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THE AVAILABLE MANGANESE CONTENT OF SOILS IN THE NETHERLANDS DETERMINED BY VARIOUS METHODS

KEY WORDS: manganese in *Avena sativa*, manganese in *Freesia hybr.*, manganese in soils. Soils in the Netherlands.

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ABSTRACT

102 Soil samples collected from arable soils in the Netherlands were analysed for manganese by various extraction methods. Two crops viz. oats (*Avena sativa* L.) and freesias (*Freesia hybr.*) were grown on the samples in pots and also analysed for manganese.

Soil manganese determined in water with the 1:2 volume method showed the best correlation with the manganese content of the crops. Morgan's manganese showed a bad correlation that could be improved by introducing the soil pH value as concomitant variable. Active manganese showed no relationship. The content of manganese of the crops was strongly depended of the pH of the soil.

INTRODUCTION

Sonneveld and Van der Ende[1] introduced the 1:2 volume extract with water for the routine analysis of glasshouse soils. This method was recently used by Sonneveld and Voogt[2] for the determination of the manganese status of soils under conditions of manganese excess in lettuce and some other glasshouse crops. Literature was reviewed by these authors.

In a fluorine investigation[3] 102 samples were collected from arable soils all over the Netherlands, moreover two crops - oats and freesias - were grown on these soils. These samples being available they were used for studying the extractable managese content of soils and its availability to the plant.

METHODS

Samples of 50 litres were collected with a spade from the surface layer of cultivated soils at 102 sites all over the country. A relatively large number of samples - 30 - came from glasshouses and only a very small number from grass land. The soil types involved differed widely in many respects. The pH ranged from 3.9 to 8.05, the calcium cabonate content ranged from 0 to 10.2%, the clay content from 1 to 46% and the organic matter content from 1.4 to 76%.

In April 1973, two 10 litre plastic buckets with a surface area of 491 cm^2 were filled from each soil sample. In one bucket freesias (I) of the variety Rijnveld's Golden Yellow were planted and in the other oats (I) variety Leanda were sown. No fertilisers were applied. After the first crop had been harvested, analar NPK chemicals were applied and a new freesia (II) and oat crop (II) were started. The crops were grown in a glasshouse. The glasshouse air was filtered through charcoal and demineralised water was used for irrigation. The oats were harvested

Other determinations

pH - using a glass electrode in a soil/water suspension, 1:5 w/v, and measured after one night.

$CaCO_3$ - with the Scheibler method.[4]

Organic matter - by loss of weight on ignition at 600°C.

Clay content - by the macro pipet method.

Manganese in crop samples

Crop samples were dried at about 80°C for 24 or 48 hours after which they were milled with an electric coffee grinder. The samples of the first oat crop (Oats I) were destructed with a nitric perchloric and sulphuric acid mixture, a modification of Schaumlöffel.[5] The samples of the other crops, (Oats II and Freesias I and II) were extracted with trichloroacetic acid (2%) according to Legget & Westerman.[6] The extraction ratio was 1:100 w/v and the suspension was shaken at room temperature for 16 hours. A few samples were also destructed. The values obtained by both methods were very similar which is in agreement with the results obtained by Legget & Westerman. In the case of the freesias only the aerial parts of the plants were used. The manganese content was determined with the atomic absorption spectrophotometer. The results are expressed as ppm Mn of the dry matter.

RESULTS

Table 1 shows the extreme and the average values of manganese obtained by three analytical methods in soil samples obtained from glass-houses and from the open. The division into two categories was made as divergent values were found in previous studies.

when the plants had reached a height of about 20 cm. The freesias were harvested just before flowering. The oats were cut off just above soil level. Of the freesias the fresh and dry weights of the aerial and subterranean parts were determined.

ANALYTICAL METHODS

Manganese in soils

Weight extract (samples collected during April 1973).

The samples were dried at 45°C for one night. Two extractants were used for the determination of manganese :

a. *Morgan's manganese.* Extracted with Morgan's solution : *Na-acetate* acetic acid buffer (pH 4.8), containing 3% Na-acetate. Extraction ratio 1 : 2½ w/v, shaking at room temperature for 30 minutes.

TABLE 1. Extreme and mean values of manganese obtained with three analytical methods in glasshouse and outdoor soils.

	watersoluble Mn ppm Mn in the 1:2 extract	Morgen's Mn ppm Mn in dry soil	active Mn ppm Mn in dry soil
outdoor soils (n = 72)			
lowest value	0.01	3	3
highest value	19.32	115	920
mean	1.27	25.4	191.9
glasshouse soils (n = 30)			
lowest value	0.01	5	28
highest value	11.51	163	465
mean	0.60	35.0	133.1
total mean (n = 102)	1.07	28.2	174.6

b. Active manganese. The extractant used is a Morgan's solution with 0.2% hydroxylammonium chloride, pH 4.8. Extraction ratio 1 : 2½ w/v, shaking at room temperature for 30 minutes.
After filtering the extracts were decolorised with charcoal. Manganese was determined in the clear extracts using the periodate method. The results are expressed as ppm Mn of the dry soil.

Volume extract (samples collected during February 1974 after the second freesia crop).

a. Mn water 1:2 v/v. A quantity of soil in field moist condition was added to two parts of water increasing the total volume by one part. The suspension was shaken at room temperature for 20 minutes. After filtration manganese was determined with the Varian Techtron model AA5 atomic absorption spectrophotometer. The results are expressed as ppm Mn of the extract.

Table 1 gives an impression of the manganese levels in the soil samples examined. Two of the methods used produced higher manganese values in outdoor soils and the third method showed higher manganese levels in the glasshouse soils. It is not clear what importance should be attached to the differences obtained between the glasshouse and outdoor soils. The active manganese determinations gave the highest values. This was to be expected as only small amounts of Mn are dissolved in water. Laske[7] found an average of 208 ppm active Mn in soils under glass.

If one wants to compare the water-soluble Mn figures with the other values it is necessary to convert the figures into dry soil values. For a rough calculation the ppm in the extract should be multiplied by 1 if the organic matter content is 0, by 2 if it is 10%, by 3 if it is 20% and by 4 if the soil contains 30% organic matter. The exact values may be obtained from Sonneveld & Van den Ende.[1]

For an average organic matter content of 10.5% an average water-soluble manganese value of 2 ppm Mn of the dry soil was found. More exactly, the average for outdoor soils was 2.70 ppm and for glasshouse soils 1.42 ppm Mn of the dry soil. The highest values calculated were 28.70 ppm water-soluble Mn of the dry soil for outdoor soils and 24.68 ppm for glasshouse soils.

In Table 2 the correlation coefficients are given for the relationship between manganese in the soil determined by three methods and some other important soil analysis figures. Organic matter is not related to the manganese content but the other figures are. Active Mn and in Morgan's solution soluble manganese contents are positively correlated with the pH and the calcium carbonate content, but water-soluble Mn is negatively correlated. The same was found in the case of the clay content but since the pH and the clay content are also related ($r = 0.47^{**}$), the question arises whether it is the clay content or the pH which has an effect on the manganese levels. The most important factor must be the pH as it regulates

TABLE 2. Correlation coefficients for the relationship between the manganese content in soil determined by various analytical methods and some other important soil analysis figures (n = 102)

	water-soluble Mn	active Mn	Morgan's Mn
pH	-0.60 **	0.40 **	0.43 **
$CaCO_3$	-0.25 **	0.50 **	0.31 **
organic matter	-0.08	0.10	-0.05
clay	-0.29 **	0.37 **	0.59 **

* : P = 0.05 ** : P = 0.01

mainly the solubility of the manganese compounds in the soil solution. Figure 1 illustrates the relationships between pH and active manganese.

In Table 3 the correlation coefficients are given for the relationship between the manganese levels in crops and various soil analysis figures. Figure 2 illustrates the relationships between the pH of the soil and the manganese content of the fertilised freesia crop (Freesia II). Figure 3 shows the relationship between water-soluble manganese in the soil and the manganese content of the second oat crop (Oats II).

No symptoms of manganese deficiency or excess were observed. It follows from the data collected in Table 3 that the pH and the water-soluble Mn content are the most important factors regulating tissue manganese. Calcium carbonate reflects the effect of the pH and the same is probably true for the clay content as the clay content and the pH are mutually highly correlated. It is noteworthy that the correlation between active Mn and the manganese content in crops is negative. The correlation with Morgan's Mn is also indistinct. The explanation may be found in the fact that the figures for active Mn and Morgan's Mn are positively corre-

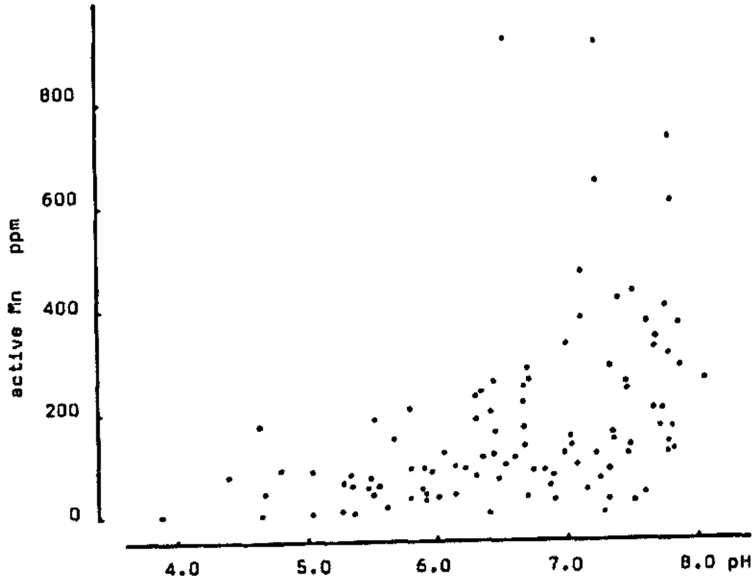

FIG. 1. The relationship between the pH of the soil and the active manganese content (ppm of the dry soil)

TABLE 3. Correlation coefficients for the relationship between the manganese contents of crops and various soil analysis figures including those for manganese.

Manganese in crops :	Freesias I	Freesias II	Oats I	Oats II
pH	-0.59 **	-0.71 **	-0.62 **	-0.62 **
$CaCO_3$	-0.21 *	-0.40 **	-0.20 *	-0.26 **
organic matter	0.02	-0.04	-0.02	-0.08
clay	-0.26 **	-0.43 **	-0.28 **	-0.40 **
water-soluble Mn	0.75 **	0.88 **	0.74 **	0.83 **
Morgan's	0.24 *	-0.10	0.11	0.83
active Mn	-0.21 *	-0.30 **	-0.22 *	-0.31 **

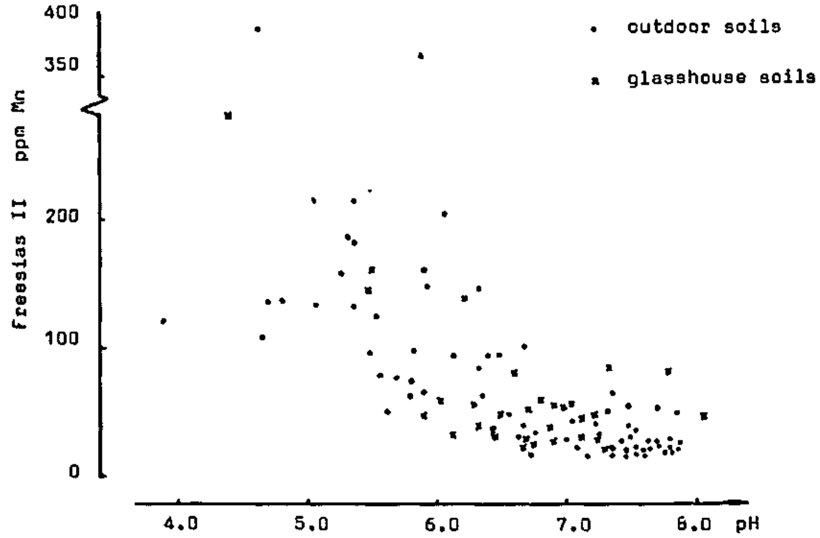

FIG. 2. The relationship between the pH of the soil and the manganese content of the second (fertilised) freesia crop (ppm Mn of the dry matter)

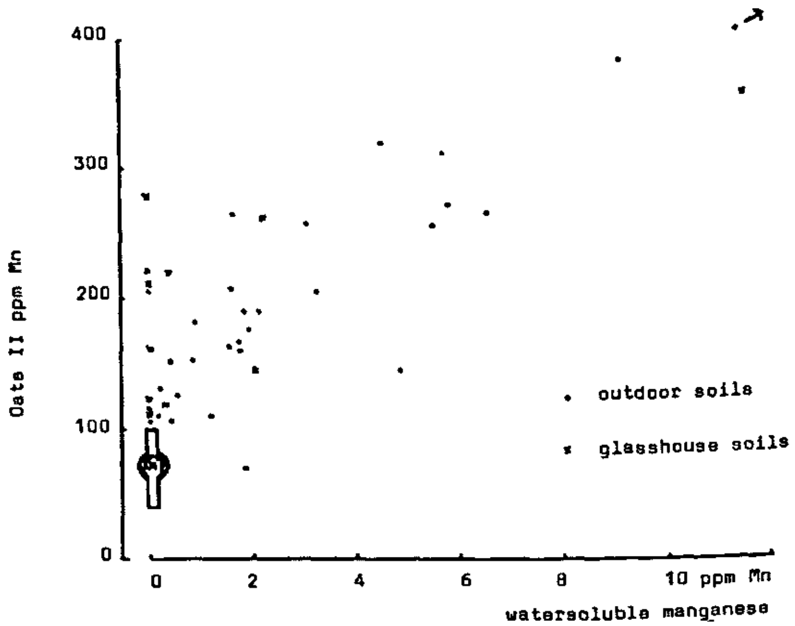

FIG. 3. The relationship between the watersoluble manganese content of the soil and the manganese content of the second (fertilised) oat crop (ppm Mn on dry weight basis)

lated with the pH (see Table 2 and Figure 1) and that the pH has a considerable negative effect on the manganese uptake by plants.

As both the pH and water-soluble Mn are highly correlated with the tissue manganese the multiple correlation coefficients were computed as multiple lineair regression equations between crop manganese and Mn water with the pH as the second independent variable. The same computations were carried out for active manganese and Morgan's manganese. The results are given in Table 4.

TABLE 4. Multiple regression equations and multiple correlation coefficients (R) for the relationship between manganese in crops (y) and in soils (x) with the pH as concomitant variable (ppm Mn of crop dry matter).

Crops	x = soil manganese	R
	Water-soluble Mn (ppm Mn of the extract 1:2)	
Freesias I	y = 11.2 x − 10.7 pH + 108.8	0.77 **
II	y = 18.3 x − 21.0 pH + 194.1	0.91 **
Oats I	y = 26.0 x − 33.3 pH + 300.1	0.77 **
II	y = 23.8 x − 17.3 pH + 210.7	0.84 **
	Morgan's Mn (ppm Mn of dry soil)	
Freesias I	y = 1.063 x − 41.4 pH + 293.4	0.79 **
II	y = 0.610 x − 58.7 pH + 445.3	0.74 **
Oats I	y = 1.952 x − 98.9 pH + 705.8	0.73 **
II	y = 1.546 x − 74.6 pH + 570.8	0.74 **
	Active Mn (ppm Mn of dry soil)	
Freesias I	y = 0.015 x − 30.9 pH + 251.4	0.59 **
II	y = 0.006 x − 52.5 pH + 420.5	0.71 **
Oats I	y = 0.041 x − 80.7 pH + 633.5	0.62 **
II	y = −0.028 x − 55.3 pH + 491.9	0.62 **

A comparison of the multiple correlation coefficients (Table 4) with the simple correlation coefficients (Table 3) shows that the introduction of the pH as the concomitant variable only slightly improves the relationship between water-soluble Mn and tissue manganese. Introduction of the pH into the relationship of active Mn and tissue manganese gives a considerable improvement, but it is remarkable that the multiple correlation coefficients are exactly the same as the simple correlation coefficients for the relationship between the pH and the manganese content of the crop. One can draw the conclusion that the introduction of the data for active Mn into the relationship between the pH and tissue manganese serves no purpose. However, the introduction of the pH as the third variable is of great importance to the relationship between Morgan's Mn and tissue manganese. It is impossible to asses the values for Morgan's Mn without taking the pH into consideration. In comparing the various methods it must be kept in mind that water-soluble manganese was determined in samples collected at the end of the experiment. According to Sonneveld & Voogt,[2] Mn water changes to some degree with the salt content of the soil which in turn may change in the course of crop development.

A logarithmic evaluation of the figures for water-soluble Mn was studied but it did not yield higher correlation coefficients. Steam sterilisation is known to have an effect on the availability of soil manganese and in Figures 2 and 3 the results obtained from glasshouse soil samples have been plotted separately. The figures show that the crops grown on glasshouse soils did not show a clear difference in manganese content.

CONCLUSION

The active manganese content of soils in the Netherlands ranged from 3 to 920 ppm Mn of the dry soil, with 175 ppm as the average. Acid sandy soils contain only small amounts of active manganese. Morgan's manganese was inadequately correlated with tissue manganese. The correlation could be improved by introducing the pH value into the multiple regression as the concomitant variable. Active manganese serves no purpose in predicting tissue manganese which can be done quite adequately by taking into account the pH. Water-soluble manganese gave the best correlation with manganese in crops.

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