

MOLYBDENUM NUTRITION OF CROP PLANTS

I. THE INFLUENCE OF PHOSPHATE AND SULFATE ON THE ABSORPTION OF MOLYBDENUM FROM SOILS AND SOLUTION CULTURES

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The object of this paper is to report further investigations of the role of phosphate and sulfate levels of soils and culture solutions as they affect molybdenum absorption by plants. It was reported earlier²⁸) that tomato plants absorbed and translocated sub-microgram amounts of radioactively tagged molybdate from single salt solutions of phosphate, chloride, nitrate, and sulfate. The greatest translocations of molybdate took place when present with phosphate salts and the least in the presence of sulfates, the difference being very large, in the order of 10 fold. As compared to the marked differential effects of phosphates and sulfate the influence of different cations on molybdate absorption was negligible. The role of sulfate ions in suppressing molybdate absorption and translocation may be explained as a direct competition between two divalent anions of the same size. However, no simple chemical explanation can be offered for enhanced accumulation of molybdate in the shoots of plants with increasing phosphate levels in the culture solution. Since in all instances roots absorbed molybdate, the amounts translocated must be related to physiological processes governing the release of root absorbed molybdate to the plant's conduction system. Inorganic phosphate levels must assume a dominate role in effecting the release of molybdate from root cells.

The present studies cover a wide variety of experimental arrangements designed to study factors influencing the molybdenum nutri-

tion of plants. Some of the investigations with soils were in progress prior to the solution culture experiments referred to ²⁸), and others have been initiated later. In all instances corroborative evidence of interrelations between phosphates, sulfate and molybdate have been found. Moreover, the effects were highly consistent under such very different experimental circumstances as short time absorption from single salt solutions and long term experiments involving pot cultures of plants grown to maturity on soil. Because of the observed consistency, generalizations of the phenomena are permitted which may be of use in field management wherein molybdenum absorption by plants presents practical agricultural problems.

The consequences of molybdenum absorption by plants may be divided into two distinctively separate categories. One deals with the molybdenum nutrition of plants *per se*, and the other with adverse effects in animal nutrition arising from ingestion of excessive amounts of molybdenum in feeds.

For our purpose, we have correspondingly differentiated between soils of high and low molybdenum supplying power. The division is arbitrary, and is based on the molybdenum content of plants grown upon them without regard to species. Our present experiments involved tomatoes, peas, and subterranean clover. Analyses of tomato and pea plants grown under comparable conditions show somewhat lower concentrations of molybdenum in the tomato plant. It has been suggested ⁷) that legumes as a class have greater power of accumulating molybdates than non-legumes. However, this generalization has not been borne out in other unreported experiments we have conducted. Having analyzed 35 species of crop plants grown on soils at both high and low soil molybdenum levels under otherwise similar cultural conditions, we can now only state that the powers of individual plant species to accumulate molybdenum are greatly different. For example on the high molybdenum soil the greatest accumulation was shown for broccoli, but upon low molybdenum soils the molybdenum absorbed by broccoli was exceeded by many other species. In characterizing soils with respect to their molybdenum supplying power, we have chosen to rate them according to the molybdenum concentrations accumulated by growing plants. Analyses of molybdenum deficient plants made in our laboratory have ranged from 0.25 to 0.03 p.p.m. dry weight. Walker ³⁰) has reported 0.11 p.p.m. and less for molybdenum deficient tomato plants grown on a

serpentine soil. Considerable variation has been found for different species, with further modifications associated with cultural conditions. From the point of view of molybdenum as an essential element for plant growth, we have tentatively set the figure of 0.5 p.p.m. molybdenum in the dry plant material as indicative of an adequate molybdenum supplying power of soils or other nutrient substrates. On the other hand soils providing in the order of 10 p.p.m. of the dry weight of plants have become known as high molybdenum soils. Concentrations of molybdenum in pasture plants of 10 p.p.m. and greater has been associated with the teart disease or molybdenosis of cattle and sheep ^{7), 9), 16), 23)}. Intermediate concentrations lying between approximately 0.5 and 5 p.p.m. molybdenum at present are not recognized as of consequence in either plant or animal nutrition.

As will be shown, the influence of phosphates in enhancing molybdate absorption and of sulfate in repressing it, is of such magnitude that the ability of soils to supply molybdenum to plants must be judged in terms other than concentrations of soil molybdenum alone.

With respect to significant levels of soil molybdenum involved in these studies, it may be pointed out that certain low molybdenum soils have been effectively converted to ones of very high molybdenum power through surface application of one part of soluble molybdenum per million parts of soil. Also, depending upon differential soil treatments with sulfate and phosphate, concentrations of molybdenum in plants have been caused to vary in the order of 10 fold.

At the time these studies were begun, interest in the role of molybdenum in plant nutrition was rapidly increasing, principally because of the remarkable field results obtained by Australian workers who were successful in increasing the yields of legumes through molybdenum applications in the field. Interpretations of the field responses to molybdenum in Australia as reviewed by Anderson ¹⁾, Anderson and Thomas ⁴⁾, and Anderson and Oertel ³⁾ were that subterranean clover showed a secondary response to molybdenum applications through the symbiotic nitrogen fixing organisms. It did not seem that the soils were in reality molybdenum deficient for plants *per se*, since no molybdenum response was obtained when their plants were fertilized with nitrates. However, the results of Davies ¹¹⁾ in New Zealand who associated the whiptail disease

of cauliflower and cabbage with molybdenum deficient soils, made it appear that the New Zealand soils either had a lower molybdenum supplying power than the soils in Australia, or that cabbage and cauliflower were plants having an exceptionally high molybdenum requirement.

There were several reasons for expending some effort toward finding soils of low molybdenum supplying power in California. First, it seemed reasonable that if the Australian soils referred to had reached a molybdenum level low enough to effectively, though indirectly, limit the growth of legumes, an intensification of the weathering factors giving rise to low molybdenum levels should reduce the molybdenum supplying power sufficiently to give rise to molybdenum deficiency for any plant specie. Second, an available supply of soil material capable of producing molybdenum deficiency in plants would permit controlled experimentation with enough different species to enable us to secure data with respect to the quantitative levels of soil molybdenum of significance in plant nutrition. Third, from the point of view of soil chemistry, an explanation of chemical weathering in relation to types of parent material involved in molybdenum supplies for plants, would represent a contribution to the general field of soil chemistry; and fourth, experience gained with growing plants on low molybdenum soils would of course be of value in extending knowledge of plant and soil factors involved in the complete mineral nutrition of plants.

In 1935, v a n N i e l ²⁹⁾ had shown that a slightly alkaline sandy soil collected at Carmel, California, was too low in molybdenum to successfully grow *Azotobacter* when dependent on the atmosphere for nitrogen. In 1939, since it was known that molybdenum was required for the growth of tomatoes ⁶⁾, one of the writers (P. R. S.) and D. I. A r n o n reasoned on the basis of v a n N i e l's reports ²⁹⁾ that soils might exist which were sufficiently low in molybdenum to show deficiency symptoms in crop plants. Being familiar with foliar symptoms of molybdenum deficiencies produced from water cultures, field examinations in the California coastal tomato growing regions were made for suggestions of similar disorders in field grown crops. However, no visually recognizable molybdenum deficiency symptoms were found, at least as they were known from molybdenum deficient plants grown in solution cultures.

A distinctly opposite problem, presented by excessive amounts of

molybdenum absorption by plants, exists in some parts of California; namely, molybdenosis of cattle. Factors contributing to the disease in California have been studied by Britton and Goss⁹⁾ and Barshad⁷⁾. It appears to be similar to the teart disease first recognized in England as reported by Lewis¹⁶⁾. Molybdenosis, or the teart disease of ruminants becomes evident when their food contains in the order of 10 parts per million or more of molybdenum. Because of van Niel's work with *Azotobacter* on a low molybdenum soil²⁹⁾ and that of Britton and Goss with molybdenosis on high molybdenum soils⁹⁾, it was obvious that molybdenum levels of California soils varied enormously.

In seeking soils of low molybdenum supplying power, it was thought that better chances of success would lie in regions where natural weathering processes were associated with freely draining surface and ground waters. In view of the Australian and New Zealand experiences associated with low molybdenum soils^{1), 2), 3), 4), 11), 13), 19)}; we were particularly interested in acid leached soils, sufficiently weathered to give rise to phosphate deficiency, but which still did not give good growth of legumes after being fertilized with N, P, K, S, Ca and Mg. Through the cooperation of the University of California Extension Service^{*)}, we were able to secure samples of acid soils which as a result of field fertilizer trials appeared to meet the above requirements.

The selected soils, described below did not produce molybdenum deficient plants, even though techniques²⁷⁾ found successful for controlled micronutrient element experiments with water cultures were applied to the soil cultures in pot tests. However, in the progress of the work it was noted that fertilization with phosphate apparently enhanced molybdenum absorption by plants. It was thought that this phenomenon might be of sufficient importance in the molybdenum nutrition of plants to deserve special study.

Molybdenum absorption by plants from soils selected as potentially low in molybdenum supply. Description of soils: Soils *a* and *b* were taken from a farm located near the coast in Marin County. The lands have not yet been mapped by the Soil Conservation Service, but the

*) We gratefully acknowledge the active cooperation of Dr. W. E. Martin, Extension Specialist in Soils.

soils are residual clay loams formed on an old marine terrace. The bedrock is of considerable depth. Field fertilizer trials showed only a slight response to phosphorus on legumes and no appreciable response by grasses or other vegetation to nitrogen, potassium, or sulfur alone or in combination with phosphorus. Greenhouse pot tests had shown a slight depressing effect from the addition of potassium and an increase in yield of leaf lettuce when lime was added.

Soils *c* and *d* are the surface and sub-soil respectively, taken from an apple orchard west of Petaluma, Sonoma County, California. It is classified as Gold Ridge fine sandy loam, a residual soil of low fertility formed from slightly consolidated sandstone, in a high rainfall zone. Soil *C* was taken from the surface 8 inches, and Soil *D* from the 20–24 inch depth where most of the apple roots grew. Trees growing on this soil were badly affected with apple die-back for which no cause has yet been found. Vetch grows well in this area provided phosphorus is added, but sweet clover requires the further addition of lime for success. Indications of response of apples to boron and zinc have been noted although neither of these elements alone or together have controlled the disease of apples. Also the symptoms of the disease shown did not seem to be completely compatible with those regularly shown by zinc and boron deficiencies.

Soil *e* was of particular interest because it had shown plant responses to manure similar to those reported for low molybdenum Australian soils. The sample represented the first 8 inches and was from a site mapped as Empire fine sandy loam, located in Humboldt County in Northwest California. This soil was brought to our attention because difficulty had been experienced with growing peas. All of the field had been treated with superphosphate, and the peas were inoculated. Only two sections of the field produced a crop. In one section where sodium nitrate had been applied at the rate of 40 pounds per acre, the crop was fair, but no nodules were observed. In another small spot in the field, growth was good and good nodulation was observed. The latter spot was one where "foreign" sheep manure had been piled prior to spreading throughout the field. It was believed that the nitrogen from the remaining sheep manure could not account for the response observed. Secondary effects of trace elements of benefit to the legume bacteria were suspected.

Method of greenhouse cropping. Because of Anderson's^{1) 2) 4)} experiences that low molybdenum levels in soils

were evidenced by failure of legumes to fix nitrogen, a legume was chosen as a test plant, on the assumption that it would be more likely to reflect a low soil molybdenum level through the higher molybdenum requirement of symbiotic nitrogen fixing micro organisms. Subterranean clover was specifically selected because of its tolerance to acid soils. Also in accord with Anderson's report that molybdenum applications of $\frac{1}{4}$ to 1 ounce of MoO_3 per acre were as effective as 4 pounds per acre, we arbitrarily decided upon molybdenum treatments of 3 mg Na_2MoO_4 per pot containing 2 kilograms of moist soil. Four millimols of $\text{Ca}(\text{H}_2\text{PO}_4)_2$ were also applied. On an area basis, the respective treatments corresponded to 1.0 pounds of molybdenum and 405 pounds P_2O_5 per acre. Clover plants were grown on the five different soils for 12 weeks. Yields and molybdenum concentrations are shown in Table I.

TABLE I

Yield and Molybdenum Content of Subterranean Clover Grown in Soils Fertilized with Molybdenum and Phosphates										
First Crop										
Treatment ¹⁾	Soil A		Soil B		Soil C		Soil D		Soil E	
	Yield g ²⁾	Mo p.p.m.	Yield g ²⁾	Mo p.p.m.	Yield g ²⁾	Mo p.p.m.	Yield g ²⁾	Mo p.p.m.	Yield g ²⁾	Mo p.p.m.
1. None	2.2	0.18	4.1	<.21	2.2	0.8	0.3	4.3	4.1	0.21
„	1.9	0.20	4.5	<.10	2.2	0.4	0.4	2.4	3.7	0.28
2. Mo	2.2	4.3	3.1	11.8	2.4	91.2	0.3	82.0	4.7	6.4
„	1.8	8.0	5.1	10.8	3.4	44.6	0.5	54.2	4.9	7.9
3. PO_4	5.1	0.9	7.2	0.4	2.8	0.8	0.1 *)	7.0	6.1	0.27
„	6.2	1.8	7.4	0.7	3.4	0.6	0.1 *)	3.3	8.6	0.28
4. $\text{Mo} + \text{PO}_4$	5.0	79.3	8.1	27.2	3.5	109	0.1 *)	58.3	6.2	123.5
„	5.3	61.4	7.5	79.0	2.9	153	0.04	68.5	8.2	69.1
pH, 1:2 susp.	5.5		5.6		4.8		5.1		4.9	

¹⁾ Applied salts were added dissolved in 400 cc of water. The solution was poured quickly over the loose soil mass in order to distribute it throughout the entire sample.

Treatments to 2 kilograms of undried soil as collected from the field

1. 400 ml of distilled water only.
2. 400 ml water containing 3 mg of Na_2MoO_4 (1 pound Mo per acre).
3. 400 ml water containing 4 m. mols $\text{Ca}(\text{H}_2\text{PO}_4)_2$ (405 pounds P_2O_5 per acre).
4. 400 ml water containing 4 m. mols $\text{Ca}(\text{H}_2\text{PO}_4)_2$ plus 3 mg Na_2MoO_4 .

²⁾ Yields are reported as total dry weight per pot of the above ground part of the plant.

*) Plants were dead at time of harvest.

In the pot cultures distinct phosphate responses were obtained with the Marin County soils A and B, and with the Humboldt county

soil E. Of the soils from Sonoma County, the surface soil (Soil C) supported subterranean clover plants but showed no significant response to phosphates. The subsoil (Soil D) however, barely supported only a scanty growth which was materially depressed by application of phosphate.

Although at no time during the cropping period were any visual effects observed that could be ascribed to molybdenum deficiency, subsequent analyses of the plants were encouraging in that the untreated soils had produced plants having a lower molybdenum content than we had previously found. For example, in Table I molybdenum concentrations in clover grown on soils A, B, and E were found to be .18, .20, < .12, < .10, .21 and .25 p.p.m. (Ter Meulen¹⁷), Barshad⁷) and Robinson and Edgington²³) who have reported molybdenum concentrations in various plant materials ranging from .3 p.p.m. upward to 120 p.p.m.

Our values for molybdenum here obtained appeared more nearly comparable with those of Anderson and Oertel³) who reported that healthy lucerne and *Phalaris tuberosa* grown on burned over land contained respectively 0.7 and 0.3 p.p.m. molybdenum whereas poorly developed plants on an adjoining area contained less than 0.1 p.p.m. This difference in the molybdenum content of plants on the two areas provided them with one of their earlier clues that the effective agent contributing to better plant growth in burned over areas was molybdenum from plant ash.

Influence of phosphate fertilization of certain acid soils in increasing molybdenum absorption by plants. The principal point of interest in the data of Table I is that for a given level of soil molybdenum, application of phosphate at the rate of 400 pounds P_2O_5 per acre caused an enormous increase in the amount of molybdenum taken up by the plants. Not only was the concentration of molybdenum in the phosphate treated plants increased, but even greater increases were obtained in the total amount of molybdenum absorbed since phosphate fertilization also increased the yields.

For example, in Table I, plants grown on Soils A and E, had 8.0, 4.3, 6.4, and 7.9 p.p.m. molybdenum when only molybdenum was applied but 79.3, 61.4, 123.5, and 69.1 p.p.m. when fertilized with phosphate. The marked increase in molybdenum uptake associated with the higher phosphate level cannot be ascribed to molybdenum

contamination in the phosphate fertilizer since treatment 3, phosphate alone, showed but 0.9, 1.8, 0.27, and 0.28 p.p.m. molybdenum in plants grown on the same soils.

Anderson and Oertel³⁾ indicated no particular influence of phosphate fertilization on the amount of molybdenum extracted by plants. Conditions imposed by these experiments, however, unmistakably demonstrate that phosphate levels in soils are important variables related to the molybdenum accumulation by plants. This interrelation with phosphate was very prominent with soils A, B, and E. The same trend though less pronounced, is shown for soil C. Similar comparisons cannot be made for Soil D because of crop failure on the phosphate treated pots.

It was assumed that calcium did not contribute to variations in the plant responses as shown by molybdenum absorption, since the calcium added with the $\text{Ca}(\text{H}_2\text{PO}_4)_2$ was shown by soil analyses to amount to only 2% or less than the soluble and exchangeable calcium already present in the soil. Other soil and culture solution experiments discussed later have adequately corroborated this assumption.

In order to show the effect of phosphate on the total molybdenum absorbed, data from plants grown on soils A, B, and E have been compiled in Table II. Columns 3 and 4 show respectively the relative increase in *molybdenum concentration*, and relative increase in *total molybdenum removed* by plants resulting from phosphate fertilization. Column 5 shows the percent recovery of 1 pound per acre of added molybdenum, with and without phosphate fertilization.

Ratios in column 3 showing increased concentration of molybdenum as a result of phosphate fertilization are in some instances very large. The increases are particularly evident when phosphate and molybdenum were added in combination, the molybdenum concentration being increased ten to thirty fold over that without added phosphate. The phosphate effect is thus seen to be operative at two widely different levels of soil molybdenum.

Increased molybdenum uptake resulting from phosphate fertilization is even greater when considered from the point of view of total amounts of molybdenum removed by plants (Column 4) since the molybdenum concentration was increased, even though higher yields were obtained.

Percent recovery of added molybdenum also illustrates the same

TABLE II

Soil Treatment	Influence of Phosphate Treatments on the Molybdenum Uptake by Tops of Subterranean Clover														
	1			2			3			4			5		
	P.P.M. Mo			Micrograms Mo Removed by Tops			Factor showing Increased Conc. of Mo due to PO ₄ fertilization			Factor showing Increased Total Removal of Mo. Due to PO ₄ fertilization			Percent Recovery of Added Mo		
	A	B	E	A	B	E	A	B	E	A	B	E	A	B	E
1. Check	0.18	< 0.21	0.21	0.4	< 0.86	0.90	—	—	—	—	—	—	—	—	—
	0.20	< 0.10	0.28	0.4	< 0.45	1.00	—	—	—	—	—	—	—	—	—
2. Plus molybdenum	4.3	11.8	6.4	9.5	36.6	30.0	—	—	—	—	—	—	0.62	2.5	2.0
	8.0	10.8	7.9	14.2	55.0	39.0	—	—	—	—	—	—	0.95	3.7	2.6
3. Phosphate only	0.9	0.4	0.27	4.6	2.9	1.6	4.7	> 2.7	1.1	11.5	> 4.4	1.7	—	—	—
	1.8	0.7	0.28	11.2	5.2	2.4	9.5	> 4.7	1.1	28.0	> 7.9	2.5	—	—	—
4. Mo. ybdenum plus phosphate	79.3	27.2	123.5	396	220	760	12.8	2.4	17.3	33.5	4.8	22.0	26.8	14.9	53.6
	61.4	79.0	69.1	325	590	580	9.9	7.0	9.7	27.5	12.9	16.8	21.8	40.4	39.8

The letters A, B, E, at the head of each column refer to plants grown in soils A, B, and E respectively.

Column 1. Concentration of molybdenum, p.p.m. dry weight, found in the tops.

” 2. Micrograms of molybdenum removed by tops of plants grown on a single pot.

” 3. Factor showing the increase in molybdenum concentration due to treatment with phosphate — obtained by calculation, using as a reference the average concentration of molybdenum in plants not treated with phosphate, but which received the same molybdenum treatment.

” 4. Increased total removal factor due to treatment with phosphate, obtained by calculation, using as reference the average total amount of molybdenum removed by the tops of plants not treated with phosphate, but which received the same molybdenum treatment.

effect, as may best be seen in Column 5, table II. Without supplemental phosphate (treatment 2) the lowest recovery of added molybdenum was 0.62% and the highest was 3.7%. With the addition of 400 pounds P_2O_5 per acre, however, the percent recovery was greatly increased, the lowest percent recovery being 14.9% and the highest 53.6%.

Although somewhat outside the scope of the principal subject of this paper, at least two quantitative aspects of the molybdenum accumulating power of clover plants, as revealed by these data, deserve comment in connection with excessive concentrations of molybdenum in leguminous cattle feeds. As earlier mentioned, workers concerned with molybdenosis have regarded molybdenum concentrations of 10 parts per million as a borderline figure above which the frequency and severity of the disease is likely to be increased.

It is seen from the results of Table I that large increases in the molybdenum content of plants may be induced solely through the application of phosphate fertilizers even though soil molybdenum is the same. It is therefore conceivable that the molybdenum content of hay could be increased from a safe to an unsafe molybdenum concentration through the indirect means of fertilization with materials other than molybdenum itself. For example, in Table I compare analyses of plants from the individual pots of treatment 2 (molybdenum only) with those of treatment 4 (molybdenum plus phosphate). As a result of adding phosphate to Soil A, the molybdenum contents of plants were raised from 4.3 and 8.0 p.p.m. to 79.3 and 61.4 p.p.m. Similarly for Soil B the molybdenum content of clover was raised from 11.8 and 10.7 p.p.m. to 27.2 and 79 p.p.m. Also, plants grown on Soil E were raised from 6.4 and 7.9 p.p.m. to 123 and 69 p.p.m. It may be noted that when molybdenum alone was added to Soil D the molybdenum concentration was raised from 4.3 and 2.4 p.p.m. to 82.0 and 54.2 p.p.m. (cf. Soil D, treatments 1 and 2 Table I) even without phosphate fertilization.

A second point of interest with regard to high molybdenum soils is that the enhanced molybdenum uptake induced by phosphates effects rapid removal of soil molybdenum. This may be seen in the data of Table II which shows that the addition of phosphate resulted in the recovery of a substantial portion of added molybdenum by a single cropping. The average percent recovery of molybdenum in the first crop from soils A, B, and E, treatment 2 (molybdenum alone) is

2.06%. An average percent recovery of 32.9 however, was obtained from the same three soils of treatment 4 (molybdenum plus phosphate).

Molybdenum absorption by garden peas following cropping with subterranean clover. After harvesting the subterranean clover, the same pots were replanted to garden peas without further fertilization. The second crop was harvested and followed by a third crop, also of garden peas. The pea plants from each pot and for both harvests were analyzed for molybdenum. Molybdenum concentrations of the second crop and third crop are given respectively in tables III and IIIa.

TABLE III

Yield and Molybdenum Content of Garden Peas Grown in Soils Fertilized with Molybdenum and Phosphates										
Second Crop										
Treatments *)	Soil A		Soil B		Soil C		Soil D		Soil E	
	Yield g	Mo p.p.m.	Yield g	Mo p.p.m.	Yield g	Mo p.p.m.	Yield g	Mo p.p.m.	Yield g	Mo p.p.m.
1. None	2.69	1.6	2.49	2.1	2.30	2.1	1.76	2.6	2.06	2.5
	2.48	1.7	2.43	2.0	1.97	2.3	1.48	4.1	2.04	2.3
2. Mo	2.22	3.5	2.69	3.3	2.42	4.5	1.94	13.5	2.30	4.5
	2.83	3.6	2.50	3.3	2.45	4.8	0.99	22.5	1.67	3.8
3. PO ₄	3.10	1.4	3.52	0.8	3.05	1.9	1.87	2.8	2.25	1.4
	3.69	1.0	2.97	0.9	2.40	1.4	1.81	1.9	2.40	2.3
4. PO ₄ + Mo	3.61	2.4	2.89	2.3	2.47	4.8	1.65	21.2	2.23	4.9
	2.96	2.5	3.26	2.9	3.11	3.5	1.30	27.8	2.08	4.8

*) Treatments were made before the first crop of subterranean clover. For method of treatment, refer to Table I. Also note, data for each replicated culture occupy the same positions as data in Tables I and IV.

The marked effects of phosphate fertilization shown so strikingly in the first crop disappeared in both the second and third crops. Reasons for such behavior are not clear but may have arisen from a number of different factors having to do with the chemistry of the soil system or to physiological peculiarities of the different plant species used.

For some soils, trends shown in the first crop appeared reversed in the second. For example, in the first crop (Table I) clover plants grown on soil A accumulated 4.3 and 8.0 p.p.m. molybdenum when treated with molybdenum alone, and 79.3 and 61.4 p.p.m. with added phosphate. Molybdenum concentrations for the respective

treatments in the second crop (Table III) were 3.5 and 3.6 p.p.m. for molybdenum alone, and 2.4 and 2.5 p.p.m. when treated with phosphate. In the third crop (table IIIa) molybdenum alone gave 3.6 and 2.9 p.p.m. and molybdenum plus phosphate 5.0 and 3.1 p.p.m.

After the first crop, further evidences of interrelations between phosphate fertilization and molybdenum accumulation by plants were found to be variable among the several soils. With soil D the effect of phosphate in increasing molybdenum absorption remained throughout all three crops, but with the other soils no consistent trend could be shown after the first crop. However, results of the

TABLE IIIa

Yield and Molybdenum Content of Garden Peas Grown in Soils Fertilized with Molybdenum and Phosphates										
Third Crop, Garden Peas										
	Soil A		Soil B		Soil C		Soil D		Soil E	
Treatment *)	Yield g	Mo p.p.m.	Yield g	Mo p.p.m.	Yield g	Mo p.p.m.	Yield g	Mo p.p.m.	Yield g	Mo p.p.m.
1. None	2.3	0.52	3.8	1.3	3.4	1.2	2.0	2.6	3.4	1.7
	3.3	1.5	4.0	1.5	1.45	2.6	1.7	2.8	3.8	2.0
2. + Mo	3.1	3.6	3.95	3.7	3.3	7.6	2.04	9.4	2.92	3.3
	4.4	2.9	4.0	3.2	4.6	6.2	2.0	12.5	3.4	3.6
3. + PO ₄	4.8	1.4	4.7	0.9	5.7	1.1	0.6	1.8	4.35	1.56
	4.4	1.0	4.3	1.1	3.3	1.8	1.1	1.4	3.36	1.8
4. + PO ₄ +Mo	4.6	5.0	5.4	2.8	4.0	12.9	3.9	18.8	3.60	3.4
	4.5	3.1	4.6	2.5	4.9	4.7	1.24	27.5	3.42	3.4

*) Treatments were made before the first crop of subterranean clover. For methods of treatment, refer to Table I, also note, data for each replicated culture occupy the same positions as data in Tables I and III.

first crop left no doubt as to an association between the phosphate levels of soils and their influence on molybdenum absorption by plants. Reasons for such effects had to be looked for with simpler systems than the complex soil medium.

An early explanation was that phosphates added to the soil might have resulted in release of molybdate from the anion adsorption complex, thus making soil molybdenum available to plants. Such exchange systems had been postulated by Stephens and Oertel²⁵⁾ to explain plant responses to molybdenum when low molybdenum acid soils were limed. Later with similar soils, Anderson and Oertel³⁾ in a series of ingeniously designed experiments,

were able to conclusively demonstrate that increased nitrogen fixation by clovers was due to rendering molybdenum available when the soils were made less acid through liming.

Fixation and exchange of molybdate ions by soil clays. Since hydroxyl ions are effective in replacing adsorbed phosphate ions^{12) 26)}, there was reason to believe that if molybdates were in fact adsorbed by soil colloidal materials they should be similarly replaceable by hydroxyl ions. So far, however, the only anions recognized by soil chemists as being strongly fixed in exchange processes with soil colloidal materials are phosphate, arsenate, fluoride and hydroxyl ions. The exchange properties of molybdate should approach those of sulfate since the two ions are of the same size and charge. Sulfate, however, is not usually regarded as being fixed by soil colloidal materials, although Reitemier²²⁾ has indicated that important amounts were fixed in adsorbed form by a moderately acid Palouse soil.

Adsorption of molybdate ions by halloysite by anion exchange. In order to check the adsorption of molybdate by a pure clay material of known structure, adsorption experiments were conducted with hydrated halloysite. Hydrated halloysite is an ideal clay mineral for studying anion exchange reactions since its crystallographic structure is characterized by an entire sheet of hydroxyl ions at one side of each neutral kaolin like packet. Moreover, it is known²⁶⁾ that its exposed lattice hydroxyl ions readily exchange for phosphate ions. It was expected that if molybdates were capable of participating in similar exchange reactions, they should also be adsorbed by this clay material.

An experimental column of hydrated halloysite was prepared as follows: One hundred grams of hitherto undisturbed lumps of hydrated halloysite were crushed in a mortar and passed through a 1 mm sieve. The screened material was suspended in distilled water and the fine material was decanted several times. A glass cylinder 2.7 cm in diameter was then filled with the halloysite to a height of 11 cm. The resulting column permitted a relatively high percolation rate of $2\frac{1}{2}$ ml per minute with a total head of 15 cm of water.

In order to remove soluble molybdenum, the column was leached with 0.1 N Na_2CO_3 . Successive 50 ml portions of the leachate were

analyzed for molybdenum. The first increment of 50 ml passing through the column removed one microgram of molybdenum. No detectable amount of molybdenum appeared in the fourth leaching. A total of 1.8 micrograms molybdenum was removed by the four leachings.

Following the sodium carbonate wash, the column was leached with .02 N HCl until all alkali disappeared. It was further washed with distilled water until free of chlorides.

Fifty ml of water containing 300 micrograms molybdenum as Na_2MoO_4 were then passed through the column followed by leaching with distilled water. Four successive 50 ml aliquots of the leachate were analyzed. No molybdenum could be detected in 200 ml of the leachate showing that the molybdate had been completely fixed.

In order to determine the position of the molybdenum, within the column the halloysite block was removed and cut into seven 1.5 cm segments. Molybdenum in the separate segments was displaced from the halloysite by heating each segment with 50 ml of 0.5 N Na_2CO_3 . After warming for 2 hours on the steam bath, the solutions were decanted and analyzed. The first five segments beginning from the uppermost, released 2.39, 0.08, 1.9, 1.1, and 1.7 micrograms of molybdenum respectively. The last two segments were not analyzed.

This experiment showed molybdates to be strongly fixed by halloysite. It also showed that much of the fixed molybdenum was released by moderately alkaline solutions presumably by an anion exchange process.

Because of the completeness of removal of molybdates by the halloysite from a water solution, it was thought that similar columns might be effectively used as a means of separating trace amounts of molybdenum from some of our stock salt solutions used for plant cultures and fertilizers. However, substantial quantities of molybdates were found to pass through the column with the percolate when a molar solution of MgSO_4 containing molybdates was substituted for water. It was assumed, pending further investigation, that in molar salt solutions of sulfates molybdates had been less effectively adsorbed by halloysite because of competition of the sulfates for anion exchange positions.

The chemistry of molybdate adsorption and exchange in soil materials is the subject of more extended investigations currently in progress in our laboratory. Goldberg¹⁵⁾ with more refined

chemical procedures has examined molybdenum fixation by soils and soil minerals over a wide range of pH values and finds that the degree of fixation continues to increase with acidity until pH values as low as 2.2 are reached, and that all molybdenum fixed by exchange can be released with alkaline solutions of pH 9. He has also shown that soluble phosphates can exchange for adsorbed molybdates.

Thus enhanced molybdenum absorption by plants from phosphate fertilized soils could be explained in part by replacement of soil molybdate from the anion exchange complex by phosphates.

Absorption of molybdenum from culture solutions in short time absorption experiments. We were fortunate in obtaining a sufficient quantity of radioactive isotopes of molybdenum (Mo^{93} and Mo^{99}) of high enough specific activity to permit short time plant absorption experiments with molybdenum levels of physiological significance. The high specific activity was attained through transmutation of zirconium by alpha bombardment. With the material available, it was possible to conduct absorption experiments using a single microgram of molybdenum for an entire culture supporting one to three vigorously growing tomato plants three to six weeks of age.

A preliminary report of the essential features of these experiments with radioactive molybdenum isotopes has been published elsewhere ²⁸). It was found that molybdenum uptake from single salt solutions was stimulated by phosphate ions to a greater extent than any other ion tested in the group consisting of Ca^{++} , Mg^{++} , NH_4^+ , K^+ , Na^+ , H_2PO_4^- , SO_4^- , NO_3^- , and Cl^- . Moreover sulfate ions appeared to interfere with molybdate absorption at least by comparison with phosphate, nitrate or chloride ions. Typical data secured from a 24 hour molybdenum absorption experiment *) given in Table IV illustrates these points.

*) It should be noted that when conducting experiments with tagged elements it is necessary to know the total amount of the element present in the system capable of diluting the radioactive isotope by isotopic exchange. If, for example, one microgram of molybdenum were to be inadvertently contained in the culture solution in addition to the one added intentionally, the amount of molybdenum estimated from measurements of radioactivity would be only one half the true value. By use of the colorimetric stannous chloride thiocyanate extraction method (24) and extraction of pentavalent molybdenum thiocyanate in 3 ml of iso-amyl alcohol, one microgram of molybdenum can be estimated within $\pm 10\%$. Direct analysis of the molar salt solutions used to prepare the culture showed less than .5 microgram of molybdenum in 25 ml of the stock salt solutions of which 1 ml was used in preparing the culture. The pyrex distilled water prepared in our

Experimental method of short time absorption experiments with molybdate.

Twelve different salts, 0.005 Normal with respect to the cation, were placed in separate quart jars used as absorption vessels. Each culture solution of 800 ml contained one microgram of molybdenum as molybdate tagged with the radioactive molybdenum isotopes Mo^{93} and Mo^{99} . Samples of the original radioactive material were set aside as standards for subsequent radioactivity assays of the various plant fractions. Marglobe tomatoes previously grown for three weeks in the same large culture tank in a complete nutrient medium were transferred to the one quart jars for the absorption experiments. The average fresh weight of the plants was 8.8 grams but with individual variations ranging from 7.5 to 12.2 grams. The plants were chosen at random for the individual treatments. Oxygen was supplied by forcing air through sintered pyrex glass aerators. The absorption period began at 4 P.M. of one day and lasted to 4 P.M. of the next. Although the experiments of table IVa were conducted on the 27th and 28th of January, the plants had previously had the benefit of good growing weather, and on the day of the absorption experiment, warm sunny weather prevailed. Thus conditions conducive to transpiration were in effect.

After harvesting the plants, they were separated into blade, stem and root fractions, fresh weights were taken, and the several fractions were ashed and assayed for radioactive molybdenum. The concentration of molybdenum referred to the fresh weight of plant material gave more consistent comparative data than when referred to the total amounts of molybdenum absorbed per plant. Because the solutions were not well buffered growing plants caused rapid shifts in pH. Therefore, pH values were measured before and after the absorption period and are given in table V.

Data shown in Table IV were secured from 15 separate culture solutions, each having a single plant. The concentrations of radioactively tagged molybdenum found in the several treatments vary greatly, but even so, certain points of consistency were revealed. Of particular note was that in each instance where sulfate salts were used, the lowest molybdenum concentrations were found in stems and blades, and wherever phosphate salts were used, the highest amounts of molybdenum were found in stems and blades. Root absorbed molybdenum was higher than for tops of plants, and did not reflect similar differences. Thus, the highest degree of contrast is

laboratories for micronutrient cultures is known to supply less than .005 micrograms per liter, as has been determined by numerous plant culture experiments. Thus the molybdenum contamination in the culture solution used in these experiments was shown chemically to be less than .02 microgram, that is, less than 2% of the amount added for the absorption experiments.

shown by the molybdenum absorbed and translocated in the presence of phosphates and sulfates as may be seen in the molybdenum concentrations of stems and blades in lines 3 and 4 of Table IV.

TABLE IV

Molybdenum Absorbed in 24 Hours from Single Salt and Complete Cultures Initially Containing 1 Microgram of Radioactively Tagged Mo (Absorption calculated as parts per billion — Fresh weight)												
Plant fraction	Blades			Stems			Roots			Percent of tagged MoO ₄ removed from culture soln. in 24 h.		
Cation/Anion	NH ₄ ⁺	K ⁺	Ca ⁺⁺	NH ₄ ⁺	K ⁺	Ca ⁺⁺	NH ₄ ⁺	K ⁺	Ca ⁺⁺	NH ₄ ⁺	K ⁺	Ca ⁺⁺
1. NO ₃ ⁻	27	17	33	2.9	4.1	10.4	44	16	31	23	11	18
2. Cl ⁻	21	7.4	11	4.2	1.4	7.8	7.0	34	10	13	9.3	11
3. H ₂ PO ₄ ⁻	39	97	44	13	21	21	60	86	86	37	61	34
4. SO ₄ ⁼	4.1	1.0	5.0	0.2	0.6	1.0	65	34	85	15	7.0	20
5. *0.1 strength culture solution			5.4			4.5			48			16

*0.1 strength Hoagland's culture solution, i.e. in m. eq. per liter Ca-10, Mg-0.4, K-0.6, NO₃-15, SO₄-0.4, H₂PO₄-0.1.

On the assumption that phosphates stimulated molybdenum uptake it also appeared that sulfate ions depressed translocation from roots to the upper parts of plants.

Since the total accumulation of molybdenum by roots in the presence of either phosphate or sulfate salts was not significantly different, these data further suggested direct competition between sulfate and molybdate ions within channels through which divalent anions are transferred from roots to the conducting system of the plants.

Further evidence of analogous mechanisms of accumulation of sulfates and molybdates is to be found in the radio-autographs reported by Stout and Meagher²⁸) and by Fried¹⁴). Stout and Meagher have called attention to the distinctly different pattern of distribution of absorbed molybdates from the patterns of other absorbed nutrient ions such as potassium, phosphorus, manganese, and zinc. They found that molybdenum was preferentially accumulated in interveinal areas of leaves whereas the other nutrient ions presented quite an opposite picture; namely, that they were preferentially absorbed in the midribs and veins.

Fried¹⁴) has found precisely the same pattern of distribution of absorbed sulfates in alfalfa as Stout and Meagher discovered for absorbed molybdate with the tomato plant. Moreover, Fried calls attention to the fact that the distribution pattern of absorbed

phosphates is directly opposite to that of sulfates in as much as his radioautographs showed a concentration of phosphorus in the transporting system of the alfalfa plant.

TABLE V

pH Values of Culture Solutions Before and After the 24 Hour Absorption Experiment of Table IV						
Cation	NH ₄ ⁺		K ⁺		Ca ⁺⁺	
	pH		pH		pH	
	before	after	before	after	before	after
NO ₃ ⁻	5.7	5.5	5.7	6.3	5.7	6.4
Cl ⁻	5.5	4.6	5.8	6.2	5.8	6.3
H ₂ PO ₄ ⁻	4.9	5.0	4.9	4.8	3.6	3.8
SO ₄ ⁼	5.5	4.4	5.7	5.6	5.6	5.6

0.1 strength culture solution, pH before absorption 5.5, pH after absorption 5.0.

The pH values of the culture solutions (Table V) showed the calcium phosphate solution to be more acid than the others. Also since some of the salt solutions were unbuffered, sizeable changes in reaction occurred in some of them. For example with NH₄Cl and CaCl₂, at the beginning of the absorption period, the pH of the NH₄Cl solution was 5.5 and the CaCl₂ solution was 5.8. After 24 hours they were found to be respectively pH 4.6 and 6.3. Because of such discrepancies in controllability of hydrogen ion concentrations in these experiments, others were undertaken for the purpose of securely establishing the interrelations between molybdates, phosphates and sulfate as they appeared to be suggested in the data of Table IV.

In order to obtain more substantial evidence of the indicated phosphate effect, it was decided to investigate separately first, the influence of the hydrogen ion concentration of the culture solution on the absorption of molybdenum from solutions containing phosphate and molybdate ions; second, the quantitative interrelations between phosphate concentration and molybdate absorption over wider ranges of phosphate concentrations at a fixed molybdenum supply; and third, the influence of sulfate ion concentration on molybdenum absorption at a fixed molybdenum supply. Also implications of interrelations between molybdate and sulfate, or molybdate and phosphate revealed in short time absorption studies were to be tested over much longer growth periods, preferably with both culture solutions and soils. All subsequent experiments have supplied

corroborative evidence of enhanced molybdenum uptake with increasing phosphate levels, and further evidence was obtained showing the opposite effect with increasing levels of sulfate ions.

Effect of hydrogen ion concentrations on molybdenum absorption by plants from culture solutions containing phosphate. Increased molybdenum adsorption by plants has been associated with increasing degree of soil alkalinity by Anderson and Oertel³⁾, Stevens and Oertel²⁵⁾ and Piper²¹⁾. They have shown that making soils less acid results in increased molybdenum absorption by plants, and have interpreted their findings as meaning that exchangeable molybdenum is released from soil materials as they are rendered less acid. Such an interpretation is proper in view of known properties of molybdate as an exchangeable anion.

Since all soils or culture solutions capable of supporting plants contain phosphates, it was decided that measurements of the hydrogen ion effect in the presence of phosphates should be informative of general situations with growing plants. In our work with culture solutions it was expected that molybdenum absorption would be found to vary with the hydrogen ion concentration since the solution pH determines the dominant type of phosphate ions in solution.

In the following experiment involving an absorption period of 6 hours the radioactive isotope used was mostly Mo^{93} of half life 6.7 hours. Procedures were the same as described earlier in this paper, with some minor exceptions to be noted. Marglobe tomatoes were first grown for two weeks in a single large tank. Three plants were later transferred to each of a series of absorption vessels containing potassium hydrogen phosphate buffers .0022 molar with respect to PO_4 , made up to cover the range of pH 3.5 to pH 8.5. Each culture was provided with 1 microgram of the radioactivity tagged molybdenum, and three replications were made of each culture.

After the absorption period the plants were harvested, separated into tops and roots, assayed for radioactive molybdenum. The pH of the culture solutions was not controlled during the absorption period, but the change in reaction for the entire period was determined from pH measurements of the cultures immediately after the plants were removed. Solutions of pH 6 remained relatively constant. Cultures either more acid or more alkaline shifted toward pH 6 as a result of the action of absorbing plants.

Data showing the absorption of molybdenum by the tops of the plants as a function of culture solution pH are given in Figure 1. Accumulations by the roots are shown in Figure 2. The amount of molybdenum absorbed is given as parts per billion fresh weight for each replicated culture. Changes of the pH of the culture solution during the absorption period are indicated by the length of the arrows drawn parallel with the abscissa. The circles on the arrow indicate the pH of the culture solution as it was at the beginning of the absorption period, and the head of the arrow the final pH. The length and direction of the arrow, therefore, shows the magnitude and direction of the shift in pH during the period of absorption.

The effect of acid reactions on molybdenum absorption is very large, the plants of the two most acid solutions having absorbed in the order of 5 times the amount of plants in the two most alkaline solutions. In this experiment, concentration of radioactive molybdenum found in plants was higher than that of the culture solution. Thus molybdenum accumulation took place against a concentration gradient, the molybdenum concentration of the culture solution initially being one part per billion, and the concentration in the plants from 1 to 8 parts per billion depending upon the particular culture solution. Molybdenum concentrations found in the roots were very much higher than in the tops — from 10 to several hundred parts per billion.

It is manifest that, under the conditions of this experiment, acid reactions favor molybdenum absorption by roots, and also the amount transported into the tops of the plants. The most rapid rise in the efficiency of absorption by tops lies within the region of pH 4.5 to pH 5.5. No reason for this behavior can be given from these data, but it is observed that the region of most rapid increase in absorption efficiency also corresponds to the pH values of solutions where the H_2PO_4^- ion predominates. One might therefore speculate that the influence of phosphates in enhancing molybdenum uptake would be more intense where the phosphates were in the form of H_2PO_4^- .

Although these data show that plants are capable of extracting molybdenum from acid solutions much more efficiently than from alkaline ones, this fact is not contradictory to the findings of other workers in experiments with soils who have reported ⁸⁾ ²¹⁾ ²⁵⁾ higher molybdenum accumulations by plants as a result of adding lime to

acid soils. It can be postulated that the release of molybdenum fixed by soil colloids must more than compensate for the inhibitory influence of alkaline solutions as shown graphically in figures 1 and 2.

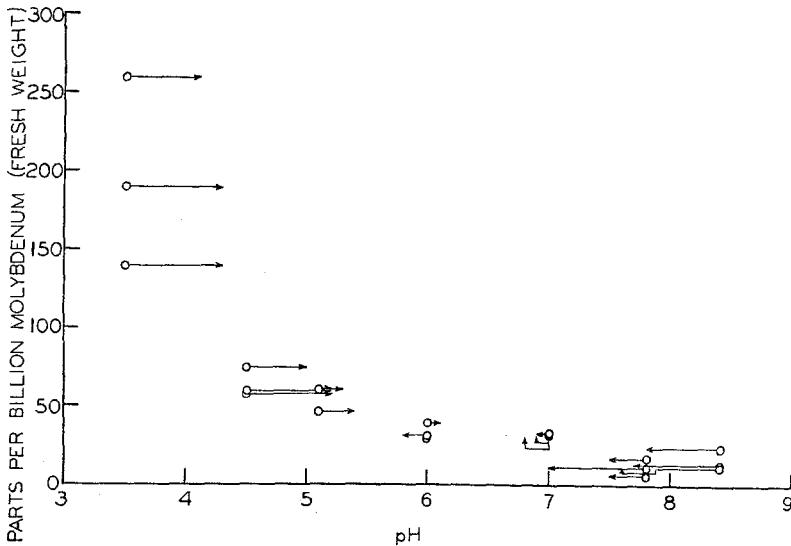


Fig. 1. Effect of pH on molybdenum absorbed and translocated to shoots of plants from solutions of .0022 M PO_4 and 1.1 p.p.b. Mo as MoO_4 .

Effect of Phosphate Concentration of Culture Solutions on Molybdenum Absorption by Plants. Since the earlier experiments with soils as well as culture solutions suggested that increased phosphate levels could be specifically associated with higher molybdenum absorption, we wished to obtain more information as to the different phosphate concentrations over which the observed interrelation with molybdenum absorption would hold. In the following experiment, culture solutions of different concentrations of KH_2PO_4 were used. The experimental procedure was analogous to the short time absorption experiments using radioactive molybdenum already described. Seedlings of marglobe tomatoes were transplanted to a single tank and grown for three weeks without supplemental additions of micro-nutrients. For the absorption experiment the plants were transferred to quart mason jars provided with aerators. Each jar contained 1 microgram of radioactivity tagged molybdenum, but the phosphate levels were made to 0, 5.0, 25, and 125 parts per million PO_4 by adding

KH_2PO_4 . There were three replicate cultures for each level of KH_2PO_4 .

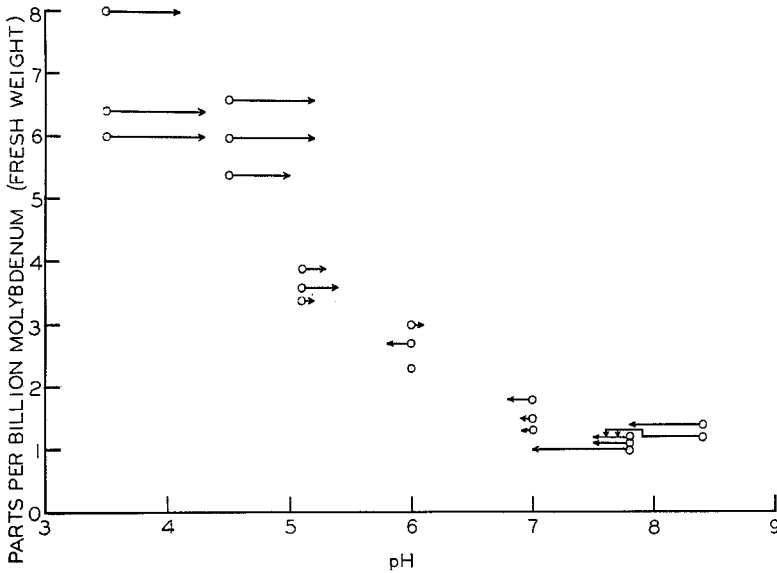


Fig. 2. Effect of pH on molybdenum absorbed and retained by roots from solutions of .0022 M PO_4 .

After an absorption period of 24 hours, the plants were harvested and assayed for radioactivity from which absorbed molybdenum was calculated. Mean values of molybdenum found in blades, stems and roots are given in Table VI. Increased molybdenum concentrations were found in all plant fractions as a result of adding KH_2PO_4 . Moreover, the increase was reflected at each higher level of potassium phosphate.

The accumulations of molybdenum in the blades of each plant in the experiment are shown graphically in Figure 3. Triangular points on the graph represent single culture and circles, the mean concentrations found for identical treatments. The line in Figure 3 was arbitrarily inserted as representing a linear relationship between the concentration of phosphate in the culture solution and molybdenum uptake, and was drawn between the mean molybdenum concentrations at the two terminal treatments. We attach no significance to the linearity of the relationship but do wish to emphasize the wide

TABLE VI

Effect of Phosphate Concentration of Culture Solutions on Molybdenum ¹⁾ Uptake by Plants ²⁾			
Treatment p.p.m. PO ₄ in culture solution	Parts per billion fresh weight ³⁾		
	Blades	Stems	Roots
None	2.5	1.4	10
5	3.2	1.85 ⁴⁾	13.5
25	11.3	6.0	20
125	35	14	41

¹⁾ 1 microgram molybdenum tagged with Mo⁹³, Mo⁹⁹ added to each culture solution of 800 cc.

²⁾ Marglobe tomatoes grown three weeks prior to the absorption experiment in a culture solution with no micronutrient supplement.

³⁾ Calculated from assays for radioactivity, each figure given is the mean of three separate plants.

⁴⁾ One sample lost: value indicated is the average of 2 samples.

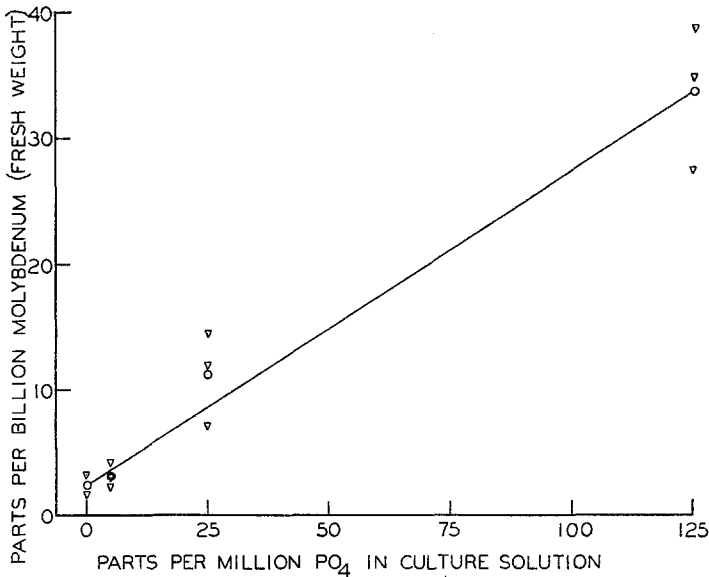


Fig. 3. The influence of phosphate concentration on molybdenum absorption as shown by tomato plants in a 24 hour absorption period.

Solutions initially contained 1 part per billion radioactively tagged molybdenum as molybdate ion.

range in phosphate concentrations over which the molybdenum-phosphate interrelation is operative.

As with other short time absorption experiments, it was found that

absorption of molybdenum by roots was not significantly influenced by the composition of the culture solution, but the amount of molybdenum translocated to the upper parts of the plant was greatly different.

It was earlier pointed out that experimental artifacts might result from isotopic dilution of the radioactive isotopes with inadvertently included non-active molybdenum isotopes. This, however, may be excluded from consideration in these experiments since the only regular variable introduced in the experiment was the amount of KH_2PO_4 added. Any effect of isotopic dilution with molybdenum impurities in the phosphate would lead to results diametrically opposite to those obtained.

The response observed is attributed to phosphates and not to potassium added concomitantly, since other experiments (Table IV) have shown no measurable effect of different cations including potassium, ammonium and calcium.

Phosphate levels of culture solutions with respect to molybdenum absorption by plants grown on culture solutions to maturity. If enhanced molybdate absorption induced by phosphates as shown in the above section for an absorption period of 24 hours were to have general significance in plant nutrition it should also be evidenced by tomato plants grown to maturity. We were able to check this point by analyzing plant parts made available to us from another study of Arnon and Hoagland⁵). In their studies in connection with the mineral composition of tomato plants they had occasion to grow plants to the fruiting stage at two different levels of phosphate supply.

It appeared that one of their experiments designed to determine the influence of phosphate on the mineral nutrition of bearing tomato plants would also serve admirably as a means of determining the influence of phosphate on molybdenum absorption. Their plants had been grown for 5 weeks on a complete culture solution at which time the first flowers had emerged. Plants were then selected for uniformity and divided into groups of 24 in other culture solutions. Some were allowed to set fruit and others were deflowered. Both kinds of plants were further grown on culture solutions with and without phosphate. The only other variation in the compositions of the culture solutions was with respect to sulfate which was used to replace

phosphate in the minus phosphate cultures. However, the total concentration of sulfate in the two culture solutions was not greatly different, being 14 m. eq. per liter in the high phosphate culture, and 16 m. eq. per liter in the minus phosphate culture. It was reasoned that the specific influence of sulfate on the absorption of molybdate should thus be minimized and even if molybdenum absorption directly decreased in proportion to sulfate concentration, the expected decrease should not be greater than $\frac{1}{7}$ or approximately 15%. Phosphate stored by the plants during their first five weeks of growth was sufficient to allow subsequent fruiting on the minus phosphate cultures, although their total growth was approximately one fifth that of the plants having a high phosphorus supply. The deflowered plants produced approximately twice the vegetative growth of those allowed to set fruit. Thus, comparisons of molybdenum absorption within this particular set of plants should provide information as to the general extent of the phosphate molybdate interrelation over a wide range of variability with respect to plant growth under different nutritional, and physiological states.

All similar plant materials available which could be paired between high and low phosphate culture solutions on a given harvest date were analyzed for molybdenum. The molybdenum contents of the several plant parts are given in table VII.

Without exception, it is shown in Table VII that comparable plant parts grown on solutions containing 200 p.p.m. phosphate have higher concentrations of molybdenum than those grown part of the time on cultures without phosphate. Averaging the concentrations of molybdenum found in leaves, without regard to position along the stem, condition of fruiting of the plant, or harvest date, the mean concentration was 1.85 p.p.m. molybdenum for leaves from plants grown on high phosphate cultures and 0.85 p.p.m. molybdenum for the low phosphate cultures. Corresponding averages for molybdenum concentrations of stem material were 1.20 and 0.54 p.p.m. molybdenum respectively for the high and low phosphate cultures. The increased molybdenum concentrations shown to be associated with higher phosphate concentrations are highly significant, exceeding the .1% level for both leaves and stems.

Another point of interest in the analyses shown in Table VII was the lower molybdenum content of stems as compared to leaves, which provided corroborative evidence earlier established with radio

TABLE VII

Relation of the Phosphate Level to Molybdenum Uptake by Tomato Plants Grown to Maturity in Culture Solution					
Harvest Date	Differential treatment other than nutritional	Plant Part	Position ¹⁾ on Plant	Molybdenum p.p.m. dry weight	
				High PO ₄ ²⁾	Low PO ₄ ³⁾
5/22/42	Fruitful	Leaves	2	1.9	0.8
			4	2.0	1.1
		Stems	4	1.2	0.6
	Deflowered	Leaves	6	1.8	1.1
			Stems	6	1.3
				5	1.3
7/10/42	Fruitful	Leaves	1	2.0	0.5
			3	2.1	0.7
		Stems	3	1.1	0.5
			22	1.1	0.6
	Deflowered	Leaves	2 and 3	1.3	0.9
Mean concentration in leaves (all data)				1.85	0.85*** ⁴⁾
Mean concentration in stems (all data)				1.20	0.54*** ⁵⁾

¹⁾ Descending from top of plant.

²⁾ Phosphate in culture solution 200 p.p.m.

³⁾ Phosphate in culture solution none after first 5 weeks.

⁴⁾ Comparing low with high PO₄ treatments for significance of increased molybdenum concentration in leaves. $t = 6.59$, 10 degrees of freedom. Significance exceeds the .1% level.

⁵⁾ Comparing low with high PO₄ treatments for significance of increased molybdenum concentrations in stems. $t = 11.0$, 8 degrees of freedom. Significance exceeds the .1% level.

autographs of plants having absorbed Mo⁹³ and Mo⁹⁹ ²⁸⁾ that molybdenum, unlike other essential elements absorbed by roots is less actively accumulated by cells adjacent to the transpiration stream, and is thus deposited in relatively higher concentrations in the leaves.

Effect of sulfate on molybdenum absorption in the presence of phosphate ion. Whereas earlier experiments were conducted with single salt solutions the following one was designed to permit observation of the influence of sulfate ion on the absorption of molybdate from solutions also containing phosphates. As in our earlier short time absorption experiments, high specific activity radioisotopes were used in order that quantitative analysis could be made of sub-micro-

gram amounts. The total amount of tagged molybdenum added to the culture solutions of 800 ml was one microgram.

Marglobe tomato plants were grown in a single culture of one tenth the usual strength for three weeks prior to the experiment. Although the plants had the benefit of excellent growing weather and appeared healthy, they varied considerably in size as indicated by their fresh weights (Table VIII). No attempt was made to choose plants of uni-

TABLE VIII

Effect of Sulphate on Mo ¹⁾ Absorption from Solutions of KH ₂ PO ₄ . Absorption Period 41 Hours											
Culture Solution Numbers	Section	Treatment	Mo, Parts per billion (fresh weight of plant)						Mean	σ_x ⁵⁾	<i>t</i> ⁶⁾
			<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>			
1-6 ²⁾	Blades	1. PO ₄	9.9	14.4	9.3	10.7	6.6	15.1	11.0	1.31	4.10**
7-12 ³⁾	„	2. PO ₄ + SO ₄ ³⁾	4.7	5.1	5.5	5.9	5.3	6.6	5.5	0.27	
1-6	Stems	1. PO ₄	10.6	13.3	21.3	6.7	3.4	8.7	10.7	2.53	3.35**
7-12	„	2. PO ₄ + SO ₄	2.1	2.6	2.1	2.2	1.7	2.6	2.2	0.14	
1-6	Roots	1. PO ₄	22	22	20	22	16	18	20.1	1.03	1.66 n.s.
7-12	„	2. PO ₄ + SO ₄	18	13	23	18	12	17	16.8	1.62	
Fresh weight of plants — grams ⁴⁾											
1-6			6.2	5.6	6.7	11.0	8.9	12.1	8.4	1.09	0.13 n.s.
7-12			5.1	8.0	6.7	7.3	18.8	6.4	8.7	2.06	
pH of culture solutions after absorption period											
1-6		PO ₄	5.5	5.4	5.4	5.4	5.5	5.2			
7-12		PO ₄ + SO ₄	5.3	5.4	5.3	5.3	5.2	5.3			

1) Molybdenum tagged with Mo⁹⁹. 1 microgram Mo added to each culture as Na₂MoO₄.

2) 125 p.p.m. PO₄, added as KH₂PO₄ to all cultures, Columns *a, b, c, d, e, f*, correspond to solution culture numbers 1, 2, 3, 4, 5 and 6 respectively.

3) 125 p.p.m. PO₄ plus 200 p.p.m. SO₄ added as KH₂PO₄ and K₂SO₄ to all cultures, Columns *a, b, c, d, e, f*, correspond to solution culture numbers 7, 8, 9, 10, 11 and 12 respectively.

4) Fresh weights were taken after harvest, total weight included roots.

5) σ_x = standard error of the mean.

6) Comparison between treatments 1 and 2 for significance of differences in molybdenum concentrations. Student's *t* values for 10 degrees of freedom, at 10% level, *t* = 1.81; at 5% level = 2.23 at 1% level = 3.17.

The total amount of molybdenum adsorbed per plant was highly variable. From these data it is apparent that the amount of molybdenum accumulated by a plant is nearly a direct function of its size as determined by weight.

form size but 12 plants were selected from the stock culture tanks at random and transferred to 12 quart jars provided with means of aeration. Two treatments were used, one being phosphate alone, and the other phosphate plus sulfate. There were six replicate cultures

for each treatment. Solutions received 1 microgram of tagged molybdenum and sufficient KH_2PO_4 to make them 125 parts per million with respect to PO_4 . The phosphate plus sulfate cultures were made to contain 200 parts per million SO_4 added as K_2SO_4 .

Since the relatively large amount of KH_2PO_4 in the culture solutions acted as a buffer, the absorption period was extended to 41 hours (5 : 30 p.m. 4-2-48 to 10 : 30 A.M. 5-2-48). After the absorption period the plants were harvested, weighed, and separated into blade, stem and root fractions. Each fraction was assayed for absorbed molybdenum by means of the radioactivity of Mo^{99} . Results of the analyses are given in Table VIII.

The lowest molybdenum concentration found in the blades of a plant absorbing from a solution of KH_2PO_4 free from sulfate was 6.6 p.p.b. (col. e). The highest molybdenum concentration found in the blades of a plant absorbing from a solution containing added K_2SO_4 was also 6.6 p.p.b. (col. f). All other possible pairings between the two types of culture solutions showed molybdenum absorption to be depressed when sulfate was included.

Analogous comparisons between the two treatments referred to the plant stems show, without exception, that addition of K_2SO_4 reduced the concentration of molybdenum found in the stems.

Statistical treatment of the molybdenum concentrations in either the blades or stems, shows that the observed repression of molybdate absorption is highly significant, being above the 1% level for the blades, and above the 5% level for the stems.

Although this experiment in itself does not distinguish between potassium and sulfate as the factor responsible for suppression of molybdate absorption, the data of Table IV and of other experiments already discussed, make it evident that if potassium does not effect molybdate absorption, its influence is small relative to that exercised by sulfate.

Depression of Molybdenum Absorption from Soils Treated with Calcium Sulfate. Having studied the role of phosphates and sulfates in relation to molybdenum absorption from culture solutions it was thought that some gross corroborative test of the principles revealed should be made using the much more complex soil medium. If the observed influences of phosphates and sulfates were generally characteristic of the physiology of plants, it could be expected that

higher soil phosphate levels should give rise to greater molybdenum accumulation by plants. Conversely, any soil factors contributing to lower availability of phosphate should, for a given level of molybdenum, result in a lower molybdenum uptake. It should also be expected that higher soil sulfate levels should result in decreased molybdenum absorption by plants.

It was reasoned that both factors having been found to influence molybdenum absorption by plants would be simultaneously invoked if calcium sulfate were to be added to a neutral soil.

Reasons for expecting additions of calcium sulfate to suppress absorption of molybdenum through indirectly decreasing soluble soil phosphate of a neutral or slightly alkaline soil were as follows: In neutral or slightly alkaline soils, soluble phosphates in the soil solution are largely determined by the amount of soluble calcium ions present. Therefore, addition of a soluble calcium salt to such a soil should result in directly lowering the concentration of soil solution phosphate. *Burd*¹⁰⁾ has particularly emphasized this point in experiments showing a reciprocal relationship between the calcium and the phosphate concentrations of the diluted solutions coming from soil columns after the soil solution proper has been displaced by water. A second reason for expecting decreased molybdenum uptake upon supplementing soils with calcium sulfate was simply that the soil sulfate level would be thereby increased. These expectations have been entirely borne out as will be shown in the data of Table X. In order to minimize complications due to variations in growth that might result from the several treatments a fertile soil was selected for the experiment, namely, Yolo silty clay loam. The soil was regarded as highly fertile for agricultural crops. Also pot tests had shown no increased production in the first crop when fertilized with N, P or K*.

Chemical studies of the effect of additions of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and KNO_3 to the water soluble calcium, phosphate and sulfate of Yolo silty clay loam. Other physical and chemical data characterizing the soil were: moisture equivalent 24.6; cation exchange capacity 21.8 m. eq. per 100 g; and NH_4Ac extractable cations being, Ca 14.0, Mg 8.2, K .78, and Na .45 m. eq. per 100 g. Water soluble nitrate was 173 p.p.m.

*) This soil was supplied to us by Dr. A. Ulrich who had used it in connection with pot tests with sugar beet production.

The comparative figure for phosphate supplying power of this soil as given by Bingham's water extraction method⁸⁾ was .20 p.p.m. PO₄ in the 1 : 10 water extract. According to Bingham's criteria, 82 percent of randomly selected soils showing this amount of water soluble phosphate could be expected to be phosphate deficient. It must be assumed that although the phosphate supplying power of this soil was low, it was not limiting. Further testimony of the high level of fertility of this soil is given in the uniformly high yields obtained with the first crop of tomatoes as shown in column *e* of Table X.

TABLE IX

Changes in the Calcium, Phosphate, and Sulfate Concentrations of 1 : 1 Water Extracts at Various Levels of CaSO ₄ and KNO ₃ Added to a Yolo Silty Clay Loam										
Treatment	Crop numbers to which treatment apply	Salt added		Equivalents per million parts of solution in 1 : 1 water extracts			Product Ca ⁺⁺ X HPO ₄ ⁼ Moles/l × 10 ⁹	Water sol. PO ₄ in a 1 : 10 extract p.p.m.	pH of 1 : 1 suspension	g dry wt. tomatoes 1st crop
		p.p.m.	Lb per acre	Ca ⁺⁺	HPO ₄ ⁼ × 10 ³	SO ₄ ⁼				
<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>	<i>g</i>	<i>h</i>	<i>i</i>	<i>j</i>	<i>k</i>
1	1,2	None	None	4.40	2.47	0.43	1.55	0.20	6.8	138
3	1	100 p.p.m. CaSO ₄ ·2H ₂ O	196	5.04	2.16	0.96	1.55	0.20	6.8	134
4,5	1,2	400 p.p.m. CaSO ₄ ·2H ₂ O	284	6.90	1.96	2.82	2.26	0.17	6.9	133
6	2	2000 p.p.m. CaSO ₄ ·2H ₂ O	3920	18.24	1.71	12.31	3.74	0.11	6.7	
7	1	*50 p.p.m. N	64.5 N	5.50	2.08	0.36	1.63	0.19	6.8	136
8	2	*152 p.p.m. N	196 N	8.54	1.84	0.32	2.24	0.15	6.8	
9	1	*200 p.p.m. N	258 N	10.10	1.65	0.27	2.38	0.15	6.8	136
10	2	*455 p.p.m. N	586 N	16.80	1.48	0.35	2.08	0.13	6.5	

*) Added as KNO₃.

In order to determine changes in the water soluble sulfates and phosphates induced by the additions of CaSO₄·2H₂O and KNO₃, separate samples of soil were used. After treatment, 1 : 1 water extracts were analyzed. Results of the analyses are given in Table IX.

As would be expected, additions of CaSO₄·2H₂O, raised the amount of water soluble calcium and sulfate as shown in Table IX, columns *e* and *g*. With increasing water soluble calcium, phosphate concentrations in the water extract was reduced from 0.20 to 0.11

p.p.m. (column *i*). It was also noted that the solubility product $[\text{Ca}^{++}] [\text{HPO}_4^-]$, increased from 1.55 to 3.74×10^9 , when 2000 p.p.m. $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ were added to the soil. It is suspected that this was due to release of some exchangeable hydrogen even though the suspension pH was not materially effected within the degree of accuracy of the pH measurements. Increasing additions of KNO_3 also resulted in corresponding reduced water soluble phosphate. Reasons for the later are to be found in analyses of water soluble calcium shown in column *e*. It is seen that the added potassium replaced calcium from the exchange complex. Also upon addition of KNO_3 some exchangeable hydrogen may have been released, as evidenced by an increase in the product $[\text{Ca}^{++}] [\text{HPO}_4^-]$. (Column *h*, Table IX).

Procedure for determination of the effect of adding $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and KNO_3 to soils on the molybdenum absorption by plants. Seven kilograms of Yolo silty clay loam were placed in 2 gallon stoneware crocks, each having an area of 7.75×10^{-6} acres and a soil depth of 8 inches. Four separate crocks were provided for each treatment. Additions of gypsum and potassium nitrate were made by dry mixing the finely ground salts. Seeds were planted in the crocks, and after they had germinated molybdenum was added to the surface as a solution of Na_2MoO_4 .

The ten different soil treatments were distributed over two different crops as shown in columns *a*, *b*, *c* and *d* of table X. The first crop received six treatments, two of them (treatments 3 and 5) involving additions of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and two others (treatments 7 and 9) the addition of KNO_3 . Treatment 1 was the control and treatment 2 had only Na_2MoO_4 added. Between the first and second crops, some crocks having received $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ or KNO_3 , were supplemented with further additions of the respective salts. Thus the crocks of treatments 3 and 5 receiving $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ before the first crop became treatments 4 and 6 for the second crop at higher levels of added $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Similarly, treatments 7 and 9 of the first crop, upon further addition of KNO_3 became treatments 8 and 10 for the second crop.

The plants were grown in the open, each crock being thinned to five tomato plants or four pea plants. Two successive crops were grown. Crop 1 was planted April 7 and harvested July 10, 1948, and

crop 2 was planted October 6, 1948, and harvested January 3, 1949. A second crop of tomatoes was much inhibited in growth during the colder weather and was finally lost by freezing. After harvest, the plants from each crock were dried, weighed and analyzed for molybdenum content as single samples. Molybdenum contents of the plant materials are shown in Table X.

TABLE X

Suppression of Molybdenum Absorption of Tomato and Pea Plants by Additions of CaSO ₄ to a Fertile Soil												
Treatment No.	Additions to Soil ¹⁾				First Crop ²⁾ Tomatoes			First Crop Peas ²⁾			Second Crop ³⁾ Peas	
	Material added in large amount	Amt. added as p.p.m. dry soil	Amt. added as lbs per acre	Mo ¹⁾ treatment	Yield		p.p.m. Mo	Yield		p.p.m. Mo	Yield	
					Total g dry wt.	tons per acre		Total g dry wt.	tons per acre		Total g dry wt.	p.p.m. Mo
<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>	<i>g</i>	<i>h</i>	<i>i</i>	<i>j</i>	<i>k</i>	<i>l</i>	
1	None	None	None	None	138	4.9	1.25	111.2	4.0	1.3	29.8	1.7
2	None	None	None	+	115	4.1	5.25	87.3	3.1	12.8	32.5 ⁸⁾	16.0
3	CaSO ₄ ·2H ₂ O	100	196	+	134		3.52	110.0	3.9	8.05		
4	CaSO ₄ ·2H ₂ O	400	784	+		4.8					46.8	6.0
5 ⁴⁾	CaSO ₄ ·2H ₂ O	400	784	+	133	4.7	2.45	93.5	3.3	5.7		
6 ⁵⁾	CaSO ₄ ·2H ₂ O	2000	3920	+							33.6	2.75
7	*N	50	64.5	+	136	4.8	4.7	99.5	3.7	9.4		
8 ⁶⁾	*N	152	146	+							44.4	8.8
9	*N	200	258	+	136	4.8	4.8	98.6	3.7	7.1		
10 ⁷⁾	*N	455	586	+							31.8	5.5
Mean yield ± Standard Error of the Mean					132.0 ± 3.0 g			100.2 ± 3.9 g			36.5 ± 9.2 g	

¹⁾ All treatments except treatment 1 received 1.5 pounds molybdenum per acre, as Na₂MoO₄.

²⁾ Planted April 7, 1948, Harvested July 10, 1948.

³⁾ Planted Oct. 6, 1948, Harvested Jan. 3, 1949: Second planting of peas in same soil used for first crop of peas.

⁴⁾ Second crop was grown on same set of pots having 196 lb/acre CaSO₄·2H₂O during first cropping.

⁵⁾ Second crop was grown on same set of pots having 784 lb/acre CaSO₄·2H₂O during first cropping.

⁶⁾ Total N added for 2 crops. Second crop was grown on same set of pots, receiving 64 N/acre for first crop.

⁷⁾ Total N added for 2 crops: Second crop was grown on same set of pots receiving 258 N for the first crop.

⁸⁾ One pot was lost from the set — Weights of remaining 3 pots multiplied by 1.33 to obtain comparable yield for set.

*N added as KNO₃.

Discussion of molybdenum absorption by plants as influenced by addition of CaSO₄·2H₂O and KNO₃. In treatments 1 and 2, table X, it is shown that the addition of 1.5 pounds molybdenum per acre raised the molybdenum content of the tomatoes from 1.25 p.p.m. to 5.25 p.p.m. and that of peas from 1.3 to 12.8 p.p.m. The second crop

of peas were consistent with the first, the respective molybdenum concentrations being raised from 1.7 to 16.0 p.p.m.

However, addition of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (treatment 3) at the rate of 196 pounds per acre, decreased the molybdenum content of tomatoes and peas in all crops. In the first crop the molybdenum in tomatoes (column g) was reduced from 5.25 to 3.52 p.p.m. and with peas from 12.8 to 8.05 p.p.m. (column j).

A further decrease in molybdenum absorption resulted from the higher rate of application of 784 pounds CaSO_4 per acre (treatment 5), tomatoes being reduced to 2.45 p.p.m., and peas to 5.7 p.p.m. The second crop consisting only of peas had the molybdenum content reduced from 16.0 to 6.0 p.p.m. (Column l) as a result of adding 400 lbs. $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ per acre (treatment 4). Also, consistent with the trend of all other comparative data, addition of 3920 lbs. $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ per acre (treatment 6) further decreased the molybdenum content of peas to 2.75 p.p.m. Within each crop, all differences in molybdenum content of plant materials resulting from the additions of CaSO_4 have been treated statistically and shown to be significant at the 5% level or better.

Significant reductions in molybdenum absorption were also affected by additions of KNO_3 but they were not as great as for equivalent amounts of CaSO_4 added to the soil. The reduction of molybdenum absorption by plants as a result of adding KNO_3 could be regarded as the result of competition between nitrate and molybdate. However, it was also shown in Table IX that additions of KNO_3 to the soil reduced water soluble phosphate, ostensibly through the suppression of the solubility of CaHPO_4 by calcium ions released by exchange with the potassium added as KNO_3 . Therefore, it might also be deduced that the decreased level of soluble soil phosphate is compatible with a corresponding inhibition of molybdenum absorption as was indicated by studies with solution cultures discussed earlier.

Thus it has been shown that calcium sulfate added to soils exercised a marked depression of molybdenum accumulated by the two plant species, tomatoes and peas. Moreover, the degree of inhibition could be quantitatively assessed at different levels of added $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, ranging from the moderately low application of 196 pounds per acre to 3920 pounds per acre.

If, of course, cannot be specifically claimed that inhibition of

molybdenum absorption, shown in Table X can be entirely ascribed to competition between sulfates and molybdates and to the lower phosphate concentrations effected in the soil solution by adding calcium sulfate. It is of interest, however, that the predicted trend should be so nicely shown by an experiment designed to test the implications of the findings of laboratory studies of soil phosphates, coupled with short time plant absorption experiments involving sub-microgram amounts of molybdenum. Since it has been established that increased levels of calcium sulfate in the soil suppress molybdenum absorption by plants any explanations of the phenomenon must account for the contribution of the sulfate and phosphate factors as well as others which might be involved.

Summary

It has been found that 1 pound per acre of molybdenum added to soils as Na_2MoO_4 , is reflected in large increases in the molybdenum absorbed by plants. If, however, phosphate levels of the soil are increased at the same time, the molybdenum absorption is considerably enhanced, sometimes by as much as tenfold. Under conditions of intensive cropping and at high phosphate levels, added molybdenum is very rapidly removed, recoveries of 10 to 50% having been attained in a single crop.

Plants are capable of extracting molybdates from very low concentrations in culture solutions. From short time absorption experiments with radioactive molybdenum it has been shown that molybdates are absorbed from concentration of 1 part per billion of culture solution and are translocated to the upper parts of plants. Absorption is enhanced in the presence of phosphates and depressed in the presence of sulfates. Since molybdate ions are divalent and of the same size as sulfates, it may be assumed that these two ions compete directly for adsorption spots on the root during the first step of absorption. Enhanced uptake in the presence of phosphates however, is difficult to explain. At present we can only say that it is characteristic of plants since it has been observed under widely different circumstances, in short time absorption periods and in long term growth periods in culture solutions as well as in soils. Moreover, the effect of phosphates is diametrically opposite to that which would be expected from consideration of ordinary physical chemical interchanges between anions. Explanations for the effect must therefore be sought in biochemical processes involving the two ionic species.

Considering only the molybdate absorption from soil systems, it could be expected that added phosphates might exchange for soil adsorbed molybdenum and thus partially account for increased absorption of molybdenum by plants, analogous to the postulated release of soil molybdenum upon making soils alkaline by exchange of soil adsorbed molybdate for

hydroxyl ions. Though soil molybdate is fixed more strongly at acid reactions, it has been shown in culture solution studies that adsorption of molybdates by plants is greater from acid solutions than from solutions of neutral reactions. It has been reported that plants absorb greater amounts of molybdenum from acid soils upon liming. It must therefore be considered that when lime is added to such soils, the increased concentration of available soil molybdenum is more than sufficient to overcome the decreased ability of plants to absorb molybdate from increasingly alkaline media.

Interrelations between soil molybdenum and sulfate or phosphates are of such nature that important changes in the molybdenum content of plants may be brought about by additions of moderate quantities of phosphate fertilizers or gypsum likely to be used in ordinary fertilization practice. For example, it was shown that subterranean clover grown on an acid, phosphate deficient soil having been given one pound of molybdenum per acre contained an average of 6 p.p.m. molybdenum in the plants. Fertilization with 405 pounds P_2O_5 per acre increased the yield $2\frac{1}{2}$ times but even with the increased plant growth, the concentration of molybdenum in the plants was raised from 6 to 70 p.p.m.

Decreased molybdenum absorption by soil grown plants can be affected by lowering soluble phosphate and increasing soil sulfate levels. This was shown with a fertile soil of neutral reaction to which the addition of 196 pounds $CaSO_4 \cdot 2H_2O$ per acre decreased the molybdenum content of pea plants from 12.8 to 8.05 p.p.m. and tomato plants from 5.25 to 3.52 p.p.m. molybdenum. Higher applications of 3920 lbs. $CaCO_3 \cdot 2H_2O$ per acre further reduced the molybdenum content of peas from 16.0 to 2.75 p.p.m.

The experiments and findings so far discussed have brought out some of the important chemical features of soils and culture solutions governing molybdenum absorption by plants from levels of molybdenum supply adequate for their nutrition requirements. Another paper now in preparation deals with California soils which have produced molybdenum deficiency in a number of different species of crop plants.

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REFERENCES

- 1) Anderson, A. J., Molybdenum Deficiency on a South Australian Ironstone Soil. *J. Australian Inst. of Agr. Sci.* **8**, 73-75 (1942).
- 2) Anderson, A. J., Molybdenum in Relation to Pasture Improvement in South Australia, *J. Council Sci. and Ind. Research* **19**, 1-15 (1946).
- 3) Anderson, A. J. and Oertel, A. C., Factors Affecting the Response of Plants to Molybdenum. *Bull.* **198** Council Sci. and Ind. Research (Australia) 25-44 (1946).
- 4) Anderson, A. J. and Thomas, M. P., Molybdenum and Symbiotic Nitrogen Fixation. *Bull.* **198** Council Sci. and Ind. Research (Australia) 5-25 (1946).
- 5) Arnon, D. I. and Hoagland, D. R., Composition of the Tomato Plant As Influenced by Nutrient Supply, in Relation to Fruiting. *Botan. Gaz.* **104**, 576-590 (1943)).

- 6) Arnon, D. I. and Stout, P. R., Molybdenum As An Essential Element For Higher Plants, *Plant Physiol.* **14**, 599-602 (1939).
- 7) Barshad, I., Molybdenum Content of Pasture Plants in Relation to Toxicity to Cattle, *Soil Sci.* **66**, 187-195 (1948).
- 8) Bingham, F. T., Soil Test for Phosphate. *Calif. Agric.* **3**, 11 (1949).
- 9) Britton, J. W. and Goss, H., Chronic molybdenum poisoning in cattle. *J. Am. Vet. Med. Assoc.*, **108**, 176-178 (1946).
- 10) Burd, J. S., Chemistry of the Phosphate Ion in Soil Systems, *Soil Sci.* **65**, 227-247 (1948).
- 11) Davies, E. B., A case of Molybdenum Deficiency in New Zealand. *Nature* **156**, 392 (1945).
- 12) Dean, L. A., and Rubins, E. J., Anion-Exchange in Soils. I. Exchangeable Phosphorus and the Anion-Exchange Capacity. *Soil Sci.* **63**, 377-387 (1947).
- 13) Ferris, H. M. and Trumble, H. C., Exploratory Investigations of Soil Deficiencies by Means of Small Pot Cultures. *J. Australian Inst. of Agric. Sci.* **9**, 179-182 (1943).
- 14) Fried, M., The absorption of sulfur dioxide by plants as shown by the use of radioactive sulfur. *Soil Sci. Soc. Amer. Proc.* **13**, 135-138 (1948).
- 15) Goldberg, I., Master's Thesis, University of California (1950).
- 16) Lewis, A. H., The Teart Pasture of Somerset, II. Relation between Soil and Teartness. *J. Agr. Sci.* **33**, 52-57 (1943).
- 17) Meulen, H. Ter, Distribution of Molybdenum. *Nature* **130**, 966 (1932).
- 18) Murphy, H. F., The Role of Kaolinite in Phosphate Fixation. *Hilgardia* **12**, 342-382 (1939).
- 19) Oertel, A. C., Prescott, J. A., and Stephens, C. G., The Influence of Soil Reaction on the Availability of Molybdenum to Subterranean Clover. *Australian J. of Science* **IX**, 27-28 (1946).
- 20) Piper, C. S., *Soil and Plant Analysis 1944*, Interscience N.Y.
- 21) Piper, C. S., Reported at the British Commonwealth Scientific Official Conference (Specialist Conference in Agriculture — Australia 1949) Melbourne.
- 22) Reitemeier, R. F., Effect of Moisture Content on the Dissolved and Exchangeable Ions of Soils of Arid Regions. *Soil Sci.* **61**, 195-214 (1946).
- 23) Ribonson, W. O., and Edgington, G., Toxic Aspect of Molybdenum in Vegetation, *Soil Sci.* **66**, 197-198 (1948).
- 24) Sandell, E. B., *Colorimetric Determination of Traces of Metals*. Interscience Publishers Inc. 1944, N.Y.
- 25) Stephens, C. G., and Oertel, A. C., Responses of Plants to Molybdenum in Pot Experiments on the Cressy Shaley Clay-Loam. *J. Council Sci. and Ind. Research* **16**, 69-73 (1943).
- 26) Stout, P. R., Alterations in the Crystal Structure of Clay Minerals as a Result of Phosphate Fixation. *Soil Sci. Soc. Amer. Proc.* **4**, 177-82 (1939).
- 27) Stout, P. R., and Arnon, D. I., Experimental Methods for the Study of the Role of Copper, Manganese, and Zinc in the Nutrition of Higher Plants. *Am. J. Botany* **26**, 144-149 (1939).
- 28) Stout, P. R. and Meagher, W. R., Studies of the Molybdenum Nutrition of Plants with Radioactive Molybdenum. *Science* **108**, 471-73 (1948).
- 29) van Niel, C. B., A Note on the Apparent Absence of Azotobacter in Soils. *Arch. Mikrobiol.* **6**, 215-218 (1935).
- 30) Walker, R. B., Molybdenum deficiency in Serpentine Barren Soils. *Science* **108**, 473-475 (1948).