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Molybdenum uptake by beets in Dutch soils

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Abstract

In the Netherlands a soil may induce Mo-deficiency symptoms in beet if it contains more than 1 or 2% iron; whether such deficiency did occur depended primarily on pH, but particle size and kind of iron also played a role: αFe_2O_3 and $\alpha FeOOH$ sharply reduced Mo content of the plant; γFe_2O_3 had only little effect. When no molybdenum was supplied, three groups of soils could be distinguished by the interaction Mo $\times$ P: soils where P almost completely prevented Mo deficiency; soils where P aggravated deficiency; and soils where P dressing hardly affected response to Mo. Steaming soils influenced Mo content of the plant. The effect of adding Mo differed when it was supplied before from when it was supplied after steaming. Applying Mo before steaming reduced its availability but after steaming increased it. Application of manganese sulphate reduced Mo content of the plant to a degree depending on the amount of available Mo in soil. Beet could take up Mo as a cation, the cation was less effective within the plant. A scheme summarizes processes affecting the availability of Mo in Dutch soils.

Contents

1 Molybdenum deficiency in the Netherlands

1.1 Incidence of molybdenum deficiency

Molybdenum deficiency in the Netherlands was first detected by Mulder. In 1954, after his first trials (with water cultures) he obtained some Australian soils of which it was known that clover responded favourably to molybdenum applications (Mulder, 1954). These soils were slightly acid and rich in bog-ore. Later he tested similar Dutch soils along brooklets in low moor areas. He found molybdenum deficiency in cauliflower and legumes grown on these soils.

Mulder's results prompted us to further investigate the occurrence of molybdenum deficiency. Sugar beet was used as an indicator plant because it is a most sensitive agronomic crop. It is true that cauliflower and spinach are even more sensitive to molybdenum deficiency, but since they are grown on a limited scale only, their use as indicator plants would have meant pot trials with every soil.

Molybdenum deficiency was observed on soils along the rivers Vecht, Regge, Schipbeek (Overijssel), Berkel, Vordense Beek, Oude IJssel and Hummelose Beek (Gelderland), Aa (Noord-Brabant), Oude Diep (surroundings of Hoogeveen), along some rivers in eastern Groningen and Drenthe, on soils developed on Meuse sediments, e.g. near Venlo and very frequently, around 's-Hertogenbosch. These soils are quite similar. The topsoil contains much iron and some clay, while the subsoil consists of sand with small silt lenses, with or without iron. Comparable soils, but mixed with peat, occur in the Nieuw-Weerdinge (Drenthe) area.

On these soils, beet was molybdenum-deficient if the pH (measured with the Hellige Truog pH meter) was below 6.0 (= pH-KCl ca 5.4).

Molybdenum deficiency was found too on the Randwijk Experimental Farm of the Research and Advisory Institute for Field Crop and Grassland Husbandry on a field of the reservation; its poor phosphate status perhaps enhanced the symptoms.

On Pleistocene sands and on 'dalgronden'[1], molybdenum deficiency occurred only in river valleys and on fields irrigated with effluent from potato-starch factories. In the village of De Krim (Overijssel), this resulted in an estimated reduction in beet yields of 60%. Molybdenum deficiency was also found near Smilde (Drenthe) on similar sands.

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1. Reclaimed cutover high-moorland, peat remnants covered with about 20 cm humiferous sand.

Table 1. Data on the cultivated layer of some river deposits showing molybdenum deficiency in the beet crop.

Origin	River	Fe_2O_3 soluble[1] in 10% HCl (%)	Loss ignition (%)	Fraction $< 16\,\mu m$ (%)	pH-KCl
Anerveen 1	Vecht	19.3	7.7	15	5.3
Anerveen 2	Vecht	3.0	3.2	7	4.4
Hellendoorn	Vecht	3.0	7.1	9	4.1
Brucht	Vecht	6.5	3.8	9	4.6
Bathmen 1	Schipbeek	28.4	12.1	24	5.1
Bathmen 2	Schipbeek	36.0	5.7	21	4.9
Bathmen 3	Schipbeek	20.2	5.9	27	5.3
Vorden	Vordense Beek	4.2	6.4	18	4.4
Wichmond 1	Vordense Beek	7.9	5.3	12	4.7
Wichmond 2	Vordense Beek	20.7	7.9	16	5.0
Rosmalen	Maas	6.5	11.1	72	3.9
Lithoyen	Maas	5.7	6.6	64	3.8
Asten	Astense Aa	7.2	9.0	6	5.2
Onstwedde	Ruiten A	11.6	4.4	12	3.9
Nieuw Weerdinge	Mussel A	7.6	19.1	13	4.9

1. See Appendix.

1.2 Description of the molybdenum-deficient soils

To find whether molybdenum-deficient soils have characteristics in common, they were examined further with assistance from the Soil Survey Institute at Wageningen. Because these soils contain much iron, it seems desirable to give a general description of the pedological characteristics of iron-rich soils before reporting specifically on the soils that were studied.

On soils without accumulation or eluviation of iron a relation existed between the soil fraction $< 50\,\mu m$ and iron content (Pons, 1959). Knibbe (1966) reported that iron content of soils along the IJssel was somewhat above one-tenth of the clay ($< 2\,\mu m$) content, and he suggested to consider the iron content relative to the clay percentage rather than the absolute amount. If the iron content is higher than expected on the basis of the clay content, the soil has been 'enriched' with iron.

The iron[2] content of these molybdenum-deficient soils may vary considerably. Comparison of the iron content with the fraction $< 16\,\mu m$ shows that all soils are iron-rich by Knibbe's criterion, because the iron content is already at least 0.1 of the fraction $< 16\,\mu m$ (Table 1).

The iron in the soil may be distributed in different ways. In 'rodoorn' soils it is uniformly distributed, the soil being uniformly red or reddish to a depth of 20 to

2. In the following referred to as Fe_2O_3; this is the amount of iron compounds extracted with 10% HCl and calculated as Fe_2O_3.

Table 2. Main characteristics of soils under crops showing molybdenum deficiency.

Place	River	Unit[3]	Degree of mottling (o) or rodoorn (+)[1]	Texture of profile[2]	Depth of G horizon (cm)
1 Bathmen	Schipbeek	38	+++	cl/s	90
2 Between Mariënberg and Hardenberg	Overijsselse Vecht	38	+++	cl/s	120
3 Den Ham	Regge	38	o	s	60
4 Almen	Berkel	38	++	cl/s	70
5 Hackfort	Vordense Beek	38	+	s	100
6 Wichmond	Vordense Beek	38	++	s	80
7 Dichteren	Oude IJssel	22	−	cl	>120
8 Kreynenberg	Hummelose Beek	38	+++	cl/s	60
9 Nuland I	Beerse Maas	41	++	cl/s	80
10 Nuland II	Maas	8	+	cl/p/s	100
11 Nuland III	Maas	8	+	cl/p	100
12 Lithoyen	Maas	26	o	cl	>120
13 Maren	Maas	26	o	cl	>120
14 Someren I	Astense Aa	38	+	s/p/s	90
15 Someren II	Astense Aa	38	+++	s/p/s	90
16 Baarlo I	Maas	21	o	cl	80
17 Baarlo II	Maas	22	−	cl	>120
18 Dubbroek	Maas	38	+++	cl/p	90
19 Zuidbroek I	Munte	8R	+++	cl/p/s	80
20 Zuidbroek II	Munte	8R	+++	cl/p/s	90
21 Muntendammerdiep	Munte	8R	++	s/p/s	70
22 Smeerling	Ruiten A	38	o	s/p/s	80
23 Vledderhuizen	Mussel A	38	++	s/p/s	90
24 Ter Apel	Ruiten A	38	+++	s	90
25 Moersloot	Ruiten A	38	++	s/p/s	90
26 Nieuw Weerdinge	Vledderdiep	37	+	s/p/s	90
27 Eerste Exloërmond	Hunze	37	+	p/s	60

1. + = weakly; ++ = moderately; +++ = strongly rodoorn; o = mottled; − = not mottled.
2. cl   = clay or loamy texture to a depth of >120 cm.
   cl/s   = clay or loamy texture to a depth of 50–120 cm.
   s   = sandy texture.
   cl/p   = clay or loamy texture, peat at 60–80 cm.
   cl/p/s = 20–30 cm clay or loamy texture, peat with sand at 80–120 cm.
   s/p/s   = 20–30 cm sand over peat with sand at 80–120 cm.
   p/s   = peat with sandy subsoil at 80 cm.
3. According to Edelman (1950).

40 cm; in rusty soils it occurs as mottles. These mottles are usually soft, but may be concreted into crumbs (a few millimeters in diameter), cylinders, often hollow pipes (ore pipes), or sometimes plates or large pieces of slag. Hence the characteristic difference between a rusty and a 'rodoorn' soil is not the iron content but its distribution. Strongly rusty soils may become uniformly reddish through cultivation.

Table 2 lists the chief characteristics of the soil of fields with molybdenum deficiency, together with their mapping units according to Edelman (1950). The topsoil of all soils reported in this table was more or less red due to iron. Many of the soils examined were 'rodoorn', either weakly (+), moderately (++) or strongly (+++). Some soils were mottled (0).

Soils 7 and 17 were alfisols developed on Pleistocene river deposits. They are identical to 16, except that 16 was mottled below 20 cm. Soil 17 showed brick-red spots caused by a field-oven, but some distance away an old river course was filled up with a strongly 'rodoorn' sandy loam. Although 7 and 17 were classified as 'not mottled' (−), they were clearly reddish. The impression was that molybdenum deficiency in alfisols on Pleistocene river deposits occurs only when they are reddish. This would agree with the patchiness of molybdenum deficiency on these soils.

The molybdenum-deficient soils are almost always in or near river basins. Hence they are practically limited to the Pleistocene part of the Netherlands. The watertable of these soils is usually high with a range of 80–130 cm in summer and 20–60 cm in winter.

The G-horizon (the permanently reduced subsoil), which is light-brown in peat soils and blue-grey in mineral soils, is usually at 60–120 cm. Seepage may occur from higher ground nearby.

These soils are often used as grassland, because they are low-lying. But fealure of field crops through molybdenum deficiency may well have contributed.

The subsoil usually consists of sand with little silt and clay. A characteristic feature of these soils is the absence of calcium carbonate, though ferrous carbonate (siderite) is frequently present, especially in iron-rich peat soils.

1.3 Discussion

That fields with molybdenum deficiency are rich in iron does not justify the converse conclusion that the occurrence of molybdenum deficiency is a characteristic of these soils. This would be true only – even though logically not permissible – if also other soils of the same kind elsewhere in the Netherlands exhibited molybdenum deficiency at low pH. If so, molybdenum deficiency would not necessarily have to occur in all the instances where both conditions are met (low pH and presence of iron); other factors could prevent this.

To test this, samples were collected from soils with a range of iron contents, of which was not known whether or not molybdenum deficiency occurred. They belonged partly to Edelman's mapping units (1950) mentioned in Table 2, partly to other units and they were used for a pot trial with beet and spinach (Table 3).

Table 3. Occurrence of molybdenum deficiency and growth of beet and spinach on iron-rich soils.

Soil type and origin	General soil characteristic	Unit[1]	pH-KCl	Fe_2O_3	P-Al	P-value	Mo deficiency		Growth	
							beets	spinach	beets	spinach
Gley soils										
1 Woudenberg	brown	39	4.0	1.02	61	1.8	no	yes	good	fair
2 Rijsbergen	brown	38	4.4	3.84	12	0.5	no	yes	good	poor
3 Zwartebroek	black	39	3.9	0.64	11	0.5	no	no	fair	poor
4 Terschuur	black	39	4.6	0.83	29	1.8	no	no	good	good
5 Klein Achterveld	black	39	4.7	0.44	25	1.5	no	no	fair	fair
Plaggen epipedon										
6 Hamersveld	brown A_1	45	3.7	1.18	41	2.0	yes	yes	poor	poor
7 Driebergen	brown A_1	45	4.3	0.41	47	2.8	no	no	good	good
8 Mussedorp	black A_1	45	4.3	0.63	61	6.8	no	no	poor	fair
9 Zeumeren	black A_1	45	3.8	1.97	8	0.5	yes	yes	fair	poor
10 Hoevelaken	black A_1	45	3.6	1.16	24	0.8	no	no	fair	poor
River levee soils										
11 Cothen		25	3.8	2.38	5	0.5	no	no	fair	fair
12 Bunnik		25	3.8	2.22	3	0.3	light	yes	fair	poor
13 Leur		25	4.6	4.72	5	0.5	no	yes	good	good
14 Ingen I		25	3.8	2.64	30	3.5	no	yes	good	poor
15 Ingen II		25	4.1	3.51	25	2.3	yes	yes	fair	poor
16 Houten[2]		25	4.4	1.97	37	6.5	no	no	good	good
17 Werkhoven[2]		25	3.7	1.83	5	0.5	no	no	good	fair
River basin Clay soils										
18 Pollenkamp		23	4.0	3.80	2	0.3	light	yes	good	poor
19 Tielerwaard	subsoil	23	6.9	6.07	15	0.3	no	no	good	fair
20 Tielerwaard	topsoil	23	4.1	6.43	14	0.5	yes	yes	good	good
Mixed soils										
21 Leersum		41	3.9	2.42	20	0.5	yes	yes	fair	poor
22 Hogerheide-Woensdrecht		41	3.7	4.13	16	0.0	yes	yes	poor	poor
23 Koewacht		41	4.0	3.63	23	1.8	no	yes	good	fair
24 Karnemelkspolder		41	4.2	1.52	52	5.5	no	no	good	good
Marine clay										
25 Ierseke		5	4.4	3.51	41	4.8	no	no	good	good
Peat with clay cover										
26 Abcoude		8	4.0	3.99	18	0.5	no	no	good	fair

1. According to Edelman (1950).
2. Decalcified river levee soil with weakly developed brown podsoloic characteristics (Alfisol) intergrading to unit 22.

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This means that the independent variable (iron content) is now under consideration, while in the foregoing the dependent variable (deficiency symptoms) formed the starting point in our observations.

Table 3 gives information about the various soils used and about the growth of the test crops. The black gley soils were low in iron; they gave no molybdenum deficiency in the crops; but on the brown soils, spinach, which is much more sensitive did.

The A_1 in soils with a 'plaggen' epipedon is thought to be man-made, either by the spreading of heather litter from stables (black A_1), or by applying forest litter and grass sods from river valleys (brown A_1). These soils were included in the pot experiments because their iron contents may be either low or reasonably high (Pape, 1970). One of the brown (7) and one of the black (8) soils was low in iron; neither exhibited molybdenum deficiency.

In the discussion of the profile descriptions the hypothesis was advanced that alfisols on Pleistocene river deposits would not show molybdenum deficiency unless they were clearly rusty or reddish. These soils (16 and 17) were therefore included. Plants grown on them showed no symptoms, in spite of the high iron contents (almost 2%). The same was observed in the field. Thus it seems that the form of iron rather than the total percentage determines whether or not deficiency occurs.

The molybdenum-deficient soils along the River Meuse in Noord-Brabant are either 'mixed soils' (Table 2; Sample 9), river basin clay soils (Table 2; 10 and 11) or river levee soils (Table 2; 12 and 13). Some similar soils from the provinces of Utrecht and Gelderland were included in the pot trial. Again, it was not known whether they were molybdenum-deficient: four out of the five river levee soils induced symptoms in spinach, two in beet.

The test plants grown on the basin soils also exhibited molybdenum deficiency. In the Tielerwaard both the topsoil (20) and the subsoil (19) were sampled. The subsoil was high in pH and free of molybdenum deficiency; the topsoil was low in pH and induced symptoms.

Four 'mixed soils' (21, 22, 23 and 24) were investigated. Three of them induced symptoms in spinach; two of them in beets. Sample 24 had a high phosphate status, which perhaps prevented molybdenum deficiency.

In Zeeland, reddish and strongly mottled marine clay soils are found locally, represented by soil 25 from Ierseke. Both test plants remained healthy, perhaps because it was rich in phosphate (P-value 4.8).

The last soil listed in Table 3 is a peat with clay cover. Against expectation, it induced no symptoms.

1.4 Conclusions

All soils with a Fe_2O_3 content of 1–2% or higher (soluble in 10% HCl), may be subject to molybdenum deficiency. Whether it actually occurs depends primarily on pH, although other factors may also play a role as will appear from the fol-

lowing chapters.

These iron-rich soils include rodoorn soils, gley soils, river levee soils, basin soils, mixed soils, and old arable lands with a plaggen epipedon. In the introduction to this chapter, the occurrence of molybdenum deficiency on the experimental farm at Randwijk was treated as a more or less isolated case, but as it is on a river basin clay, the occurrence of molybdenum deficiency fits into the general pattern.

Although alfisols contain as much iron as river levee soils, they induce no symptoms. They are, however, much older and have been leached more.

One of the characteristics of molybdenum-deficient soils is their relatively high iron content coupled with a low pH. This prompted us to investigate the influence of iron.

2 Influence of iron on the incidence of molybdenum deficiency

2.1 Literature data

The interaction between molybdenum and iron in water culture has been studied by Katherine Warington (1956). It occurred partly inside, partly outside the plant. Kirsch (1960) reported that addition of iron to nutrient cultures stimulated molybdenum transport from the roots to the leaves, but reduced uptake of molybdenum. Stout et al. (1951) and Barshad (1951) found that molybdenum was bound as anions to clay minerals. Stout et al. demonstrated that OH^- liberated previously sorbed molybdate and Barshad showed that adsorption of molybdate decreased with pH. Jones (1957) studied molybdate sorption by clay minerals as well as by ferric oxide and aluminium oxide. Sorption of molybdate by the oxides, as well as by the clay minerals, was pH-dependent. Maximum sorption occurred at low pH. For neutral soils fixation was in the order ferric oxide $>$ aluminium oxide $>$ metahalloysite $>$ nontronite $>$ kaolinite.

Jones also studied the solubility of sodium molybdate in solutions of $FeCl_3$ and $AlCl_3$ in relation to pH. Solubility in $FeCl_3$ solution was minimum at pH 2.7 and in $AlCl_3$ at pH 4.8. From an analysis of the precipitate Jones concluded that the precipitated iron was not iron molybdate but a polymolybdate. The fact that ferric oxide binds such high quantities of molybdenum led Jones to sorption experiments in soils rich and poor in iron. An iron-rich soil sorbed much more molybdate than an iron-poor soil. After removal of the iron from the iron-rich soil both soils retained almost equal amounts of molybdate. Retention was greatest at low pH.

The work of Jones agrees well with the results of Williams & Moore (1952). Through chemical analysis of plants and soils, they arrived at the equation:

$$\lg 100 \, [Mo] \text{ (in the plant)} = a \, pH - b \, [Fe] + c$$

where Fe constitutes the content of iron soluble in 6 N HCl.

Wells (1956) reported that iron concretions are rich, and aluminium oxide poor in molybdenum. He concluded that molybdate is bound to amorphous oxides, but remains available to the plant. During maturation of basaltic soils, the exterior surface area of the amorphous oxides decreases, as crystals grow, so that less molybdenum is retained but in such a way is no longer available. The form rather than the amount of iron oxides seemed to determine the sorptive capacity. Molybdenum present as an impurity became unavailable as the iron oxide crystallized.

He therefore considered that retention of molybdate, as found by other authors, did not necessarily, cause molybdenum deficiency.

The scheme shows the relation between the various iron compounds in the soil (Weenig, 1951).

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hydrolysis of ──────→ βFeOOH              oxidation of Fe(OH)₂
FeCl₃                  time                or iron rust
                        │                      │
                        ↓                      ↓
oxidation of  ──────→ αFeOOH              γFeOOH (lepidocrocite)
ferrous salt          (goethite)          dehydration
solutions             dehydration         at low temperature
                        │                      ↑
                        ↓        heating        ↓
           αFe₂O₃ (haematite) ←───────────── γFe₂O₃ (maghaemite) ←──── yellow amorphous
                        ↑        (slow at 20°C)      ↑                 ferric hydroxide
                        │                            │
           heating in autoclave            careful heating
           at 150-160°C                    Fe₃O₄ (magnetite)
                        ↑
           red amorphous
           ferric hydroxide
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The work of Perkins & King (1944) showed that haematite (αFe_2O_3) and limonite ($\alpha FeOOH$) strongly fix phosphate, but that magnetite does not.

The small iron concretions, found locally in the Veluwe area (central Netherlands), consist of γFe_2O_3 (Weenig, 1951). Town refuse also contains γFe_2O_3. According to van der Marel (1951), γFe_2O_3 occurs in 'rodoorn' soils. The bog-ore, frequently found in the north-eastern of the Netherlands consists of $\gamma FeOOH$ (van der Marel). Van der Marel believes that γFe_2O_3 must occur in all sediments rich in iron and organic matter, especially when this material has been heated, as on sites of prehistoric fires, in town refuse and as in peat soils burnt during reclamation.

2.2 Iron content of the soil

Pots were filled with soils with a wide range of Fe_2O_3 (soluble in 10% HCl), but practically equal in pH-KCl in each group. The soils were dressed with sodium molybdate and yield of beet was estimated (Table 4).

Table 4 shows that yield increases due to sodium molybdate varied considerably between soils almost identical in pH. The differences were not related with the Fe_2O_3 contents. The P-value seemed to have some effect, since the soil responding least to molybdenum had the highest P-value in 3 pH groups. Indeed Mulder (1954) and others showed that phosphate supply influences availability of molybdenum.

2.3 Particle-size distribution of iron in soil

Although the content of iron does not determine the availability of molybdenum, its particle-size distribution in the soil may well. The literature shows that iron oxide sorbs molybdate but does not establish that sorbed molybdenum is unavail-

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Table 4. Increase in yield (%) with dressings of 7.065 mg sodium molybdate per pot on various soils with equal pH, but varying in iron content (1.5 kg soil per pot, 6 weeks old plants, average of 3 replicates).

pH-KCl	Yield increase (%)	Fe_2O_3 in 10% HCl	P-value[1]	P in citric acid	Humus (%)	Fraction $< 16 \mu m$ (%)	K-value	Reducible Mn (ppm)
4.4	48	3.0	3.8	23	3.2	7	42	89
	198	5.1	1.0	15	4.9	15	21	115
	389	4.2	0.6	10	6.4	18	35	190
	457	1.8	0.8	15	3.3	9	43	93
4.7	133	2.6	3.0	49	4.7	15	45	74
	175	24.5	0.3	8	10.9	18	14	203
	402	7.9	0.5	11	5.3	12	10	156
5.0	43	7.3	5.0	42	7.6	18	28	172
	114	20.7	0.9	11	7.9	16	12	185
	370	1.7	0.8	21	3.4	8	51	122
5.6	14	3.6	0.8	13	5.2	17	14	261
	223	35.1	1.0	9	9.9	14	30	62
5.8	112	27.4	0.3	7	13.9	30	11	93
	197	31.7	1.0	13	9.0	14	25	59

1. See appendix.

able to the plant. Consequently we have checked whether addition of iron concretions to a non-deficient soil would decrease the availability of molybdenum. If deficiency resulted from molybdenum occlusion, iron concretions taken from molybdenum-deficient soils should not cause molybdenum deficiency in a healthy soil. But if decreased availability of molybdenum were due to adsorption on concretions, addition of concretions to a healthy soil could well decrease the availability of molybdenum. If so, particle-size distribution of iron would be crucial, since a certain amount of iron in fine particles has a greater adsorptive surface than in coarse particles.

Thus iron concretions of different origin were added to a sandy soil of pH-KCl 4.2, on which beet developed no molybdenum deficiency symptoms. 'Red sand' from the Veluwe was used too, but because it was in short supply, only 75 g (5%) of it was added instead of the 150 g (10%) in the other trials. In addition the same series of soils were supplied with molybdenum.

Table 5 shows that molybdenum uptake from this soil was satisfactory and that a dressing of sodium molybdate caused a high content of molybdenum in the leaves. Material from the ochre horizon sharply lowered the molybdenum content of the leaves, especially of plants dressed with molybdenum.

Thus added molybdenum is rendered almost completely unavailable; it seems to be more strongly fixed than native molybdenum. The difference may also be due

Table 5. Effect of adding iron to a sandy soil without molybdenum deficiency on molybdenum uptake by beet.

Origin of iron	Quantity (g per 1.5 kg soil)	pH-KCl after dressing	Mo in leaves (mg/kg DM)	
			no Mo dressing	with Mo dressing[1]
Control	0	4.2	0.63	15.40
Balkbrug (ochre layer)	150	4.3	0.16	1.22
Eastern Netherlands (concretions)	150	4.3	0.28	3.39
Onstwedde (concretions)	150	4.8	0.44	7.55
Red sand	75	4.3	0.52	16.55

1. 2.65 mg $Na_2MoO_4.2H_2O$/pot.

to the molybdenum concentration. Added bog-ore from the eastern Netherlands and Onstwedde also reduced molybdenum uptake, albeit to a lesser extent. Added 'red sand' had no effect on the molybdenum content of the plant, insofar as the data with the smaller amount of iron could be compared.

To determine whether size of the iron concretions affects molybdenum uptake, bog-ore from Onstwedde was fractionated by sieving. Of each fraction, 150 g was mixed with 1350 g of soil.

Table 6 shows that the finest fraction gave the greatest reduction in molybdenum content of the plant. Without added molybdenum the fraction < 0.3 mm reduced the molybdenum content by almost 75%, whereas for the fraction 3.4–4.6 mm this was only 27%. When sodium molybdate was added, these fractions lowered the content by 96 and 50%, respectively.

Although molybdenum uptake decreases with decreasing fraction size of the iron,

Table 6. Effect of size of iron concretions on molybdenum uptake by beet.

Fraction (mm)	Amount added g/pot[1]	pH-KCl	Mo in leaves (ppm)	
			without Mo	with Mo[2]
	0	4.2	0.63	15.40
3.4 – 4.6	150	4.8	0.44	7.55
2.0 – 3.4	150	4.8	0.23	6.29
1.0 – 2.0	150	4.8	0.50[3]	5.08
0.6 – 1.0	150	4.8	0.30	3.46
0.3 – 0.6	150	4.8	0.24	1.39
<0.3	150	4.7	0.16	0.67

1. Each pot contained 1500 g soil.
2. 2.65 mg $Na_2MoO_4.2H_2O$/pot.
3. Leaves contaminated by leakage water from the glasshouse.

Table 7. Molybdenum in beet leaves after adding various fractions of iron concretions to the soil[1] (average of 3 replicates).

Substrate (g)		Fraction 2–2.5 mm, not ground				Fraction 2–2.5 mm, ground to <0.5 mm				Sieved fraction <0.5 mm			
soil	iron concretions	pH-KCl	Fe_2O_3 (%)	Mo in leaves (ppm)		pH-KCl	Fe_2O_3 (%)	Mo in leaves (ppm)		pH-KCl	Fe_2O_3 (%)	Mo in leaves (ppm)	
				−Mo	+Mo[2]			−Mo	+Mo[2]			−Mo	+Mo[2]
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)
1500	0	3.67	0.53	0.22	4.77	4.02	1.90	0.18	1.65	3.91	2.00	0.15	1.31
1470	30	3.93	1.53	0.27	4.35	4.27	2.90	0.13	0.90	4.06	2.85	0.10	0.77
1440	60	4.26	2.65	0.36	6.26	4.75	5.37	0.13	0.69	4.45	5.24	0.13	0.41
1380	120	4.79	4.72	0.38	8.41	5.16	7.67	0.09	0.63	4.87	7.70	0.07	0.41
1320	180	4.98	6.62	0.45	13.20	5.52	10.47	0.09	0.55	5.12	9.89	0.09	0.38
1260	240	5.38	8.53	0.66	6.71	5.82	12.80	0.10	0.55	5.30	12.08	0.09	0.30
1200	300	5.60	11.70	0.67	9.76								

1. Iron concretions from Onstwedde; soil from Zuidlaren.
2. +Mo = 2.65 mg $Na_2MoO_4.2H_2O$/pot.

the finer and coarser fractions were not identical, because the material was sieved. So in another pot trial the effect of adding various amounts of a coarser fraction, both in their original form and ground to < 0.5 mm was compared. The sieved fraction < 0.5 mm was included. Table 7 shows that the < 0.5 fractions, whether obtained by grinding or by sieving, caused a marked decrease in molybdenum content of leaves.

Unlike Table 6, the effect of the 2.0–2.5 mm fraction which was used to prepare the < 0.5 mm fractions was positive. This reversal seems unreal, since iron concretions raised the pH-KCl of the soil (Table 7, column 3). Obviously the positive effect on pH counteracted the negative effect of iron concretions. The pH also increased with more of the fine fractions added (columns 7 and 11), but then its effect was too small to cancel the decrease in molybdenum content of the leaves (columns 10 and 14).

In conclusion, molybdenum deficiency on iron-rich soils is not necessarily a consequence of molybdenum occlusion during formation of iron concretions, but is rather a result of adsorption on the iron particles. The availability of molybdenum would therefore be expected to depend closely on the surface area of the particles.

2.4 Types of iron compounds in the soil

Section 2.3 has shown that particle size of iron concretions in the soil is crucial for molybdenum uptake by the plant. Different types of iron oxides were then compared to see whether they behaved in the same way.

X-ray analysis at the Physics Laboratory of Philips Ltd showed that the iron concretions from Onstwedde, as used in the previous trial contained $\alpha FeOOH$, αFe_2O_3 and amorphous components, and that the ochre layer from Balkbrug contained αFe_2O_3. This data disagrees with that of van der Marel, who reported that γFe_2O_3 is found in rodoorn soils and $\gamma FeOOH$ in 'bog-ore' (Onstwedde).

To test the influence of different iron oxides on molybdenum content of the plant, synthetic $\alpha FeOOH$, αFe_2O_3 and γFe_2O_3 were added to a soil from Zuidlaren. The αFe_2O_3 was obtained by heating $\alpha FeOOH$ in a muffle furnace for a few hours at 600°C. The $\alpha FeOOH$ became paramagnetic after being heated for some time during which already some of the water had disappeared. The end-product (αFe_2O_3) however was not paramagnetic.

Each pot contained 1600 g soil, to which 100 g of the different forms had been added. Furthermore, 100 g bog-ore of the < 0.5 mm fraction was added to a few pots. Beet was the test crop. Colour was assessed after 21 and 29 days.

Table 8 shows that the plants in the pots with 100 g αFe_2O_3 developed severe molybdenum deficiency symptoms. The plants in the bog-ore treatment were also definitely paler than the controls. The γFe_2O_3 treated pots yielded plants of the same colour as the controls. The colour of plants in the $\alpha FeOOH$ and bog-ore treatments improved gradually between the 21st and 29th day indicating that molybdenum deficiency was alleviated.

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Table 8. Influence of synthetic iron oxides on molybdenum uptake by beet leaves (averages of 3 replicates).

Substrate	Colour rating[1] after		Dry matter yields after 29 days (g/pot)	Mo content after 29 days (ppm)
	21 days	29 days		
1600 g soil	7.0	7.9	2.49	0.24
1600 g soil + 100 g αFeOOH[2]	4.3	6.5	1.85	0.12
1600 g soil + 100 g αFe$_2$O$_3$	1.7	2.3	0.94	0.08
1600 g soil + 100 g γFe$_2$O$_3$	7.1	7.3	1.82	0.18
1600 g soil + 100 g bog-ore <0.5 mm	5.3	6.4	2.90	0.11

1. Low rating plants yellow; high rating plants green.
2. We thank Dr G. W. van Oosterhout of the Physics Laboratory of Philips Ltd, Eindhoven, for analysing and supplying αFeOOH and γFe$_2$O$_3$.

Table 9. The influence of synthetic iron oxides on colour (indicating molybdenum deficiency) stand, molybdenum and phosphate content of beets.

Substrate 1600 g soil	Content of molybdenum and phosphate				Colour rating[1] after 21 days		Stand after 21 days	
	without Mo		with Mo[2]		−Mo	+Mo	−Mo	+Mo
	Mo ppm	P$_2$O$_5$%	Mo ppm	P$_2$O$_5$%				
untreated	0.20	1.88	1.33	1.65	9.0	9.0	9.3	9.1
+ 111 g αFeOOH	0.06	1.51	0.16	1.38	5.3	8.0	5.3	4.3
+ 100 g αFe$_2$O$_3$	0.18	1.27	0.15	1.34	4.1	4.0	2.9	4.9
+ 100 g γFe$_2$O$_3$	0.13	1.48	0.42	1.45	8.5	10.0	8.0	7.3
+ 100 g bog-ore (<0.5 mm)	0.07	1.08	0.20	1.00	5.8	9.0	7.6	9.3

1. Low rating plants yellow; high rating plants green.
2. 1.45 mg Na$_2$MoO$_4$.2H$_2$O/pot.

Plants in the αFe$_2$O$_3$ treatment showed a very low molybdenum content and a very low dry matter yield, in conformity with the symptoms. Molybdenum content of the plant at harvest in αFeOOH was obviously lowered. Added γFe$_2$O$_3$ reduced the molybdenum content only slightly.

These data point to a considerable difference between the influence of αFe$_2$O$_3$ and γFe$_2$O$_3$ on molybdenum uptake by the plant, but they do not indicate whether there is a difference between αFeOOH and αFe$_2$O$_3$, because 100 g αFeOOH contains 63 g Fe, whereas 100 g Fe$_2$O$_3$ contains 70 g Fe.

Therefore in another pot trial, the pots received an extra 11 g αFeOOH (Table 9). The plants in 100 g αFe$_2$O$_3$ and 111 g αFeOOH grew more slowly than the controls. Without molybdenum, they showed severe symptoms of molybdenum deficiency, as did the plants in pots with bog-ore added.

In the αFe_2O_3-treatment the application of molybdenum had no effect: the symptoms of molybdenum deficiency remained. Crop analysis did not reveal any difference in molybdenum content between plants that did and did not receive molybdenum. But molybdenum content was higher than expected from the severe symptoms, perhaps because crop samples were contaminated with soil. Washing did not remove all the soil from the leaves, which were red due to presence of αFe_2O_3. Added $\alpha FeOOH$ on bog-ore lowered the molybdenum content so much that the plants exhibited symptoms of molybdenum deficiency. Molybdenum dressing obviously raised the molybdenum content of plants of both treatments, but less than without iron oxides. Added γFe_2O_3 hardly affected development of the crop, but lowered molybdenum content, though not enough to cause molybdenum deficiency.

There was, therefore, a considerable difference between γ and αFe_2O_3 in molybdenum fixation. $\alpha FeOOH$ and αFe_2O_3 behaved alike.

All added iron compounds also reduced the phosphate content of the plant. Bog-ore had the greatest effect on phosphate content of the plant (Table 9, columns 3 and 5).

In conclusion: the availability of molybdenum to the plant was primarily determined by the amount of iron oxide of a certain particle size.

The type of oxide also had an effect: αFe_2O_3 and $\alpha FeOOH$ strongly lowered the molybdenum content of the plant, γFe_2O_3 had less effect.

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3 Influence of phosphate on severity of molybdenum deficiency

3.1 Literature data

Soils with a favourable phosphate status are less likely to show molybdenum deficiency than those with an unfavourable one. Many workers report an interaction between the uptake of phosphate and molybdenum by the plant.

The work of Stout (1951) showed that phosphate dressing considerably raised the molybdenum content of the plant, especially when molybdenum was supplied too. Addition of sulphate inhibited molybdenum uptake. Experiments with radioactive molybdenum showed that the leaves, and not roots, were responsible for the differences in molybdenum content between the phosphate and sulphate treatments. Transport from the roots was enhanced by phosphate but inhibited by sulphate.

Barshad (1951) suggested that phosphate converted molybdate into phospho-molybdate ion, which is more easily absorbed. Mulder (1954) reported that, in general, phosphate dressing had no effect on plant response to molybdenum and that in some soils, phosphate dressing strongly decreased plant response to molybdenum. He concluded that the phosphate liberated molybdenum in the soil, as apparent when the molybdenum content was assayed with *Aspergillus niger*. If the nutrient solution contained sufficient phosphate, phosphate had no effect on molybdenum uptake. However Rubens (1955) found that molybdenum deficiency in lettuce grown on clay soils was not overcome by phosphate: there phosphate increased response to molybdenum on clay soils whereas on sandy loams it decreased it. Williams (1956) found that phosphate reduced molybdenum content of grass: the yield response to a molybdenum dressing was greater when phosphate was applied simultaneously.

Crafts (1954) obtained a stronger response to phosphate when molybdenum was supplied. Superphosphate alone gave an increase in yield of 74%; added molybdenum resulted in an increase of 91%. Also Walker (1955) found that grass responded more to phosphate if molybdenum was supplied simultaneously.

3.2 Own trials

Evidently the literature on the influence of phosphate on molybdenum deficiency and molybdenum uptake are contradictory. This prompted us to determine once more, in pot trials, the response of beet to molybdenum in different soils with increasing levels of phosphate (Table 10). Table 11 gives some general data on the

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Table 10. Design of pot trials with beet on the interaction between molybdenum and phosphate.

Sodium molybdate (mg per pot)	Dicalcium phosphate (g P_2O_5 per pot)			
0	0	0.177	0.530	1.06
1.766	0	0.177	0.530	1.06
3.532	0	0.177	0.530	1.06
7.065	0	0.177	0.530	1.06

3 replicates. Content of pots 1.5 kg soil. General dressing: 0.3 g N per pot as NH_4NO_3, 0.53 g K_2O per pot as K_2SO_4, 0.075 g MgO per pot as $MgSO_4$. Plants harvested about 6 weeks after emergence.

Table 11. General data on the soils used in trials on the interaction between phosphate and molybdenum in beet.

Origin	Map unit[2]	pH-KCl	Org. matter (%)	Fraction <16 μm (%)	P-value	P-citr	K-HCl	Reducible Mn[1] (ppm)	Fe_2O_3 soluble in 10% HCl (%)
1 Hardenburg I	38	5.2	4.9	16	0.5	5	17	89	26.7
2 Hardenburg II	38	4.5	2.5	10	0.5	11	10	265	4.5
3 Stadskanaal I	37	5.5	20.3	17	0.5	23	16	118	22.4
4 Brucht	38	4.8	3.0	12	0.3	13	20	802	11.0
5 Oss	8	3.8	11.3	63	0.8	11	19	194	6.1
6 Vorden	38	4.2	4.6	22	1.0	9	24	148	5.3
7 Bathmen	38	5.1	6.5	23	0.5	5	15	94	31.4
8 Stadskanaal II	37	4.8	25.0	14	0.6	19	24	88	25.6
9 Hedel	26	4.4	5.5	54	1.0	16	10	286	4.2

1. Leeper method.
2. According to Edelman (1950).

soils; Table 12 supplies the results.

Figure 1 shows the effect of sodium molybdate on yield for the different soils. The lines were obtained by three-dimensional graphical fitting. From the results (Fig. 1; Table 12) the molybdenum-deficient soils can be divided into three groups:
a. Soils 1, 2, 3 and 4 where phosphate almost completely overcomes the molybdenum deficiency. When these soils were dressed with sufficient molybdenum, they did not respond to phosphate.
b. Soils 5 and 6 where phosphate aggravates the molybdenum deficiency. With a molybdenum dressing crop response to phosphate increased.
c. Soils 7, 8 and 9 where phosphate dressing hardly affects the response to molybdenum.

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Table 12. Effect of sodium molybdate and dicalcium phosphate on yield of dry matter and on molybdenum and phosphate content of beet leaves (dry matter basis).

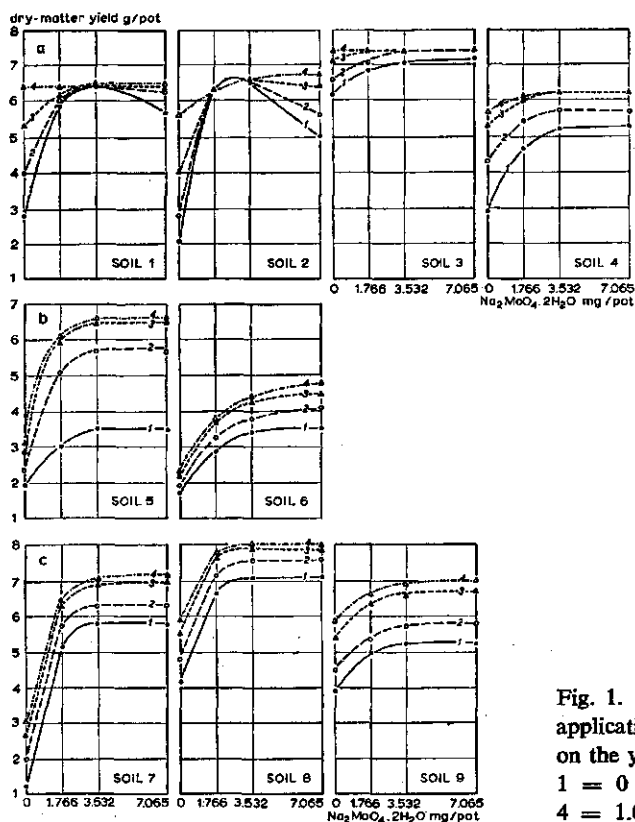| Sodium molyb-date (mg/pot)	Yield (g/pot) after P_2O_5 dressing (g/pot) of				Leaf composition after a dressing of P_2O_5 (g/pot) of							
					0		0.177		0.530		1.06	
	0	0.177	0.530	1.06	P_2O_5 g/kg	Mo mg/kg	P_2O_5 g/kg	Mo mg/kg	P_2O_5 g/kg	Mo mg/kg	P_2O_5 g/kg	Mo mg/kg
Soil 1												
0	2.8	3.7	5.1	6.3	6.7	0.08	8.0	0.06	9.3	0.06	12.2	0.08
1.766	5.9	6.8	6.4	6.1	5.9	0.14	7.4	0.16	10.4	0.24	14.7	0.35
3.532	6.2	6.2	6.0	6.2	5.0	0.21	6.3	0.25	9.2	0.36	15.3	0.56
7.065	5.4	6.4	7.1	6.6	5.7	0.32	6.7	0.50	8.8	0.64	14.3	0.97
Soil 2												
0	2.5	2.1	3.5	6.1	12.7	0.08	13.5	0.08	13.8	0.04	16.6	0.06
1.766	6.1	6.9	6.5	6.1	9.0	0.16	9.6	0.19	11.9	0.20	14.9	0.42
3.532	6.2	6.7	6.8	6.4	8.8	0.23	9.8	0.36	12.1	0.42	15.7	0.59
7.065	5.1	5.3	6.8	6.4	9.8	0.44	10.2	0.51	12.4	0.67	15.7	1.17
Soil 3												
0	5.8	6.1	7.1	7.1	7.1	0.08	8.5	0.07	10.1	0.08	11.2	0.12
1.766	7.4	7.7	7.6	7.5	7.2	0.29	8.3	0.32	10.0	0.44	12.3	0.49
3.532	6.4	6.8	6.8	7.2	7.0	0.38	8.1	0.41	9.6	0.51	11.7	0.64
7.065	7.4	7.8	7.7	8.0	7.8	0.60	9.2	0.76	10.8	0.97	12.6	1.35
Soil 4												
0	2.5	4.0	5.0	5.7	10.0	0.07	10.4	0.06	11.9	0.06	14.7	0.09
1.766	5.3	6.3	6.8	6.1	8.3	0.18	9.0	0.23	12.3	0.38	15.3	0.45
3.352	4.8	5.7	6.3	5.7	8.0	0.32	10.1	0.44	11.3	0.58	15.8	0.70
7.065	4.8	5.6	6.3	6.1	8.6	0.57	9.7	0.85	12.1	0.88	15.9	1.39
Soil 5												
0	1.6	2.4	2.5	2.7	4.3	0.00	6.2	0.00	9.1	0.01	14.1	0.02
1.766	3.1	5.2	7.0	6.1	4.5	0.05	5.3	0.06	5.9	0.04	10.0	0.17
3.532	3.1	6.0	6.4	6.9	3.9	0.10	4.5	0.05	6.4	0.21	9.8	0.27
7.065	3.6	5.6	6.5	6.2	4.1	0.25	5.4	0.24	6.4	0.37	9.9	0.42
Soil 6												
0	1.2	2.0	1.7	2.3	9.9	0.00	5.9	0.00	14.8	0.00	13.3	0.00
1.766	3.4	3.1	4.5	3.4	5.4	0.06	6.3	0.03	7.1	0.15	14.0	0.19
3.532	2.9	3.8	4.9	3.2	5.2	0.07	6.3	0.18	9.0	0.19	13.5	0.26
7.065	3.7	4.4	4.0	5.8	5.3	0.34	6.2	0.39	8.7	0.45	12.6	0.67
Soil 7												
0	0.9	1.4	2.8	2.3	9.2	—	11.0	(0.07)	10.0	0.05	11.9	—
1.766	5.6	6.8	6.6	6.7	6.1	0.10	6.2	0.12	7.7	0.14	8.0	0.20
3.532	5.5	5.9	5.7	7.2	5.9	0.15	6.1	0.17	7.8	0.17	8.3	0.26
7.065	6.1	6.5	7.0	8.0	6.0	0.21	6.5	0.29	7.6	0.45	8.9	0.48
Soil 8												
0	3.9	4.5	5.3	5.6	8.8	0.04	10.1	0.04	10.9	0.06	12.2	0.04
1.766	7.2	7.5	8.2	8.2	8.2	0.23	9.9	0.29	11.9	0.33	12.7	0.33
3.532	6.5	7.3	7.8	8.1	8.6	0.29	9.3	0.32	12.1	0.47	13.5	0.44
7.065	7.3	7.8	7.8	7.6	7.0	0.46	8.6	0.61	11.3	0.73	14.1	0.75
Soil 9												
0	3.4	4.4	5.5	6.1	5.6	0.01	8.1	0.04	10.0	0.05	15.8	0.10
1.766	5.2	5.8	5.6	6.9	4.8	0.19	6.4	0.32	11.5	0.37	16.1	0.48
3.532	5.2	5.2	6.5	7.4	5.0	0.29	6.5	0.45	9.7	0.54	14.8	0.77
7.065	5.5	5.8	6.4	6.7	5.9	0.56	7.7	0.74	10.6	0.88	15.6	1.05

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dry-matter yield g/pot
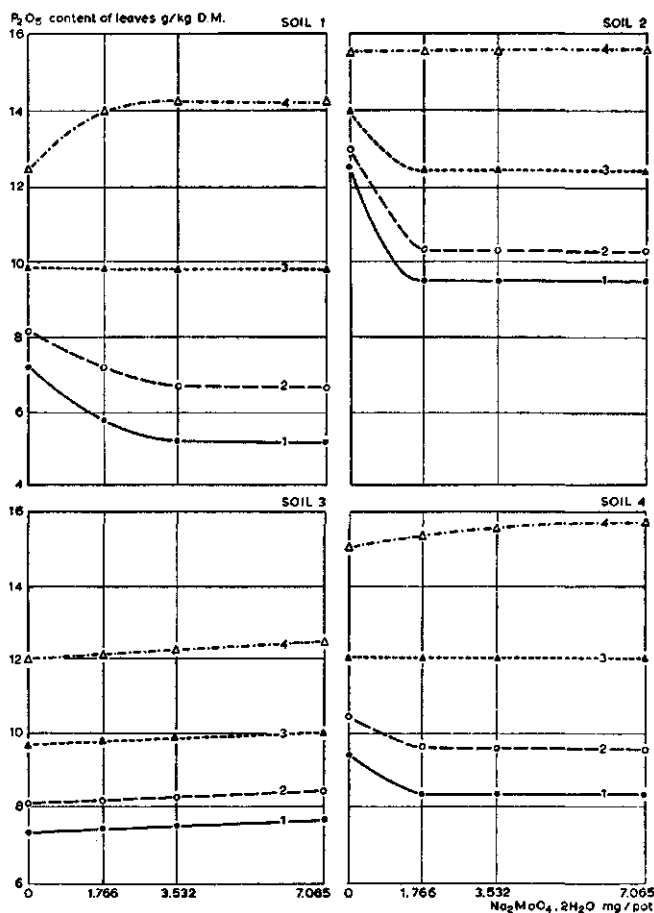
Fig. 1. The effect of sodium molybdate application at different phosphate levels on the yield of beets (adjusted).
1 = 0 g, 2 = 0.177 g, 3 = 0.530 g, 4 = 1.06 g P_2O_5 per pot.

Group a: heavy application of P corrects Mo deficiency (soil 1, 2, 3 and 4)

Though for soils 1 and 2, the highest rate of molybdenum was detrimental to dry-matter yield, this was compensated by the phosphate. This negative response is statistically significant for both soils ($P < 0.05$).

Without molybdenum response to phosphate was obvious on these soils (Fig. 2), but with molybdenum the response almost completely disappeared. Response to phosphate was clearly, in essence, an effect of the molybdenum. In soils 1 and 2 response to phosphate returned with excess molybdenum.

In soils 1, 2 and 4, molybdenum lowered the phosphate content of the crop when little phosphate was supplied (Table 12 and Fig. 3). With a higher phosphate application, the negative effect disappeared or even changed into a positive one.

In Fig. 4 the reduction in phosphate content of the plant due to 3.532 mg sodium molybdate has been plotted against the increase in yield. The reduction can be attributed to a dilution effect caused by increase in yield. This explains the differences between the four soils: the phosphate content was lowered only if the yield increases sharply with molybdenum; if not, the phosphate content rose. This indicates that molybdenum increased phosphate uptake, though not enough to com-

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Fig. 2. The effect of dical-
cium phosphate application
on the yield of beets, with
and without added sodium
molybdate (adjusted).
+ Mo = average of 1.776
and 3.532 mg sodium mo-
lybdate per pot for soils 1
and 2; average of 1.766,
3.532 and 7.065 mg for soils
3 and 4.

pensate for the dilution effect.

Although phosphate, especially at high rates considerably increased yield when
no molybdenum was applied, (Fig. 2) the molybdenum content of the plant was
barely affected. In soils 1 and 2 content was not affected; in soils 3 and 4 only
slightly. When, however, molybdenum was applied, phosphate considerably raised
the molybdenum content of the plant (Fig. 5). The increase in molybdenum content
with 1.06 g P_2O_5/pot was about equal for the four soils: an average of 0.19, 0.34
and 0.55 mg/kg with 1.766, 3.532 and 7.065 mg of sodium molybdate per pot
respectively.

That phosphate did not lower the molybdenum content of the plant when molyb-
denum was omitted indicates, that phosphate liberated molybdenum in the soil; the
extra available molybdenum compensated for the dilution.

The plants were healthy in spite of their low molybdenum content when no mo-
lybdenum but a high level of phosphate was supplied.

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Fig. 3. The effect of sodium molybdate application at different phosphate levels on the phosphate content of beets (adjusted).
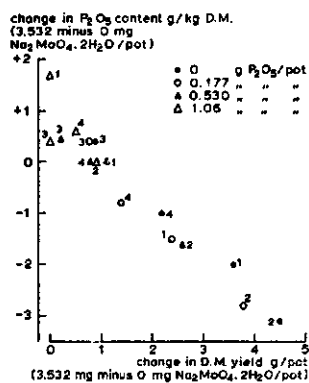1 = 0 g, 2 = 0.177 g, 3 = 0.530 g, 4 = 1.06 g P_2O_5 per pot.

Fig. 4. The relation between the yield increase due to 3.532 mg sodium molybdate and the reduction on P_2O_5 content of the plant at different levels of applied P_2O_5, for soils 1, 2, 3 and 4.
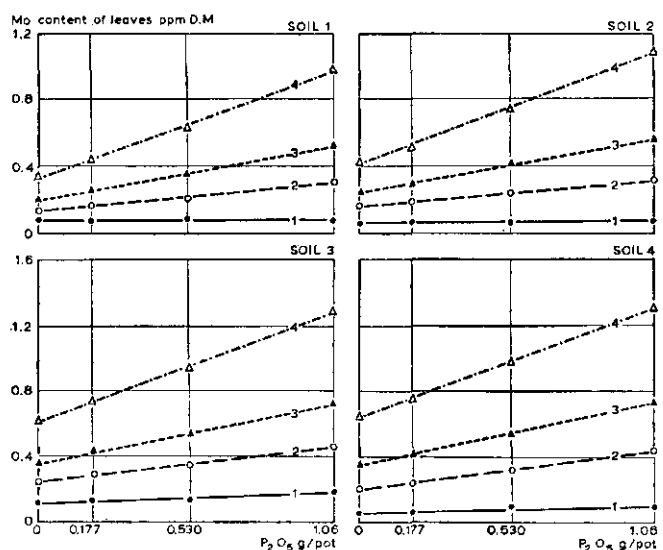
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Fig. 5. The effect of phosphate application at different levels of sodium molybdate on the molybdenum content of beets (adjusted). 1 = 0 mg, 2 = 1.766 mg, 3 = 3.532 mg, 4 = 7.065 mg $Na_2MoO_4.2H_2O$ per pot.

If the effectiveness of molybdenum in the plant were increased by phosphate, molybdenum in combination with phosphate would be more active in the plant than molybdenum alone. Hence Barshad used the term phospho-molybdenum complex. To test this, in a pot trial plants were sprayed with phosphate solution. The chlorophyll content of the plants was estimated to obtain a more exact colour rating. Table 13 shows that the chlorophyll content is increased by both means of phosphate application indicating that phosphate exerts its action on molybdenum not only via the soil, but also within the plant.

Group b: phosphate has no influence on Mo deficiency (soils 5 and 6)

Table 12 and Fig. 1 show that, in contrast to the soils of Group a, molybdenum deficiency in soils 5 and 6 persisted with high rates of phosphate. The yield increases were less without phosphate. This is more evident in soil 5 than soil 6.

Table 13. The effect of phosphate in soil and sprayed on leaves on chlorophyll content of beet leaves (average of 3 replicates).

Treatment	Chlorophyll content (mg/g)	
	fresh material	in dried material
0 Mo	0.39	5.7
0 Mo + foliar application of P_2O_5	0.72	7.8
0 Mo + 1.06 g/pot P_2O_5	0.90	9.7

I thank Dr W. van Driel (Institute for Soil Fertility) for estimating the chlorophyll.
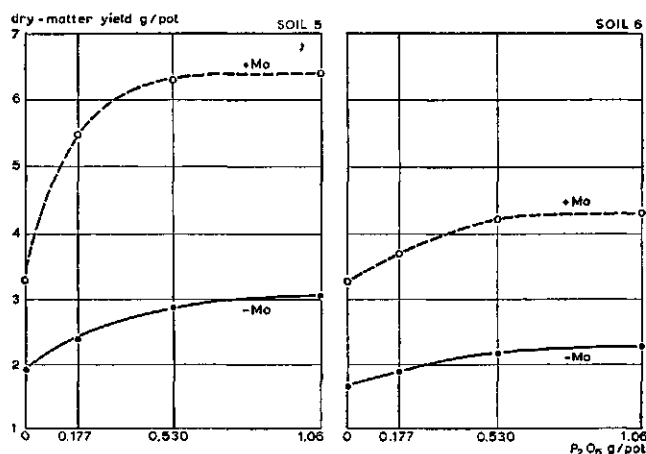
22

Fig. 6. The effect of dical-
cium phosphate application
on the yield of beets with
and without added sodium
molybdate (adjusted).
+ Mo = average of 1.766,
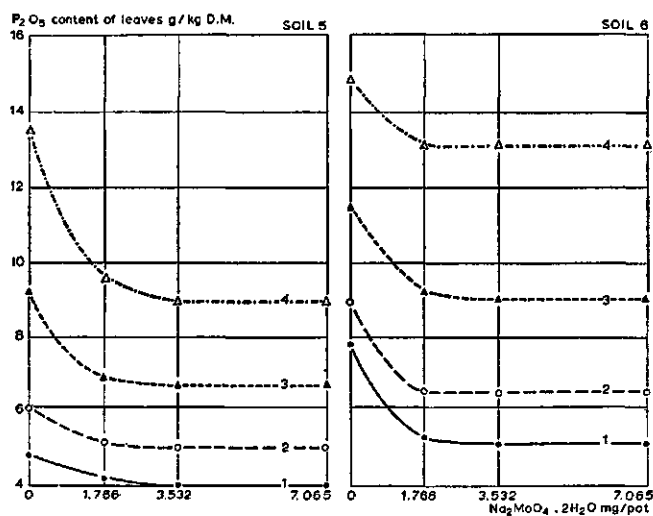3.532, and 7.065 mg sodi-
um molybdate per pot.

Fig. 7. The effect of sodi-
um molybdate application
at different phosphate lev-
els on the phosphate con-
tent of beets (adjusted).
1 = 0 g, 2 = 0.177 g,
3 = 0.530 g, 4 = 1.06 g
P_2O_5 per pot.

Thus there was a greater response to phosphate with molybdenum (Fig. 6). These
soils lacked phosphate as well as molybdenum. Response to one element was in-
hibited while the other remains deficient (Liebig's law). Table 22 in Mulder's publi-
cation (1954) shows that most of his soils also responded more to molybdenum
after phosphate application. Hence his conclusion that phosphate does not affect
plant response to molybdenum is not justified.

In Group a, molybdenum gave the greatest reduction in phosphate content of the
beet when no phosphate was applied. Fig. 7 shows that this was not so for the soils
of Group b. Corresponding with the yield increase due to molybdenum, for soil 5
the greatest decrease in phosphate content by molybdenum is found at the highest
phosphate level. For soil 6 molybdenum applications have similar effects at all
phosphate levels. The latter is in agreement with the fact that molybdenum applied
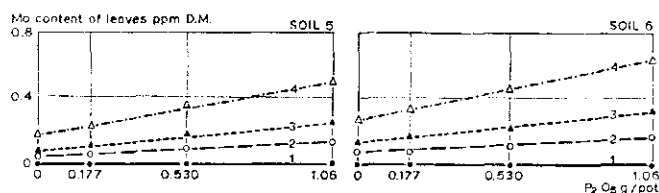
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Fig. 8. The effect of phosphate application at different levels of sodium molybdate on the molybdenum content of beets (adjusted).
1 = 0 mg, 2 = 1.766 mg, 3 = 3.532 mg, 4 = 7.065 mg $Na_2MoO_4.2H_2O$ per pot.

to this soil lowers the phosphate content of the plant almost equally for all phosphate levels.

The effect of phosphate on the molybdenum content of the plant (Fig. 8) was similar for the soils of Group a and b.

Even high rates of phosphate did not prevent the beet from developing molybdenum deficiency symptoms. Hence in these soils, phosphate did not liberate sufficient molybdenum. The availability of molybdenum was there much lower than in the soil of Group a. From the added molybdenum also less becomes available to the plant: Group b, that received 7.065 mg sodium molybdate without phosphate, the crop's molybdenum content was only 0.19 and 0.27 mg/kg, respectively; for the soils of Group a these figures were 0.35, 0.44, 0.62 and 0.64. Though for the soils of Group b dressing with phosphate increased the molybdenum content of the plant when molybdenum was applied, this increase was only about half that for the soils of Group a.

Group c: application of P did not affect response to Mo (soils 7, 8 and 9)

Fig. 1 and Table 12 show that for soils 7, 8 and 9 the yield curves for the different phosphate levels run practically parallel. Thus phosphate does not affect the crop's response to molybdenum. These three soils are not only deficient of molybdenum, but also of phosphate. But in contrast to the soils of Group b, elimination of phosphate deficiency did not alter the response to molybdenum. Yield response to an application of phosphate is practically the same whether or not molybdenum is added (Fig. 9). The effect of molybdenum dressing on phosphate content varied. For soil 7 application of molybdenum gave a strong yield response, but lowered phosphate content of the crop (Fig. 10). However this reduction decreased with increasing phosphate. In contrast with Group a, the reduction in phosphate content was not due to dilution through an increase in yield.

Though the yield increases due to molybdenum are practically equal at all rates of phosphate, also for soil 8, phosphate content was reduced most at the lowest rate of phosphate.

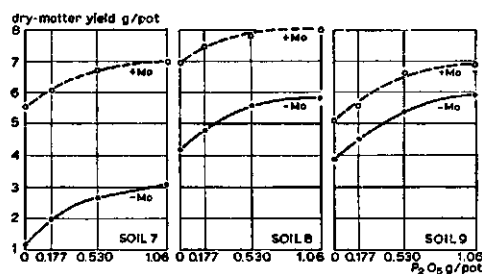The molybdenum content of beet grown on soil 7 was low even after molyb-

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Fig. 9. The effect of dicalcium phosphate application on the yield of beets with and without added sodium molybdate (adjusted). + Mo = average of 1.766, 3.532 and 7.065 mg sodium molybdate per pot.
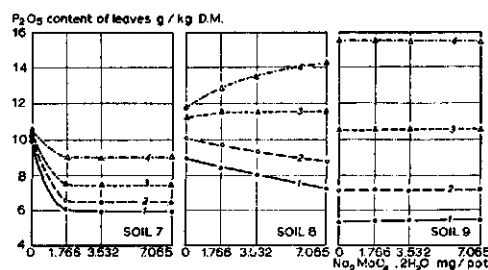

Fig. 10. The effect of sodium molybdate application at different phosphate levels on the phosphate content of beets (adjusted). 1 = 0 g, 2 = 0.177 g, 3 = 0.530 g, 4 = 1.06 g P_2O_5 per pot.
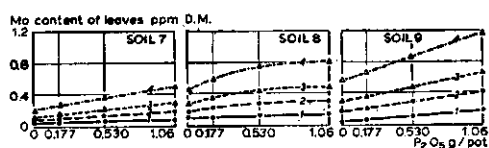
Fig. 11. The effect of phosphate application at different levels of sodium molybdate on the molybdenum content of beets (adjusted).
1 = 0 mg, 2 = 1.766 mg, 3 = 3.532 mg, 4 = 7.065 mg $Na_2MoO_4.2H_2O$ per pot.

denum application. In this respect this soil resembled the soil from Group b. For Group c, as for the soils of groups a and b, uptake of dressings of molybdenum increased with phosphate (Fig. 11).

3.3 Discussion

The results have been discussed separately for each group of soils. Here they will be discussed briefly in general.

For the soils of Group a the depression in yield could be effectively eliminated with phosphate as well as with molybdate (Fig. 1). Phosphate could also counteract yield depression caused by excess molybdenum. The effect of phosphate was indirect, since phosphate corrects molybdenum deficiency.

Fig. 2 with yield plotted against applied phosphate shows another aspect: molybdenum appeared indirectly to eliminate phosphate deficiency. But this was not so, since crop analysis demonstrated an increase in phosphate content despite the large increase in yield with phosphate.

Molybdenum, however, lowered the phosphate content of the plant when little

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or no phosphate was applied; Fig. 4 shows that this reduction could be due entirely to 'dilution' resulting from the yield increase.

In spite of the large increase in yield due to phosphate, the molybdenum content of the crop remained constant even when no molybdate was applied, and increased with phosphate if molybdate was supplied (Fig. 5). Therefore, phosphate acted by making more molybdenum in the soil available. Perhaps the molybdenum taken up by the plant was rendered more effective by phosphate, since a foliar spray of phosphate had about the same effect on chlorophyll content as a phosphate dressing (Table 13).

The soils of Group b behaved differently. Fig. 1 shows that response to molybdenum persisted even with high rates of phosphate. The response to molybdate was even greater with phosphate. Fig. 6 shows that molybdate stimulated response to phosphate. Hence the soils of Group b were deficient both of molybdenum and phosphate. Also for these soils molybdenum lowered the phosphate content of beet, because of the 'dilution effect'.

For the soils of Group b, symptoms of molybdenum deficiency persisted even with high rates of phosphate without molybdenum. Thus in these soils phosphate liberated little or no molybdenum unlike the behaviour of the soils of Group a. The effect of phosphate dressing on the molybdenum content of the plant was otherwise the same for Group b as for Group a. The main difference between the two groups was probably the molybdenum content of the soil: the molybdenum content of the plants grown on the soils of Group b were generally much lower. A definite conclusion could not be drawn without a suitable soil test.

The soils of Group c were like those of Group b in response to phosphate, because they, too remained molybdenum-deficient despite addition of phosphate. But, in contrast with Group b, phosphate and molybdenum did not interact on yield of dry-matter.

The differences in Mo $\times$ P interactions between the soils of the groups cannot be related to any soil data or the mapping units mentioned in Table 11.

3.4 Conclusions

The experiments described in the foregoing lead to the conclusion that phosphate stimulates uptake by the plant of freshly applied molybdenum.

When no molybdenum is applied, three groups of soils can be distinguished:

Group a. Soils where application of phosphate eliminates molybdenum deficiency
Possible only for soils containing sufficient molybdenum which, however, is unavailable because it is adsorbed on iron particles. Phosphate liberates this molybdenum. The fineness of the iron is an important factor in the adsorption (Chap. 2). Yield responds sharply to phosphate without molybdenum. Phosphate requirement can not actual be assessed before an adequate amount of molybdenum has been provided.

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Group b. Soils where application of phosphate increases the response to molybdenum dressing, and vice versa

These soils are governed by the law of the minimum. Presumably molybdenum deficiency does not result solely from adsorption on iron particles.

Group c. Soils without interaction between phosphate and molybdenum

As for Group b, the molybdenum content of the plant is low even after application of molybdenum.

Perhaps a high phosphate content of the plant increases the activity of the molybdenum, since foliar application of phosphate also improves the colour of molybdenum-deficient plants. The phosphate content increased with molybdenum, if there was no yield response. Hence molybdenum stimulates the uptake of phosphate.

The success of phosphate as a cure for molybdenum deficiency cannot yet be forecast. So dressings of phosphate and molybdenum are not interchangeable.

4 Effect of soil steaming on molybdenum uptake

4.1 Introduction

During the investigation I observed that reducing conditions in the soil aggravated molybdenum deficiency. Places that were heavily trodden so that their soil structure was destroyed always showed worst symptoms in the plants. Poorly drained fields were more sensitive.

Hence, perhaps, plants in a pot trial were more deficient than in the same soil in the field. Manganese however, is more available in reducing conditions. Manganese deficiency was more difficult to demonstrate in pots than in the field, because pots are supplied with more moisture and a small proportion is gas phase. Manganese deficiency showed up quickly in appropriate soils if pots were kept dry.

Steaming produces strong reducing conditions. Jager et al. (1969, 1970) and many other authors have found that available nitrogen, potassium and manganese in soil was raised by steaming; the manganese may even reach a toxic level. Jager found no clear effect of steaming on the content of water-soluble phosphate, but reported that other authors usually did.

The observations in pot and field trials suggest a decrease of the molybdenum content of the plant by soil steaming as long as other processes favouring the uptake of molybdenum do not counteract.

4.2 Own trials

To assess the effect of steaming on molybdenum deficiency, the response of beets to dressing of sodium molybdate in a steamed and unsteamed soil was investigated. Soils 5 from Oss and 7 from Bathmen (Table 11) were dressed with 0.3 g N as NH_4NO_3, 0.4 g P_2O_5 and 0.53 g K_2O as K_2HPO_4, and 0.05 g MgO as $MgSO_4.7H_2O$. The plants were harvested after 4 weeks.

All yields (Table 14) were low because of the short period of growth. A dressing of molybdenum increased them, especially if the soil had not been steamed. Contrary to expectation the plants in steamed soil that received no molybdenum showed less severe symptoms of molybdenum deficiency than those in the unsteamed soil. The molybdenum content of the plants grown on the steamed soil was clearly higher. Rather striking, however, the difference in molybdenum content between plants from steamed and unsteamed soil increased with higher rates of molybdenum (Fig. 12).

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Table 14. Effect of a dressing of sodium molybdate on yield and molybdenum content of young beet plants grown in steamed and unsteamed soil (average of 3 replicates).

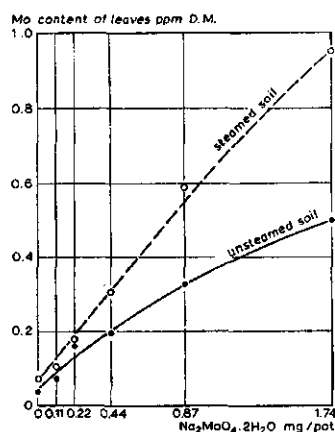| Soil	Sodium molybdate mg/pot	Dry matter yield (g/pot)		Mo content of leaves (mg/kg)	
		steamed soil	unsteamed soil	steamed soil	unsteamed soil
Oss	0	1.20	1.04	0.06	0.04
1.5 kg/pot	0.11	1.25	1.41	0.11	0.07
	0.22	1.20	1.56	0.18	0.16
	0.44	0.85	1.36	0.31	0.20
	0.87	1.27	1.31	0.59	0.33
	1.74	1.30	1.40	0.95	0.50
Bathmen	0	1.50	0.74	0.02	0.00
1.7 kg/pot	0.11	2.12	1.74	0.08	0.02
	0.22	1.94	1.84	0.09	0.04
	0.44	1.85	1.95	0.15	0.09
	0.87	1.94	1.99	0.33	0.17
	1.74	1.93	1.70	0.54	0.27

Fig. 12. The effect of sodium molybdate application on the molybdenum content of young beet plants grown in steamed and unsteamed soil from Oss.

The higher content of molybdenum could be due to an increased content of available molybdenum caused by steaming. That the lines in Fig. 12 are not parallel suggests that factors are present in the steamed soil enhancing molybdenum uptake. Perhaps steaming decreased fixation by the soil of added molybdenum. The addition of phosphate increased the molybdenum content of the plant more strongly when more molybdenum was applied (Chap. 3). Perhaps some phosphate was liberated by steaming, increasing the availability of molybdenum applied after steaming.

The trial does not show whether molybdenum was partially or completely transformed in to a form unavailable to the plant as would happen if it were reduced by steam treatment. However, a dressing of molybdenum caused a much larger

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Table 15. Effect of a dressing of sodium molybdate before and after steaming on yield and contents of molybdenum and phosphate of young beet plants.

Soil	Sodium molyb-date mg/pot	Dry matter yield (g/pot)			Composition of plant					
		un-steamed	steamed after dressing	steamed before dressing	unsteamed		steamed after dressing		steamed before dressing	
					Mo mg/kg	P$_2$O$_5$ g/kg	Mo mg/kg	P$_2$O$_5$ g/kg	Mo mg/kg	P$_2$O$_5$ g/kg
Bathmen	0	3.09	3.64	3.64	0.04	8.7	0.10	10.2	0.10	10.2
1.7 kg/pot	1.09	4.52	3.71	3.96	0.11	7.8	0.31	9.3	0.25	9.7
	2.18	4.28	3.95	3.97	0.17	7.5	0.47	10.7	0.38	10.0
	4.36	4.11	4.03	4.00	0.30	8.1	0.70	9.6	0.71	9.9
	8.72	4.85	4.03	4.36	0.48	6.9	0.95	8.9	1.23	9.6
	17.44	4.68	4.04	4.37	0.85	7.4	1.63	9.9	2.02	9.0
Hardenberg	0	1.95	2.88	2.88	0.02	12.4	0.08	13.4	0.08	13.4
1.6 kg/pot	1.09	3.34	2.95	3.40	0.04	8.0	0.12	10.3	0.11	11.2
	2.18	2.98	3.28	3.41	0.08	8.1	0.16	10.7	0.24	12.4
	4.36	3.11	3.37	3.40	0.12	8.8	0.53	11.2	0.40	11.2
	8.72	3.27	3.62	3.39	0.31	7.7	0.64	9.8	0.77	10.7
	17.44	3.22	3.07	3.38	0.38	8.9	0.98	10.9	1.16	10.5

increase in the molybdenum content of the plant in steamed soil than in unsteamed soil.

In the trial described, sodium molybdate had been applied after the soil had been steamed. The effect on beet of steaming if the molybdate were applied before steaming was studied in two soils, from Bathmen and Hardenberg (Overijssel), subjected to three treatments: not steamed, steamed before dressing with sodium molybdate, and steamed afterwards. The basal dressing was the same as before; applied after steaming. The plants were cut after 5 weeks. The results are shown in Table 15.

In both soils only plants in the unsteamed soil without molybdenum dressing exhibited symptoms of molybdenum deficiency. Thus in these soils too steaming had increased availability of molybdenum.

Fig. 13, referring to the Bathmen soil, again shows that a dressing of sodium molybdate increased molybdenum content of the plant in steamed soil more than in the unsteamed soil. But, when the soil was first treated with molybdenum and then steamed, the molybdenum content of the crop was indeed higher than in the unsteamed soil, but lower than when the sodium molybdate was applied after steaming. Thus the availability of sodium molybdate was decreased by steaming, although the positive effect of the steam treatment in itself was much greater.

Fig. 14 indicates that the phosphate content of plants was higher in the steamed soil than in the unsteamed soil. Sodium molybdate lowers this phosphate content of

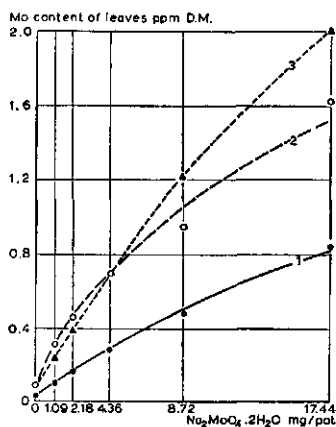30

Mo content of leaves ppm D.M.

Fig. 13. The effect of sodium molybdate application on the molybdenum content of young beet plants after different soil treatments (Bathmen soil; Table 15).
1 = not steamed; 2 = soil steamed after application of sodium molybdate; 3 = soil steamed prior to sodium molybdate application.

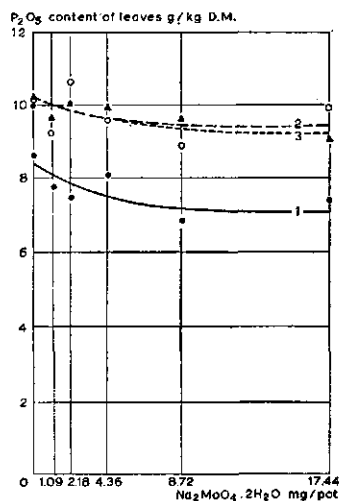P₂O₅ content of leaves g/kg D.M.

Fig. 14. The effect of sodium molybdate application on the phosphate content of young beet plants grown in Bathmen soil (Table 15).
1 = not steamed; 2 = soil steamed after sodium molybdate application (o); 3 = soil steamed prior to sodium molybdate application (▲).
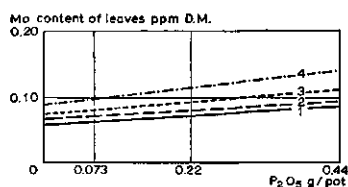
Mo content of leaves ppm D.M.

Fig. 15. The effect of phosphate application on the molybdenum content of young beet plants at different levels of sodium molybdate (unsteamed soil; adjusted).
1 = 0 mg, 2 = 0.73 mg, 3 = 1.45 mg, 4 = 2.90 mg Na₂MoO₄.2H₂O per pot.

the plant. This completely agrees with results in Chapter 3.

The above results suggest that a study of the interaction between phosphate and molybdenum might provide a link with the results of Chapter 3. For this purpose the treatments mentioned in Table 16 were compared in steamed and unsteamed soil from Bathmen, the treatments applied to the steamed soil were separated into dressing with molybdenum dressing prior to and after steaming. Phosphate was

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Table 16. Lay out of pot trials on interaction between molybdenum and phosphate in steamed and unsteamed soil.

Rate of sodium molybdate	Rates of dicalcium phosphate (g P_2O_5/pot)			
0	0	0.073	0.22	0.44
0.73 mg/pot	0	0.073	0.22	0.44
1.45 mg/pot	0	0.073	0.22	0.44
2.90 mg/pot	0	0.073	0.22	0.44

applied after steaming. The results are in Table 17.

Chapter 3 has proved that phosphate increased uptake of molybdenum supplied as sodium molybdate. Fig. 15 shows that here the same occurs.

To trace any difference between the effects of sodium molybdate applied to steamed and unsteamed soil, and to find any difference between molybdenum application before and after steaming, molybdenum content of the plant was considered in relation to the phosphate application, especially since phosphate was always applied after steaming.

Because the effect of phosphate was more evident at higher molybdenum levels, Figs 16a and 16b include only the quantities of 1.45 mg and 2.90 mg sodium molybdate. They show that when a soil was steamed and then dressed with molybdenum and phosphate, the molybdenum content of the plant was raised much more by phosphate than in unsteamed soil. Steaming caused the soil to lose the property of limiting the mobility of sodium molybdate. This assumption sounds reasonable, since as more sodium molybdate was given, the increase in molybdenum content of the plant due to phosphate was enhanced.
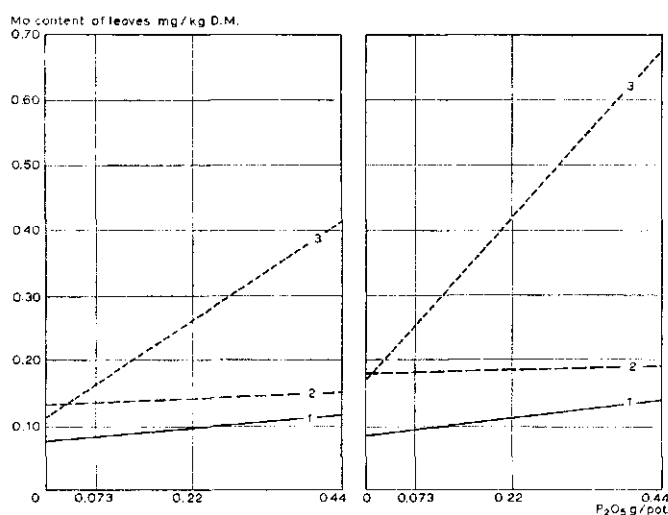

Fig. 16. The effect of phosphate application on the molybdenum content of young beet plants (adjusted).
left = 1.45 mg, right = 2.90 mg $Na_2MoO_4.2H_2O$ per pot.
1 = unsteamed soil; 2 = steamed after sodium molybdate application; 3 = soil steamed before sodium molybdate application.

Table 17. The effect of sodium molybdate and dicalcium phosphate, without and with steaming at different moments, on yield and molybdenum and phosphate content of young beet plants.

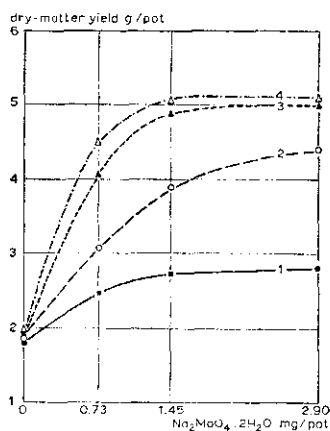| Treatment	Sodium molybdate mg/pot	Dry matter yield g/pot after rates of P_2O_5 per pot of				Composition of leaves after rates of P_2O_5 per pot of							
		0 g	0.073 g	0.22 g	0.44 g	0 g		0.073 g		0.22 g		0.44 g	
						Mo mg/kg	P_2O_5 g/kg	Mo mg/kg	P_2O_5 g/kg	Mo mg/kg	P_2O_5 g/kg	Mo mg/kg	P_2O_5 g/kg
Not steamed then Mo + P	0	1.5	1.7	1.5	2.3	0.07	10.0	0.08	10.9	0.07	13.1	0.10	12.8
	0.73	2.8	3.2	4.2	4.5	0.02	5.3	0.07	6.3	0.07	6.8	0.10	8.0
	1.45	2.5	3.6	5.0	5.2	0.12	5.3	0.09	5.7	0.09	6.4	0.02	8.0
	2.90	2.9	4.9	4.8	5.1	0.08	5.1	0.08	5.2	0.13	7.0	0.16	8.0
Steamed first then Mo + P	0	1.6	2.2	3.2	3.7	0.09	6.0	0.07	6.8	0.11	8.2	0.18	9.9
	0.73	1.6	3.0	4.0	4.4	0.05	5.6	0.11	7.3	0.14	7.1	0.14	8.4
	1.45	2.0	2.8	3.8	4.5	0.08	6.4	0.19	7.2	0.26	8.2	0.38	9.2
	2.90	2.1	3.2	4.4	4.8	0.28	6.7	0.23	6.6	0.48	8.2	0.62	9.5
First Mo, then steamed, then P	0	1.6	2.3	3.4	3.9	0.08	6.4	0.07	7.4	0.07	8.3	0.11	9.2
	0.73	1.8	2.7	3.7	4.1	0.11	6.2	0.10	7.4	0.12	6.9	0.12	8.8
	1.45	2.1	2.3	3.4	3.8	0.15	5.8	0.15	7.6	0.16	8.2	0.17	9.2
	2.90	1.2	1.8	2.9	3.5	0.14	5.9	0.16	6.6	0.15	8.0	0.19	8.9

Fig. 17. The effect of sodium molybdate application on the yield of young beet plants at different phosphate levels (unsteamed soil; adjusted).
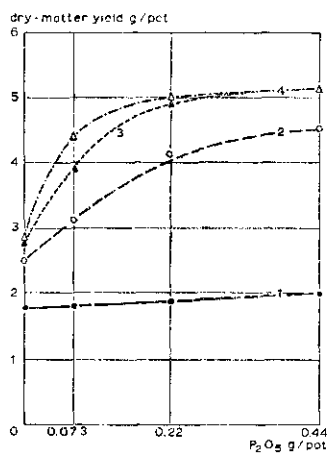$1 = 0$ g, $2 = 0.073$ g, $3 = 0.22$ g, $4 = 0.44$ g P_2O_5 per pot.

Fig. 18. The effect of dicalcium phosphate application on the yield of young beet plants at different levels of sodium molybdate (unsteamed soil; adjusted).
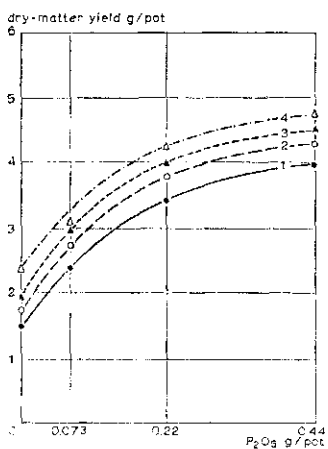$1 = 0$ mg, $2 = 0.73$ mg, $3 = 1.45$ mg, $4 = 2.90$ mg sodium molybdate per pot.

Fig. 19. The effect of dicalcium phosphate application on the yield of young beet plants at different levels of sodium molybdate, applied *after* steaming of the soil (adjusted).
$1 = 0$ mg, $2 = 0.73$ mg, $3 = 1.45$ mg, $4 = 2.90$ mg sodium molybdate per pot.
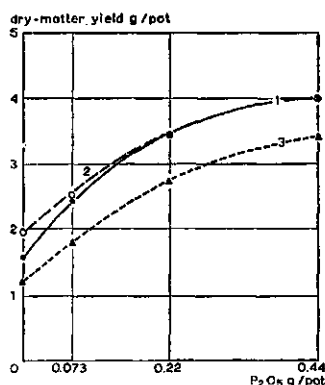
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Fig. 20. The effect of dicalcium phosphate application on the yield of young beet plants at different levels of sodium molybdate applied *before* steaming (adjusted).
1 = no molybdenum; 2 = average effect of 0.73 and 1.45 mg sodium molybdate per pot; 3 = 2.90 mg sodium molybdate per pot.

When the soil dressed with sodium molybdate was steamed the molybdenum content of the plant did indeed increase, but phosphate barely affected its uptake. Thus steaming must have reduced the mobility of sodium molybdate; the change in the soil caused by steaming could hardly depend on whether sodium molybdate was added. Figs 16a and 16b also indicate that steaming so strongly reduces the availability of sodium molybdate that the decrease in fixing capacity of the soil was largely counteracted. Yet more of the molybdenum in the soil became available through steaming, as is evident from the higher molybdenum content of the plants grown in steamed soil without molybdenum. The yields corroborate this.

Fig. 17 shows that yield increased less with sodium molybdate in the absence than in the presence of phosphate. This soil behaved like soil 5 in Group b (Chapter 3).

The plants did not respond to phosphate when no molybdenum was applied (Fig. 18). But after a dressing of molybdenum, phosphate increased yield. When the soil was first steamed and then dressed, there was a response to phosphate application in the absence of molybdenum. Thus molybdenum was liberated by steaming. Hence, application of sodium molybdate had only slight effect (Fig. 19).

Unlike Fig. 19 Fig. 20 shows that yield was clearly lower at the highest molybdenum level but there were no differences in yield between the lower rate of molybdenum and the treatment without molybdenum. This negative action of molybdenum could not be the result from excess molybdenum, since the molybdenum content of the plant was much lower than in the corresponding treatments where molybdenum was applied after steaming. The cause of this negative response is not clear.

4.3 Discussion

Chapter 3 and the above experiments refer to the same two soils, deficient of molybdenum and phosphate. They were therefore dressed with phosphate. Chapter 3 has shown that phosphate did not relieve molybdenum deficiency, whereas the present chapter has indicated that steaming does. The increase in availability of

molybdenum is not due to an increased availability of phosphate. However, the sharper increase in molybdenum content of the plant caused by the application of sodium molybdate, could be due to the increase in availability of phosphate with steaming. It could, however, be that the capacity of the steamed soil to fix sodium molybdate was lower. The plant took up less of the molybdenum applied before steaming than of the molybdenum applied afterwards, but the effect of the molybdenum dressing on the molybdenum content of the plant was much greater in both cases than in unsteamed soil.

To link up the results of Chapter 3 with those mentioned above the phosphate × molybdenum interaction was studied in the steamed and unsteamed soil from Bathmen. Once again sodium molybdate when applied before raised the molybdenum content much less than after steaming. But the differences were much greater than in the first trials. The lower molybdenum content could hardly be due to fixation by the soil: if so, this would also have occurred when the molybdenum was applied after steaming.

A comparison between the yields from the phosphate × molybdenum interaction trial (Fig. 17; Table 17) reveals that beet in unsteamed soil and soils of Group b in Chapter 3 responded simularly, i.e. a dressing of phosphate enhanced the response of the crop to sodium molybdate.

As in soils of Group b, the crop hardly responded to phosphate in the absence of molybdenum, but responded sharply to phosphate when molybdenum was added.

The response to phosphate after steaming indicates that soil molybdenum was liberated by steaming, or at least that the supply of molybdenum was increased in the soil that did not receive molybdenum.

A comparison of Figs 19 and 18 reveals that steaming caused the soil behaved more like Group c (Fig. 9) than Group b in Chapter 3 (Fig. 6).

The soils of Group c seem to have a higher molybdenum content than those of Group b; only soil analysis could prove this.

4.4 Conclusions

1. Steaming increases the availability of molybdenum in the soil.
2. A dressing of sodium molybdate increases molybdenum content of the plant more in a soil steamed before dressing than in an unsteamed soil. Thus the binding of molybdenum in a steamed soil is less.
3. If sodium molybdate is added just before steam treatment, it becomes less available the plant. The reduction in availability does not occur when molybdenum is applied after steaming, so it is not due to binding in the soil but to formation of compounds not available to the plant.

5 Influence of manganese on molybdenum deficiency

5.1 Literature data

Many investigators have studied the interaction between manganese and molybdenum. Millikan (1947, 1948) found that molybdenum retarded the onset of lower leaf necrosis in flax grown in water culture, and also decreased its severity, though it is symptomatic of manganese toxicity. The same symptom developed in water cultures without molybdenum but with a normal supply of manganese. Molybdenum also prevented the symptom on strongly acid soils in Victoria (Australia). As iron deficiency in water cultures, induced by excess manganese, zinc, copper, cobalt and nickel could also be diminished by adding molybdenum, he concluded that molybdenum is required in regulation of the effect of these elements on the availability of iron.

Yet, Warington (1951) reported that in soya and flax molybdenum aggravated chlorosis induced by excess of manganese. But in oats molybdenum and manganese did not interact.

Anderson et al. (1953) found that on a red basaltic soil a dressing of manganese sulphate reduced yield of white clover. The reduction was counteracted by adding molybdenum. As magnesium sulphate and potassium sulphate did not lower the yield, they concluded that manganese caused the reduction.

Hewitt (1954), working with beet in sand cultures, reported that extra molybdenum aggravated chlorosis induced by excess manganese. Results of Hannay & Street (1954) agreed with those of Hewitt and Warington: molybdenum aggravated manganese toxicity in excised tomato roots, whereas rates of manganese strongly toxic in the presence of molybdenum proved to encourage growth when molybdenum was absent.

Mulder (1954) found that the improvement in growth of cauliflower with sodium molybdate on molybdenum-deficient soil was nullified by manganese sulphate. With increasing rates of manganese sulphate to such soils, more molybdenum was required for normal growth and the molybdenum content of the plant was low. In acid soil with sufficient molybdenum molybdenum did not eliminate the negative effect of manganese. He demonstrated that the countereffect of manganese sulphate and molybdenum was due both to the manganese and to the sulphate. Unlike cauliflower, white clover, tomatoes and spinach, responded alike to molybdenum when manganese sulphate was present or absent. He did not analyse these plants.

In water cultures, Mulder found no interaction between manganese and molyb-

denum even in cauliflower. These results resembled those of Warington and Hewitt: a high rate of molybdenum retarded growth, especially at high rates of manganese. Thus Mulder concluded that the antagonism between manganese and molybdenum was confined to certain species growing in soil.

Heintze (1955) reported that adding sodium molybdate aggravated manganese deficiency (marsh spot) in peas if nitrogen was applied as ammonium nitrate. However sodium molybdate reduced the incidence of marsh spot if the nitrogen was supplied as urea. That the results depended on the form in which the nitrogen was supplied could mean that molybdenum affected metabolic processes as well as lowered manganese uptake, since it reduced manganese content of peas.

Candela & Hewitt (1957) report that in sand culture lack of molybdenum decreased weight increment of tomato plants and that this effect was aggravated by excess manganese. Increasing rates of manganese increased the molybdenum content of the plant, both at high and low molybdenum rates. They reason that both excess manganese and molybdenum deficiency lowered the content in free amino acids. Thus manganese excess could further decrease the already inadequate amino acid content of molybdenum-deficient plants, and a possible favourable effect from an increase in molybdenum content could thus be eliminated by the effect of manganese. The increasing incidence of manganese deficiency in peas with molybdenum dressing (Heintze, 1956) could be partly explained in the same way.

Peas with marsh spot contain more amino acids than healthy peas. Addition of molybdenum may raise amino acid content beyond a critical limit when manganese supply is poor. It should be noted, however, that Heintze found a reduction in the manganese content of peas dressed with molybdenum. Candela & Hewitt conclude that the interaction of manganese and molybdenum included two components: metabolic derangement due to an excess manganese and absence of molybdenum, and enhanced uptake of molybdenum under the influence of manganese.

That molybdenum and manganese separately affect the oil content of *Helianthus annuus*, but not in combination, led Soboleva (1959) to the idea that manganese and molybdenum are antagonists.

Kirsch et al. (1960), in studies on the interaction between iron, manganese and molybdenum in tomatoes grown in water cultures, concluded that molybdenum alleviates manganese toxicity (Millikan, Anderson) only if the iron supply is ample. As reported by Hewitt and Warington, they observed aggravation of the manganese-induced iron chlorosis, only when iron was in poor supply. Thus, Kirsch et al. concluded that the interaction was indirect through uptake of iron.

Published results are contradictory. Probably at least partly because of the growing medium: where soil was used (Anderson, Heintze, Mulder), there was a negative interaction between molybdenum and manganese (although in a few crops Mulder did not observe it).

Only Heintze and Mulder analysed plants: Heintze found a reduction in manganese content due to molybdenum, Mulder a reduction in molybdenum content due to manganese.

The picture presented by water and sand cultures differ from those in soils. Only Mulder checked whether manganese caused molybdenum deficiency in water cultures. The other workers were concerned with the influence of molybdenum on manganese toxicity. They all agree that excess of manganese caused iron deficiency. Whether iron deficiency was alleviated by molybdenum, as Millikan found, or aggravated by it, as other workers reported, depends on supply of iron (Kirsch et al.). The plants grown in water cultures were not analysed except by Kirsch. He reported the molybdenum uptake per pot, but as yield also responded sharply his data give no indication on changes in content.

Candela & Hewitt found, however, that manganese increased the molybdenum content of plants grown in sand culture. Mulder concluded that the interaction varied with the growing medium and the plant species.

5.2 Own trials

In view of the contradictory results, I studied the influence of manganese sulphate on production of dry matter and molybdenum content of young beet in a soil from Zuidlaren (pH-KCl 3.67) with sufficient molybdenum but with different amounts of added iron concretions (Table 18). None of the treatments resulted in molybdenum deficiency symptoms.

Table 19 shows that manganese sulphate did not affect weight of dry matter from untreated soil neither did the addition of iron concretions without manganese sulphate. A supply of manganese together with iron concretions increased yield. The highest yield was with much iron and much manganese, though the weights were little more than on untreated soil.

Table 20 shows the effect on molybdenum and manganese contents of leaves. After adjustment for the variation in molybdenum content the effect of applying manganese sulphate at different rates of iron concretions is evident (Fig. 21). Man-

Table 18. Lay out of pot trials on the influence of iron concretions and manganese sulphate on young beet plants.

Soil (g/pot)	Iron concretions, fraction < 0.5 mm (g/pot)	Manganese sulphate (g/pot)			
1500	0	0	0.11	0.22	0.44
1450	50	0	0.11	0.22	0.44
1400	100	0	0.11	0.22	0.44
1350	150	0	0.11	0.22	0.44

Number of replicates 3. Basal dressing 0.3 g N/pot as NH_4NO_3; 0.4 g P_2O_5 as K_2HPO_4 and 0.05 g MgO as $MgSO_4.7H_2O$. Plants harvested one month after emergence.

Table 19. Effect of manganese sulphate on dry weight of young beet plants grown on sandy soil (pH-KCl 3.67) mixed with various amounts of iron concretions (< 0.5 mm).

Soil (g/pot)	Iron concretions (g/pot)	Average dry matter yield (g/pot) after adding			
		No manganese sulphate	0.11 g manganese sulphate	0.22 g manganese sulphate	0.44 g manganese sulphate
1500	0	2.54	2.39	2.41	2.55
1450	50	2.52	2.66	2.77	2.68
1400	100	2.57	2.73	2.59	2.77
1350	150	2.46	2.69	2.69	2.82

Table 20. Effect of manganese sulphate application on molybdenum and manganese contents of leaves of young beet plants on sandy soil (pH-KCl 3.67) supplied with different amounts of iron concretions (< 0.5 mm).

Soil (g/pot)	Iron concretions (g/pot)	0 g manganese sulphate per pot		0.11 g manganese sulphate per pot		0.22 g manganese sulphate per pot		0.44 g manganese sulphate per pot	
		Mo	Mn	Mo	Mn	Mo	Mn	Mo	Mn
1500	0	0.23	442	0.20	1152	0.18	1594	0.16	1465
1450	50	0.12	766	0.11	1285	0.07	1923	0.07	1480
1400	100	0.07	791	0.07	1134	0.09	1517	0.07	1452
1350	150	0.07	802	0.02	1172	0.07	1326	0.07	1430

ganese sulphate lowered the molybdenum content of the plant, especially in the absence of iron concretions. With much iron, the molybdenum content of the plant was low, and was not further reduced by manganese sulphate.

The manganese content of plants increased with increasing levels of manganese sulphate (Table 20). There is little difference between the manganese contents of the plants grown at the two highest rates of manganese.

Fig. 22 indicates that iron concretions increased the manganese content of the crop when no manganese was supplied. Upon addition of manganese a small decrease in the manganese content is apparent due to the concretions. This does not necessarily mean that the iron concretions themselves increase the manganese content: they may have contained some manganese, as manganese oxides are often clearly discernible in large concretions encountered in the field.

Though the preceding paragraphs have demonstrated that manganese sulphate lowered the molybdenum content of the plant, after adding iron concretions this effect disappeared. Thus the effect of iron oxides counteracts that of manganese: the molybdenum was so rapidly fixed in particles that the amount available for reaction with manganese was too small.

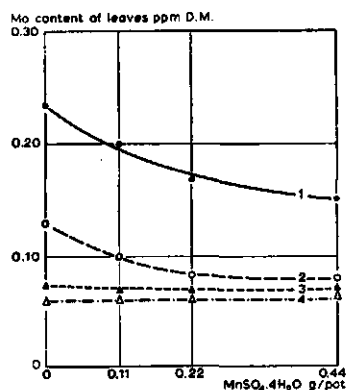This would mean that the effect of manganese on the molybdenum content of

Fig. 21. The effect of manganese sulfate application on the molybdenum content of young beet plants, grown on a sandy soil supplied with various amounts of iron concretions (<0.5 mm; adjusted).
1 = 0 g, 2 = 50 g, 3 = 100 g, 4 = 150 g iron concretions per pot.
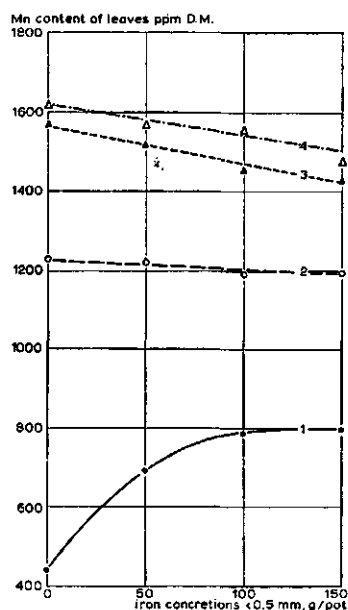

Fig. 22. The effect of adding iron concretions, supplied to a sandy soil, on the manganese content of young beet plants at different levels of manganese sulfate (adjusted).
1 = 0 g, 2 = 0.11 g, 3 = 0.22 g, 4 = 0.44 g manganese sulfate per pot.

the plant is much greater when the molybdenum content of the soil is high. To test this the influence of manganese sulphate on the molybdenum content of the plant was tested in the presence of various amounts of iron concretions, both with and without added sodium molybdate. Since yields were scarcely affected by the treatments, they were not included in Table 21.

Fig. 23 shows that, in agreement with the preceding trial (Fig. 21), the effect was indeed absent at high rates of iron. When, however, the molybdenum content of the soil was raised by applying sodium molybdate, application of manganese lowered the molybdenum content of the plant, even in the presence of much iron. The effect of manganese sulphate was greater in the treatment without iron concretions. Without molybdenum, there was no difference in molybdenum content between the treatments which received 0.22 and 0.44 g manganese sulphate per pot.

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Table 21. Effect of manganese sulphate on the molybdenum and manganese content of leaves of young beet plants grown on a sandy soil mixed with various amounts of iron concretions (fraction < 0.5 mm) without Mo or with Mo (2.90 mg/pot $Na_2MoO_4.2H_2O$).

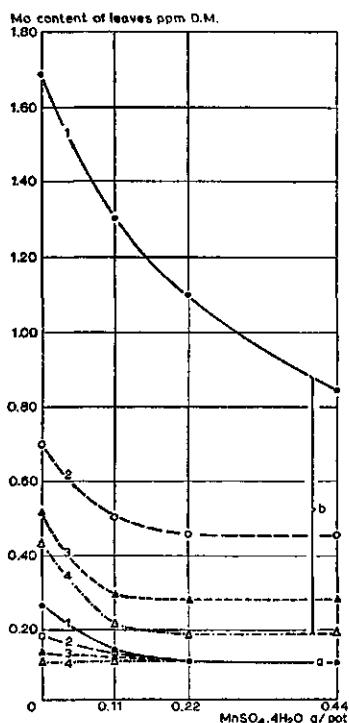| Soil (g/pot)	Iron concretions (g/pot)	Mo and Mn content of leaves (mg/kg)														
		with no $MnSO_4.4H_2O$ per pot and				with 0.11 g $MnSO_4.4H_2O$ per pot and				with 0.22 g $MnSO_4.4H_2O$ per pot and				with 0.44 g $MnSO_4.4H_2O$ per pot and			
		-Mo		+Mo		-Mo		+Mo		-Mo		+Mo		-Mo		+Mo	
		Mo	Mn	Mo	Mn	Mo	Mn	Mo	Mn	Mo	Mn	Mo	Mn	Mo	Mn	Mo	Mn
1500	0	0.27	416	1.71	446	0.14	1234	1.14	1281	0.14	2281	1.26	1934	0.11	4175	0.84	4347
1450	50	0.17	653	0.61	734	0.14	1345	0.62	1277	0.09	2161	0.43	2086	0.08	3731	0.49	3779
1400	100	0.15	600	0.52	625	0.10	1033	0.28	1004	0.13	1536	0.31	1476	0.13	2722	0.27	2687
1350	150	0.10	533	0.44	536	0.19	789	0.24	823	0.11	1146	0.11	1103	0.24	1915	0.23	1893

Fig. 23. The effect of maganese sulfate application on the manganese content of young beet plants, grown on a sandy soil supplied with different amounts of iron concretions (<0.5 mm; adjusted).
a = 0 mg, b = 2.90 mg $Na_2MoO_4.2H_2O$ per pot.
1 = 0 g, 2 = 50 g, 3 = 100 g, 4 = 150 g iron concretions per pot.

Upon application of sodium molybdate the molybdenum content continued to decrease over the entire range of manganese rates. But when part of the molybdenum was adsorbed by iron, resulting in a lower concentration of free molybdenum in soil, there was no difference in the molybdenum contents of the plant grown at the highest manganese levels. Thus an equilibrium had been established.

5.3 Discussion

The trials show that manganese sulphate may lower the molybdenum content of the plant. The reduction depended on the availability of molybdenum in the soil: the effect was only slight when this availability is decreased by for instance iron oxides. Chapter 4 indicated that less sodium molybdate was absorbed by the plants under reducing conditions (i.e. when it was applied before the soil was steamed). But uptake of manganese was enhanced by exposure to such reducing conditions. The literature shows that in water cultures manganese does not lower the molybdenum content of the plant. The oxygen supply is usually better in water cultures than in soil so that the availability of molybdenum may be decreased by manganese only under anaerobic conditions.

The phenomena could be ascribed to oxidation-reduction processes if: (1) the plant can not absorb molybdenum in reduced form, (2) manganese can reduce molybdate (Chapt. 6).

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6 Molybdenum regime in the soil

The first two chapters, based on field observations, have shown that coincidence of molybdenum deficiency and iron in the soil was no chance. Addition to a soil of iron concretions from field samples lowered the molybdenum content of the plant, especially if the iron concretions were fine. Addition of phosphate and hydroxyl ions released the fixed molybdenum. Thus molybdenum must have been sorbed onto iron particles as an anion.

From trials and published data, Davies (1956) inferred that a considerable proportion of molybdenum was present as an exchangeable molybdate anion and that soil reaction had a marked effect on its availability. Reisenauer et al. (1962) concluded that molybdate-sorption reactions with the hydroxides of Fe, Al, Ti and of acid soils all show analogous pattern. Sorption of molybdate by $Fe_2O_3.nH_2O$ was accompanied by the release of two hydroxyl ions and a mole of water. In an acid system Na_2MoO_4 reacted with $Fe(OH)_3$ to form $Fe_2(MoO_4)_3$; in solid phase, molybdate was chemically sorbed onto an iron-waterhydroxyl-complex.

Reyes & Jurinak (1967) found that adsorption of molybdenum on the oxide surface of αFe_2O_3 was five times as much at pH 4.0 as at pH 7.75. Adsorption at low pH was temperature-sensitive. By comparing the surface area of three forms of molybdate with nitrogen surface areas of the molybdated oxides, they concluded that the principle form adsorbed was the monomeric, $H_n(MoO4)^{n-2}$. The para-molybdate form $Mo_7O_{24}{}^{6-}$ condensed as the temperature was increased at high molybdenum concentrations.

According to Jurinak (1966), the potential adsorption sites (hydroxyl-groups) of haematite (αFe_2O_3) cover a mean surface area of 22 to 23 Å². The tetrahedral form of molybdate $H_n(MoO_4)^{n-2}$ with its surface area of 25 Å² closely approaches this value.

That adsorption processes in the soil strongly influence molybdenum uptake by the plant does not imply that molybdenum is exclusively absorbed as an anion. In a pot trial with a molybdenum-deficient soil from eastern Overijssel I compared the behaviour of molybdenum sulphide (97.7% MoS_2; 58.6% Mo) with that of sodium molybdate (39.6% Mo). Like copper sulphide, molybdenum sulphide is insoluble. Tests with barley by Mulder (1938) had shown that copper as the sulphide was equal or superior to the sulphate. Molybdenum sulphate was used rather than molybdenum trioxide, which could be converted to molybdates in the soil nullifying the purpose of the experiment. Molybdenum sulphide would be oxidized in the soil into molybdenum sulphate. Although sulphate decreases the molybdenum

Table 22. Effect of sodium molybdate or molybdenum sulphide on production of dry matter and molybdenum content of young beet plants.

mg Mo per pot	Dry matter (g/pot) with Mo from		Molybdenum content (mg/kg) with Mo from	
	sodium molybdate	molybdenum sulphide	sodium molybdate	molybdenum sulphide
0	1.2		0.00	
0.29	4.5	1.2	0.06	0.02
0.58	4.6	1.3	0.19	0.02
0.88	4.4	1.4	0.32	0.03
1.16	4.8	2.0	0.55	0.08
1.46	4.4	1.6	0.63	0.09
1.75	4.7	2.0	0.59	0.10

Number of replicates 3. Plastic pots with 1.5 kg soil. Plants harvested 8 weeks after emergence; MoS_2 contained 58.6%; sodium molybdate 39.6% Mo.

content of the plant (Mulder, 1954), the amount of sulphate formed would be negligible.
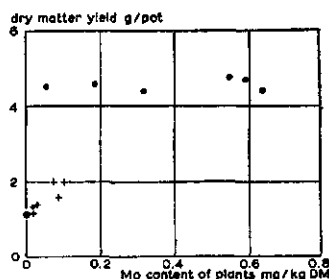
The plants supplied with molybdenum sulphide showed symptoms of molybdenum deficiency throughout growth. So did the pots without molybdenum. Plants supplied with sodium molybdate remained healthy.

Table 22 shows that sodium molybdate increased yield: 0.29 mg Mo/pot as sodium molybdate was optimum. But molybdenum as sulphide had little effect.

The molybdenum content of the plants increased sharply with sodium molybdate. Molybdenum sulphide also increased it, but not much. A dressing of 1.75 mg molybdenum as sulphide had less effect on molybdenum content than 0.58 mg molybdenum as sodium molybdate.

Fig. 24 shows that molybdenum taken up by the plant from the sulphide was not so effective: 0.1 mg Mo from sodium molybdate per kg plant dry matter gave healthy plants and a good yield, but plants with the same amount from molybdenum sulphide were sickly and grew poorly.

The trial demonstrates that the plant could take up molybdenum as a cation, but only to a small extent. This molybdenum proved less effective within the plant.

Fig. 24. The relation between molybdenum content of young beet plants and dry matter yield.
$\odot$ = without molybdenum added; $\bullet$ = sodium molybdate added; $+$ = molybdenum sulfide added.

Amin et al. (1958), in their study on the availability of different molybdenum oxides to the plant showed that less oxidized forms (MoO_2 and Mo_2O_5) were not taken up. They supposed that molybdenum occurred in three forms in the soil:
a. Water-soluble molybdenum, especially soluble molybdates.
b. Molybdenum soluble in NH_4OH, not available to the plant but easily converted by cations in the soil to available form.
c. Oxidizable molybdenum oxides, which have to be oxidized before they become available to the plant.

Thus, the trial and data of Amin et al. demonstrate that the type of ion can influence the availability of molybdenum as well as its adsorption. The results with steamed soil support this view.

Most probably steaming worked in two ways:
1. It destroyed the complex that adsorbed molybdenum: molybdenum deficiency disappears after steaming, and the molybdenum content of the plant becomes higher. That this resulted from more available molybdenum was shown by the response to phosphate (Figs 18 and 19). In the unsteamed soil production of dry matter did not increase with phosphate unless sodium molybdate was supplied. It did increase, however, in the steamed soil. Steaming had the same effect on response to phosphate as did sodium molybdate. Another argument in favour of the contention that steaming attacks the molybdenum adsorbant is that sodium molybdate had much more effect on molybdenum content of the plant after the soil had been steamed (Fig. 12).
2. Steaming, renders molybdates unavailable, for the molybdenum content of the plants was lower when the sodium molybdate was supplied before steaming instead of afterwards (Fig. 16). This reduced availability could not have been caused by manganese, because manganese remains more mobile for a considerable time (some months) after steaming, so that sodium molybdate supplied after steaming should also be affected by it.

Although, according to Reyes & Jurinak, a higher temperature increased the adsorption of molybdenum by αFe_2O_3 at higher concentrations, this fact cannot explain the lower availability of sodium molybdate applied before steaming: in the foregoing it has been made plausible that the adsorption complex was attacked by steaming.

Amin's data supports my view that, during steaming, sodium molybdate was transformed into strongly reduced molybdenum compounds. But another explanation would be that polymolybdates are formed, which are less available to the plant.

The question remains if the negative effect of manganese on the molybdenum content of the plant can be explained by reduction of molybdates. A small exploratory test, in which solutions of 0.02 M $MnSO_4$ and 0.02 M Na_2MoO_4 were combined, seemed to affirm this hypothesis. Theoretical data concerning the involved pH range are lacking. Novozamsky of the Department of Soils and Fertilizers at the Agricultural University has tested whether Mn^{2+} reduces MoO_4^{2-} at pH 4 and 6, but his potentiometric, spectrophotometric and polarographic meas-
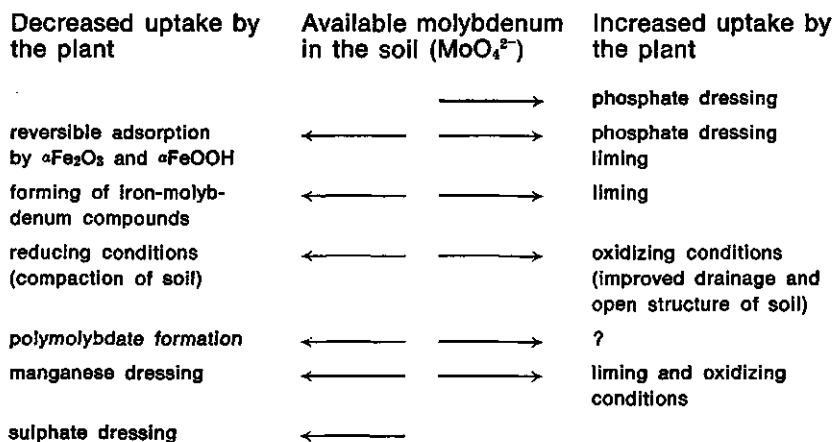
urements gave no evidence of reduction.

The negative effect of manganese on molybdenum uptake cannot be due to competition during uptake, because manganese is taken up as a cation and molybdenum chiefly as an anion. Novozamsky's tests and my own exploratory investigation have shown, however, that molybdate reacts with manganese: apparently compounds are formed that are less available to the plant. A detailed chemical study will be required.

Although less molybdate is available after reduction, it is yet uncertain if these processes play an essential role in molybdenum deficiency in the pH range in which the deficiency occurs in practice.

If αFe_2O_3 or $\alpha FeOOH$ is present in the soil, the molybdate ions are adsorbed and become unavailable to the plant. Conversely, other negative ions ($H_2PO_4^-$ and OH^- ions) may liberate them again. If molybdenum deficiency in the Netherlands were caused solely by adsorption onto iron, a phosphate dressing would be beneficial on all soils. Iron exerts its influence not only by a reversible adsorption, but also in some other way.

The fact that phosphate always increases the molybdenum content of plants grown on molybdate-enriched soils indicates that, besides the reactions in the soil, a synergy exists between phosphate and molybdenum in uptake by the plants.

The following scheme outlines and summarizes the processes to which plant-available molybdenum in Dutch soils is subject.

Decreased uptake by the plant	Available molybdenum in the soil (MoO_4^{2-})	Increased uptake by the plant
	$\longrightarrow$	phosphate dressing
reversible adsorption by αFe_2O_3 and $\alpha FeOOH$	$\longleftarrow \quad \longrightarrow$	phosphate dressing liming
forming of iron-molybdenum compounds	$\longleftarrow \quad \longrightarrow$	liming
reducing conditions (compaction of soil)	$\longleftarrow \quad \longrightarrow$	oxidizing conditions (improved drainage and open structure of soil)
polymolybdate formation	$\longleftarrow \quad \longrightarrow$	?
manganese dressing	$\longleftarrow \quad \longrightarrow$	liming and oxidizing conditions
sulphate dressing	$\longleftarrow$	

The outline is based solely on plant analysis and on the literature; unfortunately no analytical data on the soils were available. Such an analysis, would allow, for instance study of the differences in the phosphate $\times$ molybdenum interaction in the soils. Also a more definite statement on the manganese $\times$ molybdenum interaction would be possible. But so far, no method of soil analysis is available that can supply meaningful data. I hope this study may encourage soil chemists and physiologists to clarify some of the problems.

Summary and conclusions

An investigation was conducted into the occurrence of molybdenum deficiency in beets in the Netherlands. In addition, the factors which influence molybdenum uptake were studied by means of pot trials.

In Chapter 1 the soils have been described on which beets show molybdenum deficiency symptoms in the field. Pot trials with beets and spinach demonstrated furthermore that other soils with similar properties, but not identified as molybdenum-deficient, in most cases exhibited molybdenum shortage. These trials showed that a soil should be considered susceptible to molybdenum deficiency when the content of iron (expressed as Fe_2O_3) soluble in 10% HCl amounts to 1 to 2% or higher. Whether or not molybdenum deficiency will occur depends primarily on the pH.

It was shown in Chapter 2 that the simultaneous presence of molybdenum deficiency and iron oxides in the soil is no coincidence. Adding iron concretions, collected in the field, to a soil lowered the molybdenum content of the plant. Furthermore, it was demonstrated that this reduction is caused by sorption of molybdenum onto the iron. The molybdenum content of the plant decreases with increasing fineness of the iron oxides. Not only the fineness, but also the kind of iron is important: synthetically prepared αFe_2O_3 and $\alpha FeOOH$ strongly reduce the molybdenum content of the plant; γFe_2O_3, on the other hand, has only a small effect. X-ray analysis showed that the material collected in the field contained αFe_2O_3 and $\alpha FeOOH$.

Chapter 3 reports on the influence of the phosphate supply on the occurrence of molybdenum deficiency in a number of soils. It has often been observed in the field and reported in the literature that an ample supply of phosphate prevents molybdenum deficiency, but this situation was not found to be generally true. When no molybdenum was applied, three groups of soils could be distinguished: soils in which phosphate application eliminates the molybdenum deficiency, soils in which phosphate application aggravates the molybdenum shortage, and soils without interaction between phosphate and molybdenum.

On all soils, however, the application of phosphate increased the uptake by the plant of freshly applied molybdenum. It is often apparent in agricultural practice that reducing conditions in the soil aggravate molybdenum deficiency. Because steaming of the soil caused strongly reducing conditions to occur, the effect of steaming on the degree of molybdenum deficiency was also studied (Chapter 4). This study showed that steaming improves the availability to the plant of the molyb-

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denum that is naturally present in the soil. The molybdenum-fixing power of the soil is decreased by steaming. However, freshly applied sodium molybdate that was included in the steam treatment was found to be less available to the plant than molybdenum applied after steaming. Steaming apparently transforms sodium molybdate into compounds which are unavailable to the plant.

In Chapter 5 the effect of manganese sulphate on the molybdenum content of young plants was studied. In agreement with other authors, it was found that applying manganese sulphate lowers the molybdenum content of the plant. The magnitude of this reduction depended on the quantity of the plant-available molybdenum.

In Chapter 6 it was made plausible that the kind of molybdenum ion can influence its availability in the soil. The plant was shown to be able to take up molybdenum as the cation, be it to a slight extent. This molybdenum, however, is not very effective within the plant. The results obtained in the preceding chapters were discussed against this background. It was concluded that steaming results in the transformation of added sodium molybdate into reduced compounds. Potentiometric, spectrophotometric, and polarographic measurements led to the conclusion that reduction processes do not play a role in the manganese × molybdenum interaction. It was considered likely that manganese and molybdenum react with each other to form compounds which are less available to the plant. On the basis of the fact that applying phosphate does not always alleviate molybdenum deficiency, it is surmised that the influence of iron on molybdenum uptake should be ascribed to yet another factor, in addition to reversible adsorption.

Finally, a chart has been presented which summarizes the processes to which plant-available molybdenum in Dutch soils is subject.

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Appendix: Analytical methods

Plant material

Molybdenum
a. Following wet digestion of the ground plant material with nitric, sulfuric and perchloric acids, molybdenum was determined spectrophotometrically with toluene 3,4 dithiol (modified method Scharrer & Eberhardt, 1956).
b. Following dry ashing of the ground plant material in a muffle furnace at 600°C for 15 h, molybdenum was determined spectrophotometrically with toluene 3,4 dithiol (modified method Scholl, 1962).

Manganese
Following wet digestion of the ground plant material with nitric, sulfuric and perchloric acids, the manganese was determined spectrophotometrically with formaldoxim (Henkens & Mebius, 1965).

Phosphate
Following wet digestion of the ground plant material with nitric, sulfuric and perchloric acids, the phosphate was determined spectrophotometrically according to the molybdenum blue method (Rameau & ten Have, 1951).

Soils

Reducible manganese
Following extraction of the soil with 1 N ammonium acetate containing 0.2% hydroquinone for 1 h, the manganese was determined spectrophotometrically with formaldoxim (Leeper, 1947).

K-HCl
The amount of K_2O in the soil (in mg/100 g) was assessed by extracting the soil with a 0.1 N HCl-solution. Determination by flame photometer (de Vries, 1945).

K-value
A transformation of K-HCl, in which the empirically assessed influence of organic matter and clay content was taken into account (van der Paauw, 1958; van der Paauw & Ris, 1960). The K-value was used in the agricultural interpretation of the K-HCl.

P-value (mg P_2O_5/100 g soil)
Following extraction of the soil with water (5 g soil + 50 ml H_2O) during 24 h at 50°C, the P-concentration was determined at room temperature according to the molybdenum blue method (de Vries & Hetterschij, 1937).

P-citr (mg P_2O_5/100 g soil)
Following extraction of the soil with citric acid (1%) for 2 h at room temperature, the P-concentration was determined after 24 h according to the molybdenum blue method (de Vries & Hetterschij, 1937).

P-Al (mg P₂O₅/100 g soil)

P-Al (mg P_2O_5/100 g soil)

Following extraction of the soil with a mixture of 0.1 N ammonium lactate and 0.4 N acetic acid, the P-concentration was determined according to the molybdenum blue method (Egner et al., 1960).

Fe_2O_3

Following extraction of the soil with a 10% HCl solution, the iron was determined colorimetrically with O-phenanthroline (Snell, 1949).

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