INFLUENCE OF AGE AND ORGANIC MATTER ON THE AVAILABILITY OF MANGANESE IN MARINE AND ESTUARY SOILS

by

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I. Introduction

Manganese deficiency is rather common on holocene marine and fluvial sand and clay soils with high pH in the Netherlands. In contrast to our pleistocene sandy soils, where manganese deficiency is generally caused by overliming, both deficient and healthy soils have a high pH in consequence of their calcium-carbonate content. There is a marked difference between the manganese economy of marine sediments and that part of the fluvial clays which have been deposited in the fresh-water tidal area. A study of the manganese status in relation to the availability for crops of these two soil types will be given in this paper.

II. Methods of analyses

Leeper (4, 5) formulated the Mn-status of a soil as a dynamic oxidation-reduction system in which the following forms of Mn are in equilibrium:

$$\underset{\text{exchangeable}}{Mn^{++}} \rightleftarrows \underset{\text{easily reducible}}{MnO_2 \text{ (colloidal size)}} \rightleftarrows \underset{\text{rather inert.}}{MnO_2 \text{ (coarse)}}$$

Besides in size the reducible and inert forms differ in that the latter have a higher order in their crystal lattice.

The three forms of Mn mentioned are studied. The exchangeable Mn was extracted by means of a solution of neutral normal ammonium acetate. From a technical point of view the easily reducible Mn was directly determined without eliminating the exchangeable forms by treating the soil immediately with a neutral solution of normal ammonium acetate, containing 0.2% hydroquinone as a reducing agent. The sum of the three forms of Mn, called total Mn, was determined according to Kurmies (3) by ashing the sample at 500—550° C with ammonium nitrate and subsequent treating with 25% hydrochloric acid.

The Mn in the extracts was in all cases analysed by means of the formaldoxime method of Kniphorst (2). The soil samples were taken from the field to a depth of 20 cm over smaller or larger areas.

III. Experimental results

Both in marine and estuary soils existed a correlation between the clay + silt separate (fraction < 16 microns) and amount of reducible Mn. In figure 1 this relation is plotted for three marine regions and the estuary soils of the Biesbosch. The fifth line with a swarm of dots represents the correlation in the North East Polder area (one of the reclaimed polders of the former Zuiderzee), of which the marine or fluvial origin is not quite certain.

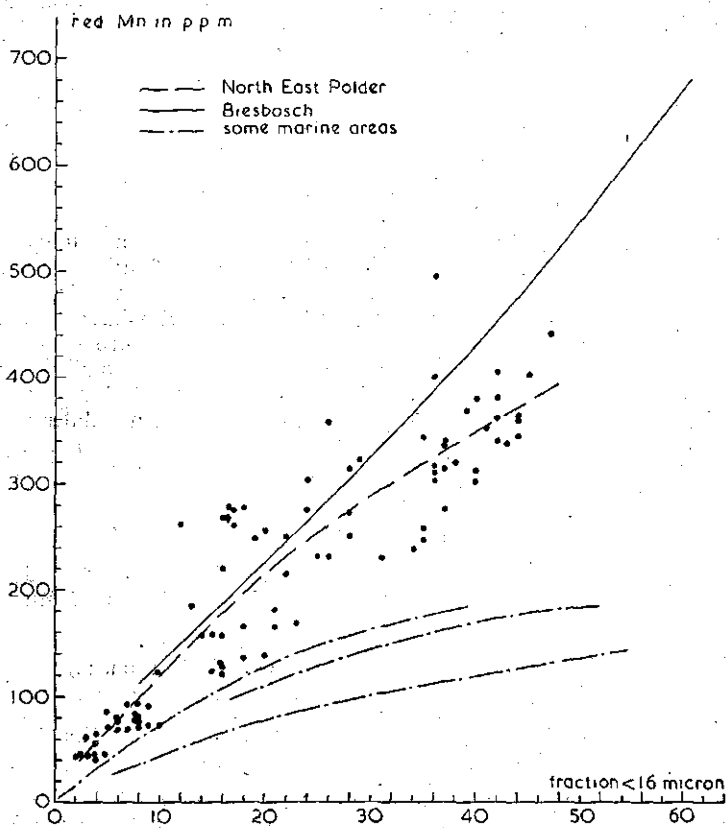

Fig. 1

Relation between content of reducible Manganese and clay + silt separate for marine and estuary soils.

a) *Availability in marine soils*

On marine soils the availability of Mn for cereals and beets could partly be characterized by the amount of reducible Mn in relation to the organic matter content of the soil (figure 2). With organic matter contents < $2\frac{1}{2}$% crops are deficient with < 60 p.p.m. reducible Mn and are healthy with Mn-contents > 70 p.p.m. At higher contents of organic matter at least 100 p.p.m. reducible Mn *is needed* for the plants to be healthy, although deficiency may occur.

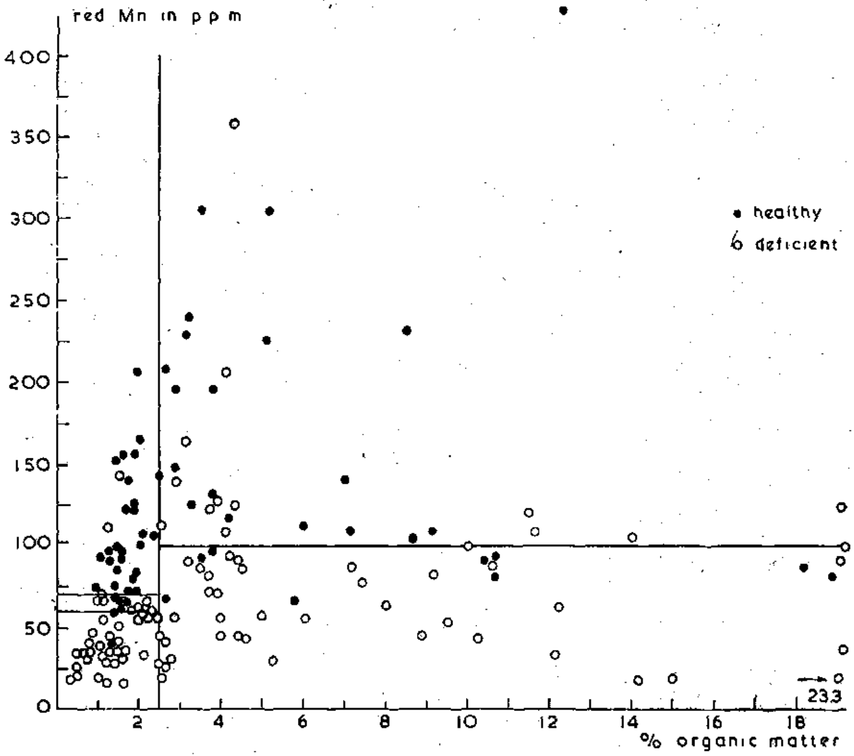

FIG. 2

Distinction of deficient and healty marine soils with regard to Manganese (Beets and cereals).

b) *Availability in estuary soils*

As demonstrated in figure 1 the amount of reducible Mn at a given content of the fraction < 16 microns in the estuary soils is much higher than in the marine soils. In contradiction to this high status of reducible Mn is the fact that Mn deficiency is very common on these soils but that it is not at all possible to make a distinction between deficient and healthy soils which fits into the above mentioned scheme for marine sediments. Mn deficiency in this area even appears with 600—700 p.p.m. reducible Mn in the soil. The same applies to the North East Polder soils, where also a high Mn-status is found (figure 1). This paradoxical behaviour of estuary soils gave rise to a more detailed study of the changes in forms of Mn during the principal process of ripening of the original fluvial mud to arable land.

c) *The ripening process of estuary sediments*

In the fresh-water tidal area of Rhine and Meuse (Biesbosch) we have to do with a sequence of stages of ripening. Physically increasing ripening is characterized by a loss of water content and shrinkage of the sediment.

On the forelands we have progressively in stages of ripening mud flats, muds with rush vegetation, reed marshes (Phragmites communis), and willow tidal forests. Luxuriant vegetation begins slightly above low water level (rushes) and at this stage the physical ripening process begins. For further details concerning the physical ripening of these sediments is referred to Zonneveld (6), thanks to whose expert advice manganese research in the Biesbosch could be carried out.

With regard to the manganese problem it proved to be more suitable to use the redox-potential as a measure of stage of ripening than the water content (water bound to 1 g of the fraction $<$ 2 microns).

The determinations of redox-potentials were carried out according to Flaig (1) by putting the wet soil sample in a water suspension, by forcing nitrogen bubbles through it, and measuring the potential in relation to a calomelectrode. The potentials, which could be measured with an accuracy within 20 mV, were converted into the normal hydrogen-electrode. As all sediments of the Biesbosch area vary within a narrow pH-limit (7.0—8.0) no corrections for pH were made.

Aside from the relation of soil factors to ripening stages within one group of sediments (within one group of sediments, e.g. Willow tidal forest, the accompanying vegetation of the willows varies according to the redox-potential of the sediment), the average results for each group are given in table 1. The healthy and deficient arable soils also given in the table are found on the inner side of an embankment.

TABLE 1

RELATION BETWEEN SOME SOIL FACTORS (AVERAGE VALUES FOR THE MENTIONED AMOUNTS) AND STAGES OF RIPENING IN THE BIESBOSCH

Ripening stage	Amount of samples	Exchangeable Mn in ppm	Reducible Mn in ppm	Redox-potential in mV	C/N-ratio of organic matter	% Moisture
Mud flats	25	47	54	60	26	39
Reed-marshes..	7	87	485	140	26	45
Willow tidal forests........	17	6	904	410	20	40
Deficient arable soils........	33	negligible	447		16.0-11.0	
Healthy arable soils........	25	negligible	357		11.0- 7.0	

Table 1 shows that in the very reduced condition of the muds appreciable amounts of exchangeable Mn are found. Considering that the contents of reducible Mn were determined without eliminating the manganous ions, it is clear that the fractions of real easily reducible

Mn were very small. The greater part of Mn in the muds consists of inert oxides. When the mud flats ripen to the stage of reed-marsh a mobilization of the inert oxides takes place and results in a rather high status of reducible Mn.

The simultaneous rise in the level of exchangeable Mn proves that the first stage of the mobilization of the inert oxides is a reduction to manganous ions, followed by a reoxidation to reducible Mn. With rising redox-potential the mobilization of inert oxides reaches a maximum value in the willow tidal forests. In consequence of oxidation only a small fraction of exchangeable Mn remains. After enclosing the sediments, a part of the mobilized oxides recrystallize to the inert forms, but only in so far as a high level of reducible oxides remains. In the young arable soils a lack of available Mn is soon apparent, in spite of a high status of reducible oxides.

Table 1 further shows that during the ripening process of the foreland there is a decrease in the C/N-ratio of the organic matter. This decrease continues after the enclosure of the sediments.

On occount of C/N-determinations we could sharply distinguish between deficient and healthy soils in the arable areas of the Biesbosch, as is seen from the table. In consequence of a further decrease of the C/N-ratio during cultivation, deficient soils will get healthy after a shorter or longer time. This corresponds to the experience that in the Biesbosch area Mn deficiency is only common on the younger sediments.

These changes in the Mn status of estuary soils are plotted against the fraction $<$ 16 microns in fig. 3. To show that besides a certain fraction of reducible Mn (mainly manganous ions), mud flats contain a very high content of inert oxides, the total Mn-contents of a number of these mud flats have been plotted. The figure further clearly demonstrates the regression in reducible oxides, in consequence of recrystallizing to the inert forms, by reclaiming willow tidal forests (sediments enclosed after 1920). A further regression of mobilization has taken place as compared with sediments reclaimed in the period 1600—1850. The latter sediments do not show any difference from sediments older than 1600 (not plotted).

d) *Availability in North East Polder soils*

As has been described, Mn deficiency is also very common at high levels of reducible Mn in the North East Polder area. Here both deficient and healthy soils have high C/N-ratios in the organic matter ($>$ 11). A distinction between deficient and healthy soils as in the Biesbosch is not possible here. Of the organic matter in this area it is known that the decomposition after enclosure of the sediments was negligible, which is in sharp contrast to the Biesbosch soils. An investigation of the changes in Mn during the principal ripening process of soils equivalent to that of the North East Polder has been projected.

e) *The ripening process of marine sediments*

In connection with the above mentioned changes in the Mn status of estuary soils an equivalent investigation was carried out in the marine forelands of the north of the country (N. Groningen). The status of exchangeable and reducible Mn in the fresh mud flats with low redox-potential resembled the muds in the fresh-water tidal area. In

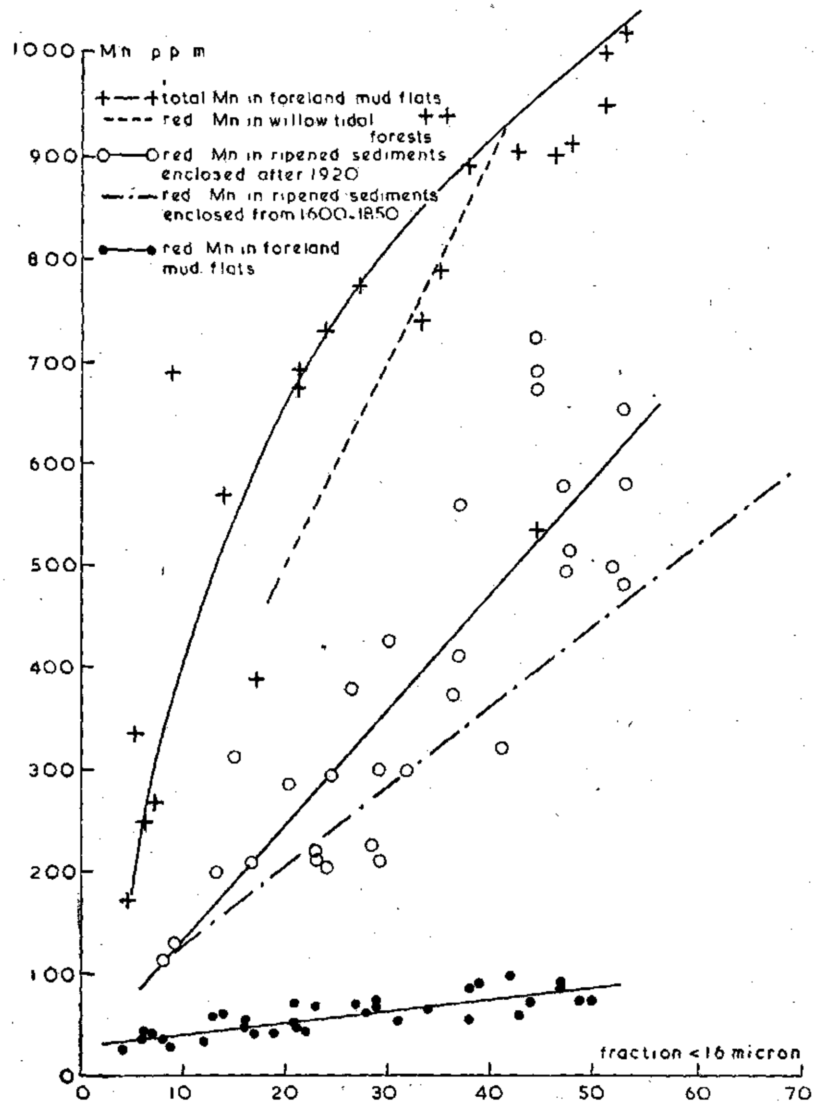

FIG. 3
Comparison of contents of reducible Manganese in different stages of ripening in the Biesbosch.

consequence of the marine origin of the sediments total Mn contents were much lower. At a comparable redox-potential the mobilization in the marine sediments attain much lower values than in estuary deposits.

Comparison of the contents of reducible Mn from marine foreland soils with high redox-potential with arable soils reclaimed from 1250 to 1718 showed only a small regression in mobilization. This demonstrates that mobilization of inert oxides does not give rise to such a labile state of reducible oxides as is the case in estuary soils. The average value of the C/N-ratio of the organic matter in the marine foreland sediments was 12 (in the whole range of redox-potentials it varied between the narrow limits 11—13) which is sharp contrast with corresponding soils under estuary conditions.

IV. DISCUSSION

In a separate investigation it was shown that under high pH conditions the amount of exchangeable Mn was not a reliable method for determining the available Mn in soils. According to Leeper the possibilities of reduction of higher oxides (due to root environment or reducing circumstances in the soil) determine the Mn-supply of crops. This hypothesis is practicable for our marine soils in so far as the contents of organic matter are low. The influence of higher humus contents needs further investigation. The unavailability of Mn in estuary soils, despite high amounts of reducible oxides, may be explained by the fact that the small amounts of manganous ions necessary for the plant uptake and reduced from the abundance of higher oxides are fixed to unavailable organic chelate compounds under conditions of high C/N-ratio. A high C/N-ratio under estuary conditions means an active decomposition of organic matter which may give rise to an accumulation of compounds with high chelating capacity. As to the further ripening process of arable land, it is worth noting that in the course of recrystallization of reducible Mn, which actually means lower availability, Mn-deficiency disappears in consequence of decreasing C/N-ratio of the organic matter.

The deviating behaviour of the North East Polder soils according to C/N-ratio and availability of Mn may be explained from the fact that high C/N-ratio and healthy soil point to an admixture of the organic matter (consisting in stable humification products), which despite their high C/N-ratio shows no symptoms of decomposition.

The most striking fact in these investigations is the mobilization of inert oxides. Three possible causes for this effect will be discussed.

a) With low redox-potentials accumulation of sulfides takes place to a high extent in the estuary soils in consequence of favourable conditions for vegetation (sulfates reduced by an abundance of organic matter as oxygen-acceptor). Increasing redox-potentials give rise to considerable sulfuric acid formation, which might be able to dissolve the inert Mn-oxides. Under marine conditions a smaller amount of decomposable organic matter is available with a smaller sulfide production in consequence. This would be in agreement with the lower mobilization in the latter soils. The hypothesis is however contradicted, by our experience that under marine conditions the largest mobilization is attained at the lowest sulfate production.

b) Organic matter directly reduces the inert oxides. As there is an intensive decomposition of organic matter during the mobilization process, (especially in the fresh-water tidal foreland soils), this possibility must not be ignored.

c) Special attention should be paid to our observation concerning diatoms and mobilization of inert oxides.

By sampling marine foreland muds in some cases we separately sampled the upper 1 cm and the underlying 19 cm. Both layers showed very low redox-potentials, but the upper layers had increased levels of manganous ions. The increases were abnormally high with vegetations of diatoms. In consequence of the low redox-potentials no reoxidation of these high levels of manganous ions occurs.

Further investigations are planned to solve the problem of mobilization of inert oxides.

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ZUSAMMENFASSUNG

Während der Untersuchungen von niederländischen Kulturböden auf Mangan, im Zusammenhang mit der Verfügbarkeit für die Pflanzen, ergab sich ein erheblicher Unterschied zwischen *marinen* und *fluvialen* Sedimenten.

In den mässig mit Mangan versorgten marinen Böden wurde der Einfluss vom Humus auf die Verfügbarkeit des reduzierbaren Mangans studiert.

Trotz sehr hoher Gehalte des reduzierbaren Mangans in den Aestuariumböden des Süsswassergezeitengebietes (fluviatile Böden), treten starke Mangelerscheinungen auf. Ein Zusammenhang zwischen Verfügbarkeit des Mangans und C/N-Verhältnis des organischen Stoffes konnte in diesem Gebiete festgestellt werden.

Zur Erklärung der Unterschiede der Manganversorgung in Sedimenten vom Salz- und Süsswassergezeitengebiet wurde die Bodenbildung hinsichtlich des Mangans in beiden Gebieten von den frischen Schlämmen bis zum endgültigen Ackerland untersucht. Bei den Aestuariumböden war während der Reifungsprozesse eine stark ausgeprägte Mobilisierung von unverfügbaren Manganoxyden zu erkennen, im Gegensatz zu den marinen Sedimenten, wo diese Prozesse nur in beschränkter Weise hervorgehen. Die Ursachen von diesem verschiedenen Verhalten werden diskutiert.

RESUME

Lors des recherches sur la teneur en manganèse des sols cultivables aux Pays-Bas et l'assimilabilité de celui-ci pour les plantes, nous avons trouvé une différence remarquable entre les sédiments marins et alluviaux.

Dans les sols marins avec des teneurs en manganèse moyennes, l'influence de l'humus sur la disponibilité du manganèse réductible fut étudiée.

Malgré les fortes teneurs en manganèse réductible dans les sols des estuaires de la zone des marais d'eau douce (sols fluviatiles), de fortes carences de manganèse furent constatées. Nous avons pu déterminer une relation entre l'assimilabilité du manganèse et le quotient C/N de la matière organique des sols en question.

Pour éclaircir les différences d'assimilabilité respectives du manganèse dans les sédiments des zones de marais salins et d'eau douce, la genèse des sols des deux zones fut étudiée depuis les sédiments frais jusqu'aux sols cultivables en résultant finalement. Lors de la maturation des sols des estuaires une très forte mobilisation des oxydes de manganèse difficilement assimilables put être constatée, contrairement aux sédiments marins, où ce processus ne se passait que sur petite échelle. Les causes de ce comportement différent sont discutées.