

THESIS

THE CHEMISTRY, AVAILABILITY AND MOBILITY OF MOLYBDENUM IN
COLORADO SOILS

Submitted by
Paul L. G. Vlek

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for the Degree of Doctor of Philosophy

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WE HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER OUR SUPERVISION
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Committee on Graduate Work

T. N. Solie
Carol Klute
M. E. McCallum
William L. Lindsay
Adviser

W. F. Keim
Head of Department

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FORT COLLINS, COLORADO 80521

COLORADO STATE UNIVERSITY

ABSTRACT OF THESIS

THE CHEMISTRY, AVAILABILITY AND MOBILITY OF MOLYBDENUM

IN

COLORADO SOILS

The purpose of this study was to investigate the impact of molybdenum contamination in irrigation water on soils and pastures in Colorado. The chemistry, availability and mobility of Mo was studied in the laboratory, greenhouse, and field. These results were incorporated into a dynamic computer simulation model that predicts Mo accumulation in forages.

Solubility diagrams were constructed from thermodynamic data for naturally occurring molybdenum minerals. The solubility of molybdenum in selected Colorado soils was compared with that predicted by the solubility diagrams. Molybdenum minerals were found to control the solubility of Mo in only one of the thirteen soils studied. Addition of wulfenite (PbMoO_4), the most stable Mo mineral, raised the Mo solubility to conform to the solubility isotherm of wulfenite in soils.

In the remaining twelve soils the solubility of Mo was controlled by specific adsorption processes, and changed with the degree of Mo saturation and pH. The Freundlich adsorption isotherm was extended with a pH term to describe the solubility relationship of Mo in soils.

The availability of Mo in soils was studied in both greenhouse and field. Additions of Na_2MoO_4 to soils increased the uptake of Mo by alfalfa, clover, and bluegrass; the uptake increased with alkalinity. Water-extractable or $(\text{NH}_4)_2\text{CO}_3$ -extractable soil Mo accurately predicted

the concentration of Mo in alfalfa grown on neutral and alkaline soils ($r = .97$ in the greenhouse, and $r = .85$ in the field).

The information obtained in the laboratory and greenhouse studies was used to develop a computer model to simulate the impact of high-Mo irrigation water on soils and forages. The model used simulated daily growth of alfalfa under climatic conditions typical for Colorado. Changes in the Mo content of the rhizosphere were evaluated daily by considering inputs from irrigation water and losses from leaching and plant uptake.

The impact of Mo contamination on forage was shown to depend on the quality and amount of irrigation water applied to the field, as well as on the type and leachability of the soil. Toxic levels of Mo were predicted for alfalfa grown on a clayey soil after 15 years of irrigation with 300 mm of water containing 100 ppb Mo. It was demonstrated that most soils irrigated with water containing more than 25 ppb Mo will eventually produce toxic forages.

Paul Louis Gerhard Vlek
Agronomy Department
Colorado State University
Fort Collins, Colorado 80521
December, 1975

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Voor mijn onvolprezen vriend,

Gemma

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1. INTRODUCTION

Molybdenite (MoS_2) deposits are widespread in the Colorado Rocky Mountains. Approximately 40% of the world's supply is mined here, primarily at Climax, Urad and Henderson (Fig 1.1.). The Climax mine is the world's largest molybdenum producing operation. The Urad deposit was exhausted after eight years of mining and was closed in late 1974. The nearby Henderson mine is scheduled to start operation in 1976.

Mining activities in the Rocky Mountains have increased the Mo levels in some of the streams draining the mined areas. Voegeli and King (1969) found the highest levels of molybdenum in Colorado streams draining areas with molybdenum deposits or areas where molybdenum ore is processed. Table 1.1 lists the maximum molybdenum levels of water from the major river basins of Colorado. Concentrations higher than 5 ppb are generally associated with molybdenum mineralization, whereas levels above 60 ppb are associated with mining activities.

Table 1.1. Maximum Mo Contents Recorded in Colorado Streams
(from Voegeli and King, 1969)

River	Maximum
	Mo Concentration ppb
Eagle River	3800
Blue River	1200
Clear Creek	600
Platte River	240
Colorado River	87
Arkansas River	19
Rio Grande	18
Gunnison River	8
Dolores River	8
Kansas River	6
San Juan River	6
Green River	5

Elevated Mo levels in Colorado's natural waterways pose a potential environmental hazard mainly because these waterways are principle sources of irrigation water. Use of high-Mo irrigation water on pastures may adversely effect the quality of forages produced on these fields. Even though Mo toxicity to plants is rare and has only been observed under experimental conditions, high levels of molybdenum in forages often induce Cu deficiencies in livestock by interfering with sulfide-oxidase and precipitating highly insoluble copper sulfides. This disorder is referred to as molybdenosis and has various clinical symptoms and occasionally results in the death of animals.

The levels of Mo in forages that are hazardous to ruminants depend on the levels of copper and sulfur in the diet. Molybdenosis has been reported in cattle grazing forages with as low as 5 ppm Mo but forages containing greater than 10 ppm Mo are generally considered toxic to livestock.

The areas in Colorado of prime concern are those using irrigation water derived at least in part from the Climax and Urad mines. In the past, the Climax mine drained both into Tenmile Creek and the Eagle River (Fig 1.1.). Presently this mine is drained by Tenmile Creek into Dillon Reservoir which is discharged either by the Blue River into the Colorado River, or through Roberts Tunnel into the South Platte River. The Urad mine is drained by Woods Creek into Clear Creek which enters the South Platte River just north of Denver. When the Henderson mine is in operation this mine will be drained by Williams Fork into the Colorado River.

Cases of molybdenosis have been reported in the Blue River and Eagle River Valleys, which have a long history of irrigation with Mo

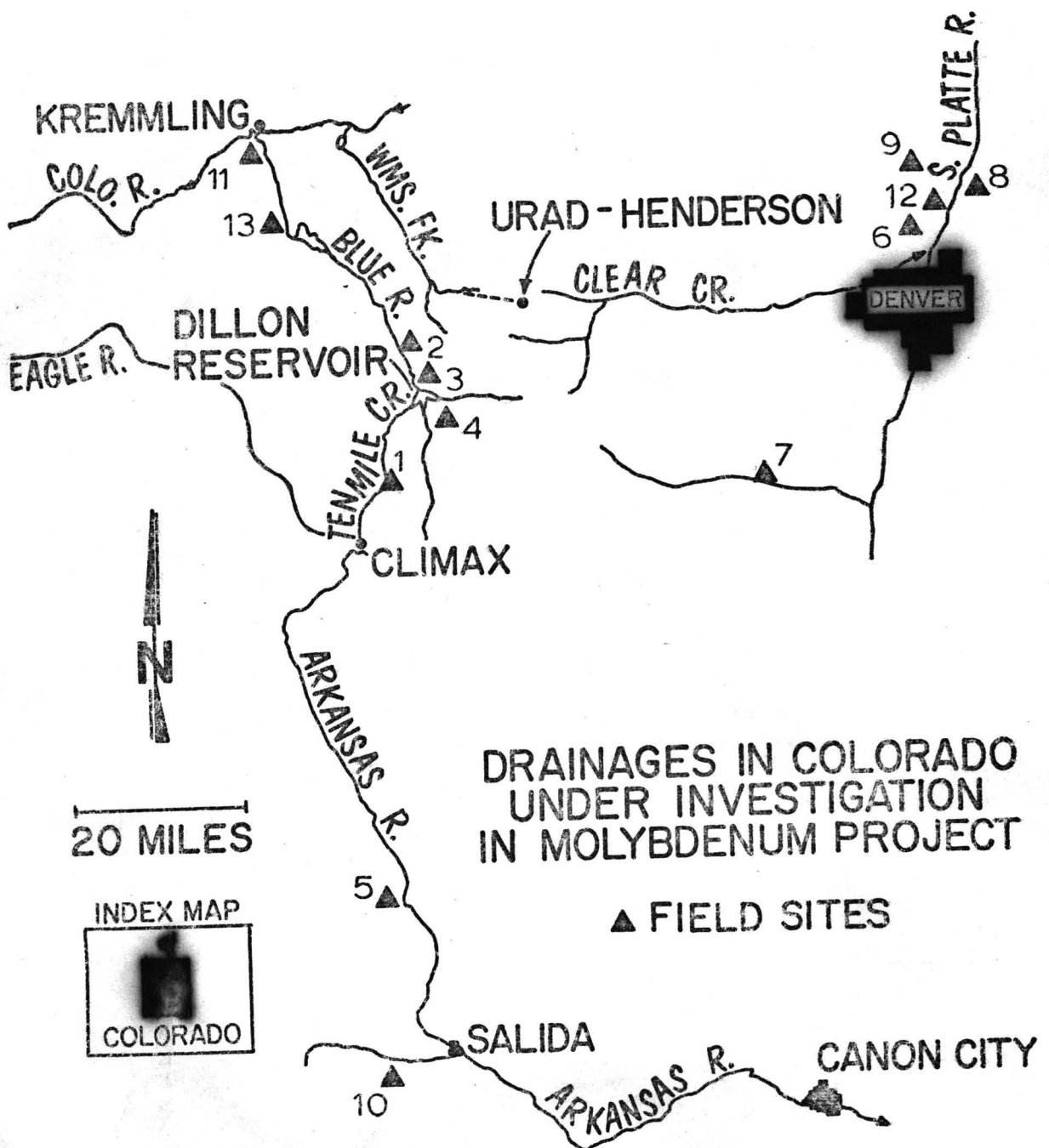


Fig. 1.1. River systems and soil sampling sites in central Colorado.

enriched water. So far no cases of molybdenosis have been reported in the Brighton area north of Denver where water from the eight year old Urad mine has been used for irrigation.

The objective of the present study was to determine the fate of molybdenum applied to soils through irrigation water and the possibility that Mo accumulation in soils may lead to the production of toxic herbage. The form in which a nutrient is retained by soils determines the solubility of that nutrient and its availability to plants. If solid phases of Mo are present in soils, the solubility of Mo can be predicted at any pH from thermodynamic data of these minerals. If adsorption controls the solubility of Mo, development of quantitative relationships between molybdenum in solution and other soil parameters permits the prediction of the Mo solubility in soils. Once the chemistry of Mo in soils is known, the impact of Mo-enriched irrigation water on soils and forages can be better understood.

Laboratory studies were carried out to describe the solubility relationships of Mo in selected Colorado soils. A greenhouse experiment was used to relate the solubility of molybdenum in soils to the accumulation of Mo in forages under controlled environmental conditions. Soil tests were evaluated for predicting the concentration of Mo in forages under both greenhouse and field conditions.

The information obtained in laboratory, greenhouse, and field was used to develop a dynamic computer model simulating Mo accumulations in soils and forage as a result of high-Mo irrigation. The study was made for two alfalfa pastures in the South Platte Valley. The model gives an insight into the long term problems of Mo pollution and helps to evaluate water quality standards for Mo in irrigation water.

2. LITERATURE REVIEW

2.1. Molybdenum Minerals and Their Stability

The chemical affinity of molybdenum is highly temperature dependent. At high temperatures molybdenum tends to associate with Fe, Ni, Ti, Mn, and Mg, suggesting high concentrations of Mo metal in the earth's core. At intermediate temperatures Mo is very chalcophilic which explains the abundance of molybdenite (MoS_2) in hydrothermal deposits. There is little evidence that molybdenum enters the silicate minerals of igneous rocks (Goldschmidt, 1958). At temperatures commonly found in supergene environments and soils, molybdenum shows a preference for associations with Ca, Pb, and Fe(III) (Rankama *et al.*, 1950).

Only few naturally occurring molybdenum minerals are known. The most common mineral is molybdenite (MoS_2); occasionally molybdate (MoO_3) and ilsemanite (Mo_3O_8) are found as alteration products of MoS_2 . The more familiar secondary molybdate minerals are powellite (CaMoO_4), wulfenite (PbMoO_4), ferrimolybdate ($\text{Fe}_2(\text{MoO}_4)_3 \cdot n\text{H}_2\text{O}$), lindgrenite ($\text{Cu}_3(\text{MoO}_4)_2(\text{OH})_2$), melkovite ($\text{H}_6\text{CaFe}(\text{PO}_4)\text{MoO}_4 \cdot 6\text{H}_2\text{O}$), betpakdalite ($\text{CaFe}_2(\text{As}_2\text{Mo}_5\text{O}_{24}) \cdot 14\text{H}_2\text{O}$), and possibly pateraitite ($\text{CoMoO}_4 \cdot n\text{H}_2\text{O}$) (Poverennykh, 1972). In uranium bearing systems, the following minerals may form: Sedovite ($\text{U}(\text{MoO}_4)_2$), iriginite ($\text{U}(\text{MoO}_4)_2(\text{OH})_2 \cdot 3\text{H}_2\text{O}$), cousinite ($\text{Mg}(\text{UO}_2)_2(\text{MoO}_4)_2(\text{OH})_2 \cdot 5\text{H}_2\text{O}$), and calcurnolite ($\text{Ca}(\text{UO}_2)_3(\text{MoO}_4)_3(\text{OH})_2 \cdot 8\text{H}_2\text{O}$).

Titley and Anthony (1961) studied the stability of various molybdenum minerals and ionic species in the system H_2O , H_2MoO_4 , H_2SO_4 . They concluded that molybdenite eventually oxidizes to molybdate (MoO_4^{2-}) or

bimolybdate (HMoO_4^-) ions. The molybdate ions exist under a wide range of conditions and are available to form secondary minerals such as wulfenite, powellite, lindgrenite, or ferrimolybdate. It appears that ferrimolybdate may form under acid, oxidizing conditions as an end product in the weathering of molybdenite, whereas ilsemanite (Mo_3O_8) may occur as an intermediate product (Titley, 1963).

The forms of molybdenum present in aqueous media depend on the pH and concentration of the solution. Polymers of molybdenum are reported in acid solutions with Mo concentrations of 10^{-4}M or higher (Carpeni, 1947; Aveston *et al.*, 1964). In solutions with Mo concentrations less than 10^{-4}M , molybdate and bimolybdate ions are the major species. The neutral molybdic acid species is important only in highly acid solutions (pH 2.5), (Burclova *et al.*, 1973).

No agreement has yet been reached on the value of the second dissociation constant of molybdic acid. An early estimate of pK_2 calculated by Brewer (1953) from the solubility of MoO_3 in water, gave a value of 6.00. This value has been used in many geochemical calculations (Titley *et al.*, 1961, 1963, Hansuld, 1966). Considerable evidence suggests that a value for pK_2 of 4.0 may be more accurate (Sasaki *et al.*, 1965). Based on pK_2 values of 3.89 and 3.87 reported by Sillen and Martell (1964) and Chojnacki *et al.* (1965) respectively, a pK_2 of 3.88 was used herein (Table 2.1).

In dilute solutions of slightly acid to alkaline reaction, the $\text{MoO}_4^{=}$ ion predominates (Burclova *et al.*, 1973). In highly reduced aqueous systems molybdenum may be present in valence states lower than Mo(VI). The most important of these is the Mo (V) species as MoO_2^+ (Burclova *et al.*, 1973). Thermodynamic constants for the aqueous species of molybdenum are listed in Table 2.1, Reactions 1-5.

Thermodynamic data of molybdenum minerals have been reported by scientists from many different disciplines. The solubility products for reactions involving molybdenite and ilsemanite (Table 2.1, Reactions 6-9) were derived primarily from work by Titley (1963). The solubilities of molybdate minerals and sparingly soluble molybdenum salts were critically reviewed by Urusov (1967) listing values for Ca, Sr, Ba, Fe(II), Pb, Zn, and Cu molybdates. In a more recent review O'Hare et al. (1974) list solubilities for the molybdates of Ba, Sr, Ca, and Fe(II). A value for $pK_{sp}^O(Fe_2(MoO_4)_3 \cdot nH_2O)$ was reported by Titley (1963). The solubilities of molybdate minerals of possible importance in soils is given in Reactions 10-15 (Table 2.1). The list is incomplete due to the lack of thermodynamic data for the more complex molybdate minerals of possible importance in soils (e.g. lindgrenite and melkovite).

Of the molybdate salts listed in Table 2.1 only the Fe(III), Ca and Pb salts have been found in nature. The solubility of ferrimolybdate was adopted from Titley (1963) and corrected for the updated second dissociation constant of 3.88. The $pK_{sp}^O(Fe_2(MoO_4)_3)$ of 31.1 agrees with the solubility of ferrimolybdate determined by Sarafian and Furbish (1965). Values for $pK_{sp}^O(CaMoO_4)$ vary from 7.19 to 8.50. The value accepted as most reliable was 7.84, taken from the National Bureau of Standards (Wagman et al., 1968).

The solubility products of $PbMoO_4$ reported in the literature are not consistent. Muldrow and Hepler (1958) estimated a pK_{sp}^O for $PbMoO_4$ of 13, based on calorimetric studies of enthalpies of precipitation from aqueous lead nitrate - sodium molybdate solutions. Using Muldrow

Table 2.1. The Equilibrium Constants for Various Reactions of Molybdenum Minerals and Complexes in Soil for 25C and Infinite Dilute Solution

Equation	Log K°	Source
<u>Hydrolyses</u>		
1. $\text{H}_2\text{MoO}_4 \rightleftharpoons \text{HMoO}_4^- + \text{H}^+$	-	-
2. $\text{HMoO}_4^- \rightleftharpoons \text{MoO}_4^{--} + \text{H}^+$	-3.88	Chojnacki et al. (1965)
		Sillen and Martell (1964)
<u>Redox</u>		
3. $\text{Mo}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{MoO}_2^+ + 4\text{H}^+ + 2\text{e}^-$	-9.96	Titley (1963)
4. $\text{MoO}_2^+ + 2\text{H}_2\text{O} \rightleftharpoons \text{HMoO}_4^- + 3\text{H}^+ + \text{e}^-$	-15.97	Titley (1963)
5. $\text{MoO}_2^+ + 2\text{H}_2\text{O} \rightleftharpoons \text{MoO}_4^{--} + 4\text{H}^+ + \text{e}^-$	-19.85	Titley (1963)
6. $\text{MoS}_2 + 10\text{H}_2\text{O} \rightleftharpoons \text{MoO}_2^+ + 2\text{SO}_4^{--} + 20\text{H}^+ + 17\text{e}^-$	-111.89	Titley (1963)
7. $\text{MoS}_2 + 12\text{H}_2\text{O} \rightleftharpoons \text{MoO}_4^{--} + 2\text{SO}_4^{--} + 24\text{H}^+ + 18\text{e}^-$	-131.74	Wagman et al. (1968)
8. $3\text{MoS}_2 + 32\text{H}_2\text{O} \rightleftharpoons \text{Mo}_3\text{O}_8 + 6\text{SO}_4^{--} + 64\text{H}^+ + 52\text{e}^-$	-335.22	Titley (1963)
9. $3\text{MoO}_2^+ + 2\text{H}_2\text{O} \rightleftharpoons \text{Mo}_3\text{O}_8 + 4\text{H}^+ + \text{e}^-$	0.45	Titley (1963)
<u>Sparingly Soluble Mo- Salts</u>		
10. $\text{Ag}_2\text{MoO}_4 \rightleftharpoons 2\text{Ag}^+ + \text{MoO}_4^{--}$	-11.77	O'Hare et al. (1974)

Table 2.1 (Cont.)

Equation	Log K°	Source
<u>Sparingly Soluble Mo- Salts</u>		
$\text{Ag}_2\text{MoO}_4 \rightleftharpoons 2\text{Ag}^+ + \text{MoO}_4^{2-}$	-11.55	Wagman et al. (1968)
11. $\text{BaMoO}_4 \rightleftharpoons \text{Ba}^{2+} + \text{MoO}_4^{2-}$ (20 C)	-8.34	Urusov et al. (1967)
	-7.46	Wagman et al. (1968)
	-7.42	O'Hare et al. (1974)
12. $\text{FeMoO}_4 \rightleftharpoons \text{Fe}^{2+} + \text{MoO}_4^{2-}$	-10.45	Wagman et al. (1968)
	-9.11	O'Hare et al. (1974)
	-7.70	Weller (1963)
13. $\text{Fe}_2(\text{MoO}_4)_3 + 6\text{H}_2\text{O} \rightleftharpoons 2\text{Fe}(\text{OH})_3 + 3\text{HMoO}_4^- + 3\text{H}^+$	-31.10*	Titley (1963)
14. $\text{CaMoO}_4 \rightleftharpoons \text{Ca}^{2+} + \text{MoO}_4^{2-}$	-8.50	O'Hare et al. (1974)
	-7.85	Spitsyn et al. (1952)
	-7.84*	Wagman et al. (1968)
	-7.19	Bokiy (1956)
		Weller and King (1963)

Table 2.1 (Cont.)

Equation	Log K ^o	Source
<u>Sparingly Soluble Mo- Salts</u>		
15. $\text{PbMoO}_4 \rightleftharpoons \text{Pb}^{2+} + \text{MoO}_4^{=}$	-15.89	Wagman et al. (1968)
	-13.00*	Muldrow and Hepler (1958)
	-11.48	Skobets et al. (1970)
	-10.60	Fomin et al. (1952)
(22 C)	-9.72	Chepelevetskii et al. (1967)
(20 C)	-7.45	Weller and King (1963)

*Indicate values selected for use in this study.

and Hepler's data in combination with a more accurate value of ΔG_f° (MoO_4^{2-}), O'Hare (1974) estimated a $\text{pK}_{\text{sp}}^\circ$ for PbMoO_4 of 15.0. Skobets et al. (1970), employing an inverse polarographic method for determining the lead concentration of slightly soluble salts determined a $\text{K}_{\text{sp}}^\circ$ for freshly precipitated PbMoO_4 of 3.3×10^{-12} . Discrepancies in reported wulfenite solubilities illustrate the difficulty in obtaining accurate thermodynamic data for this mineral. Reliable solubility data for wulfenite and other less common molybdenum minerals are needed to determine their possible significance in soils.

2.2. Adsorption of Molybdenum in Soils

Considerable research has been carried out to characterize the mode of Mo adsorption by various soils and soil minerals. The role of Fe(III) oxides and hydroxides as a molybdenum adsorbent in soils has been emphasized by several investigators (e.g. Jones, 1956; Reisenauer et al., 1962; Mikhailov, 1962; Reyes and Jurinak, 1967; Taylor and Giles, 1970). Other molybdenum sorbing minerals in soils that have been given some attention are metahalloysite, nontronite, and kaolinite (Jones, 1957), illite and allophanes (Theng, 1971) and oxides of titanium and aluminum (Reisenauer et al., 1962). Others consider soil organic matter as an important adsorbent for molybdenum in humus rich soils (Tuev et al., 1965; Szilagyi, 1967).

The mechanism of molybdenum adsorption has been studied with Fe(III)-oxides. Reisenauer et al. (1962) studied the stoichiometry of surface adsorption of molybdate on Fe(III) oxides at pH 4.0 and found that each adsorbed MoO_4^{2-} ion displaces two hydroxyls from the oxide surface. Reyes and Jurinak (1967) concluded that at pH 4.0 adsorption of Mo

onto hematite is a definite fixed site adsorption process involving the OH-groups of the hematite surface and the tetrahedral form of monomeric $H_xMoO_4^{x-2}$. Each ion completely covers an adsorption site but strongly interacts with neighboring adsorbed molybdate ions (Reyes and Jurinak, 1967).

Specifically adsorbed ions are to some degree covalently bound to their adsorbent. Wakatsuki et al. (1974) tested the tendency of several anions to form covalent bonds by measuring their effectiveness in reducing the surface charge of adsorbent at a specified pH. Molybdate was placed in the class of high specificity together with arsenate, vanadate, and phosphate.

Specific adsorption of anions is often studied by developing Langmuir (1918) or Freundlich (1926) adsorption isotherms (Olsen and Watanabe, 1957). The Langmuir equation is based on the kinetic theory of gaseous adsorption onto solids, but is often used to relate the adsorption of ions from solution onto solids. The Langmuir equation states that the amount of adsorbed ion (N) is related to the equilibrium concentration of that ion (C) and the amount of available adsorption sites remaining ($N_{max} - N$):

$$N = kC(N_{max} - N)$$

where k is a constant related to the bonding energy of the adsorbent for the adsorbate (Ellis and Knezek, 1972).

The Freundlich equation has no sound theoretical basis but is an empirical relationship used to describe the adsorption of ions or molecules from a liquid onto a solid phase. The amount adsorbed (N) is related to the equilibrium concentration of the adsorbate (C) as follows:

$$N = kC^A$$

where k and A are constants. Other, more complicated adsorption isotherms have been developed (Gunary, 1970; Adamson, 1963), but they add little to the understanding of adsorption processes, and are rarely used for soils.

Reisenauer et al. (1962) found that adsorption of molybdate onto soils at a fixed pH followed the Freundlich equation. Reyes and Jurinak (1967) and Theng (1971) in studying molybdenum adsorption onto hematite and soil at pH 4.0, found two adsorption reactions, each conforming to a Langmuir isotherm. The isotherms were interpreted to show two energetically distinct binding sites for Mo. Adsorption sites for Mo in soils are likely to be energetically different. The Langmuir theory which is based on equality of binding sites is therefore expected to be inadequate for describing Mo adsorption in soils (Barrow, 1970).

Molybdenum adsorption depends not only on the kind of adsorbent but also on the pH of the system. Since H^+ and OH^- are considered potential determining ions, they cause a change in surface potentials of minerals with pH. Hingston et al. (1967, 1968, 1970) showed that the capacity of an adsorbent for binding molybdenum is pH dependent and that an adsorption maximum occurs at $pH = pK_2 = 3.88$. Indeed, Jones (1957) and Theng (1971) found maximum retention of molybdenum by soils, clay minerals, or sesquioxides at pH 4.0. Reyes and Jurinak (1967) demonstrated that the adsorption maximum of molybdate on hematite was reduced by 80% if the pH was changed from 4.0 to 7.75. The zero point of charge of the hematite sample occurred at pH 8.0.

The pH dependence of Mo adsorption in the pH range of soils was described by Reisenauer et al. (1962) who concluded that at a fixed

concentration of Mo in solution, the log of Mo adsorbed ($\log N$) is linearly related to pH:

$$\log N = B \cdot \text{pH} + k$$

where B and k are constants. Reisenauer et al. (1962) recognized that the solubility of Mo in soils is a function of the minerals present, the degree of molybdenum saturation, and pH, but no sound quantitative relationship relating these parameters has been developed.

2.3. Molybdenum Availability to Forage Plants

The availability of soil Mo to plants varies significantly and is dependent on soil parameters as well as plant parameters. The uptake of Mo is well correlated with the amount of Mo in the soil solution (Evans, 1950, 1956) which ranges from 10^{-8}M in low Mo soils (Lavy and Barber, 1964) to 10^{-5}M in soils producing toxic herbage (Kubota et al., 1963). Soil parameters affecting molybdenum solubility include pH, mineralogy, degree of Mo saturation, and presence of competing anions such as phosphate and sulfate (Reisenauer, 1967; Davies, 1956).

The pH dependence of Mo availability was recognized as early as 1943 when Lewis showed that basic fertilizers increased the uptake of Mo by grasses growing on acid soils. Ahlrichs et al. (1963), James et al. (1968) and Gupta (1969, 1970) reported increased contents of Mo in alfalfa after liming. Barshad (1948) found that acidifying alkaline soils greatly reduced water-soluble Mo. The importance of the Mo status of soils is evident from the positive effect of Mo fertilization on the Mo uptake by plants (Cunningham and Hogan, 1949; Reisenauer, 1956; Ahlrichs et al., 1963; Gupta and MacKay, 1968; James et al., 1968).

High levels of available phosphate in soils often increase the adsorption of Mo by the crop (Barshad, 1951; Mulder, 1954; Jones and Ruchman, 1973). In nutrient solutions high levels of phosphate do not greatly affect the Mo uptake by plants (Gorlach *et al.*, 1971). High levels of sulfate in soils often decrease Mo adsorption (Reisenauer, 1963; Gupta and Munro, 1969).

The ability of plants to extract Mo from soils depends on the plant species (Johnson, 1966), the nutrient status of plants (Jones, 1965), pH and degree of reduction of the growth media (Giordano, 1966). With aerobic conditions increasing pH favors the uptake of Mo by corn and tomatoes from hydroponic solutions. The reverse was found with anaerobic conditions. Even though redox potential has little effect on the solubility of Mo in soils (Kereszteny and Nagy, 1963), the uptake of Mo from hydroponic solutions was significantly lowered by anaerobic conditions (Giordano, 1966).

Environmental conditions greatly affect the uptake of Mo by plants. Plant absorption of soil molybdate increases with increased soil moisture (Bortels, 1949; Cannell *et al.*, 1960; Kubota *et al.*, 1963; Lavy and Barber, 1964). Similarly, climatic factors such as rainfall solar radiation, wind, and relative humidity affect the rate of transpiration of crops and thereby modify the uptake of Mo by plants.

With so many factors affecting the availability of Mo in soils and the uptake of Mo by plants, it is understandable that soil tests are often unsuccessful in predicting Mo deficiencies and toxicities.

In 1953, Grigg published a 12-hour ammonium oxalate extraction for assessing Mo deficiency in soils. Gorlach (1964) reduced the extraction time without significantly changing the results. The method has been used

extensively by many workers (e.g. Davies, 1956; Massey et al., 1967; Reisenauer, 1967).

Extraction of soil with 5% ammonium hydroxide was proposed by Amin and Joham (1958) as a measure of plant available Mo. Little work has been done to substantiate the accuracy of this test.

Lavy and Barber (1964) used the *Asparagillus niger* - bioassay method (Mulder, 1948) as an indicator for plant available molybdenum in soils. Although useful, the method is elaborate and not easily amenable to routine soil testing.

Lowe and Massey (1965) endeavored to improve Barshad's (1951) simple water extraction method by using a continuous hot water leaching method in order to extract detectable amounts of Mo from soil. Though tedious, the method appears to be far superior to Grigg's method for predicting plant uptake of Mo from soils (Lowe and Massey, 1965; Pathak et al., 1969).

Bhella and Dawson (1972) used an anion exchange method similar to that used by Mosher et al. (1959) for phosphate availability to assess plant available molybdenum in 30 soils from Western Oregon. Jackson (1973) evaluated this procedure for predicting plant uptake in Mo contaminated soils from Colorado and found it to be suitable for calcareous soils. In an effort to develop a Mo soil test for detecting potentially toxic pastures, Williams and Thornton (1973) evaluated EDTA and ammonium acetate (Evans et al., 1951) as possible extractants. Only ammonium acetate gave a satisfactory indication of the molybdenum uptake by herbage.

Soils supplying excessive amounts of Mo (> 10 ppm) commonly yielded higher correlation coefficients than those limited to the

response range. Barshad (1951) and Kubota et al. (1963) showed good correlations between plant Mo up to 40 ppm and extraction of the soil with water. Correlation coefficients between Mo uptake and Mo dissolved by 0.1 M NaOH or acid oxalate were 0.85 and 0.80, respectively, for plant contents up to 11 ppm Mo (Haley and Melsted, 1957).

Davies (1956) and Reisenauer (1967) concluded that the only soil test adequately checked with field trials is the acid oxalate extraction. Due to its performance, there is a need for a versatile soil test that is accurate over a wide range of soils, and that has been evaluated for both greenhouse and field.

2.4. Movement of Molybdenum in Water-Soil-Plant Systems

From geochemical studies it appears that Mo tends to be concentrated in the topsoils derived from igneous rocks, indicating the resistance of this element to leaching processes as bases are removed (Wells, 1960). In alkaline soils molybdenum is more mobile and, if not leached from the profile by rain or irrigation water is highly available to plants (Johnson et al., 1952; Muller et al., 1964).

Transport of Mo through soils has been studied to a very limited extent (Jones and Bellings, 1967). Employing radioactive isotopes they studied the retention of Mo, applied as a topdressing of ammonium molybdate to 16-cm columns of soil, during a simulated rain. They found that Mo leached through most soils, particularly soils with an alkaline reaction. Some accumulation of Mo occurred in the top two inches of the soil column. No effort was made to describe the transport of Mo by one of the commonly used chromatographic models (Frissel and Poelstra, 1967).

Pratt and Bair (1964) used lysimeters in irrigated fields to measure the net change of Mo in the soils as the amount added in irrigation water minus the amount removed by crops and drainage water. With a leaching fraction of 7-8%, the molybdenum accumulation was about three fourths of the amount added in the irrigation water.

Jackson (1973) developed a compartmental simulation model of molybdenum flow in a water-soil plant system based on greenhouse and laboratory studies of calcareous soil. Assumptions were made to simulate alfalfa growth, irrigation practices and Mo retention by soils. A regression model from a greenhouse study was used to relate plant concentration to resin extractable molybdenum in the soil on a daily basis. Jackson points out that extending the Mo model by including an adequate transport theory and plant uptake mechanism would greatly improve its usefulness.

Examples of models for nutrients other than Mo are available in the literature. Various approaches to transport of ions are discussed by Frissel and Poelstra (1967) including continuous and discontinuous flow theories. Continuous flow theories of the transport equation give the concentration of the tracer in the fluid phase at any time and depth. If analytical solutions to the transport equations are desired, only simple source term expressions can be included in the mass balance equation (Cameron, 1973). In discontinuous flow theories the soil is regarded as being built from a large number of segments and flow is discontinued periodically to establish equilibrium between liquid and solid phase. The height of the segment can be determined experimentally.

Compartmental flow models such as the one developed by Dutt and coworkers (1963) allow for simulation of solute movement through soils as well as inclusion of plant uptake and other external processes. Although only remotely based on a physical theory this type of modeling can be very useful in soils. The development of digital computer models of the water - soil - plant relationships, including biotic and abiotic factors, permits sensitivity studies of the effect of one or more of these factors on the behavior of the total system (Dutt, et al., 1972). A dynamic Mo model would thus be useful to study the effect of Mo pollution on soil and plants.

3. MATERIALS AND METHODS

3.1. Analytical Procedures

Molybdenum analysis

The procedure used for analyses of Mo in solution was dependent on the Mo concentration range and the total composition of the sample. The conventional thiocyanate procedure (Bradford, et al., 1965), preceded by a H_2O_2 - H_2SO_4 digestion to remove interfering organic matter (Jackson and Meglen, 1975) was used to analyze solutions with strong matrices - e.g., $(\text{NH}_4)_2\text{CO}_3$ - extracts, plant digests - containing 50 ppb of Mo or more.

The thiocyanate procedure was modified to allow analyses of HClO_4 - HF digested soils as follows:

Possible copper interferences were avoided by pre-extracting the 50 ml solution sample for 10-15 minutes with 1 gram of citric acid and 2 ml of iso-amyl alcohol. The organic phase was discarded. The procedure described by Bradford et al. (1965) was then followed up to the extraction of Mo from the aqueous sample into 10 ml iso-amyl alcohol. Interferences of iron and titanium were eliminated by washing the yellow colored organic phase with 25 ml of the aqueous phase of a blank. Generally one but sometimes two washings were sufficient to remove the interfering yellow color, leaving the amber color of the molybdenum thiocyanate complex for spectrophotometric analyses.

Analyses of Mo by means of flameless atomic absorption spectrophotometry has only been possible since the introduction of graphite furnaces.

The analytical procedure has many advantages including speed, accuracy and reduced sample requirement. A sample of 20 or 50 μl is inserted into the carbon rod by means of an Eppendorf micropipette. The carbon rod is then heated to 120C for 20 seconds to dry the sample. A 20-second charring cycle with a temperature of 1600C removes organics and other more volatile elements. Atomization of Mo by heating the carbon rod to 2700C for 10 seconds is recorded on an automatic recorder and the concentration in the sample is determined by comparison with peak heights of standards containing 0 to 100 ppb Mo. Between runs the carbon rod was heated for another 5 seconds at 2700C to suppress the memory effect caused by incomplete atomization of the previous sample. The largest limitation of the procedure at this point is the interference of strong matrices making the procedure unsuitable for Mo analysis of plant and soil digests or soil extracts high in salt.

Aqueous extracts of soils were analyzed both by thiocyanate procedure and by flameless atomic absorption spectrophotometry. Linear regression analyses of 50 samples containing between 25 and 300 ppb Mo analysed colorimetrically (x) and by flameless A (y) resulted in:

$$y = 1.12 x - 12$$

with $r = 0.975$ and a standard error of 15.8 ppb. The intercept of the regression line as well as the deviation from a unit slope are due to the overestimation of the Mo content in low Mo solutions. For samples containing 100 ppb or more the two procedures were equally good. Recovery by flameless AA of 10 ppb Mo additions to solutions containing less than 25 ppb Mo ranged from 70 to 116% with an average recovery of 87%, indicating a high accuracy of the AA method at low Mo concentrations.

3.2. Soil Testing and Plant Analyses

The total analyses of Mo in soils has puzzled many researchers. Reisenauer (1965) proposed a procedure of dissolving Mo in a HClO_4 digestion and analyzing it colorimetrically as the Ferric molybdatethiocyanate complex. The procedure is claimed to be replicable within 5%. The accuracy of this procedure has not been evaluated.

For this study total Mo was determined by dissolving Mo in HClO_4 - HF as outlined by Pratt in Methods of Soil Analyses (1965) and analyzing it as previously described. The accuracy of the procedure was verified by analyses of six standard samples from USGS. Results of these analyses were given in Table 3.1 with the multilaboratory data obtained from the United States Geological Survey.

Table 3.1. Multilaboratory Mo analyses of six USGS standards (ppm). Atomic absorption (AA), Emission Spectroscopy (EMS), Colorimetrically (COL), and by X-ray fluorescence (XRF).

		USGS								CSU	
Sample #		AA		EMS		COL		XRF		COL	
GRX	1	24.8±	17.1	34.4±	43.8	20.2±	20.8	30.5±	6.4	25.8±	1.2
	2	9.2	13.5	12.3	5.8	4.1	5.8	12.0	0	9.4	1.9
	3	16.6	22.3	16.7	35.7	22.8	64.5	14.0	1.4	14.5	0.5
	4	353.8	154.1	400.0	261.0	232.4	137.8	301.0	27.5	332.0	70.0
	5	39.6	17.3	42.4	28.0	33.0	20.5	31.8	5.6	38.1	1.6
	6	--		4.2	3.0	4.0	.9	10.0	0.0	3.4	.1

From the analytical data submitted by the USGS it is learned that an accurate procedure for Mo analyses is still not available. Results obtained utilizing the above described method are in agreement with the best USGS estimates and reproducibility of the results is excellent.

Additions of 0.5 ppm Mo as sodium molybdate to perchlorate digests containing approximately 1 ppm Mo were completely (90 - 110%) recovered.

Water-extractable Mo in soils was determined by extracting 15 grams of soil (<16 mesh) with 30 ml of distilled-deionized water for a period of 12 hours. Extractions were done on a rotary shaker at 25C. The suspensions were centrifuged at 25C for 15 minutes and subsequently filtered through filter paper, Whatman No. 1, to remove floating organic matter. Molybdenum was measured in the clear filtrate by flameless AA.

Extraction of Mo from two soils indicated that a plateau was reached between 8 and 12 hours of extraction. A twelve hour extraction with H₂O was highly reproducible for most soils.

DTPA - extractable Mo was determined in the DTPA - micronutrient extract (Lindsay and Norvell, 1969). Molybdenum was analyzed by flameless AA, using standard solutions containing a similar matrix.

Ammonium carbonate extractable Mo in soils was determined by extractions of 15 grams of soil (<16 mesh) with 30 ml freshly prepared 1 M (NH₄)₂CO₃ of pH 9.0. The suspensions were shaken for 12 hours at 25C on a rotary shaker, centrifuged and filtered, and Mo measured colorimetrically in the filtrate. Extractions of two soils for various lengths of time revealed that 2 to 4 hours of equilibration sufficed to reach a plateau. The extraction time could thus be halved without loss of reproducibility of the method.

Plant available Fe, Mn, Zn, and Cu in soils was determined with the DTPA - micronutrient soil test (Lindsay and Norvell, 1969). The sodium bicarbonate extraction method (Olsen et al., 1954) was used to assess

available phosphorus in soils. Available potassium was determined by extractions of the soil with ammonium acetate (Richards et al., 1954).

Plant tissues were dried at 70C for 48 hours. Field samples were then ground in a stainless steel mill. A two gram ground sample was predigested for 1 hour on a hot plate with 5 ml 50% $\text{Mg}(\text{NO}_3)_2$. Samples were subsequently ashed for 16 hours at 550C and the white residue was dissolved in 40 ml 4N HCl, filtered and brought to 50 ml final volume. Molybdenum was determined colorimetrically.

3.3. Soils and Soil Preparation

Twelve surface soils were collected from the South Platte, Blue River, and Arkansas River areas of Central Colorado. The selected sites numbered 2 through 13 are shown in Fig. 1.1. An acid soil (No. 1) from South Colorado was included for laboratory studies. The soils ranged in pH (saturated paste) from 5.5 to 7.7. Soil #4 was a mountain forest soil collected east of Breckenridge. All other sites were irrigated pastures at the time of sampling in 1974.

Soils 6, 8, 9, and 12 correspond to soils 73-1, 72-15, 72-17, and 72-21 from the Brighton area (Jackson, 1973) and have been irrigated with water ranging in Mo from 95-225 ppb. Soil 7 is from the North fork of the South Platte, approximately a mile downstream from where Roberts tunnel adds high-Mo Dillon Reservoir water to this stream. Soils 5 and 10 are uncontaminated soils from the Arkansas Valley. Soils 2, 3, 11, and 13 were collected in the Blue River Valley between Dillon Reservoir and the Colorado River. Soil 2 has been flooded with Blue River water containing suspended mine tailing material accumulated prior to

construction of Dillon Reservoir. A light colored surface layer had formed as a result of deposition of these tailing fines. Soils 11 and 13 were irrigated with Blue River water, whereas Soil 3 was irrigated with water from a tributary of the Blue River containing 1 ppb Mo.

The extent of Mo contamination in the Blue River soils is difficult to evaluate. Total Mo values (Table 3.2) for Soils 3, 11 and 13 are 5 to 10 times higher than for soils in the Brighton Area or from the Arkansas Valley. The relatively high total Mo content of the non-irrigated forest soil (4) suggests that a large percentage of the Mo found in the Blue River soils may be native Mo.

The soils were air-dried, crushed with a wooden mallet and sieved through a 0.5 cm stainless steel screen and used for greenhouse experiments. A representative subsample of the soils was pulverized with a wooden rolling pin and screened through a 16-mesh stainless steel sieve prior to being used for laboratory experimentation. Some characteristics of the topsoils (0-30 cm) including pH (saturated paste), total Mo, and nutrient status are listed in Table 3.2.

3.4. Equilibrium Studies

Wulfenite solubility

Duplicate samples (100 mg) of natural wulfenite (PbMoO_4) were washed with dilute nitric acid and water and subsequently suspended in 100 ml distilled deionized water. After shaking for one month at 25C, the supernatant solutions were centrifuged and decanted.

Solutions (100 ml) of 10^{-2} M $\text{Pb}(\text{NO}_3)_2$ and 10^{-3} M Na_2MoO_4 were slowly mixed under continuous stirring, allowing precipitation of the sparingly soluble PbMoO_4 . The supernatant solutions were decanted and replenished

Table 3.2. Nutrient Status of Colorado Soils Used in Greenhouse Experiment

Soil	Total Mo ppm	pH Sat. paste	K exch. ppm	P HCO ₃ ppm	DTPA extractable			
					Fe	Cu	Mn	Zn
					ppm			
1	2.5	5.5	-	-	62.0	0.4	44.0	3.6
2	9.9	5.8	120	12.0	129.0	12.5	34.0	125.0
3	20.7	5.8	83	9.5	347.0	4.0	14.3	3.2
4	13.3	6.5	111	14.0	87.0	0.7	37.0	2.3
5	3.5	6.7	163	19.0	71.0	2.7	38.0	4.9
6	3.1	7.0	300	37.0	52.0	12.6	24.0	13.5
7	36.3	7.1	178	11.5	169.0	7.5	54.0	16.8
8	2.3	7.2	246	34.0	27.0	1.2	16.9	2.0
9	3.0	7.3	435	54.0	17.4	6.5	15.0	11.9
10	4.8	7.3	404	43.0	113.0	3.5	32.0	5.8
11	25.5	7.5	178	8.0	64.0	3.6	21.0	4.9
12	3.6	7.6	355	15.0	11.3	2.2	15.5	1.3
13	22.0	7.7	110	13.0	78.0	2.6	22.0	8.5

with 200 ml distilled-deionized water and allowed to age at 25C. After six months the suspensions were centrifuged and the precipitate was examined petrographically. The yellowish-white precipitate appeared well crystallized, and resembled natural wulfenite. X-ray diffractions confirmed the crystallinity of the fresh precipitate showing a pattern identical to that of natural wulfenite. Both x-ray patterns checked perfectly with the A.S.T.M. x-ray diffraction pattern for synthetic PbMoO_4 (J. V. Smith, 1969).

Lead activities in the equilibrium solutions were measured with a lead electrode-double junction reference electrode. Total molybdenum in solution was measured by flameless atomic absorption spectrophotometry. Mo activities were calculated from total Mo and activity coefficient obtained from the extended Debye-Huckel equation. Ionic strengths were estimated from the electrical conductivity (EC) of solution (Griffin and Jurinak, 1973). Formation of Mo ion pairs in aqueous solution was not taken into account due to lack of thermodynamic data.

Solubility of Mo in soils

Saturated pastes of thirteen test soils were prepared and allowed to equilibrate open to the air at 25C. After two weeks of incubation, the soils were transferred to a high pressure cell allowing filtration under high Argon pressure. The clear solutions were analyzed for pH, Mo, and EC.

Subsamples (25g) of the test soils were equilibrated with 50 ml demineralized water on a rotary shaker at 25C. Air was continuously replenished above the suspensions through a connecting airline. Eh

and pH were measured in the soil suspensions at weekly intervals. After 28 days the suspensions were centrifuged at 25C and filtered. Measurements of Mo and EC were made on the clear filtrates. In a separate experiment, soil suspensions (25g/50 ml) were amended with 30 mg wulfenite obtained from Los Lamentos, Mexico, equilibrated for four weeks with aeration, and analyzed for Mo, pH and EC.

All solubility studies were done in quadruplicate, and analytical results were averaged.

Suspensions (1:2 soil-water) of Soils 2, 9, 10, and 13 were altered in pH by adding nitric acid or sodium hydroxide to obtain soils ranging in pH from 6.5 to 9. After shaking for 10 days at 25C the clear filtrates were analyzed for EC, Mo, and pH. In addition, suspensions of Soil 10 were prepared to contain 4000 mg of added Pb as $\text{Pb}(\text{NO}_3)_2$ per gram of soil prior to equilibration at various pH values. Additional Pb in the form of wulfenite was given to suspensions of Soil 10 that were brought to pH 8.6 - 8.8. Molybdenum and EC analyses of the clear filtrates were carried out after 10 days of shaking at 25C.

Adsorption studies

Adsorption isotherms were determined in 1:2 suspensions of Soils 7, 8, 9, and 12 by equilibrating the soils with solutions containing up to 5 ppm Mo as Na_2MoO_4 . The impact of pH on the adsorption isotherms was studied on Soils 9 and 10 by repeating the experiment at 0.5 pH unit below the natural pH of these soils. Soil 9 was also equilibrated with solutions containing 0.5 and 1 ppm Mo as Na_2MoO_4 at pH values between 6.5 and 9. After 10 days of aerated shaking at 25C the clear solutions were analyzed for Mo and EC.

The formation of wulfenite in soils contaminated with lead was studied by determining the adsorption isotherm of Soils 9 and 10 after addition of 200 ppm Pb as $\text{Pb}(\text{NO}_3)_2$ to the soils.

3.5. Greenhouse Experiments

Two greenhouse experiments were conducted: one with four soils (# 3; 4; 9; and 13), and one with all 12 soils. In the first experiment, six kilograms of each soil was fertilized with monocalcium phosphate (MCP) to provide at least 40 ppm NaHCO_3 -extractable phosphorus (Olsen et al., 1954) after mixing in a twin shell blender. Three plastic lined pots were filled with 2 kg of soil and brought to field capacity* with a solution supplying 50 ppm K as K_2SO_4 and 50 ppm N as $\text{Ca}(\text{NO}_3)_2$. Three series of three pots were thus prepared for each soil and assigned randomly to positions within the greenhouse.

The soils were allowed to dry for a week prior to being rewetted to field capacity. After a second wetting and drying cycle three pots of each soil were planted with inoculated alfalfa seeds (WL 215), three pots with inoculated Alsike clover and three pots with Merion bluegrass. The soils were brought to field capacity and covered with filterpaper. After emergence, the filterpaper was removed and the alfalfa and clover were thinned to six and twelve plants per pot, respectively. The soils were watered daily to field capacity during the entire growing period.

Harvesting took place two months after seeding by clipping the tops one inch above the soil surface. Plants were washed in 0.1 N NaOH, rinsed twice in distilled water, and then dried for 48 hours at 70°C.

*Field capacity is defined here as the percentage of moisture retained against gravity by a 20 cm column of soil.

Yields were determined by weighing the oven-dried plants. Soils were air-dried and freed of roots, pulverized to pass a 16-mesh stainless steel sieve, and stored in plastic lined cans.

In the second experiment, carried out concurrently, all soils were fertilized with monocalcium phosphate as indicated above. Three pots of each soil received 0, 0.5, 1.0, or 2.0 ppm Mo in the form of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ along with the phosphate fertilizer. Sodium molybdate solutions were sprinkled onto the soil prior to mixing in the twin-shell blender. All pots were treated similarly to the first experiment and seeded with inoculated alfalfa (WL 215).

3.6. Field Sampling

Four sampling sites (#6, 8, 9, and 12) in the South Platte River Valley around Brighton (Fig. 1. 1) were selected for monitoring the impact of High-Mo water on the Mo concentration of alfalfa. Yearly sampling of topsoil (0-25cm), plants, and irrigation water, started in 1972 by Jackson (1973) and was continued through 1974 and 1975. Table 3.3 lists the sampling sites with corresponding soil numbers assigned by Jackson (1973), soil texture, and source of irrigation water. The description and physiography of these alluvial soils are given by Jackson (1973).

Table 3.3. Soils sampled over a period of 4 years (1972-1975)

Site #	Jackson's Soil #	Texture (0-25cm)			Irrigation Source
		Clay	Silt	Sand	
6	73-1	38	18	44	Clear Creek
8	72-15	20	6	65	Burlington
9	72-17	44	30	26	Brantner
12	72-21	56	31	13	Stanley

Waters were dip-sampled from the respective irrigation canals. The top 25 cm of soil was sampled by shovel in a 10 m^2 area. Alfalfa was sampled from the same area by clipping it one inch above the ground. The validity of critical soil test levels for Mo in alfalfa obtained in the greenhouse experiments were evaluated by sampling twenty additional alfalfa pastures during the summer of 1975. The sites are all located in the area between Brighton, Greeley and Fort Collins, Colorado, and all were irrigated. Samples were taken and treated as described above.

To study the extent of Mo contamination in various test soils, profile distributions of total Mo and various soluble Mo fractions were determined for Soils 2, 3, 6, 8, 9, 11, 12 and 13 by sampling at various depths with a twin-blade auger. Profile samples were collected in 1974, pretreated as the topsoils and analysed for total Mo, and Mo extracted with water or $1\text{M } (\text{NH}_4)_2\text{CO}_3$.

3.7. Movement of Mo in Soil Columns

The objective of this study was to determine the rate of molybdenum depletion of a soil irrigated with Mo free water, and the subsequent accumulation of Mo upon irrigation with high-Mo water. No attempt was made to fit the data to a mathematical transport equation simulating molybdenum transport and retention.

Soil 8 was ground to pass a 16-mesh sieve and uniformly packed in a plexiglass tube with an inside diameter of 5 cm forming a soil column of 30 cm height. The bulk density was determined as 1.76 g/cc . The particle density measured by a standard technique (Blake, 1965) was 2.62 g/cc . The columns were inundated with distilled-deionized water allowing a progress of the infiltration front by 1.0 to 2.5

cm/min. Solutions were collected at the bottom of the columns by means of a fraction collector with a $10 \text{ ml} \pm 0.2 \text{ ml}$ delivery device. The saturated flow rate was regulated with a brass needle valve.

Solutions entering the columns were made up using Na_2MoO_4 and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$. The collected solutions were analyzed for pH, molybdenum and chloride described previously.

The experimental set up described above does not represent natural conditions, but information thus obtained can be helpful in gaining an understanding of processes taking place in irrigated fields.

3.8. Computer Simulation of Mo Accumulation and Uptake

A computer simulation language called SIMCOMP (Gustafson and Innis, 1973) was used to simulate molybdenum flow in an irrigated alfalfa pasture (Soil 8). A CDC-6400 computer was used to do the mathematical calculations of the daily flows between state variables (Forrester, 1968) (plant Mo, Soil Mo in five distinguished soil layers, and Mo in irrigation water). The actual flows were functions written in Fortran.

Even though this kind of modeling calls for many simplifying assumptions, it results in a simple picture of the long term effects of irrigation with Mo contaminated water on the Mo status of the soil at various depths and the accumulation of Mo in forages produced by this soil.

4. RESULTS AND DISCUSSION

4.1. The Chemistry of Mo in Colorado Soils

The solubility of wulfenite

Results of the determination of the solubility product of wulfenite (PbMoO_4) are given in Table 4.1.

Table 4.1 Measurement of the solubility products of synthetic and natural wulfenite.

Sample	Equilibration Time	pH	pPb^{2+}	$\text{pMoO}_4^{=}$	$\text{pK}_{\text{sp}}^{\circ}$
Synthetic	7 month	7.98	5.28	7.52	12.80
Natural	1 month	6.63	6.05	6.90	12.95
Natural	4 month	6.43	5.27	7.71	12.98

Equilibrium appears to be reached within one month as no change in the $\text{pK}_{\text{sp}}^{\circ}$ of natural wulfenite was found between one and four months of equilibration. The synthetic wulfenite, precipitated from solutions of $\text{Pb}(\text{NO}_3)_2$ and Na_2MoO_4 was slightly more soluble than naturally formed wulfenite. The slight difference in solubility, if significant, may be due to the presence of amorphous coatings on the crystalline precipitate, that persisted even though the sample was washed several times.

The values obtained for the two wulfenite samples are in close agreement with the $\text{pK}_{\text{sp}}^{\circ}$ of 13.0 reported by Muldrow and Hepler (1958), based on calorimetric studies. The solubility of wulfenite determined by activity measurements of lead and molybdenum in aqueous solutions

by other investigators is invariably higher than 10^{-13} . These differences may be due to a) insufficient aging of freshly precipitated lead molybdate, b) inadequate accounting for ion-pair formation in calculating Pb^{2+} activity from concentration measurements, and c) low sensitivity of analytical techniques (Skobets et al., 1970; Busev, 1964; Chepelevetskii et al., 1963; Fomin et al., 1953). The procedure used in this study avoided all of these problems by measuring the lead activity directly and employing the flameless atomic adsorption spectrophotometer to analyze the extremely low Mo concentrations. The method seems equally promising for determining the solubility product of other sparingly soluble Pb minerals.

Development of stability and solubility diagrams

The ultimate source of Mo enrichment in Colorado soils is the primary mineral molybdenite, MoS_2 . The various transformations that may take place upon weathering and oxidation of molybdenite can be studied by developing stability diagrams. In constructing stability and solubility diagrams for molybdenum minerals use was made of the most reliable thermodynamic constants (indicated with an asterik in Table 2.1).

The system H_2MoO_4 , H_2SO_4 , and H_2O which represents the weathering environment of MoS_2 , contains four known inorganic monomeric molybdenum species. Predominance fields for these ionic species were calculated according to the methods described by Garrels and Christ (1965) from Reaction 1-5 of Table 2.1, and plotted in a pe-pH diagram (Fig 4.1). The pe is the negative log of the electron activity (e^-) similar to the use of pH. A pe + pH of zero represents a highly reduced environment corresponding to 1 atm of H_2 . The pe + pH in equilibrium with air containing 20% of O_2 is approximately 20.61.

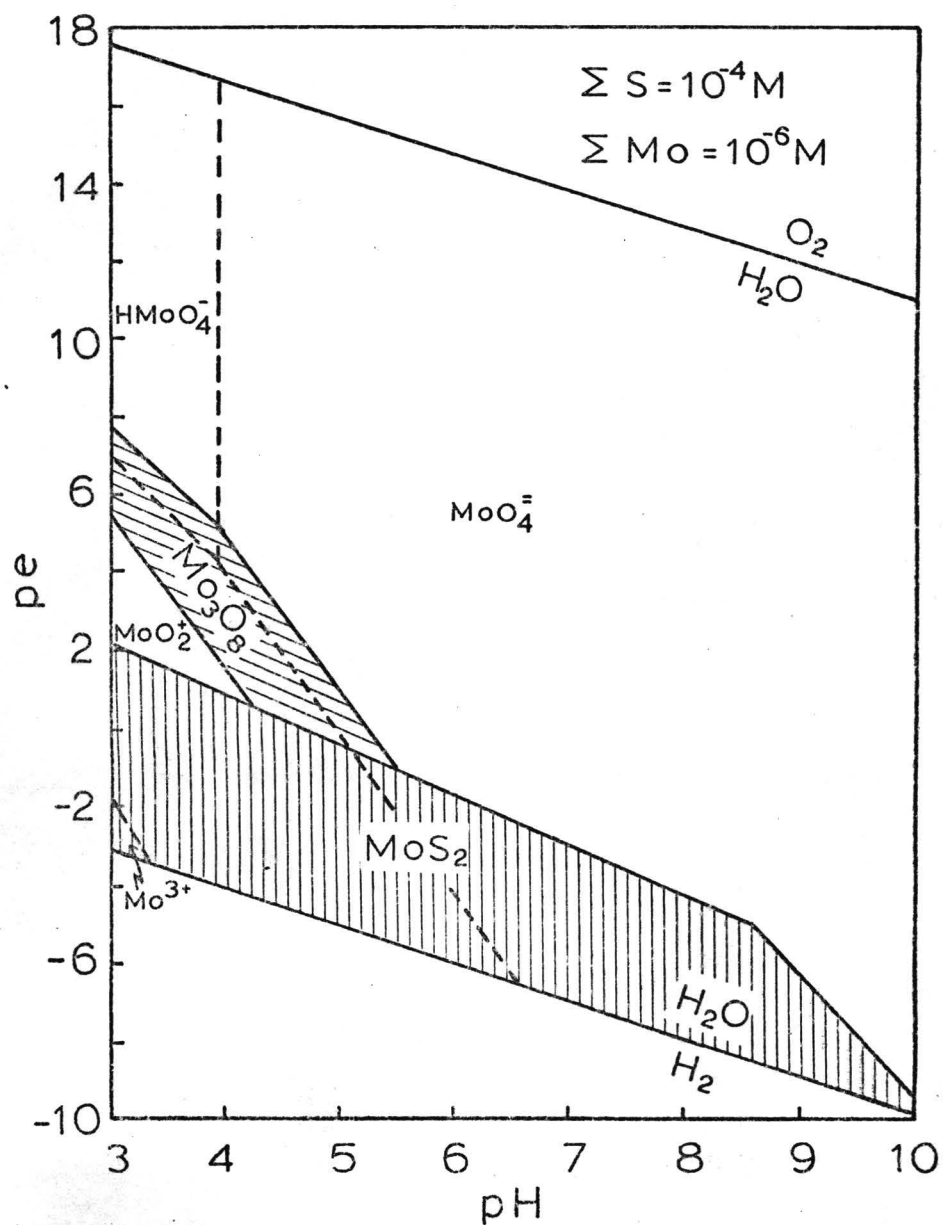


Fig. 4.1. Stability fields of MoS_2 and Mo_3O_8 (hatched areas) superimposed on the stability fields of ionic Mo-species. $T = 25^\circ C$ and $P = 1 \text{ atm}$.

The largest predominance field in this system is occupied by the molybdate ion. At pH values less than 3.88 and at $pe + pH$ values over 8, bimolybdate ($HMoO_4^-$) is the most important species. Cationic MoO_2^{+} becomes predominant below pH 7 if reduced conditions prevail, Mo^{3+} becomes significant only under extremely reduced and very acid conditions which are rarely encountered in soils. Polymerization of molybdate ions under acid conditions is restricted to solutions $>10^{-4}$ M (Carpeni, 1947; Aveston *et al.*, 1964). The products of polymerization are ill-defined and stability constants of the products are unknown. Molybdenum concentrations in acid soil solutions never exceed 10^{-4} M Mo, and no efforts were made to include polymerization products in Fig. 4.1.

The stability fields of minerals that can exist in the system H_2MoO_4 , H_2SO_4 , and H_2O , (molybdenite and ilsemaninite) were calculated using equations 6 through 9 of Table 2.1, and are depicted in Figure 4.1 as well. In plotting the stability of these minerals the total concentration of Mo and S were fixed at 10^{-6} and 10^{-4} M, respectively, levels which are likely to occur in weathering environments and soils. An increase of the total Mo concentration enlarges the stability fields of both minerals, whereas increasing total S results in an increased stability of molybdenite.

Under the specified conditions molybdenite is stable only in extremely reduced environments ($pe + pH < 5.2$) similar to the stability of pyrite (Vlek *et al.*, 1974). At pH values higher than 6, MoS_2 oxidizes to form simple molybdate and sulfate ions. At pH values below 6 ilsemaninite may form as an intermediate alteration product. Further oxidation causes Mo_3O_8 to redissolve, yielding the molybdate ion at pH

values higher than 3.88 and bimolybdate at pH values below 3.88. Under the specified condition molybdenite and ilsemanite can coexist at $pe + pH$ of 5.2.

Redox conditions permitting the existence of molybdenite or ilsemanite are found only in highly reduced soils, e.g. mangrove subsoils or acid bog soils. Redox potentials of eleven irrigated agricultural soils from Colorado after 6 weeks of aerated agitation of 1:2 soil-water suspensions are given in Table 4.2. Differences between measurements after 2, 4 and 6 weeks of incubation were insignificant and indicate that equilibrium was established within two weeks of equilibration. The $pe + pH$ values for these soils varied over a limited range from 12.9 to 14.1 conditions which are too oxidized for ilsemanite or molybdenite to persist. The predominant ionic species in these naturally well aerated soils is the molybdate ion ($MoO_4^{=}$).

Table 4.2. Equilibrium redox conditions ($pe + pH$) in 1:2 suspensions of agricultural soils of Colorado.

Soil #	pH	pe	$pe + pH$
2	6.10	6.84	12.94
3	5.78	7.11	12.89
5	6.95	6.55	13.50
6	6.88	6.08	12.96
7	7.99	6.08	14.07
8	7.90	5.22	13.12
9	7.72	5.38	13.10
10	7.80	6.15	13.95
11	7.95	5.49	13.44
12	7.99	5.49	13.48
13	8.17	5.36	13.53

Several molybdate minerals could form under the oxidized conditions prevailing in a majority of the soils included in this study. Minerals of most probable importance are ferrimolybdate, powellite, and wulfenite.

Solubility diagrams relating the $\text{MoO}_4^{=}$ activity to soil pH were developed for these minerals using reactions 13-15 of Table 2.1 and appropriate reactions for common soil minerals (Table 4.3).

Fig. 4.2 shows the predicted $\text{MoO}_4^{=}$ activity in the soil solutions if ferrimolybdate or powellite are present in soils. The solubility of $\text{Fe}_2(\text{MoO}_4)_3 \cdot n\text{H}_2\text{O}$ in equilibrium with Soil- $\text{Fe}(\text{OH})_3$ ($\text{pK}_{\text{sp}}^{\circ}$ of 39.5, Norvell, 1971), maintains a $\text{MoO}_4^{=}$ activity of $10^{-8.25}$ at pH 3.0 and this activity increases 100-fold for each unit increase in pH. At pH between 4 and 5 ferrimolybdate becomes more soluble than CaMoO_4 . The actual Mo level maintained in the soil by powellite depends on the mechanism controlling the Ca^{++} activity in the soil solution. Ca^{++} activities in in soils not containing calcite are generally controlled by the exchange complex at levels between $10^{-3.5}$ and $10^{-2.5}$ M. Increasing Ca activity reduces the equilibrium activity of molybdate as shown by the dashed line for $\text{pCa} = 2.5$ (Fig. 4.2). If calcite is present and the CO_2 pressure is held constant, the activity of $\text{MoO}_4^{=}$ will increase 100-fold per unit increase in pH.

If wulfenite is present in soils the $\text{MoO}_4^{=}$ activity is directly affected by the solubility of Pb. A solubility diagram (Fig. 4.3) for lead compounds that may govern the Pb^{++} activity in soils was developed using appropriate reactions in Table 4.3.

In soils of pH 5 and lower that generally maintain a $\text{SO}_4^{=}$ activity between 10^{-4} and 10^{-3} M, lead sulfate (PbSO_4) apparently is the most stable phase. In soils of intermediate pH (5-8) lead phosphates may form. In acid soils, variscite ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$) in equilibrium with gibbsite ($\text{Al}(\text{OH})_3$) establishes a limit on phosphate solubility (Lindsay and Moreno, 1960), whereas the phosphate activity in slightly

Table 4.3. Solubility Products of Soil Constituents Considered in this Study

Reaction	Log K ^o	Source
$\text{Al}(\text{OH})_3 \rightleftharpoons \text{Al}^{3+} + 3\text{OH}^-$	33.96	Singh, 1974
$\text{AlPO}_4 \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{Al}^{3+} + \text{PO}_4^{3-} + 2\text{H}_2\text{O}$	22.52	Taylor and Gurney, 1964
$\text{CaCO}_3 + 2\text{H}^+ \rightleftharpoons \text{Ca}^{2+} + \text{CO}_2(\text{g}) + \text{H}_2\text{O}$	9.79	Sillen and Martell, 1964
$\text{Ca}_3(\text{PO}_4)_2 \rightleftharpoons 3\text{Ca}^{2+} + 2\text{PO}_4^{3-}$	-28.92	Gregory et al., 1974
$\text{Ca}_5\text{OH}(\text{PO}_4)_3 \rightleftharpoons 5\text{Ca}^{2+} + \text{OH}^- + 3\text{PO}_4^{3-}$	-53.20	Avnimelech et al., 1974
$\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O} \rightleftharpoons 8\text{Ca}^{2+} + 2\text{H}^+ + 6\text{PO}_4^{3-} + 5\text{H}_2\text{O}$	-93.96	Wagman et al., 1968
$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O} \rightleftharpoons 2\text{Ca}^{2+} + \text{PO}_4^{3-} + \text{H}^+ + 2\text{H}_2\text{O}$	-18.95	Patel et al., 1974
$\text{PbCO}_3 + 2\text{H}^+ \rightleftharpoons \text{Pb}^{2+} + \text{CO}_2 + \text{H}_2\text{O}$	5.00	Sillen and Martell, 1964
$\text{PbSO}_4 \rightleftharpoons \text{Pb}^{2+} + \text{SO}_4^{2-}$	-7.66	Sillen and Martell, 1964
$\text{Pb}(\text{OH})_2 \rightleftharpoons \text{Pb}^{2+} + 2\text{OH}^-$	-20.44	Nriagu, 1974
$\text{Pb}_3(\text{PO}_4)_2 \rightleftharpoons 3\text{Pb}^{2+} + 2\text{PO}_4^{3-}$	-44.40	Nriagu, 1974
$\text{Pb}_5(\text{PO}_4)_3\text{OH} \rightleftharpoons 5\text{Pb}^{2+} + 3\text{PO}_4^{3-} + \text{OH}^-$	-76.80	Nriagu, 1974
$\text{Pb}_4\text{O}(\text{PO}_4)_2 + 2\text{H}^+ \rightleftharpoons 4\text{Pb}^{2+} + 2\text{PO}_4^{3-} + \text{H}_2\text{O}$	-36.86	Nriagu, 1974

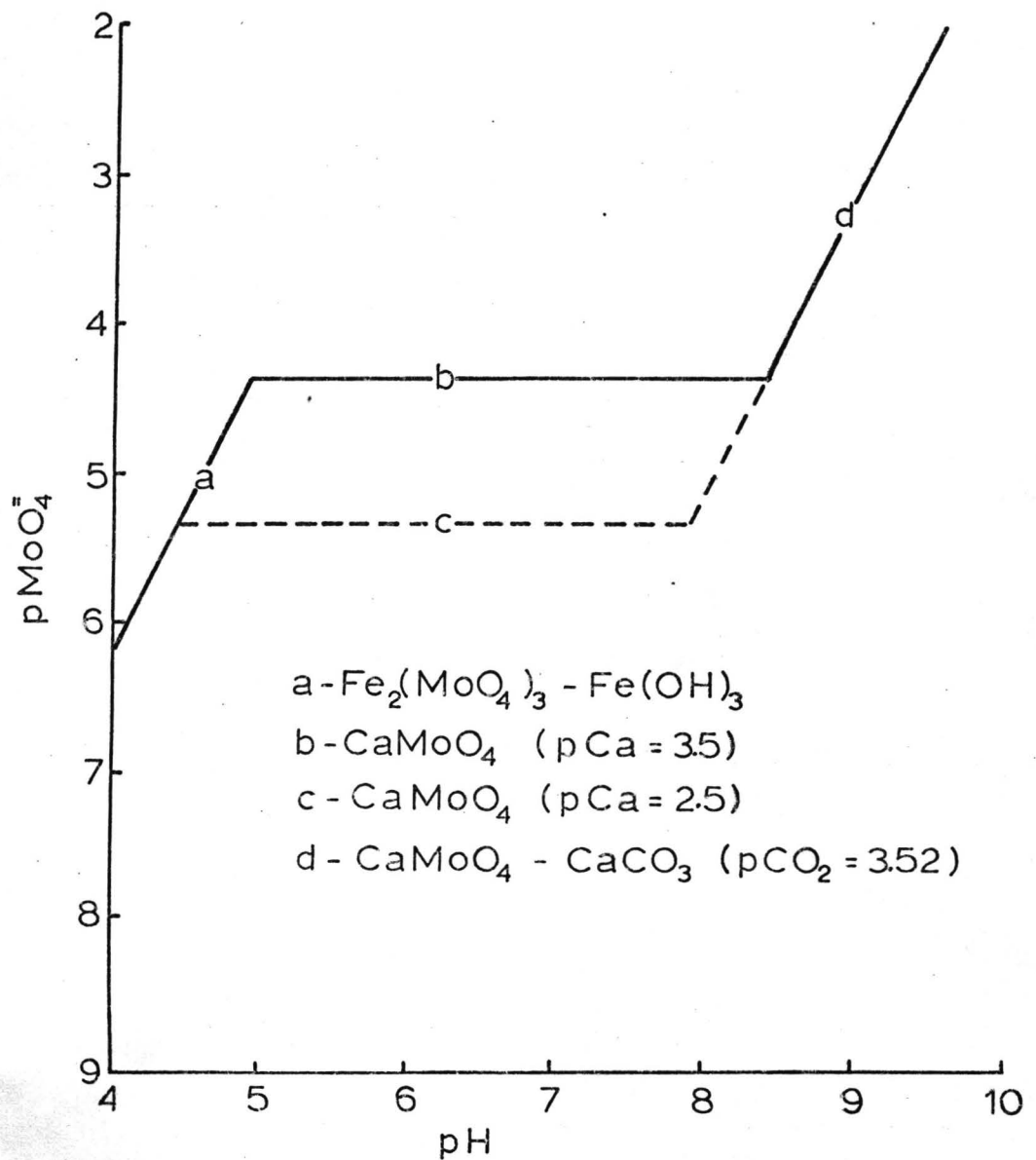


Fig. 4.2. Solubility of ferrimolybdate and powellite in equilibrium with soil constituents at 25°C and 1 atm.

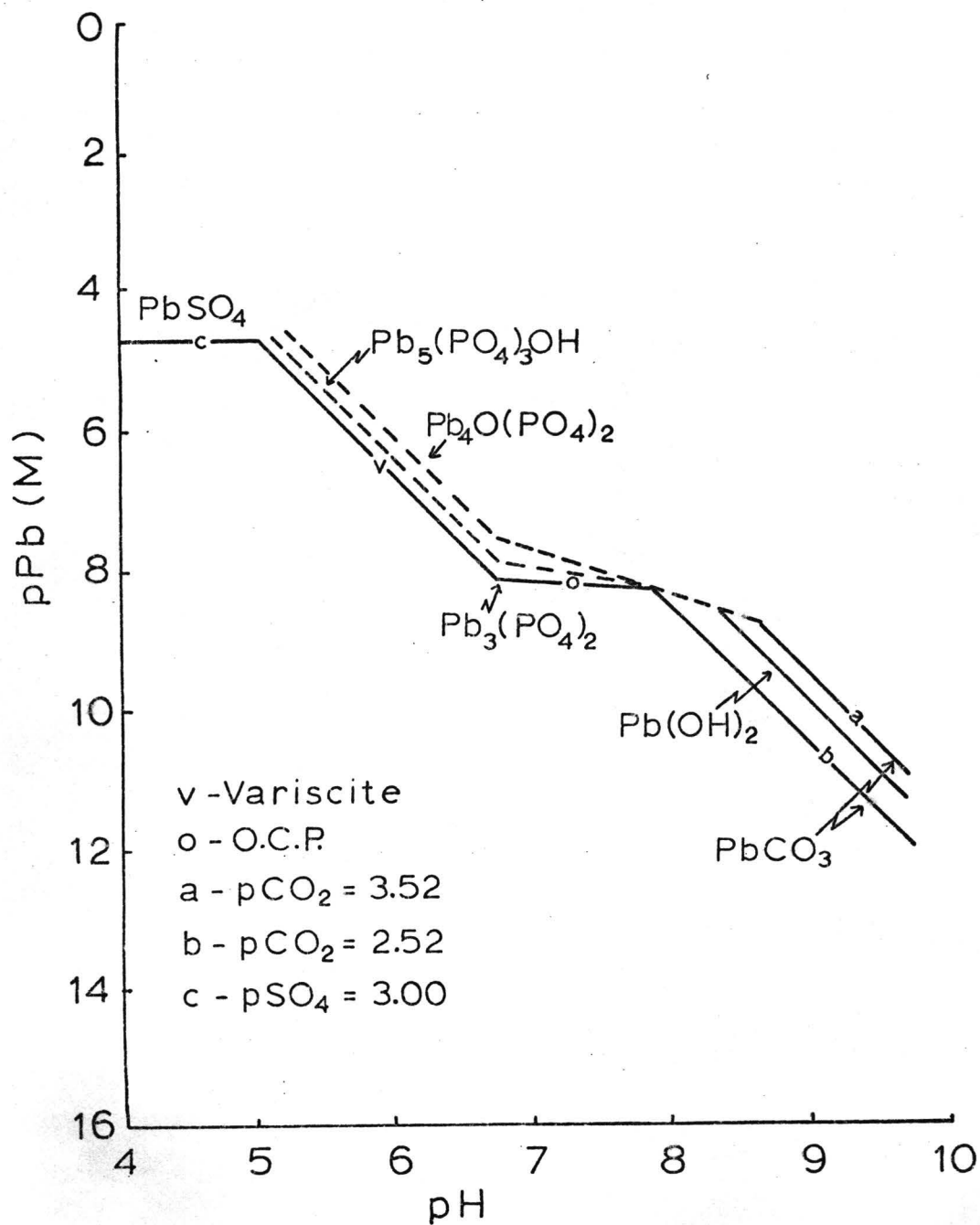


Fig. 4.3. The solubility relationships of Pb in soils at 25°C and 1 atm.

alkaline agricultural soils can be controlled by tricalcium phosphate (TCP), octocalcium phosphate (OCP), or dicalcium phosphate dihydrate (DCPD) (Webber and Mattingly, 1970, I and II). There is little doubt that cerussite (PbCO_3) can control the Pb^{++} solubility in calcareous soils. The existence of the above mentioned lead-compounds in natural, uncontaminated soils has not been fully established, but their formation in soils to which Pb has been added seems quite certain.

Lead activities measured in three soils with pH between 4.8 and 6.2 conform to the solubilities predicted for lead sulfate and lead phosphate in soils. The same was true for these soils equilibrated with 10^{-3} M lead nitrate. For soils of pH higher than 6.5 the equilibrium Pb^{++} activities were below the detection limit of the lead-electrode (Lindsay, 1973).

Fig. 4.4 was constructed with the assumption that PbMoO_4 controls $\text{MoO}_4^{=}$ solubility and that PbSO_4 , $\text{Pb}_3(\text{PO}_4)_2$, or PbCO_3 controls the solubility of Pb^{2+} in soils. It was further assumed that CO_2 of the soil air is $10^{-3.52}$ atm, that $\text{SO}_4^{=}$ and Ca^{++} activities are 10^{-3} and $10^{-2.5}$ M respectively, and that phosphate activity is controlled by variscite and gibbsite below pH 7 and by tricalcium phosphate, octocalcium phosphate, or dicalcium phosphate dihydrate above pH 7.

The $\text{MoO}_4^{=}$ activity in equilibrium with PbMoO_4 and PbCO_3 is lower by a factor of 4.5 compared to that maintained by CaMoO_4 and CaCO_3 . Thus, in calcareous soils containing cerussite, wulfenite is slightly more stable than powellite. In the pH range of 7-8 and in the absence of PbCO_3 , the molybdate activity in equilibrium with PbMoO_4 , and octocalcium phosphate (OCP) is approximately 10^{-5} M. Increasing phosphate solubility increases the $\text{MoO}_4^{=}$ activity (DCPD line), whereas lowering

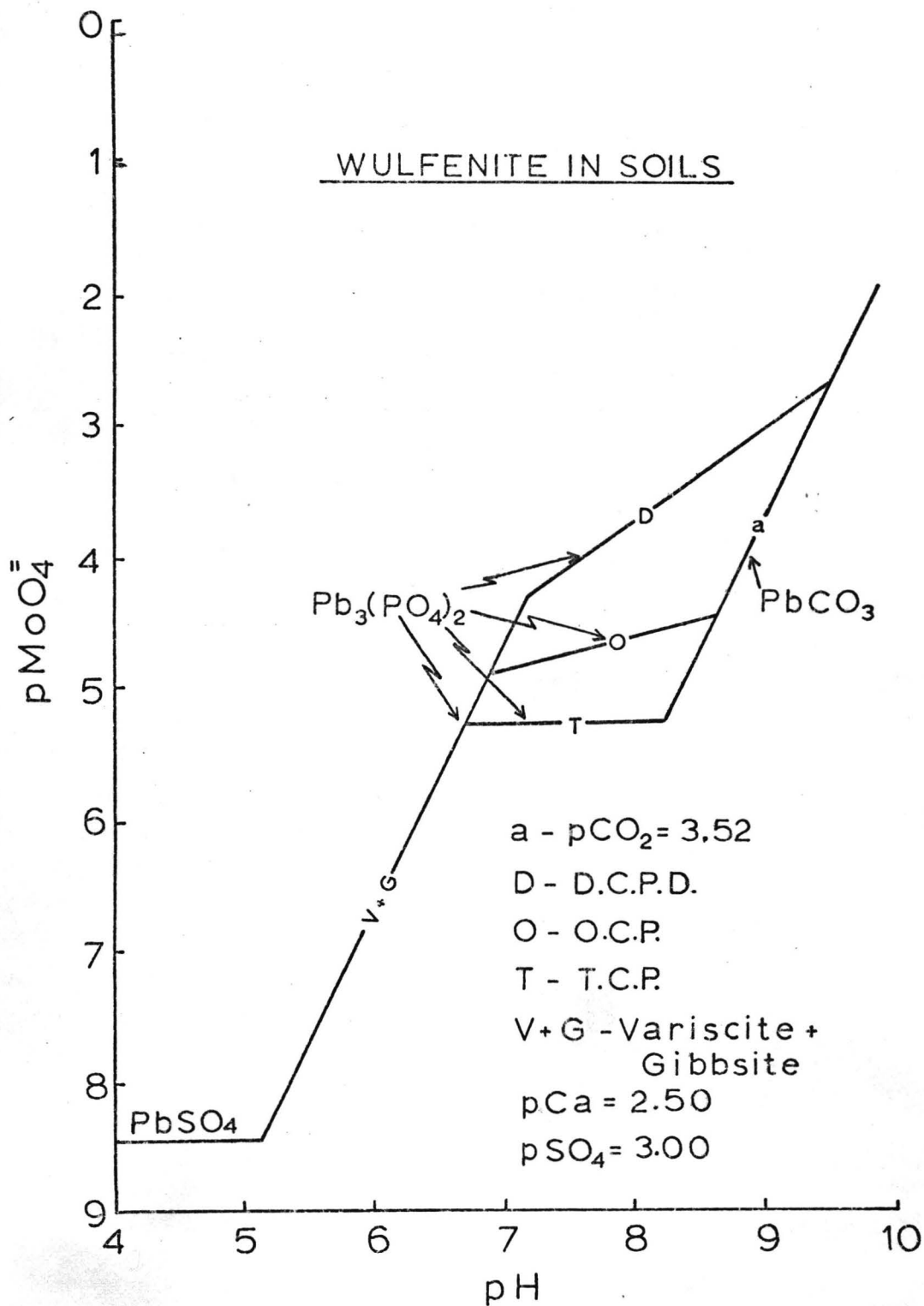


Fig. 4.4. The solubility relationships in soils containing wulfenite (PbMoO_4) at 25C and 1 atm.

phosphate activity depresses $\text{MoO}_4^{=}$ in solution. In acid soils containing variscite in equilibrium with gibbsite, the molybdate activity becomes highly pH dependent, decreasing 100-fold for each unit decrease in pH. Below pH 5, PbMoO_4 in equilibrium with PbSO_4 maintains a molybdate level of $10^{-8.5}$ M when $\text{pSO}_4 = 3$. A lower $\text{SO}_4^{=}$ activity decreases the activity of $\text{MoO}_4^{=}$.

Solubility of molybdenum in soils

The molybdate activities and pH of solutions, extracted from saturated pastes and 1:2 soil-water suspensions after 28 days of equilibration, are given in Table 4.4. Equilibrium in these soils appeared to be reached within 3 days, as no significant change in Mo activity was apparent thereafter. The results of Table 4.4 are represented graphically in Figure 4.5.

Table 4.4. Equilibrium pH and molybdate activities of saturation extracts, and 1:2 soil-water extracts with and without wulfenite for selected Colorado soils.

Soil	Saturation			1:2 Suspension		1:2 Suspensions + Wulfenite	
	Sat % H ₂ O	pH Sat-extr	$\text{pMoO}_4^{=}$	pH	$\text{pMoO}_4^{=}$	pH	$\text{pMoO}_4^{=}$
1	29	8.05	6.68	5.97	7.44	6.29	5.97
2	32	7.49	7.02	6.17	7.57	6.16	7.39
3	66	7.63	6.64	5.70	7.90	5.74	7.09
4	53	7.89	6.88	—	—	—	—
5	35	8.48	6.29	6.91	6.86	6.91	5.33
6	41	8.55	6.12	6.88	6.90	7.02	5.09
7	66	8.62	5.41	8.02	5.89	7.95	4.80
8	56	8.56	6.03	7.69	6.54	7.68	4.76
9	41	8.57	5.82	7.72	6.07	7.85	4.61
10	43	8.22	6.32	7.61	6.35	7.89	4.70
11	47	8.74	5.49	7.99	5.69	8.11	4.53
12	47	8.37	5.95	7.97	6.06	8.10	4.58
13	70	8.33	5.06	8.12	5.32	8.32	4.64

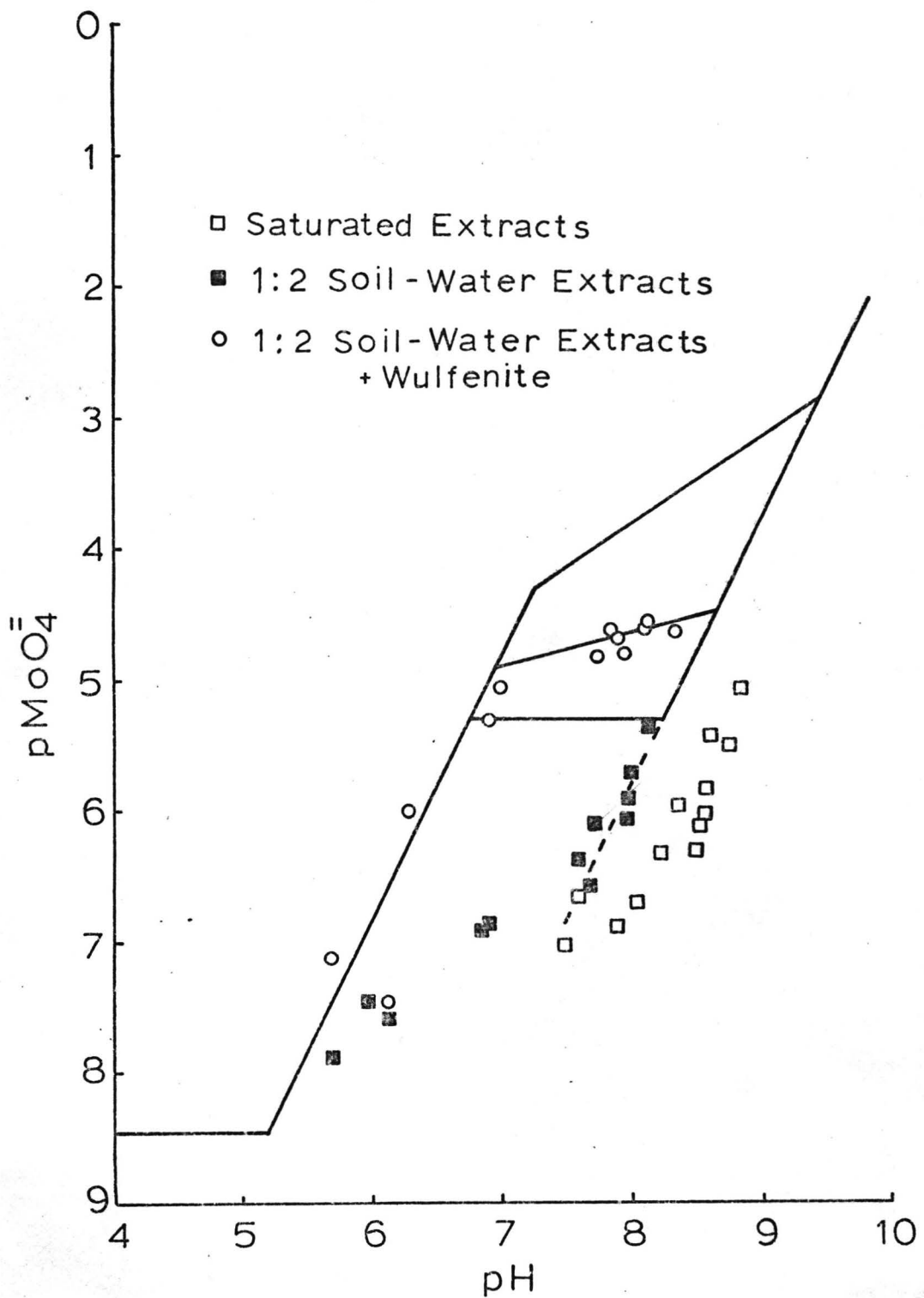
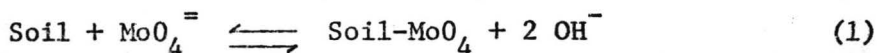


Fig. 4.5. Solubility of Mo in saturated extracts, and 1:2 soil: water suspensions with and without wulfenite for selected Colorado soils, compared to the predicted solubility of wulfenite in soils from Fig. 4.4. (solid lines).

Solutions extracted from saturated soil pastes appear under-saturated with respect to wulfenite. However, the significance of OH^- and $\text{MoO}_4^{=}$ activities measured in saturated soil extracts is doubtful. Anion exclusion causes the pH measured in extracts of saturated pastes to be higher than the pH measured directly in the saturated suspension (c.f. Table 3.2). A similar anion exclusion effect is likely to affect molybdate ions in solution. Anion exclusion makes saturated extracts unsuitable for equilibrium studies.

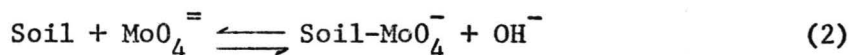
The effect of anion exclusion on the OH^- and $\text{MoO}_4^{=}$ activities of 1:2 soil-water extracts appears negligible. Soil water suspension (1:2) with a pH between 7.0 and 8.0 suggest the presence of wulfenite in equilibrium with lead carbonate, despite the predicted thermodynamic instability of lead carbonate in this pH range. Addition of natural wulfenite to these alkaline soils resulted in a 10-100 fold increase in $\text{MoO}_4^{=}$ activity (Table 4.4), which closely approximates the $\text{MoO}_4^{=}$ activities predicted for soils containing wulfenite in equilibrium with lead phosphate and octocalcium phosphate (open circles in Fig. 4.5). According to the chemical phase rule, wulfenite can not maintain two different molybdate activities in the same system, which leads to the conclusion that wulfenite was not present in the soils prior to the addition of PbMoO_4 .

Interpretation of the Mo solubility of the unamended alkaline soil suggests the existence of some mineral fitting the reaction:



This reaction has an apparent solubility product of 10^{-16} , giving a 100-fold decrease in Mo solubility per unit decrease in pH.

The pH dependence of the molybdate solubility of three soils that appeared to fit reaction (1) was studied by changing the pH of the equilibrating suspensions. All three soils (9, 10, and 13) then followed the relationship:



showing a 10-fold decrease in $\text{MoO}_4^{=2}$ activity per unit decrease in pH (Fig. 4.6). A solubility product for reaction 2 can not be evaluated since each soil follows a different isotherm. A similar pH dependence was noted in molybdate adsorption studies on Australian soils by Jones (1957) when his results were replotted on a solubility diagram.

Wulfenite can be precipitated by supplying an adequate lead source to soil. The addition of 4000 ppm Pb as $\text{Pb}(\text{NO}_3)_2$ to Soil 10 depressed the Mo activity due to the formation of wulfenite (Fig. 4.7). Reducing pH in the presence of lead lowered the activity of molybdenum 100-fold per unit change in pH instead of 10-fold found in the absence of lead. The 100-fold slope in the presence of lead is identical to that expected if wulfenite were in equilibrium with PbCO_3 or $\text{Pb}(\text{OH})_2$. At pH values above 7.8, a plateau was reached in the solubility of Mo due to exhaustion of the soluble Mo in the soil. Addition of a Mo source in the form of wulfenite brought about a predictable 100-fold increase in the Mo activity per unit increase in pH (Fig. 4.7).

Addition of wulfenite to acid soils also yielded 10-100 fold increase in $\text{MoO}_4^{=2}$ activity, with the exception of Soil 2 (Fig. 4.5). The $\text{MoO}_4^{=2}$ activities in Soil 1, 3, 4, and 5 with added wulfenite seem to verify the predicted wulfenite isotherm with variscite controlling the phosphate activity in these soils. Soil 2 did not show a significant

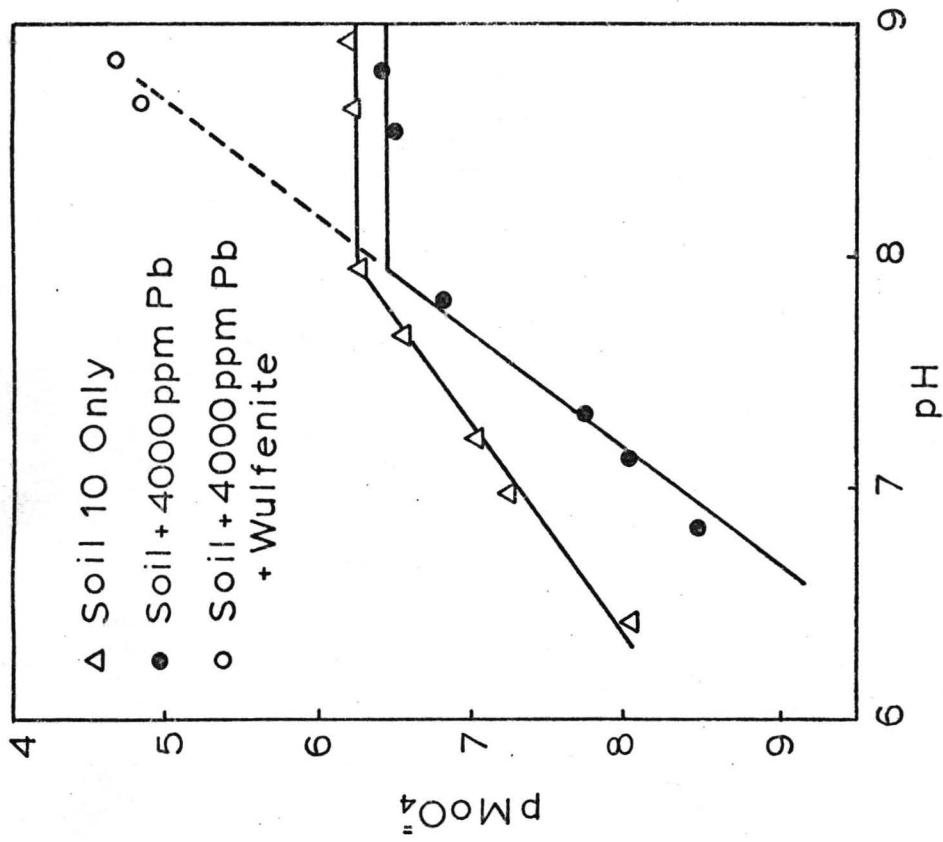


Fig. 4.6. Effect of pH on the Mo activity of four Colorado soils.

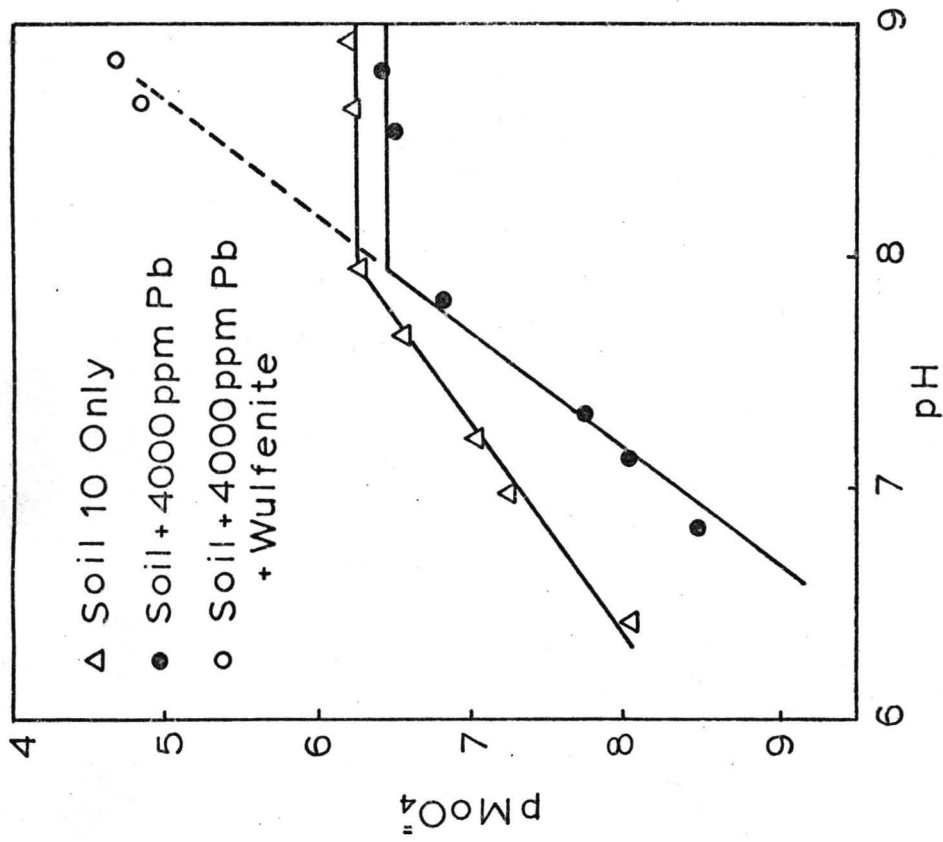


Fig. 4.7. Effect of pH on the Mo activity of Soil 10 with and without added Pb.

increase in $\text{MoO}_4^{=}$ activity upon addition of wulfenite, suggesting that this soil might have contained wulfenite initially. The apparent undersaturation with respect to the $\text{PbMoO}_4 - \text{Pb}_3(\text{PO}_4)_2$ isotherm may be due to the presence of more stable lead phosphates (Fig. 4.3). Even though Soil 2 did not fit the predicted wulfenite isotherm it showed a 100-fold increase in the molybdate solubility per unit increase in pH (Fig. 4.6), as would be expected if wulfenite were present. Only at pH values higher than 7 did the molybdenum activity become less pH dependent.

The possible presence of PbMoO_4 in Soil 2 may be related to the existence of solid mine tailing material in the top 2 inches of this soil. However, identification of wulfenite in this soil by scanning electron microscopy was unsuccessful.

The results of these studies lead to the conclusion that, with the possible exception of soils contaminated with mine-tailing, agricultural soils in Colorado do not contain Mo minerals such as ferrimolybdate, wulfenite, or powellite. Other Mo minerals, yet unknown or not studied, could possibly be present in these soils. The pH dependence of the Mo solubility of individual soils, however, suggest that adsorption reactions of the molybdate ion onto soil constituents is the mechanism controlling the molybdenum solubility in these soils.

Adsorption reactions of Mo in soils

Since the impact of Mo contamination is expected to be most drastic on soils of alkaline nature, adsorption studies were limited to Soils 7, 8, 9, 10 and 12. Data pertaining to these batch experiments including the soil texture and suspension pH are listed in Table 4.5.

Table 4.5. Adsorption Isotherm Studies of Five Colorado Soils

Soil Texture pH	7 Sandy Loam 8.06		8 Sandy Clay Loam 8.39		9 Clay 7.81		10 Loamy Sand 7.67		12 Clay 8.01	
	Mo added (ppm)	Mo Soln (ppm)	Mo ads (ppm)	Mo Soln (ppm)	Mo ads (ppm)	Mo Soln (ppm)	Mo ads (ppm)	Mo Soln (ppm)	Mo ads (ppm)	Mo Soln (ppm)
.0	.365	.71	.043	.11	.105	.47	.048	.23	.115	.44
.2	.385	.87	.145	.11	.165	.55	.099	.33	.184	.50
.4	.430	.99	.252	.11	.215	.65	.130	.47	.255	.56
1.0	.560	1.32	.545	.11	.445	.79	.300	.73	.428	.81
2.0	.845	1.74	1.080	.11	.875	.93	.600	1.13	.846	.98
5.0	2.175	2.31	--	--	2.140	1.40	1.690	1.95	2.300	1.07
10.0	4.450	2.55	--	--	4.350	1.98	3.890	3.20	4.750	1.17

The difference between water-extractable Mo at the natural soil pH, and Mo extracted at pH 9 was considered to be the amount of adsorbed Mo in equilibrium with the natural Mo level of the soil solution (c.f. Fig. 4.6). The amount of Mo adsorbed by soils amended with Na_2MoO_4 was calculated as the difference between Mo added and Mo remaining in solution:

The relationship between Mo concentration in solution and adsorbed Mo for the five selected soils are depicted in Fig. 4.6. The coarse textured Soil 8 has a very low adsorption capacity (.11 ppm) due to both its coarse texture and the high pH of the suspensions. The inertness of this soil for Mo also explains the constancy of the product of soil water content and Mo concentration in solution (Table 4.4). Soil 12 has the next lowest adsorption capacity (1.17 ppm) followed by soil 7 (2.5 ppm). Adsorption maxima for soils 9 and 10 were not reached in the range of Mo concentrations studied, nor could they be calculated from the Langmuir equation due to non-linearity of the Langmuir isotherms (Fig. 4.9).

When the Langmuir equation is written in the linear form:

$$C/N = 1/kN_{\max} + C/N_{\max} \quad (3)$$

where C is the equilibrium concentration and N is the amount of adsorbed Mo per unit of soil, the constant $1/k$ can be related to the bonding energy of the adsorption sites. The non-linearity between C/N and C suggests that low energy adsorption sites are made available for adsorption of $\text{MoO}_4^{=}$ with increased Mo concentration. Since the Langmuir theory assumes the availability of adsorption sites to be constant and energetically equal, the basic requirement for Langmuir adsorption of

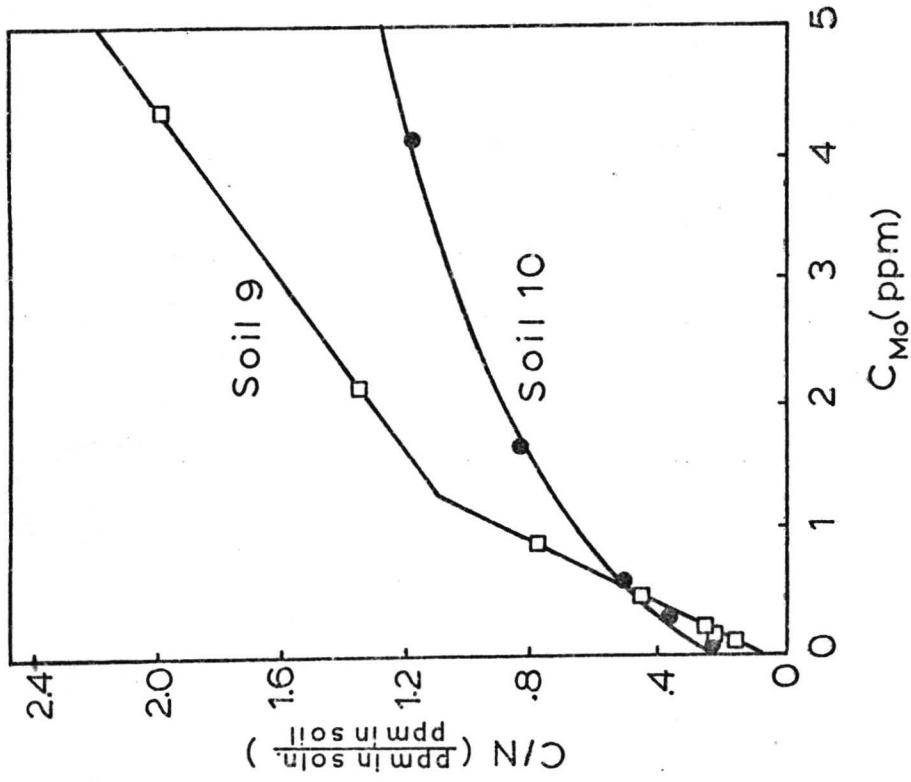


Fig. 4.9. Langmuir plot of adsorption isotherms of Soils 9 and 10.

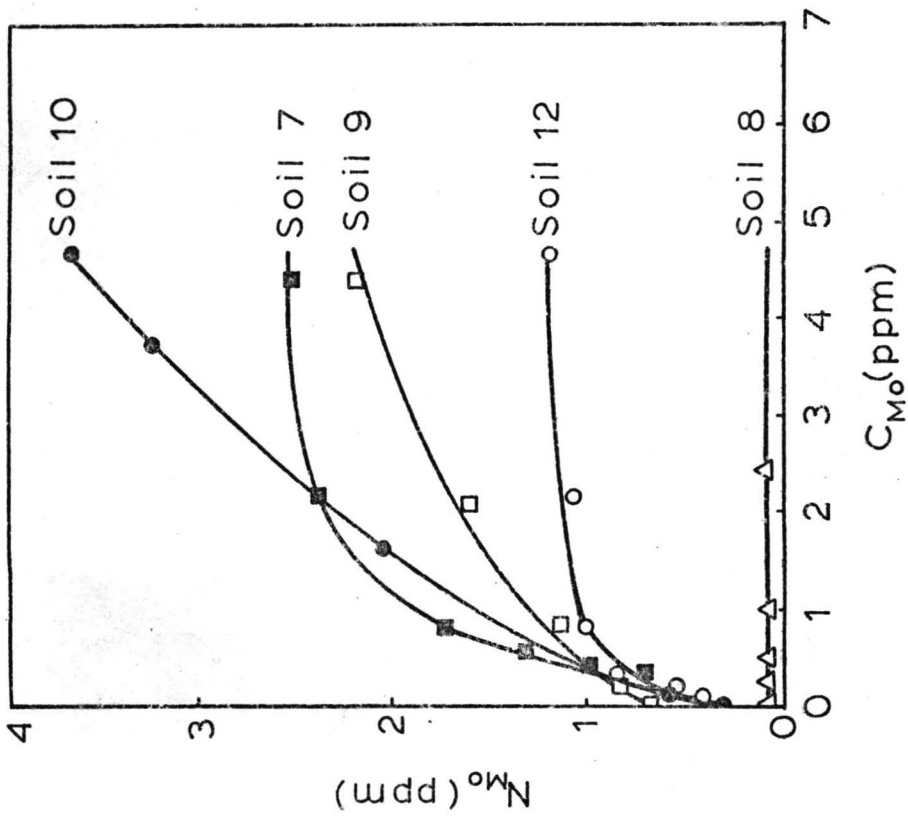


Fig. 4.8. Adsorption isotherms for five Colorado soils.

Mo in soils seem unsatisfied. A similar observation was reported by Barrow (1970).

The adsorption of Mo by the soils studied here was better described by the simple Freundlich isotherm:

$$\log N = A \cdot \log C_{\text{Mo}} + k_1 \quad (4)$$

with N and C defined previously and A and k_1 being soil constants.

Table 4.6 shows the linear regression parameters for soils 7, 9, 10, and 12 for their fit to Equation (4). High correlation coefficients (r) and low Standard Errors (S.E) show the usefulness of the Freundlich equation.

Table 4.6. Regression analyses of Freundlich isotherms of 4 alkaline soils from Central Colorado.

Soil		Regression Parameters			
#	pH	A	$\log k_1$	r	S.E.
7	8.06	.615	.209	.941	.060
8	8.39	---	---	---	---
9	7.81	.370	.032	.994	.022
9	7.30	.362	.238	.996	.021
10	7.67	.600	.164	.998	.025
10	7.34	.637	.435	.992	.055
12	8.01	.325	-.036	.957	.043

The constant "A" varied from 0.325 to 0.615 for the different soils. A change in pH of the soil does not change "A" significantly as is demonstrated for soils 9 and 10. The parameter " k_1 ", however, decreased with increasing pH due to an increased molybdenum adsorption capacity of the soil. Fig. 4.10 depicts this adsorption behavior for soil 9 at pH 7.81 and 7.30.

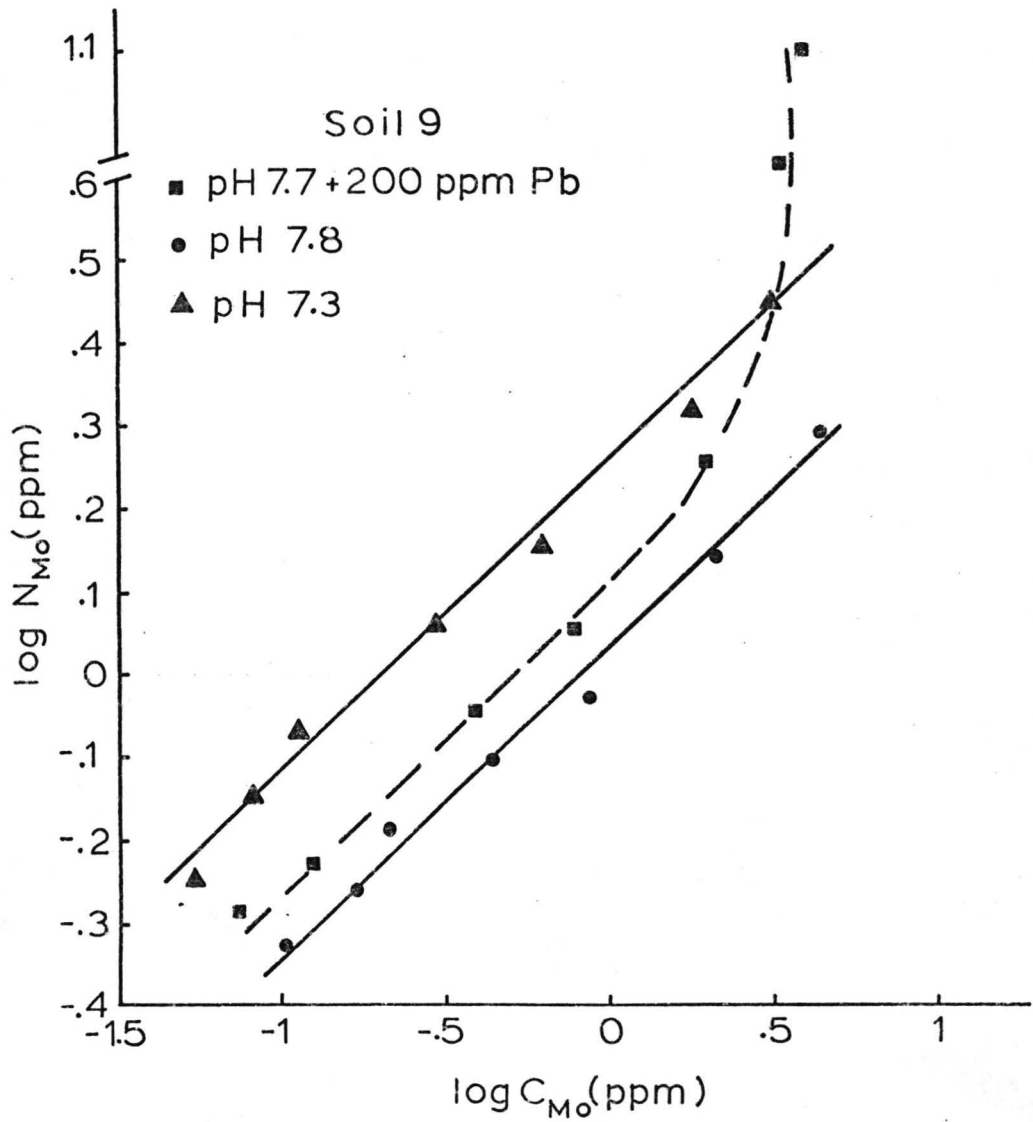


Fig. 4.10. Freundlich plots of adsorption isotherms for Soil 9 at pH 7.8 and 7.3, and, in the presence of 200 ppm Pb at a pH of 7.7.

Reisenauer et al. (1962) observed a similar pH dependence of " k_1 " for Mo adsorption of California soils. They also found that the adsorption of Mo at a fixed Mo concentration is dependent on pH and fits the equation:

$$\log N = B \cdot \text{pH} + k_2 \quad (5)$$

where B is a constant and k_2 depends on the Mo equilibrium concentration.

Equations (4) and (5) can be combined in the following manner to generate a more useful relationship. If pH and $\log C_{\text{Mo}}$ are set at zero, k_1 and k_2 are equal to $\log N_{(0,0)}$. The amount of molybdenum adsorbed at any pH or any Mo concentration is defined by the plane:

$$\log N = A \cdot \log C_{\text{Mo}} + B \cdot \text{pH} + \log N_{(0,0)} \quad (6)$$

or, in terms of Mo solubility:

$$\log C_{\text{Mo}} = - (B/A) \cdot \text{pH} + (\log N - \log N_{(0,0)})/A \quad (7)$$

Equation (7) describes the adsorption behavior observed in various Colorado soils as depicted in Fig. 4.6 and 4.11. The constant $(-B/A)$ is equal to one for all soils at any degree of Mo saturation (Fig. 4.11). Reisenauer et al. (1962) and Jones (1957) also found the ratio of $(-B/A)$ to be close to unity for soils from California and Australia.

Figure 4.11 demonstrates the dependence of the Mo solubility on the degree of Mo saturation of the soil. Included in this graph are Soil 9 with three levels of added Mo (0, 1, and 2 ppm) and some re-plotted data reported by Jones (1957) for an Australian soil. The degree of Mo saturation is determined by the exchange capacity of a soil and the amount of Mo absorbed.

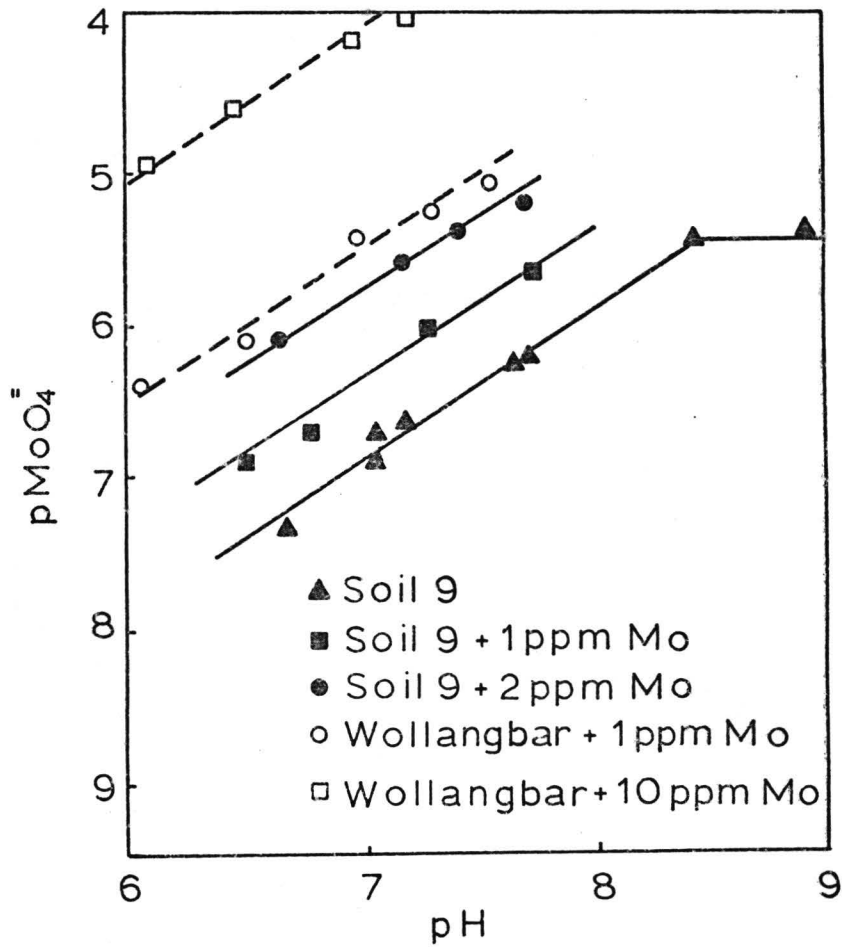


Fig. 4.11. Effect of pH and Mo ammendments on the Mo solubility of Soil 9 and an Australian soil (Wollangbar) studied by Jones (1957).

The adsorption behavior of Mo was also studied after 200 ppm of Pb was added to Soils 9 and 10. The results for Soil 9 are included as a dashed line in Fig. 4.10. In the presence of lead the Freundlich isotherm is followed until wulfenite precipitates at a Mo concentration of $10^{-4.75}$ M. The concentration of Mo at which wulfenite starts to precipitate in these soils closely agrees with the Mo solubility of these soils amended with wulfenite (Table 4.4).

A unified solubility diagram applicable to soils containing wulfenite (Fig. 4.4) does not adequately predict the Mo solubility in Colorado soils, but may be applicable to some contaminated soils elsewhere. The Freundlich equation, modified to include a term accounting for the effect of pH (Eq. 6) seems to be applicable to a wide range of soils where Mo is held through adsorption processes. The constant "B/A" in Eq. 7 seems to be close to unity for soils from Colorado, California, and Australia. The effect of the Mo status of a soil on its Mo solubility has to be determined for each individual soil by developing a Freundlich adsorption isotherm at a specific pH.

4.2. Availability of Mo in Agricultural Soils of Colorado

Greenhouse studies

Mean yields of tops of alfalfa, clover, and bluegrass, harvested after 2 months of growth on unamended soils are given in Table 4.7. Dry matter yields for alfalfa vary largely between soils (0.95 - 5.72 gram/pot). Low yields were probably caused by acidity of the soil (#2 and 4), inadequate fertilization (#4 and 11) or toxicity of heavy metals other than Mo (#2 and 11). Addition of molybdenum to the soils

Table 4.7. Yields and Mo concentrations of three forage crops grown in a greenhouse experiment using Colorado soils.

Soil	Yield (g of oven-dry tops)			Mo ($\mu\text{g/g}$ oven-dry tops)		
	Alfalfa	Clover	Bluegrass	Alfalfa	Clover	Bluegrass
2*	0.95			4.7		
3	2.44	3.20	5.05	1.0	1.1	3.1
4	1.23	2.00	3.60	1.3	1.1	2.9
5	2.93			1.3		
6*	3.39			7.7		
7*	3.79			12.3		
8*	2.89			3.9		
9*	3.47	4.48	4.71	8.7	32.2	3.4
10	5.72			4.2		
11*	1.40			21.1		
12*	2.46			12.7		
13*	2.85	3.83	3.93	38.2	69.2	11.1

*Mo contaminated

in the form of Na_2MoO_4 (0, 0.5, 1.0 and 2.0 ppm) did not significantly affect the yield of alfalfa on any of these soils, indicating that Mo was not a growth limiting factor.

Molybdenum concentrations of the crops grown on unamended soils are included in Table 4.7. Four soils (#7, 11, 12, and 13) produced alfalfa hazardous to livestock if the threshold level of 10 ppm Mo is accepted (Lesperence, 1967). Subclinical effects might be found in livestock grazing on alfalfa produced by Soils 6 and 9. All these soils have a history of irrigation with high-Mo water. The only Mo-contaminated soil producing nontoxic alfalfa is of acid nature (Soil 2), but alfalfa yields from this soil were very low. Soils 3, 4, 5, and 10 were control soils and supported healthy crops.

On alkaline soils, clover seems to accumulate molybdenum most efficiently followed by alfalfa and bluegrass. On acid soils leguminous forages contain less Mo than bluegrass.

The effect of Na_2MoO_4 addition (0, 0.5, 1.0, and 2.0 ppm) on the molybdenum content of alfalfa is depicted in Fig. 4.12 for some of the soils included in this study (a table containing all greenhouse data is presented in Appendix A). The Mo content of alfalfa increased linearly with Mo added to the soils. The more alkaline the soil, the more pronounced the effect on the uptake of Mo by the plant. The Mo status and pH of a soil have a direct effect on the Mo level in the soil solution (equation 6), and thus indirectly affect the uptake of molybdenum by plants.

A soil test that adequately predicts the Mo content of a crop should be sensitive to the Mo solubility in soils and assess the

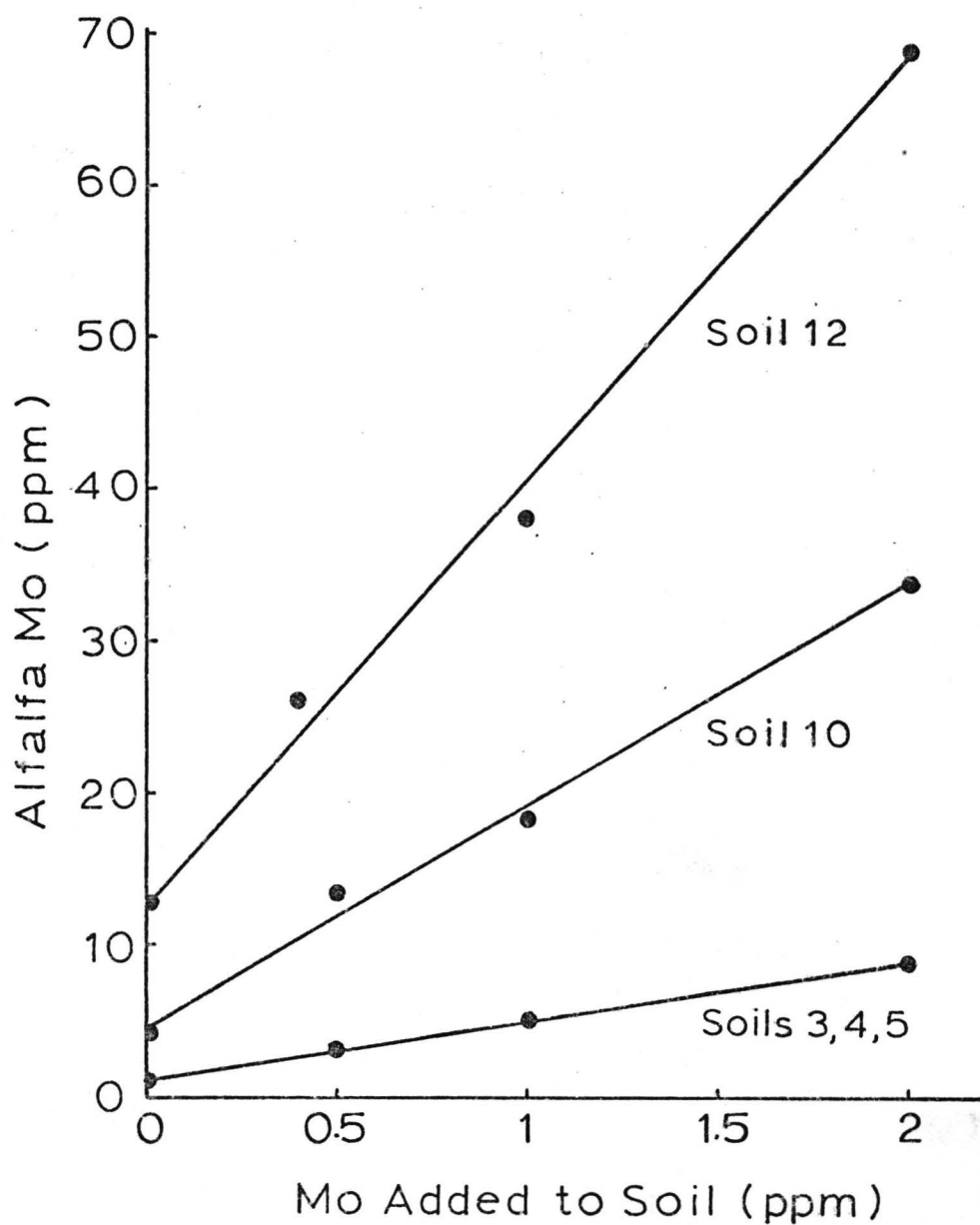


Fig. 4.12. Effect of Mo addition (0, 0.5, 1.0, 2.0 ppm) to soil on the Mo content of alfalfa.

ability of the soil to replenish the soil solution. A 12-hour water extraction (1:2) was thought to be reasonable estimate of the Mo solubility, but gives little information about the labile Mo pool of the soil. The procedure is simple but requires a flameless atomic absorption spectrophotometer to analyze Mo concentrations below 20 ppb.

The ammonium carbonate soil test was developed on the basis that a large fraction of the total Mo in soils is in solution at pH's above 8.5. An increase in this "labile Mo pool" resulting from Mo contamination can thus be monitored by extracting a soil at a pH of 8.5 or higher. For this purpose a 12-hour extraction with 1 M $(\text{NH}_4)_2\text{CO}_3$ at pH 9 was attempted as a means of evaluating the Mo status of soils. Ammonium carbonate has the advantage of being an excellent buffer, volatilizes during digestion, and leaves a decolorized extract when treated with H_2O_2 prior to the colorimetric Mo analyses. The amount of Mo extracted from soils is generally high enough to permit Mo analyses by the thiocyanate method.

It has been reported that molybdenum in soils is mainly associated with surfaces of iron oxides or hydroxides (Smith, 1967). It was thought that by dissolving surfaces of soil-Fe(III) oxides, the amount of Mo solubilized would relate to the amount of molybdenum taken up by plants. The DTPA-micronutrient soil test, developed for Fe, Mn, Cu, and Zn, extracts some of the iron present in soils and was therefore tested as a possible Mo extractant.

The results of the three proposed soil tests for Mo are reported in Appendix A. Table 4.8 summarizes these results by giving linear regression parameters for the equation:

$$\text{alfalfa Mo} = A \cdot (\text{Extr-Mo}) + B \quad (8)$$

Table 4.8. Regression parameters of Mo concentrations in alfalfa with Mo extracted by various soil tests (Equation 8).

<u>Soil test</u>	<u>Regression Parameters</u>			
	A	B	r	S.E.
H ₂ O	66.0	-.049	.990	.74
(NH ₄) ₂ CO ₃	13.8	-1.870	.950	3.20
DTPA	1.0	1.230	.985	1.80

Correlations are equally good for water and DTPA extractions. DTPA is only half as efficient as water in extracting Mo from soils, suggesting that iron oxide surfaces do not play an important role as Mo absorbent in soil. The strong organic matrix of the DTPA extracts makes accurate Mo analyses tedious and decreases the value of this soil test on a routine basis.

The need for flameless AA analyses of the water extracts was demonstrated by an improvement of approximately 0.2 unit in the correlation coefficient of equation 8 when compared to colorimetric analyses of the solutions. The improvement was primarily due to more accurate analyses of samples containing less than 20 ppb Mo.

The correlation coefficient of alfalfa Mo with Mo extracted by ammonium carbonate was lower than with water or DTPA extractable Mo.

In acid soils the ammonium carbonate soil test overestimates the amount of Mo available to plants. The correlation between alfalfa Mo and $(\text{NH}_4)_2\text{CO}_3$ - extractable Mo improved significantly (.986) by excluding soils below pH 7.

The use of water and ammonium carbonate as possible molybdenum soil test extractants was further evaluated on these soils amended with 0, 0.5, 1 and 2 ppm Mo as Na_2MoO_4 and cropped with alfalfa. The results of the water extraction are depicted in Fig. 4.13. The correlation coefficient for soils producing alfalfa with less than 30 ppm Mo was .98. Extraction of the amended soils with 1 M $(\text{NH}_4)_2\text{CO}_3$ yielded an acceptable correlation ($r = 0.977$), but only for soils with a pH of 7 or higher (Fig. 4.14).

Mo toxicity problems are mainly expected in alkaline soils, and the vast majority of agricultural soils in Colorado fall in this category. The ammonium carbonate and water soil tests for Mo may therefore be considered equally good for predicting Mo toxicity in Colorado. Critical levels above which toxic forages can be expected should be evaluated individually for each forage crop in field tests and surveys.

Field validation of Mo soil tests

The water and ammonium carbonate soil tests were performed on 23 soil samples from alfalfa fields and correlated with the Mo content of the alfalfa growing thereon. All soils were collected in the Front Range Area between Greeley and Brighton, Colorado and were alkaline. The fields were sampled in July 1975 when most of the alfalfa was blooming. Four soils, used in the greenhouse experiment (Soils 6, 8, 9, and 12), were also sampled in 1974.

A large difference is observed between the regression lines obtained in the greenhouse experiment and those from field samplings. The regression lines obtained under greenhouse conditions (Figs. 4.13 and 4.14) are included in Figs. 4.15 and 4.16 for comparison.

The lower accumulation rate of Mo in alfalfa grown in the field compared to that grown in the greenhouse is likely due to differences in soil water regimes. Plant absorption of soil Mo increases with increased water availability (Cannell, 1960; Kubota, 1963; Lavy and Barber, 1964). Under greenhouse conditions, where soils are brought to field capacity daily, crops tend to transpire large quantities of water as a result of both high temperatures and ample water supply. In the Front Range Area of Colorado alfalfa is grown on irrigated land where luxury consumption of water is avoided. Higher uptake of Mo in the greenhouse could be explained by the higher mass flow of Mo to the root system. Other factors such as greater root density and higher soil temperatures in the greenhouse may also contribute to higher Mo uptake.

The range of Mo concentrations of alfalfa sampled in the field was limited to nontoxic levels. Based on the greenhouse results it seems that extrapolation of the regression lines is warranted. The alkaline soils of the Northern Colorado Front Range should then be considered hazardous for cattle, grazing on alfalfa, if greater than 0.5 ppm Mo is extracted from these soils by water during a 12-hour period. The critical level for $(\text{NH}_4)_2\text{CO}_3$ extraction can be set at 1.7 ppm Mo. Potentially toxic soils should preferably be kept in grass and used for hay production.

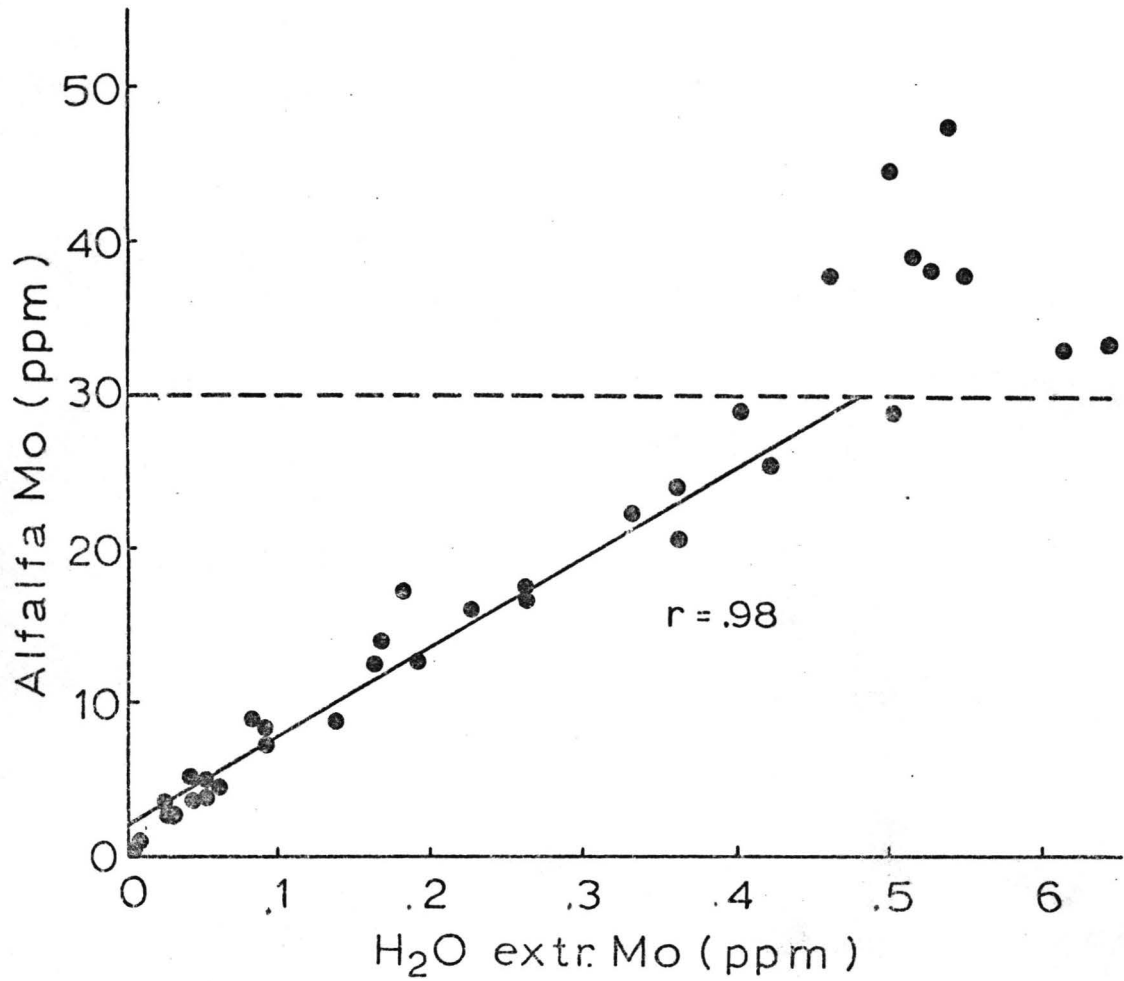


Fig. 4.13. The relationship between water-extractable Mo and Mo in alfalfa grown in the greenhouse on Colorado soils.

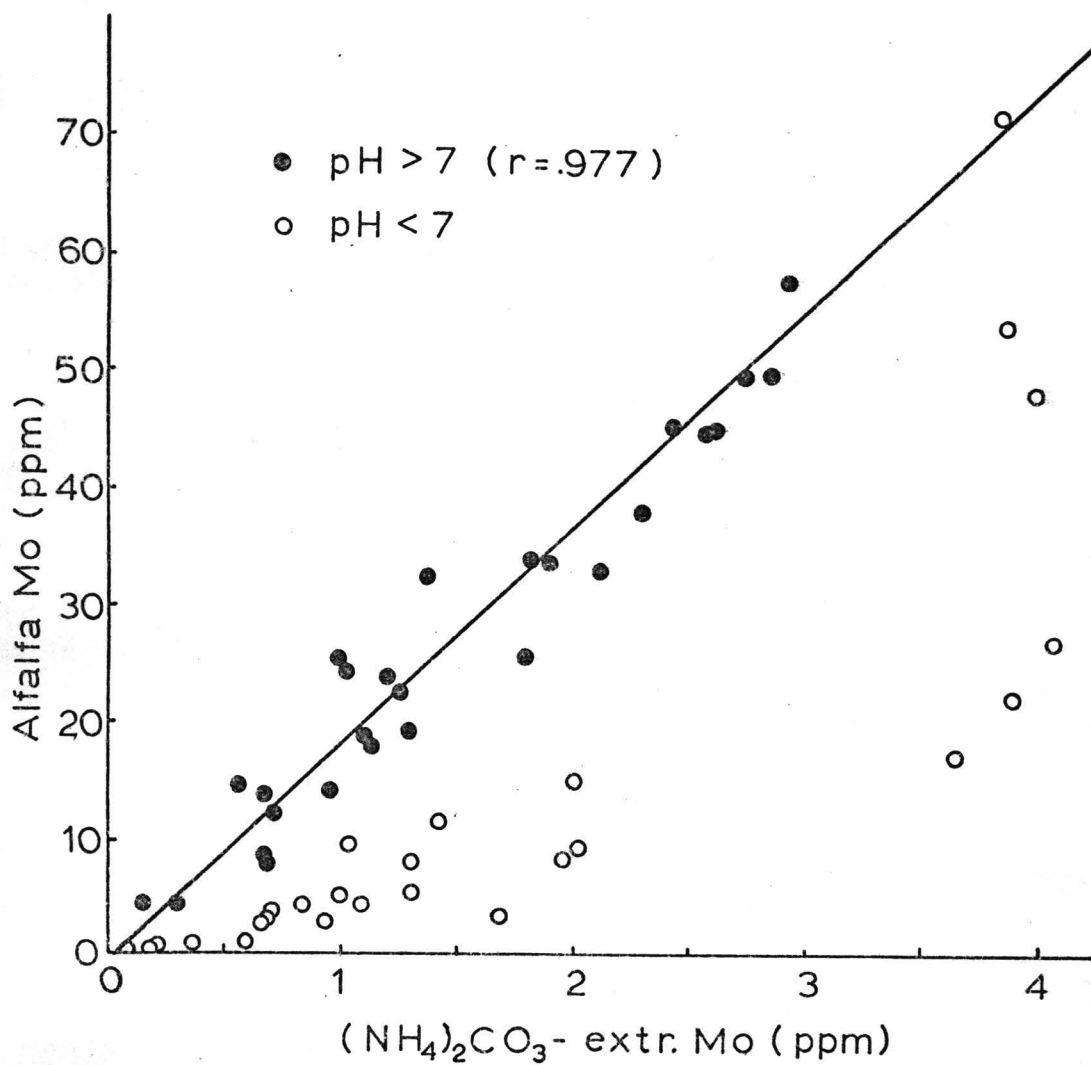


Fig. 4.14. The relationship between ammonium carbonate-extractable Mo and Mo in alfalfa grown in the greenhouse on Colorado soils.

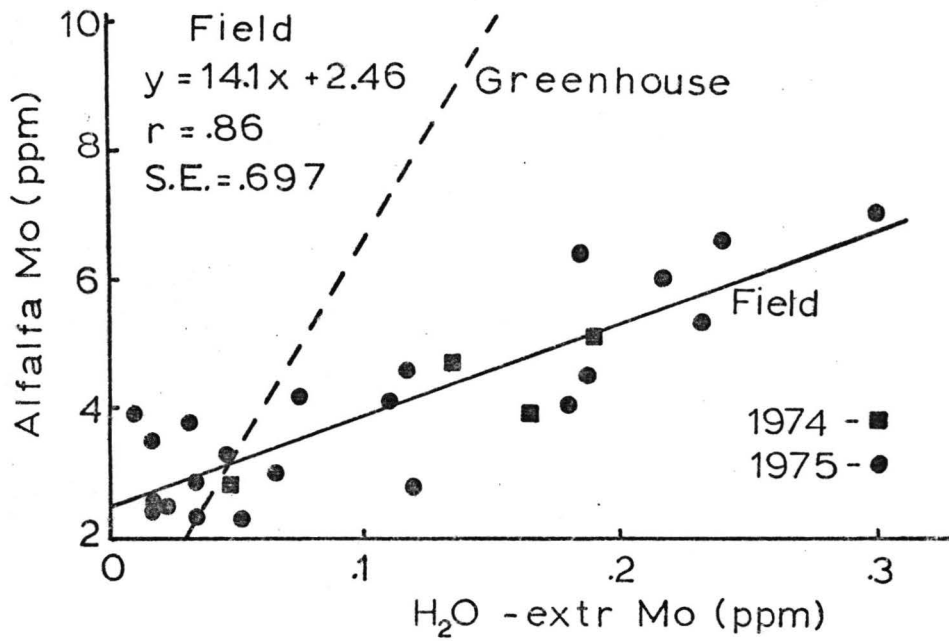


Fig. 4.15. The relationship between water-extractable Mo and Mo in alfalfa sampled in the Front Range area of Colorado.

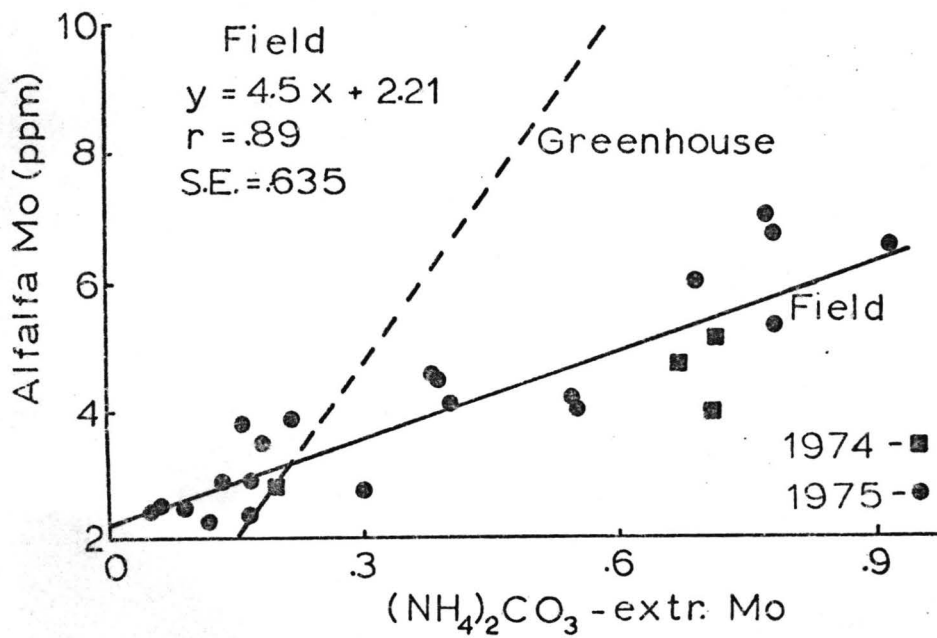


Fig. 4.16. The relationship between ammonium carbonate-extractable Mo and Mo in alfalfa sampled in the Front Range area of Colorado.

Mo accumulation in contaminated soils

Soils 6, 8, 9, and 12 from the South Platte Valley were irrigated from irrigation canals contaminated by water from Clear Creek. Prior to 1973 the fluctuations in Mo content in the irrigation waters were monitored by Jackson (1973). Through 1975 water samples were taken from these sources for Mo analyses and the results are given in Table 4.9. Blue River water sampled in May 1974 at three points approximately 10 miles apart showed an average Mo content of 181 ± 10 ppb. No effort was made to monitor fluctuations in Mo concentrations of Blue River water. The history of Mo contamination of soils in this area goes back as far as a century and is not likely related to present Mo levels in irrigation water.

Table 4.9. The Mo levels of four irrigation waters from the Denver area.

Ditch	Soil	Mo (ppb)			
		1973*	May 1974	July 1974	July 1975
Standley	12	213	93	215	240
Brantner	9	91	48	172	68
Burlington	8	27	22	94	15
Clear Creek	6	158	--	184	78

*Average of biweekly sampling by Jackson, 1973

The impact of Mo contamination of a soil can be estimated as the difference between Mo input from irrigation water and the Mo removed in the harvested crop. Disregarding deep percolation beyond the alfalfa rhizosphere (6 feet) and assuming a yearly irrigation of

25 cm water, 2.5 g of Mo is added per hectare for each ppb Mo in the water. An average alfalfa yield in the Front Range Area of 10 metric tons/hectare will remove 10 g of Mo/ha for each ppm of Mo in the crop. In order to assure healthy crops (<5 ppm Mo) the inputs of Mo should not exceed the maximum allowable outputs, thus the concentration of Mo in irrigation water should not exceed 20 ppb.

The results of excessive additions of Mo to soils over a period of a decade are demonstrated for Soils 8 and 12 in Fig. 4.17. Both soils contain about 1.5 ppm total Mo in the subsoils which is the indigenous Mo level for the parent material of these soils. Soil 8 contained slightly over 2 ppm Mo in the top horizon, which decreases with depth. According to the adsorption isotherm (Fig. 4.8) the topsoil of Soil 8 is unable to retain further added Mo. The topsoil of Soil 12 contains 3.75 ppm Mo and is able to fix another one ppm of Mo (Fig. 4.8). In both cases irrigation with high Mo water increased the Mo content in the top 50 cm of the soil.

The long term effect of Mo contamination is seen from Fig. 4.17 where a Mo profile distribution is shown for Soil 11 taken from the Blue River Valley. This topsoil contains 28 ppm of Mo which decreases to 11 ppm at 50 cm depth. Apparently Mo contamination has affected this soil to a greater depth than soils from the Denver Area.

The amounts of Mo extracted by ammonium carbonate and water from the various layers of Soils 8, 11, and 12 are included in Fig. 4.17. In Soils 8 and 12 the shapes of the profile distributions of $(\text{NH}_4)_2\text{CO}_3$ and H_2O extractable Mo are similar to those of total Mo. Ammonium carbonate extracted between 6 and 17% of the total Mo present whereas water extracted only 1.9 to 4.5%. The fraction of total Mo

Soil-Mo-(ppm)

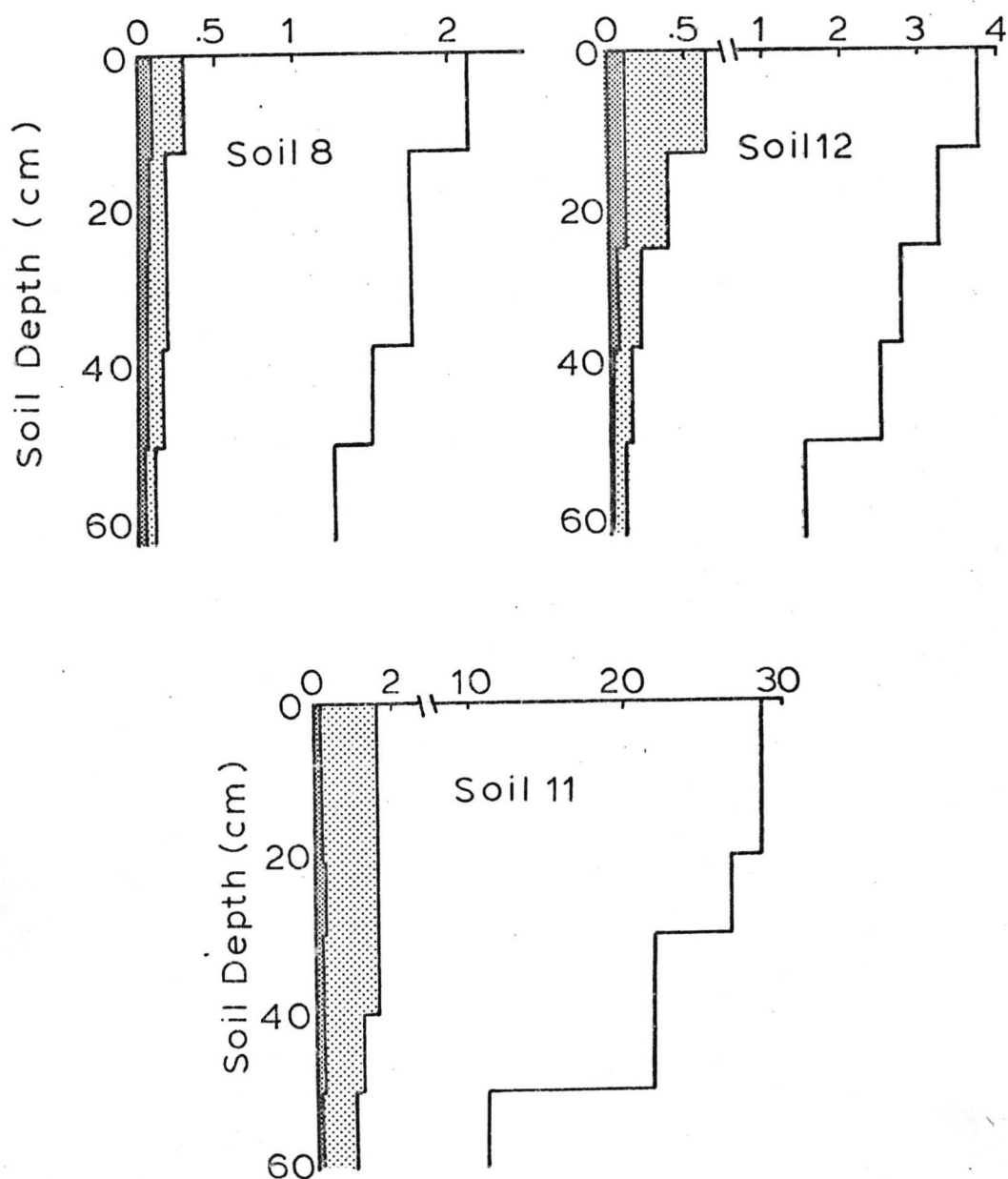


Fig. 4.17. Various Mo fractions in three soil profiles contaminated by high Mo irrigation water.

soluble in $(\text{NH}_4)_2\text{CO}_3$ or H_2O decreased with increasing soil depth. Both extractions were useful for monitoring the extent of molybdenum contamination in moderately contaminated soils.

A 12-hour extraction with ammonium carbonate or water dissolved only a small percentage of the total Mo present in the highly contaminated soil (#11). Extraction for 36 hours with either extractant removed almost double the amount of Mo, indicating that a plateau had not been reached in 12 hours. The sluggish release of Mo by H_2O and $(\text{NH}_4)_2\text{CO}_3$ makes these tests less suitable for monitoring the molybdenum status of very polluted soils.

The ammonium carbonate extractable Mo in profiles from South Platte Soils 6, 8, and 9 and Blue River Valley Soils 2, 3, 11, and 13 are shown in Figure 4.18. The South Platte soils all show some accumulation of Mo in the top soils. The Blue River soils (11 and 13) of alkaline pH released high quantities of Mo into 1 M $(\text{NH}_4)_2\text{CO}_3$ in contrast to the acidic soils (2 and 3) even though the degree of contamination in those soils was about equal (Table 3.2). The high amounts of ammonium carbonate extractable Mo in the top 5 cm of soil 2 undoubtedly arises from mine tailing debris deposited in the topsoil.

4.3. Mobility of Molybdenum in Agronomic Systems

Molybdenum transport in a sandy clay loam

The results of transport studies of Mo through soil columns of a sandy clay loam (Soil 8) are summarized in Figs. 4.19 and 4.20.

Leaching the soil with distilled-deionized water resulted in loss of Mo from the soil as demonstrated by the presence of Mo in the leachate. The total amount of Mo leached from the soil accounts for 75% of the labile Mo determined by extraction with $(\text{NH}_4)_2\text{CO}_3$ (Fig. 4.19).

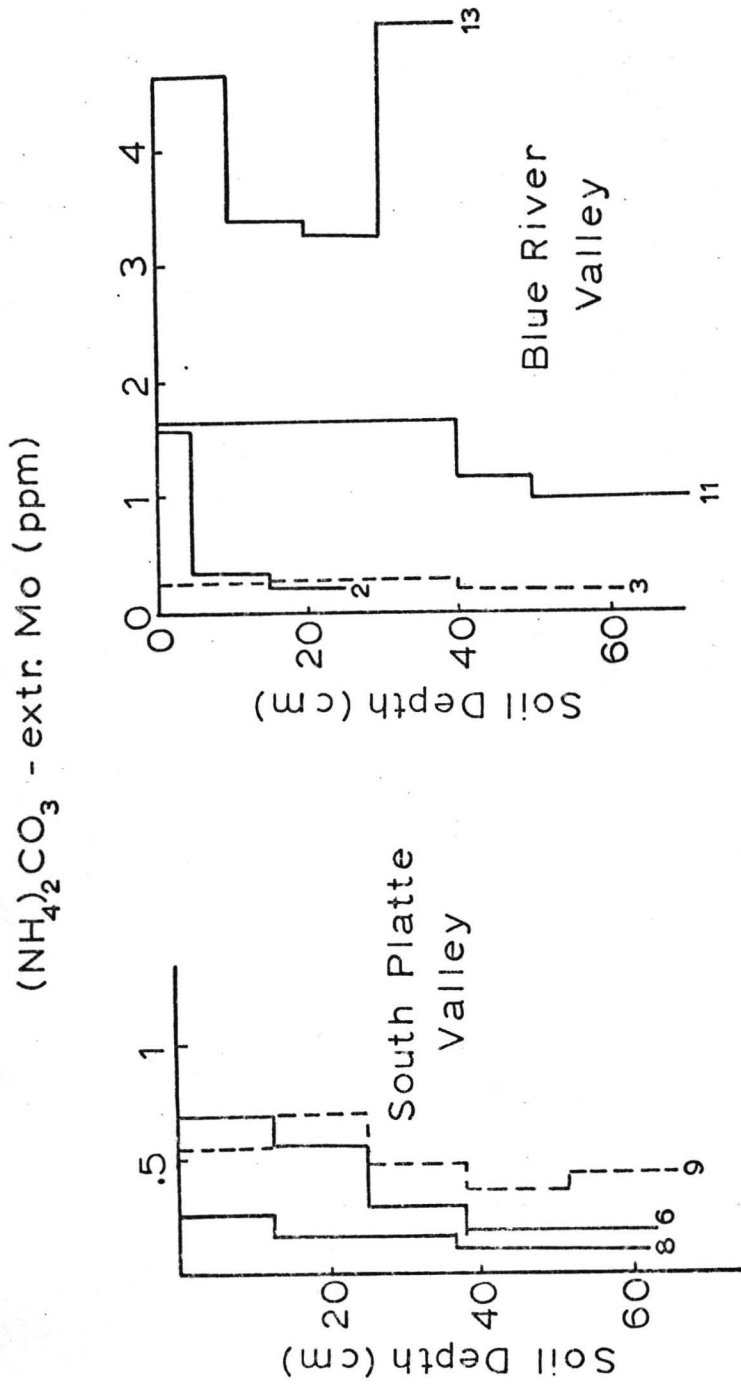


Fig. 4.18. Ammonium carbonate extractable molybdenum in soil profiles of the South Platte Valley (6,8,9) and the Blue River Valley (2,3,11,13).

The concentration of Mo in the effluent showed a peak after approximately one pore volume of solution (230 ml) was passed through the column (Fig. 4.19). The peak concentration was approximately 250 ppb. After reaching a maximum the molybdenum in the effluent decreased rapidly due to depletion of the labile molybdenum pool, which was exhausted after approximately 1500 milliliter of water had leached through the column. The average molybdenum concentration of the first pore volume collected after infiltration was approximately 150 ppb or about four times the equilibrium concentration of a 1:2 soil-water suspension.

Unlike molybdenum, chloride in the effluent did not exhibit a delayed concentration peak. The first 10 ml aliquot of leachate contained close to 1500 ppm chloride, which decreased rapidly in subsequent aliquots to become negligible once 200 ml of leachate had been collected. A delayed Cl^- leaching was reported by Dyer (1965) in soils infiltrated at a slow rate instead of under ponded water conditions. The cause of delayed solute leaching may be found in dispersion effects and soil-solute interaction (Dyer, 1965). The phenomenon deserves further study.

Movement of molybdenum under saturated steady state conditions was studied by comparing breakthrough curves of molybdenum with those of chloride. Chloride breakthrough curves in these experiments resembled the theoretical breakthrough curves for the solute transport equation without a source function, and may be fitted to this equation by using optimization techniques developed by Cameron (1973). Forward and backward breakthrough curves determined under identical waterflow conditions were symmetrical.

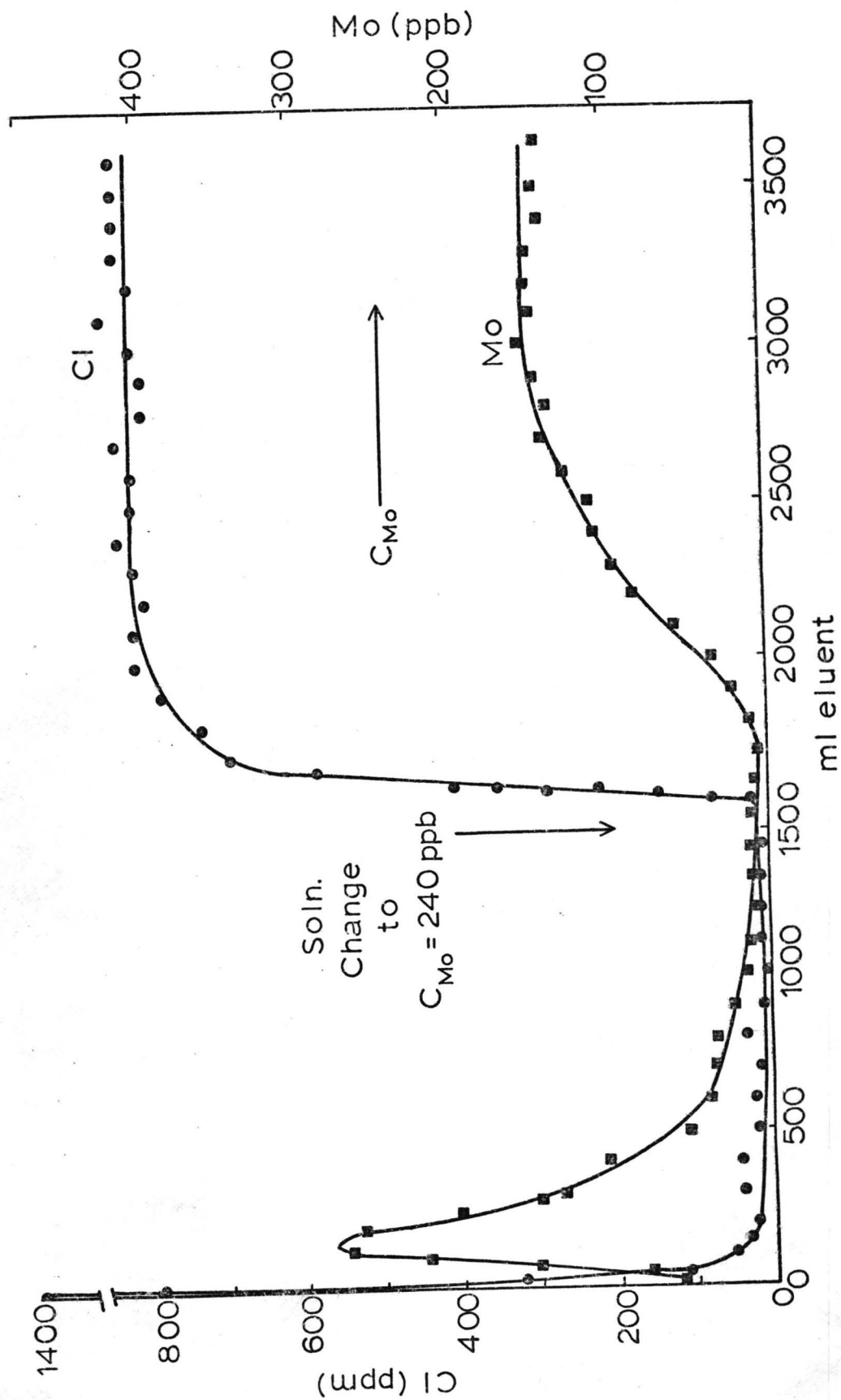


Fig. 4.19. Measured Mo and Cl breakthrough curves of a Mo depleted soil column.
(1 pore volume = 230 ml)

After leaching the column with 1500 ml of distilled water the influx solution was changed to 800 ppm Cl and 240 ppb Mo (Fig. 4.19). The molybdenum breakthrough curve was delayed from that of the chloride. An instantaneous adsorption reaction between solution and solid phase caused a "hold-up" in breakthrough of the Mo tracer. The concentration of molybdenum in the effluent did not return to the 240 ppb level of the influx solution but, after a delayed breakthrough, leveled off at approximately 150 ppb.

A linear Freundlich isotherm used by Cameron (1973) as the source function in the transport equation for silver may be useful in describing the delayed Mo breakthrough as well. The irreversible Mo removal from solution causing the breakthrough curve to level off at 150 ppb resembles a precipitation reaction where the precipitate serves as an infinite Mo sink. Cameron (1973) extended his transport model to describe this process by including a kinetic expression in the source term. This model allows prediction of irreversible precipitation reactions where the rate of molybdenum removal from solution greatly exceeds the rate of molybdenum dissolution.

A second soil column was leached with a solution containing 42 ppb Mo and 475 ppm Cl (Fig. 4.20). After the molybdenum and chloride concentrations of the outflowing equaled those of the inflowing solution, the influx solution was changed to 200 ppb Mo only. The resulting forward molybdenum breakthrough curve and backward breakthrough curve for chloride are depicted in Fig. 4.20. These curves are both typical of non-reactive solutes moving through a porous medium. The non-reactivity of the soil for Mo resulted from the fact that the anion exchange complex was already saturated by the initial 42 ppb

level. The non-reactivity implies also that a precipitate is not formed in the absence of CaCl_2 in the influx solution.

Extraction with ammonium carbonate of the soil from the columns cut in 5 cm sections after termination of the experiment, revealed that column II (Fig. 4.20) was saturated with molybdenum (0.11 ppm) whereas the amount of molybdenum in the top 5 cm of column I (Fig. 4.19) exceeded the adsorption capacity of Soil 8 several times. Apparently, in the presence high levels of CaCl_2 Mo was precipitated soon after it entered the column. The precipitating compound has not been identified but may well be a powellite-type mineral.

Molybdenum uptake simulation model

A simulation model developed by Gilbert (1974) for modeling plant growth in grasslands was modified to simulate alfalfa growth in the Front Range area around Denver. The rhizosphere was considered to comprise five soil layers of 25 cm each. Weather data were the principal driving variables for the model which is represented as a box and arrow diagram in Fig. 4.21. Solid arrows represent mass flows whereas dashed arrows refer to control mechanisms of the flows.

Daily precipitation data were generated stochastically, while average daily temperatures were computed from a sine function based on historical weather data (Gilbert, 1974). Irrigation took place after each harvest. Rain or irrigation water was considered to enter the top-soil. When water in the top layer exceeded field capacity, the amount of water above field capacity was drained to the next soil layer, or below the rhizosphere.

Water was lost from the various soil layers by evapotranspiration. Potential evapotranspiration was calculated as a function of temperature

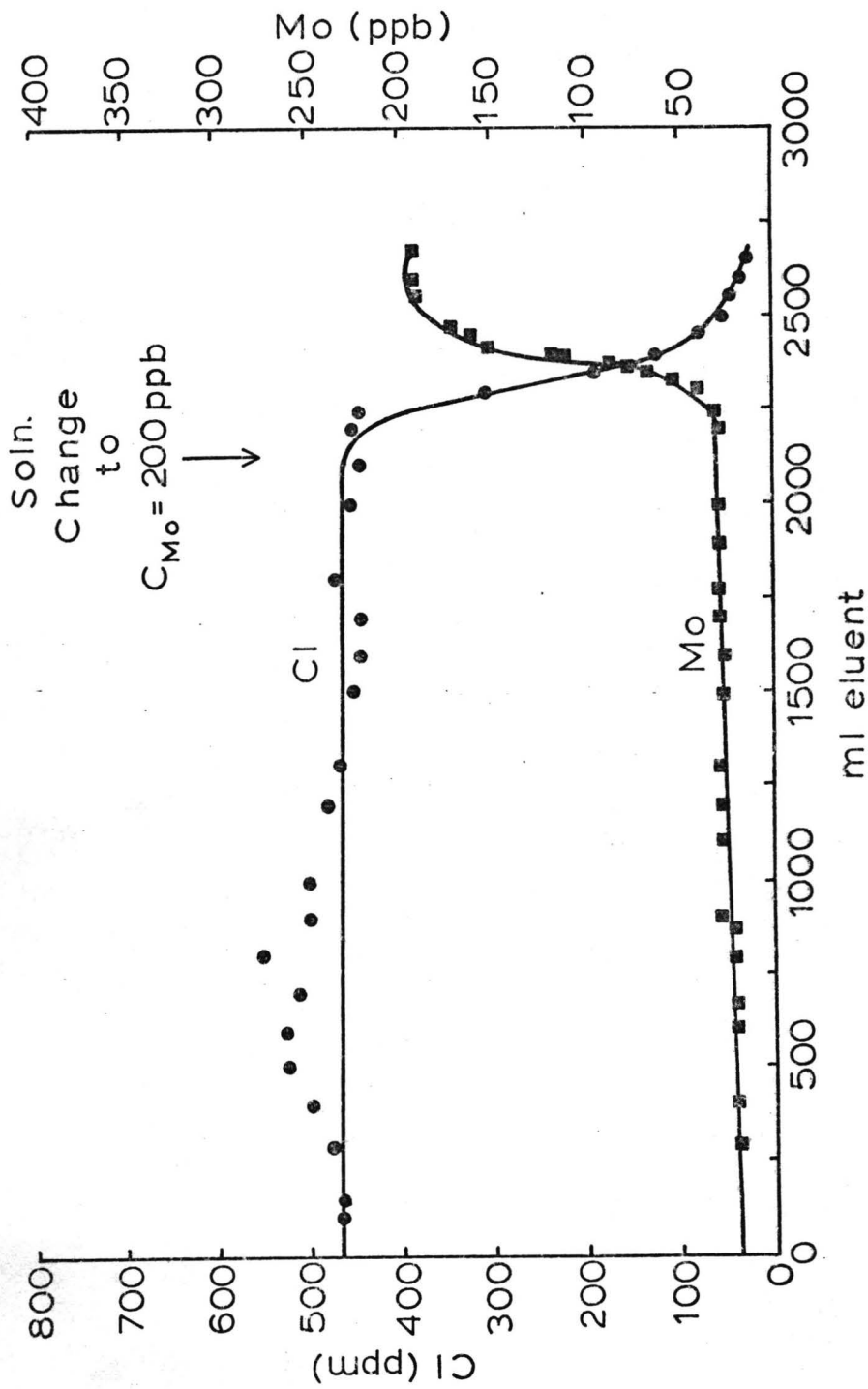


Fig. 4.20. Measured Mo and Cl breakthrough curves of a Mo saturated soil column.
(1 pore volume = 230 ml)

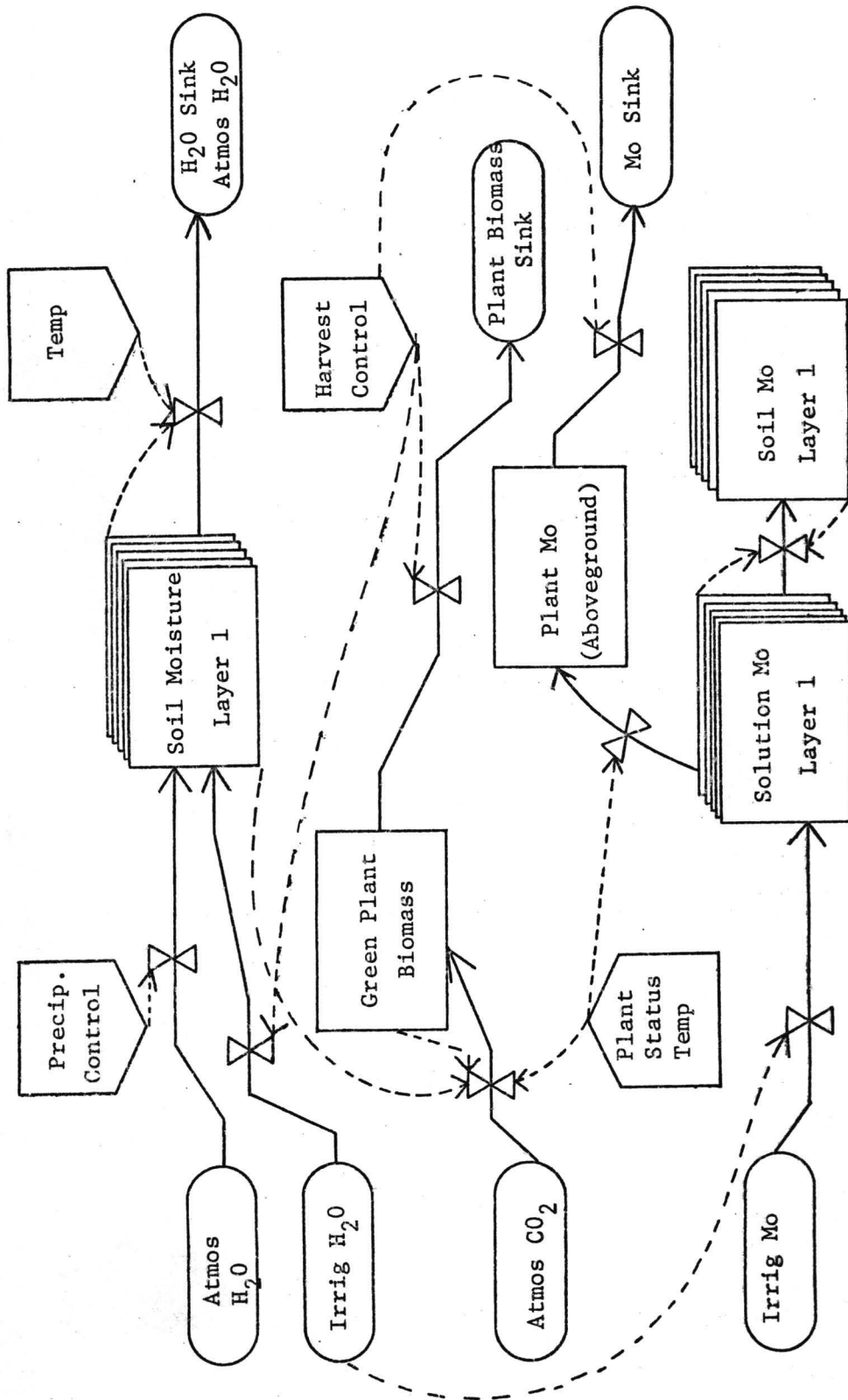


Fig. 4.21. Box-and-arrow flow diagram for the alfalfa-molybdenum simulation model.

and was used to calculate actual ET as a function of the soil water present in each layer (Gilbert, 1974). Transpiration was set equal to ET if the green plant biomass exceeded 1 ton/ha, or was assumed to be proportional to the green plant biomass if less than 1 ton/ha.

Plant growth was controlled by the average ambient temperature, the soil water status, green plant biomass, and phenological stage of the crop (Gilbert, 1974). By introducing adequate growth factors the model was made to mimic sigmoidal growth curves representative for Colorado. An example of a one-year simulation run of alfalfa growth on site 8 is given in Fig. 4.22. The first yield was approximately 5 ton/ha, followed by two cuttings of 2 ton/ha each. Harvesting times were set for the middle of June, first week of August and late September. Winterkill was considered to occur in late October.

For the purpose of this study a Mo submodel was added to Gilbert's plant growth model. A daily evaluation was made of the amount of labile (ammonium carbonate extractable) molybdenum for each soil layer. Labile Mo changed as a result of plant uptake, addition of Mo in the irrigation water, and drainage into the subsoil. The amount of Mo present in the equilibrium solution of a 1:2 soil suspension was calculated for each layer using experimentally determined isotherms (section 4.1). The Mo concentration in the actual soil solution was found by concentrating the 1:2 suspension to the actual water content assuming no further soil-solution interaction.

It was assumed that the amount of Mo taken up by plants is proportional to the water taken into the plant as determined by transpiration. Trial simulation runs for uncontaminated soils, assuming Mo absorption by unobstructed mass flow yielded crops with 50 times more molybdenum than

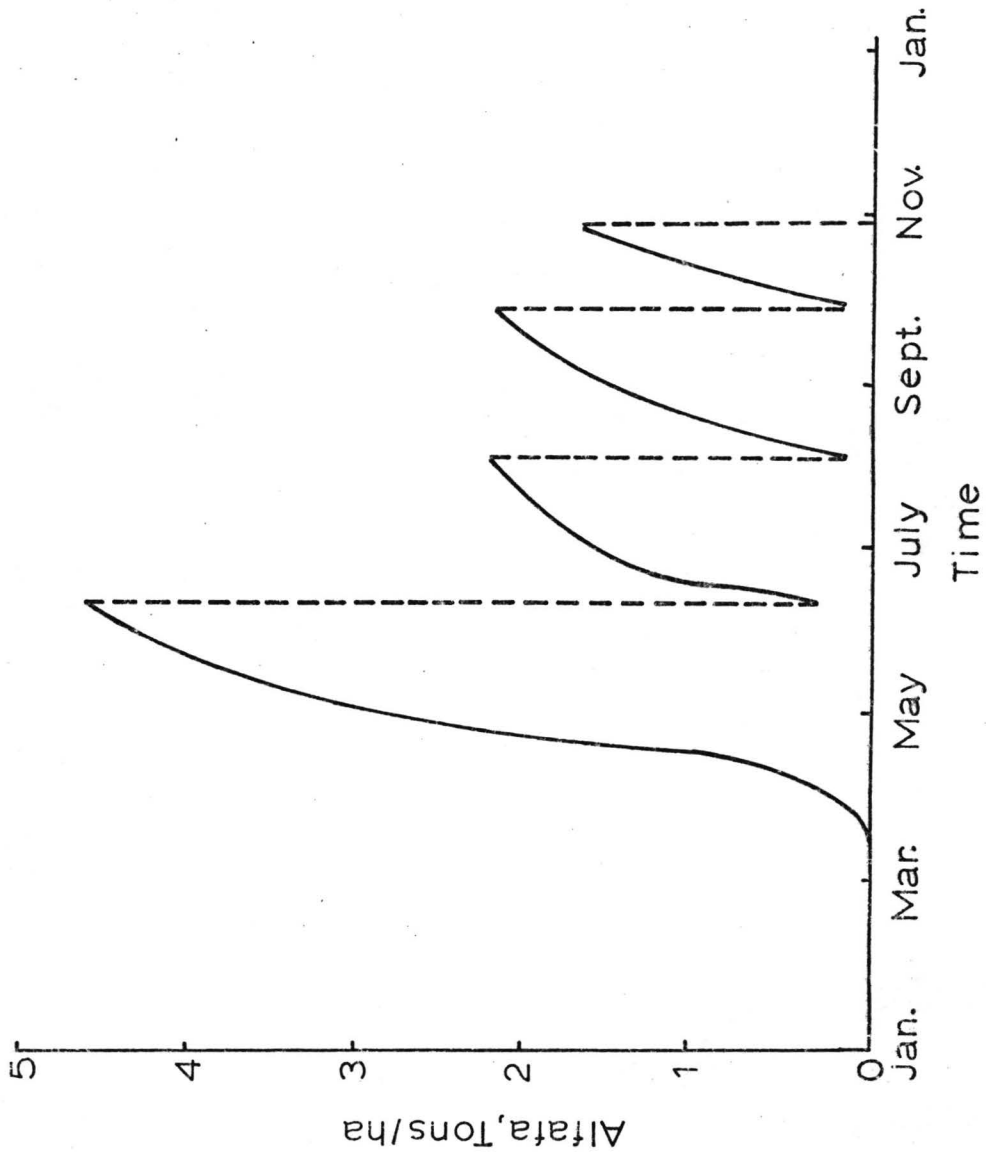


Fig. 4.22. One year of simulated growth for an alfalfa pasture of the Front Range Area around Denver, Colorado.

observed in the field. Discriminative Mo uptake (Lavy and Barber, 1964) and Mo retention by plant roots are mechanisms responsible for this discrepancy. A selectivity factor of 1/50 for Mo absorption was adopted in order to simulate Mo uptake as it is observed in the field.

The results of 5-year simulation runs for two different soils (8 and 9) using various qualities and amounts of irrigation water are represented in Figs. 4.23 and 4.24. Represented in Fig. 4.23 is the molybdenum content of alfalfa in three different cuts for five consecutive years of cropping on a sandy clay loam. Irrigation with 100 mm of water after each harvest did not allow drainage of water and Mo below the rhizosphere. With a Mo level in irrigation water of 30 ppb and with an initial level of 20 ppb "labile" Mo homogeneously distributed throughout the soil, alfalfa accumulated approximately 1.6 ppm of Mo during the first year. After each cutting the Mo concentration was temporarily diluted due to a rapid regrowth not matched by Mo uptake. Subsequent years showed a slight increase in alfalfa Mo due to accumulation of Mo in the soil. The fifth year had a very dry and cool spring resulting in sharply reduced yields and low Mo accumulation.

If the concentration of Mo in irrigation water was set at the maximum level allowed by EPA in Colorado (150 ppb) the trend in Mo accumulation in the alfalfa crop gave more reason for concern. Within three years the soil was polluted enough to support toxic alfalfa. The limited capacity of this soil to adsorb Mo renders Mo highly soluble, causing a rapid increase in the Mo concentration of alfalfa.

An increase in the application of irrigation water to 150 mm per cycle allowed drainage of Mo below the rhizosphere and decreased the

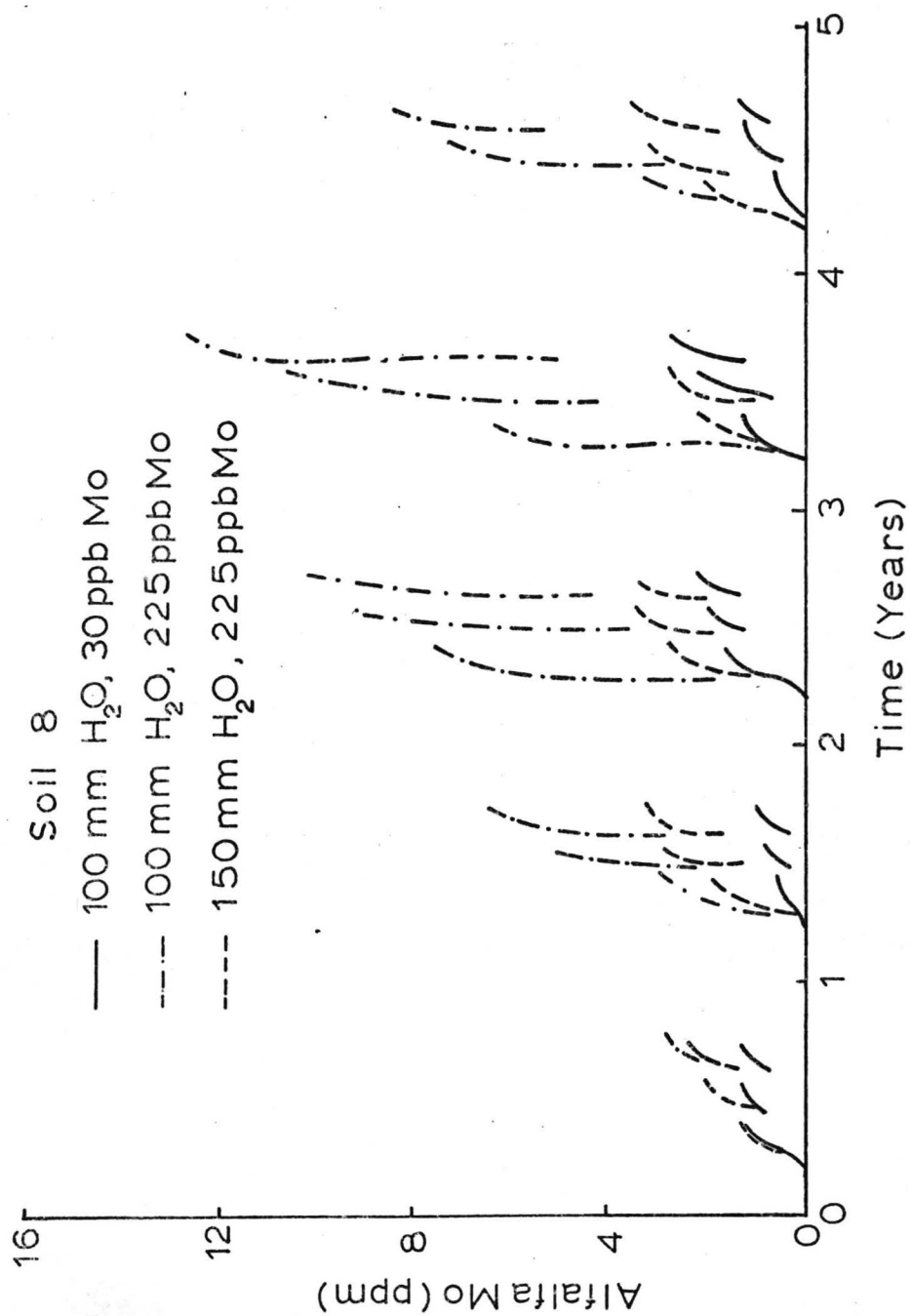


Fig. 4.23. Simulated accumulation of Mo in alfalfa grown on a sandy loam soil under different irrigation regimes (100 or 150 mm 3 times yearly) using relatively clean (30 ppb) and severely contaminated (225 ppb) water.

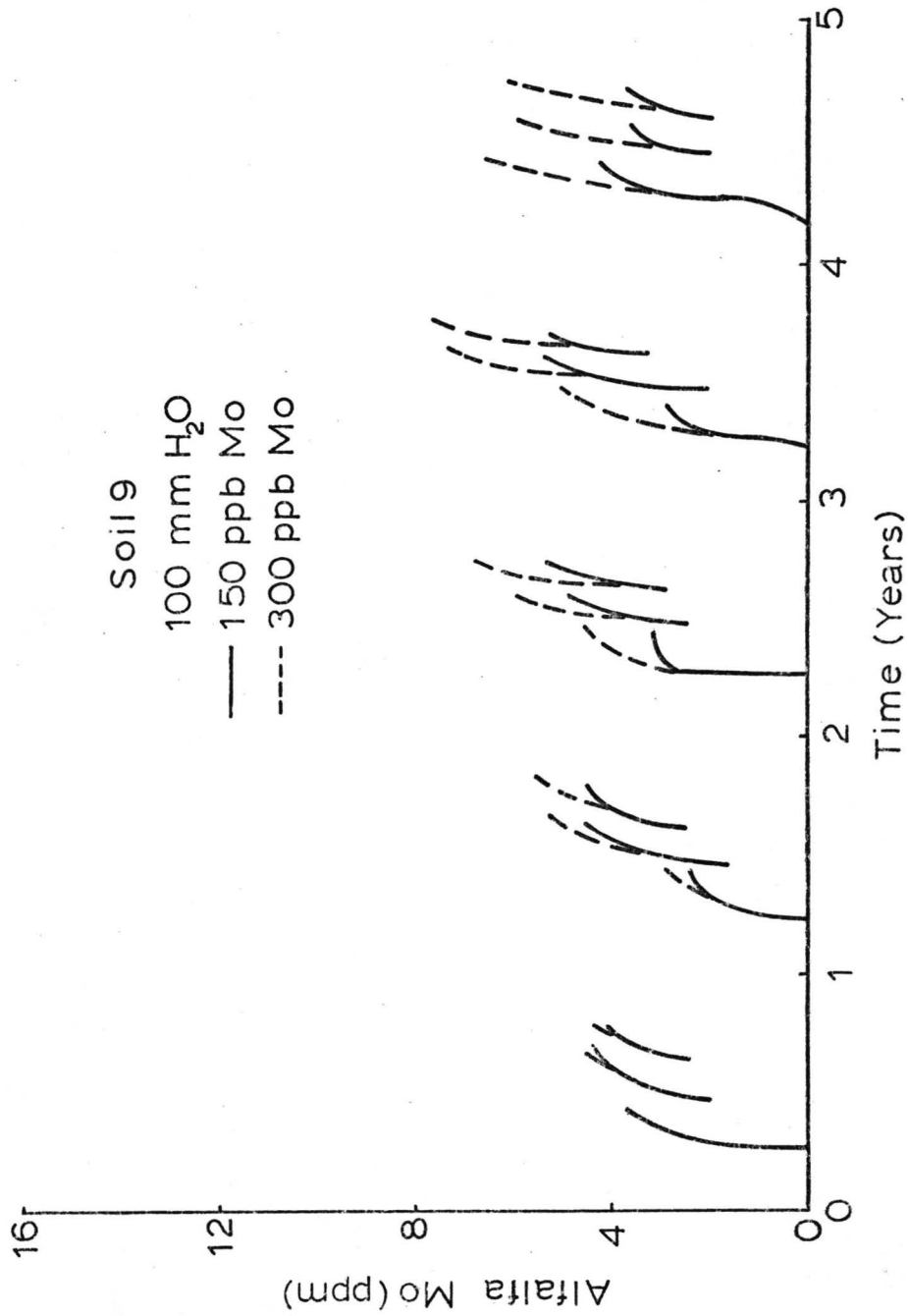


Fig. 4.24. Simulated accumulation of Mo in alfalfa grown on a clayey soil applying 100 mm of water with two molybdenum levels 3 times a year.

rate at which soils were polluted. The high level of Mo in irrigation water caused a rapid increase of alfalfa-Mo following each irrigation. However, the loss of excessive Mo in the profile by leaching prevented development of toxic forage, even after several years of high-Mo irrigation.

The results of two 5-year simulations of Mo uptake by alfalfa from a clay soil (Soil 9) are given in Fig. 4.24. The solid lines represent the Mo concentration in alfalfa if the soil was irrigated with 100 mm H_2O containing 150 ppb Mo. Soil 9 has a high capacity to adsorb Mo and to buffer the Mo concentration in solution. Yearly fluctuations in Mo content of alfalfa were small compared to seasonal variations. The impact of irrigation with high-Mo water became more apparent if the Mo concentration in irrigation water was assumed to be 300 ppb. A definite trend towards toxic Mo levels in alfalfa was seen, reaching as high as 8 ppm Mo within 4 years. Leaching of molybdenum beyond the rootzone by over-irrigation might slow down the rate of soil pollution, but 200-300 mm of irrigation water per cycle is needed on such a clayey soil before leaching will take place.

Validation data for alfalfa Mo contents are summarized in Table 4.10 for both sites. The differences in Mo concentrations between years are irregular and could be accounted for by seasonal fluctuations alone.

Table 4.10. Mo concentrations in alfalfa pastures sampled for three consecutive years.

Soil #	Alfalfa Mo (ppm)		
	1973	1974	1975
8	4.2	3.3	4.6
9	7.3	5.6	4.0

A 25-year simulation run on Soil 9 using parameters that are representative for present field conditions (i.e., 100 mm water per cycle and 100 ppb Mo in the water) is depicted in Fig. 4.25. The results show that continued irrigation with high Mo water was more harmful than was anticipated from the short term field monitoring. Within 15 years alfalfa grown on this pasture contained toxic levels of Mo (>10 ppm). After 25 years alfalfa containing 14 ppm Mo was produced. With the present levels of Mo in irrigation water (Table 4.9) toxic levels of Mo in forages can eventually be expected.

Although many assumptions made in building the model need experimental verification, the model is able to predict Mo concentrations in alfalfa grown in different soils under various management conditions. The model is sensitive to Mo retention capacity and texture of soils, as well as to the amounts of Mo and water applied. The lower the capacity of soil to adsorb added Mo and buffer the solution concentration, the faster the soil will grow toxic forages. On coarse textured soils the rate of soil pollution may be reduced at the cost of over-irrigation by leaching excess Mo into the subsoil.

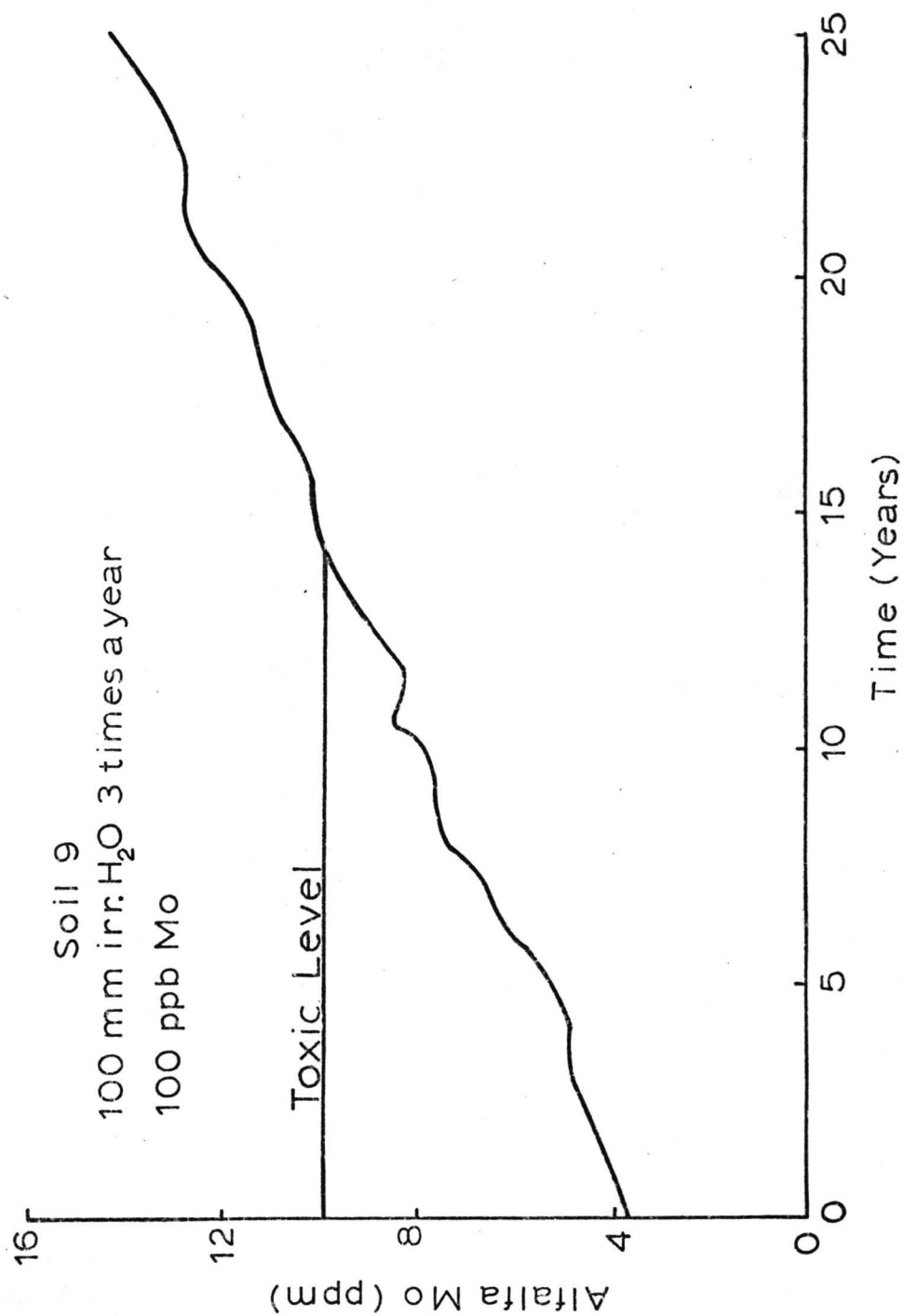


Fig. 4.25. Simulated accumulation of Mo in alfalfa grown on a clayey soil irrigated after each harvest with 100 mm H₂O containing 100 ppb Mo.

5. SUMMARY AND CONCLUSIONS

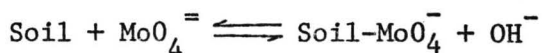
Mining activities in the Rocky Mountain areas of Colorado have caused an increase in the Mo levels of drainage waters, many of which are being used for irrigation. The objective of this study was to evaluate the impact of high-Mo irrigation water on Colorado soils and forages supported by these soils.

The chemical reactions between soil and molybdenum were studied in the laboratory. Solubility diagrams were constructed from thermodynamic data obtained from the literature or determined on pure minerals. Included in these diagrams were solubility relationships for molybdenite (MoS_2), ilsemanite (Mo_3O_8), ferrimolybdite ($\text{Fe}_2(\text{MoO}_4)_3$), powellite (CaMoO_4), and wulfenite (PbMoO_4). From these diagrams it was learned that wulfenite is the most stable mineral and most likely to form in soils. Lack of thermodynamic data on other, less abundant molybdenum minerals prevented evaluation of their possible existence in soils.

The solubilities of molybdenum in selected Colorado soils, ranging in pH (sat. paste) from 5.5 to 7.7, were plotted on the wulfenite diagram. All but one soil appeared undersaturated with respect to the minerals included in this study. This was confirmed by a significant (10-100 fold) increase in molybdenum solubility when wulfenite was added to the soils, indicating that wulfenite was not present initially. The Mo solubility of wulfenite amended soils validated the wulfenite solubility diagram by closely fitting the wulfenite isotherm.

In the absence of solid phase Mo compounds, the solubility of Mo in soils was apparently controlled by specific adsorption processes. The Mo

solubility in such soils was dependent on the degree of molybdenum saturation of the soil and on the pH. At a fixed pH the Freundlich isotherm adequately predicted the dependence of the Mo solubility on the degree of Mo saturation. The pH dependence of the Mo exchange reaction caused a 10-fold increase in the Mo solubility for each unit increase in pH, as described by the reaction:



The Freundlich isotherm was extended to include a term for pH, thus relating the Mo solubility of an individual soil to its Mo saturation and pH.

The availability of Mo in soils was studied in a greenhouse experiment. The results of this study show an increased Mo uptake by forages upon additions of Na_2MoO_4 to the soils. The effect of Mo amendments was more pronounced in alkaline than in acid soils in accordance with the modified Freundlich isotherm. The uptake of Mo was different for different forages; clover yielded the highest Mo contents, followed by alfalfa and bluegrass. It appears that growing leguminous forages should be avoided in areas where Mo pollution poses a problem.

The two important parameters in soils that influence the availability of molybdenum to plants, the intensity and capacity factors, were evaluated using two separate soil tests. The intensity factor or concentration of molybdenum in the soil solution was determined by extraction of the soil with water. The capacity factor or ability of the soil to replenish the solution as it is depleted by the plant was evaluated by extracting the soil at a pH of 9 using $1\text{M } (\text{NH}_4)_2\text{CO}_3$.

The H_2O soil test was most successful in predicting Mo levels in forages grown in the controlled environment of the greenhouse. The

regression line between water soluble Mo for all soils, irrespective of pH, and Mo in alfalfa yielded a correlation of .98. The correlation for the field survey dropped to .86 due to varietal and environmental differences between sampling sites. The slope of the regression line obtained in the field was one fifth of that found for the greenhouse study, which indicates that greenhouse data, (e.g., critical levels) are not readily transferable to field situations.

Extraction with $1M (NH_4)_2CO_3$ proved to be a good soil test for neutral and alkaline soils, and can be used in most of the Western States. Differences between regression lines of field and greenhouse data were similar to those found for the H_2O -soil test. The ammonium carbonate soil test gave a good estimate of labile Mo and can be used as a monitoring device for Mo contamination in soils.

The use of these soil tests for predicting Mo deficiencies has not been evaluated. With the ability of analyzing low concentrations of Mo in solutions the H_2O -soil test may turn out to be quite universal. The extraction power of ammonium carbonate may be useful for extracting detectable amounts of Mo from Mo deficient soils. The application of $(NH_4)_2CO_3$ for testing Mo deficient soils warrants further investigation.

The information obtained in the laboratory and greenhouse studies was used in developing a model simulating the impact of high-Mo irrigation water on soils. The model was made to simulate daily alfalfa growth under climatic conditions representative for the Front Range area near Denver, Colorado. Molybdenum contents in 5 soil layers comprising the rhizosphere were evaluated on a daily basis taking into account inputs from irrigation water and losses due to deep drainings and plant uptake.

Five year simulation runs for two of the experimental soils revealed that short term hazards are to be expected only in soils with a limited Mo adsorption capacity. In such soils the inputs of molybdenum into the rhizosphere should match the losses by deep percolation and plant uptake. If deep percolation was avoided then 20-30 ppb Mo in irrigation water was the maximum tolerable concentration to produce non-toxic alfalfa in the future. Higher Mo concentrations in irrigation water could be tolerated if leaching by over-irrigation is economically feasible.

In soils able to adsorb as much as 2-3 ppm Mo, forages are less likely to become toxic within a 5 year period. If Soil 9 was irrigated with water from Brantner ditch with an average Mo content of 100 ppb, the model predicted development of toxic forages within 15 years. After 25 years the accumulation of Mo in the soil caused alfalfa to contain as much as 14 ppm Mo.

The molybdenum simulation model is simplistic and makes various assumptions with respect to the mechanism of Mo uptake and transfer to the shoots. A worthwhile research problem would be to investigate whether the Mo uptake is indeed controlled by the Mo concentration in solution and the amount of water transpired by the plant. Studying Mo uptake from hydroponic solutions of known Mo concentration under various environmental conditions affecting the rate of transpiration may give some answers to this problem.

Despite the assumptions being made, the Mo model seems to predict Mo content in alfalfa quite accurately, and is sensitive to soil parameters as well as irrigation parameters. The model indicates that safe levels of Mo in irrigation water depend on the soil being considered and

the period of time this water is being applied. Absolutely safe waters should not contain more than 25 ppb Mo.

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Appendix A

Yields, Mo concentrations, and soil test results for alfalfa (Alf.), clover (Clo.) and bluegrass (Blg.) grown in the greenhouse on selected Colorado soils.

Soil	Mo application (ppm)	Yield (grams)		Mo conc. (ppm)		H ₂ O	Extr. Mo (ppm)	
		Alf.*	Clo. Blg.	Alf.	Clo. Blg.		DTPA	(NH ₄) ₂ CO ₃
2	0	0.95		4.7		0.028	0.028	0.86
	0.5			9.4				1.06
	1.0			11.7				1.43
	2.0			15.0				2.02
3	0	2.44	3.20 5.05	1.0	1.1 3.1	0.007	0.010	0.20
	0.5			3.0		0.024		0.67
	1.0			5.2		0.049		0.99
	2.0			8.2		0.066		1.30
4	0	1.23	2.00 3.60	1.3	1.1 2.9	0.005	0.004	0.24
	0.5			3.8		0.023		0.71
	1.0			5.5		0.039		1.31
	2.0			8.9		0.080		2.05
5	0	2.93		1.3		0.010	0.018	0.37
	0.5			3.0		0.025		0.72
	1.0			4.4		0.051		1.01
	2.0			8.4		0.092		1.94
6	0	3.39		7.7		0.166	0.071	0.71
	0.5			17.4		0.264		1.31
	1.0			-		-		-
	2.0			45.0		0.520		2.44

*Average for all treatments

Appendix A: (Cont.)

Soil	Mo application (ppm)	Yield (grams)		Mo conc. (ppm)		H ₂ O	Extr. Mo (ppm)	
		Alf.*	Clo.	Alf.	Clo.		DTPA	(NH ₄) ₂ CO ₃
7	0	3.79		12.3		0.164	0.074	1.44
	0.5			22.4		0.330		1.74
	1.0			39.0		0.516		2.35
	2.0			45.2		0.560		3.09
8	0	2.89		3.9		0.048	0.021	0.20
	0.5			17.5		0.274		0.57
	1.0			29.0		0.500		1.06
	2.0			74.0		1.21		1.55
9	0	3.47	4.48	8.7	32.2	0.134	0.072	0.67
	0.5			14.3		0.166		0.94
	1.0			24.3		0.360		1.19
	2.0			33.0		0.616		2.13
10	0	5.72		4.2		0.042	0.044	0.33
	0.5			13.5		0.225		0.72
	1.0			16.9		0.264		1.13
	2.0			33.9		0.642		1.82
11	0	1.40		21.1		0.368	0.172	1.79
	0.5			25.6		0.420		2.30
	1.0			38.3		0.526		2.84
	2.0			49.5		0.920		--

*Average for all treatments

Appendix A: (Cont.)

Soil	Mo application (ppm)	Yield (grams)		Mo conc. (ppm)			H ₂ O	Extr. Mo (ppm)		
		Alf.*	Clo.	Blg.	Alf.	Clo.		Blg.	DTPA	(NH ₄) ₂ CO ₃
12	0	2.46			12.7		0.190	0.070	0.71	
	0.5				26.0		0.400	1.01		
	1.0				37.9		0.623	1.36		
	2.0				69.0		1.26	1.89		
13	0	2.85	3.83	3.93	38.2	69.2	11.1	0.346	2.57	
	0.5				51.9				0.540	2.72
	1.0				58.2				0.740	2.93
	2.0				71.5				1.51	3.85

*Average for all treatments