51-86.