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FACTORS AFFECTING SOIL MOLYBDENUM AVAILABILITY AND MOLYBDENUM FERTILIZATION OF TROPICAL PASTURE LEGUMES

A THESIS SUBMITTED TO THE GRADUATE DIVISION OF THE UNIVERSITY OF HAWAII IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

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by

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Introduction

Nitrogen occupies a unique place in man's life. Although the element is abundant and essential for all living things, supplies of the forms available to plants are inadequate in many parts of the world. Where such inadequacies exist, life has become unbearable because of low crop production and poor harvest. To compensate for the limited supply of nitrogen in soils, man has resorted to chemical N_2 fixation amid the dwindling natural gas and oil resources. For this reason, enhancement of our knowledge of biological N_2 fixation and the processes involved would undoubtedly play an important role in the cropping patterns of the tropics.

In many areas in the tropics and most efficient and economical way of producing good pastures has been the growing of a mixture of grass and legume species. The legume component of the mixture provides nitrogen to the soil-plant system as well as increasing the much-desired protein content of the herbage. The direct transfer of fixed nigrogen by the legumes to the associated grass species, varies considerably. Whitney (1970) reported 53 per cent transfer in a Digitaria decumbens - Desmodium intortum mixture, and 43 per cent in a Paspalum plicatulum - Phaseolus atropurpureus mixture (Jones et al., 1967).

The ability of a legume to nodulate and consequently fix nitrogen relies on many factors. With the unraveling of the structure of the nitrogen-fixing enzyme nitrogenase and nitrate reductase, molybdenum and lime have been found to be increasingly indispensable in nitrogen metabolism of plants. Anderson (1942) observed increased symbiotic nitrogen

fixation due to the lime/Mo interaction in nodulated clover. In these soils, low solubility of iron and aluminum molybdates caused deficiency of Mo for crops. As a result of liming, hydroxyl ion activity increases thereby increasing the ion exchange activity between hydroxyl ions and molybdate ions. The molybdate released into soil solution can readily be utilized by the legume rhizobia and plants for nitrogen metabolism.

Increasing research work in the last two decades has transformed Mo into a fertilizer of great significance. In certain places, dressings of as little as 1 or 2 ounces of Mo per acre have brought about substantial increases in pasture and crop growth. Many of these responses, according to Anderson and Thomas (1946) have been due to the effect of Mo in symbiotic N_2 fixation. Frequently, however, the small amounts that legumes obtain in deficient soils can suffice for metabolism in the host plant.

On the average, Mo in agricultural soils varies from 0.5 to 5.0 ppm. Since the total content of the element is not the best index of availability to the plant, skill and good judgement in the use of lime are required in pasture plants growing on high-Mo soils. In acid soils, Mo solubility approaches the critical levels below which nutrient deficiencies are encountered. It is obvious, therefore, that liming would increase solubility and availability of Mo sufficient to cause injury to livestock.

In Hawaii, Fujimoto and Sherman (1951) discounted the so-called "Molokai disease" on grounds that the range of Mo concentration (2 - 2.5 ppm) in the tissues of the plants studied was too low to cause injury to the cattle. Younge and Takahashi (1953), in an alfalfa

variety test in a high-manganese soil, obtained results that suggested a greater response to side dressings of 4 lb Mo/acre than 2 lb Mo/acre of the element. In a greenhouse experiment, Watson (1968) noted that at soil pH less than 5.0, Mo uptake was so low that it limited dry matter yields of centrosema. However, rates of 1 lb Mo/acre and/or liming soils to pH 6.0 and higher significantly increased yield, Mo uptake, and nitrogen content of Centrosema pubescens and Pueraria phaseoloides. At such pH levels, the amount of Mo sorbed by these high Fe, Al and Mn oxide soils decreased, defective nodulation was minimized, and Ca content of forage increased. The evidence discussed shows that lime stimulated symbiotic N_2 fixation by increasing availability of Mo. Kurmarohita (1964) obtained a darker green desmodium plant side dressed with 2 lb Mo/acre, a fact restricted to active N_2 fixation in nodulated legumes. In Australia, Johansen (1978) compared Mo concentration of desmodium, siratro, lotonis and glycine with their growth response to application of rates from 0 to 200 g Mo/ha. He found different growth responses between the species which reflected their abilities to absorb Mo.

Unlike other micronutrients, the greater affinity for Mo of Fe and Al compounds in soils has made it a major limitation of legume growth in the acid soils of the tropics. Therefore, appropriate use of Mo as a fertilizer would require knowledge of both "native" and fertilizer Mo within specific soil systems. In light of the above, this study was directed toward obtaining information on the effect of Mo and pH on yield and composition of tropical legumes (Desmodium intortum and Centrosema pubescens) and biological nitrogen fixation in a Hawaiian

Ultisol. Therefore, the objectives of this study were:

1. To study the effect of soil pH on the availability of molybdenum in Hawaiian soils;
2. To study the sorption of molybdenum in Hawaiian soils;
3. To determine the effect of molybdenum on nitrogen fixation of tropical pasture legumes; and
4. To determine the effect of molybdenum and lime on dry matter yield, nitrogen content, nodulation, and mineral composition of Centrosema pubescens and Desmodium intortum.

Review of the Literature

I. Molybdenum Availability in Soil

The problem of availability of a nutrient is closely related to its retention or release in soil. The greater the retention, the less is the water-soluble portion present in the soil solution. Soils developed from highly-weathered parent materials have a tremendous capacity to retain molybdate anions, thereby making them unavailable to plants. The resulting decrease in concentration suggests adsorption on gibbsite and geothite by ligand exchange. Jones (1957), who extensively studied Mo reactions in different mineral systems, noted strong affinity of Mo for iron oxide and to a lesser extent aluminim oxides, halloysite, nontronite, and kaolinite. Reisenauer et al. (1962) suggested the following equation for the reaction of Mo with Fe oxides:

$$Fe_2O_3 + 3H_2O \rightleftarrows 2Fe(OH)_3$$

$$2Fe(OH) + 3MoO_4^{2-} \rightleftarrows Fe_2(MoO_4)_2 + 6OH^-$$

The above relationship suggests a pH dependence on Mo solubility which provides a direct measure of soil capacity to retain or release the element for plant uptake.

Soluble Mo in the soil exists in three forms. Below pH 4, $HMoO_4^-$ and H_2MoO_4 predominate as a result of protonation of the divalent molybdate anion. As the pH increases above 5, the MoO_4^{2-} species becomes dominant. In most soils Mo can be characterized in some major forms: (1) water-soluble Mo; (2) Mo combined with organic matter; (3)

exchangeable MoO_4^{2-} anion, adsorbed on colloidal complexes; and (4) unavailable Mo held in the crystal lattices of minerals. These forms of potential plant-available soil Mo would depend on soil parameters, such as pH, minerology of the soil and the levels of other plant nutrients (Davies, 1956; Reisenauer et al., 1962). The pH of a soil is acknowledged by researchers as the most important factor affecting availability of Mo to plants. As pH is increased, OH^- ions are produced which would replace MoO_4^{2-} ions held by soils.

A. Effect of pH on Molybdenum Availability in Soils

The concentration of a given molybdate species in soil varies with the pH of the system. Under conditions of acidity the MoO_4^{2-}, $HMoO_4^-$ and $HMoO_4$ are present; while above pH 5.0, MoO_4^{2-} predominates. Maximum retention of Mo occurs in the acid range because the second dissociation constant, pK_2, of molybdic acid is around pH 4 (Jones, 1957; Barrow, 1970). At pH between 5.0 and 7.0, the pH of most agricultural soils, Mo availability increases because the most highly charged form of the anion persists. At still higher pH values (> 8), clay surfaces would not be able to donate protons resulting in negligible retention of MoO_4^{2-} (Theng, 1971). Equally important in the relation between soil pH and Mo availability is the surface chemistry of these highly weathered soils. The predominant clay minerals in the tropics belong to those of the constant-surface-potential type colloids (Uehara and Keng, 1975). Their surfaces have uncoordinate metal ions in their lattice. In the presence of H^+ ions, positive charge is formed on these sites due to protonation of hydroxyl groups. Increasing the pH results in more OH^-

ions in solution which favors the development of a negatively-charged surface (Figure 1). Such surfaces would allow unrestricted mobility of MoO_4^{2-} anions in soil solution. Therefore, in order to reduce the fixative capacity of these highly-weathered soils of the tropics, one generally resorts to liming.

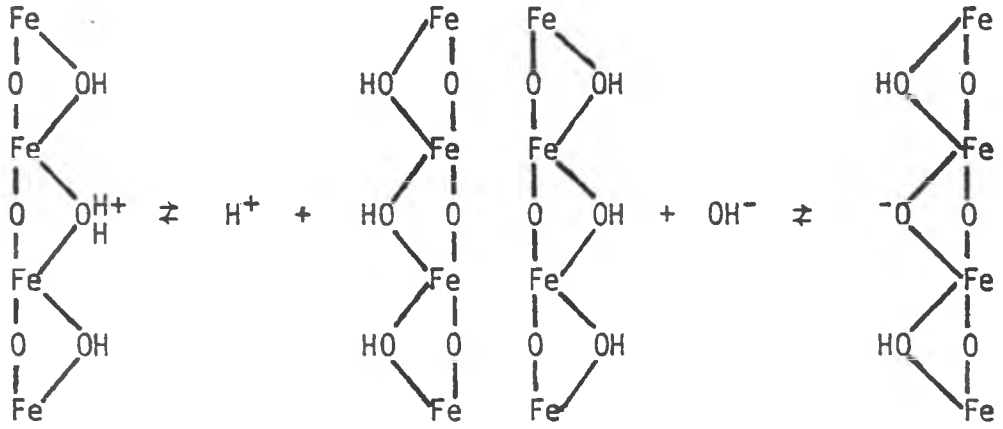


Figure 1: Origin of surface charge for a constant potential colloid (e.g. hematite) through protonation and deprotonation of surface hydroxyls.

The availability of soil Mo in plants depends on soil as well as the efficiency of uptake by the crop in question. In a Hawaiian study Kikuyu grass was found to absorb Mo according to the amount of Mo in soil solution above pH 6.4. The addition of Mo showed a significant increase in plant tissues leading to what would become a toxic situation due to high Mo accumulation in forages with time (Kurmarohita, 1964). Tang (1974) reported poor growth of Siratro in a pot experiment on heavy textured lateritic soils of pH 4.7. At this pH, Mo

deficiency was apparent; however, with liming yield was increased by 40 per cent. The relationship between soil pH and Mo availability has been shown to be affected by the mineralogical makeup of soil, an index of great potential for retention of molybdate ions (Barrow and Spencer, 1971).

B. Molybdenum Sorption in Soils

In reviewing factors affecting the availability of soil Mo to plants, Davies (1956) listed the precipitation of the molybdate anion by hydrous oxides of iron and aluminum as a major process in the formation of unavailable Mo in soils. Data by Jones (1957) and Wells (1956) showed strong sorption of Mo by iron oxides and hydrous oxides, but Al oxides also complex Mo (Jones, 1957; Reisenauer et al., 1962). In general, they found Mo adsorption by soils, clays and the hydrous oxides to decrease with increasing pH.

Reisenauer et al. (1962) reported that adsorption of molybdate was accompanied by a release of two hydroxyl groups and a water molecule. The molybdate at low pH forms a chemical bond with mineral surfaces not fully coordinated, thus becoming unavailable to plants (Barrow, 1977). Adsorption therefore would be more marked in soils of the constant-surface-potential type colloids, which are predominant in the tropics, than in the constant-surface-charge colloids of the temperate regions.

The relationship between phosphorus, sulfur and the availability of soil Mo to plants has been studied by many researchers. Barrow (1970) reported similarity between phosphate and molybdate adsorption except in the extent to which they respond to pH. In soils with high

pH, adsorption of both molybdate and sulfate was much lower relative to phosphate. However, molybdate retention may be substantially decreased by adding phosphate or by raising the pH of the soil by liming (Theng, 1971). The increase in Mo content of the plant on phosphate application is simply a result of phosphate replacing molybdate in the exchange complex.

II. Molybdenum Content of Soils and Plants

With the exception of few soils, total Mo content in agricultural soils varies from 0.3 to 4 ppm (Evans and Purvis, 1951; Robinson et al., 1951). As discussed earlier, the most important factor affecting Mo supply to the plant is change in soil pH. Walsh et al. (1952) found Mo deficiency in acid soils with total Mo of 0.4 to 3.5 ppm. However, at the same total Mo content, but at soil pH greater than 7, pastures were found harmful to livestock. In Hawaii, arguments on levels of the element in the soils have been around the question of accuracy in analytical techniques, because of high Mo contents reported (Fujimoto and Sherman, 1951). Due to possible interference by titanium, vanadium and chromium, the high soil Mo readings did not correlate with Mo uptake. The strong acid extractants used in their study reportedly brought other elements into solution, thereby interfering with Mo determination. On the average, Hawaiian soils contain over 2 ppm of the world average of soil Mo contents (Huang, 1962).

The ability of plants to extract Mo from soils depends on plant species (Johnson, 1966), soil pH and mineralogy (Davies, 1956) and nutrient status of the plant. In general, the Mo status and

pH of a soil have the greatest effect on the Mo level in the soil system which relates significantly to the uptake of the element by plants. Gupta (1970) reported increased contents of Mo in alfalfa after liming. At the high Mo treatment, level of toxicity effect was evident in the forage (> 10 ppm). Consequently, that high-Mo soil at neutral to alkaline pH can cause injury to livestock at the threshold level of 10 ppm, is accepted. Johansen et al. (1977) compared five tropical pasture legumes, G. wightii, D. intortum, M. atropurpureum, S. humilis and L. bainesii and their response to Mo accumulation over a five-year period. From the data it was not possible to estimate critical deficiency concentration in the plant tops.

III. Molybdenum in Biological Nitrogen Fixation

Following the discovery by Bortels in 1930 that Mo was essential as a catalyst in nitrogen fixation by free-living microorganisms the element has become a fertilizer of great importance. In Steinberg's (1939) work with microorganisms it was emphasized that Mo was essential for nitrate utilization, while the requirement for the element was considerably less for the cultures grown with ammonium nitrogen. Plants absorb nitrogen in the nitrate or ammonium form. Before utilization in the plant metabolism, the nitrate nitrogen must be reduced to the ammonium form. The conversion of nitrate nitrogen to ammonium nitrogen in plants is mediated by enzymes. Proofs came when Nicholas (1955) purified the nitrate reductase enzyme responsible for reduction of nitrate to nitrite from soybean leaves. The enzyme involved was shown to contain molybdenum and flavium. Another significant aspect of Mo

participation in plant metabolism is in fixation of molecular nitrogen by microorganisms through the enzyme nitrogenase. Nitrogenase has been isolated from Clostridium pasteuriana and other free-living nitrogen-fixing microorganisms as well as from root nodule bacteroids of legumes. These roles therefore make Mo an indispensable element in plant nitrogen metabolism.

Response of pasture legumes to Mo has been associated with the effect of Mo in symbiotic nitrogen fixation. In the absence of Mo, Mulder (1954) observed smaller, paler yellow-brown nodules than in the normal plants with pinkish nodules. 't Mannetje et al. (1963) observed that plants grown on soils low in Mo had numerous small nodules, which were white or geen in color whereas in sufficient Mo, the nodules were fewer, larger, branched and pinkish. In a pot experiment with an Ultisol, N_2 fixation in Desmodium intortum, Glycine javanica and Centrosema pubescens was markedly improved by liming and addition of Mo (Trigoso and Fassbender, 1973). Means and Barkus (1970) reported that Mo increased dry matter yield and nitrogen content of glycine because of improved symbiotic nitrogen fixation.

Peres et al. (1976), studying the increase in nitrogenase activity of Azobacter paspali growing in a soil medium with and without Mo, showed positive correlation between the activity of the microbe due to Mo and total increase in plant N content of C. pubescens. Correlation coefficients (r) of 0.97 in Oxisols and 0.96 in Ultisols were obtained in the above study.

IV. Molybdenum as a Fertilizer

In practically all studies of Mo as a fertilizer, small quantities have been required to correct deficiency. Evidence has shown, however, that amounts required varied with the crop, soil, and other factors.

The first plant response to Mo fertilizer was reported in 1942 in Australia, which led to immediate widespread use of commercial Mo fertilizer. Anderson (1942) identified Mo as a limiting factor in production of clovers in some Australian pastures and showed remarkable increases in pasture production with dressings of 5 g Mo/ha. Younge and Takahashi (1953) in Hawaii found alfalfa growth was much better with 4 lb Mo/acre than with 2 lb Mo/acre in a soil high in manganese.

Response of non-legumes to Mo was first reported by Davies (1945) in New Zealand. He showed that the "whiptail" of cauliflower could be corrected by the use of Mo. The disease known as "yellow spot" of citrus in Florida was due to Mo deficiency (Steward and Leonard, 1952).

Tropical pasture legumes have not received as much attention on fertilizer studies as their counterparts in temperate countries. In trials on three soil types (Kerridge *et al.*, 1973), MoO_3 at the rate of 100 g/ha was as effective when applied in a rock phosphate seed pellet, as when applied to the soil directly in correcting Mo deficiency. Nodulation, dry matter yield, N and Mo content of *D. intortum*, *G. wightii*, *L. bainesii* and *M. atropurpureceum* were similar with both methods of application. Field trials in Chile by Wernberger and Wenzel (1973) showed that Mo at 200 g/ha markedly increased yields of leguminous plants. A recent study by Andrew (1976) showed increased per cent nitrogen and dry matter yield of *D. intortum* with the application of

rates up to 300 g Mo/ha.

In some soils molybdate at 100 to 200 g Mo/ha have been found adequate to correct deficiency. In soils high in colloidal iron oxides, which are generally Mo deficient, higher rates of Mo would be needed (Anderson, 1956). Because of the various soil characteristics that affect Mo availability to plant, rate and frequency of application have been well studied. Anderson (1970), who studied Mo fertilization of D. intortum for three years, found that in the first year 25 g Mo/ha was sufficient for maximum yield. After three years a supply of 200 g Mo/ha was needed for maximum growth.

It seems quite evident that the use of Mo fertilizers will continue to improve nutritional quality of forages, especially those produced in soils high in available copper. The use of Mo fertilizers to raise Mo levels to counteract copper toxicity may prove to be worthwhile in view of Mo-Cu balance required in forages.

V. Lime-Molybdenum Interaction

The focus on Mo in pasture production in the tropics has been a result of its availability due to liming of soils. The relationship between availability of the micronutrients and soil pH is widely recognized. However, since Mo is a micronutrient soluble at high pH, liming tropical soils can lead to deficiencies in other plant nutrients. In Hawaii, Zn deficiency has been noted in D. intortum as a result of overliming (Fox and Plucknett, 1964).

Individually, Mo or lime have tremendous impact on the nutrition of tropical pasture legumes. In most tropical soils, lime may be

needed in addition to Mo to correct the problem of defective nodulation. By increasing the availability and uptake of Mo, lime application increases symbiotic nitrogen fixation and corrects nitrogen deficiency in plants.

Anderson and Oertel (1946) showed that by increasing the availability of Mo, lime stimulated nitrogen fixation in clover plants. The effect of lime on color, per cent nitrogen, growth and nodulation of the clover plants was similar to the effect of Mo. In soils with pH less than 5, Anderson and Moye (1952) found a substantial response to subterranean clover of 1 oz Mo/acre mixed with 224 lb calcium carbonate per acre. An interaction between Mo and lime was found for alfalfa, birdsfoot trefoil, and ladino clover by Kliewer and Kennedy (1960). Molybdenum applied with lime at rates less than 2 tons/acre increased the yield and nitrogen content of the forage. The marked interaction effect of Mo and lime suggested that the effect of lime was to increase the uptake of Mo which, in turn, increased symbiotic fixation. However, at rates greater than 2 tons/acre there was no response to Mo. Gupta (1970) noted that even when soils were limed to pH 6.5, alfalfa, bromegrass and cauliflower did not give maximum yields. Addition of Mo gave substantial increase in yield.

Because of the high buffering capacity of soils in the tropics, heavy liming has been practiced extensively in pasture fertilization. The components of soil acidity, low pH, Ca and Mo deficiencies, Al and Mn toxicities, and P deficiency, have made such a practice a necessity in these areas. Souto et al. (1969) noted that tropical soils high in Mn impaired nodulation and nitrogen fixation in C. pubescens,

S. gracilis and P. atropurpureum. The result of work by Truong et al. (1971b) did indicate, however, that if Ca, pH and P are not limiting, Mo could overcome Mn toxicity by promoting greater plant fiber, allowing the plant to dilute the absorbed Mn concentration. Munns and Fox (1976) reported a decrease in relative yield of D. intortum and S. gracilis at low pH. Liming rates up to 10 tons/ha in these high-Mn soils increased yields and other yield components tremendously. In these soils, liming reduced toxicity, permitted effective nodulation, solubilized Mo, and increased P availability. In the lateritic soils of Taiwan, Tang (1970) found that Mo x lime increased dry matter yield of siratro by 40 per cent more than Mo treatments alone. In many field trials in the tropics, the benefits of the lime x Mo interaction have led to reduced demands for higher lime rates.

Materials and Methods

Description of Soils Used

The soils used in this study represent distinct physical, chemical and mineralogical properties. They represent some of the major soil series of the Hawaiian Islands as described by Cline *et al*. (1955) and U.S.D.A. Soil Taxonomy (1972). Pertinent information regarding these soils is given in Table 1.

Paaloa Soil: This soil was collected in Helemano from a Waialua Agricultural Company field on the island of Oahu. It belongs to the family of Humoxic Tropohumult, clayey oxidic isothermic. This soil is formed from olivine basalt. The elevation is about 366 m above sea level and has an average annual rainfall of 2000 mm. The mean annual soil temperature is 21^{o}C. The soil is dark brown, well drained with fine and very fine subangular blocky structures at the surface. The clay fraction is abundant in haematite, magnetite, gibbsite, geothite, kaolinite and mica. Paaloa soils are cultivated to pastures and sugar cane.

Lualualei Soil: This soil, classified as a Typic Chromustert, very fine, montmorillonitic, isohyperthermic, was collected from Lualualei Valley on the island of Oahu. It is derived from alluvium in an area with annual rainfall of 600 mm. The soil has a mean annual temperature of about 24^{o}C. It is sticky and plastic, imperfectly drained and very dark greyish-brown in color. The clay fraction is dominated by montmorillonite. The soil is cultivated to sugar cane, pastures and truck crops. It is chemically superior in terms of production agriculture

TABLE 1 Important Characteristics of the Experimental Soils

Soil	Total N %	Organic C %	CEC (me/100 g)	Exchangeable Bases[f] Ca (me/100 g)	Mg (me/100 g)	Na (me/100 g)	K (me/100 g)	P[1] (ppm)	Al (ppm)	Mo[2] (ppm)
Kaiwiki	0.72	10.40	51.9	0.10	0.13	0.16	0.11	12	0.14	---
Molokai	0.21	1.52	24.5	6.20	2.80	0.25	0.47	54	---	1.64
Lualualei	0.10	1.21	59.2	20.24	19.80	2.50	1.40	221	---	1.06
Wahiawa	0.16	1.12	22.3	5.56	1.14	0.22	0.75	48	0.10	1.84
Paaloa	0.27	3.26	21.4	2.07	0.47	0.20	0.15	11	1.50	1.29

f CEC determined by 1 N ammonium acetate technique, pH 7.0

1 Extractable P by modified Troug technique

2 Mo content by alkaline digestion (1948, 1953)

but physically poor because of its shrinking and swelling properties.

Wahiawa Soil: This soil was collected from the University of Hawaii Agricultural Experimental Station farm at Poamoho, on the island of Oahu. It is classified as a Tropeptic Eutrustox, clayey, kaolinitic, isohyperthermic. The soil is derived from olivine basalts in areas with an annual rainfall of about 1000 mm. The mean annual temperature is 21.7°C. This soil is dark red in color, hard, friable, sticky, and plastic, and well drained. Their clay fraction is abundant in kaolinite, haematite and gibbsite. The soil is cultivated to pineapple.

Molokai Soil: This soil was sampled from Kunia on the island of Oahu. It is derived from olivine basalt and classified as a Typic Torrox, clayey, kaolinitic, isohyperthermic. The soil occurs in areas with an annual rainfall of about 500 mm and has a mean annual temperature of 23°C. It is dark reddish-brown in color, friable, slightly sticky and plastic. Their dominant clay minerals are kaolinite, haematite, magnetite and gibbsite. Molokai soils are cultivated to sugar cane.

Kaiwiki Soil: This is a volcanic-ash derived soil sampled from Kaiwiki, on the island of Hawaii. It is classified as a Typic Hydrandept, thixotropic, isothermic. The annual rainfall is 4350 mm and the mean annual temperature is 21°C. This soil is yellowish-brown in color, slightly sticky and plastic. It is highly permeable and has good drainage. The Kaiwiki soil is dominated by x-ray amorphous mineral colloids with additional amounts of gibbsite, geothite, haematite, magnemite, magnetite and ilminite. The soil is mostly devoted to forestry and wildlife habitat.

Experiment 1: Effect of Soil pH on Availability of Molybdenum

The five soils mentioned earlier were selected for this investigation. The Kaiwiki series, a Hydrandept, was passed through a 6 mm sieve, stored in double polyethylene bags, and refrigerated until needed for experimentation. The other soils were air-dried, ground to pass through 20 mesh sieve and stored in double polyethylene bags at room temperature until needed.

Five-gram samples (O.D. basis) of each soil were placed in a series of 50 ml centrifuge tubes. The samples were suspended in 20 ml of 0.001 M $CaCl_2$. To these 5-ml portion of 500 ppm Mo as Na_2MoO_4 were added. The suspension was adjusted to pH values of 2, 4, 6, 8 and 10 by adding either 0.1 N HCl or 0.1 N KOH solutions. The suspensions were stoppered and shaken at room temperature for 18 hours in a reciprocating shaker. After equilibration the pH of the soil suspension was measured using a Beckman Digital pH meter. The samples were centrifuged at 15,000 rpm for 15 minutes, then filtered through Whatman No. 42 filter paper. The molybdate concentration in the filtrate was determined colorimetrically by the thiocyanate-stannous chloride method of Johnson and Arkley (1954).

Experiment II: Effect of Equilibration Time on Molybdenum Adsorption

Five-gram samples (O.D. basis) of each soil were placed in a series of 50-ml centrifuge tubes, each containing 20 ml of 0.001 M $CaCl_2$. Then 5 ml of 500 ppm Mo as $NaMoO_4$ was added to each tube. The suspension contained in stoppered centrifuge tubes was shaken at room temperature in a reciprocating shaker for different time periods, varying from 0 to 1,

TABLE 2 Charge and Mineral Properties of the Experimental Soils

Soil	Mineralogy (dominant)	Sub-Group	Depth cm	pH 1:1 H_2O	pH 1 N KCl	ΔpH
Kaiwiki	A	Typic Hydrandept	0-16	3.72	3.87	+0.15
Molokai	K,O	Typic Torrox	0-16	6.40	5.41	-0.99
Lualualei	M	Typic Chromustert	0-16	7.24	6.58	-0.66
Wahiawa	K,He,O	Tropeptic Eutrustox	0-16	5.80	4.87	-0.93
Paaloa*	Go,Gi,He,K	Humoxic Tropohumult	0-16	4.60	3.92	-0.68

A = Amorphous materials
K = Kaolinite
Gi = Gibbsite
He = Haematite
Il = Ilminite
M = Montmorillonite
O = Oxides
Go = Geothite

* Total soil N = 21 ppm after corn depletion of soluble N

4, 8, 24, 48 and 72 hours. The suspensions were centrifuged at 15,000 rpm for 15 minutes, then filtered through Whatman No. 42 filter paper. The final concentrations of molybdenum in the solutions were determined colorimetrically by the method of Johnson and Arkley (1954).

Experiment III: Sorption of Molybdenum by Soils

Molybdenum adsorption isotherms for each soil were determined by equilibrating soil samples at 25°C with Mo solutions of varying concentrations.

Five-gram samples (O.D. basis) were suspended in 20 ml of 0.001 M $CaCl_2$ in a series of 50-ml centrifuge tubes. To the suspension was added 5 ml of solution containing 0, 50, 100, 200, 400 and 600 ppm of Mo as $NaMoO_4$. The samples were allowed to equilibrate for six days at room temperature on a reciprocal shaker. During this time they were shaken for 30 minutes twice daily, according to the procedure developed by Fox and Kamprath (1970) for phosphate sorption studies. After shaking for six days the phases were separated by centrifuging for 15 minutes at 15,000 rpm, then filtered through Whatman No. 42 filter paper. The final concentration in the solution was determined colorimetrically by the method of Johnson and Arkley (1954).

Experiment IV: Effect of pH and Molybdenum on Growth of Desmodium intortum and Centrosema pubescens - Greenhouse Study

A. Soil Preparation

This experiment was conducted at the Mauka Campus Greenhouse on a Paaloa silty clay. The soil was sieved through a 1-cm

sieve to preclude gravels, stones and large roots, and spread on flat benches to air dry. After air drying and thoroughly mixing to attain homogeneity, a representative sample was taken to determine moisture content as well as to conduct routine soil tests for fertilizer application; e.g., tests for pH, lime requirement, available P, CEC, etc. (see Table 1, Figures 2 and 3). Six kg of soil on the basis of oven-dry weight were bagged in double polyethylene bags and secured for subsequent fertilization.

B. Fertilizer Application

The chemical fertilizers used in this study were all analytical reagent grade. The chemical source of Mo was $Na_2MoO_4.2H_2O$. The Mo treatments were 0, 1, 2 and 5 kg Mo/ha, which were equivalent to 0, 6.5, 13.0 and 32.5 mg Mo/pot of $Na_2MoO_4.2H_2O$, respectively. Lime as $Ca(OH)_2$ was added to raise the pH values of soils from 4.6 to 5.5, 6.0 and 6.5. The calculated amounts of lime were evaluated from a titration curve of the experimental soil (Figure 3). The basal fertilizer added to all pots was as follows:

800 kg P/ha as $Ca(H_2PO_4)_2.2H_2O$

200 kg Mg/ha as $MgSo_4.7H_2O$

200 kg K/ha as KCl

20 kg Zn/ha as $ZnSO_4.7H_2O$

2 kg B/ha as H_3BO_3

It is important to note that lime was applied first and allowed

Figure 2: Adsorption Curve of Paaloa Silty Clay for Estimation of Fertilizer P Required to Maintain 0.2 ppm P in Solution.

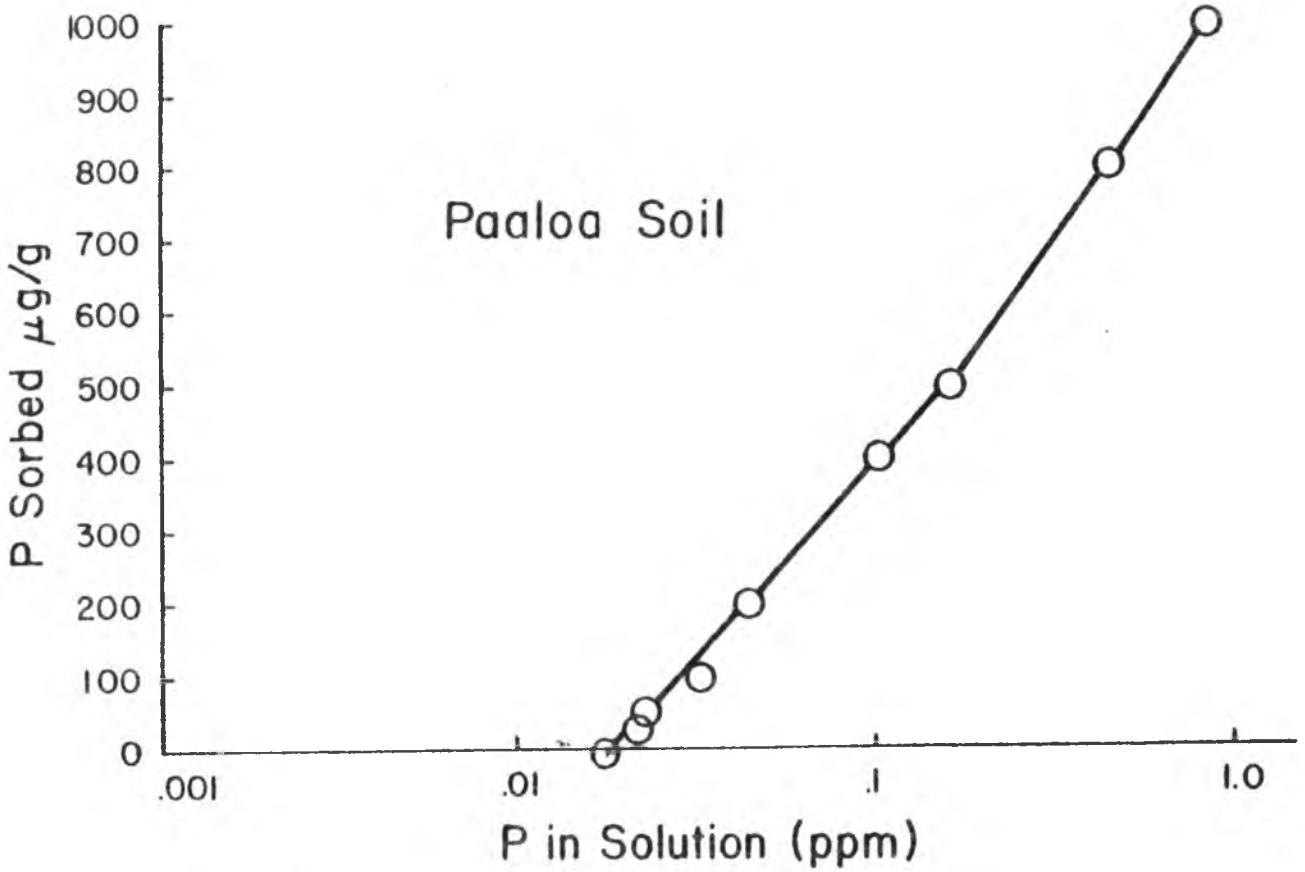
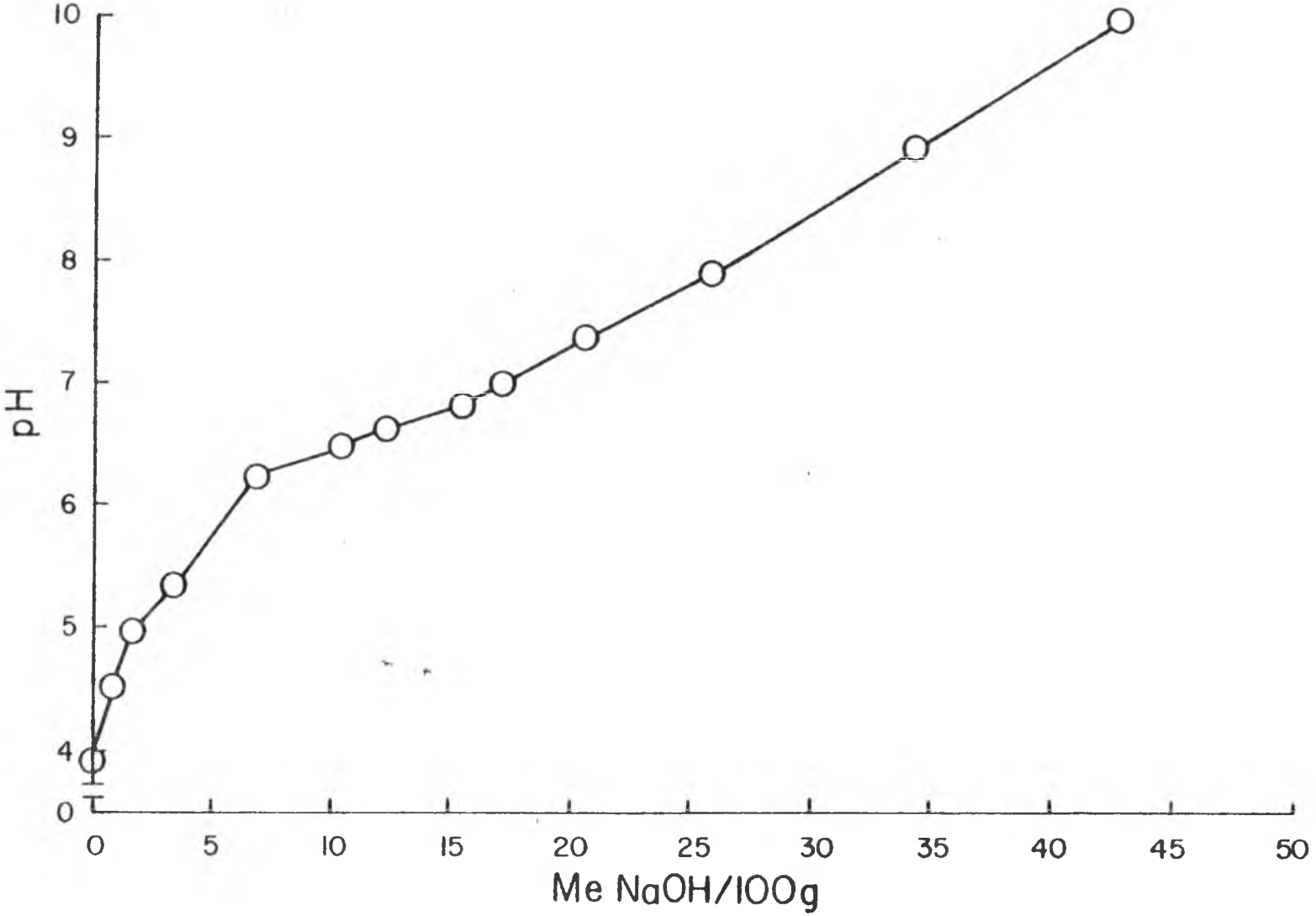

Paaloa Soil
P Sorbed µg/g
1000
900
800
700
600
500
400
300
200
100
0
.001
.01
.1
1.0
P in Solution (ppm)

Figure 3: Titration Curve for the Estimation of Lime Requirement of a Paaloa Silty Clay Soil.


pH
10
9
8
7
6
5
4
0
0
5
10
15
20
25
30
35
40
45
50
Me NaOH/100g

to equilibrate for two weeks before the rest of the nutrients were added. All treatments, in solution where possible, were mixed thoroughly into the soil.

C. Experimental Layout

The fertilized soils were transferred to 2.5-gallon pots lined with polyethylene bags. The experimental layout in the greenhouse was carried out as a 2 (plant) x 4 (Mo) x 4 (pH) factorial in a split-plot design with three replications.

D. Seed Preparation

Seeds of Desmodium intortum (c.v. Greenleaf) and Centrosema pubescens (c.v. Centro) were obtained from NifTAL (Nitrogen fixation by Tropical Agricultural Legumes) project field laboratories on the island of Maui. They were scarified by immersion in sulphuric acid (concentration 98 per cent) for two minutes. After draining they were washed ten times with distilled water. The final washing was saved to test for any evidence of sulfate by using barium chloride solution. The scarified seeds were then pregerminated in a petri dish until their radicles emerged.

E. Innoculation

After emergence of their radicles, the seeds were transferred to petri dishes containing the specific Rhizobium suspension. In the case of D. intortum the Rhizobium strain TAL 309 was used. C. pubescens, relatively specific, had TAL 655. The petri dishes were swirled to ensure contact between the radicles and the Rhizobium strains. A week after planting,

1 ml of the Rhizobium suspension of each strain was added directly into the roots by means of a pipette.

F. Cultivation Practice

Due to the possible interference of mineralized N with response of the legumes to Mo fertilization, it was decided to deplete the soil of some of the soluble forms of N by growing corn until deficiency symptoms of N were evident. This was done prior to fertilization of the soil. (Note: Amount of nitrogen left was sufficient for Rhizobium starter nitrogen; see Table 2).

The seeds already treated as above were planted in the pots using 10 seeds per pot. Throughout the experiment the pots were watered to 75 per cent field capacity. After a week of germination the seedlings were thinned to three uniformly growing plants per pot. Pots were randomized within replications for each indicator crop every week, in order to avoid microclimatic effects. Plants were harvested 79 days after seeding by cutting the shoots 1 cm above the surface of the soil. The roots were carefully removed with minimum detachment of the nodules and put into jars for acetylene reduction experiment. Plant samples were washed, placed in paper bags and oven dried at 70°C for two days for determination of dry matter yield. The oven-dried samples were ground in a stainless steel Wiley Mill using a 20 mesh screen and subsequently analyzed for elemental composition.

Analytical Procedures for Soil and Plant Analyses

The determination of Mo in this study was done colorimetrica-ly. Because of its sensitivity and general freedom from interference, the thiocyanate-stannous chloride method is usually superior to others. In acid solution in the presence of a suitable reducting agent, such as stannous chloride, thiocyanate gives an orange-red color with Mo. The colored compound which is a thiocyanate complex of Mo can be extracted by a 1:1 mixture of carbon tetrachloride and isoamyl alcohol.

Details of the methods of extraction and determination of the other nutrients are given in Methods of Soil Analysis (Black et al., 1965).

Procedure for Total Molybdenum in Soils

To eliminate the interference of such elements as vanadium, chromium, titanium, nickel and copper, which are abundant in Hawaiian soils, the alkaline digestion method of Robinson and Alexander (1953) was used in this study with some modification. For color development, the procedure of Johnson and Arkley (1954) was followed.

A 1.0 g sample of finely-ground soil (325 mesh) was mixed with 0.5 g anhydrous sodium carbonate in a porcelain crucible and fused at low heat for 15 minutes on a hot plate. The crucible was transferred to a muffle furnace and slowly brought to complete fusion at 1000^{0}C for 30 minutes. The crucible was removed, swirled and allowed to cool. The cake was detached with the aid of a rubber policeman and dissolved in 1 N HCl. The beaker was placed on a steam bath and evaporated to dry-ness. The residue was taken up to 2 ml of 30 per cent H_2O_2 in order to

complete the oxidation of any reduced Mo, and brought to dryness. The residue was cooled, washed with 70 ml of distilled water and heated to boiling for one minute. Ten ml of concentrated HCl was added, filtered, allowed to cool and made up to 100 ml.

The filtrate was transferred to a 125-ml separatory funnel and treated with 10 ml of 6.5 N hydrochloric acid-ferric chloride solution. A 10-ml aliquot of 1:1 mixture of isoamyl alcohol-carbon tetrachloride was added and the funnel shaken vigorously by hand for two minutes, releasing pressure as necessary. The phases were allowed to separate for 15 minutes and the extractant (the organic phase) discarded quantitatively. The following reagents were added into the separatory funnel, and shaken after each addition: 1 ml of 40 per cent potassium thiocyanate, 1 ml of 40 per cent stannous chloride tin 6.5 N HCl, and exactly 10 ml of the isoamyl alcohol-carbon tetrachloride extractant. The flask was subsequently shaken for two minutes and allowed to stand for about 15 minutes. To ensure that the colored extract was free of turbidity caused by traces of water, the exit tip of the funnel was dried with cotton swabs. The colored extract was transferred directly into the spectrophotometric cell and the optical density of the solution measured by a Klett Summerson Colorimeter using filter #47 (475 millimicrons).

Procedure for Soil-Extractable Molybdenum

Twenty-gram soil samples were shaken with 200 ml of each of the extranctant $|(NH_4)_2C_2O_4$ pH 3.3 and 0.1 N NaOH)|, respectively, for 18 hours at room temperature. The suspension was filtered using Whatman No. 42 filter paper. In the case of the NaOH extraction, due to the

dispersion of the soil, the extract was centrifuged before filtering to remove the finer particles. Exactly 150 ml of the filtrate was evaporated to dryness in a 100-ml Pyrex beaker. The beaker was heated in a muffle furnace at 450°C for four hours to destroy organic materials. The residue was taken up in 10 ml of distilled water. To this was added 10 ml of concentration HCl and filtered. The filtrate was made up to 100 ml volume. This solution contained the extractable Mo from 15 g of soil. The solution was transferred to a 125-ml separatory funnel and Mo determined as described under total soil Mo analysis.

Soil pH

The pH of the soil samples was determined using a 1:1 soil-water mixture and a 1:1 soil-KCl (1 N KCl) solution mixture after an hour equilibration with occasional stirring. The readings were made with a Beckman Digital pH meter.

Procedure for Molybdenum in Plants

The wet ashing method of Purvis and Peterson (1956) was followed in this study with a few modifications. Two-gram samples of oven-dried finely-ground plant material contained in a 100-ml Pyrex beaker was predigested in 15 ml of concentrated HNO_3 for 48 hours. Samples were then heated on a hot plate at low heat until solid material disappeared. A 2 ml portion of 70 per cent perchloric acid was added and digested to dryness at low heat. This should require a maximum of 10 hours. The residue was taken up in 5 ml of concentrated HNO_3 and 1 ml of 70 per cent perchloric acid, and evaporated to dryness, reducing heat to avoid

spattering. Two ml of 30 per cent H_2O_2 was added and again evaporated to dryness. The residue was treated with 70 ml of distilled water and heated to boiling for one minute. To the warm solution was added 10 ml of concentrated HCl, filtered, allowed to cool and made up to 100 ml. A blank digest was carried through the same procedure for every group of samples studied. The solution was then transferred to a 125-ml separatory funnel and Mo determined by the thiocyanate-stannous chloride method described above.

A standard curve was constructed by transferring 0, 0.25, 0.5, 1, 2, 4, 8, 10 and 20 ml of standard 5 ppm Mo as $NaMoO_4$ into separatory funnels. These were brought to 100 ml by adding blank digests. The Mo concentration in each sample was determined as described above.

Procedure for Acetylene Reduction Assay

Roots with nodules attached were put into 500 ml incubation jars. Each jar was sealed with a screw cap into which had been installed a rubber serum stopper. A 25-cc portion of air was taken from the jar such that the inner pressure was 1 atmosphere. Exactly 25 cc of acetylene from a portable balloon was then injected through the serum stopper into the jars. The jars were incubated for one hour at room temperature. Two cc of gas were withdrawn from the incubated jars and transferred to 38 ml vaccine bottle for subsequent determination of ethylene by gas chromatography.

Nodules were then detached from the roots, washed, blotted, and weighed.

Procedure for Other Plant Nutrients

Plant samples from each treatment were ground in a stainless steel Wiley Mill and analyzed for P, K, Ca, Mg, S, Mn and Zn by x-ray quantometer. Total N was determined by use of Technicon Autoanalyzer System.

Statistical Analysis

The experimental data such as dry matter yield and nutrient concentration were analyzed statistically through use of a factorial analysis of variance in split-plot design. Statistical significance of the differences among treatment means was carried out by means of Duncan's Multiple Range Tests. Correlation coefficient, regression equations and other statistical parameters were also used to further explain the data.

TABLE 3. Analysis of Variance for Data on Effect of pH and Molybdenum on Yield and Mineral Content of Pasture Legumes

Source of Variation	d.f.
Main Plot	
Plant	1
Rep	2
Plant x Rep	2
Error (a)	2
Sub-Plot	
Mo	3
pH	3
Mo x pH	9
Mo x plant	3
pH x plant	3
Mo x pH x plant	9
Error (b)	60
Total	95

Results and Discussion

Experiment I: Effect of Soil pH on the Availability of Molybdenum

The effect of pH on Mo availability is shown in Figure 4, where the general trend is for Mo adsorption to decrease as pH increases with a change in slope occurring between pH 4 and 6. Figure 4 shows also that irrespective of the mineralogical makeup of the soil maximum retention was shown at the extreme acid levels. As the pH is increased, the concentration of Mo in solution increases in all soil samples. The pH range used in this study includes both dissociation constants (pK_1 and pK_2) of molybdic acid, which is close to pH 4. Accordingly, the pH of maximum retention should coincide with the second dissociation constant pK_2, which in this study is around pH 4.7. Such a change from the predicted pK_2 value of molybdic acid can be attributed to the differenc- between the clay mineral surface pH and the pH of the bulk solution, as shown in Table 4. Theng (1971) observed that maximum retention was close to pH 4, above which Mo in soil solution increased. Above pH 5.0 MoO_4^{2-} predominates (Chojnacka, 1963; Theng, 1971). At pH values higher than 8, the clay surface is incapable of donating protons. This would lead to increased availability of Mo. At the acidic end of the scale the free acid forms predominate, resulting in low concentrations of detectable Mo.

The change in the pH after equilibration is associated with the one-to-one replacement of MoO_4^{2-} for OH^-. Where retention occurred at the low pH 2, release of OH^- ions meant an increase in the equilibrium pH (Table 4).

Figure 4: Effect of pH on Molybdenum in Solution by Five Hawaiian Soils.

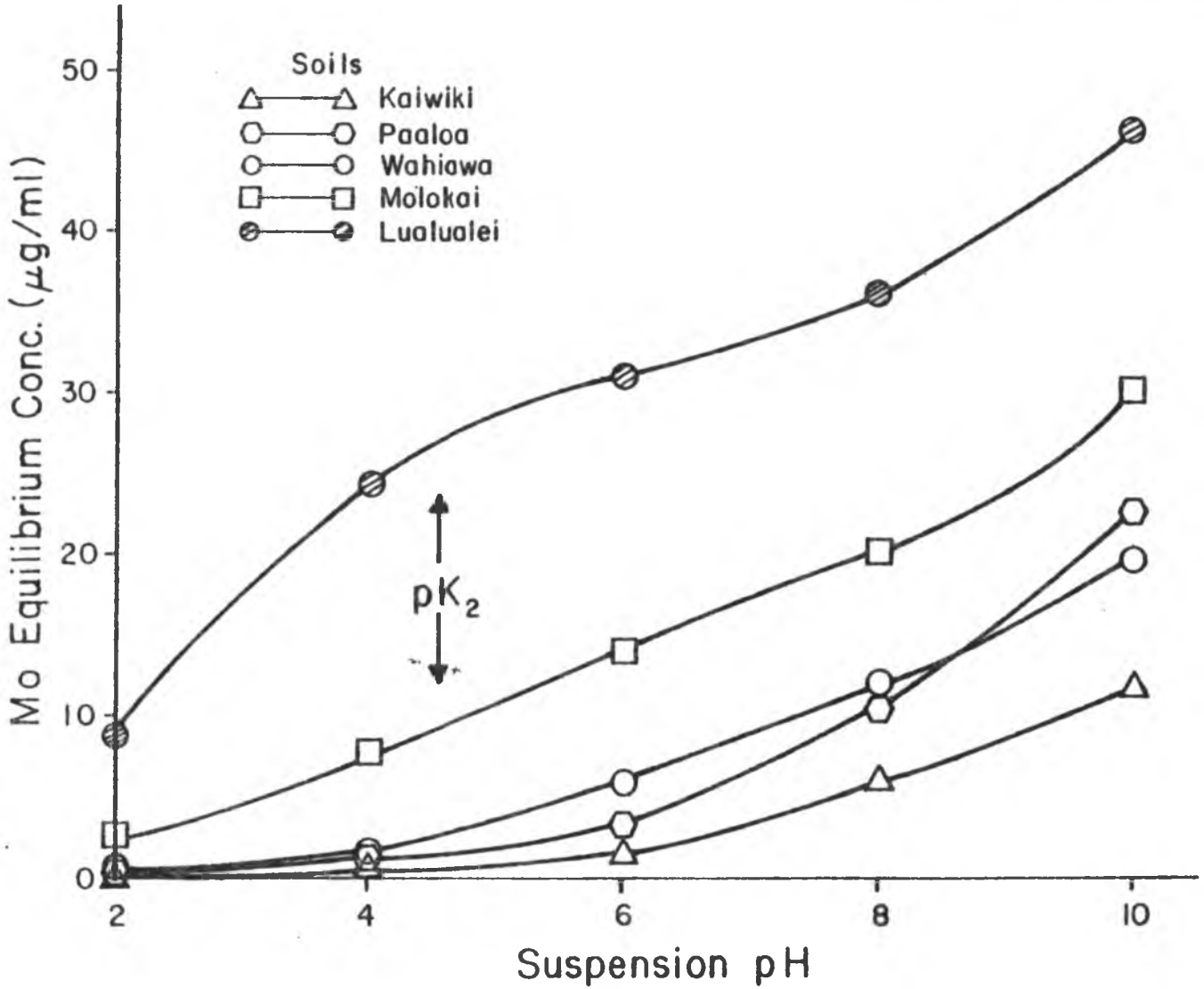

Soils
Kaiwiki
Paaloa
Wahiawa
Molokai
Lualualei
pK2
Mo Equilibrium Conc. (µg/ml)
Suspension pH
0
10
20
30
40
50
2
4
6
8
10

TABLE 4 Molybdate in Solution as Affected by Soil pH of Five Soils

Soil	Adjusted pH	Equilibrium pH	Mo in Solution µg/ml
Kaiwiki	2.0	3.14	0.03
	4.0	3.80	0.20
	6.0	4.57	1.34
	8.0	5.04	6.97
	10.0	5.57	11.87
Paaloa	2.0	3.34	0.12
	4.0	4.55	0.77
	6.0	4.92	3.20
	8.0	5.01	10.02
	10.0	5.57	22.51
Wahiawa	2.0	3.74	0.30
	4.0	5.37	1.18
	6.0	5.68	6.10
	8.0	5.88	12.00
	10.0	5.57	19.88
Molokai	2.0	3.97	0.48
	4.0	6.14	8.00
	6.0	6.40	14.01
	8.0	6.51	20.00
	10.0	6.87	30.00
Lualualei	2.0	5.04	8.90
	4.0	6.64	24.37
	6.0	6.91	31.20
	8.0	7.16	36.00
	10.0	7.91	45.81

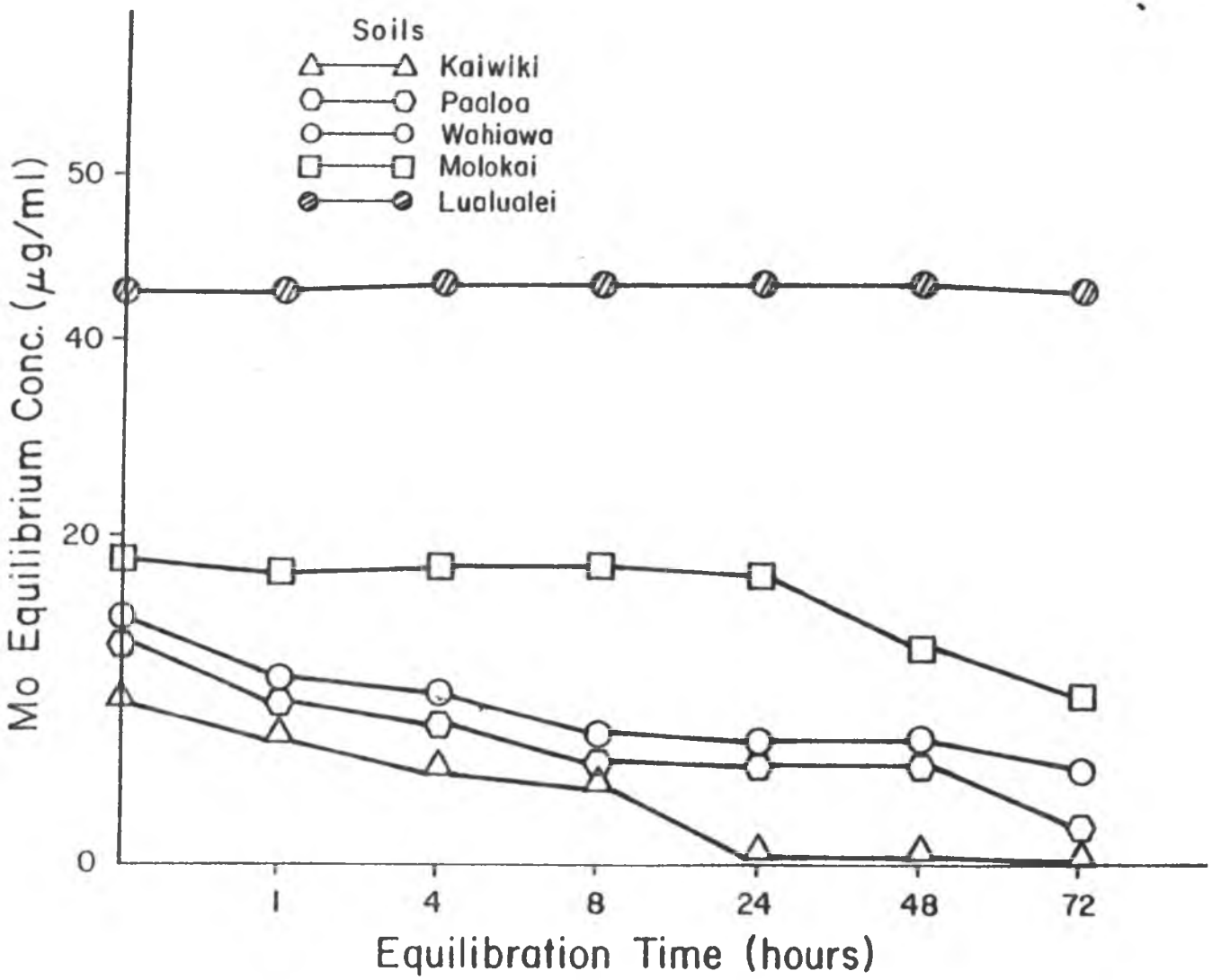
The relationship between pH and the solubility of molybdate shows that all the soils represented exhibit different capacities to release Mo because of their mineral contents. The order of maximum retention at the pK_2 level is: Kaiwiki > Paaloa > Wahiawa > Molokai > Lualualei. The mineralogy of the soil less than 325-mesh or the silt and clay fraction were examined by x-ray diffraction analysis. The Kaiwiki colloid with its amorphous materials and a different charge characteristic (ΔpH net positive) showed a higher retention capacity than the montmorillonitic Lualualei soil at the same pH level. These observations support the findings of Jones (1957) who, by removing the free iron oxides from the Wollongbar soil, found less Mo retention at the low pH levels than with the untreated soil.

It is obvious from Figure 4 that the liming would increase the availability of Mo and that Mo deficiency is expected only in acid soils.

Experiment II: Effects of Equilibration Time on Molybdenum Adsorption

The results obtained for Mo adsorption as a function of time in the foregoing soils showed that 1 to 8 hours was sufficient time to attain equilibrium condition (Figure 5). In the case of the Kaiwiki soil, a Typic Hydrandept with a much larger capacity factor than the rest of the soils, a sharp decline in Mo concentration was evident between 24 and 72 hours of shaking. Figure 5 shows that adsorption was rapid at first and then continued at a decreasing rage, which agrees with earlier observations (Barrow, 1970). The Lualualei soil, dominated by montmorillonite, did not show any change in Mo concentration with time.

Figure 5: Effect of Time of Shaking on the Molybdenum in Solution by Five Soils.


Soils
Kaiwiki
Paaloa
Wahiawa
Molokai
Lualualei
Mo Equilibrium Conc. (µg/ml)
50
40
20
0
1
4
8
24
48
72
Equilibration Time (hours)

The results obtained clearly reflected the mineralogy of the soils as the determining factor in the Mo concentration at different shaking times. The critical rapid stage of mobilization of Mo may be attributed to reaction with the surface of the clay mineral. When these surfaces or "sinks" are fully saturated with Mo, a slow reaction phase ensues as shown between 8 and 24 hours. Regarding equilibration time, Gonzales et al. (1974) found 1 to 4 hours to be adequate to attain equilibrium in an allophanic and highly amorphous soil of Chile. This study, in concordance with observations by Barrow (1970), showed rapid adsorption of Mo at first which declined with time. However, he also found Mo adsorption to be affected by the soil solution ratio and the concentration of the supporting electrolyte. In this study 0.001 M $CaCl_2$ was used, since the objective for the use of a supporting electrolyte was to simulate soil solution concentration of Ca, which is far less than the 0.01 M $CaCl_2$ commonly used in adsorption work. The Kaiwiki soil pH 3.7 showed a distinct drop in the Mo concentration between 8 and 24 hours, which would indicate the presence of two energetically distinct sites on which adsorption can take place. A similar situation was arrived at by Muljadi et al. (1966) in an adsorption study. Paaloa and Wahiawa soils behaved similarly except that the more acid Paaloa soil had a lower Mo concentration in solution at all times. With increasing time, the Molokai soil showed a decrease in Mo remaining in solution. Fox (1966) showed a similar response by the Molokai soil on P immobilization with time. In this same study, the Lualualei soil had the lowest per cent retention at all times. In contrast to P and S, the more acid the soil the more Mo is retained. Figure 5 indicates that comparatively high Mo

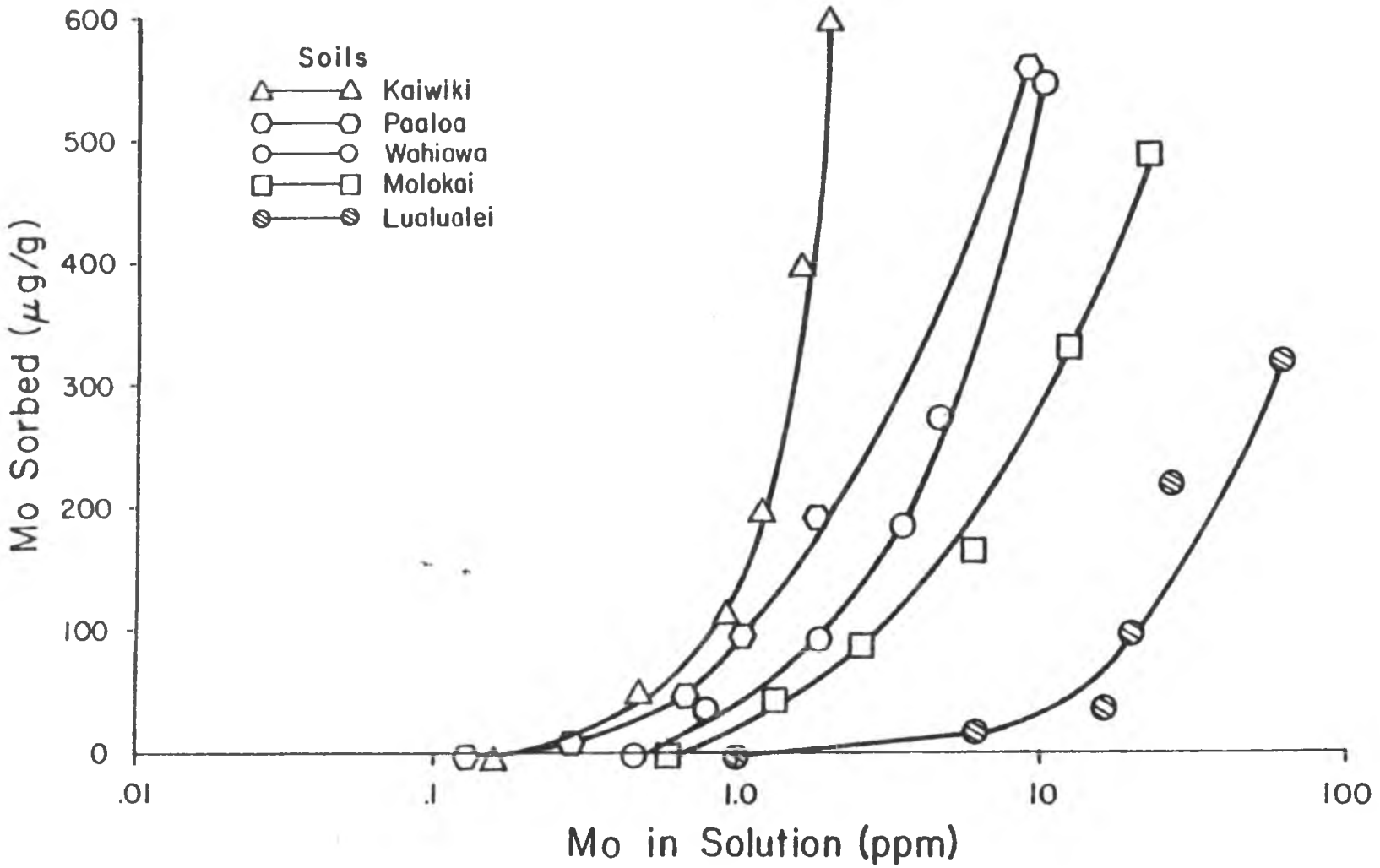
fertilization would be required to maintain adequate growth of plants in the Kaiwiki soil than in the Lualualei soil. In general, the Mo sorption as a function of time for all samples follows this order: Kaiwiki (amorphous hydrated oxides) > Paaloa (gibbsite, geothite, ilminite) > Wahiawa (haematite, kaolinite) > Molokai (kaolinite) > Lualualei (montmorillonite).

Experiment III: Sorption of Molybdenum by Soils

The equilibration conditions in this experiment were modified to eliminate interaction effects between the supporting electrolyte and the Mo concentration in solution. A preliminary investigation on the effect of shaking time on Mo concentration using 300 µg/ml Mo as Na_2MoO_4 resulted in almost total fixation by the Kaiwiki soil (amorphous hydrated oxide) after 1 hour of continuous shaking. As a result, higher concentrations were needed and a much lower supporting electrolyte concentration than the commonly used 0.01 M $CaCl_2$, which would precipitate Mo at concentrations greater than 50 ppm. In order to accomodate a wider range of Mo concentrations, as well as the adsorption capacities of these soils, an electrolyte concentration of 0.001 M $CaCl_2$ was used.

Figure 6 shows the isotherms for Mo adsorption by the surface samples of five soils of Hawaii, representing different physical, chemical and mineralogical properties. The curve of the Kaiwiki soil is characterized by the amorphous nature of its dominant minerals. Derived from volcanic ash, these soils have a net positive-charge surface (Table 2) which gives them a tremendous capacity to adsorb anions. From the slope of these curves, which reflect their buffering capacities, Mo

Figure 6: Molybdate Adsorption Curves of Five Soils of Different Mineralogies.


Soils
Kaiwiki
Paaloa
Wahiawa
Molokai
Lualualei
600
500
400
300
200
100
0
Mo Sorbed (µg/g)
.01
.1
1.0
10
100
Mo in Solution (ppm)

adsorption will follow this order: Kaiwiki > Paaloa > Wahiawa > Molokai > Lualualei. Sorption of Mo by the Lualualei soil was very small. The equilibrium concentration of Mo increased markedly as the initial Mo concentrations were increased. The Kaiwiki soil, with high buffering capacity, adsorbed more than the other samples. It is convenient to use a single value with which to characterize Mo sorption by these soils. Two equations have been used to characterize sorption of Mo in soils. They are the Langmuir and Freundlich equations. The Langmuir theory assumes a surface free of interaction between the adsorbed elements, which in the soil system is impossible. For this reason many investigators of Mo adsorption by soils have resorted to the Freundlich equation. Fitting of experimental data to the Freundlich curve nevertheless has to be interpreted with caution because of the empirical nature of the equation, and the fact that it does not predict maximum adsorption. Therefore by choosing an arbitrary concentration of Mo in soil solution the sorption characteristics of these soils were compared. At the concentration of 1 µg/ml Mo in solution, sorption of Mo would reflect the cominant mineralogies of these soils. In the case of Paaloa and Wahiawa soil, near-identical isotherms reflected similar parent materials. Both have an olivine-basaltic origin. The Paaloa, however, has less kaolinite and more gibbsite, geothite, haematite and some ilminite (see Appendix 1) than the Wahiawa. Compared to Kaiwiki and Lualualei soils, the Molokai soil was intermediate in sorption tendencies.

The least adsorption was associated with crystalline montmorillonite type clays as in the case of the Lualualei soil. It seems from the x-ray diffractograms (Appendix 1) that the high content of Al and Fe

oxides, especially in the amorphous forms in the Kaiwiki soil, was responsible for high Mo sorption. This observation is supported by the findings of Theng (1971) for a range of soils in New Zealand which covered both crystalline and amorphous soil clays. He found greater Mo adsorption in soils containing allophane (Taupo-allophane) than in those soils with predominantly crystalline minerals (Taita-kaolin, illite). As in our Kaiwiki soil, Gonzales et al. (1974) obtained high adsorption of Mo by Trumao soil, which reflected its high content of amorphous material. These soils are derived from volcanic ash.

The relationship established here suggests that soil mineralogy which controls Mo solubility also determines to a large extent the uptake of the element by plants. The high fixing capacity of the Kaiwiki soil suggests more Mo in the soil than is required by the other soils.

Experiment IV: The Effect of pH and Molybdenum on the Growth of *Desmodium intortum* and *Centrosema pubescens*

Dry Matter Yield

Mean values for the dry matter yields of *Desmodium intortum* and *Centrosema pubescens* are shown in Table 5. Although yields were increased by both Mo and increasing soil pH alone, highest yields were obtained by the addition of both together as indicated by the Mo x pH rate interaction. Application of Mo alone at the rate of 1 kg $NaMoO_4$/ha increased yields by 44 per cent above the control in the case of *D. intortum*. However, *C. pubescens* showed a mere 15 per cent increase above the control in the presence of Mo alone. By increasing the pH of the

TABLE 5 Effect of Molybdenum and Soil pH on D.M. Yield of *Desmodium intorum* and *Centrosema pubescens*

Mo Applied (kg/ha)	Soil pH 4.6	Soil pH 5.5	Soil pH 6.0	Soil pH 6.5
	Yield g/pot[ʃ]			
	Desmodium intortum			
0	11.13f	23.60cd	21.60de	21.00e
1	20.14e	27.11a	24.80abc	24.18bc
2	20.36e	26.16ab	25.31abc	25.00abc
5	21.03e	26.4ab	24.43abc	24.21abc
	Centrosema pubescens			
0	17.10c	20.60b	21.50ab	21.70ab
1	21.10ab	23.20a	22.10ab	22.80ab
2	21.50ab	23.80a	21.70ab	23.13a
5	22.20ab	22.40ab	22.00ab	23.20a

ʃ Mean of three replications for each plant.

Any two means in the body of the table or any two averages on a line or column of the table not followed by the same letter or letters are significantly different at the 5 per cent level as measured by Duncan's Multiple Range Test.

soil or by liming, yields of both plants were increased. The increase due to liming was significant at the pH of 5.5 in both cases. In the absence of lime, as in pH 4.6, Mo rates did not differ significantly beyond the 1 kg Mo/ha rates. A combination of Mo and lime was essential for maximum yield. At pH 5.5 and Mo at the 1 kg $NaMoO_4$/ha rate, D. intortum reached optimum yield. In the case of C. pubescens, the third rate of Mo (2 kg Mo/ha) was adequate for optimum yield. The general trend in the yield differences between D. intortum and C. pubescens is shown in Figures 7 and 8 respectively. The foregoing results indicate that at the highest lime rate, pH 6.5, there was no significant effect from the addition of higher than 1 kg Mo/ha for both indicator plants.

The results indicate that adding lime alone increased yield above the control. This suggests the creation of a more conducive soil/root/rhizobium environment which in turn would facilitate effective nodulation and subsequently fix nitrogen. Under very acid conditions, Andrew (1962) indicated that tropical legumes will respond to increased pH. Dradu (1974) in Uganda found that increase in lime rate increased dry matter yield of D. intortum. Munn et al. (1977) showed positive lime response in D. intortum. In this study, liming to raise pH to 5.5 increased yield significantly. Above pH 6.0 yield decline was evident in D. intortum. C. pubescens equally responded to liming significantly above the control; however, the percentage increase in this instance was much lower than was the case with D. intortum because of the difference in their tolerance to extremely acid conditions. Increase in the lime rate above pH 5.5 for C. pubescens did not increase significantly. These results are in agreement with Munns and Fox (1976), who found maximum

Figure 7: Effect of Soil pH and Mo Levels on D.M. Yield of Desmodium intortum.

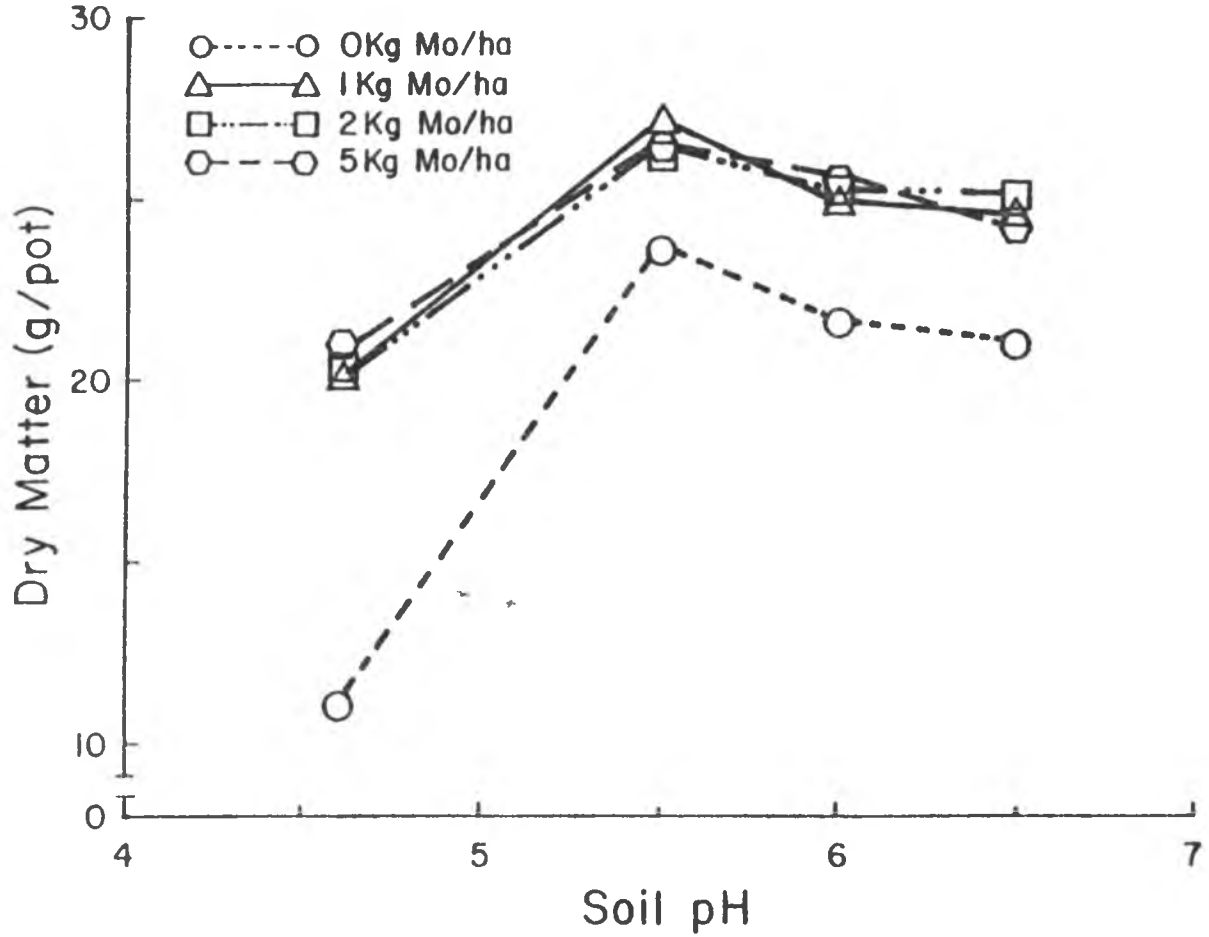
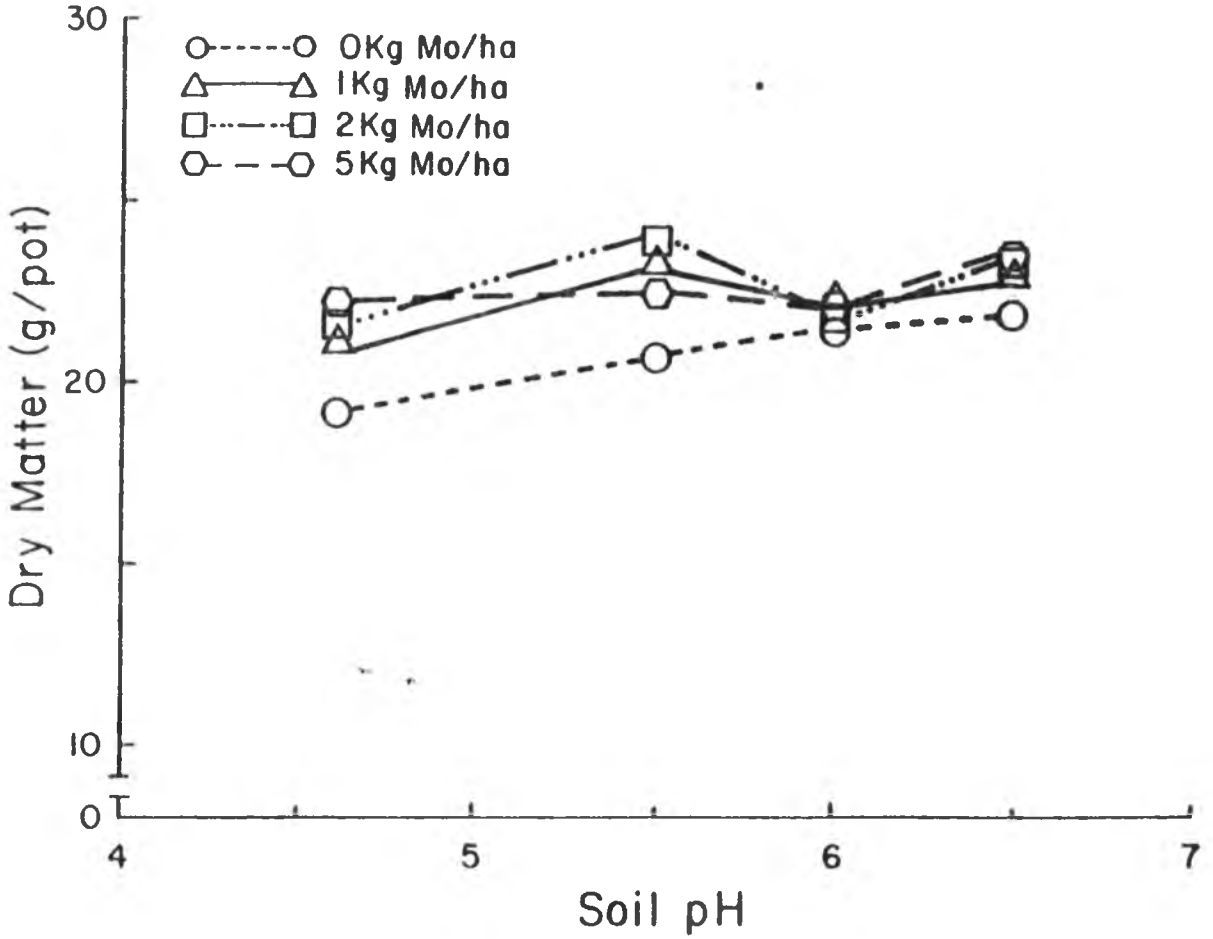

30
20
10
0
4
5
6
7
Dry Matter (g/pot)
Soil pH
0Kg Mo/ha
1Kg Mo/ha
2Kg Mo/ha
5Kg Mo/ha

Figure 8: Effect of Soil pH and Molybdenum Levels on D.M. Yield (g/pot) of Centrosema pubescens.


30
20
10
0
Dry Matter (g/pot)
0Kg Mo/ha
1Kg Mo/ha
2Kg Mo/ha
5Kg Mo/ha
4
5
6
7
Soil pH

response for D. intortum at pH 5.5

Similarly, Mo alone increased yield significantly in both plants. The effect can be attributed to Mo nutrition by leguminous plants. Since the requirement of nitrate reductase enzyme for Mo is very small incomparison to the nodule nitrogenase enzyme needs, it is reasonable to assume that uptake of Mo made the difference. Even the highest Mo level alone failed to give maximum yield except when lime was added. The Mo x lime (pH) interaction increased yield significantly. In the presence of lime, Mo availability is increased, which would improve the general metabolism of the Mo-dependent enzymes. Mo deficiency has been associated with soil acidity. In a red-yellow podzolic soil, De-Potti et al. (1976) found significant yield increases with Mo fertilization of siratro and centrosema. However, when liming soils to pH 5.8, there was also a good response to Mo. At the highest pH level (6.5), Mo addition made no significant yield increases. This is probably because the soil Mo level can suffice for the needs of the plants at high pH levels. The soil used in this study strongly adsorbs molybdate ions. Thus the effect of liming in increasing the uptake of Mo by the plants is due to the effect of OH^- ions displacing MoO_4^{2-} thereby increasing the availability of Mo in the soil rather than any effect of lime increasing the ability of the plant to take up Mo.

Mineral Composition

Plant N: The results in Table 6 show that the application of Mo significantly increased nitrogen content of D. intortum and C. pubescens and that this effect was particularly marked at increasing pH. In both

TABLE 6 Effect of Molybdenum and Soil pH on Total N Content of *Desmodium intortum* and *Centrosema pubescens*

Mo Applied (kg/ha)	*Desmodium intortum*			
	Soil pH			
	4.6	5.5	6.0	6.5
	per cent N[ʃ]			
0	1.41g	1.49fg	1.73efg	2.53abc
1	1.85ef	2.75ab	2.55abc	2.64abc
2	1.83ef	2.58abc	2.45bc	2.33cd
5	2.03de	2.65abc	2.54abc	2.82a
	Centrosema pubescens			
0	1.38i	1.68hi	1.94fgh	2.58bcd
1	1.65hi	2.40cde	2.50bcd	3.04a
2	1.48i	2.00fgh	2.24def	2.79ab
5	1.90gh	2.10efg	2.42cde	2.68abc

ʃ Mean of three replications for each plant.

Any two means in the body of the table or any two averages on a line or column of the table not followed by the same letter or letters are significantly different at the 5 per cent level as measured by Duncan's Multiple Range Test.

plants, the N content was also increased by the application of lime alone. In the absence of both lime and Mo, N levels were low and reached a maximum when soil pH was increased to 6.5. In the presence of Mo, N levels were low but reached maximum when the soil pH was increased to 6.5. In the presence of 1 kg Mo/ha, N levels reached 97 per cent of the maximum at pH 5.5, or at the first increment of lime, in D. intortum. C. pubescens showed similar response to Mo, although their N levels reached maximum at the highest pH level. The addition of both lime and Mo increased the N content of the forage. However, lime did not completely correct N deficiency until the soil had a pH of 6.5 for both legumes. Both gave about 40 per cent increase in N content at the highest pH level over the control, pH 4.6. Application of 1 kg Mo/ha significantly increased the N content for both legumes at every increment of lime (Figures 9 and 10). Adding Mo alone increased the per cent N in both D. intortum and C. pubescens. Lime, too, significantly increased the N content of both plants. The marked interaction of Mo and lime for N content suggests that one of the effects of adding lime is to increase the uptake of Mo, which in turn would increase the symbiotic N_2 fixation. Figure 11 illustrates the effect of such interaction on the leaf color of D. intortum. Anderson and Oertel (1946) showed that lime, by increasing the availability of Mo in the soil, stimulated symbiotic N_2 fixation in nodulated clover. This is particularly true in soils which have high fixation capacities. Mo fertilization of such soils would be economically unfeasible, unless limed.

As a constituent of nitrogenase and nitrate reductase enzyme, the significance of Mo in plant N metabolism cannot be underestimated. Peres

Figure 9: Effect of Soil pH and Molybdenum Levels on the Total N (%) of Desmodium intortum.

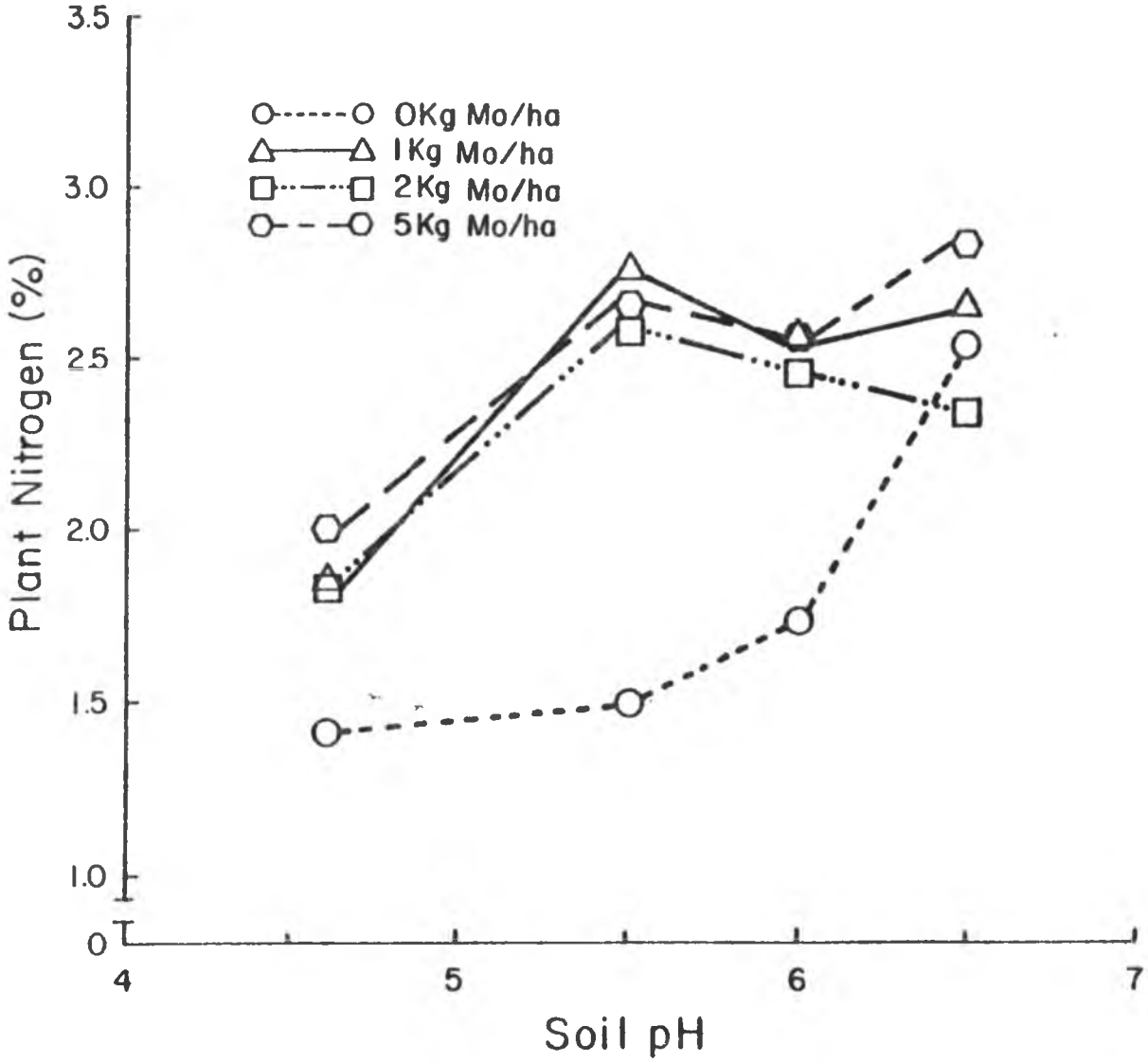
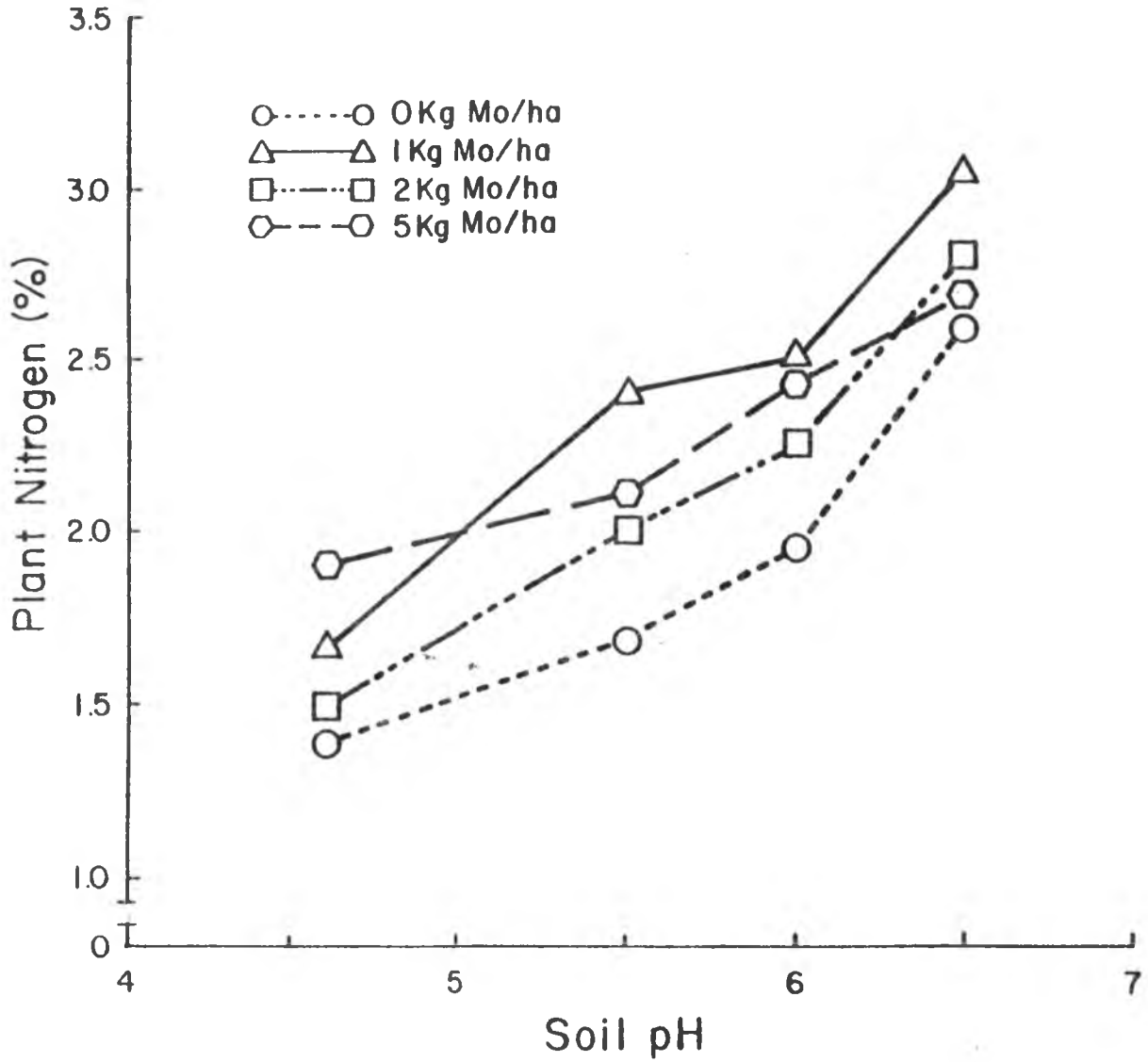

0Kg Mo/ha
1Kg Mo/ha
2Kg Mo/ha
5Kg Mo/ha
Plant Nitrogen (%)
3.5
3.0
2.5
2.0
1.5
1.0
0
4
5
6
7
Soil pH

Figure 10: Effect of Soil pH and Molybdenum Levels on the Plant N (%) of Centrosema pubescens.


0Kg Mo/ha
1Kg Mo/ha
2Kg Mo/ha
5Kg Mo/ha
Plant Nitrogen (%)
3.5
3.0
2.5
2.0
1.5
1.0
0
4
5
6
7
Soil pH

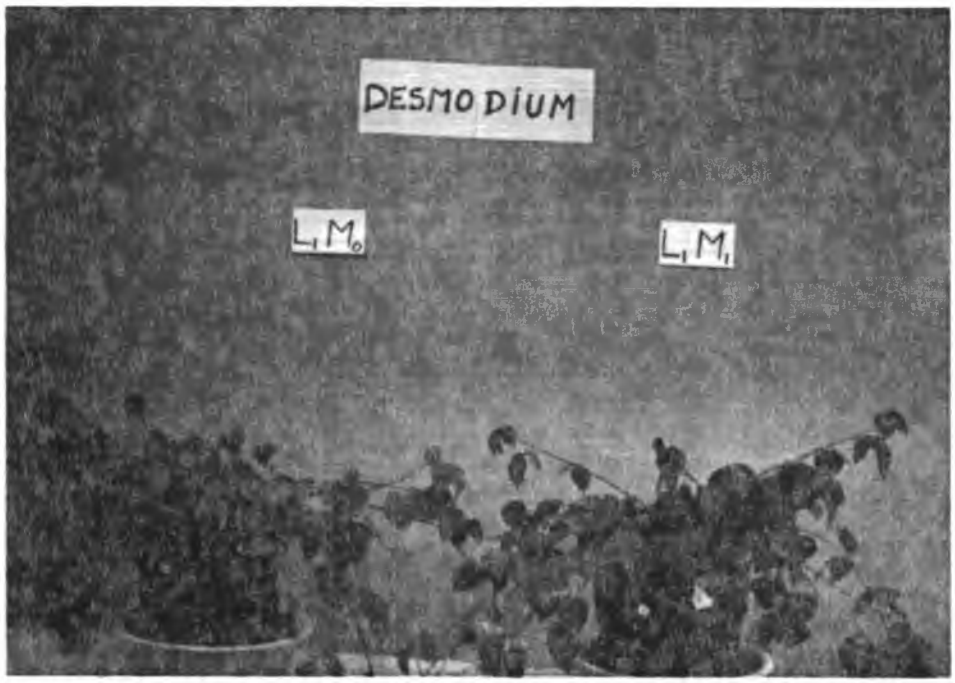


Figure 11: The effect of lime (pH) on the availability of molybdenum in D. intortum (pH x Mo).

L_1M_0: L_1 = pH 5.5

M_0 = 0 kg Mo/ha

L_1M_1: L_1 = pH 5.5

M_1 = 1 kg Mo/ha

et al. (1976) showed an increase in N_2ase activity due to Mo fertilization in the Mo-deficient soils of Rio de Janeiro state. The results of our study supported the findings of Peres et al. (1976) even though their investigation was on a microorganism, Azobacter paspali (Figures 12 and 13). In the presence of 1 kg Mo/ha, N_2ase activity increased with a total increase in plant N of D. intortum and C. pubescens. In general, where the effect of Mo deficiency is evident in leguminous plants, yellowing of the leaves persists (Figure 14). Since the enzymatic transformation of nitrate to ammonium form is mediated by Mo, its deficiency in pasture legumes is reflected as N deficiency (Andrew, 1976).

Plant Phosphorus

Table 7 shows data on P concentration in the plant tissues of D. intortum and C. pubescens. There were no significant differences in P concentration among treatments. Basal fertilization of P was calculated on the basis of P required to give equilibrium concentration of 0.2 ppm P in solution from the sorption curve of Paaloa soil (Figure 2). Neither Mo nor pH nor pH x Mo interaction had any significant effect.

Plant Calcium

In both D. intortum and C. pubescens, Ca levels were increased by liming or increase in pH, as expected. From Table 8 it is evident that Ca concentration at pH 4.6 in all Mo increments were significantly different from the limed treatments in both plants. However, Mo alone without lime (pH 4.6) caused no significant increase in the Ca

Figure 12: Plant N (%) and Nitrogenase Activity of Desmodium intortum as Affected by Soil pH and Molybdenum Fertilizer.

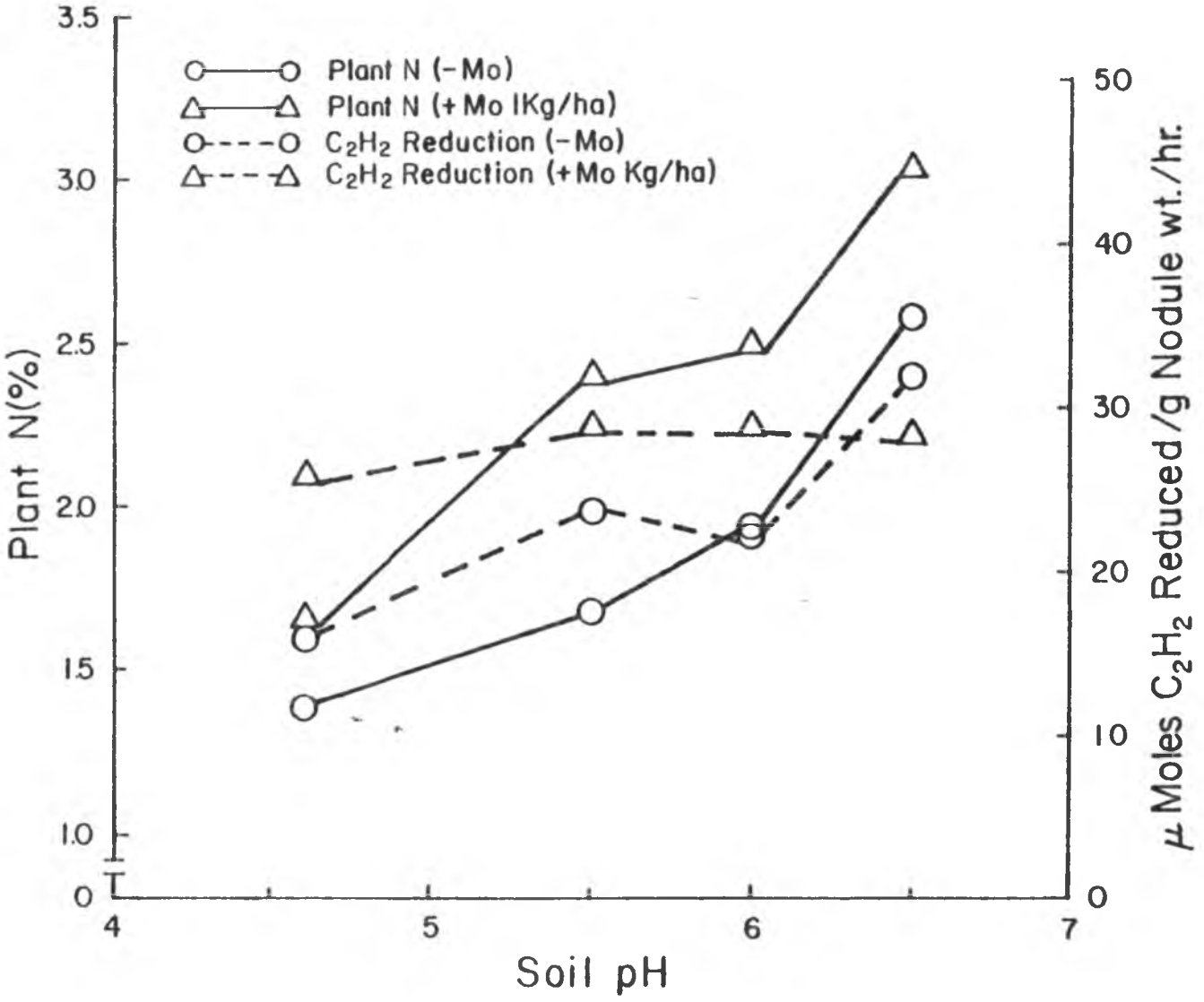

Plant N (-Mo)
Plant N (+Mo 1Kg/ha)
C_2H_2 Reduction (-Mo)
C_2H_2 Reduction (+Mo Kg/ha)
Plant N(%)
μ Moles C_2H_2 Reduced/g Nodule wt./hr.
Soil pH
3.5
3.0
2.5
2.0
1.5
1.0
0
50
40
30
20
10
0
4
5
6
7

Figure 13: Plant N (%) and Nitrogenase Activity of Centrosema pubescens as Affected by Soil pH and Molybdenum Fertilizer.

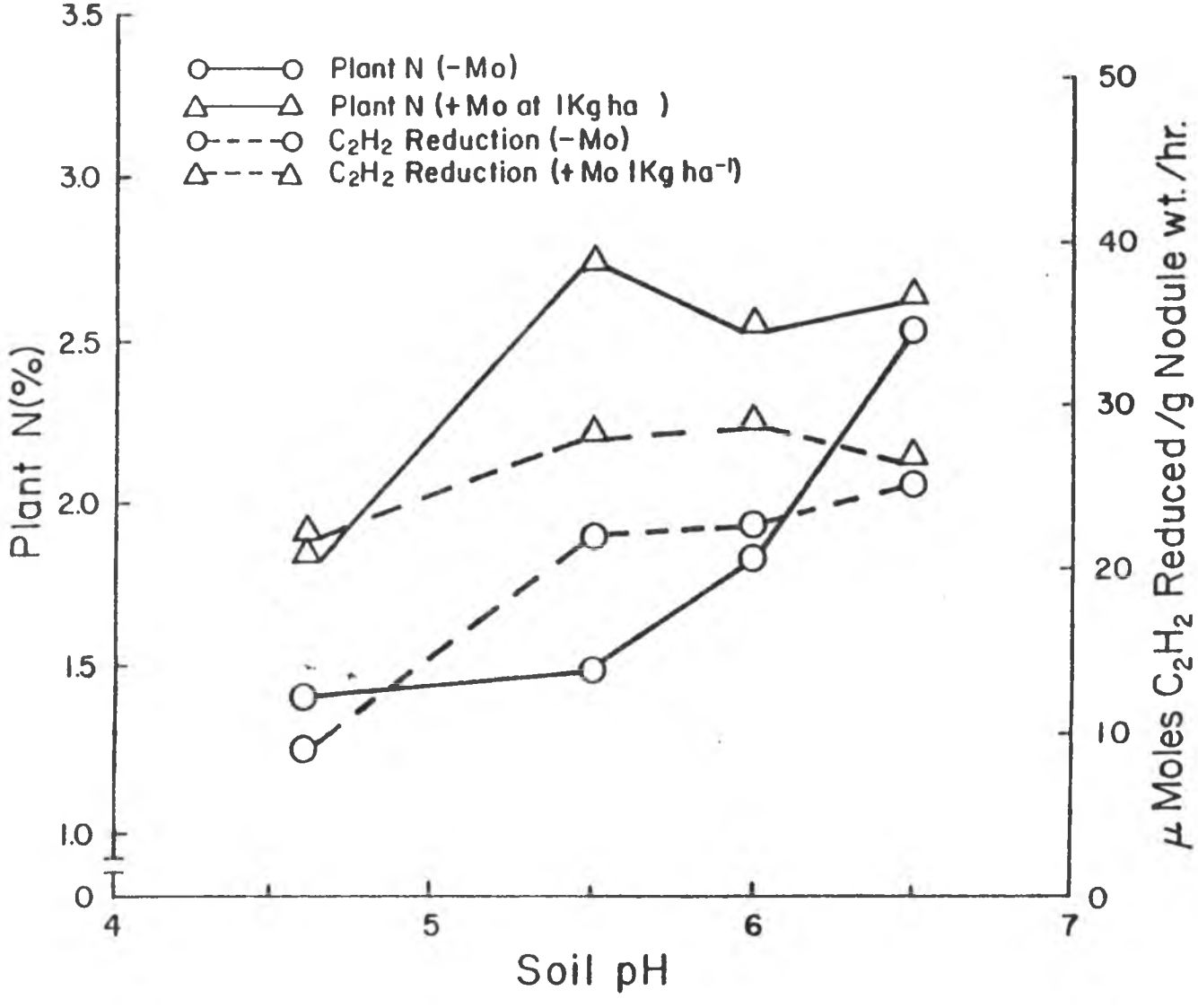

Plant N (-Mo)
Plant N (+Mo at 1Kg ha)
C_2H_2 Reduction (-Mo)
C_2H_2 Reduction (+Mo 1Kg ha^{-1})
Plant N(%)
3.5
3.0
2.5
2.0
1.5
1.0
0
4
5
6
7
Soil pH
50
40
30
20
10
0
μ Moles C_2H_2 Reduced /g Nodule wt./hr.

TABLE 7 The Effect of Mo and Soil pH on the Concentrations of P in the Tops of Desmodium intortum and Centrosema pubescens

Mo Applied (kg/ha)	Desmodium intortum			
	Soil pH			
	4.6	5.5	6.0	6.5
	per cent P∫			
0	0.23a	0.20a	0.20a	0.19a
1	0.20a	0.19a	0.20a	0.20a
2	0.22a	0.18a	0.18a	0.19a
5	0.19a	0.21a	0.17a	0.20a
	Centrosema pubescens			
0	0.21a	0.19a	0.19a	0.19a
1	0.19a	0.17a	0.20a	0.20a
2	0.19a	0.19a	0.20a	0.19a
5	0.18a	0.19a	0.18a	0.20a

∫ Mean of three replications for each plant.

Any two means in the body of the table or any two averages on a line or column of the table not followed by the same letter or letters are significantly different at the 5 per cent level as measured by Duncan's Multiple Range Test.

TABLE 8 Effect of Molybdenum and Soil pH on the Concentration of Calcium in the Tops of Desmodium intortum and Centrosema pubescens.

Mo Applied (kg/ha)	Desmodium intortum			
	Soil pH			
	4.6	5.5	6.0	6.5
	per cent Ca[f]			
0	0.67f	1.30e	1.38de	1.57ab
1	0.72f	1.41cd	1.50bc	1.53ab
2	0.70f	1.41cd	1.41cd	1.42cd
5	0.68f	1.49bc	1.41cd	1.61a
	Centrosema pubescens			
0	0.72e	1.42d	1.46cd	1.59a
1	0.73e	1.41d	1.52abc	1.53abc
2	0.78e	1.53abc	1.45cd	1.53abc
5	0.80e	1.47cd	1.48bcd	1.57ab

[f] Mean of three replications for each plant.

Any two means in the body of the table or any two averages on a line or column of the table not followed by the same letter or letters are significantly different at the 5 per cent level as measured by Duncan's Multiple Range Test.

concentration of the plant tops of C. pubescens and D. intortum. Mo x lime (pH) interaction did not differ significantly except at pH 6.5 and 5 kg Mo/ha for D. intortum.

As expected, the lowest Ca concentrations occured at pH 4.6 in both D. intortum and C. pubescens, because of low Ca in this unlimed treatment. Calcium percentage found in the plant tops falls within the range set by Andrew (1976) for tropical pasture species (0.27 - 1.33 per cent for nodulated species). The high Ca concentrations at high pH level x Mo interaction reflects luxury consumption. These concentrations did not translate into higher D.M. yields either, because at pH 6.5 and 5 kg Mo/ha, yields were not significantly different from pH 5.5 in all Mo increments.

Plant Manganese

It is clear from the data in Table 9 which are averaged graphically in Figures 15 and 16, that level of Mn decreased linearly as pH increased. Application of Mo did not seem to have any significant effect on the Mn concentrations of the plant tissues of both D. intortum and C. pubescens.

The high Mn levels in the treatments without lime (pH 4.6) suggest the possibility of Mn toxicity. However, Munns (1976) established the critical concentration of Mn in the plant tissues of C. pubescens and D. intortum at 1600 and 1260 ppm, respectively. At these levels of Mn concentration yield reduction of 10 per cent will occur. In our experiment the Mn concentration at the pH 4.6 is too low to cause any yield reduction. Nevertheless, the successive drop in Mn concentration

TABLE 9 Effect of Molybdenum and Soil pH on Concentration of Mn in Tops of Desmodium intortum and Centrosema pubescens

Mo Applied (kg/ha)	Desmodium intortum			
	Soil pH			
	4.6	5.5	6.0	6.5
	ppm Mn∫			
0	174a	123bc	96de	47f
1	185a	132b	92e	45f
2	175a	112cd	91e	34f
5	173a	125bc	88e	51f
	Centrosema pubescens			
0	155ab	118c	95d	52e
1	152b	115c	95d	56e
2	168ab	119c	91d	51e
5	172a	126c	84d	55e

∫ Mean of three replications for each plant.

Any two means in the body of the table or any two averages on a line or column of the table not followed by the same letter or letters are significantly different at the 5 per cent level as measured by Duncan's Multiple Range Test.

Figure 15: Effect of Soil pH and Molybdenum Level on the Plant Manganese (ppm) of Desmodium intortum.

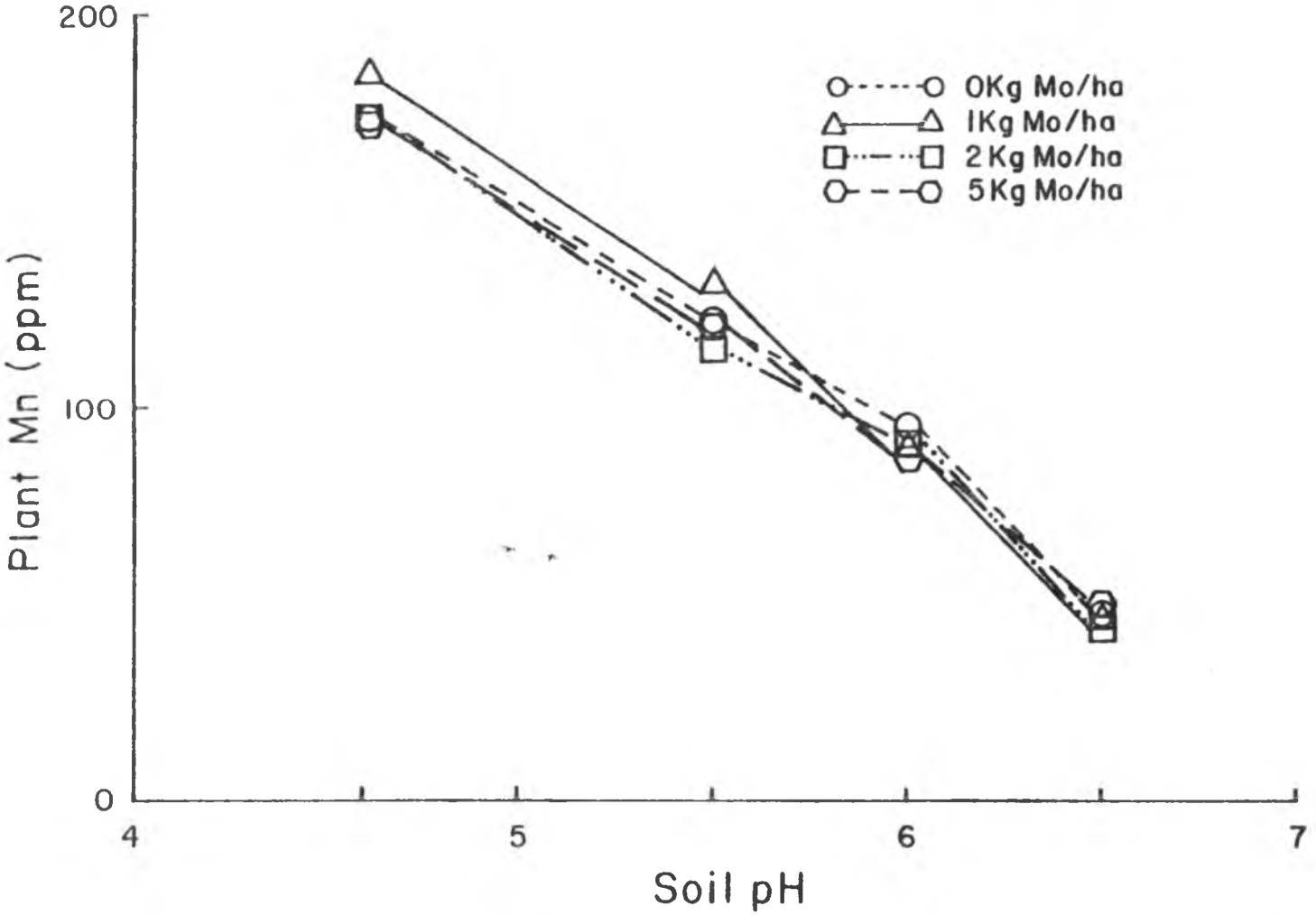
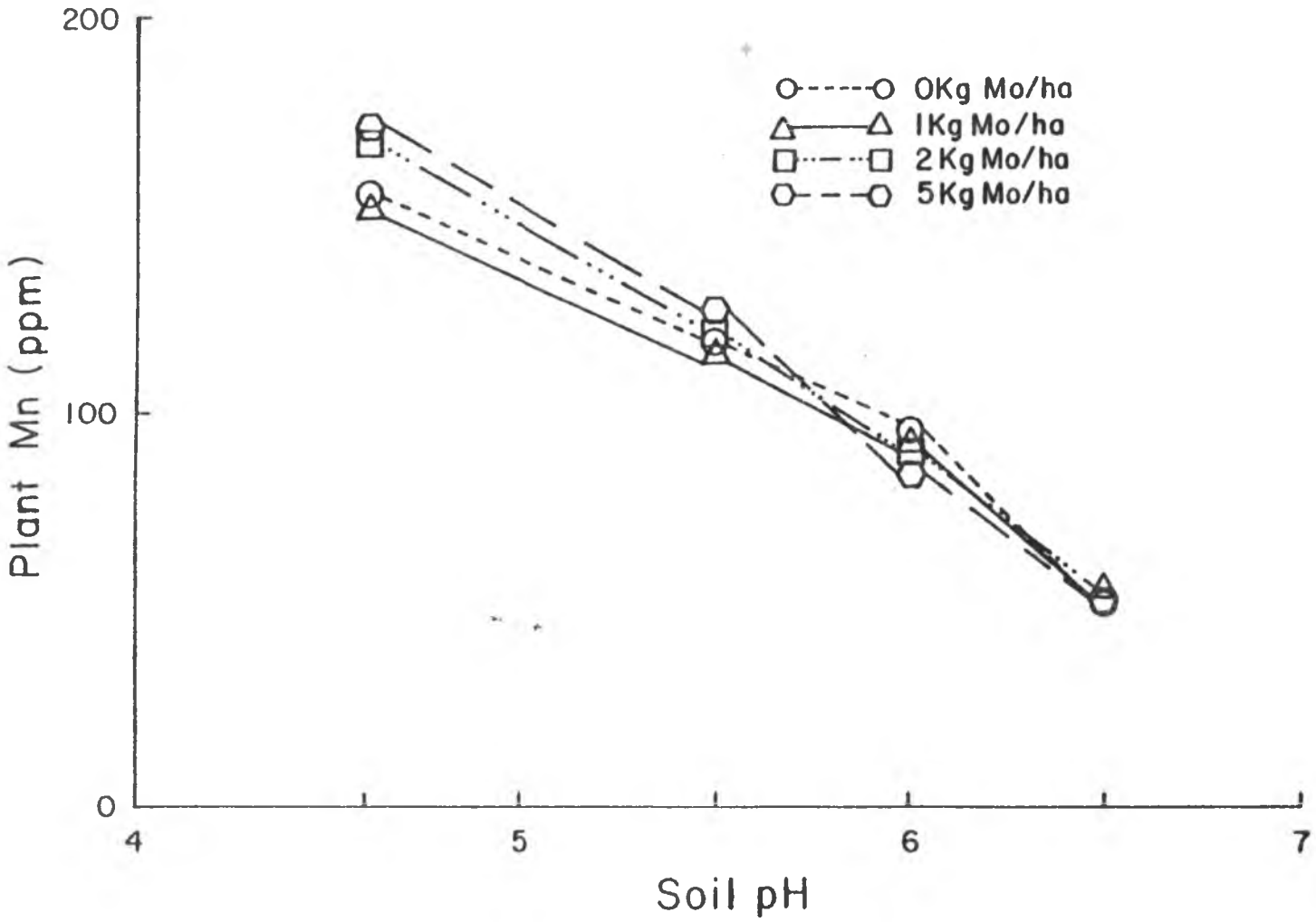

200
100
0
Plant Mn (ppm)
4
5
6
7
Soil pH
0Kg Mo/ha
1Kg Mo/ha
2Kg Mo/ha
5Kg Mo/ha

Figure 16: Effect of Soil pH and Molybdenum Levels on the Plant Manganese (ppm) of Centrosema pubescens.


200
100
0
Plant Mn (ppm)
4
5
6
7
Soil pH
0Kg Mo/ha
1Kg Mo/ha
2Kg Mo/ha
5Kg Mo/ha

is attributable to liming or change in pH. It is interesting to note that at the 0 kg Mo/ha level, increments of lime not only depressed Mn concentration but gave higher N per cent concentration as shown in Table 5. Thus liming made Mn less soluble for uptake, ensured nodulation which eventually led to higher N content in plant tissues.

Plant Zinc

Zinc levels accompanying the basal fertilizers were determined through soil test. Even though Zn concentrations in the plant tissues decreased with increasing pH (Figures 17 and 18), final tissue concentration was within the range of normal growth.

Plant Molybdenum

The concentration of Mo in the plant material is given in Table 10. The concentration of Mo increases significantly with increasing levels of Mo application for D. intortum and C. pubescens. At 0 kg Mo/ha, increased pH did not who any significant difference in the Mo content of the plant top. In the case of D. intortum the low Mo content at 0 kg Mo/ha and pH 4.6 showed acute deficiency symptoms. Since at pH 4.6 every increment of Mo showed no symptom of Mo deficiency, it is reasonable to attribute the deficiency symptom shown (Figure 19) for D. intortum at the zero Mo level solely to Mo. C. pubescens showed no apparent evidence of cupping of the leaves but, like desmodium, total plant N per cent at this zero Mo treatment was low and showed leaf yellowing (Figure 14). The interaction effect of Mo and lime on the Mo content of both plant samples were significantly different from individual

Figure 17: Effect of Soil pH and Molybdenum Levels on Plant Zinc (ppm) of Desmodium intortum.

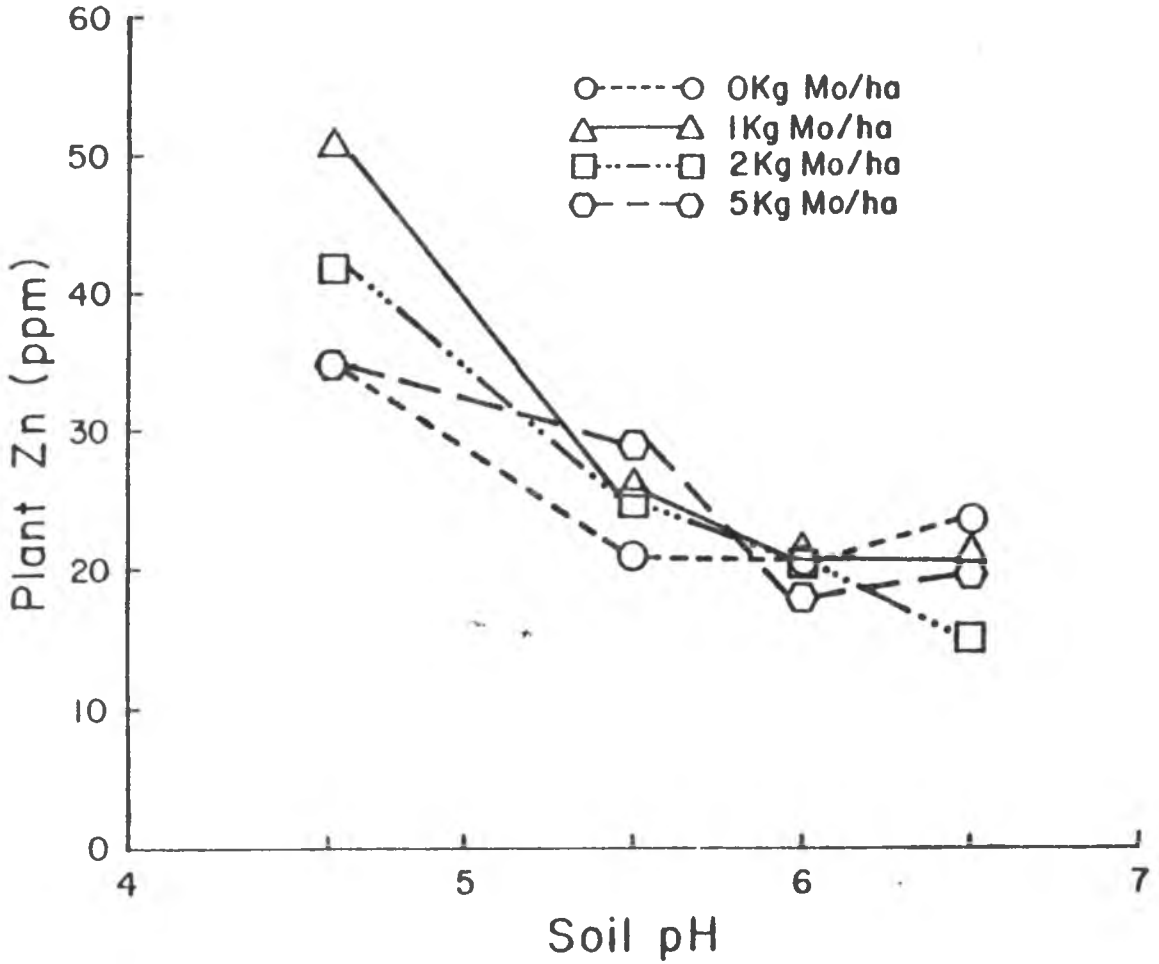

0Kg Mo/ha
1Kg Mo/ha
2Kg Mo/ha
5Kg Mo/ha
Plant Zn (ppm)
60
50
40
30
20
10
0
4
5
6
7
Soil pH

Figure 18: Effect of Soil pH and Molybdenum Levels on Plant Zinc (ppm) of Centrosema pubescens.

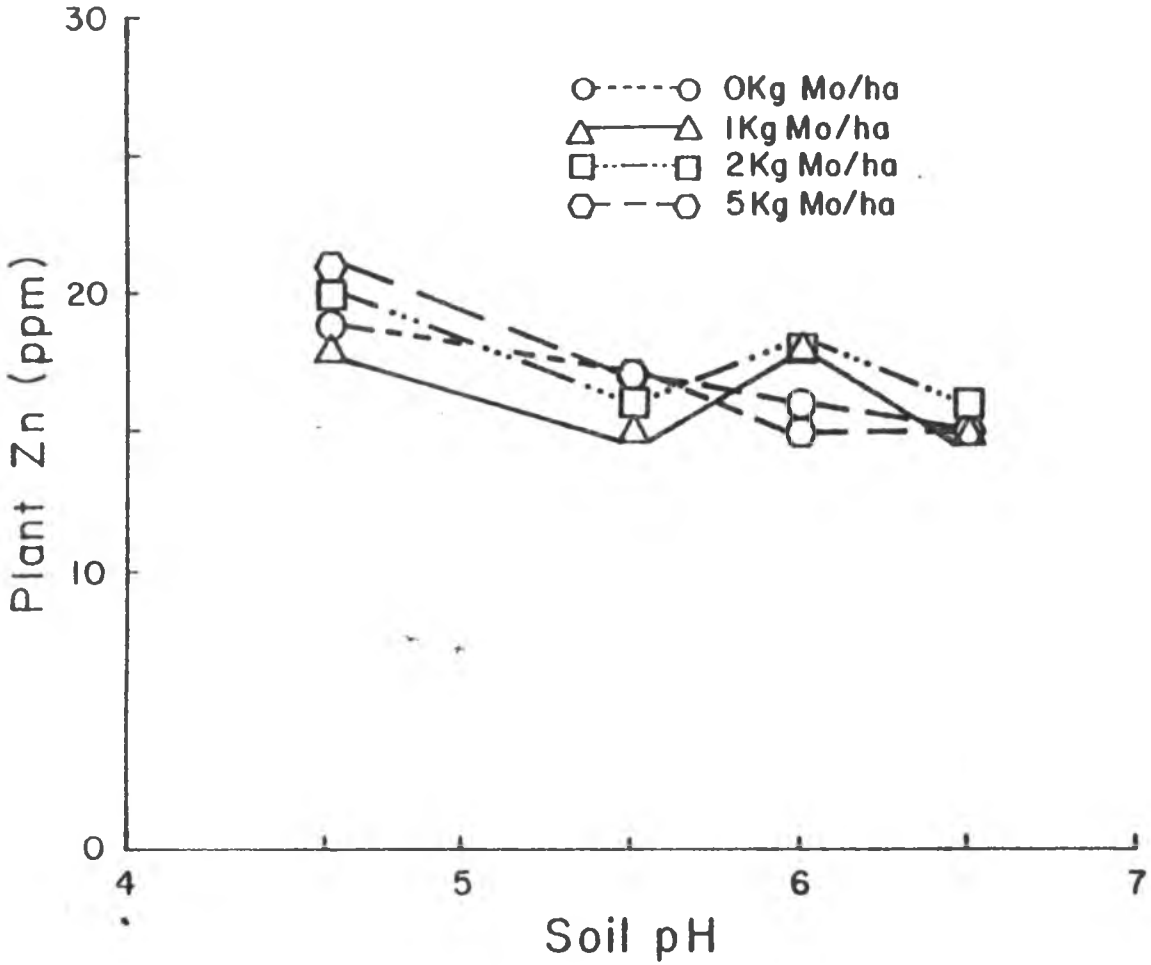

30
20
10
0
Plant Zn (ppm)
4
5
6
7
Soil pH
0Kg Mo/ha
1Kg Mo/ha
2Kg Mo/ha
5Kg Mo/ha

TABLE 10 Effect of Mo and Soil pH on the Concentration of Molybdenum in Tops of Desmodium intortum and Centrosema pubescens

Mo Applied (kg/ha)	Desmodium intortum			
	Soil pH			
	4.6	5.5	6.0	6.5
	ppm Mo[f]			
0	0.03k	0.05jk	0.06jk	0.06jk
1	0.17ij	0.28hi	0.38gh	0.73e
2	0.33h	0.48fg	0.56f	1.82c
5	0.57f	1.35d	0.80b	8.35a
	Centrosema pubescens			
0	0.03i	0.04i	0.07hi	0.07hi
1	0.19h	0.47g	0.96f	1.78d
2	0.48g	0.89f	1.50e	3.36b
5	1.00f	1.86d	2.94c	5.32a

[f] Mean of three replications for each plant.

Any two means in the body of the table or any two averages on a line or column of the table not followed by the same letter or letters are significantly different at the 5 per cent level as measured by Duncan's Multiple Range Test.

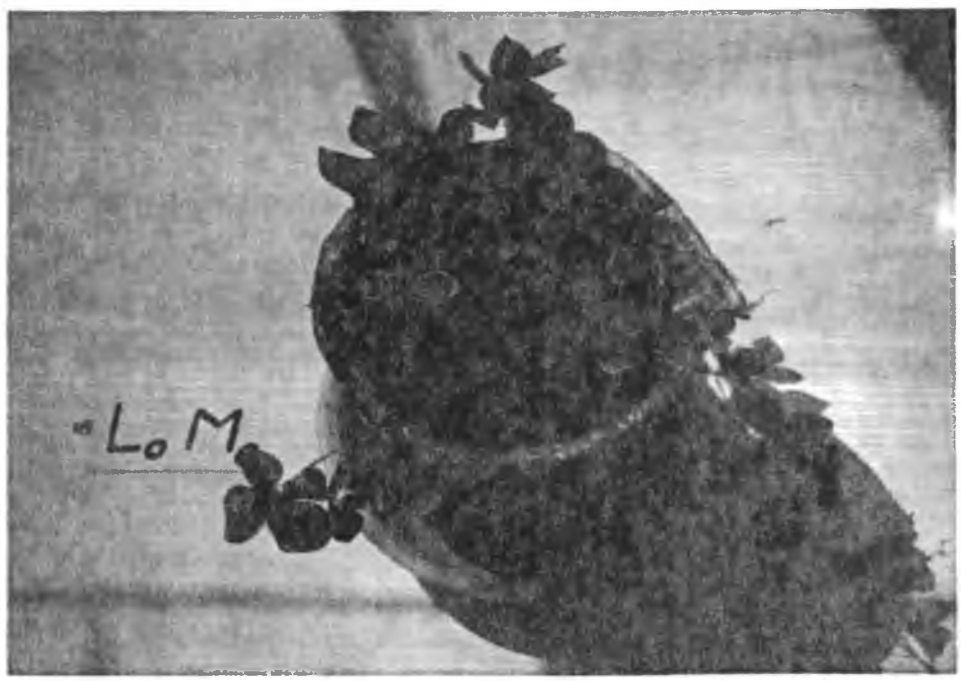


Figure 19: Growing D. intortum in a molybdenum-deficient soil (Paaloa, a Tropohumult). Cupping and interveinal chlorosis emerging.

L_0M_0: L_0 = pH 4.6

M_0 = 0 kg Mo/ha

treatment effect. The Mo content of the forage increased as the pH of the soil increased at successive increments of Mo (Figures 20 and 21). In C. pubescens the 1 kg Mo/ha treatment differs signficantly at every pH level, but with D. intortum the corresponding treatments were not significantly different except at pH 6.5. D. intortum receiving 5 kg Mo/ha at pH 6.5 had a concentration of Mo in the forage which may correspond to toxicity from the standpoint of animal feed.

The response of Mo in this study can clearly be measured from the control treatment, which contained 0.03 ppm. A value of 0.1 ppm of Mo in the dry matter of plant tissues has been considered to represent a value below which Mo deficiency is likely to appear, but the value may vary widely (Anderson, 1956). In an experiment with subterranean clover, Anderson (1956) reported response at 0.5 ppm Mo in plant tissue. This figure appears to be higher than the data reported by Shorrock (1964), who found moderate and extreme deficiencies at 0.22 ppm Mo and 0.06 ppm Mo, respectively, in the leaves of Pueraria phaseoloides. Johansen (1978), in a comparative study on the Mo concentration of some tropical legumes including D. intortum, reported 0.02 ppm or less as sufficiency levels. In our study shoot values less than 0.04 ppm can be reported as maximum to avert severe Mo deficiency symptoms for D. intortum and moderately for C. pubescens (Figure 22). Increases in Mo concentrations at every Mo increment was high at every pH level other than pH 4.6. Because of the fixative capacity of the soil (Paaloa), addition of lime increases the hydroxyl ion concentration which, in effect, will replace molybdate ions on the clay. Therefore, application increases the availability of molybdenum in soil. Liming the soil in the absence of Mo

Figure 20: Effect of Ferilizer Molybdenum at Different Soil pH Levels on the Molybdenum Content of Desmodium intortum (tops).

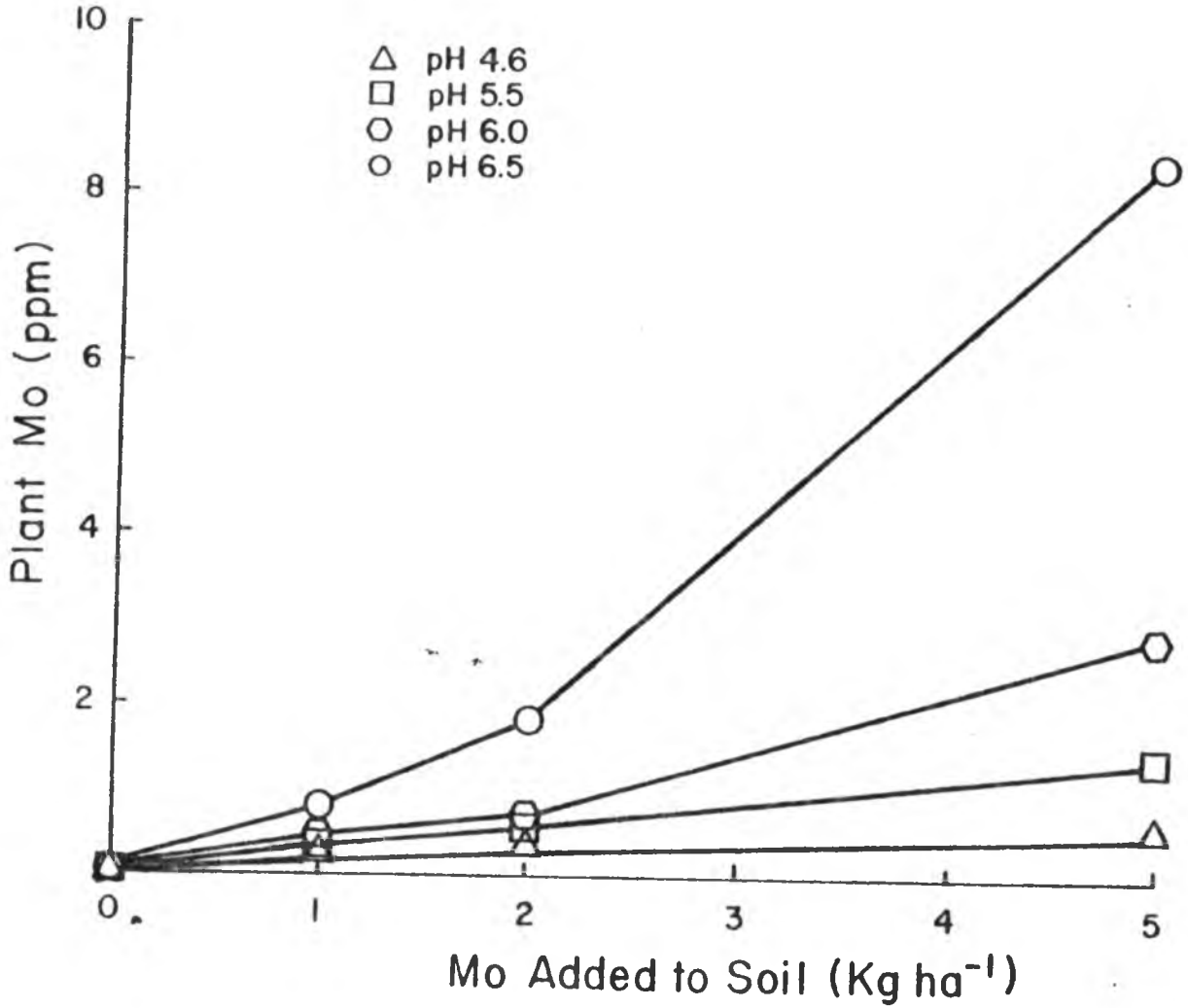
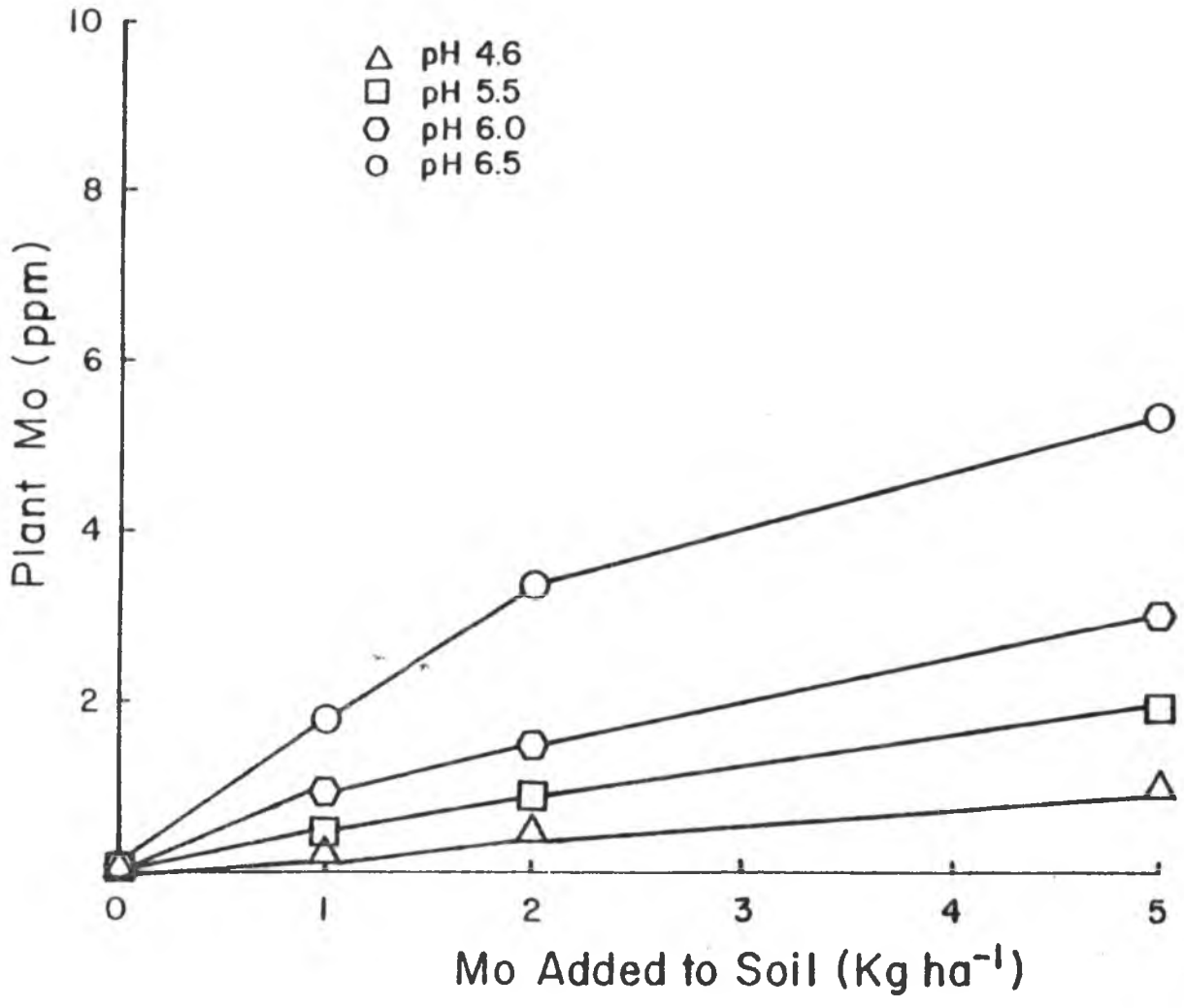

pH 4.6
pH 5.5
pH 6.0
pH 6.5
Plant Mo (ppm)
10
8
6
4
2
0
1
2
3
4
5
Mo Added to Soil (Kg ha^{-1})

Figure 21: Effect of Fertilizer Molybdenum at Different Soil pH Levels on the Molybdenum Content of *Centrosema pubescens* (tops).


pH 4.6
pH 5.5
pH 6.0
pH 6.5
Plant Mo (ppm)
10
8
6
4
2
0
1
2
3
4
5
Mo Added to Soil (Kg ha⁻¹)

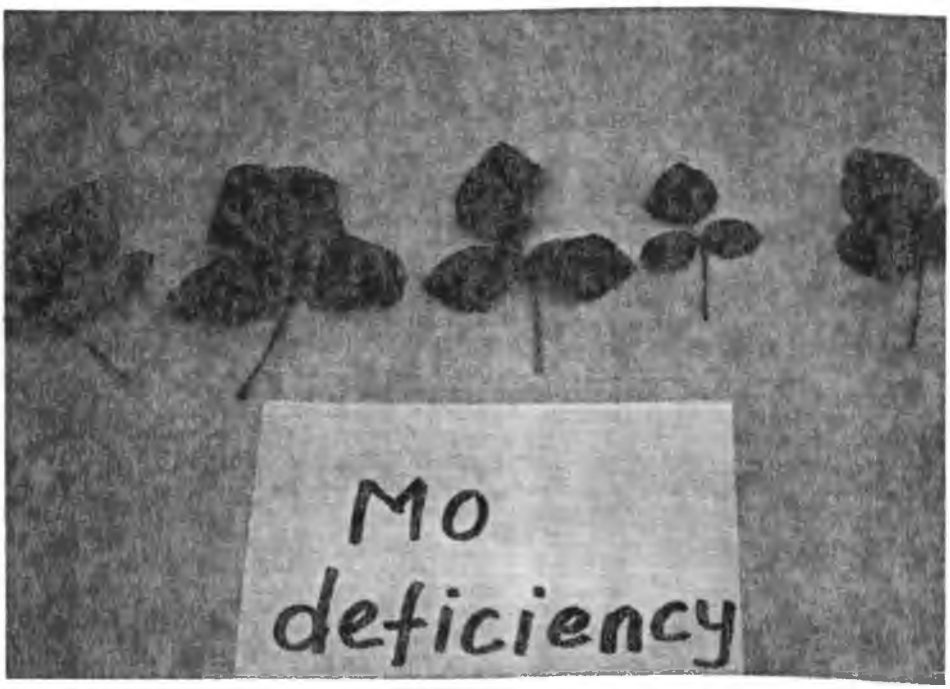


Figure 22: Leaf samples taken from molybdenum-deficient plants (cupping of leaves, diffuse chlorosis).

(0 kg Mo/ha) had no significant effect in the Mo concentration of plant tissues. However, the amount of soil Mo released at these pH levels was sufficient to catalyze reduction of nitrate to ammonium in the nitrate reductase enzyme where the Mo requirement is considerably lower than those of the nitrogenase enzyme. If the soil contains high Mo, liming may increase the Mo content of plants to levels which may cause toxicity. A feed containing 10 ppm of Mo was found toxic to livestock (Dick, 1953, 1956). In Hawaii, forage which caused the so-called "Molokai disease" or "teartness" in cattle was discounted by Fujimoto and Sherman (1951), who found levels too low (2 to 2.5 ppm) to cause alarm. Nevertheless, depending on the concentration of copper in the animal feed tissue Mo contentrations of 8.35 ppm, as evident in this study, may cause "teartness" or molybdenosis. Since there were no cattle on which to test this forage, the toxicity level mentions in this study is purely speculative.

Soil Molybdenum

Soil test values have become useful indices for the establishment of fertilizer needs of crops for a given element. In this study an attempt was made to graphically set a critical level for Mo in soil by plotting relative yields as a function of soil test values, as shown in Figures 23 and 24. Soil samples from this experiment were extracted for Mo availability by using ammonium oxalate buffered at pH 3.3 and 0.1 N NaOH. In the case of 0.1 N NaOH, difficulty in bringing the residues into solution made it difficult to accept their extractable Mo data. From the plots relating per cent relative yields

Figure 23: Relation of $(NH_4)_2C_2O_4$ extractable Molybdenum and Relative Yield at Different pH Levels in Desmodium intortum.

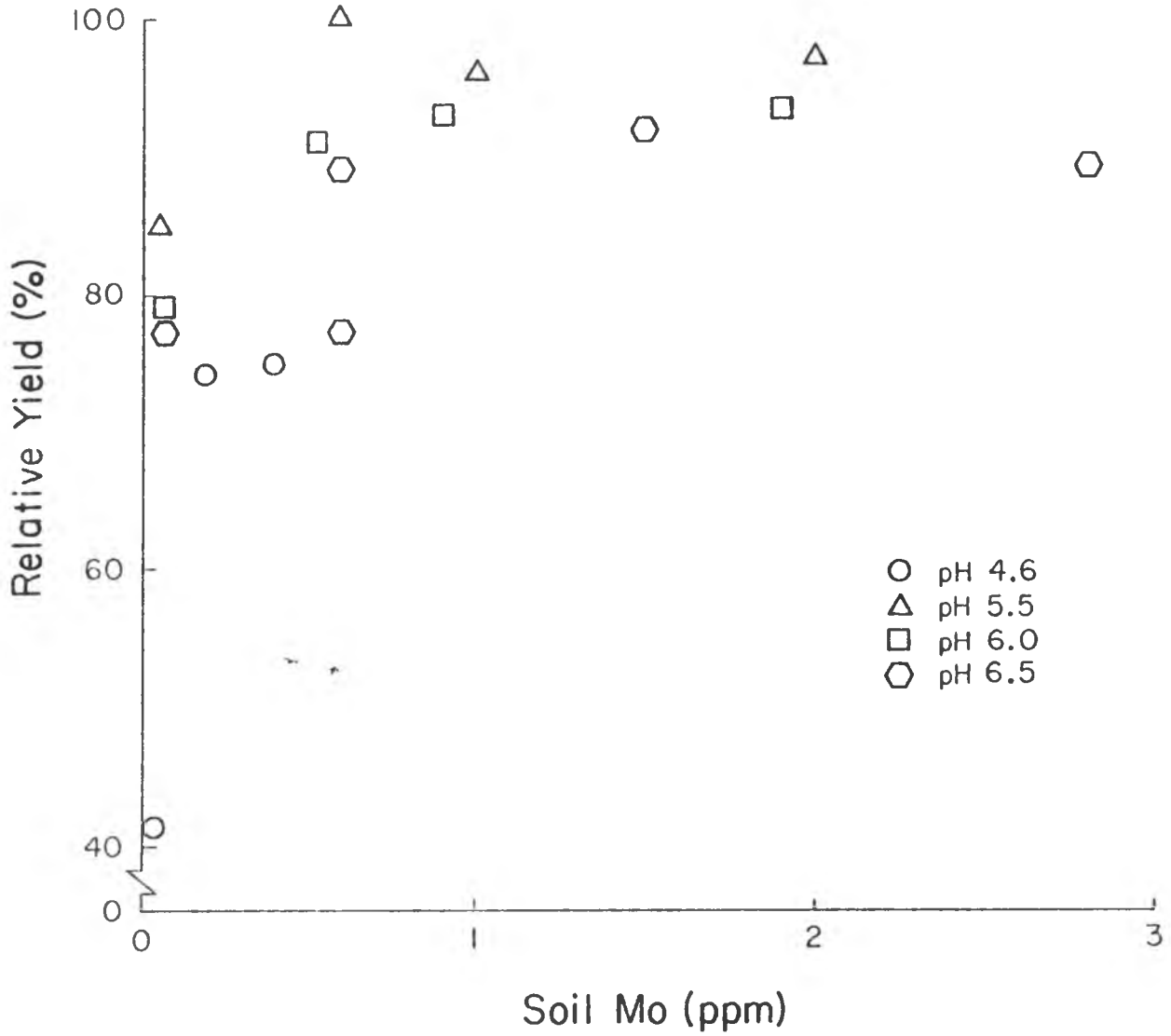
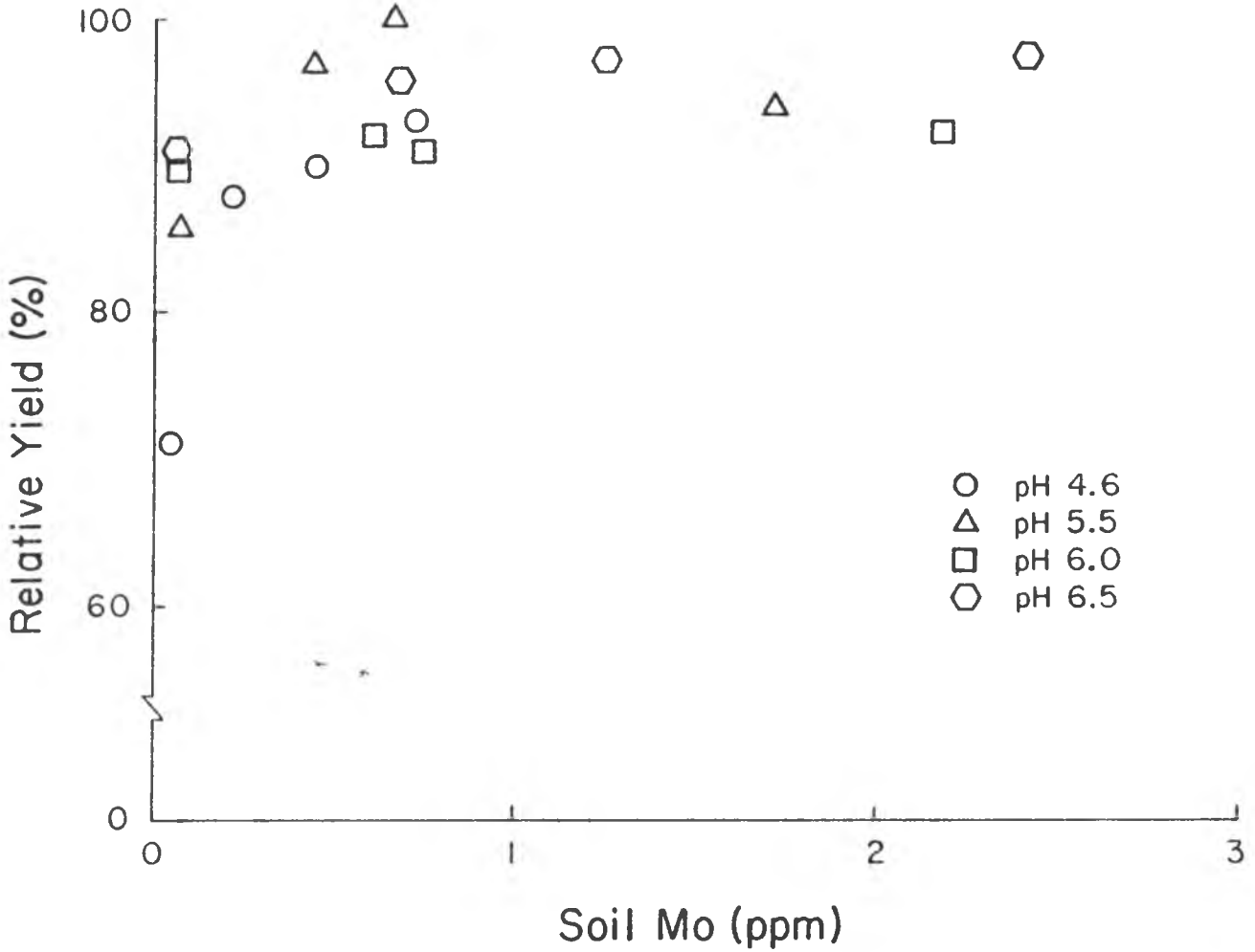

100
80
60
40
0
Relative Yield (%)
0
1
2
3
Soil Mo (ppm)
pH 4.6
pH 5.5
pH 6.0
pH 6.5

Figure 24: Relation of $(NH_4)_2C_2O_4$ Extractable Molybdenum and Relative Yield at Different pH Levels in Centrosema pubescens.


100
80
60
0
Relative Yield (%)
0
1
2
3
Soil Mo (ppm)
pH 4.6
pH 5.5
pH 6.0
pH 6.5

and ammonium oxalate extractable Mo, it was found that at 0.02 to 0.42 ppm of Mo in soil deficiency will occur for D. intortum, and 0.02 to 0.32 ppm for C. pubescens. Walsh et al. (1951) found 0.04 to 0.12 ppm of Mo in the soils where Mo deficiency occurred. The discrepancy in this instance could be due to the characteristics of the soil in use. Soil test for Mo is still a problem, because current methods are cumbersome and researchers have concluded differently in correlation studies by some common extractants.

Acetylene Reduction Assay

Data in Table 11 show the effect of Mo and pH on acetylene reduction by the root nodules of D. intortum and C. pubescens. An application of 1 kg Mo/ha significantly increased the rate of C_2H_2 reduction by 59 per cent over the control in D. intortum and by 36 per cent over the control for C. pubescens. The different rates of Mo addition gave significantly higher C_2H_2 reduction values than of the control. Raising the soil pH at the 0 kg Mo/ha treatment significantly increased the rate of C_2H_2 reduction over that of the original soil pH of 4.6 in both plants (Table 11). Except at pH 6.5 in C. pubescens, C_2H_2 reduction at pH 5.5 and 6.0 were not significantly different. The Mo x pH interaction gave significantly higher reduction at high Mo and high soil pH levels. However, in both plant samples C_2H_2 reduction rates were extremely high at the 5 kg Mo/ha rate without lime. It seems evident from the foregoing that Mo made the difference (Figures 25 and 26). This deviates from the advantages that the interaction effect displayed in the other parameters already discussed.

TABLE 11 Effect of Molybdenum and Soil pH on Acetylene Reduction by *Desmodium intortum* and *Centrosema pubescens*

Mo Applied (kg/ha)	Soil pH			
	4.6	5.5	6.0	6.5
	Desmodium intortum			
	C_2H_2 reduction µmole/g nodule wt/hr∫			
0	9.10e	22.63d	22.67d	25.03bcd
1	22.52d	28.41abc	29.31ab	26.92bcd
2	23.26cd	22.82d	28.49abc	27.05bcd
5	28.11abc	32.97a	27.52bcd	27.43bcd
	Centrosema pubescens			
0	16.19e	23.82cd	22.47d	32.08a
1	25.00bcd	29.11ab	29.17ab	28.49abc
2	29.40ab	27.24abcd	28.65abc	32.68a
5	28.83abc	25.21bcd	28.44abc	31.16a

∫ Mean of three replications for each plant.

Any two means in the body of the table or any two averages on a line or column of the table not followed by the same letter or letters are significantly different at the 5 per cent level as measured by Duncan's Multiple Range Test.

Figure 25: Effect of Soil pH and Molybdenum Levels on the Nitrogenase Activity of *Desmodium intortum*.

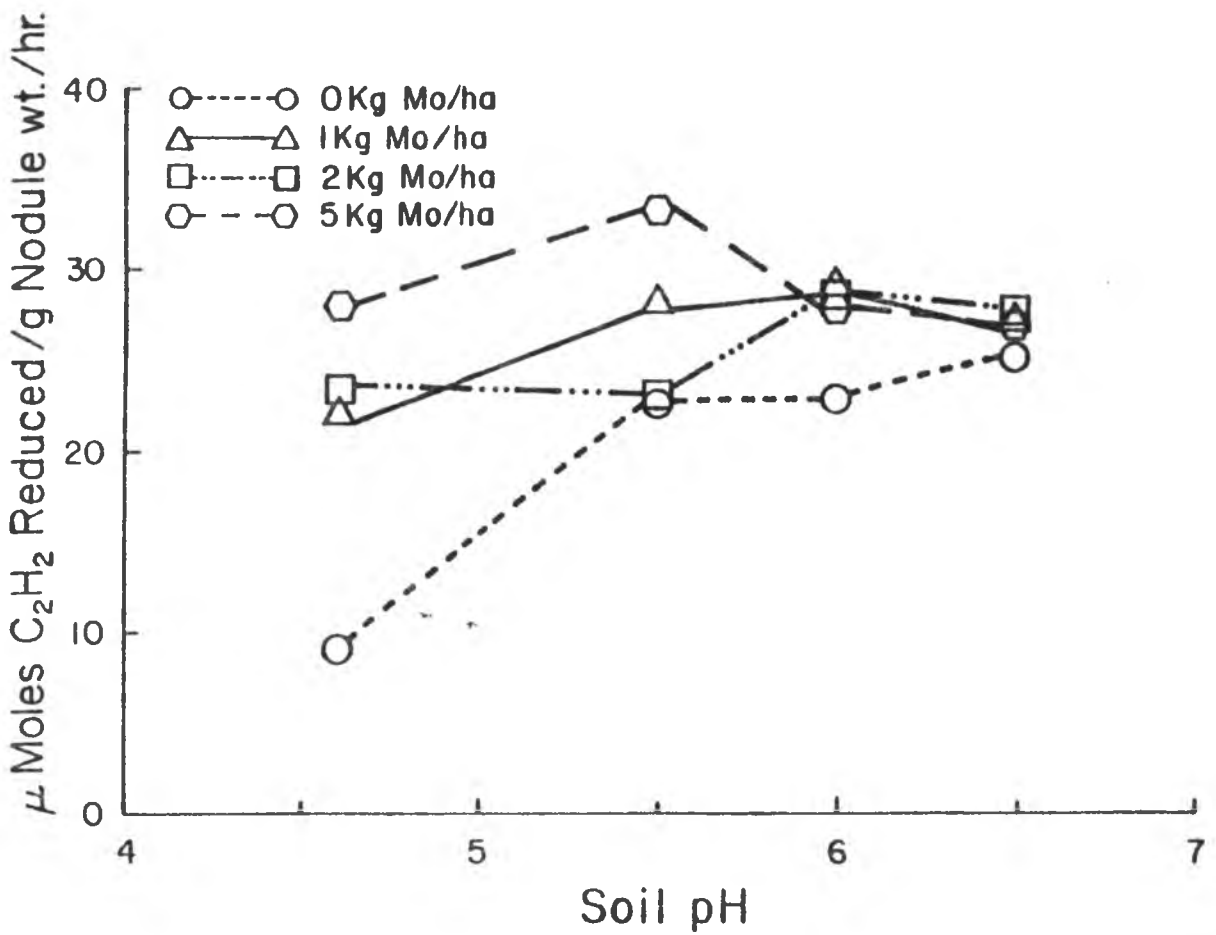
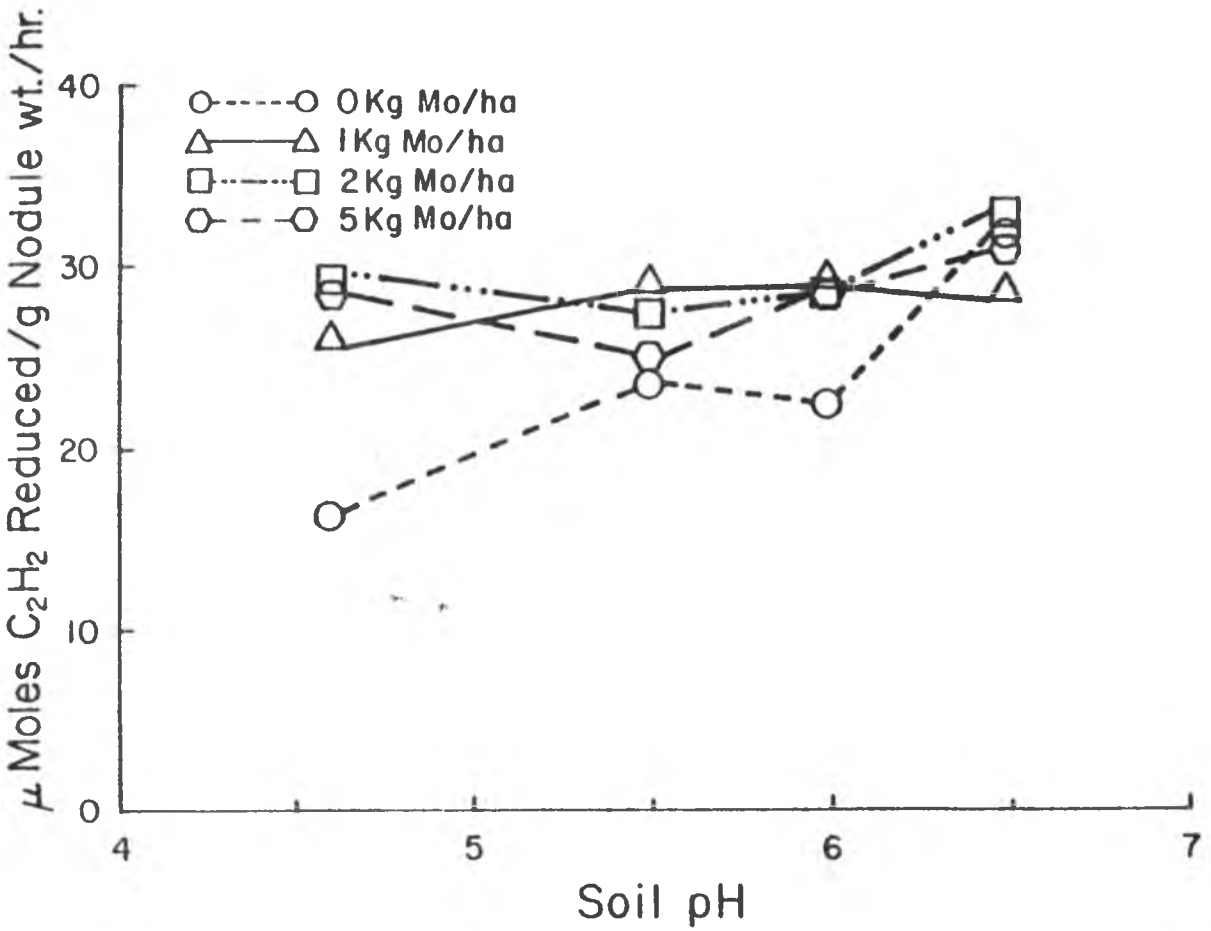

0Kg Mo/ha
1Kg Mo/ha
2Kg Mo/ha
5Kg Mo/ha
μ Moles C_2H_2 Reduced/g Nodule wt./hr.
40
30
20
10
0
4
5
6
7
Soil pH

Figure 26: Effect of Soil pH and Molybdenum Levels on the Nitrogenase Activity of Centrosema pubescens.


0 Kg Mo/ha
1 Kg Mo/ha
2 Kg Mo/ha
5 Kg Mo/ha
μ Moles C_2H_2 Reduced/g Nodule wt./hr.
40
30
20
10
0
4
5
6
7
Soil pH

Acetylene reduction is mediated through the nitrogenase enzyme system where Mo is a constituent. Therefore if the element is not limiting, the H_2 evolved by the nitrogenase, an untapped energy resource, would reduce the highly bonded acetylene to ethylene. For this reason 5 kg Mo/ha at pH 4.6 did not differ significantly with treatments of high Mo and high pH. However, the inference one can deduce from this has to be tentative because of the inevitable loss of nodules during the harvest of roots for acetylene reduction assay. Franco (1976) reported great increases in acetylene reducing activity and total N with liming and Mo fertilization. This is in concordance with the findings of this study. In the presence of Mo, acetylene reduction activity increased significantly over the nil Mo application for both plant samples (see Figures 12 and 13). The effect of Mo in nitrogenase activity or C_2H_2 reducing activity was studied by dissecting the nodules in the Mo treatments. The observations indicated the presence of a red leghemoglobin pigment that is associated with plant actively fixing N. In the nil treatments, the nonactive greenish pigments were evident.

The nodule size for D. intortum showed differences but no difference was observed in the case of C. pubescens. The nodules of the Mo-treated pots were large in size and few in number. Nodule count and per cent N in forage has been inversely related (Anderson and Spencer, 1950). The higher the nodule count the lower the total N content of the forage. Since root nodules are the site of N_2ase activity, the low nodule counts on the Mo-treated roots supports the fact that the lower the nodule count the higher the N content of the plant tissues. In the case of C. pubescens the nodules, naturally large, were not affected

Figure 27: The Relationship Between Nodule Weight (g/pot) and Nitrogenase Activity of Desmodium intortum.

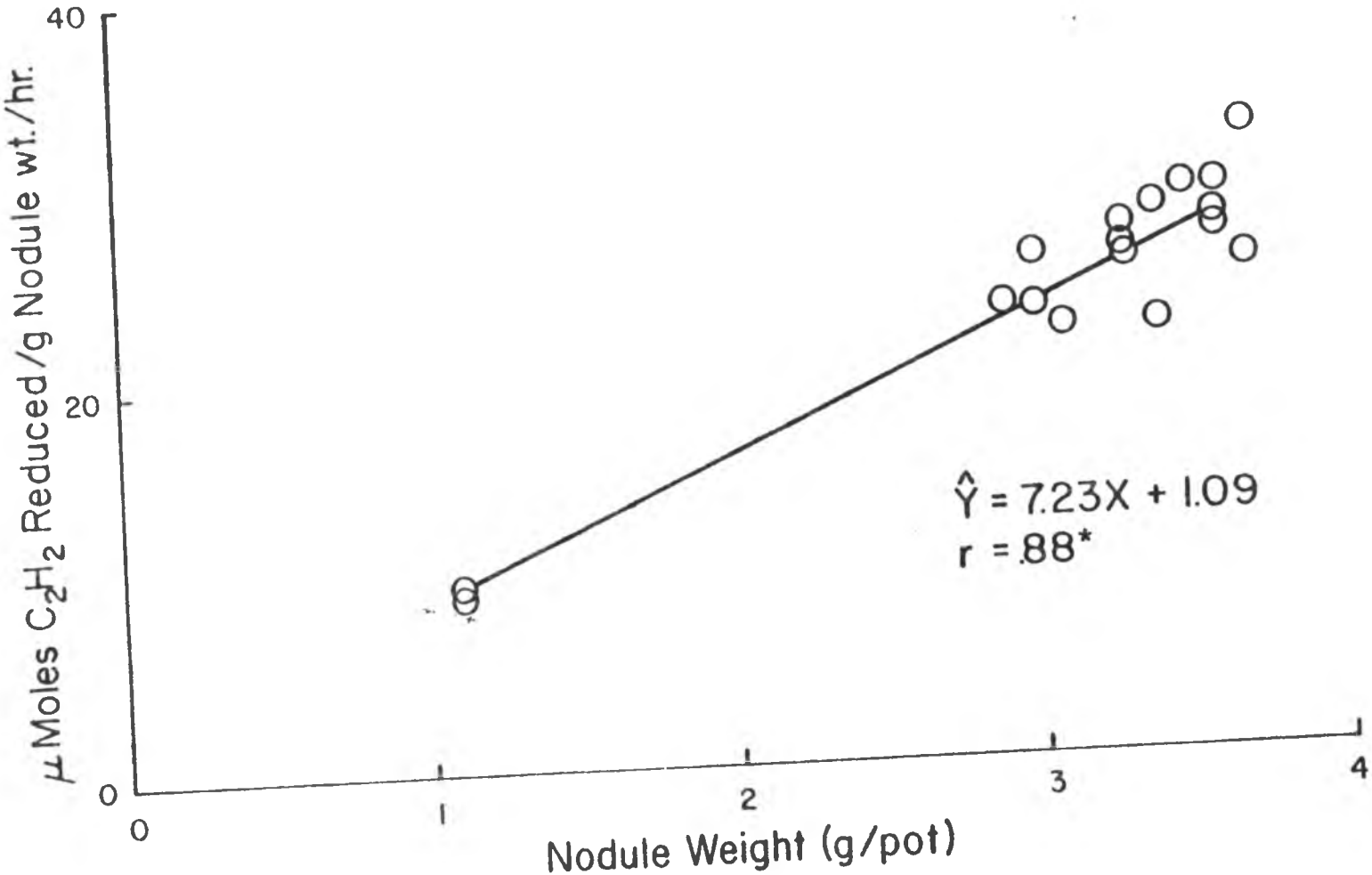
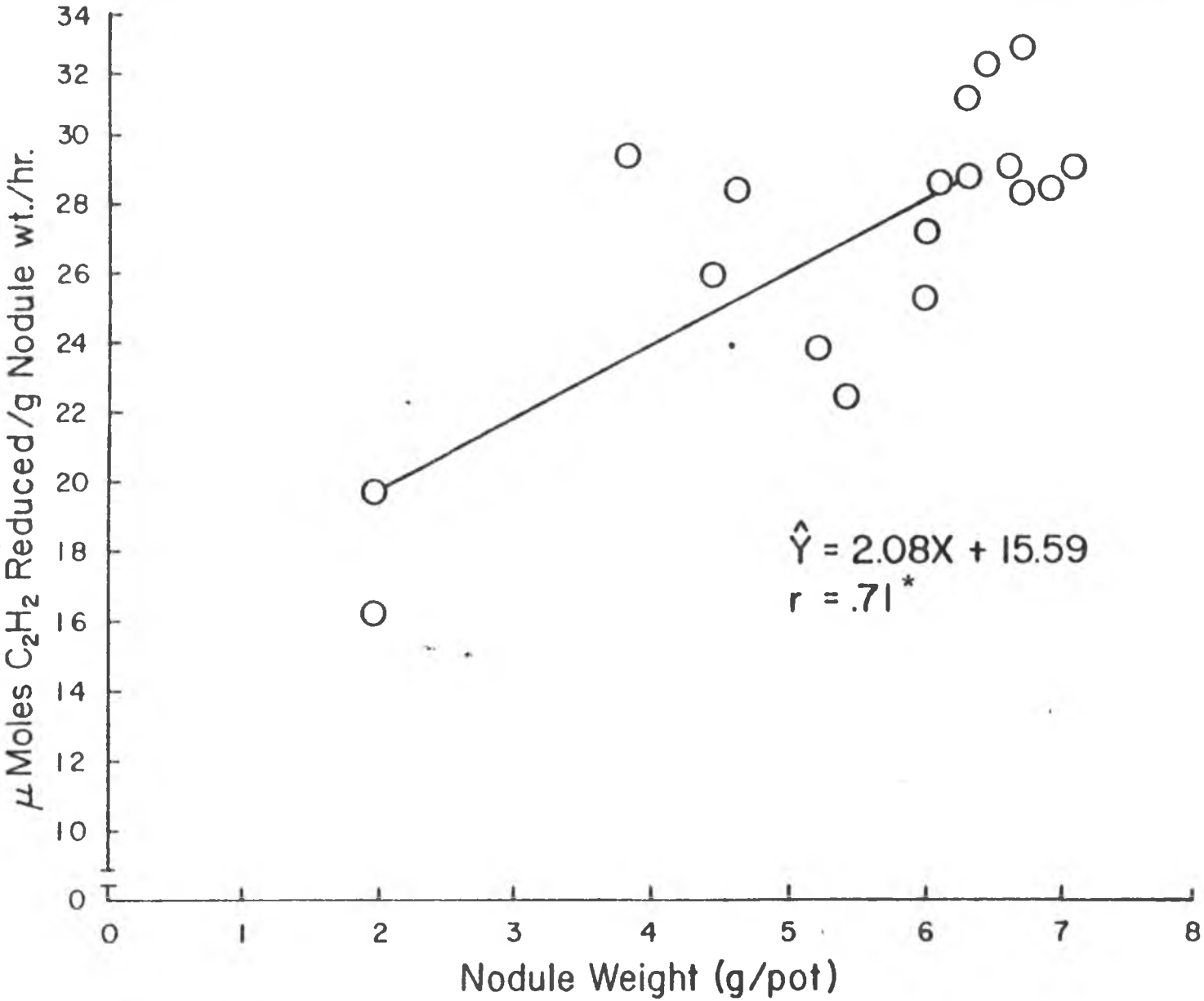

40
20
0
0
1
2
3
4
μ Moles C_2H_2 Reduced/g Nodule wt./hr.
Nodule Weight (g/pot)
$\hat{Y} = 7.23X + 1.09$
r = .88*

Figure 28: Relationship Between Nodule Weight (g/pot) and Nitrogenase Activity of Centrosema pubescens.


34
32
30
28
26
24
22
20
18
16
14
12
10
0
μ Moles C_2H_2 Reduced/g Nodule wt./hr.
0
1
2
3
4
5
6
7
8
Nodule Weight (g/pot)
$\hat{Y} = 2.08X + 15.59$
$r = .71^*$

by Mo fertilization. However, their leghemoglobin reflected Mo treatments and we did see a significant correlation between their weights and nitrogenase (C_2H_2) activity (Figures 27 and 28).

Nodule Weight

Figures 29 and 30 show the effect of soil pH and Mo level on the nodule weight of C. pubescens and D. intortum. At the initial pH level (pH 4.6) few nodules were found. With each lime increment there was increased nodulation. Application of 1 kg Mo/ha increased nodule weight. Further increases in Mo rate did not give any significant change. The pH x Mo interaction showed increased fresh weight at high level of both pH and Mo in C. pubescens over D. intortum. Low fresh weights at pH 4.6 for both plants can be attributed to the effect of H^+ ion concentration on nodulation, because of a sensitivity of Rhizobium root infection to H^+ ion concentration. With increasing pH, the medium becomes more conducive to nodulation or survivability of the Rhizobium in the soil medium. Adding Mo reduced the number of nodules but increased their sizes (Anderson and Spencer, 1950). The difference in the average nodule weights of both plants can be explained in terms of the different morphological structure of the nodules. C. pubescens, large and oblong, weighed more than the tiny numerous nodules of D. intortum.

Figure 29: Effect of Soil pH and Molybdenum Levels on Nodule Weight (g/pot) of Desmodium intortum.

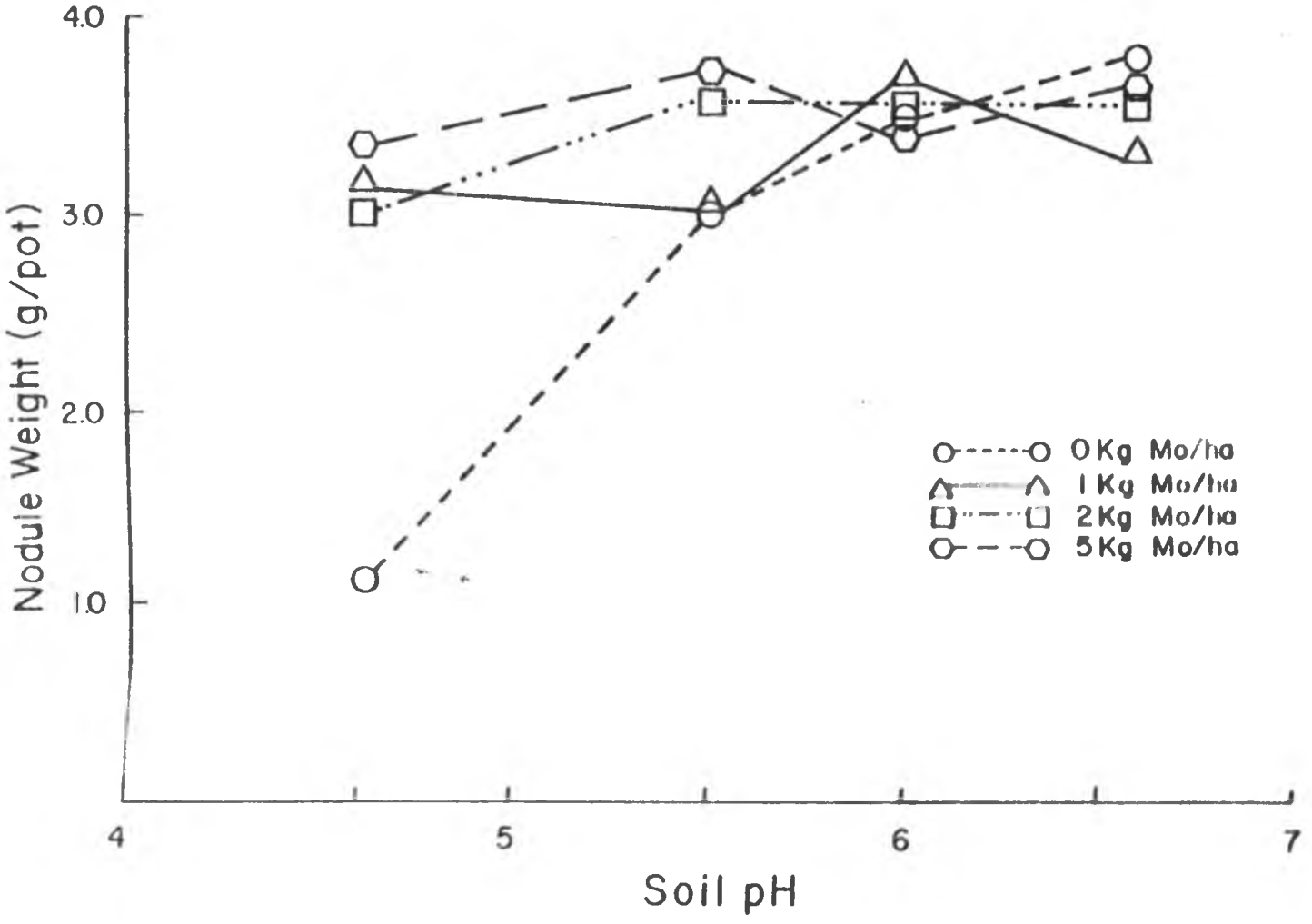
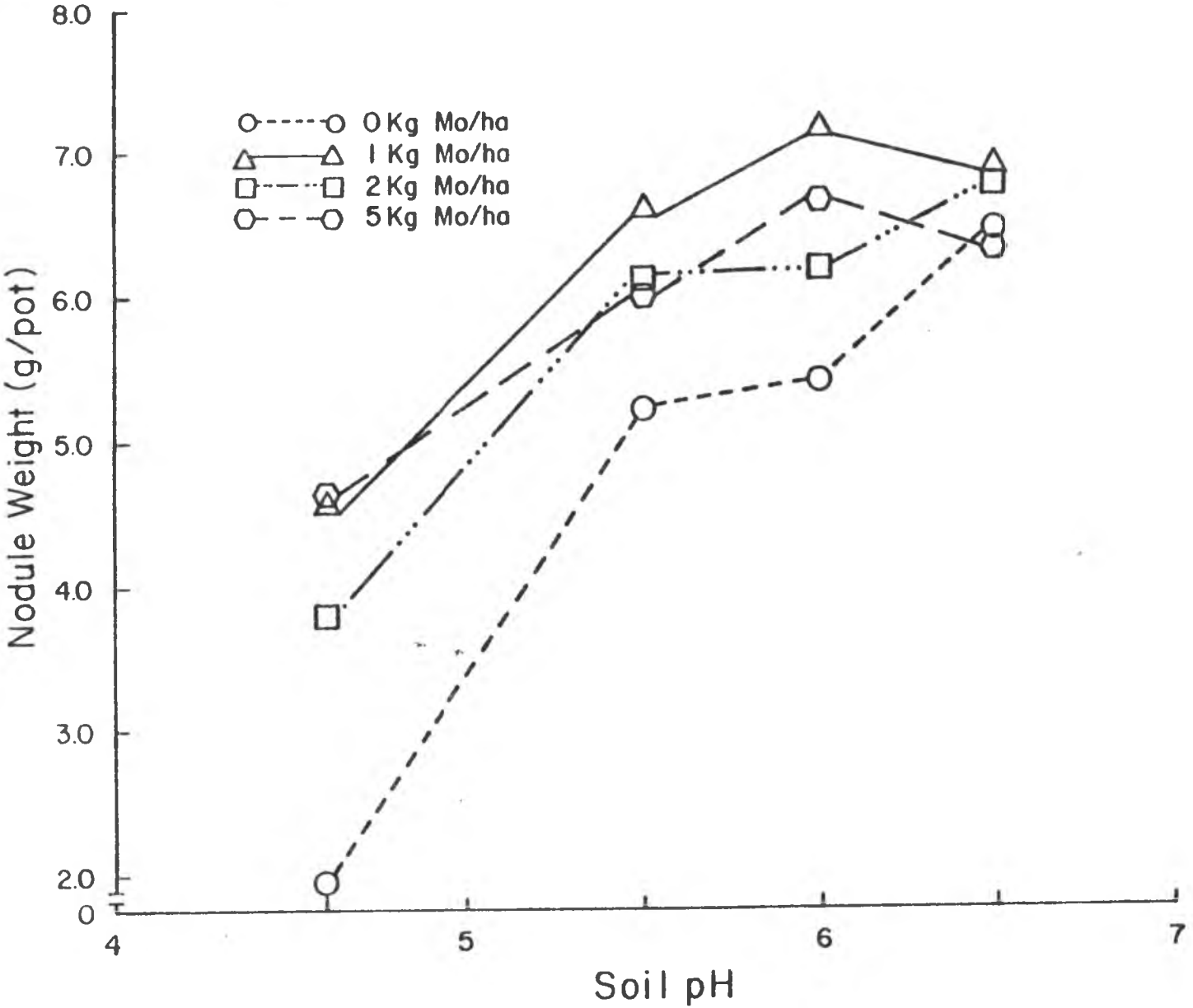

4.0
3.0
2.0
1.0
Nodule Weight (g/pot)
4
5
6
7
Soil pH
0 Kg Mo/ha
1 Kg Mo/ha
2 Kg Mo/ha
5 Kg Mo/ha

Figure 30: Effect of Soil pH and Molybdenum Levels on the Nodule Weight (g/pot) of *Centrosema pubescens*.


8.0
7.0
6.0
5.0
4.0
3.0
2.0
0
Nodule Weight (g/pot)
0 Kg Mo/ha
1 Kg Mo/ha
2 Kg Mo/ha
5 Kg Mo/ha
4
5
6
7
Soil pH

Conclusion

The evidence discussed in this study shows that legume rtilization in the highly weathered soils of the tropics cannot be rrowed down into a single parameter effect. A series of chain reacons takes place. These soils which belong to the constant-surface-tential type colloidal are inherently devoid of nutrients. Their clay actions are dominated by amorphous materials, gibbsite, geothite, ematite, ilminite and kaolinite, which give them a tremendous capacity adsorb nutrients such as phosphate, sulfate and molybdate anions. herefore to manage these soils in order to improve their cation exhange characteristics, liming has become a matter of course in the ropics.

With the exception of the Lualualei soil, a montmorillonitic clay ineral, all the soils used in this study adsorbed molybdate anion. By ncreasing the pH of the soil suspension beyond 4.5, Mo adsorption was ecreased tremendously in the order: Lualualei < Molokai < Wahiawa < aaloa < Kaiwiki. The capacity to adsorb was found to be a function f the mineralogical composition of the investigative soil. More MoO_4^{2-} nion was adsorbed by amorphous material of the Kaiwiki soil than by he montmorillonite of the Lualualei soil. The time at which equilirium condition was reached varied from one to eight hours for most of the soil samples. In the case of the Lualaulei soil, Mo adsorption as a function of time was constant because of the virtual absence of any surface minerals with fixing capabilities.

From the foregoing it is reasonable to conclude that liming can

·ove Mo nutrition of plants grown in the highly weathered soils of tropics. The application of Mo alone increased yield, per cent ·ogen and Mo content of D. intortum and C. pubescens. Increasing pH of the soil tends to increase yield and per cent N. At the st increment of lime, pH 5.5, Mo increased both yield and per cent ignificantly for both plants. The response to Mo was essentially a rogen response. Since there was a definite beneficial effect of Mo lication on yield, per cent nitrogen, and mineral composition, even the absence of liming, it is reasonable to conclude that the effect the first increment of lime, pH 5.5, was mainly to increase the ıilability of Mo in the soil. Since these legumes are quite adaptable low soil Ca content, the benefits of liming can be attributed to the lease of their limiting nutrients. For all practical purposes, the rst increment of lime (pH 5.5) and Mo (1 kg Mo/ha) can be considered equate to ensure both increased yield and nitrogen content of plants, d effective and efficient nodules. This recommended rate averts de- ciency or toxicity, provides availability of Mo, and ensures maximum ·owth of tropical pasture legumes growing in an acid soil.

APPENDIX I

X-Ray Diffraction Studies

The five soils used in this study were ground and screened through a 325-mesh seive. The powdered samples were filled into an aluminum slide underlined by a glass slide to ensure fill and fit. The sample slide was fitted into a holder in the Philips XRG 3100 x-ray diffractometer and analyzed for its mineral composition. The x-ray diffractometer has a long, fine focus, copper target x-ray tube operated at 40 kv, 40 mA constant potential.

The goniometer was fitted with a curved graphite crystal monochrometer, operated in a high resolution configuration.

Continuously compensating slit system was employed which ensured that exactly the same amount of sample was exposed to the x-ray beam at all diffraction angles.

Figure 1: X-Ray Diffractogram of the Silt, Clay Fractions of a Paaloa Soil.

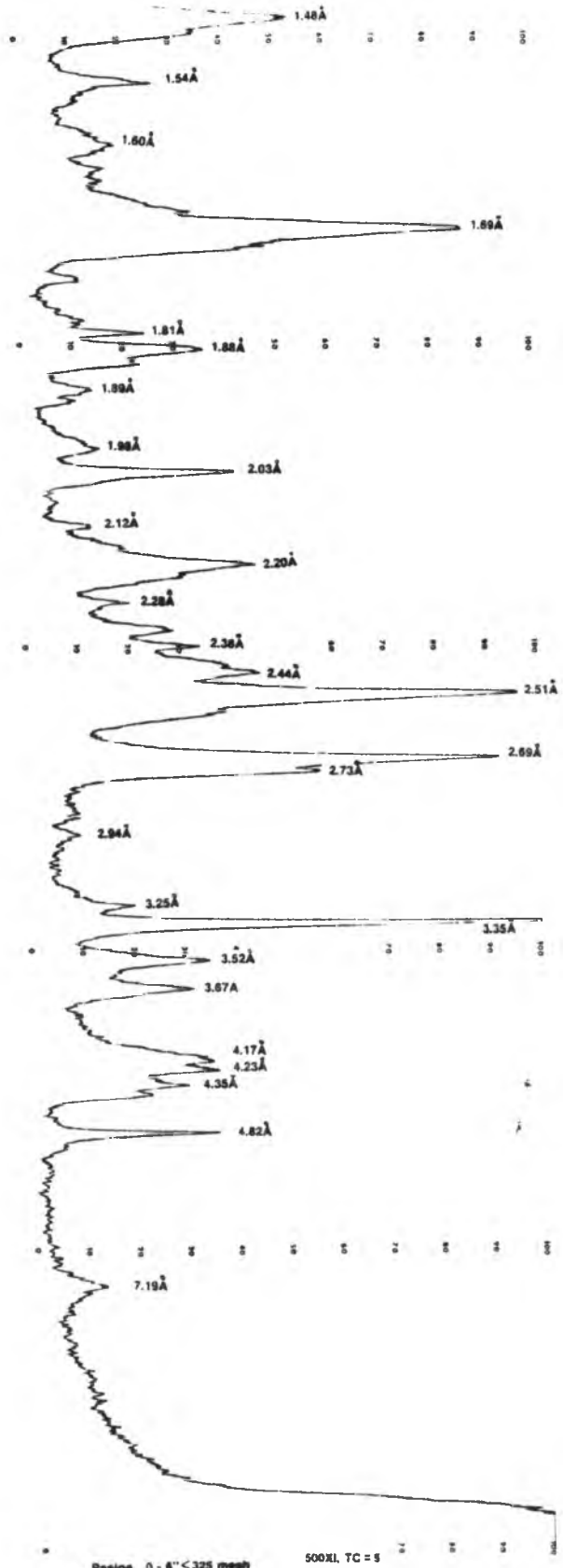
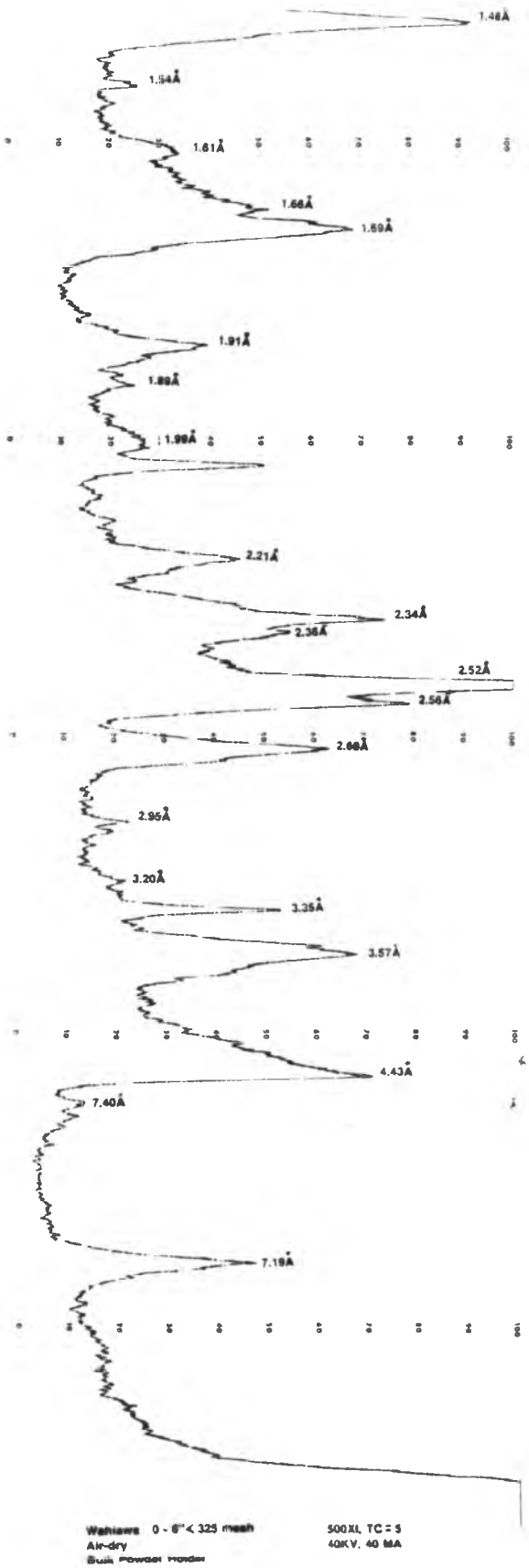

1.48Å
1.54Å
1.60Å
1.69Å
1.81Å
1.88Å
1.89Å
1.98Å
2.03Å
2.12Å
2.20Å
2.28Å
2.36Å
2.44Å
2.51Å
2.69Å
2.73Å
2.94Å
3.25Å
3.35Å
3.52Å
3.67A
4.17Å
4.23Å
4.35Å
4.82Å
7.19Å
Pasico 0 - 6" < 325 mesh
Air-dry
Bulk Powder Holder
500XI, TC = 5
40KV, 40 MA

Figure 2: X-Ray Diffractogram of the Sil, Clay Fractions of a Wahiawa Soil.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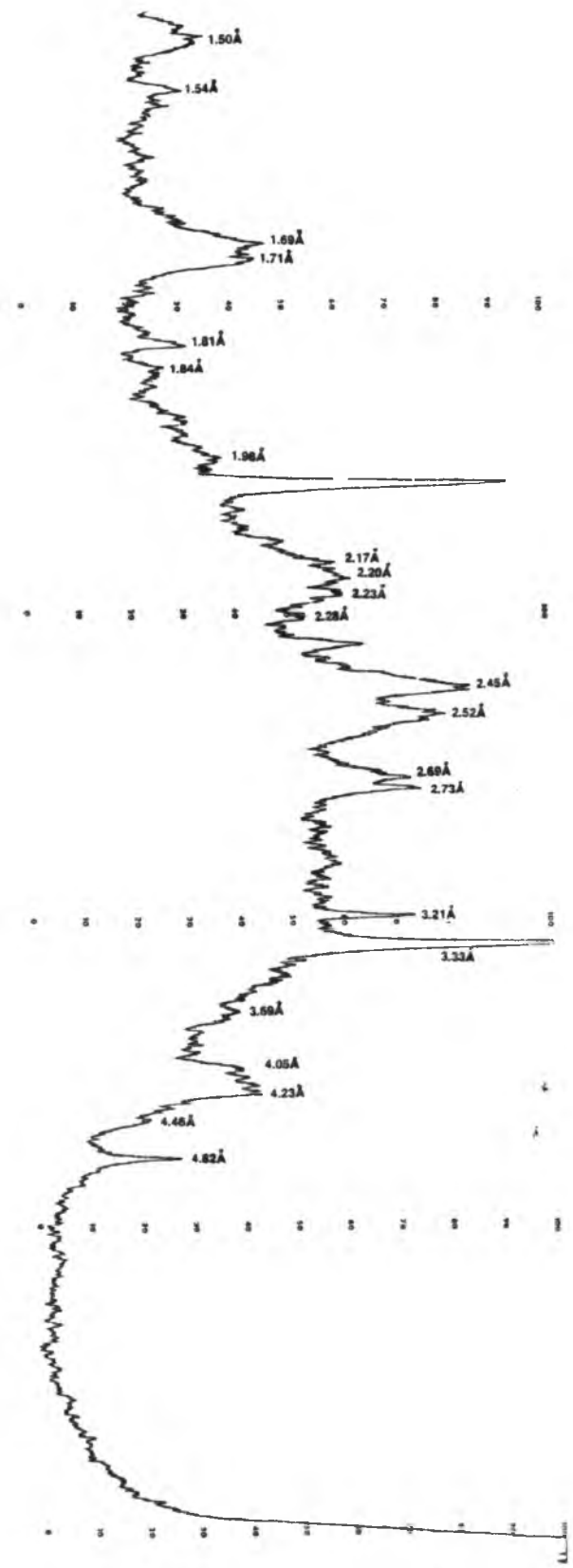
1.54Å
1.61Å
1.66Å
1.69Å
1.91Å
1.99Å
2.21Å
2.34Å
2.38Å
2.52Å
2.56Å
2.66Å
2.95Å
3.20Å
3.35Å
3.57Å
4.43Å
7.40Å
7.19Å
Washawa 0 - 6" < 325 mesh
Air-dry
Bulk Powder Holder
500 XL TC = 5
40KV, 40 MA

Figure 3: X-Ray Diffractogram of the Silt, Clay Fractions of a Kaiwiki Soil.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1.54Å
1.69Å
1.71Å
1.81Å
1.84Å
1.96Å
2.17Å
2.20Å
2.23Å
2.28Å
2.45Å
2.52Å
2.69Å
2.73Å
3.21Å
3.33Å
3.59Å
4.05Å
4.23Å
4.46Å
4.82Å
Kaheriki 0 - 6" < 325
Field Moisture
Bulk Powder Holder
500XL TC = 5
40KV, 40 MA

Figure 4: X-Ray Diffractogram of the Silt, Clay Fractions of a Molokai Soil.

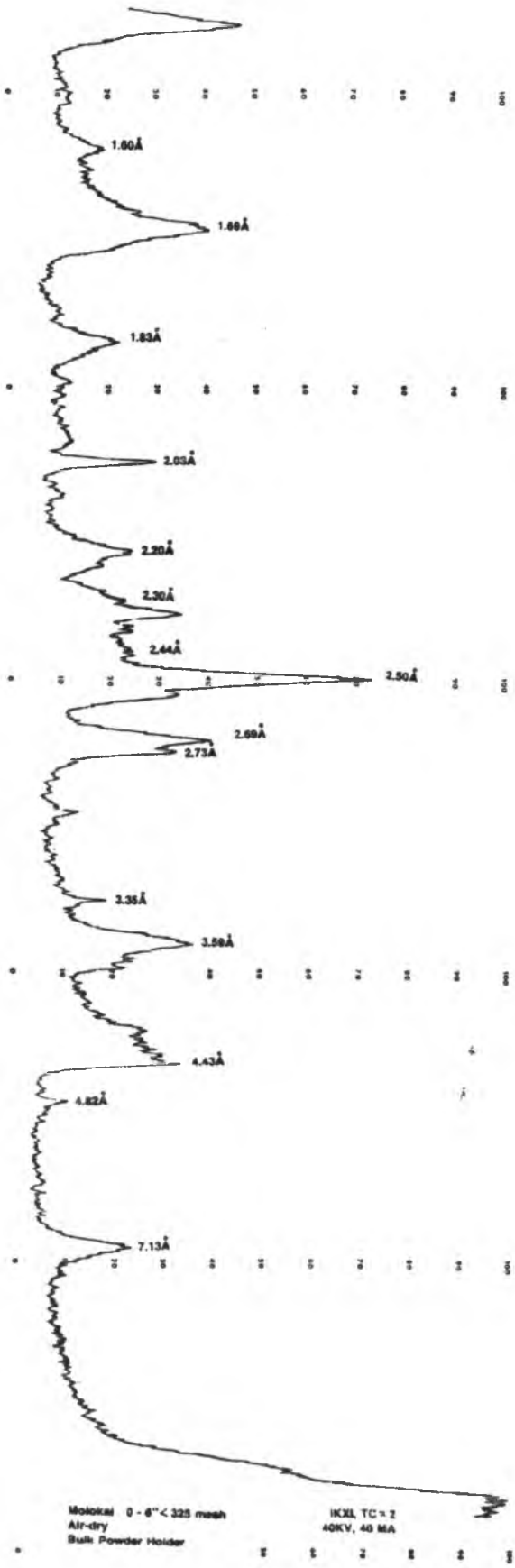
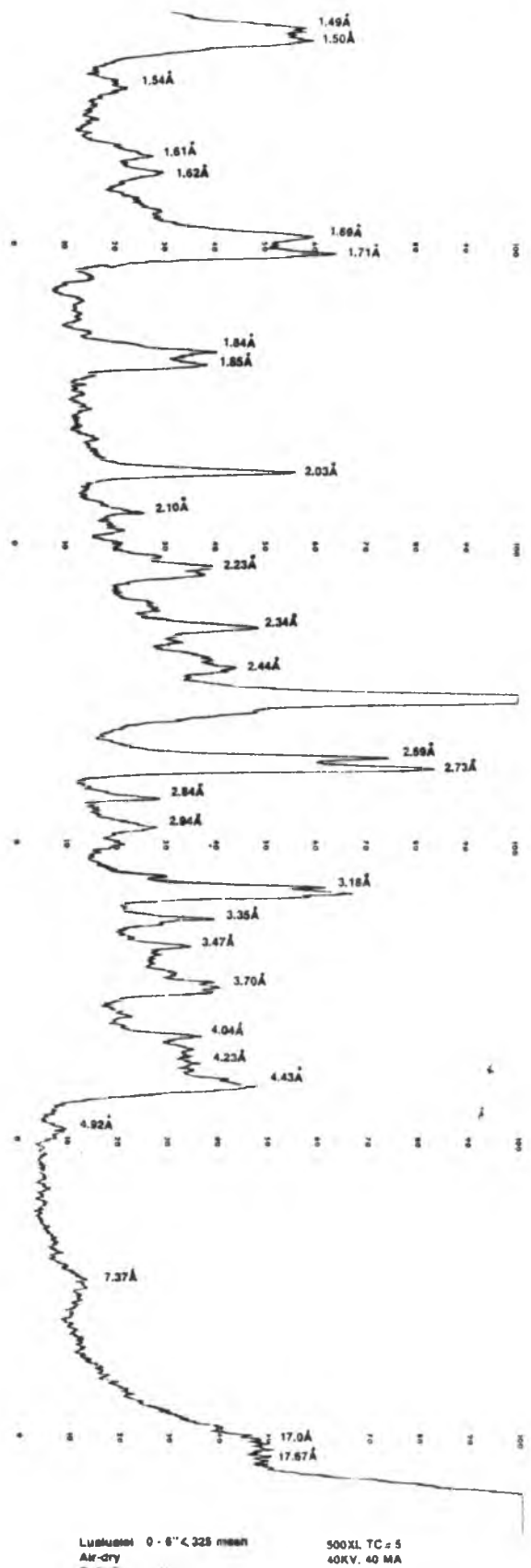

1.60Å
1.66Å
1.83Å
2.03Å
2.20Å
2.30Å
2.44Å
2.50Å
2.69Å
2.73Å
3.35Å
3.59Å
4.43Å
4.82Å
7.13Å
Molokai 0 - 6" < 325 mesh
Air-dry
Bulk Powder Holder
IKXL TC = 2
40KV, 40 MA

Figure 5: X-Ray Diffractogram of the Silt, Clay Fractions of a Lualualei Soil.



Lustusion 0 - 6° < 325 mesh
Air-dry
Sum Powder reader

500XL TC = 5
40KV, 40 MA

APPENDIX II

TABLE 1 Data on Mean Elemental Concentration of Plant Tissues of Centrosema pubescens

Mo Applied (kg/ha)	Centrosema pubescens							
	Soil pH 4.6							
	Mean Elemental Concentration							
	%					ppm		
	N	P	K	Ca	S	Mn	Zn	Mo
0	1.38	0.21	1.07	0.72	0.14	155	19	0.03
1	1.65	0.19	1.17	0.73	0.15	152	18	0.19
2	1.48	0.19	1.15	0.78	0.14	168	20	0.48
5	1.90	0.18	1.23	0.80	0.17	172	21	1.00
Ave	1.60	0.19	1.15	0.76	0.15	162	19.5	0.43
	5.5							
	%					ppm		
	N	P	K	Ca	S	Mn	Zn	Mo
0	1.68	0.19	1.09	1.42	0.17	118	17	0.04
1	2.40	0.17	1.09	1.41	0.16	115	15	0.47
2	2.00	0.19	1.04	1.52	0.18	119	16	0.89
5	2.10	0.19	1.08	1.47	0.17	126	17	1.68
Ave	2.04	0.19	1.08	1.45	0.17	119	16	0.83

Continued...

Table I -- Elemental Concentrations
Page two

Mo Applied (kg/ha)	Centrosema pubescens							
	Soil pH							
	6.0							
	%					ppm		
	N	P	K	Ca	S	Mn	Zn	Mo
0	1.94	0.19	1.19	1.46	0.17	95	16	0.07
1	2.50	0.20	1.24	1.52	0.18	93	18	0.96
2	2.24	0.20	1.24	1.45	0.17	91	18	1.50
5	2.42	0.18	1.15	1.48	0.17	84	15	2.94
Ave	2.28	0.19	1.20	1.48	0.17	91	17	1.43
	6.5							
	%					ppm		
	N	P	K	Ca	S	Mn	Zn	Mo
0	2.53	0.19	1.23	1.59	0.18	52	15	0.07
1	3.04	0.20	1.21	1.53	0.20	56	16	1.78
2	2.79	0.19	1.25	1.54	0.20	51	16	3.36
5	2.68	0.20	1.24	1.57	0.19	55	15	5.32
Ave	2.77	0.20	1.23	1.56	0.19	53	15	2.75

TABLE II Data on Mean Elemental Concentration of Plant Tissues of Desmodium intortum

Mo Applied (kg/ha)	Desmodium intortum							
	Soil pH							
	4.6							
	Mean Elemental Concentration							
	%					ppm		
	N	P	K	Ca	S	Mn	Zn	Mo
0	1.41	0.23	1.90	0.67	0.17	174	35	0.03
1	1.85	0.26	2.10	0.72	0.18	185	51	0.17
2	1.83	0.22	1.92	0.70	0.18	175	42	0.33
5	2.03	0.19	1.62	0.68	0.18	173	35	0.57
Ave	1.78	0.22	1.88	0.69	0.18	177	41	0.30
	5.5							
	%					ppm		
	N	P	K	Ca	S	Mn	Zn	Mo
0	1.49	0.20	1.38	1.30	0.15	123	21	0.05
1	2.75	0.19	1.50	1.41	0.17	132	26	0.28
2	2.58	0.18	1.59	1.41	0.16	112	25	0.48
5	2.65	0.21	1.79	1.49	0.17	125	29	1.35
Ave	2.37	0.20	1.59	1.40	0.16	123	25	0.54

Continued...

Table II -- Elemental Concentrations
Page two

Mo Applied (kg/ha)	Desmodium intortum							
	Soil pH							
	6.0							
	%					ppm		
	N	P	K	Ca	S	Mn	Zn	Mo
0	1.73	0.20	1.52	1.38	0.17	96	21	0.06
1	2.55	0.20	1.53	1.50	0.17	92	22	0.38
2	2.45	0.18	1.50	1.41	0.15	91	21	0.56
5	2.54	0.17	1.47	1.41	0.15	88	18	2.80
Ave	2.32	0.19	1.50	1.42	0.16	92	20	0.97
	6.5							
	%					ppm		
	N	P	K	Ca	S	Mn	Zn	Mo
0	2.53	0.22	1.81	1.57	0.17	47	24	0.06
1	2.64	0.19	1.68	1.54	0.19	45	22	0.73
2	2.33	0.16	1.47	1.42	0.14	45	15	1.82
5	2.82	0.20	1.71	1.61	0.18	51	20	8.35
Ave	2.58	0.19	1.67	1.53	0.17	47	20	2.80

LITERATURE CITED

Anderson, A. J. 1942. Molybdenum deficiencies on a South Australian Ironstone soil. J. Aust. Inst. Agr. Sci. 8:73-75.

Anderson, A. J. 1956. Molybdenum as a fertilizer. Adv. Agron. 8:163-202.

Anderson, A. J. 1970. Trace elements for sheep pastures and fodder crops in Australia. J. Aust. Inst. Agr. Sci. 36:15-29.

Anderson, A. J. and D. V. Moye. 1952. Lime and molybdenum in clover development on acid soils. Aust. J. Agr. Res. 3:95-110.

Anderson, A. J. and A. C. Oertel. 1946. Factors affecting response of plants to molybdenum. Aust. Coun. Sci. Ind. Res. Bull. I. 198:25-44.

Anderson, A. J. and D. Spenser. 1950. Molybdenum in nitrogen metabolism of legumes and nonlegumes. Aust. J. Sci. Res. Ser. B3:414-430.

Anderson, A. J. and M. P. Thomas. 1946. Factors affecting the response of plants to molybdenum. Aust. Coun. Sci. Ind. Res. Bull. II. 198:25-44.

Andrew, C. S. 1962. In: A review of nitrogen in the tropics with particular reference to pastures. Bull. 46., Comm. Bur. Pasture Field Crops, Hurley.

Andrew, C. S. 1976. Effect of calcium, pH and nitrogen on the growth and chemical composition of some tropical and temperate pasture legumes. I. Nodulation and growth. Aust. J. Agr. Res. 27:611-623

Barrow, N. J. 1970. Comparison of the adsorption of molybdate, sulfate, phosphate by soils. Soil Sci. 100(5):282-288.

Barrow, N. J. 1977. Factors affecting the molybdenum status of soils. In: W. R. Chappell and K. K. Peterson (Ed's). Molybdenum in the Environment. Vol. 2. Marcel Dekker, N. Y.

Barrow, N. J. and K. Spenser. 1971. Factors in the molybdenum and phosphate status of soils on the Dorrigo Plateau of N. S. Wales. Aust. J. Expt. Agr. Anim. Husb. 11:670-676.

Black, C. A., D. D. Evans, J. L. White, L. E. Ensminger and F. E. Clark. 1965. In: Methods of soil analysis. Part II. Chemical and mineralogical properties. Amer. Soc. Agron. Inc. Madison, Wis.

Bortels, H. 1930. Molybdenum as a catalyst in biological nitrogen fixation. Arch. Mikrobiol. 1:333-342.

Chojnacka, J. 1963. Influence of pH on the ionic mobilities of molybdic isopolyacids. Roczniki Chomii 37: 259-272.

Cline, M. G. et al. 1955. Soil survey of the territory of Hawaii. U.S.D.A. Series, 1939. No. 25.

Davies, E. B. 1945. A case of molybdenum deficiency in New Zealand. Nature 156:392.

Davies, E. B. 1956. Factors affecting molybdenum availability in soils. Soil Sci. 81:209-221.

DePolli, H., S. R. Carvalha, P. F. Lomos and A. A. Franco. 1977. Intern. Symp. on Biol. Nitrogen fixation in the tropics. Brasilia, Brazil.

Dick, A. T. 1953. The effect of molybdenum and of lime dressings on the copper and molybdenum contents of some pasture species in the Murray Valley. Aust. J. Agr. Res. 4:52-56.

Dradu, E. A. A. 1974. Soil fertility studies on loam soils for pasture development in Uganda. Pot experiments. East African Agr. For. J. 40(2):125-131.

Evans, J. and D. Purvis. 1951. Effect of soil reaction on availability of molybdenum. Soil Sci. 71:117-124.

Fox, R. L. 1967. Phosphorus fixation by Hawaiian soils and what to do about it. First Ann. Hawwaii Fert. Conf. Honolulu, Hawaii.

Fox, R. L. and D. L. Plucknett. 1964. Overliming Hawaiian soils creates problems. Hawaii Farm Sci. 13:9-10.

Fox, R. L. and E. J. Kamprath. 1970. Phosphate sorption isotherms for evaluating the phosphate requirement of soils. Proc. Soil Sci. Soc. Am. 34:902-907.

Franco, A. A. 1976. Nutritional restraints for tropical grain legume symbiosis. In: J. M. Vincent, A. S. Whitney and J. Bose (Eds). Exploiting the legume - Rhizobium symbiosis in tropical agriculture. Proc. Workshop. Kahalui, Maui. Hawaii. College Trop. Agr. Misc. Pub. 145. pp. 237-252.

Fujimoto, G. and G. D. Sherman. 1951. Molybdenum content of typical soils and plants of the Hawaiian Islands. Agron. J. 43:424-429.

Gonzalez, R., H. Appelt, E. B. Schalscha and F. T. Bingham. 1974. Molybdate adsorption characteristics of volcanic-ash-derived soils in Chile. Proc. Soil Sci. Soc. Am. 38:903-906.

Gupta, U. 1970. Effect of interaction of molybdenum and limestone on growth and molybdenum content of cauliflower, alfalfa and bromegrass on acid soils. Proc. Soil Sci. Soc. Am. 33:929-932.

Huang, Yoong Lee. 1962. A study of the status of molybdenum in Hawaiian soils and the reaction of vegetation to the application of molybdenum. M. S. Thesis, University of Hawaii.

Johansen, C., P. C. Kerridge, P. C. Luck, B. G. Look, K. F. Lowe and H. Ostrowski. 1977. The residual effect of molybdenum fertilizer on growth of tropical pasture legumes in a subtropical environment. Aust. J. Expt. Agr. Amin. Husb. 17:961-968.

Johansen, C. 1978. Comparative molybdenum concentration in some tropical pasture legumes. Comm. in Soil Sci. and Plant Anal. 9(10):1009-1017.

Johnson, C. M. 1966. Molybdenum. In: H. D. Chapman (Ed). Diagnostic Criteria for Plants and Soils. University of California. Div. Agr. Sci. pp. 286-301.

Johnson, C. M. and T. H. Arkley. 1954. Determination of molybdenum in plant tissue. Anal. Chem. 26:572-574.

Jones, L. H. P. 1957. The solubility of molybdenum in simplified systems and aqueous soil suspensions. J. Soil Sci. 8:313-327.

Jones, R. J., J. G. Davies and R. B. Waite. 1967. The contribution of some tropical legumes to pasture yields of dry matter and nitrogen at Samford, Southeastern Queensland. Aust. J. Expt. Agr. Anim. Husb. 7:57-65.

Kerridge, P. C., B. C. Cook and M. L. Everette. 1973. Application of molybdenum trioxide in the seed pellet for subtropical pasture legumes. Trop. Grassl. 7:229-232.

Kliewer, W. M. and W. K. Kennedy. 1960. Studies on response of legumes to molybdenum and lime fertilization on Mardin silt loam soil. Proc. Soil Sci. Soc. Am. 24:377-380.

Kurmarohita, Kunchit. 1964. Molybdenum content of pasture species and some factors that affect it. M. S. Thesis. University of Hawaii.

t'Mannetje, L., N. H. Shaw and T. W. Elich. 1963. Residual effect of molybdenum fertilizer on improved pastures on a prarie-like soil in subtropical Queensland. Aust. J. Expt. Agr. Anim. Husb. 3: 20-25.

Mears, P. J. and B. Barkus. 1970. Response of Glycine wightii to molybdenized superphosphate on a Krasnozem. Aust. J. Expt. Agr. Anim. Husb. 10:415-425.

Mulder, E. G. 1954. Molybdenum in relation to growth of higher plants and microorganisms. Plant and Soil 5: 368-415.

Muljadi, D., A. M. Posner and J. P. Quirk. 1966. Mechanism of phosphate adsorption by kaolinite, gibbsite and pseudohaematite. J. Soil Sci. 17:212-247.

Munns, D. N. 1976. Soil acidity and related factors. In: J. M. Vincent, A. S. Whitney and J. Bose (Eds). Exploiting the Legume - Rhizobium Symbiosis in Tropical Agriculture. Proc. Workshop. Kahalui, Maui Hawaiian College. Trop. Agr. Misc. Publ. 145: 211-236.

Munns, D. N. and R. L. Fox. 1976. Depression of legume growth by liming. Plant and Soil 45:701-705.

Munns, D. N., R. L. Fox, and B. L. Koch. 1977. Influence of lime on nitrogen fixation of tropical and temperate legumes. Plant and Soil 46:591-601.

Nicholas, D. J. 1955. Role of molybdenum as a constituent of nitrate reductase from soybean leaves. Plant Physiol. 30:195-198.

Peres, J. R. R., M. Nery and A. A. Franco. 1976. Ann. XV. Cong. Bras. Solo Campinas. S. P. p. 163.

Reisenauer, H. M., A. A. Tabikh and P. R. Stout. 1962. Molybdenum reaction with soil and hydrous oxides of iron, aluminum and titanium. Proc. Soil Sci. Soc. Am. 26:23-27.

Robinson, W. O. 1948. The presence and determination of molybdenum and rare earth in phosphate rock. Soil Sci. 66:317-322.

Robinson, W. O. and C. T. Alexander. 1953. Molybdenum content of soils. Soil Sci. 75:287-292.

Robinson, W. O., G. Edgington, W. H. Armiger and A. V. Breen. 1951. Availability of molybdenum as influenced by liming. Soil Sci. 72:267-274.

Shorrocks, V. M. 1964. Mineral deficiencies in Hevea and associated cover plants. Rubber Res. Inst. of Malaya, Kaula Lumpar, Malaysia.

Souto, S. M. and J. Döbereiner. 1969. Toxidez de Manganes em leguminosas ferrageiras tropicals. Pesg. Agropoc. Bras. 4:129-138.

Steinberg, R. A. 1937. Role of molybdenum in the utilization of ammonium and nitrate nitrogen by Aspergillus niger. J. Agr. Res. 55: 891-902.

Steward, I. and C. D. Leonard. 1952. Molybdenum deficiency in Florida citrus. Nature 170:714-715.

Tang, C. N. 1974. Effect of lime and molybdenum on yield of siratro on lateritic soil. Taiwan Agr. Quart. 10(4):112-119.

Tang, C. N. and P. W. Lin. 1970. Study of nutrition of a tropical pasture legume on lateritic soil. Taiwan Livestock Res. 3(1): 98-105.

Theng, B. K. G. 1971. Adsorption of molybdate by some crystalline and amorphous soil clays. New Zealand J. Sci. 14:1040-1956.

Trigoso, R. and H. W. Fassbender. 1973. Effect of application of Ca, Mg, P, Mo, B on yield and nitrogen fixation in four tropical legumes. Turrialba 23:172-180.

Truong, N. V., C. S. Andrew, and G. L. Wilson. 1971. Manganese toxicity in pasture legumes. II. Effect of pH and molybdenum levels on the substrate. Plant and Soil 34: 547-560.

Uehara, G. and J. Keng. 1975. Management implication of soil mineralogy in Latin America. In: E. Bornemisza and A. Alvarado (Eds). Soil Management in Tropical America. N. C. State University, Raleigh. pp. 351-362.

Walsh, T., M. Neeman and L. B. O'Moore. 1952. The importance of molybdenum in relation to cropping and livestock problem under Irish conditions. Eire Dept. Agr. J. 48:32-43.

Watson, G. A. 1960. Interaction of lime and molybdate in the nutrition of Centrosema pubescens and Pueraria phaseoloides. J. Rubber Res. Inst. Malaya 16:126-130.

Wells, N. 1956. Soil studies using sweet Vernal to assess element availability. Part 2. Molybdate ion fixation in New Zealand soils. New Zealand J. Sci. Tech. 3:482-502.

Weinberger, P. and H. Wenzel. 1973. Molybdenum in volcanic ash soils and its effect on nitrogen metabolism in cultivated plants, particularly legumes. Turrialba 23(2):119-127.

Whitney, A. S. 1970. Effect of harvesting intervals, height of cut, and nitrogen fertilization on the performance of Desmodium intorum mixture in Hawaii. IN: Proc. XIth Intern. Grassl. Congr. Australia. pp. 632-636.

Younge, O. R. and M. Takahashi. 1953. Response of alfalfa to molybdenum in Hawaii. Agron. J. 45:420-428.