INTERACTION OF ADDED GYPSUM IN ALKALINE SOILS WITH UPTAKE OF IRON, MOLYBDENUM, MANGANESE, AND ZINC BY SORGHUM*

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ABSTRACT

Experiments with tomato plants in nutrient cultures indicated previously that Mo accentuated Fe deficiency at low levels of available Fe. This interaction may be important in alkaline soils where pH favors a low Fe availability and high Mo availability from native soil levels. When such interactions exist, this information will help interpret the relationship between response predicted by a soil test for available Fe and actual response. This interaction was confirmed in six soils where sorghum plants showed an increase in Fe uptake and/or Fe concentration as Mo was decreased by adding $CaSO_4$ at 30 ppm of S. The Ca SO_4 decreased Mo from 2.33 to 1.26 ppm and increased Fe from 56 to 65 ppm in sorghum. An increased in Mo supply above native levels decreased the Fe concentration from 57 to 51 ppm and Fe uptake from 369 to 306 ug/pot in sorghum. Also, $CaSO_4$ consistently increased Mn concentrations from 70 to 90 ppm, Zn from 56 to 80 ppm and Mg from 2760 to 3090 ppm, in sorghum. Knowledge of these interactions will help interpret plant responses to natural levels of these micronutrients in soils and disturbed lands or to induced levels from sewage, other wastes, and from fertilizers.

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INTERPRETIVE SUMMARY

In alkaline and calcareous soils, typically located in semiarid regions, many palnt species may exhibit symptoms of iron chlorosis indicated by yellow or pale green leaves with a darker green near the veins. A high pH in such soils usually decreased available iron and this condition was generally the cause of iron chlorosis. In some soils, well supplied with available molybdenum, however, the plants absorbed less iron and became deficient in this nutrient. Uptake of molybdenum by sorghum was decreased by adding gypsum ($CaSO_4$) at a rate of 30 ppm of sulfur. This decrease in molybdenum uptake increased Fe uptake and/or Fe concentrations in sorghum in six test soils and increased the yield. Addition of iron chelate (sequestrene-138 or Fe EDDHA) in separate treatments likewise increased the yields indicating a low supply of native available iron. An addition of gypsum offered a less expensive way, however, to improve the iron supply to plants in these soils. Gypsum also increased magnesium, manganese, and zinc concentrations in the sorghum.

INTRODUCTION

In alkaline and calcareous soils, typically located in semiarid regions, many plant species exhibited symptoms of iron chlorosis indicated by yellow or pale green leaves with a darker green near the veins. A high pH in such soils usually contributed to a low supply of available iron and this condition was generally the cause of iron chlorosis. In some of these soils, well supplied with available Mo, however, the plants absorbed less Fe and became deficient in the nutrient.

Experiments with tomato plants (Lycopersicon esculentum Mill., var. Marglobe) in nutrient culture indicated that Mo accentuated Fe deficiency at low levels of available Fe (Gerloff et al., 1959; Kirsch et al., 1960). When Mo was added at low Fe levels, yields were depressed. Addition of Mo at high Fe levels increased yields. As the Mo supply was increased, higher Fe levels were required to obtain maximum yields at all Mn levels. This interaction of Fe and Mo could be important in alkaline soils where pH favors a low Fe availability and a high Mo availability from native soil levels (Gerloff et al., 1959). If such interactions exist, this information would help interpret plant responses in soils and disturbed lands to natural levels of these micronutrients or to induced levels from sewage, other wastes, and fertilizers.

The purpose of this paper is to report an experiment designed to test the hypothesis that an interaction operates in plant uptake between Fe and Mo in alkaline soils. Other experiments have shown that Mo uptake was reduced in plants by increasing sulfate levels in the soil (Stout et al., 1951; Reisenauer et al., 1963; Gupta and Munro, 1969; Jones and Ruckman, 1973). Therefore, a gypsum treatment was included to test an associated hypothesis that $CaSO_4$ would increase the Fe availability to plants in those soils where an Fe x Mo interaction exists. The Fe uptake would increase presumably because the SO_4^{-2} would depress MoO_4^{-2} uptake.

METHODS AND SOILS

Six soils were collected from eastern Colorado for the experiment. Two selective criteria were followed in choosing the soils, i.e. a pH above 7 and absence of gypsum in the 0-30 cm layer. The pH and extractable nutrients found in the soils are listed in Table 1. The variable treatments for each soil are shown in Table 2. The Fe was added as Fe EDDHA (ethylenediaminedi-o-hydroxyphenylacetic acid), S as gypsum ($CaSO_4 \cdot 2H_2O$), and Mo as sodium molybdate (Na_2MoO_4). Each soil received a uniform treatment of 5 ppm Zn as ZnDTPA (diethylenetriaminepentaacetic acid), and 200 ppm N as $Ca(NO_3)_2$ and KNO_3 (one-half N as each form). The Platner sandy loam did not receive P. The Stoneham loam received 25 ppm P and the other soils received 50 ppm P, all as concentrated superphosphate. There were three replications.

The amendments were added to 2 kilograms of soil, mixed, and the treated soils and the control were placed in two-liter containers. The test crop was Sorghum (Sorghum bicolor (L.) Moench. var. RS-610). Water was added daily or as needed to a level equivalent to .33 bars suction. The plants were grown during the period January 16 to March 12 in a greenhouse. The above ground portion of the plants were harvested, dried at 70^oC, weighed, and ground in a Wiley mill for analyses.

Following wet digestion of the above-ground plant material with nitric and perchloric acids, analyses were made for Fe, Mn, and Zn (atomic absorption), for Mo (Johnson and Arkley, 1954; Bradford et al., 1965), and for S (Bardsley and Lancaster, 1965). Extractable soil nutrients (Table 1) were measured by the following methods: $NaHCO_3$-soluble P (Watanbe and olsen, 1965); DTPA extractable Fe and Zn (Lindsay and Norvell, 1969; soluble SO_4 in .016 M $Ca(H_2PO_4)_2$ (Fox, et al., 1964); and anion-exchangeable Mo (Bhella and Dawson, 1972; Jackson and Meglan, 1975).

Table 1. Extractable Nutrients and pH in Soils

Soil	pH (paste)	P	S	Mo	Fe	Zn
		-------PPM-------				
Stoneham l.	7.60	27	1.25	.20	10.4	1.57
Platner sa.l.	7.50	50	4.60	1.35	7.2	2.90
Otero f.sa.l.	7.50	7.8	2.50	.09	3.4	.46
Anselmo f.sa.l.	7.45	14	1.50	.10	3.4	1.37
Keith si.l.	7.75	9.4	1.25	.45	3.6	1.13
Bridgeport l.	7.70	6.1	3.85	.18	4.6	1.06

Table 2. Soil Treatments

No.	Fe	S	Mo
		------PPM------	
1	0	0	0
2	5	0	0
3	0	30	0
4	0	0	.062
5	5	30	0
6	5	0	.062
7	0	30	.062
8	5	30	.062

RESULTS AND DISCUSSION

The yield of sorghum, concentrations of Fe, Mo, S, Mn, Zn, and Fe uptake are shown in Table 3 in relation to treatments. Iron chelate increased yields in five of the six soils. Iron chelate did not increase yield on the Platner sandy loam, but gypsum significantly increased yield. Gypsum significantly increased yield in four of the six soils, i.e. Shoneham, Platner, Otero, and Anselmo. The combination of Fe chelate and $CaSO_4$ significantly increased yields over either treatment alone in three of the six soils, i.e. Otero, Anselmo, and Keith. Added Mo had no effect on yield of sorghum.

Table 3. Yield of sorghum and concentrations of Fe, Mo, S, Mn, and Zn in plants as affected by treatments.

Soil	Treatment	Yield g/pot	Fe	Mo	S	Mn	Zn	Fe Uptake ug/pot
			---ppm---					
Stoneham	0	12.0	62	1.5	650	58	33	745
Loam	Fe	13.6	64	.8	755	48	34	876
	S	13.9	71	.8	1175	75	40	988
	Mo	11.5	55	2.9	773	54	32	624
	Fe + S	14.3	72	.5	1108	53	35	1024
	Fe + Mo	14.7	65	2.0	817	46	30	952
	Fe + S	14.1	71	1.4	1450	71	33	972
	Fe + Mo + S	14.5	71	1.0	1333	50	33	1028
Platner	0	8.4	63	1.5	892	61	81	527
Sandy	Fe	9.2	82	1.2	1275	36	71	751
Loam	S	10.0	75	.8	1542	87	96	748
	Mo	8.0	57	4.9	958	83	72	459
	Fe + S	10.7	75	.6	1200	38	57	804
	Fe + Mo	8.8	78	4.1	1225	45	61	691
	Mo + S	9.9	70	2.6	1408	85	91	689
	Fe + Mo + S	9.8	73	2.4	1358	42	67	711
Otero	0	1.7	51	1.7	508	36	55	84
Fine	Fe	9.5	62	.9	600	14	37	587
Sandy	S	13.2	55	1.0	955	40	61	726
Loam	Mo	1.4	37	6.6	600	28	65	54
	Fe + S	16.2	73	.6	875	21	39	1173
	Fe + Mo	10.7	74	5.0	502	14	40	785
	Mo+ S	14.1	63	3.3	943	55	66	883
	Fe + Mo + S	15.5	74	2.8	967	27	44	1150
Anselmo	0	2.4	49	2.0	570	65	55	117
Fine	Fe	11.6	62	.9	557	18	34	718
Sandy	S	9.6	53	.9	1350	82	78	514
Loam	Mo	2.6	49	8.2	604	62	63	128
	Fe + S	16.3	69	.7	978	30	42	1119
	Fe + Mo	11.9	57	3.7	649	20	41	674
	Mo + S	7.6	57	4.0	1433	72	91	432
	Fe + Mo + S	16.6	70	2.1	1008	27	40	1163
Keith	0	4.4	62	2.6	687	107	63	273
Fine	Fe	11.6	75	1.0	670	45	48	862
Sandy	S	5.3	49	1.4	1658	150	143	264
Loam	Mo	4.3	38	9.5	649	100	63	164
	Fe + S	16.3	53	.6	1143	44	46	864

	Fe + Mo	12.9	57	4.7	640	37	50	737
	Mo + S	5.6	50	5.4	1723	132	128	282
	Fe + Mo + S	16.5	59	2.0	777	44	46	971
Bridgeport	0	8.6	54	4.7	783	93	50	469
Loam	Fe	13.0	50	3.0	887	46	42	644
	S	9.6	52	2.6	1507	109	62	492
	Mo	9.0	46	7.6	770	83	47	409
	Fe + S	14.3	52	2.2	1407	56	42	751
	Fe + Mo	11.2	58	5.5	960	64	39	651
	Mo + S	10.6	52	4.1	1500	106	61	536
	Fe + Mo + S	13.6	57	3.3	1373	64	42	769
	LSD (.05)	1.4	7.3	0.9*	126	9.8	4.4	100
	(within soils)			1.5				

*0.9, native Mo levels; 1.5, added Mo.

Two primary objectives were tested in this experiment. The yield responses and nutrient concentrations will be examined in relation to these two objectives:

A. Evidence of a Fe and Mo interaction.

Yield variations were inconclusive as evidence for this interaction with respect to initial or added Mo levels, because Mo had no effect on yields. Since five of the six soils were deficient in available Fe, based on yield response, presumably the depressive effect of added Mo on Fe concentration in the plants did not produce and additional decrease in yield. Added Mo decreased the Fe in the plants from 56.8 to 50.8 ppm and Fe uptake from the 369 to 306 ug/pot (average for six soils). The effect of added Mo on the plant's Fe concentration is shown in Figure_1 for each soil. The depressive effect of Mo on the plant's Fe concentration was evident on five of the six soils. Omitting the Anselmo, added Mo decreased the plant's Fe from 58.4 to 46.5 ppm. The reason is unknown for the different behavior of the Anselmo in Fig. 1. The data indicated generally that a reciprocal relationship existed between available Mo and available Fe in these soils.

Iron chelate decreased the Mo concentration in sorghum as shown in Table 3. In Figure 2 Mo Concentrations are shown for the control and added Mo treatments. Added Mo increased the plant's Mo concentration in all soils (an estimated value was used for the Otero soils because of an insufficient sample for analysis). Data in Fig. 3 and Fig. 4 showed that Fe chelate decreased the plant's Mo concentration for native Mo levels and for soils with added Mo.

The effect of Fe chelate on the plant's Mo concentration was difficult to interpret because large changes in yield were usually associated with added Fe which could cause a dilution effect of Mo concentration. However, small changes in yield occurred in response to added Fe chelate in the Stoneham soil (Table 3), where Fe chelate decreased the plant's Mo concentration and total Mo uptake. These data indicated an Fe x Mo interaction.

Gerloff et al., (1959) found that Mo and Mn affected Fe availability in tomato. As Mo was increased in the nutrient solution from .067 to 6.7 ppm, the yield of tomato was decreased from 3.28 to .39 g. These decreases correlated with a marked intensification of Fe chlorosis, although the Fe concentration of the tops remained constant at near 30 ppm. These authors suggested that Mo accentuated Fe deficiency because an insoluble Fe molybdate precipitated in the roots. They observed that increased Fe levels of the nutrient solution accentuated Mo deficiency and decreased yields.

A marked interaction between Fe and Mo with tomato plants in nutrient culture was observed by Kirsch et al. (1960), but the effects of Fe and Mo uptake by the roots differed from Gerloff's data (Gerloff et al., 1959). Molybdenum uptake by roots was decreased while uptake by leaves generally increased as Fe was added in Kirsch's experiment. Kirsch et al. (1960) implied that Fe additions stimulated Mo translocation from roots to leaves. However, the total Mo uptake by the plant was decreased by Fe additions. In this respect, the data of Kirsch et al. (1960) agreed with Gerloff et al. (1959) and both sets of data agreed with the results in Table 3.

Hanger (1965) found that excess Mo caused Fe chlorosis in red clover. By increasing the Fe concentration in a nutrient culture as Mo increased, he eliminated this symptom and he observed normal plants. He suggested that Mo blocked Fe movement from the roots to tops and interfered with a metabolic function of Fe.

Berry and Reisenauer (1967) showed that Fe accumulation by tomato tops depended on Mo levels in the nutrient solution. Molybdenum increased Fe uptake at a marginally adequate Mo level, but at a higher level, Mo decreased Fe uptake. Plants deficient in Mo showed the least Fe uptake. Iron translocation from the central vein to leaf margins was less in Mo-starved leaves. These data indicated various aspects of Fe x Mo interactions.

B. Evidence of an Fe x Mo x S interaction.

The purpose of the gypsum treatment was to determine whether SO_4 ions would reduce Mo concentration in sorghum plants. As a consequence of the Fe x Mo interaction, this SO_4 effect could increase the plant's concentration and increase yields in soils with low available Fe. The effect of added SO_4 on yields and on Fe, Mo, and S concentrations is shown in Table 3. Added SO_4 increased the plant's Fe concentration in four of the six soils as shown in Fig. 1. Added SO_4 increased Fe uptake by sorghum in all soils as indicated by data in Table 3 from average values for plants without added SO_4 compared with added SO_4. Apparently, SO_4 caused the effect on Fe by decreasing the plant's Mo concentration, as shown in Fig. 3. The SO_4 effect on Mo occurred in all six soils, with native Mo levels (Fig. 3), or with added Mo (Fig. 4).

Five of the six soils were deficient in available Fe (except Platner) since added Fe chelate increased the yield on these five soils. Added SO_4 increased yield of sorghum in four of six soils. This response could be caused by a lack of available SO_4 effect on the plant's Fe concentration. In the Stoneham loam, available SO_4 appears to be adequate for a high yield level, but added SO_4 increased the plant's Fe concentration. In this soil, the yield response or SO_4 seems to be caused by its effect on available Fe. These data supported the concept that SO_4 may increase Fe uptake by reducing Mo uptake or concentration in the plants.

Plant yields were higher with added Fe or SO_4 in two soils (Otero and Anselmo) and yields were higher with the combination treatment (Fe + SO_4) than with either treatment alone. The additive response, or interaction, was non-linear. Part of the SO_4 response may be caused indirectly to an Fe effect (as a consequence of an Fe x Mo interaction) but this kind of effect was not obvious from the yield data on these two soils. With Otero, the yields with SO_4 (and SO_4 + Mo) were in between the yields for Fe and Fe + SO_4, which indicated the added SO_4 may have corrected a small S deficiency. However, the Fe concentration increased from 51 ppm in the untreated plants to 59 ppm in SO_4-treated plants (ave. for SO_4 and SO_4 + Mo). The untreated plants were markedly Fe deficient. The plants with added SO_4 were slightly Fe deficient. Uptake of Fe (Table 3) increased from 84 ug/pot in the untreated plants to 805 ug/pot in SO_4-treated plants (ave. for SO_4 and SO_4 + Mo). These data indicated the Fe supply increase with added SO_4. Iron uptake was 687 ug/pot for Fe and Fe + Mo treatments and the soil SO_4 supply was sufficient for 10.1 g yield with adequate Fe.

A possible SO_4 effect on Fe availability for sorghum was less clear for the Anselmo compared with the Otero soil. The plant yields with added SO_4 (and SO_4 + Mo) were less than yields with added Fe (and Fe + Mo) for the Anselmo soil. This lower yield was not caused by S deficiency because the soil SO_4 supply was sufficient to produce 11.6 g with added Fe. Thus the increase in yield from added SO_4 above the control seems to be caused by an increase in Fe uptake, although the plants appeared moderately Fe deficient. Added SO_4 increase the Fe concentration from 48.5 ppm in untreated plants in 55.2 ppm in SO_4-treated plants (ave. of SO_4 and SO_4 + Mo) and increased the Fe uptake from 117 ug/pot (untreated) to 514 ug/pot with added SO_4. These data indicated that added SO_4 increased available Fe less in the Anselmo compared with the Otero. A possible explanation of this soil-plant difference may be related to the relative SO_4 effect on the plant's Mn and Zn concentrations in the two soils. (Table 3). Added SO_4 increased Mn and Zn to higher levels in the Anselmo compared with the Otero and these higher levels may have reduced the physiological effectiveness of Fe in the plants. (Olsen, 1972).

In two soils, Keith and Bridgeport, yield of sorghum increased in response to Fe chelate and the yield increased additionally to added Fe and SO_4, but added SO_4 by itself did not increase yield. Yield data offered no evidence that added SO_4 had any effect on available Fe as a result of an Fe x Mo interaction for the Keith soil. Iron concentration was less in the SO_4-treated plants showed very large increases in Mn and Zn concentrations (Table 3 and Fig. 5). In Keith silt loam, for example, added SO_4 increased the Zn concentration twofold. High levels of Mn and Zn could have interfered with the uptake of Fe and its metabolic function in the plant (Brown and Tiffin, 1962; Lingle et al., 1963; Olsen, 1972). Possibly, this large effect of added SO_4 on Mn and Zn uptake decreased the effect that SO_4 could have on Fe uptake. However, Fe uptake was 595 ug/pot for the four treatments with added SO_4 compared with 509 ug/pot for four treatments without SO_4. This difference was significant (LSD =50). Iron uptake increased from 43 to 637 ug/pot in plants without SO_4 treatment compared with plants that received SO_4 for the Bridgeport soil.

Calcium sulfate also increased the plant's Mg concentration in four of the six soils from 0.252 to .309% and Mg uptake in all soils from 22.6 to 36.3 mg/pot.

The effect of added Fe and SO_4 on the average Fe, Mn, and Zn concentrations in the plants is shown in Fig. 6 (average of Fe is for first four soils in Table 3). Added Fe decreased Mn and Zn concentrations in sorghum. Added SO_4 increased Fe, Mn, and Zn concentrations above the untreated plants. Thus, changes in the plant's Fe concentration related to added SO_4 cannot be evaluated independently from changes in Mn and Zn.

The mechanism by which $CaSO_4$ increase the plant's Fe, Mn, and Zn concentration is unknown. Calcium sulfate may lower the pH which would increase uptake of these nutrients (Lindsay, 1972). The amount of $CaSO_4$ added (30 ppm S) would produce a solution of .oo78 M $CaSO_4$) for a soil water content of 12 percent. This $CaSO_4$ concentration is quite similar to the concentration of (Ca + Mg) observed in saturation extracts of similar soils. The pH of the saturated paste was measured in the soils after cropping by sorghum as shown in Table 4. Mean values are shown for treatments 1 and 2 (no SO_4) and treatments 3, 5, 7, and 8 (with SO_4). A small decrease in pH occurred with added SO_4in three soils (Stoneham, Otero, and Anselmo). No change in pH occurred from added SO_4 in other three soils. The pH in the rhizosphere around the roots could have been higher than these measured values on the bulk soil (Riley and Barber, 1969, 1971).

Table 4. Effect of added $CaSO_4$ on soil pH of the saturated paste after cropping.

Soil	pH	
	Control	Added SO_4
Stoneham loam	7.27	7.12
Platner Sandy loam	7.85	7.81
Otero fine sandy loam	7.27	7.09
Anselmo fine sandy loam	7.65	7.37
Keith silt loam	7.67	7.59
Bridgeport loam	7.62	7.60

Control- mean value for treatments 1 and 2 (table 2)
Added SO_4- mean value for treatments 3, 5, 7, 8 (table 2)

The relationship of pH to the mechanism by which $CaSO_4$ increases the plant's Fe, Mn, and Zn concentration is not consistent for these six soils. The lower pH with added SO_4 in three soils may explain, in part, the increase in uptake, but additional experiments will be needed to confirm whether small changes in pH could account for the observed differences in uptake. Data in Table 3 showed that added SO_4 consistently increased plant uptake and Mn and Zn concentration in all six soils. Since added SO_4 had no appreciable effect on pH in three soils (less than 0.1 pH unit), a change in pH seems unlikely to be a cause of the increased uptake.

Iron, Mn, Zn will form uncharged ion-pairs with SO_4 in the soil solution (Adams, 1971), which suggests a mechanism by which SO_4 could contribute to the uptake rate. There is no evidence to support this mechanism for plants at this time.

Figure #1

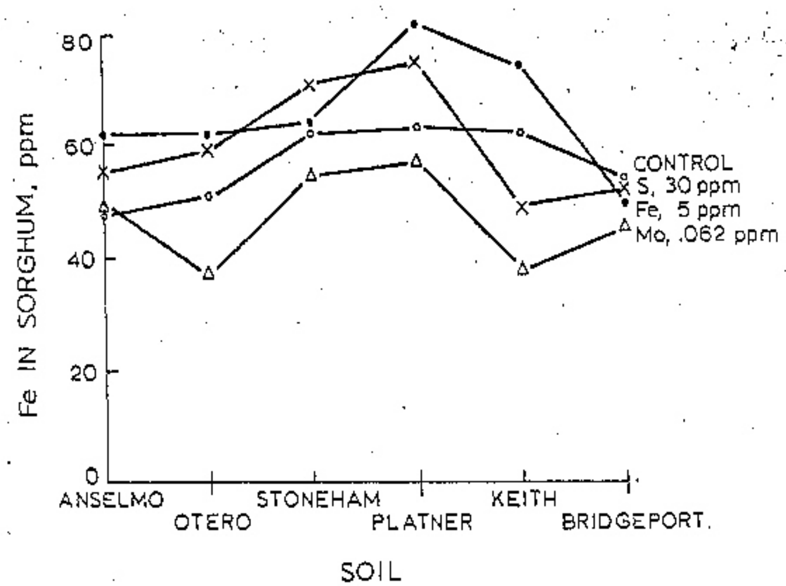


Figure #2

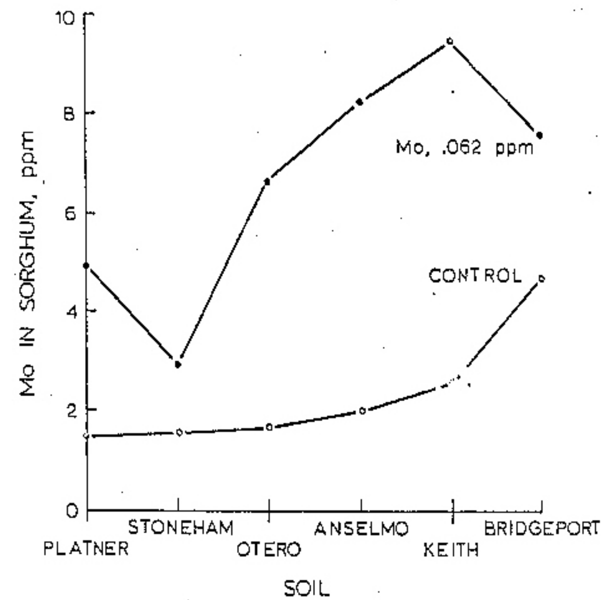


Figure #3

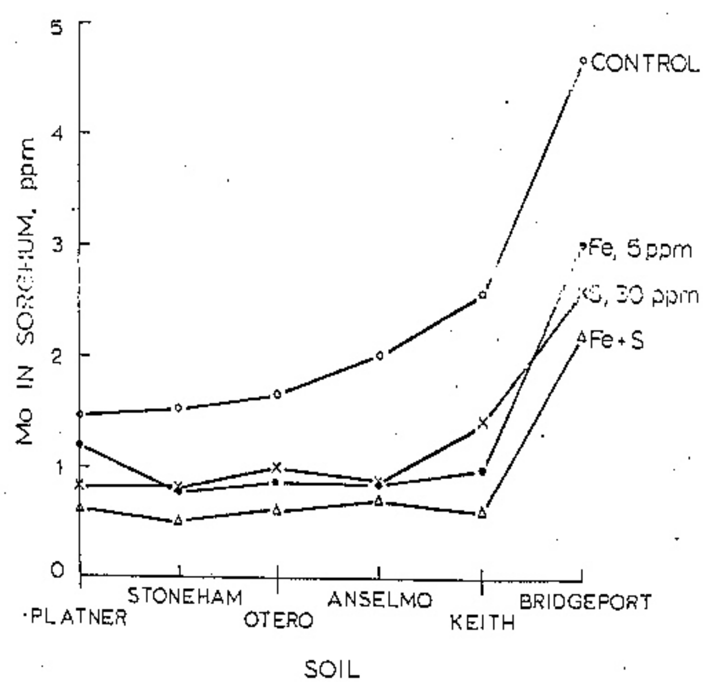


Figure #4

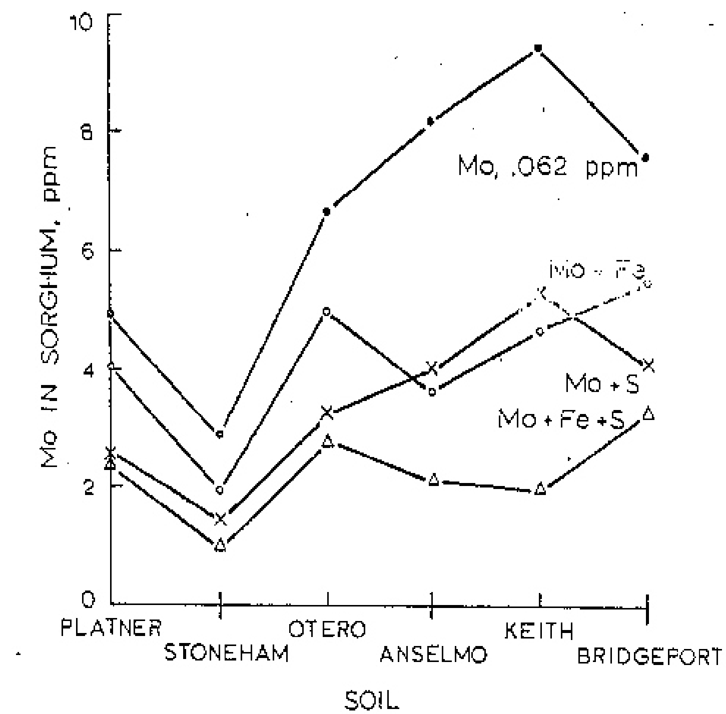
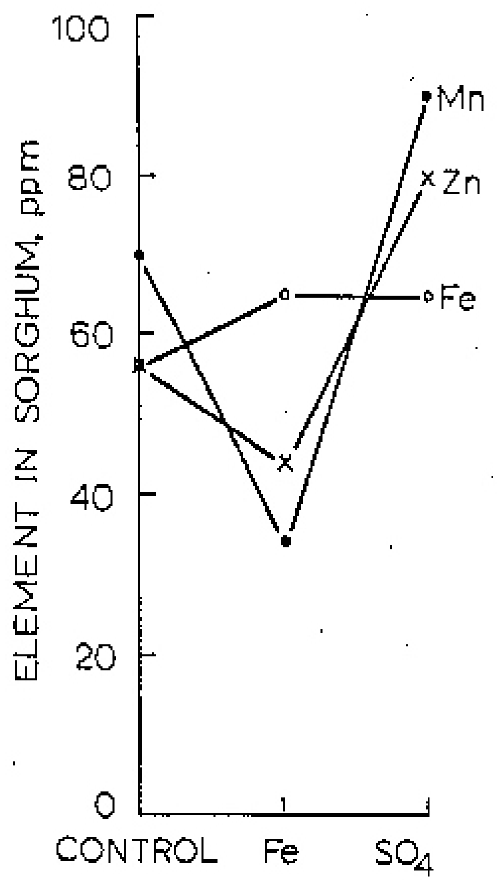


Figure #5



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