

AN ABSTRACT OF THE THESIS OF

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Title: MOLYBDENUM STATUS OF SUBCLOVER (TRIFOLIUM
SUBTERRANEUM) AS AFFECTED BY Mo AND S
FERTILIZATION AND SOIL TYPE

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Field studies designed to study residual effects from fertilizer molybdenum were initiated in September 1971 on established grass-clover pastures at ten sites in Western Oregon. Treatments were 0.0 and 1.12 kg molybdenum/ha on plots receiving 0-35-0-20S fertilizer (elemental sulfur-S) and 0.0, 0.56, 1.12 and 2.24 kg molybdenum/ha on plots receiving single superphosphate. Treatments were replicated four times in a randomized block design.

Forage yields were measured during the spring in 1972 and 1973. Subterranean clover samples were analyzed for nitrogen, sulfur, copper and molybdenum. Yield response to applied molybdenum was noted on three harvests of seventeen; these responses were all on plots receiving single superphosphate. Clover nitrogen and copper levels were not significantly affected by molybdenum application.

Form of sulfur fertilizer had a profound effect on molybdenum uptake by clover. On plots which received 1.12 kg Mo/ha, application of elemental sulfur (0-35-0-20S) produced plants much lower in molybdenum than did single superphosphate application. It was hypothesized that depression of Mo uptake resulted from one or a combination of the following phenomena: (1) a decrease in soil pH, (2) increased competition between sulfate and molybdate for absorption by the plant, and (3) increased leaching of molybdate due to the sulfate release pattern of the elemental sulfur material.

Samples of the surface 10 cm of soil from each treatment were analyzed for anion exchange resin extractable molybdenum. Correlation between plant molybdenum and soil molybdenum was significant where all harvests were considered together, but the correlation was improved by separating soils into two groups. The soils in one of these groups were found to sorb large amounts of molybdenum, to release high amounts of hydroxyl anions on treatment with sodium fluoride, and to contain large amounts of amorphous and exchangeable iron compared with soils in the other group.

Laboratory studies were carried on to investigate the molybdenum adsorption patterns peculiar to these soils. Surface samples were taken from eight of the field sites which showed a large range of molybdenum responses. Molybdenum solutions (0-20 ppm Mo in 0.01 M CaCl₂) were allowed to equilibrate with soil at 25°C and the

supernatant molybdenum concentration measured. Molybdate adsorption by soils was found to conform to the Freundlich adsorption isotherm in all instances. Four of the eight soils showed sorption patterns which followed the Langmuir adsorption isotherm at low equilibrium concentrations.

The increase in solution hydroxyl concentration measured two minutes after mixing soil with 1 N NaF correlated significantly with molybdate adsorption at an equilibrium concentration of 0.03 ppm Mo. The fluoride ions may be reacting directly or indirectly with soil constituents responsible for molybdate retention.

Iron extracted in ammonium acetate, pH 4.8, and ammonium oxalate, pH 3.3, correlated significantly with molybdate sorbed at an equilibrium concentration of 0.03 ppm, and with hydroxyls measured by the above sodium fluoride technique. Neither citrate-dithionite extractable iron nor aluminum in ammonium acetate and ammonium oxalate extracts were significantly correlated with molybdate sorption. Oxalate-extractable aluminum was significantly related to hydroxyls released with sodium fluoride.

No correlation was found between laboratory measurements of molybdate retention by soils and the increases in clover molybdenum following molybdenum fertilization. It is suggested that several parameters not investigated in the present study such as soil moisture content, phosphate and sulfate levels, and the soil organic regime may

affect rates of molybdate uptake into and translocation through the plant. Results indicate that it is difficult to predict the effect of molybdenum application on plant uptake of molybdenum in the field.

A larger number of samples representing a vast range of soils appears desirable to reliably predict residual effects from applied fertilizer molybdenum.

Molybdenum Status of Subclover (Trifolium
subterraneum) as Affected by Mo and S
Fertilization and Soil Type

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MOLYBDENUM STATUS OF SUBCLOVER (TRIFOLIUM
SUBTERRANEUM) AS AFFECTED BY Mo AND S
FERTILIZATION AND SOIL TYPE

INTRODUCTION

For several years significant increases in yield of grass-legume pastures have been reported after application of a few ounces of molybdenum per acre. However, recommendations have largely been on a trial and error basis, with residual effects and interactive effects (such as companion fertilizers) not considered for lack of information. To examine the effects on plant and soils of molybdenum addition to the soil, a study with the following objectives was initiated: To (1) examine clover yield and nutrient content as affected by relatively high rates of applied molybdenum (up to 2.2 kg/ha); (2) study effects of form of fertilizer sulfur on molybdenum, nitrogen, and sulfur status of the plant; (3) further explore the utility of the anion exchange resin method for use in characterizing soil Mo status; (4) determine patterns of Mo sorption by soils from field experiments; (5) relate levels of iron and aluminum removed from soil by a number of standard extractants with sorption in the laboratory and plant Mo uptake in the field; (6) develop a method for predicting plant response to applied Mo as a function of soil characteristics.

Field experiments were initiated in the fall of 1971 on a number

of contrasting sites in established subterranean clover-grass pastures. Eight sites which showed a wide range of response to Mo fertilizer were selected for further studies in the laboratory.

LITERATURE REVIEW

For convenience this review of literature on Mo has been considered in four sections:

- a. Plant response to applied molybdenum (Mo);
- b. Factors affecting Mo uptake;
- c. Methods of predicting Mo fixation and availability;
- d. Molybdenum toxicities.

Plant Response to Applied Molybdenum

Bortels (1930, 1937) first reported that Mo was required for normal activity of symbiotic N-fixing bacteria in peas, soybeans, and red clover. Since then Mo has been found to be a required cofactor for the enzyme nitrogenase, responsible for reduction of atmospheric N_2 to ammonium compounds in nitrogen-fixing organisms. Lower levels of Mo are required for the reduction of nitrate to assimilable forms in plants grown on an inorganic nitrate-nitrogen source (Bortels, 1937; Stout, 1953; Evans, 1956).

The first field response to applied Mo was reported by Anderson (1942) for clover growing on an ironstone soil in Australia.

Molybdenum responses have since been reported on many other crops including citrus, cauliflower, broccoli, tobacco, corn, tomatoes, and flax, as well as nearly all cultivated legumes (Hewitt, 1956; Evans,

1956; Peterson and Purvis, 1960; Evans et al., 1950; Vanselow and Datta, 1949; Stout and Johnson, 1956). Because Mo deficiency limits nitrogen fixation rates and assimilation of inorganic nitrate, symptoms of Mo deficiency are very similar to those of nitrogen deficiency (Johnson, 1966; Evans, 1956; Hewitt, 1956).

Factors Affecting Molybdenum Uptake by Plants

A number of physical, chemical, and biological factors affect the amount of Mo absorbed by and translocated in the plant. These include soil pH, degree of weathering, soil iron and aluminum status, levels of other anions, soil drainage, organic matter status, and the plant itself.

Soil pH

Soil reaction was early recognized as a major factor in determining Mo availability in soils. Barshad (1951) found that Mo adsorption on soils decreased as the system pH increased from 3 to 7.5. Above pH 7.5 no absorption was detectable. He attributed the decreased adsorption at high pH's to greater competition between OH^- and $\text{MoO}_4^{=}$ for sorption sites. Many workers have shown that liming may substitute for Mo fertilization (Evans, 1950; Gammons et al., 1954; Gupta, 1972; John et al., 1973). Conversely, application of Mo may substitute for lime application where optimum yields are not

attained due to Mo deficiency, but pH-related problems such as Al and Mn toxicity and Ca deficiency may only be solved by liming (John et al., 1973; Walker, Adams and Orchiston, 1955).

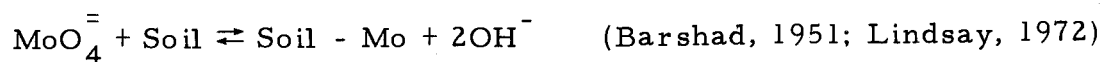
When insufficient Mo is available for exchange with hydroxyls, liming alone may not release enough Mo to satisfy plant requirements. Small amounts of fertilizer Mo must then be applied to achieve maximum yields.

Care must be taken to avoid over-liming and consequent production of toxic levels of Mo (Gammons et al., 1954), especially in situations where Mo fertilizer may have been applied earlier. This may have built up a large reserve which is released upon reaction with lime.

Solution culture experiments have shown that Mo uptake is actually enhanced by acidity, implying that any increase in plant Mo uptake after liming is a result of greater availability rather than improved absorption. Soil solution Mo must increase sufficiently to offset decreased efficiency of absorption.

Molybdenum has not been found to precipitate as a calcium molybdate at high soil pH. Its availability generally reaches a maximum near neutrality and does not diminish as pH increases (Lindsay, 1972).

Molybdenum solubility in soils increases as a function of hydroxy concentration, following the equation



Therefore Mo in solution is inversely proportional to the square of the H^+ concentration and a one unit increase in pH should increase solution Mo 100-fold. However, in the non-ideal soil systems this relationship seldom if ever holds exactly. The interaction of many forms of iron, aluminum, and organic matter in the soil preclude precise prediction of increases in Mo availability with liming.

Forms of Soil Fe and Al

As free ions, colloidal particles, or coatings on other soil constituents the reactivity of iron and aluminum seems to be a major factor in determining Mo availability in most soils (Anderson, 1942; Oertel, 1944; Jones, 1956; Reisenauer, 1962; Reyes and Jurinak, 1967; Barrow, 1970). In this and many other respects Mo seems to react with soils in a manner analogous to the phosphate ion (Barshad, 1951; Davies, 1952). This similarity may be due not only to both existing as monomeric tetrahedral anions at the dilute solutions encountered in soils (Reyes and Jurinak, 1967), but also to their approximately equal valence contributions to oxygen (Fields and Schofield, 1960). Hingston's theory of specific anion adsorption (Hingston et al., 1967) and its substantiating experimental agreement found by Barrows (1970) are further indications that phosphate and

molybdate share similar affinity for reactive soil components, especially at acid pH. A vast amount of literature on phosphate-soil interaction has been published; with some modification these findings may be applicable to Mo as well.

Jones (1956) equilibrated Mo solutions with soils and found Mo adsorption to be closely related to extractable "free" iron oxides in the soils studied. Removal of these iron oxides greatly decreased adsorption. Iron and aluminum molybdates, precipitated from chloride salt solutions of Fe and Al, showed minimum solubility at pH 2.7 and 4.8 respectively. Laboratory-prepared ferric oxide and aluminum oxide showed highest Mo adsorption within a pH range between 4 and 5; the ferric oxide adsorbed much more Mo than did the Al oxide.

Oertel and Prescott (1944), through spectrochemical analysis of ironstone nodules, found considerable Mo concentrated in them compared with bulk soil Mo levels. Reisenauer, Tabikh and Stout (1963) found Mo more strongly sorbed by iron oxides than by either Al or Ti oxides. Several other workers have correlated Mo adsorption in soils more strongly with "free" iron oxide content than with aluminum oxides (Wells, 1956; Robinson and Edgington, 1954). Barrow (1970), however, obtained results showing good correlation between oxalate-extractable aluminum and Mo sorption, but the relationship between sorption and oxalate-iron was poor.

Interactions Between Molybdenum and Other Nutrient Ions: Manganese, Phosphorus, and Sulfur

Plant uptake of molybdate may also be affected by the levels of other plant nutrients. In particular, manganese, sulfate, and phosphate ions influence the plant's ability to absorb and translocate molybdate.

Manganese. Numerous observations of apparent manganese-molybdenum interactions have been reported, but the conclusions drawn differ considerably. In reviewing the effects of Mn on Mo uptake, Mulder (1954) reported decreased cauliflower Mo after soil treatment with $MnSO_4$. Using other manganese and sulfur sources he ascertained that both ions depressed Mo uptake.

Gupta (1972) reported lower Mo in barley harvested from manganese-treated soil. He also found decreases in Cu and Fe at high rates of Mn fertilization. Plant Mo at high Mn application rates showed pronounced variation with pH; at pH 5.7, plants from high Mn plots contained 0.45 ppm Mo, while high Mn plots at pH 6.2 produced plants with average Mo concentration of 1.53 ppm.

Millikan (1947, 1948) reported that Mo at high levels in culture solution alleviated iron deficiency symptoms in flax. However, Hewitt (1954), Mulder (1954), and Warrington (1951) found that iron chlorosis induced by high levels of other metals was accentuated when solution molybdate concentration was increased. Gerloff, Stout and

Jones (1959) published similar results: plant iron content decreased with increases in either manganese or molybdate. They proposed that the interactive effect of Mo on Fe was through precipitation of iron by molybdate in the plant root. This precipitate could not be translocated to plant tops.

Kirsch, Harward and Peterson (1960) studied the effects of iron, manganese and Mo on tomato growth in culture solution. They concluded that the Mn-Mo interaction effect was actually an indirect manifestation of two more important interactions, those between Fe and Mo and Fe and Mn. Iron additions decreased Mn toxicity but the effective Fe level depended upon solution Mo concentrations. When iron was low, Mo decreased yields, while at high iron levels added Mo increased yields. Translocation of Mo from the roots to the upper plant parts was stimulated by iron but total Mo uptake was reduced. Low iron levels resulted in accumulation of Mo in the roots whereas with higher Fe levels this was not observed. At low Fe and Mn levels, added Mo had little effect on Mn uptake; on low Fe-high Mn treatments, Mo decreased Mn uptake; and at higher Fe and Mn levels, Mo increased Mn uptake.

Phosphorus. The phosphate ion also has considerable effect on plant Mo status. Stout et al. (1951) measured much greater uptake of Mo by subterranean clover when phosphate was added to the soil and Mo fertilizer efficiency was high. They hypothesized that because Mo

and P undergo similar fixation reactions, phosphate could block sorption sites on the soil colloids and exchange with fixed Mo. Molybdenum translocation within the plant was also stimulated by P-addition.

Davies (1952) found in desorption studies that ammonium molybdate shaken with soil resulted in progressive displacement of phosphate by molybdate ions. Barshad (1951) noted that Mo uptake by Ladino clover was enhanced by additions of phosphate. Mulder (1954) found that added phosphate substantially increased uptake of Mo by cauliflower on Mo-treated plots, while those soils without fertilizer Mo produced plants with no more Mo than the check.

Sulfur. Sulfur fertilization is usually reported to depress plant uptake of Mo (Stout et al., 1951; Mulder, 1954; Widdowson, 1966; Walker, Adams and Orchison, 1955; Jones and Ruckman, 1973). Stout et al. (1951) showed that Mo uptake and translocation decreased as sulfate levels increased and attributed this effect primarily to competition for uptake resulting from the ions' similarity in size and charge. Mulder (1954) reported significant depression of Mo uptake after treatment with Na, K, and Ca sulfates. The more pronounced effect of CaSO_4 may have been due to the pH depression it induced which in turn may have increased Mn solubility.

Walker, Adams and Orchison (1955) recorded depressed white clover yields relative to monocalcium phosphate alone on a soil

treated with both $\text{Ca}(\text{H}_2\text{PO}_4)_2$ and gypsum. Addition of Mo, however, increased yield over the P-alone treatment. Mn toxicity may have been overcome by the Mo dressings. Jones and Ruckman (1973) reported similar results from a seven year study on subterranean clover. Sulfate apparently accentuated the molybdenum deficiency, while phosphate alone increased total Mo uptake.

From experiments involving S and Mo fertilization of peas, Reisenauer (1963) concluded that not only did gypsum application reduce uptake of soil and fertilizer Mo, but for optimum yield higher levels of Mo were required in S-fertilized plants than in unfertilized plants.

Because P and frequently S are generally more limiting nutrient elements than is Mo (Anderson, 1956), complex fertilizer P-S-Mo interactions are frequently encountered. Single superphosphate supplies both phosphorus and sulfur. Generally the net effect of superphosphate fertilization is reduction of plant Mo levels (Cunningham and Hogan, 1956; Widdowson, 1966; Ouelette, 1963; Gupta and Cutcliffe, 1968). For example, Ouelette (1963) induced chlorosis in Ladino clover with application of 1200 lbs/A single superphosphate; the chlorosis was subsequently eliminated by fertilization with 16 oz/A $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$.

Gupta (1969), in a review of the sulfur-molybdenum interaction, concluded that the effect of sulfate on molybdate uptake was so

significant that any recommendations for Mo fertilization must include considerations of the soil sulfur status as well.

Soil Drainage

Robinson and Edgington (1954) reported higher availability of Mo in fields under waterlogged conditions than in comparable soils when well-drained. Kubota, Lemon and Allaway (1963), in a greenhouse study, found that soils maintained in a wet state had greater Mo in both the soil solution and the plant than the same soil under a drier moisture regime. It was suggested that more Mo is swept into the transpiration stream when the soil is very moist rather than relatively dry, but this does not explain the greater solubility. Robinson and Edgington (1954) suggested that inundation produces reducing conditions which allow solubilization of iron molybdates and increases Mo availability. Kee and Bloomfield (1962) found that flooding a soil resulted in increased Mo availability; upon draining, however, Mo concentration in solution did not decrease greatly although much iron precipitated. This was attributed to formation of a relatively stable soluble organic matter-Mo complex, and Mo was less available for entering into adsorption or precipitation reactions.

Organic Matter

Davies (1956) reported low Mo on organic soils. Kee and Bloomfield (1962) hypothesized formation of a soluble complex of organic matter and molybdenum which partially protected Mo from precipitation or adsorption by iron compounds.

Gupta (1971) added virgin sphagnum moss, farmyard manure, and compost to unfertilized soil and soil to which Mo and copper had been applied. Ammonium oxalate extractable Mo was lower on soils receiving organic materials without added Mo or Cu than on untreated soils. But where both organic matter and Mo fertilizer were added, extractable Mo was higher than on untreated plots. Peat application in all cases resulted in the lowest levels of Mo among organic matter treatments.

Plant Species Effect

Wide variation in Mo content among different plant species growing in the same soil has been noted (Robinson and Edgington, 1954; Barshad, 1951; Jensen and Lesperance, 1971). In general, legumes accumulate Mo to a much greater extent than non-legumes, and among legumes, clovers seem to concentrate Mo to the greatest extent (Jensen and Lesperance, 1971; Kubota, 1961).

Residual Effects of Molybdenum Fertilization

Plant response to applied Mo has been found to vary with soil type and companion fertilizer. Cunningham and Hogan (1956) found that over a four year period, three consecutive applications of 2 oz/A each resulted in grass Mo content of 10.6 ppm on a sand soil, whereas on a silt loam eight ounces of Mo per acre brought grass Mo levels to about 17 ppm. From a New Zealand study involving 64 North Island soils and 50 from the South Island, only seven North Island soils were found to produce plants with Mo levels above 3 ppm after fertilization with 2 1/2 oz Mo/A. They concluded that even this small percentage in a marginally toxic range indicates that extreme care is warranted to prevent over-fertilization with Mo because residual effects are frequently long-lasting.

Jones (1973) conducted a six year study of residual fertilizer P, S, and Mo on a Pinole silt loam under subterranean clover pasture. Phosphorus was added as concentrated superphosphate, sulfur as finely ground elemental S, and Mo as molybdic acid. A depression in yield was recorded where S was added without fertilizer Mo, indicating that the elemental S decreased Mo uptake. Jones attributed this decrease to competition of the two ions for uptake rather than to decrease in soil pH, estimated at about 0.2 pH units per acre furrow slice for the 112 kg S/ha applied.

Anderson (1956) noted that 2 oz of fertilizer Mo remained effective for several years. However, Wells (1956) and Mulder (1954) stated that on acid soils of high Mo fixing capability, more frequent applications might prove necessary.

Molybdenum Adsorption

Adsorption of molybdate from solution by soils and prepared substances has been investigated by many researchers (Barshad, 1951; Wells, 1956; Jones, 1956, 1957; Reisenauer *et al.*, 1963; Reyes and Jurinak, 1967; Barrow, 1970). The degree of adsorption has been found to be affected by pH, degree of soil weathering, and presence of iron oxides.

Barshad (1951) found that several types of soil colloids including halloysite and kaolinite adsorbed large amounts of Mo from solutions, but the amount of sorption decreased steadily as pH was increased from 4.5 to 7.5. At pH 7.5 essentially no $\text{MoO}_4^{=}$ was adsorbed. Solubility of soil molybdenum in basic solutions was greater than in neutral water; he suggested that an exchange of OH^- for $\text{MoO}_4^{=}$ occurred.

In studies of molybdate adsorption by New Zealand soils, Wells (1956) found that Mo retention increases with soil weathering to a maximum in soils with a high amorphous hydrous oxide content. As crystallization of these hydrous oxides occurs, Mo retention

decreases; on podzolized soils it approaches zero. Therefore both young soils and those highly weathered or podzolized are expected to exhibit low Mo adsorption and fixation characteristics. At an intermediate weathering stage the soil Mo will be most strongly retained and least available to plants. Phosphate, vanadate, and hydroxyl ions showed stronger affinity for soil than molybdate, while Mo sorption increased in the presence of chloride and sulfide ions. Fields and Schofield later (1960) explained this order of affinity in terms of relative electrostatic stability at tetrahedral aluminum sites. They also stated that any tetrahedral Fe present would produce a similar order of affinity.

Jones (1956) studied molybdate adsorption by hydrous ferric oxide, aluminum oxide, and clay minerals, and found that amount of adsorption depends on pH and molybdate concentration in solution. Hydrous ferric oxide adsorbed Mo most strongly, followed by aluminum oxide, halloysite, nontronite, and kaolinite. Soils highest in ferric oxide adsorbed the greatest amount of Mo; after iron oxide removal the soil's Mo retention was near that of a low-Mo fixing soil. He attributed the fixation to an exchange of MoO_4^- and OH^- ions. An equation relating plant Mo to soil pH and oxalate iron was formulated:

$$\log[\text{Mo}_{\text{plant}}] = a \cdot \text{pH} - b \cdot \text{Fe} + c,$$

where a , b , and c are empirical constants.

Using the Freundlich equation modified by a pH term, Reisenauer et al. (1962) described Mo sorption by soils and by hydrous ferric oxide:

$$\log \frac{x}{m} = A \log(1000c) + BpH + k_f,$$

where

$$\frac{x}{m} = \mu\text{g Mo adsorbed/g adsorbent}$$

$$c = \text{equilibrium concentration of molybdate, } \mu\text{g Mo/ml}$$

$$k_f = \text{constant}$$

$$A = \log \frac{x}{m} / \Delta \log (1000c)$$

$$B = \log \frac{x}{m} / \Delta \text{pH}$$

Iron oxide was found to stoichiometrically release 2 molecules of OH^- and one molecule of water for each molybdate ion adsorbed.

Reyes and Jurinak (1967), in describing molybdate adsorption on hematite found two distinct adsorption reactions at pH 4. Both followed the Langmuir adsorption isotherm. The first reaction was insensitive to temperature change and was saturated at 10 ppm Mo equilibrium concentration, while the endothermic second reaction was not saturated until 55 ppm Mo entered solution. Surface area studies indicated that at low equilibrium concentration the monomeric HMoO_4^- form was principally adsorbed.

Barrows (1970) compared phosphate, sulfate, and molybdate

adsorption by soils from 0.01 M CaCl_2 solutions. He used the interpolated adsorption at equilibrium concentrations of 0.2 ppm phosphate, 20 ppm sulfate, and 0.1 ppm molybdate as measures of retention. As the pH was decreased from 6 to 4, the ratio $\text{SO}_4:\text{PO}_4$ adsorbed increased three times, while $\text{MoO}_4:\text{PO}_4$ increased 20 times. A ready explanation of this observation is found in the work of Hingston et al. (1967). These workers proposed that both proton donor and proton acceptor forms must be present for the adsorption of a weak acid to occur. A polybasic acid may have several possible combinations, all pH-dependent. As extremes of pH are reached, adsorption decreases rapidly because both members of the required pair are not equally abundant. In the case of Mo, HMoO_4^- and $\text{MoO}_4^{=}$ are most common at acid soil pH.

Estimation of Molybdenum Requirements and Prediction of Residual Effects of Molybdenum Fertilization

Most workers have extracted soils with various reagents and attempted to determine critical levels for plant sufficiency. Below the critical level Mo may be limiting plant growth, while concentrations greater than the critical value result in no response from added Mo. Even when a fairly reliable critical level can be established, this approach tells nothing of the soil's ability to transform Mo into forms unavailable to the plant.

Solution Extractable Molybdenum

Barshad (1951) found that ladino clover uptake of Mo correlated well with water soluble Mo on a neutral Merced clay loam. A variety of other extractants, including NaOH, HCl, H_3PO_4 , ammonium tartarate, ammonium carbonate, and $(NH_4)_2HPO_4$ gave generally poor correlations with plant Mo uptake.

Grigg (1953) discovered that acid ammonium oxalate extractable Mo correlated well with plant uptake of Mo when a correction factor involving soil pH was included. However, he later (Grigg, 1960) noted that the acid oxalate extraction was not ideal because some of the totally unavailable iron-bound molybdates were also extracted. Gupta and MacKay (1966) found that among 0.1 N NaOH, 0.1 N HCl, 2% citric acid, and 0.2 N ammonium oxalate at pH 3.0, the latter extractant removed the most Mo from soils. They concluded it was the best extractant for determination of exchangeable Mo and copper. Others continue to use the oxalate method (Massey et al., 1967; Baratynski et al., 1966).

Anion Exchange Materials

Because the uptake of nutrient anions by plant roots is thought to be through an anion exchange mechanism, use of synthetic anion exchangers to assess nutrient availability has been proposed by

investigators for measurement of both phosphate and molybdate availability. Amer et al. (1955), Mosher et al. (1959), Sheard and Caldwell (1955), Cooke and Hislop (1963), Saunders (1964), and Williams (1965) have shown that plant uptake of soil phosphate correlates well with anion resin extractable phosphate. Ross (1969) and Dawson and Bhella (1972) following Olsen's suggestion (1967), developed an anion exchange resin technique for assessment of plant-available Mo. Using strongly basic Dowex 1-X4 resin, Dawson and Bhella (1973) established 1.2-1.4 $\mu\text{g Mo}/100\text{g soil}$ as the critical lower limit for normal plant growth. Soils used in their study had pH values of 5.8 or lower.

Prediction of Phosphate and Molybdate Availability After Fertilization

Measurement of phosphate adsorbed from solution by soils in the laboratory has been developed as a means of predicting response to applied phosphorus (Ozanne and Shaw, 1968; Beckwith, 1965; Barrow et al., 1965; Barrow and Spencer, 1971; Datta and Srivastava, 1962; Barrow, 1973). Where P-sorption follows the Langmuir adsorption isotherm, adsorption maxima and bonding strengths may be calculated (Olsen and Watanabe, 1957; Datta and Srivastava, 1962; Rennie and McKercher, 1959; Weir and Soper, 1962; Woodruff and Kamprath, 1965; Udo and Uzu, 1972). In other cases the Langmuir isotherm has

not been followed by all soils studied (Beckwith, 1965; Barrow, 1970; Saunders, 1965; Hsu and Rennie, 1962; Muljadi, Posner and Quirk, 1966). By calibration of adsorption with field data it is hoped that the retentive capacity of a soil may be a more accurate indication of its phosphate requirement than are the current extraction techniques. Since extraction procedures rarely yield information on the soil's ability to renew the P supply in solution or the degree of fixation expected, they do not adequately predict P-fertilization requirements for optimum growth.

Similar studies have also been reported for molybdenum. Wells (1956) reported on studies of sweet vernal Mo levels in New Zealand and the Mo adsorptive capacity of these soils as measured in laboratory equilibration experiments. He concluded that when one gram of soil retained greater than 25% of the molybdate in 25 ml of 50 ppm Mo solution, and sweet vernal Mo was less than 0.5 ppm, a response to Mo fertilization could be expected. This response, he also stated, might not be observed where the field received dressings of phosphate fertilizer or lime. On a low retention soil these dressings would have little impact because insufficient Mo would be available for replacement by phosphate or hydroxyl ions.

Following work done on sulfate adsorption by soils, Barrow and Spencer (1971) measured the ability of 50 different soils to adsorb Mo from 0.01 M CaCl_2 solutions containing various levels of Mo. When

soils were grouped by parent rock type (granitic, sedimentary, basaltic) yields of untreated and Mo-fertilized plants were observed to decrease as the soil's ability to adsorb molybdate increased. However, through multiple regression it was found that the term for Mo sorption contributed relatively little to the yield sum of squares, and the relationship between low soil pH and low yield was probably more significant.

Fluoride Anion Exchange Reactions

Kelly and Midgeley (1943) reported an exchange of fluoride ions for phosphate and hydroxyl ions on precipitated ferric hydroxide. Dickman and Bray (1941) used 0.1 N NH_4F solution to replace phosphate adsorbed on kaolinite. They also demonstrated stoichiometric release of hydroxyl ions through exchange with fluoride.

Fields and Perrott (1966) reported on a rapid test for the presence of tetrahedral aluminum in allophane. One gram of finely ground H_2O_2 -treated soil was stirred with 50 ml 1 N NaF . Soils which produced suspension pH's greater than 9.2 after two hours' equilibration were found to contain significant amounts of allophane clay.

Molybdenum Toxicities

Molybdenum toxicity was identified as the cause of "teart" on English pastures (Ferguson, Lewis and Watson, 1943) and "peat

scours" on organic soils. The interaction of molybdenum and copper has proven central in cases of both Mo and copper toxicities. Ingestion of low-Mo high-Cu forage produces symptoms of molybdenosis (Wynne and McClymont, 1955). When plant copper content is low, Mo may be toxic at plant concentrations as low as 3 (Cunningham, Hogan and Lawson, 1959) to 5 ppm (Wynne and McClymont, 1955), although generally symptoms are not observed until plant levels of 10-20 ppm Mo are reached (Barshad, 1951). Dick (1953) and Wynne and McClymont (1955) found that inorganic sulfate decreases blood Mo and increases Mo excretion. Cunningham et al. (1959) measured blood levels near those of animals fed low Mo diets when feed was supplemented with both inorganic Mo and inorganic sulfate. Relatively high sulfate levels increased neither Cu nor Mo excretion.

Cattle show greater sensitivity to induced copper deficiency than do sheep, and ruminants in general are more susceptible to molybdenosis than are monogastrics (Dick, 1956). On pastures producing forages high in Mo, copper is introduced as injections or through feeding of inorganic copper salts.

Soil and environmental factors which may produce high-Mo forage have been discussed in previous sections. They include overliming, over-fertilization, and poor soil drainage.

MATERIALS AND METHODS

Field Studies

Field trials were initiated in September 1971 at ten sites in Western Oregon on established subterranean clover pastures. Soil profile descriptions are given in Appendix 1. Experimental design consisted of a randomized block of six treatments replicated four times. Table 1 summarizes these treatments. The 0-35-0-20S product was formulated commercially from treble superphosphate, 0-45-0, and finely ground elemental sulfur (≤ 100 mesh). Fertilizer was hand-broadcast over the 1.8 meter x 6.1 meter plots. For molybdenum applications, powdered Na_2MoO_4 was mixed with the PS source before application. Where soil tests indicated a requirement for K, muriate of potash was broadcast at recommended rates.

Table 1. Summary of treatments used in field experiment. Rates: 90 kg P/ha; 45 kg S/ha; and 60 kg K/ha where required.

Treatment	Mo, kg/ha	Fertilizer Form
PS	0.00	0-35-0-20S
PSMo	1.10	0-35-0-20S, $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$
PSO_4	0.00	0-18-0-12S
PSO_4Mo_1	0.56	0-18-0-12S, $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$
PSO_4Mo_2	1.12	0-18-0-12S, $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$
PSO_4Mo_3	2.24	0-18-0-12S, $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$

To harvest the plots, a swath 91 cm wide was cut through the length of the plot, and both grass and clover weighed. At each location one clover sample per treatment was taken by lumping subsamples from all four replications together. Samples were then weighed, oven-dried at 70°C for 24 hours, and reweighed to allow calculation of dry matter percentage. After samples were ground in a Wiley mill, they were redried for four hours at 70°C and stored under sealed desiccant conditions until analysis.

Soil Sampling and Sample Preparation

The surface 10 cm of soil (Ozanne et al., 1965) were sampled at harvest with all four replications of each treatment combined. Samples were air-dried in the laboratory and ground with mortar and pestle to pass a 60 mesh sieve. The soil was stored in tightly capped glass jars.

Soil Analysis

Standard soil tests were those used by the Oregon State University Soil Testing Laboratory (Table 2). In addition, three extraction procedures were used to investigate soil forms of iron and aluminum: ammonium acetate buffered at pH 4.8; 0.2 N ammonium oxalate, pH 3.3 (McKeague and Day, 1966); and citrate-dithionite at pH 4.8 (Coffin, 1962). Iron was determined in all three extracts by

an orthophenanthroline method (Krishna Murti, Volk and Jackson, 1966) and aluminum in the acetate and oxalate extracts were assayed by an aluminon procedure (Jackson, 1958).

Table 2. Methods used in standard soil analysis.

Determination	Method	Reference
pH	1:2 soil-water suspension	Jackson, 1958
Exchangeable cations	Extraction with pH 7.0 ammonium acetate buffer, atomic absorption spectrophotometry	Schollenberger and Simon, 1945
Cation exchange capacity	Saturation with ammonium acetate, pH 7.0; micro-Kjeldahl analysis of NH_4^+	Peech <i>et al.</i> , 1957
Organic matter	1 $\underline{\text{N}}$ $\text{K}_2\text{Cr}_2\text{O}_7$ oxidation of soil organic matter and back titration with 0.4 $\underline{\text{N}}$ $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	Walkley and Black, 1934

A modification of Bhella's method (1972) was used to determine anion resin exchangeable molybdenum. Ten grams of soil prepared as above were mixed with 20 ml distilled water in a centrifuge tube containing 5 ml Ag1-X4^{1/} anion exchange resin, 20-50 mesh. After shaking overnight at 25°C in a constant temperature water bath, resin was washed free of soil with distilled water on a 60 mesh brass

^{1/} AG1-X4, because of its greater purity and narrower range of particle size, was chosen in place of Dowex 1-X4 originally used by Bhella.

screen. The resin was transferred to a column of 1 cm inside diameter, then leached with 25 ml 2 N NaCl over a 30 minute period. Molybdenum in this leachate was determined by flameless atomic absorption spectrophotometry (Henning and Jackson, 1973). A charring temperature of 2100°C maintained for 15 seconds was required to eliminate smoke interference from the vaporizing matrix.

Plant Analysis

Total plant nitrogen was analyzed by a micro-Kjeldahl method (Black, 1965). Samples for sulfur analysis were first wet ashed in perchloric acid, then S concentration determined turbidimetrically (Chesmin and Yien, 1950). Copper and molybdenum samples were dry ashed at 500°C, the residue dissolved in 5% HCl and this solution filtered. Copper was determined by flame atomic absorption, while Mo concentration was analyzed through flameless atomic absorption spectrophotometry (Henning and Jackson, 1973).

Laboratory Experiments

Adsorption

In Autumn 1972 soil samples from the 0-10 cm depth were taken from untreated areas at eight of the ten locations. These were air-dried and ground to pass a 2 mm sieve. Two grams of soil were

mixed in a 50 ml centrifuge tube with 20 ml 0.01 N CaCl_2 containing 0-20 ppm Mo. Duplicate samples were shaken for 18 hours in a constant temperature water bath at 25°C, then centrifuged. The supernatant was transferred to glass vials, acidified with HCl, and the Mo concentration was determined by flameless atomic absorption spectrophotometry (Henning and Jackson, 1973).

Rise in pH Subsequent to NaF Treatment

Soil samples from the above eight locations were treated with H_2O_2 to remove organic matter. After air-drying, one gram of this treated soil (< 100 mesh) was added to 50 ml 1 N NaF, the mixture stirred for one minute and pH determined after one additional minute. The pH increase was then converted to moles OH^- released per gram of soil.

RESULTS

Field Plot Yields

A total of 17 harvests were taken on nine of the ten soils involved in this study (Appendix 3). Significant subterranean clover responses to applied Mo were noted for three harvests (Table 3). In two instances (Rydell and Nekia soils) single superphosphate and 0.56 kg Mo/ha (Treatment 4) provided the greatest yield, while in the third case (Steiwer) single superphosphate with 1.12 kg Mo/ha (Treatment 5) yielded highest. In several instances while yields were higher than the check on treatments PSMo, PSO_4Mo_1 , and PSO_4Mo_2 (Mo at 1.12, 0.56, and 1.12 kg Mo/ha respectively), they were not statistically significant, because of high variability within treatments (Table 4).

Table 3. Subterranean clover yields as influenced by applied Molybdenum (responsive sites).

Soil	Treatment	Yield, kg/ha
Steiwer	PSO_4	843
	PSO_4Mo_1	1310* L.S.D. .05 = 390 kg/ha
	PSO_4Mo_2	1579*
	PSO_4Mo_3	1256*
Nekia	PSO_4	4269
	PSO_4Mo_1	5794* L.S.D. .05 = 710 kg/ha
	PSO_4Mo_2	5220*
	PSO_4Mo_3	5059*

Table 4. Subterranean clover yields as influenced by applied Molybdenum (possibly responsive sites).

Soil	Treatment	Yield, kg/ha	
Yoncalla	PSO ₄	4144	
	PSO ₄ Mo ₁	3660	C. V. = 23%
	PSO ₄ Mo ₂	(4682)	
	PSO ₄ Mo ₃	4252	
Dement	PSO ₄	2888	
Dement	PSO ₄ Mo ₁	2852	C. V. = 20%
	PSO ₄ Mo ₂	(3175)	
	PSO ₄ Mo ₃	(3265)	

Plant Analysis

Chemical analyses for nitrogen, sulfur, copper and molybdenum from subterranean clover samples obtained from the field trials are presented in Appendix 3.

Clover Nitrogen Content

Molybdenum seemed to have little effect on plant N content. Even in instances where yield responses were recorded, nitrogen levels were not significantly increased by molybdenum fertilization. Plant N concentrations in this study were at near-deficient or deficient levels in several instances, and only in one or two cases (e.g.,

Astoria, 1972) could they be considered adequate.

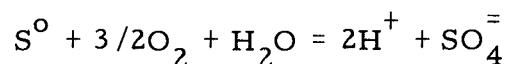
Among the several possible explanations which could account for this relatively low plant N status, problems associated with low pH must be examined with suspicion. Toxic levels of aluminum (Rorison, 1958) and manganese (Vose and Jones, 1963) have been shown to affect nodulation and rates of fixation. Furthermore, plants deficient in calcium apparently are unable to supply sufficient energy to the nodule bacteria (Loneragan and Dowling, 1958; Loneragan, 1959; Vose and Jones, 1963).

Survival of effective Rhizobium strains may be affected by the pH-related factors listed above (Loneragan and Dowling, 1958; Bergerson, 1961; Vincent, 1962). Infection of clover roots with ineffective Rhizobium strains could cause low fixation rates (Schwinghamer et al., 1970; Pate and Dart, 1961). These factors may well account for the relatively low plant nitrogen status inspite of adequate available soil molybdenum.

Clover Sulfur Content

Clover sulfur content varied considerably among samples within locations, but for all treatments averages for a harvest were above the critical level of 0.22% established by Jones (1962) (Appendix 2). Sulfur could not be considered a limiting factor in clover production at the rates of uptake measured. The form of applied S had little

effect on the plant's uptake of this nutrient; although the elemental sulfur plants contained an average of 0.30% S compared with an average of 0.28% S for single superphosphate plants, the difference was not statistically significant. These results suggest that elemental S was transformed by microbial oxidation to sulfate at a rate sufficient to supply adequate available $\text{SO}_4\text{-S}$ for the plant needs. The generally accepted biochemical transformation may be presented as:



This reaction is performed by several autotrophic bacteria including Thiobacillus species and possibly by heterotrophs as well. The sulfuric acid product decreases soil pH; an average of three pounds of pure CaCO_3 are required to neutralize acidity released from one pound elemental sulfur.

Clover Copper Content

Application of Mo fertilizer did not significantly affect plant copper uptake. Plant copper averages ranged from 5.8 ppm for the Astoria 1972 harvest to over 13 ppm for the 1973 harvests on the Steiwer, Rydell, Peavine and Mosher soils (Appendix 3). Treatments which received elemental sulfur produced plants with slightly higher (9.9 vs. 9.5 ppm) copper levels than those supplied with sulfate-sulfur,

though these differences were not significant.

Clover Molybdenum Content

As might be expected plant Mo content increased following the application of fertilizer Mo. However, the response curve varied considerably among locations. Plant Mo content increased almost linearly with application of 0.56, 1.12, and 2.24 kg Mo/ha. The first 0.56 kg increment of Mo resulted in a greater increase in plant Mo than did additional like increments (Figure 1).

One of the more interesting features from the field trials was the effect form of sulfur fertilizer had on plant Mo content. Plant Mo levels were significantly lower where Mo was applied with elemental S fertilizer compared with SO_4 -S in single superphosphate. Table 5 compares the effect of two sulfur forms on plant Mo levels from two Mo treatments, 0 and 1.12 kg Mo/ha. With no added fertilizer Mo, no significant differences were found between S treatments in amount of Mo absorbed by the plant. The average difference was slightly less than .4 ppm. On the treatments receiving 1.12 kg Mo/ha, however, the difference between means was highly significant ($P < .01$), with the elemental sulfur treatment averaging 1.4 ppm Mo less than plants which received sulfate fertilizer. Differences among Mo levels as a function of sulfur source were generally greater the second year than the first.

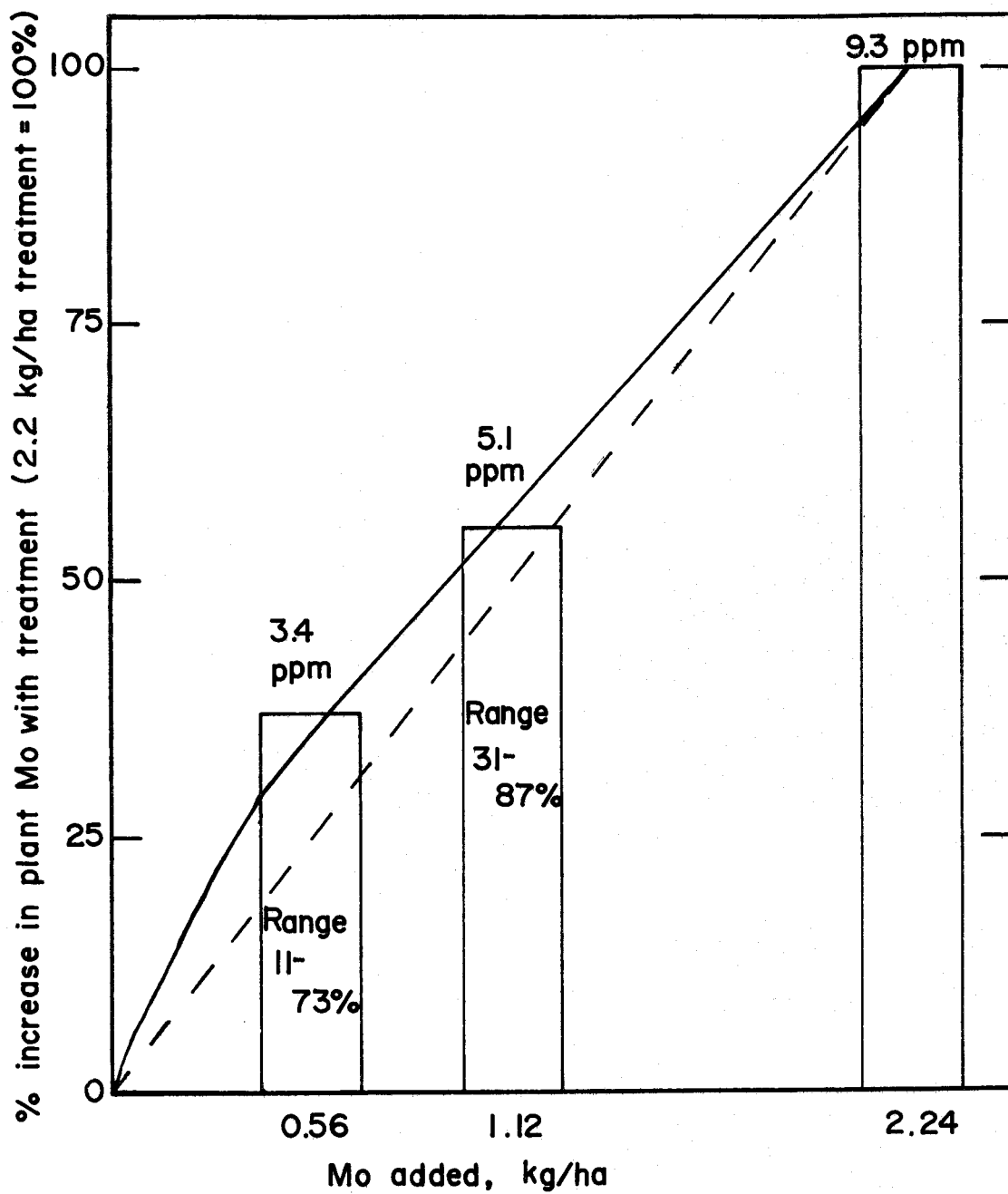


Figure 1. Plant molybdenum as affected by three rates of soil-applied molybdenum.

Table 5. Effect of form of sulfur on molybdenum uptake by clover.

Soil	Harvest	No Mo Applied (ppm Mo)		1.12 kg Mo/ha (ppm Mo)	
		PS	PSO ₄	PSMo	PSO ₄ Mo ₂
Astoria	1972I	2.0	1.1	11.9	11.8
	1972II	0.5	0.8	2.9	6.0
	1973	1.0	0.8	2.1	5.1
Peavine	1972	0.6	0.8	8.5	9.3
	1973	0.4	0.7	3.7	5.6
Steiwer	1972	0.8	0.9	4.6	7.3
	1973	0.4	0.4	0.6	2.9
Rydell	1972I	0.3	1.0	3.7	5.2
	1972II	0.4	0.5	3.7	5.6
	1973	1.0	2.0	2.4	3.4
Nekia	1972I	0.3	0.4	5.5	4.0
	1972II	1.0	1.0	3.4	3.4
	1973	0.5	0.6	0.8	4.5
Yoncalla	1973	0.3	0.4	1.5	7.4
Dement	1972	1.0	1.0	3.0	4.0
	1973	0.6	0.8	2.2	2.6
Powers	1972	0.5	0.9	1.6	4.7
	1973	0.3	0.3	2.5	3.0
McKenzie	1972	0.8	1.1	6.2	6.7
	1973	0.6	1.4	3.0	5.0
Mosher	1972II	1.2	1.6	2.4	4.7
		Average PS = 1.38		Average PSMo = 3.78	
		Average PSO ₄ = 1.76		Average PSO ₄ Mo ₂ = 5.23	
		t = 1.67 n. s.		t = 5.77***	

Sulfate may compete with molybdate for plant uptake (Stout et al., 1951). Because the ions are of similar charge and atomic configuration, similar plant uptake mechanisms may be active. The fertilizer form that released the most sulfate probably competed with molybdate and produced low Mo plants. Because elemental S must first be oxidized by micro-organisms, under the Western Oregon climate release of sulfate from this form would be most active during early fall and spring months. This is also the period of most rapid plant growth and possibly much more Mo is taken up at this time. The CaSO_4 form, though only slightly soluble, would dissolve steadily through the wet winter. A small part of the sulfate could be expected to be absorbed while much of it moved down the profile in percolating water (Dawson, 1969). Although this may be later intercepted by roots, the spatial separation of sulfate absorption from molybdate absorption may significantly decrease competition for uptake.

Application of sulfur fertilizer is frequently found to decrease soil pH. Although gypsum has been reported to depress pH (Kipps, 1947), the elemental form generally has a more pronounced effect. Duplicate samples from the surface 2.5 cm on eight of the ten locations studied were taken from the elemental S plots, the single superphosphate plots, and check samples outside the plots. This data is summarized in Appendix 4. Although the differences were not statistically significant, consistently higher pH readings were noted

on the $\text{SO}_4\text{-S}$ plots than on the elemental S plots. Both were more acid than plots that received no sulfur fertilizer. A much more drastic pH decrease may occur in a zone around the disintegrating fertilizer granule. This change in pH may solubilize Fe and Al which, after diffusing outward or downward from the zone around the granule into regions of higher pH, would precipitate as molybdates. This could substantially lower the Mo availability.

Competition for sorption sites on soil colloids may provide another explanation for the effect of sulfur on Mo uptake. Decreased Mo sorption would favor the leaching of molybdate and transfer down the profile into a zone less accessible to roots. Such a process could account for lower plant Mo levels especially during the second harvest year. Molybdate leaching could explain the large difference in plant Mo concentration on the Steiwer plot between 1972 and 1973 harvests. An alternate explanation may be found in time-dependent fixation reactions which may have been very effective the second year compared with the first.

In summary, differences in Mo uptake as a function of fertilizer S source may be due to (1) competition for uptake by the plant; (2) local decreases in soil pH, accelerating fixation reactions; (3) competition for sorption sites on soil colloids resulting in decreased Mo sorption or fixation. Further research is required to

demonstrate which of these is more important in governing Mo availability.

Residual Molybdenum

The clover Mo content obtained in plants two years after Mo fertilization on single superphosphate plots decreased markedly (Jones, 1973) (Figure 2). In only one instance was the clover Mo content higher in the 1973 harvested plant material than the 1972 harvest (Nekia soil). Here the increase may have been due to unintentional fertilization by the landowner. Excluding this special case, the PSO_4Mo_1 treatment (0.56 kg Mo/ha) yielded 24% less Mo in 1973 compared with 1972; PSO_2Mo_2 and PSO_4Mo_3 (1.12 and 2.24 kg/ha respectively) showed decreases averaging 37%; and the PSMo treatment had a 43% reduction in plant Mo the second year. Although the greater decrease in plant Mo from the PS plot is not statistically different from that in the PSO_4Mo_2 treatment (1.12 kg Mo/ha), it is consistent with increased fixation or competition for uptake noted on the PSMo plots.

Correlation Between Plant Molybdenum and Soil Anion Exchange Resin Molybdenum

The differences in plant response to applied Mo as noted above indicate that soil and environmental effects play significant roles in determining plant availability of Mo (Davies, 1956). These

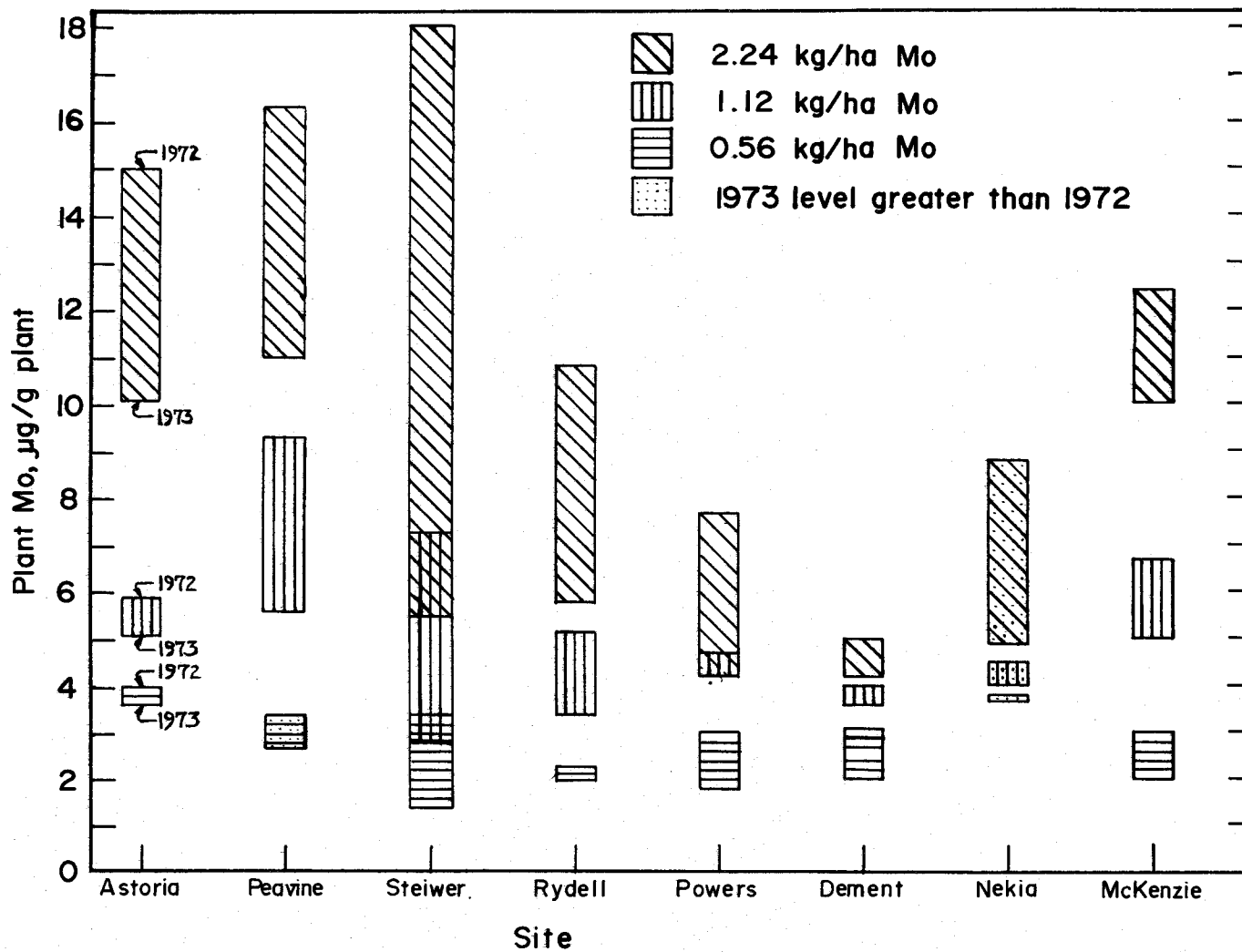


Figure 2. Schematic diagram showing decreases in clover molybdenum two years after initial application.

differences among soils are further borne out in the two curves obtained from correlation of plant Mo with anion exchange resin Mo (Figure 3).

A significant but low correlation coefficient ($r = .43$) was found between clover Mo and soil Mo as measured by the resin technique (Figure 2). However, inspection of the scatter diagram indicated that segregation of soils into two groups would greatly improve the correlation. This proved to be true, with the Astoria and Peavine soils together giving a coefficient of determination of .64 and the remainder of the ten soils producing an $r^2 = 0.70$ (Figure 3).

On the basis of soil chemical-mineralogical properties several mechanisms may account for the differences observed in anion exchange resin values among soils (see also Laboratory Results section). The Astoria (1) and Peavine (2) soils may have held Mo in a non-soluble form which was yet available to plants (e. g. , by contact exchange) during the growing season. Alternatively, molybdate may have been complexed in organic matter forms which while not desorbed from the resin by chloride leaching are indeed plant available.

It would appear that the soil anion resin technique measures a constant proportion of the plant available Mo, but that this proportion varies among soils. A greater number of samples are needed to test this hypothesis.

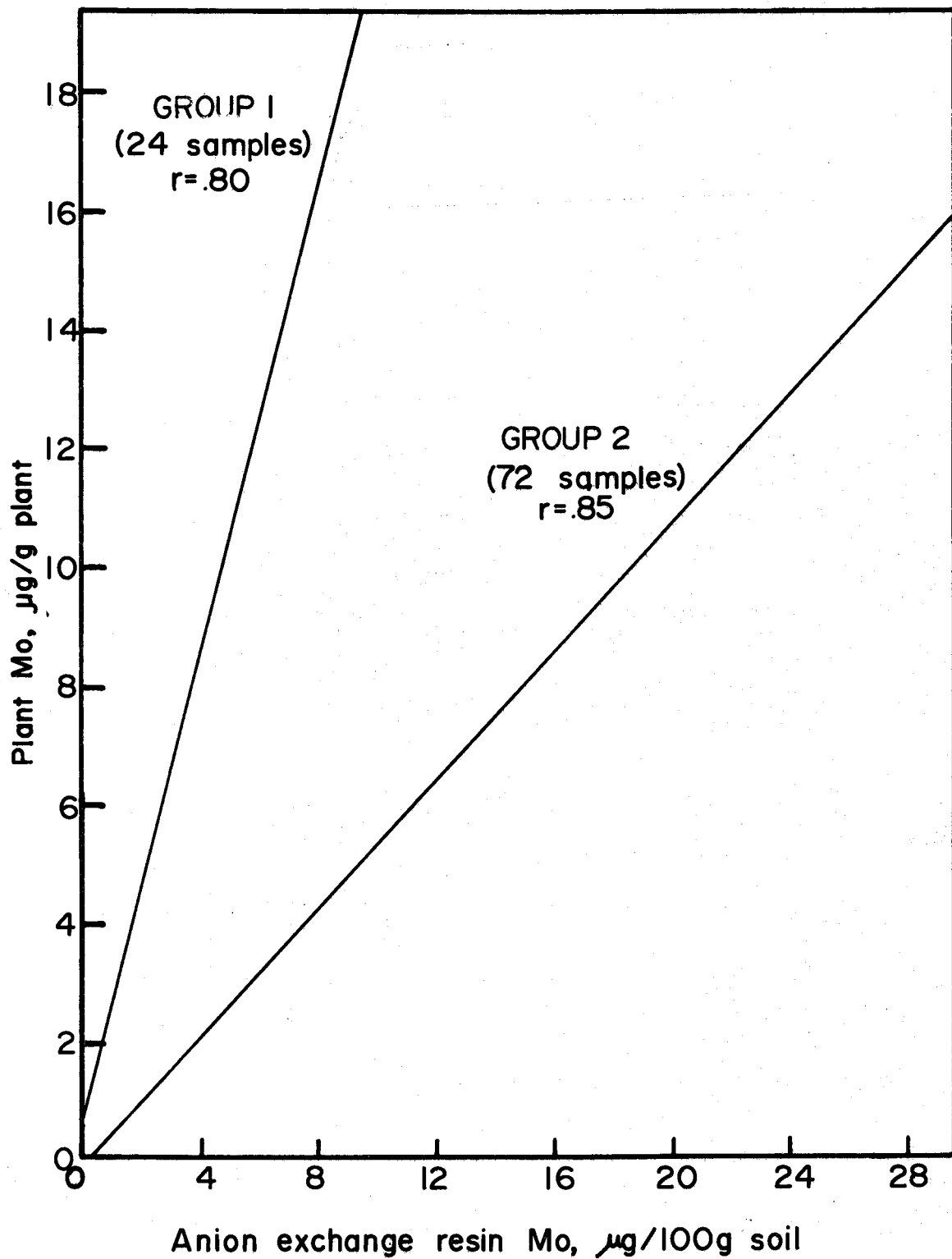


Figure 3. Relationship between plant molybdenum and soil anion exchange resin molybdenum.

Toxic Molybdenum Levels

It is to be noted that the levels of plant Mo in the 1972 harvest are for the most part in the toxic range proposed by some authors (cited below). The table below compares plant criteria developed by several researchers for ruminant molybdenum toxicity. Incipient toxicities may occur before symptoms are observed, and this can decrease production in the absence of visual symptoms of molybdenosis.

Table 6. Selected criteria for molybdenum toxicity.

Criterion Number	Criterion for Toxicity	Reference
1	Mo greater than 10-20 ppm in plant	Barshad, 1948
2	Mo greater than 3 ppm in the plant	Cunningham, 1956
3	Cu:Mo ratio less than 2:1	Miltmore <i>et al.</i> , 1967

Using criteria 2 and 3 from the above table, no toxicities were noted in the absence of applied Mo but application of 0.56 kg Mo/ha with single superphosphate or 1.12 kg Mo/ha with 0-35-0-20S each produced four samples from the 18 harvests which were potentially toxic. On SO₄-S plots treated with Mo at 1.12 and 2.24 kg/ha, 11 and 16 harvests respectively produced potentially toxic ratios (criterion 3).

This data indicates that Mo fertilization must be done with extreme care and with attention given to soil type. Use of an

elemental sulfur source may allow higher rates of Mo application with complete safety. The results suggest that Mo supplied with 0-35-0-20S may provide residual effects which will maintain Mo at sufficiency levels that preclude induction of molydenosis.

The lowest Mo application rate (0.56 kg/ha) sufficed to bring Mo levels well into the range required for maximum plant yield without inducing toxic levels in most plants.

Summary of Field Results

Molybdenum was apparently not the factor limiting plant growth in most of the harvests. Plant Mo was well above established critical levels on all fertilized plots. Plant nitrogen in general did not increase as a function of Mo fertilization or sulfur source. Plant copper levels were not significantly affected by treatment.

Clover sulfur levels were not significantly affected by fertilizer form or molybdenum application, although sulfur levels were slightly higher on elemental-S treated plots than on those receiving single superphosphate. Form of sulfur had a significant effect on plant Mo content on plots receiving molybdenum fertilizer. Where 1.12 kg Mo/ha was applied, elemental sulfur produced plants with an average of 1.4 ppm Mo less than clover from SO_4 -S plots. Residual Mo decreased slightly faster on the elemental S treatments than on those receiving single superphosphate; average Mo in plants from the 1973

harvests was slightly over 60% of the 1972 levels on molybdenum-treated plots.

The anion exchange resin measured a portion of the soil Mo which correlated well with plant uptake of Mo. However, differences among soils were noted. Apparently different proportions of the plant-available Mo pool were measured in the different soils.

The above observations prompted closer scrutiny of the soil's chemical characteristics and its reaction with molybdate; the following sections describe the results of these laboratory studies.

LABORATORY RESULTS

Adsorption of Molybdate From SolutionFreundlich Isotherm

Over the range of Mo levels utilized in this study, adsorption of Mo by these soils fits the unmodified Freundlich Equation (Freundlich, 1919) (Figure 4) very well. This equation is a useful empirical description even though sorption strengths and adsorption maxima cannot be calculated directly from it. For example, interpolation to 0.03 ppm Mo equilibrium concentration is facilitated by substitution into the Freundlich formula $x/m = kc^{1/n}$, where $x/m = \mu\text{g Mo adsorbed/g soil}$, c is the equilibrium Mo concentration, and k and n are empirically determined constants specific for each soil. Once the soil is characterized by the adsorption isotherm, Mo adsorption at any equilibrium concentration may easily be calculated. However, since the equation is empirical, extrapolation may prove misleading because linearity is not guaranteed outside the range studied.

The values of the Freundlich constants k and n are most useful in comparing soils, although some theoretical observations may be made. The k value is a direct proportionality constant relating amount of sorption to the equilibrium concentration. The n is

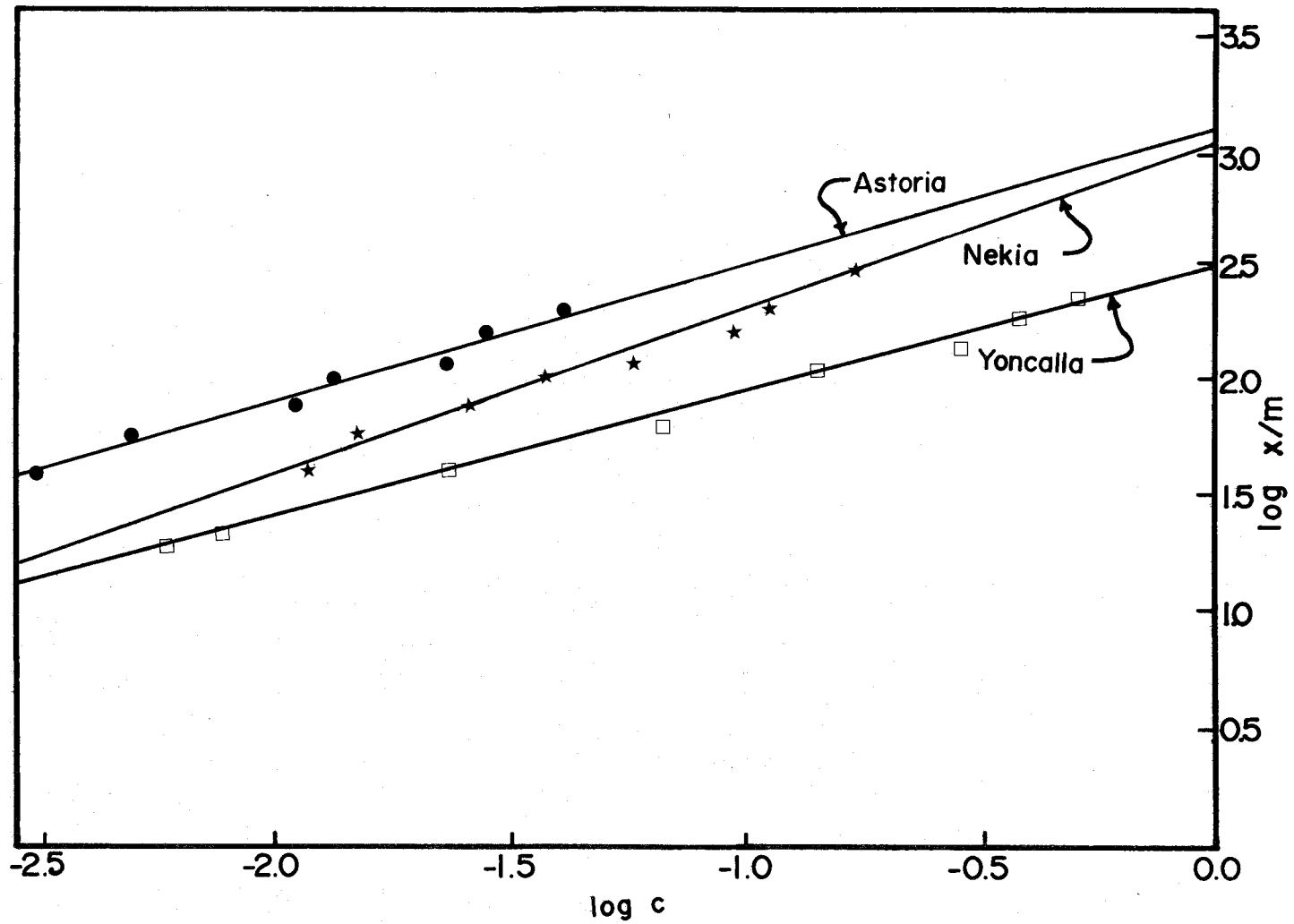


Figure 4. Freundlich adsorption isotherms for three contrasting soils.

generally found to be a number greater than one. Through analysis of the n value at limiting states of the theoretically derived Langmuir equation, a general interpretation of its meaning may be deduced (Graham, 1953). An n near two implies that relatively less of the adsorbent surface is available for fixation reactions. For instance, the low n value of the Nekia soil suggests that a fairly large proportion of its surface is available for these reactions compared with the other soils. The Yoncalla soil, with small k and large n values would be expected to show low fixation properties (Table 7).

Table 7. Freundlich constants derived for eight soils.

Soil	k	n
Astoria	1200	1.7
Peavine	1000	1.7
Steiwer	480	1.7
Rydell (unn.)	360	1.8
Nekia	1030	1.4
Yoncalla	260	1.9
Dement	350	1.8
Powers (unn.)	590	1.7

Langmuir Adsorption Isotherm

This theoretically derived adsorption isotherm may be expressed in the form $c/x/m = 1/kb + c/b$. The c value is the equilibrium concentration of molybdate, x/m is the μg Mo adsorbed per gram of soil, k is a constant related to sorption strength, and b is the

so-called adsorption maximum. Conditions necessary for this equation to be valid are the following: (1) molecules are only adsorbed in monolayer thickness, with second layer effects negligible; (2) adsorbate molecules do not interact; (3) all sorption sites possess equivalent bond strengths. In dilute solutions, (1) and (3) above are in most cases approximately satisfied in soils; if the sorption sites differ considerably in strength of sorption, only the strongest site would be active at low concentrations. Deviations from ideality in one required condition may be offset by the nonideality of another. For instance, if adsorbate molecules do interact a negative deviation is expected, while differences in sorption site strength results in a positive deviation of the curve in Figure 5.

Four of the eight soils studied obeyed the Langmuir equation up to $c_{eq} = 0.12-0.14$ ppm (Figure 5, Table 8). Above this concentration a significant negative deviation was encountered; whether this deviation represented a shift to another Langmuir isotherm was indeterminable because insufficient points were plotted. Molybdate has pronounced tendencies to polymerize (Reyes and Jurinak, 1967) and some interaction of sorbed ions may be occurring.

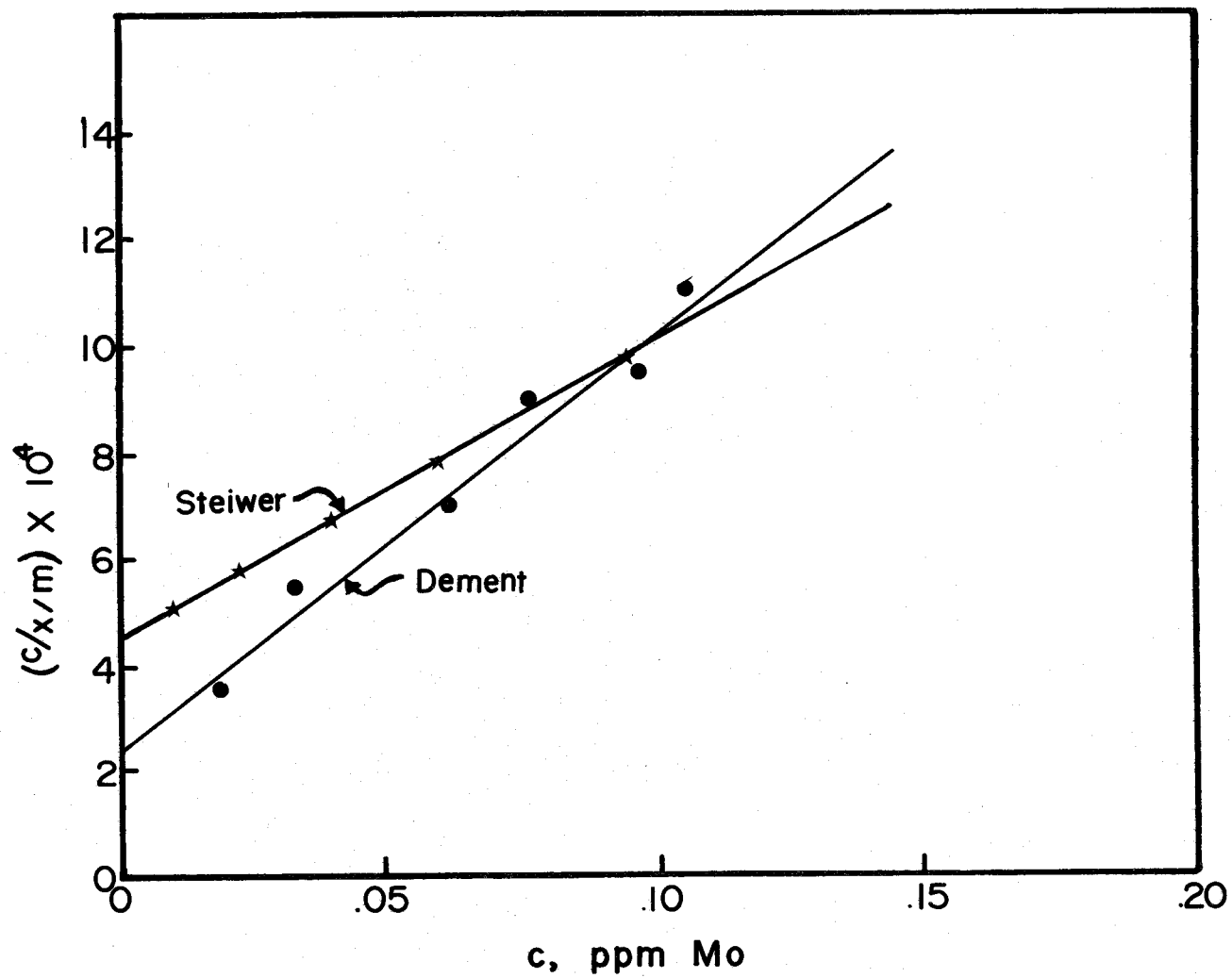


Figure 5. Langmuir adsorption isotherms for two soils.

Table 8. Langmuir constants for four soils.

Soil	k (function of bond strength)	b (adsorption maximum)
Steiwer	11.7	.0186
Rydell (unn.)	24.3	.0150
Yoncalla	16.1	.0150
Dement	21.9	.0151

Hydroxyls Released From Soil With Fluoride Treatment

Because generation of an adsorption isotherm is a laborious task, a more rapid means of determining potential anion adsorption capacity is desirable. If the mechanism of adsorption is one of exchange of hydroxyls and molybdate anions, measurement of the pool of "replaceable" hydroxyls may be a useful additional soil parameter with some predictive value.

Fluoride is a highly reactive anion in soil systems and rapidly replaces hydroxyl ions on soil constituents (Kelly and Midgeley, 1943). One could imagine that the more labile hydroxyls would initially be replaced by fluoride, followed by the less accessible or more strongly held forms. Alternatively, short exposure of soil to a neutral fluoride solution may effect the dissolution of more soluble soil iron and aluminum compounds, with a resultant increase in solution hydroxyl concentration (Huang and Jackson, 1965).

Mixing of one gram H_2O_2 -treated soil with 50 ml 1.0 N NaF produced the following pH increases after two minutes:

Table 9. Hydroxyls released from soils with 1 N NaF.
pH of 1 N NaF = 6.8.

Soil	pH After 2 min.	Moles OH ⁻ released/g x 10 ⁷
Astoria	8.70	50
Peavine	8.60	40
Steiwer	7.70	5
Rydell (unnamed)	8.15	14
Nekia	8.40	25
Yoncalla	7.60	4
Dement	8.60	40
Powers (unnamed)	7.90	8
$r^2 = 0.97^{**}$ for 7 soils, excluding Dement $r^2 = 0.74^*$ for 8 soils, including Dement		

When sorption of Mo at $c_{eq} = 0.03$ ppm (Table 10) was graphed against moles of OH⁻ released by NaF after two minutes (Table 9), a significant correlation was found (Figure 6). The Dement soil deviated most drastically from the regression curve, showing much greater release of OH⁻ than would be expected from its adsorption characteristics. This may be due to the presence of sites such as tetrahedral aluminum OH⁻ groups which may not participate in exchange with MoO₄⁻ at low concentration but can be replaced by F⁻. Until more soils with a wider range of characteristics have been examined, the potential of this quick test for indirect characterization of anion adsorption capacity is not known. Possibly work with pure, well-defined mineral systems could show where the fluoride is acting, and whether in fact the correlation between its activity and molybdate sorption is direct or indirect (Huang and Jackson, 1965).

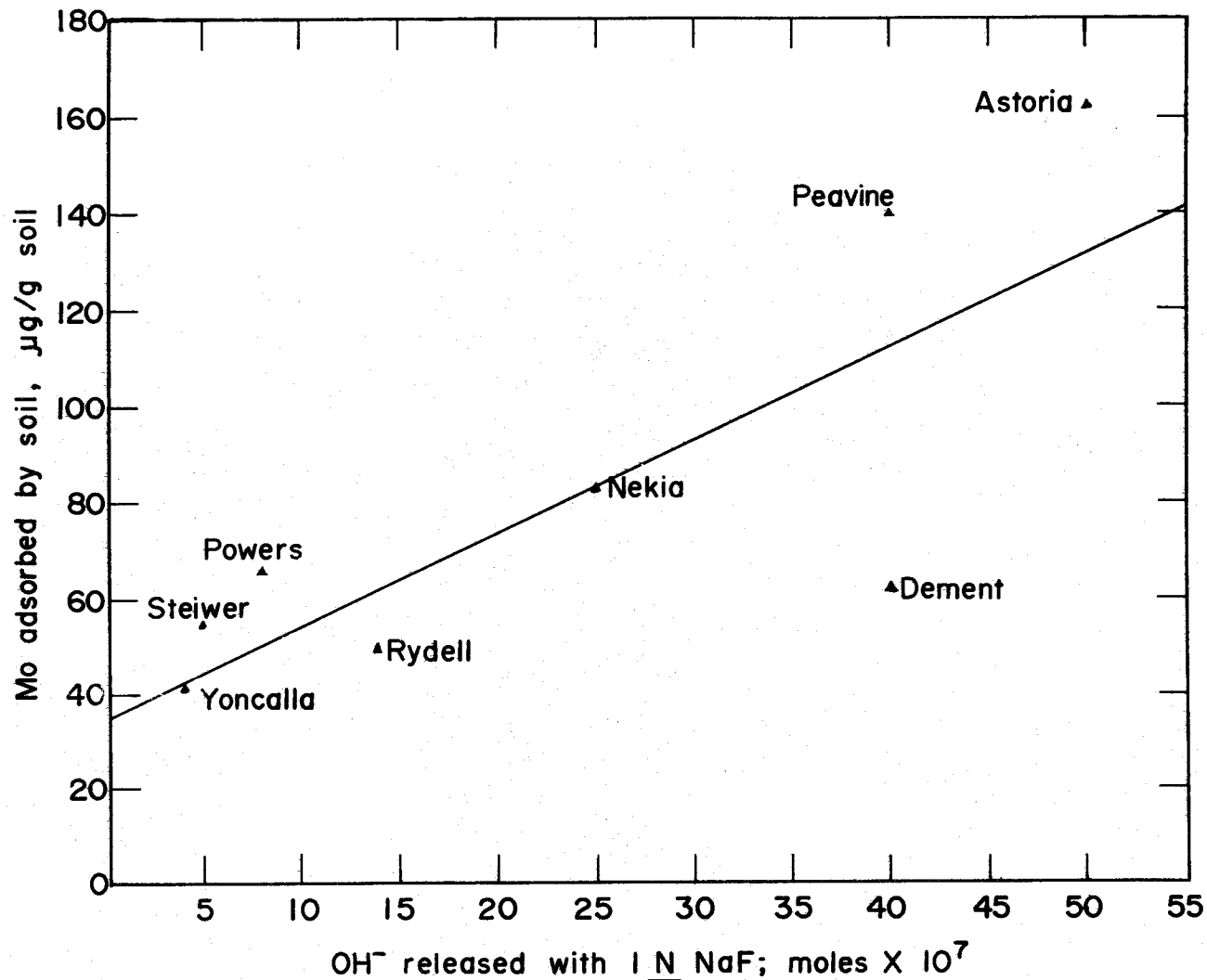


Figure 6. Relation of molybdenum adsorbed by soil at an equilibrium concentration of 0.03 ppm to hydroxyls released from soils with 1 N NaF.

Table 10. Molybdenum adsorbed on soils at an equilibrium concentration of 0.03 ppm Mo.

Soil	Molybdenum Sorbed, $\mu\text{g Mo/g Soil}$
Astoria	162
Peavine	120
Steiwer	55
Rydell (unn.)	50
Nekia	83
Yoncalla	42
Dement	62
Powers (unn.)	66

Soil Iron and Aluminum

Forms of soil aluminum and iron have frequently been correlated with sorption of anions by the soil (Saunders, 1965; Barrow, 1970; Jones, 1956). In this study, extractions with 1 $\underline{\text{N}}$ $\text{NH}_4\text{OOCCH}_3$ at pH 4.8, 0.2 $\underline{\text{N}}$ $\text{NH}_4\text{OOC}(\text{COOH})$, pH 3.3, and a citrate-dithionite procedure were used as measures of soil forms of these elements. Each method is considered to remove a fraction of the soil iron and aluminum, although these fractions are not mutually exclusive.

Ammonium Acetate Extraction, pH 4.8

Both pH and the complexing character of the acetate anion are significant in determining the amounts of iron and aluminum extracted with ammonium acetate. Since the soil pH fell between 5.0-5.5 for the samples used there was reasonable basis for considering

elements extracted with ammonium acetate buffered at pH 4.8 as "exchangeable" (Table 11). Iron and aluminum so extracted were found to be significantly correlated (Figure 7), an indication that during soil weathering a change in the solubility of one element was paralleled by a change in the other's solubility (Wells, 1956). The highest Mo-fixing soils, Astoria and Peavine (Table 10) also contain high iron and aluminum levels. These observations would suggest these soils are moderately well weathered. The Rydell and Yoncalla soils on the other hand were low molybdate absorbers. They contained relatively little extracted ammonium acetate, iron and aluminum which indicated they were either young or strongly weathered (Wells, 1956). Acetate-extractable iron correlated significantly with Mo adsorption while aluminum did not. Acetate-extractable iron may be in equilibrium with a soil fraction capable of sorbing Mo from solution.

Table 11. Soil iron and aluminum extracted with ammonium acetate, ammonium oxalate, and citrate-dithionite.

Soil	1N NH ₄ OAc		0.2 N NH ₄ Oxalate		Citrate-dithionite Fe, %
	Al, meq/100 g	Fe, meq/100 g	Al, %	Fe, %	
Astoria	5.2	0.55	1.0	1.4	3.4
Peavine	4.5	0.38	1.0	0.7	2.8
Steiwier	2.7	0.26	1.6	0.6	2.9
Rydell (unn.)	2.3	0.14	0.5	0.2	2.1
Nekia	2.2	0.07	0.8	0.5	5.6
Yoncalla	1.6	0.09	0.4	0.3	1.9
Dement	5.8	0.26	3.4	0.6	2.7
Powers (unn.)	4.0	0.45	1.0	0.6	2.0

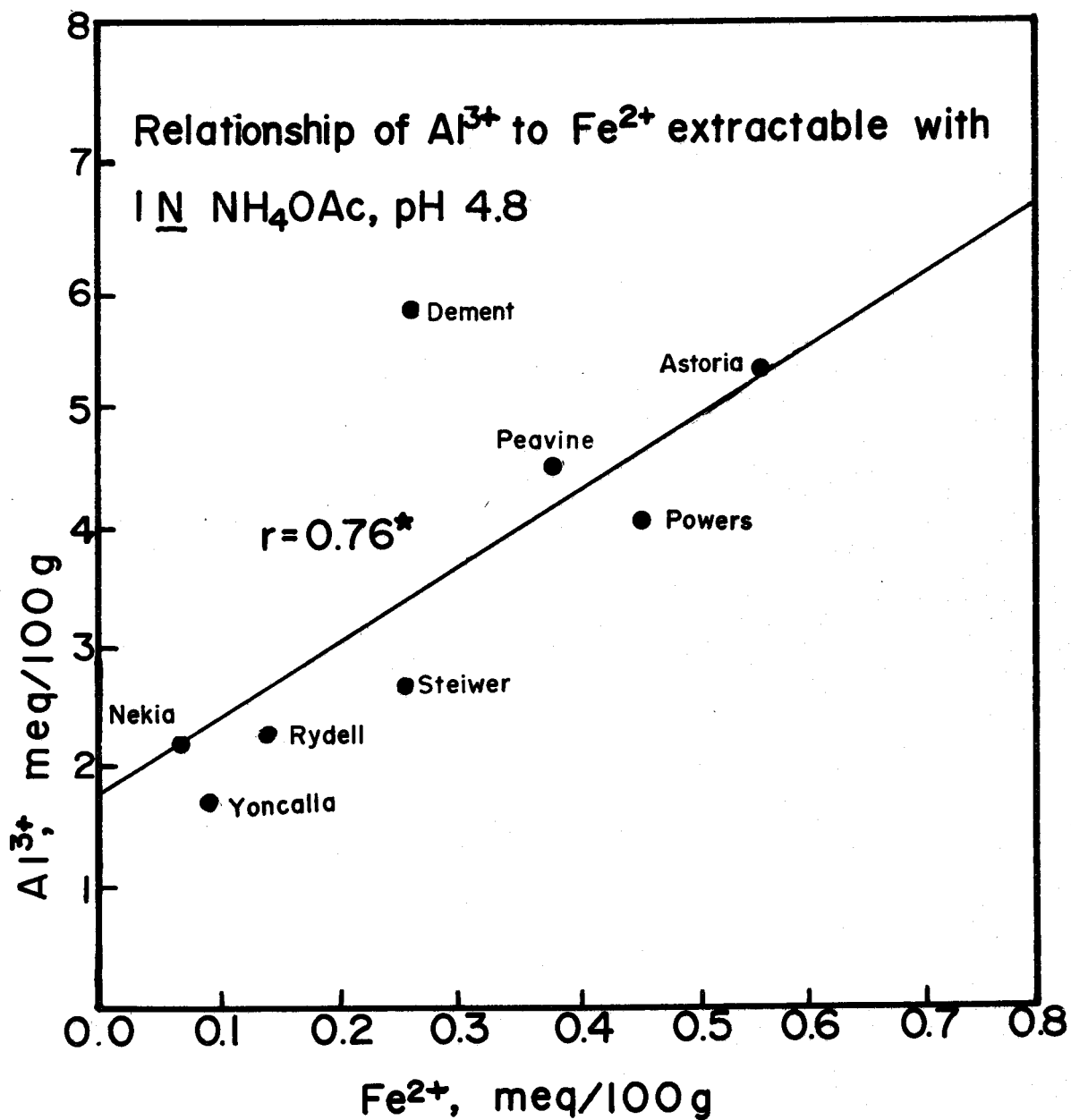


Figure 7. Relationship of Al^{3+} to Fe^{2+} extractable with $1 \text{ N } \text{NH}_4\text{OAc}$, pH 4.8.

Ammonium Oxalate Extraction

Amorphous Fe and Al compounds are extracted with ammonium oxalate pH 3.3 (McKeague and Day, 1966). Such extraction includes hydrous oxides which have recently precipitated or have a very low degree of crystallinity. Some fraction of the amorphous forms may be solubilized by the ammonium acetate extractant. However, no significant correlation between the two forms of extracted Al and Fe was found.

Iron extracted with the ammonium oxalate method correlated significantly ($r^2 = 0.79$) with Mo adsorption at an equilibrium concentration of 0.03 ppm Mo. Oxalate-extractable Al, on the other hand, showed a poor correlation ($r^2 = 0.32$). Both elements were significantly correlated with soil hydroxyls measured by the NaF technique, aluminum providing a better correlation than iron ($r_{Al}^2 = 0.62$ versus $r_{Fe}^2 = 0.50$).

Amorphous forms of iron, but not those of aluminum, appear to be related to the soil fraction responsible for sorption of molybdate. This seems plausible since oxalate-extractable iron may be freshly precipitated, somewhat stable, and capable of reacting with molybdenum. Such a reaction could result in Mo remaining sparingly available to the plant.

Citrate-Dithionite Extraction

Iron extracted by the citrate-dithionite procedure constitutes both amorphous (oxalate-extractable) and the more stable crystalline fractions of soil iron. The dithionite treatment reduces Fe^{3+} to Fe^{2+} , a much more soluble ion, and thus solubilizes even quite stable forms. "Crystalline" iron as determined by this extraction [(Fe extracted by citrate method) - (Fe extracted by oxalate procedure)], Table 11, was significantly correlated with neither adsorption nor hydroxyls released by NaF treatment. Still, a portion of this "crystalline" iron may be reactive enough to participate in molybdate sorption reactions, although the bulk is inactive (Reyes and Jurinak, 1967).

GENERAL SUMMARY AND DISCUSSION

The laboratory phase of this study was conducted to determine whether observations from the field work could be explained in terms of soil parameters as measured by physical and chemical techniques. Portions of the field results which we sought to explain included: (1) change in soil and plant Mo with time on fertilized plots; (2) the effect of form of sulfur on molybdenum uptake; (3) the differences among soils in the correlation of plant Mo with anion exchange resin molybdenum.

Plant availability of molybdenum may change with time either as a result of long-term fixation reactions or movement of molybdate below the root zone. Removal of molybdenum in harvested plants is not appreciable. "Aging" reactions of iron and possibly aluminum molybdates produce more stable and therefore less soluble molybdenum compounds as amorphous forms become more crystalline. High levels of oxalate-extractable iron could therefore be presumed to produce more drastic decreases in molybdenum availability with time. Experimental results however do not support this hypothesis. The two instances of greatest residual effect (Dement and Astoria soils) showed relatively high levels of oxalate iron. Interestingly, there appears to be a negative correlation between residual effect and soil hydroxyls measured by the NaF procedure. High levels

of somewhat exchangeable hydroxyls may have a "buffering" effect upon molybdenum availability, maintaining a fairly constant molybdenum concentration in the soil solution.

The laboratory results reported herein do not explain differences among soils from the effect of fertilizer form on molybdenum uptake. More precise measurement of soil pH and a study of the sulfate release pattern of the two materials appear necessary to resolve these questions. Acidification of soils by these fertilizers would not only increase the solubility of iron oxides but as the pH approaches or passes the isoelectric point of Fe or Al oxides their anion exchange capacities could become more significant. Within the pH range of the soils studied (5-5.5) changes of a few tenths of a pH unit could produce significant differences in solubility (Jones, 1957; Reisenhauer, Tabikh, and Stout, 1962; Theng, 1971).

If plant levels of molybdates in the first harvest after fertilization are compared, significant differences are found within treatments. For example, on the Astoria and Peavine soils very high plant molybdenum levels were noted in samples from both Treatments PSMo and PSO_4Mo_3 . These soils possessed high sorption characteristics, high amorphous and exchangeable iron and exhibited much release of hydroxyls with NaF. Apparently large amounts of molybdate were adsorbed on amorphous iron, but much of this remained available to plants. Plant molybdenum from Treatment PSO_4Mo_3

on the Steiwer soil was highest of all treatments. Sorption was relatively low on this soil while iron levels were intermediate. This contrasts with the Dement soil which showed iron and sorption levels similar to the Steiwer soil but produced plants much lower in molybdenum.

As noted in an earlier section, the correlation coefficients for plant molybdenum versus anion exchange resin molybdenum were much higher when soils were separated into two sets. The Astoria and Peavine soils constitute one group (Group 1) while the remainder of the soils are in another (Group 2). Apparently the resin was not acting in a manner exactly analogous to that of the plant root, but was measuring only a portion of the plant-available molybdenum. This proportion varied among soils as was evidenced by the difference in slope of the two correlation curves.

In examining the soil parameters characterized in the laboratory studies, Group 1 soils are markedly similar in several respects. They show the highest molybdate sorption among the soils studied. Moreover amorphous and exchangeable iron levels are among the highest. These soils also released the most hydroxyls as measured by NaF. The Dement soil showed somewhat similar properties with those soils in Group 1 except that its Mo sorption value was considerably lower.

Apparently in the Group 1 soils a significant proportion of the

plant available molybdenum is held with a higher bonding energy than the resin exchange sites can exert. That is, the resin method measures a smaller portion of plant available molybdenum in Group 1 than in Group 2 soils. This may be due to differences in surface bond strengths among the soil hydrous oxide fractions. Alternatively in soils such as those of Group 1 with high oxalate-extractable iron, some of this iron may be solubilized by root exudates such as citric or oxalic acids (Wallace, 1963) with substantial release of molybdates to the plant. It is well known that allophane forms humus complexes and this gel may be present in the Astoria and Peavine soils. The Ando-like horizon associated with allophane may exhibit a molybdate sorption pattern which differs from that found in the Group 2 soils.

In addition to the physical and chemical properties of soils discussed above, factors such as soil morphology, climate, environment and plant morphology and physiology can affect molybdenum uptake by the plant. Among important soil chemical characteristics, organic matter status, soil pH, and soil phosphate and sulfate status which are in a continued state of flux make single measurements difficult to interpret. For example, levels of phosphate and sulfate ions are annually renewed by fertilization on these soils. They may compete with molybdate both for sorption sites on soil colloids and for adsorption by the plant root. The degree of competition is

concentration-dependent, so these variations may cause significant differences in plant molybdenum uptake which are time dependent.

Soil moisture content also fluctuates greatly and can have a profound effect on molybdenum availability (Kee and Bloomfield, 1961). The Yoncalla and Steiwer soils in particular were in somewhat poorly drained positions. The high molybdenum levels of plants grown on these soils following fertilization may be due to restricted drainage. Differences in moisture from year to year could also cause variation in the residual molybdenum effect. The drier spring of 1973 may partially account for the lower plant uptake of molybdenum on the Steiwer soil compared with 1972.

Not unrelated to soil pH and drainage are the levels of exchangeable aluminum, iron and manganese present. Any excesses of these ions may precipitate molybdate in areas of concentration such as the root surface or within the root, significantly reducing translocation within the plant.

In general, while laboratory sorption studies appear to be useful in predicting soil requirements for a macronutrient such as phosphorus, difficulties are compounded when using a similar method for characterization of a micronutrient such as molybdenum. Too many uncharacterized variables may affect molybdenum availability for a single test to suffice. Sorption of molybdenum from solution provides insufficient basis for recommendations. Nevertheless, studies such

as those described above provide a better understanding of many of the reactions molybdenum undergoes in the soil. With better understanding a more substantial foundation is developed on which recommendations for molybdenum application may be based.

SUGGESTIONS FOR FURTHER STUDY

Numerous unanswered questions remain as a result of this study. Problems requiring further research include the following:

Adsorption on Soils

Characterization of sorption site strength and population is difficult without reference to those of a known substance. A material with well-defined sorption sites, such as the anion exchange resin, could be introduced into a system to compete with soil for uptake of solution Mo. Measurement of solution and resin Mo would allow the formation of a clear picture of molybdate fractionation between soil and resin, and help in characterizing numbers and sorption energies of sites.

Temperature dependence of Mo adsorption would allow description of reaction kinetics. If these reactions were allowed to occur over long periods of time (e.g., months) a clearer understanding of the fixation kinetics, as encountered in the field, could be developed.

Desorption From Soils

The desorption of soil molybdate to anion exchange resin was only examined for field study. This desorption could also be measured for soils receiving Mo under carefully controlled laboratory conditions.

Desorption over time would indicate how rapidly molybdenum becomes "unavailable" to the resin.

A procedure analogous to that of Chang and Jackson (1957) for inorganic phosphate fractionation may also prove useful for examining the soil fractions responsible for molybdenum fixation. In addition incubation studies could be designed to detect those soil components by which molybdenum is initially adsorbed and whether the molybdate distribution among these components changes with time. Use of acid ammonium oxalate and citrate-dithionite extracts from iron may also show forms responsible for Mo fixation over time. Molybdate may be sorbed initially by aluminum but finally "fixed" as the highly insoluble ferric molybdate. Sequential reactions such as these could account for disparities between laboratory sorption (short term) and field availability (long term).

Field Studies

The spatial effects of fertilizer granule reaction with the soil as its materials become available require further investigation. For instance, the pH near a granule of 0-35-0-20S is expected to decrease sharply as elemental sulfur is oxidized microbiologically. Iron and aluminum may be solubilized and become much more reactive toward molybdate. These reactions should be examined, as well as effects of changes in microbial populations near the fertilizer particle.

Movement of molybdenum down the soil profile could provide information on the degree of retention exerted by the various soil horizons. Sampling at incremental depths and analysis by oxalate extraction or anion exchange resin equilibration would allow description of Mo movement. Rainfall data especially would be required, and soil temperature monitoring would likely prove useful.

Hydroxyl Release

Although the hydroxyls released by fluoride correlate well with molybdate adsorption, little insight has been gained at this point into the soil components from which the hydroxyls were released. Use of adsorption studies and fluoride-labile hydroxyl measurements on well-defined hydrous oxides of iron and aluminum could indicate likely soil iron and aluminum forms which participate in these reactions and whether the relationship between sorption and hydroxyl release was direct or indirect.

Organic Matter — Molybdenum Interactions

Although little relationship has been found between total organic matter and soil molybdenum (except under poorly drained conditions) (Kubota, 1963), the association of molybdate with specific forms of soil organic matter has received very little attention. Some interaction between organic matter and Mo has been reported. This deserves further scrutiny (Gupta, 1971; Kee and Bloomfield, 1962).

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APPENDICES

APPENDIX 1

Descriptions of Soil Profiles

<u>Horizon</u>	<u>Depth</u>	<u>Description</u>
<u>Astoria Soil</u>		
A _p	0-6"	very dark greyish brown (10YR 3/1) silt loam, many fine moderate roots; granular structure; soft, friable, slightly sticky, slightly plastic, many fine interstitial pores.
A ₂	6-15"	very dark greyish brown (10YR 3/2) silty clay loam; weak subangular blocky; soft, friable, slightly sticky, slightly plastic; may fine roots; fine interstitial pores; dark coating on ped surfaces; gradual, smooth boundary.
B ₁	15-22"	dark brown (10YR 4/3) silty clay loam; medium subangular blocky; soft, friable, sticky, plastic; common fine roots; common interstitial pores.
B ₂	22-40"	dark yellowish brown (10YR 4/4) silty clay loam; weak coarse breaking to medium fine subangular blocky; slightly hard, friable, sticky, plastic; few fine, few large roots; medium tubular pores; few fragments of shale.
B ₃	40-50+"	dark yellowish brown (10YR 4/4) heavy silty clay loam; moderate medium subangular blocky; slightly hard, friable, sticky, plastic; common shale fragments; fine pores.
<u>Peavine Soil</u>		
A ₁	0-4"	dark brown (7.5YR 2/2 and 3/2) silty clay loam; moderate fine subangular blocky; friable, sticky, plastic; abundant very fine and fine roots; common fine tubular pores; abrupt smooth boundary.

<u>Horizon</u>	<u>Depth</u>	<u>Description</u>
A ₃	4-10"	dark brown (7.5YR 3/2) silty clay loam; moderate fine subangular blocky; hard, sticky, plastic; abundant fine and very fine roots; common fine tubular pores; few very fine shale fragments; clear smooth boundary.
B ₁	10-15"	dark reddish-brown (5YR 3/4) silty clay, 5YR 4/6 dry; moderate fine subangular blocky; hard, very sticky, very plastic; many fine and medium roots; many very fine tubular pores; thin clay films; many fine pores; diffuse smooth boundary.
B _{2t}	15-26"	yellowish-red (5YR 4/6) silty clay, 5YR 5/6 dry; moderate medium subangular blocky; hard, very sticky, very plastic; few medium roots; many very fine tubular pores; common thin clay films; many very fine shale fragments.
B ₃	26-36"	yellowish red (5YR 4/6) silty clay, 5YR 5/6 dry; moderate fine subangular blocky; firm, very sticky, very plastic; common fine roots; many very fine pores; thin clay films.

Steiwer Soil

A _p	0-6"	very dark brown (10YR 3/2) light silty clay loam; weak fine subangular blocky; friable, slightly sticky, slightly plastic; many interstitial pores; common fine roots; clear smooth boundary.
A ₁	6-14"	very dark brown (10YR 3/2) light silty clay loam; weak medium subangular blocky; friable, slightly sticky, slightly plastic; many fine roots; many interstitial pores, common fine tubular pores; clear smooth boundary.
B ₁	14-21"	dark yellowish brown (10YR 4/4) silty clay loam; weak medium subangular blocky structure, friable, sticky, plastic; common roots, common fine roots; clear, smooth boundary.

<u>Horizon</u>	<u>Depth</u>	<u>Description</u>
B ₂	21-28"	greyish brown (10YR 5/3) silty clay loam; moderate, coarse and medium subangular blocky; firm, plastic and sticky; few coarse roots; few large tubular pores; fragments of shale saprolite.

Rydell Soil

A _p	0-6"	dark reddish brown (5YR 3/4) heavy silt loam; light brown (7.5YR 6/4) dry; moderate coarse granular to weak medium subangular blocky in lower part; slightly hard, friable, slightly sticky, slightly plastic; many fine roots; clear boundary.
B _{1t}	6-14"	reddish brown (5YR 4/4) light silty clay loam; moderate medium subangular blocky, slightly hard, friable, sticky, plastic; many fine roots; common thin clay films; clear boundary.
B _{21t}	14-24"	reddish brown (5YR 4/4) silty clay; moderate fine subangular blocky; slightly hard, slightly firm, sticky and plastic; common thin clay films; gradual boundary.
B _{22t}	24-40"	yellowish red (5YR 4/6) silty clay; moderate fine subangular blocky; firm, very sticky and plastic; thin continuous clay films; diffuse boundary.
B _{23t}	40-50"	yellowish red (5YR 7/6) silty clay; moderate coarse subangular blocky; firm, sticky, and plastic; thin patchy clay films.
B _{3t}	50-60"	red (2.5YR 4/6) silty clay; weak coarse subangular blocky; few patchy clay films; common olive soft shale fragments; increasing with depth.

<u>Horizon</u>	<u>Depth</u>	<u>Description</u>
<u>Nekia Soil</u>		
A _p	0-7"	dark reddish brown (5YR 3/4) heavy silty clay loam; 5YR 4/4 crushed; strong medium and coarse granular; slightly hard, friable, sticky and plastic; clear smooth boundary.
A ₁₂	7-14"	dark reddish brown (2.5YR 3-4/4) light silty clay; moderate fine subangular blocky; slightly firm, sticky and plastic; many fine roots; clear smooth boundary.
B ₁	14-18"	red (25YR 4/6) silty clay; moderate, medium subangular blocky; firm, sticky, and plastic; common fine roots; gradual boundary.
B _{2t}	18-26"	red (2.5YR 4/6) medium silty clay; strong medium subangular to angular blocky; firm, very sticky and plastic; common roots; gradual boundary.
B _{3t}	26-36"	red (2.5YR 4/8) heavy silty clay loam; weak medium subangular blocky; friable, sticky and plastic; common yellowish saprolite patches, increasing with depth.
C ₁	36-44"	very soft basalt saprolite with variegated reddish and yellowish colors and dark manganese streaks.

Yoncalla Soil

A _p	0-6"	dark brown (10YR 4/3) silt loam (7.5YR 5/4) dry, weak coarse granular, partly cloddy in lower part; slightly hard dry, friable, slightly sticky, slightly plastic; many fine roots; clear boundary.
B ₁	6-13"	dark brown (7.5YR 4/3) silty clay loam; weak medium subangular blocky; slightly hard, friable, sticky and plastic; few medium and common fine pores; gradual boundary.

<u>Horizon</u>	<u>Depth</u>	<u>Description</u>
B ₂₁	13-20"	brown (7.5YR 4/4) silty clay loam; moderate medium subangular blocky; slightly hard, friable, sticky, and plastic; many large and medium pores; slightly mottled; few manganese stains; gradual boundary.
B ₂₂	20-30"	strong brown (7.5YR 5/6) and brown (7.5YR 4/4) clay loam; weak, medium, and coarse subangular blocky; slightly hard, slightly firm, sticky and plastic; common pores; common 7.5YR 7/2 and 7/4 mottles and dark stains; abrupt boundary.
IIC ₁	30-37"	olive (5YR 5/3) clay; massive, very sticky, very plastic; many strong brown (7.5YR 5/6) mottles; clear irregular boundary.
IIC ₂	37"+	Soft shale saprolite.

Dement Soil

A ₁	0-4"	dark reddish-brown (5YR 3/3) silt loam; moderate fine granular; very friable, not sticky, slightly plastic; common very fine and fine roots, common very fine interstitial pores; abrupt smooth boundary.
A ₁₂	4-8"	dark reddish-brown (5YR 3/4) silt loam; moderate fine granular; very friable, slightly sticky, slightly plastic; many very fine and fine roots; common very fine interstitial pores; abrupt smooth boundary.
B ₁	8-16"	yellowish red (5YR 4/6) silty clay loam, moderate fine and medium subangular blocky; friable slightly sticky, plastic; many very fine and fine roots; common very fine interstitial and tabular pores; clear smooth boundary.

<u>Horizon</u>	<u>Depth</u>	<u>Description</u>
B ₂₁	16-28"	yellowish red (5YR 4/6) clay; weak fine and medium subangular blocky; friable, sticky, plastic; few very fine roots; common very fine tubular, few very fine interstitial pores; clear smooth boundary.
B ₂₂	28-38"	red (5YR 4/8) silty clay loam and loam; weak coarse subangular blocky; friable to firm, slightly sticky, plastic; very few very fine roots; few very fine tubular pores; clear boundary.
C ₁	38"+	variegated (7.5YR 7/4, 6/4, 8/6, 5/4) stratified saprolite (loam); massive; friable, not sticky, slightly plastic.

Powers Soil

A ₁	0-3"	dark reddish brown (5YR 3/3, 3/4) light silty clay loam, (no dry colors); moderate very fine granular structure; friable, slightly sticky and slightly plastic; many very fine and few fine roots; slightly acid (pH 6.2); abrupt smooth boundary.
B ₂₁	3-13"	reddish brown (5YR 4/4) heavy silty clay loam; weak fine and medium subangular blocky structure; friable, sticky and plastic; common very fine and few fine roots; few thin clay flows in pores and on ped faces; medium acid (pH 6.0); clear smooth boundary.
B ₂₂	13-21"	reddish brown and yellowish red (5YR 4/4, 5/6) silty clay; weak fine subangular blocky structure; firm, sticky and plastic; few very fine and fine roots; about 20 percent pebbles of subangular siltstone fragments; medium acid (pH 6.0); gradual wavy boundary.
C	21-24"	dark yellowish brown (10YR 4/4) fractured, weathered siltstone bedrock, pale brown (10YR 6/3) dry; about 3 percent soil material in fractures; few reddish brown and black (5YR 4/4, 2/1) stain and coatings on fracture faces in the rock.

APPENDIX 2

Standard Analysis of Soils Used in This Study

	pH	Ca	Mg	meq/100g		% Organic Matter
				K	Cation Exchange Capacity	
Astoria	5.1	6.2	1.9	0.69	25	18.0
Peavine	5.3	6.2	0.9	0.50	17	7.7
Steiwer	5.1	12.7	7.7	1.35	24	7.9
Rydell	5.2	5.1	1.9	0.62	22	7.2
Mosher		5.6	0.54	0.30	32	4.4
Nekia	5.4	9.4	6.4	0.65	26	11.0
Yoncalla	5.1	5.0	5.5	0.45	15	4.2
Dement	5.4	5.0	1.5	0.62	21	14.0
Powers	5.3	7.5	5.8	0.65	26	7.5

APPENDIX 3

Forage Yields and Levels of Clover Nitrogen, Sulfur,
Copper and Molybdenum From Field Experiments

Soil		N %	S %	Cu ppm	Mo ppm	$\frac{\mu\text{g Mo}}{100\text{g soil}}$	Ave. Yield kg/ha
Astoria 1972	1	2.74	0.24	5.2	0.5	0.8	*
	2	2.84	0.21	5.6	2.9	5.3	
	3	2.77	0.22	6.1	0.8	0.7	
	4	2.82	0.23	6.6	4.0	4.3	
	5	2.75	0.21	6.0	6.0	5.4	
	6	2.67	0.20	8.0	15.0	6.4	
1973	1	2.25	0.24	8.0	1.0	0.8	*
	2	2.36	0.22	8.8	2.1	1.2	
	3	2.32	0.21	10.6	0.8	0.9	
	4	2.31	0.22	11.6	3.6	1.8	
	5	2.42	0.20	14.4	5.1	2.9	
	6	2.68	0.22	7.0	10.2	5.0	
Peavine 1972	1	2.56	0.28	11.6	0.6	0.6	3642
	2	2.56	0.33	10.2	8.5	1.4	3337
	3	2.45	0.37	11.5	0.8	0.9	4054
	4	2.63	0.29	9.2	2.7	1.2	3749
	5	2.58	0.31	10.0	9.3	2.3	4521
	6	2.60	0.33	12.8	16.3	5.8	3965
1973	1	2.25	0.37	13.2	0.4	0.5	2547
	2	2.32	0.28	13.6	3.7	1.2	2516
	3	2.39	0.26	11.4	0.8	0.6	2332
	4	2.31	0.30	10.6	3.3	1.2	2619
	5	2.31	0.32	11.0	5.6	2.4	2404
	6	2.24	0.33	13.2	11.0	4.0	2458
Steiwer 1972	1	2.05	0.54	12.6	0.8	0.4	1310
	2	2.16	0.40	11.2	4.6	13.5	1094
	3	2.07	0.27	10.9	0.9	0.4	843
	4	2.21	0.26	8.8	3.4	8.2	1310
	5	2.30	0.24	12.2	7.3	17.0	1579
	6	2.33	0.37	10.4	18.0	31.0	1256

*Not harvested for yield.

Soil		N %	S %	Cu ppm	Mo ppm	$\frac{\mu\text{g Mo}}{100\text{g soil}}$	Ave. Yield kg/ha
Steiwer 1973	1	2.61	0.23	12.0	0.4	0.8	2189
	2	2.30	0.22	11.6	0.6	12.0	2153
	3	2.59	0.21	10.8	0.4	1.2	2045
	4	2.66	0.26	13.2	1.4	4.2	2422
	5	2.56	0.22	13.4	2.9	9.2	2799
	6	2.46	0.16	13.0	5.5	17.0	2081
Rydell 1972I	1	2.59	0.29	8.0	0.3	0.5	4503
	2	2.59	0.31	9.0	3.7	1.7	4646
	3	2.59	0.27	6.8	1.0	0.7	4521
	4	2.55	0.28	6.0	2.3	1.0	4557
	5	2.56	0.26	6.0	5.2	2.7	4449
	6	2.56	0.25	6.4	10.8	4.2	4413
1973	1	2.68	0.32	15.6	1.0	0.3	4862
	2	2.51	0.33	16.0	2.4	1.2	4951
	3	2.79	0.35	15.2	1.0	0.3	4987
	4	2.76	0.29	10.0	2.1	2.8	4754
	5	2.60	0.28	10.4	3.4	2.9	4880
	6	2.79	0.29	12.2	5.8	8.2	4682
1972II	1	1.96	0.49	7.0	0.4		933
	2	2.13	0.43	6.8	3.7		789
	3	2.20	0.25	5.7	0.5		825
	4	2.38	0.40	5.8	3.0		1005
	5	2.23	0.44	6.2	5.6		870
	6	2.28	0.35	6.4	8.0		879
Nekia 1972I	1	2.86	0.29	8.8	0.3	0.8	1991
	2	2.51	0.28	6.8	5.5	6.9	2117
	3	2.56	0.38	6.8	0.4	0.9	1991
	4	2.18	0.33	6.7	3.8	8.9	2404
	5	2.43	0.40	7.4	4.0	12.6	2045
	6	2.39	0.38	8.0	4.9	13.5	1991
1972II	1	2.40	0.38	10.8	1.0		6150
	2	2.23	0.43	12.0	3.4		6692
	3	2.33	0.38	12.4	1.0		5990
	4	2.46	0.45	13.3	3.3		8290
	5	2.27	0.27	13.6	3.4		7044
	6	2.24	0.36	11.0	6.6		6485

Soil		N %	S %	Cu ppm	Mo ppm	µg Mo 100g soil	Ave. Yield kg/ha
Nekia 1973	1	2.25	0.30	14.2	0.5	1.7	4646
	2	2.29	0.28	16.0	0.8	3.9	4162
	3	2.01	0.34	16.0	0.6	1.2	4269
	4	2.38	0.30	8.6	3.9	2.2	5794
	5	2.27	0.30	10.0	4.5	2.7	5220
	6	2.21	0.28	10.4	8.4	10.0	5059
Yoncalla 1973I	1	2.60	0.36	10.2	0.3	0.7	3803
	2	2.91	0.31	9.5	1.5	9.0	3570
	3	2.46	0.30	11.2	0.4	0.8	3803
	4	2.47	0.34	9.8	2.6	7.2	3731
	5	2.46	0.34	10.5	7.4	8.2	3516
	6	2.42	0.37	10.2	12.0	18.0	3965
1973II	1	2.29	0.34	14.8	0.3		3139
	2	2.29	0.27	9.8	1.2		4072
	3	2.30	0.27	10.8	0.3		4144
	4	2.33	0.26	12.6	6.0		3660
	5	2.67	0.29	12.0	7.0		4682
	6	2.13	0.28	11.8	8.0		4252
Dement 1972	1	1.95	0.24	7.8	1.0	1.2	3032
	2	1.94	0.25	5.0	3.0	6.6	2547
	3	2.20	0.21	6.9	1.0	0.9	2888
	4	2.11	0.25	7.6	3.1	4.0	2852
	5	2.10	0.24	5.8	4.0	7.7	3175
	6	1.96	0.30	7.8	5.0	11.1	3265
1973	1	2.16	0.20	6.8	0.6	1.4	*
	2	2.04	0.19	8.4	2.2	6.8	
	3	2.30	0.16	7.6	0.8	1.4	
	4	1.91	0.15	9.6	2.0	3.6	
	5	2.18	0.16	7.8	2.6	6.4	
	6	1.99	0.23	8.4	4.2	10.0	
Powers 1972	1	1.96	0.27	8.2	0.5	0.5	*
	2	1.95	0.27	7.0	1.6	3.2	
	3	1.94	0.27	7.8	0.9	0.6	
	4	1.83	0.27	7.6	4.3	1.7	
	5	1.93	0.24	6.8	4.7	4.1	
	6	1.87	0.20	7.0	7.7	14.9	

*Not harvested for yield.

Soil		N %	S %	Cu ppm	Mo ppm	$\frac{\mu\text{g Mo}}{100\text{g soil}}$	Ave. Yield kg/ha
Powers 1973	1	2.65	0.28	8.0	0.4	0.8	1794
	2	2.49	0.22	6.4	2.5	1.6	1974
	3	2.49	0.20	6.8	0.4	0.8	1794
	4	2.56	0.18	9.4	1.8	1.2	2404
	5	2.23	0.21	8.2	3.0	3.6	1650
	6	2.26	0.21	6.4	4.4	4.4	1920
McKenzie 1972	1	2.90	0.30	8.0	0.8	0.5	2250
	2	3.60	0.46	7.6	6.2	8.3	2200
	3	3.00	0.36	7.6	1.1	0.6	1780
	4	3.30	0.33	5.0	2.0	7.5	2410
	5	3.50	0.31	7.0	6.7	19.2	3110
	6	3.50	0.34	8.8	12.5	28.0	2720
1973	1	3.00	0.26	7.4	0.6	1.3	2800
	2	3.02	0.29	8.6	3.1	8.0	2220
	3	2.98	0.22	7.2	1.4	1.15	2490
	4	2.88	0.22	7.8	3.0	7.0	2720
	5	2.82	0.33	6.4	5.0	15.4	2820
	6	2.86	0.20	6.4	10.0	62.0	2460
Mosher 1972I	1	2.8	0.28	8.6	4.4		4330
	2	2.6	0.31	8.2	8.8		4450
	3	2.7	0.27	9.4	2.0		4270
	4	2.7	0.27	11.5	3.5		4170
	5	3.0	0.26	10.0	5.5		4200
	6	2.7	0.25	8.8	24.0		4640
1972II	1	2.20	0.30	13.8	1.2	5.4	2140
	2	2.4	0.48	13.2	2.4	12.2	2250
	3	2.2	0.23	13.2	1.6	6.7	2170
	4	2.6	0.25	13.8	3.6	10.0	2280
	5	2.1	0.22	13.8	4.7	32.0	2310
	6	2.2	0.24	13.8	11.1	48.0	2430
1973I	1	2.91	0.35	10.0	4.5		2860
	2	2.84	0.24	13.0	14.0		2970
	3	2.42	0.32	10.2	6.0		2790
	4	2.82	0.28	10.4	7.5		3130
	5	2.54	0.30	12.8	14.0		2800
	6	2.89	0.31	9.8	20.0		2640

Soil		N %	S %	Cu ppm	Mo ppm	$\frac{\mu\text{g Mo}}{100\text{g soil}}$	Ave. Yield kg/ha
Mosher	1	2.18	0.22	11.3	1.8	5.5	1920
1973II	2	2.17	0.32	12.2	15.0	26.2	2050
	3	2.13	0.20	12.5	6.0	14.0	2140
	4	2.23	0.24	11.9	16.5	32.0	1830
	5	2.10	0.18	12.8	6.0	9.2	2190
	6	2.09	0.18	13.0	16.0	28.0	1940

APPENDIX 4

Effect of Form of Sulfur on Soil pH

Soil	Soil pH		
	Untreated	0-35-0-20S	Single Superphosphate
Steiwer	5.7	5.1	5.3
Rydell	4.7	4.5	4.6
Nekia	5.4	5.0	5.1
Yoncalla	5.1	4.8	4.8
Dement	5.2	5.0	5.0
Powers	5.2	5.0	5.1
McKenzie	5.6	5.2	5.4
Mosher	5.4	5.3	5.4