

## Manganous oxide (MnO) as a fertilizer for controlling manganese deficiency in oats

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### Summary

In pot experiments on 'Wieringermeerpolder' soil fertilizing with 50 kg of Mn/ha as manganous oxide (MnO; 55 or 63.5% Mn) or manganese sulphate ( $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ ; 32.5% Mn), raised reducible soil manganese to 50–60 ppm. At this level no manganese deficiency occurred in oats. These treatments were as effective as foliar sprays with manganese sulphate or manganese 'Rayplex' (a polyflavonoid). Under field conditions to equal the effect of foliar sprays in controlling manganese deficiency in crops much larger amounts of manganese fertilizer were needed. This would make broadcasting too costly in practice, even when using the relatively cheap manganous oxide.

In a pot experiment with 'Biesboschpolder' soil fertilizing with manganous oxide at quantities of up to 176 kg of Mn/ha was not completely sufficient to control manganese deficiency in oats. Increasing reducible soil manganese had little effect on this soil where manganese availability is primarily associated with the C/N ratio.

### Introduction

In The Netherlands manganese deficiency in field crops frequently occurs on calcareous marine sandy clay soils. Its incidence on one group of soils (e.g. 'Wieringermeerpolder', reclaimed from the Zuyderzee) containing less than 2.5% organic matter, is associated with a low reducible manganese\* concentration (< 60 ppm). Another group comprises young, ripening soils (e.g. 'Biesboschpolder', an estuary soil), where manganese deficiency is not closely related to the level of reducible manganese, but associated with the C/N ratio. It is likely to occur under these conditions until the C/N ratio has decreased to a value less than 11 (De Groot, 1957, 1963).

The usual method to correct manganese deficiency in field crops is foliar spraying with manganese sulphate. In field and pot experiments with grain crops, potatoes and sugar beets on 'Wieringermeerpolder' soil (Henkens, 1959, 1962; Henkens and Smilde, 1967) it could also be controlled by application of large quantities of manganese sulphate (at least 400 kg  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ /ha) to the soil. Reducible manganese was then found to increase to a level sufficiently high to prevent manganese deficiency. As the residual effect of soil-applied manganese sulphate was rather poor this method

\* Extraction with 1 N ammonium acetate + 0.2% hydroquinone at pH 7 (1:20 ratio) according to Leeper (1947).

cannot be considered economical (Henkens and Smilde, 1967).

New interest in fertilizing with manganese was gained by the production of another compound, water-insoluble manganous oxide ( $\text{MnO}$ , prepared by reduction of  $\text{MnO}_2$ ), which is much cheaper than manganese sulphate per kg of manganese. Its low solubility, preventing rapid fixation, might be an additional advantage. It was thought worthwhile to test this material in pot experiments with oats on both the 'Wieringermeerpolder' and the 'Biesboschpolder' soil with their different characteristics as regards manganese availability. The results of these pot experiments conducted in 1965 to 1967 inclusive, are described below. In the same period the Agricultural Advisory Service tested the effectiveness of soil-applied manganous oxide and foliar-applied manganese sulphate in controlling manganese deficiency in potatoes in two field experiments in the 'Wieringermeerpolder'. The results referred to here will be published elsewhere (Borst and Mulder, 1968).

The manganous oxide used in the experiments was kindly provided by the 'Algemene, Industriële, Mineraal- en Ertsmaatschappij', now incorporated in NVCP, Amsterdam.

### Materials and methods

The response of oats (variety Marne) to  $\text{MnO}$  (55% Mn\*\*) was studied on a soil from the 'Wieringermeerpolder' (5.1% particles  $< 16 \mu$ ; pH-KCl 7.9; 1% organic matter; 6.1%  $\text{CaCO}_3$ ; 34 ppm reducible Mn; C/N ratio 8.3) and a soil from the 'Biesboschpolder' (43.4% particles  $< 16 \mu$ ; pH-KCl 7.2; 10.5% organic matter; 9.3%  $\text{CaCO}_3$ ; 692 ppm reducible Mn; C/N ratio 16.9) in 1965. All pots (5.2 l Mitscherlich pots, containing 6.7 and 5.6 kg of soil, respectively) received the following quantities of A.R. chemicals: 2.86 g  $\text{NH}_4\text{NO}_3$ , 1.85 g  $\text{K}_2\text{HPO}_4$ , 1.93 g  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , 0.08 g  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . The treatments (3 replicates) were: 0, 0.25, 0.50, and 1.00 g  $\text{MnO}$  (55% Mn) per pot, which is equivalent to 0, 80, 160, and 320 kg  $\text{MnO}$ /ha respectively, and spraying with a 1% manganese sulphate solution (40 ml per pot). The crop was sown on 27th April (40 seeds per pot). Spraying with manganese sulphate was carried out on 3rd June, when the first symptoms of manganese deficiency were visible (3rd leaf), and on 24th June. On 11th June the number of plants per pot was reduced to 25, the harvested plants (stage 3-4) being analysed for manganese with the exception of the sprayed ones. Because of contamination there is not much point in analysing the latter (cf. Coic and Coppenet, 1958). Soil moisture was kept at 60% of the water holding capacity. Plants were watered with deionized water only. Dry weights of grains and straw were determined after harvesting (27th August). Results were analysed statistically with the Cochran and Cox methods and the Duncan test was used to assess the significance of treatment differences.

The above experiment was continued in 1966 to study the residual effect of manganous oxide on oats. All pots received fresh applications of A.R. chemicals at rates equal to those of 1965. The crop was sown on 29th March and thinned out on 10th May, the harvested plants (stage 3-4) being used for manganese analysis. A foliar spray with manganese sulphate was given when the first symptoms of manganese deficiency appeared (10th May). The treatment was repeated on 1st June. All plants were harvested on 2nd August.

In another pot experiment carried out in 1967, only the soil from the 'Wieringer-

\*\* Additional substances 6% Fe, 5%  $\text{SiO}_2$ .

meerpolder' was used. All Mitscherlich pots received the following quantities of A.R. chemicals: 2.86 g  $\text{NH}_4\text{NO}_3$ , 1.90 g  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ , 1.85 g  $\text{K}_2\text{SO}_4$ , 1.93 g  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , 0.08 g  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . The treatments (3 replicates) were: 0, 0.124, 0.247, 0.494 g  $\text{MnO}$  (63.5% Mn) and 0.241, 0.482, 0.965 g  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  (32.5% Mn) per pot, which is equivalent to 25, 50, and 100 kg Mn/ha respectively; spraying with a 1¼% manganese sulphate or a 2½% manganese 'Rayplex'\*\*\* (9.2% Mn) solution. The oat crop (variety Marne) was sown on 22nd March and thinned out on 11th May; the harvested plants were used for manganese analysis as usual. As at stage 4-5 (plant height 25 cm) still no symptoms of manganese deficiency had appeared all plants were cut at 5 cm from the soil (May 18th). Deficiency symptoms became visible on 5th June and appropriate plants were sprayed with a manganese sulphate or 'Rayplex' solution. All plants were harvested on 15th August. Experimental conditions were similar to those of the previous experiments.

## Results

The results of the 1965 pot experiment are shown in Table 1. Fertilizing with manganous oxide was as effective as foliar application of manganese sulphate in controlling manganese deficiency in oats grown on the 'Wieringermeerpolder' soil. Even the smallest quantity of manganous oxide given (44 kg Mn/ha) was found to be adequate.

Table 1 Grain and straw yields of oats following soil application of  $\text{MnO}$  (55% Mn) or spraying with  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  (1¼% solution); means of 3 pots. Also results of leaf and soil analyses (1965 experiment)

	Yield (g)		Mn deficiency index <sup>1</sup>		Leaf Mn on 11/6 (ppm)	Mn soil on 19/11 in ppm	
	grain	straw	21/6	21/7		exchange-able <sup>2</sup>	reducible <sup>3</sup>
'Wieringermeerpolder' soil							
0 kg $\text{MnO}$ /ha	28.1	30.8	5.1	3.7	6	3	34
80	39.7	39.9	10.0	10.0	19	6	56
160	40.9	41.4	10.0	10.0	29	6	70
320	38.5	40.8	10.0	10.0	41	6	110
$\text{MnSO}_4$ spraying on 3/6, 24/6	40.8	40.2	9.8	10.0	— <sup>4</sup>		
'Biesbosch' soil							
0 kg $\text{MnO}$ /ha	38.0	34.8	8.8	6.3	13	3	692
80	40.6	35.6	9.0	7.7	13	3	728
160	38.2	34.5	9.5	8.3	13	3	740
320	42.4	36.8	10.0	9.3	19	3	788
$\text{MnSO}_4$ spraying on 3/6, 24/6	43.3	39.5	10.0	10.0	— <sup>4</sup>		

<sup>1</sup> Scale 1-10, 10 = healthy

<sup>2</sup> Extraction with 1 N ammonium acetate pH 7 (Leeper, 1947)

<sup>3</sup> As 2; 0.2% hydroquinone added

<sup>4</sup> Not analysed

\*\*\* Manganese 'Rayplex' is an organic manganese compound (polyflavonoid).

Grain and straw yields increased by 40 and 30% respectively. Plant manganese increased from 6 to 19 ppm and reducible soil manganese from 34 to 56 ppm. Larger doses of manganous oxide did not result in further significant increases in grain and straw yields but plant and reducible soil manganese were raised to 41 and 110 ppm respectively.

On the 'Biesboschpolder' soil which has a much higher reducible-manganese and organic-matter content and a higher C/N ratio, the response to manganese was smaller. Maximum yield increases were 13% for both grain and straw. Manganese applied to the soil (manganous oxide) was less effective than foliar-applied manganese (manganese sulphate). Only at the largest quantity of manganous oxide supplied (176 kg Mn/ha) a significant increase in grain yield was obtained which was equal to that produced by spraying. Straw yields were not significantly affected, however. Fertilizing with manganous oxide could not completely suppress manganese deficiency symptoms in oats, but spraying with manganese sulphate fully controlled the disorder. Plant manganese was raised from 13 to 19 ppm following application of 320 kg/ha manganous oxide (176 kg Mn/ha). Smaller doses were ineffective. Reducible soil manganese increased with increasing quantities of manganous oxide supplied.

In 1966 a second crop of oats was sown. According to Table 2 there was a significant residual effect of manganous oxide on the 'Wieringermeerpolder' soil, even at 80 kg/ha (44 kg Mn/ha), applied in 1965. Significantly higher yields were obtained with soil application of 160 kg/ha (88 kg Mn/ha) or more, and with manganese sprays. No significant differences were found between these treatments. Grain and straw yields increased by 84 and 50% respectively, relative to the control plants. In spite of the increase in plant manganese resulting from application of manganous oxide in 1965, manganese deficiency symptoms were not completely suppressed. Oat plants on the 'Biesboschpolder' soil hardly showed symptoms of manganese defi-

Table 2 Grain and straw yields of oats following soil application of MnO (residual effect of 1965) or spraying with  $MnSO_4 \cdot H_2O$  (1¼% solution); means of 3 pots. Also results of leaf analyses (1966 experiment)

	Yield (g)		Mn deficiency index <sup>1</sup>		Leaf Mn on 10/5 (ppm)
	grain	straw	20/5	3/6	
'Wieringermeerpolder' soil					
0 kg MnO/ha in 1965	30.1	36.3	4.3	3.3	9.9
80	43.0	40.2	5.8	5.2	11.9
160	53.7	53.9	7.3	7.8	13.9
320	56.7	56.4	9.4	9.5	15.3
$MnSO_4$ spraying on 10/5, 1/6	55.8	54.0	8.3	10.0	—*
'Biesbosch' soil					
0 kg MnO/ha in 1965	58.3	49.7	9.1	9.3	16.6
80	57.9	48.3	9.3	9.5	14.6
160	57.5	49.4	9.9	10.0	17.6
320	57.0	49.8	10.0	10.0	16.9
$MnSO_4$ spraying on 10/5, 1/6	56.8	49.2	10.0	10.0	—*

<sup>1</sup> Scale as in Table 1

\* Not analysed

ciency. None of the treatments affected yield significantly, nor was plant manganese raised.

In the 1967 pot experiment fertilizing with manganese (manganous oxide or manganese sulphate) was compared with foliar application (manganese sulphate or manganese 'Rayplex'). The results are presented in Table 3. Both manganous oxide and manganese sulphate applied to the soil significantly increased yields of oats. There was found to be no significant difference between the two manganese fertilizers. A quantity of 25 kg of Mn/ha as manganous oxide (63.5% Mn) or manganese sulphate (32.5% Mn) was insufficient to attain maximum grain and straw yields and to control manganese deficiency. Significantly higher yields and practically complete suppression of manganese-deficiency symptoms were obtained with quantities of 50 kg of Mn/ha or more, and with foliar sprays of manganese sulphate or manganese 'Rayplex'. No significant differences were found between these treatments. Maximum yield increases relative to the control plants amounted to 177 and 36% for grain and straw, respectively.

Average grain weight (not mentioned in Table 3) was significantly increased by both soil and foliar applied manganese. In the previous experiments the differences were smaller in this respect.

Table 3 Grain and straw yields of oats following soil application of MnO and MnSO<sub>4</sub>.H<sub>2</sub>O, or spraying with MnSO<sub>4</sub>.H<sub>2</sub>O (1¼% solution) and the polyflavonoid Mn 'Rayplex' (2½% solution); means of 3 pots. Also results of leaf and soil analyses (1967 experiment)

	Yield (g)		Mn deficiency index*		Leaf Mn on 11/5 (ppm)	Reducible soil Mn in nov. 1967 (ppm)
	grain	straw	9/6	27/6		
0 kg Mn/ha; MnO (63.5% Mn)	12.6	29.5	5.8	3.5	13.6	32
25	28.7	25.9	10.0	6.9	28.9	41
50	33.9	28.4	10.0	9.1	40.1	52
100	35.8	28.6	10.0	9.6	67.2	64
25 kg Mn/ha; MnSO <sub>4</sub> .H <sub>2</sub> O	29.1	25.3	9.8	6.3	24.7	41
50 (32.5% Mn)	35.9	28.6	10.0	9.8	39.7	51
100	34.4	27.0	10.0	9.8	56.5	63
MnSO <sub>4</sub> spraying on 5/6	34.6	27.6	10.0	9.0	—	—
Mn 'Rayplex' (9.2% Mn) spraying on 5/6	35.1	27.5	10.0	9.9	—	—

\* Legend as in Table 1

Equivalent amounts of manganous oxide and manganese sulphate produced similar increases in reducible manganese in this 'Wieringermeerpolder' soil. The same applies to plant manganese, showing that the fertilizers supplied equal quantities of plant available manganese. Manganese deficiency was almost completely controlled at 51 ppm reducible soil manganese, which confirms the results of the 1965 experiment. It should be stated here that the plant analysis data (Table 3) refer to stage 3-4. As pointed out on p. 199 the crop was cut at stage 4-5 because no symptoms of manganese deficiency appeared (probably due to temporarily high soil moisture conditions).

## Discussion

In the above pot experiments on 'Wieringermeerpolder' soil about 50 kg of soil-applied manganese per ha in the form of manganous oxide or manganese sulphate was effective in controlling manganese deficiency in oats in the year of application. Under field conditions at least 400 kg of manganese sulphate per ha (100 kg Mn/ha) proved necessary to control manganese deficiency in various crops, as was shown in previous experiments (Henkens, 1962; Henkens and Smilde, 1967). From the results of some potato-field experiments by the Agricultural Advisory Service (Borst and Mulder, 1968), it would appear that this also holds for manganous oxide. As a matter of fact, on 'Wieringermeerpolder' soil broadcasting 80–160 kg of manganous oxide per ha (50–100 kg Mn/ha) increased potato yields to some extent, but was insufficient to control manganese deficiency. Spraying with manganese sulphate not only gave markedly better results but was also less costly.

The data above show that the results obtained in pot experiments are not quantitatively applicable to field conditions. Stenuit (1963) had the same experience when testing the manganese effect of basic slag. This can partly be attributed to better soil moisture and soil temperature conditions in pot experiments favouring manganese availability to plants (Mc Cool, 1935; Mederski and Wilson, 1955). Another important factor is the distribution of manganese-fertilizer particles through the soil (Shepherd et al., 1960) which is usually better in pots than under field conditions.

According to the results of the 1965 pot experiment on the 'Biesboschpolder' soil manganese deficiency in oats was not easily controlled by soil-applied manganous oxide. In fact there was an increase in reducible soil manganese but plant-manganese content was only little affected. As was pointed out in the Introduction, on this type of soil manganese availability is not closely related to reducible soil manganese. It is interesting to note the high level of reducible manganese as compared with the 'Wieringermeerpolder' soil. Leeper (1947) also reports manganese deficiency on marsh soils high in reducible manganese.

In evaluating fertilizing with manganese compounds relative to spraying with manganese sulphate the following literature data should be mentioned. In field experiments with cereal crops on calcareous soils broadcasting manganese sulphate was inferior to spraying (Nicholas and Fisher, 1951; Walsh and Mc Donnell, 1957; Hammes and Berger, 1960; Mc Gregor et al., 1960). Drilling with the seed (25–56 lb/acre of manganese sulphate) was, however, far more efficient than broadcasting and equalled the effect of spraying. Unfortunately, data on placement are lacking in The Netherlands.

Soil-applied manganous oxide and manganese sulphate were equally effective in controlling manganese deficiency in tomatoes grown on calcareous marl, peat and sand soils in pot experiments (Fiskel et al., 1953; Fiskel and Mourkides, 1955). Jones and Leeper (1951) report similar results for oats. In field studies with onions on calcareous muck soil good results were obtained with manganous oxide, banding being more effective than broadcasting (Shepherd et al., 1960). Whereas on acid soils broadcasting manganese sulphate corrected manganese deficiency in citrus trees, equivalent amounts of manganous oxide and manganese dioxide failed to do so. On calcareous soils none of the manganese compounds were effective, but application of a mixture of equal quantities of manganese sulphate and calcium chloride in piles around the trees corrected manganese deficiency (Leonard and Stewart, 1959).

Summarizing the results, it can be concluded that whereas in pot experiments soil application of manganous oxide may be a satisfactory alternative for spraying with manganese sulphate in controlling manganese deficiency, this is not the case under field conditions in The Netherlands. An additional advantage of the latter method is that weed killers or insecticides can be added to the spraying liquid (Toms, 1968). More research is needed to test the effectiveness of manganous oxide when drilled with the seed.

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