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Determination of plant-available manganese from soils by acid ammonium acetate-EDTA extraction

OILI MOHAMMADI[a], MARKKU YLI-HALLA[a] and VÄINÖ MÄNTYLAHTI[b]

[a] *Kemira Oy, Espoo Research Centre, Luoteisrinne 2, SF-02270 Espoo, Finland*

[b] *Viljavuuspalvelu Oy — Soil Analysis Service Ltd, Vellikellontie 4, SF-00410 Helsinki, Finland*

Abstract. Manganese was extracted with a solution containing 0.5 M NH_4-acetate, 0.5 M acetic acid and 0.02 M Na_2-EDTA at pH 4.65 (AAAc-EDTA) from 86 soil samples collected from plough layers in Finland. The results were compared to the quantities of exchangeable, reducible (three methods) and total Mn of the soil samples as well as to Mn uptake in a pot experiment in which four yields of ryegrass were grown. $Mn_{AAAc-EDTA}$ ranged from 1.8 to 158.8 mg/kg, mean 32.2 mg/kg. $Mn_{AAAc-EDTA}$ correlated more closely with reducible Mn (r = 0.82*** – 0.87***) than with total Mn (r = 0.50***) or exchangeable Mn (r = 0.45***), suggesting a relationship between reducible Mn and $Mn_{AAAc-EDTA}$. In order to take into account the effect of pH on plant-availability of $Mn_{AAAc-EDTA}$, the $Mn_{AAAc-EDTA}$ indices were multiplied by two different pH correction coefficients. The pH correction resulted in a closer correlation between $Mn_{AAAc-EDTA}$ and exchangeable Mn, but in a poorer correlation between $Mn_{AAAc-EDTA}$ and reducible Mn. The pH-corrected $Mn_{AAAc-EDTA}$ indices or exchangeable Mn explained the variation in the Mn content of the first ryegrass yield to a higher degree (R^2 = 33—38 %) than did the original $Mn_{AAAc-EDTA}$ indices (R^2 = 3 %). However, the original $Mn_{AAAc-EDTA}$ indices explained 38—55 % of the variation in the Mn content of subsequent ryegrass yields, whereas the pH-corrected indices explained only 16—34 % of the variation. Thus, $Mn_{AAAc-EDTA}$ is an indicator of the potentially plant-available reserves of Mn, while the pH-corrected indices reflect the quantity of the readily available Mn in the soil.

Index words: exchangeable manganese, reducible manganese, total manganese

Introduction

The supply of soil Mn to plants is of interest both at low levels where deficiency may occur and at excessive levels where toxic reactions may arise. Deficiency occurs mainly in coarse-textured soils (GOLDBERG and SMITH 1985), in soils of inherently low total Mn content, in organic and tile-drained soils, in neutral and calcareous soils, and in formerly acidic soils that have been limed (REISENAUER 1988). Mn toxicity can be a growth limiting factor in acid soils (WRIGHT et al. 1988), in soils high in total Mn or in soils of low oxygen levels caused by poor drainage, compaction or excessive irrigation or rain (REISENAUER 1988).

A number of properties control Mn availability and cause plant-available Mn levels in the soil to vary with time. These properties include: soil pH, total Mn content, soil aeration status, microbial activity and organic matter content (FOY 1984). Consequently, it has been even suspected that the estimation of plant-available Mn by simple chemical extraction is not feasible. In Denmark, the Mn fertilization recommendations are indeed based on soil pH instead of soil Mn indices (NILSSON 1984). CARLGREN (1987) found in field experiments in Sweden that only Mn deficiency symptoms were reliable indicators of need of Mn fertilization. However, several extractions have been used to assess the quantity of plant-available soil Mn, but general agreement does not exist about the most appropriate method. REISENAUER (1988) classified the extractants used for soil Mn into five groups: (1) water and dilute salt solutions, (2) ammonium acetate, pH 4 or pH 7, with or without reducing agent, (3) dilute acids, (4) chelate solutions (DTPA and EDTA) and (5) total soil Mn fusion analysis. REISENAUER (1988) reviewed, that most workers have had little success in relating soil analysis to plant uptake of Mn. In general, the acid extracts and DTPA have given the closest correlations.

For routine soil analysis, it is ideal to use a universal extractant for the simultaneous determination of many nutrients. LAKANEN and ERVIÖ (1971) compared eight extractants for the determination of Cu, Zn, Mn, Fe, Mo and Co in soils. They found that adding the chelating agent EDTA to acid (pH 4.65) ammonium acetate (AAAc) increased the extractability of Cu, Fe, Mo and Co, as compared to ammonium acetate alone. The EDTA addition did not increase the extractability of Mn markedly, neither did it make the correlation between plant and soil Mn closer. However, since 1986, in addition to other micronutrients, also Mn has been extracted with AAAc-EDTA in soil testing in Finland.

According to SILLANPÄÄ (1982), the AAAc-EDTA extraction method as such is a poor indicator of the Mn status of soil, and a pH correction is needed to eliminate the difference between the pH effects on plant Mn and soil Mn. Therefore, in Finland the $Mn_{AAAc\text{-}EDTA}$ indices are multiplied by a pH correction coefficient before interpretation of the results of a routine soil analysis.

The aim of this study was to examine the relationships between AAAc-EDTA extractable soil Mn and other soil Mn indices, including reducible Mn, which is likely to form the reserves of plant-available Mn. Further, the ability of $Mn_{AAAc\text{-}EDTA}$ to predict the content and the uptake of Mn by ryegrass in a pot experiment was investigated. The effect of pH correction of $Mn_{AAAc\text{-}EDTA}$ on the usefulness of the results was also studied.

Materials and methods

The suitability of the AAAc-EDTA extraction for the determination of plant-available Mn in soils was studied with 86 mineral soil

Table 1. Some chemical and physical characteristics of the soil samples.

	$pH(H_2O)$	$pH(CaCl_2)$	Organic C, %	Clay*, %
Minimum	4.4	3.9	0.6	4
Maximum	7.3	7.2	13.9	65
Mean	5.3	5.1	3.6	22.7

* particle size <0.002 mm

samples collected from plough layers (A_p horizons) of 84 cultivated and two virgin soils in southern and middle Finland. The soil samples were part of a larger material presented by MÄNTYLAHTI (1981). Some physical and chemical characteristics of the soil material, relevant to the present study, are presented in Table 1.

The same soil samples have earlier been analyzed for exchangeable, reducible and total soil manganese and the soils have also been used in a pot experiment in which Mn uptake by ryegrass was determined (MÄNTYLAHTI 1981). Briefly, exchangeable Mn was determined by using cation exchange resin (Amberlite IR-120), saturated with Mg^{2+}; the reducible Mn was determined by using (1) hydroquinone, (2) hydroxylammonium chloride and (3) ascorbic acid as reducing agents; the total manganese was determined by a sodium carbonate fusion method. In the pot experiment, Italian ryegrass was grown in 100 grams of soil. Four yields were harvested without reseeding, and the Mn content of the plant material was determined and the uptake of Mn per pot was calculated.

For the current study, soil Mn was extracted for 60 min by AAAc-EDTA (0.5 M CH_3COOH, 0.5 M CH_3COONH_4, 0.02 M Na_2-EDTA, pH 4.65) at the soil to solution ratio of 1 : 10 (v/v) (LAKANEN and ERVIÖ 1971). Two different coefficients were used for the pH correction of the $Mn_{AAAc\text{-}EDTA}$ indices. Coefficient 1 (SILLANPÄÄ 1982) that is based on a world-wide material was $10^{8.092-2.275\ pH+0.152\ pH^2}$. Coefficient 2 ($10^{6.321-1.761\ pH+0.111\ pH^2}$) has been calculated at the Department of Soil Science in the Agricultural Research Centre of Finland according to the method of SILLANPÄÄ (1982) by using the results of soil and plant analyses of materials originating in Finland (KÄHÄRI and NISSINEN 1978, SIPPOLA and TARES 1978). Coefficient 2 is used for pH correction of the Mn indices of routine soil test in Finland. For the calculation of coefficient 1, pH($CaCl_2$) is used and for the coefficient 2, pH(H_2O).

Results

In the extraction of Mn by the AAAc-EDTA method, the results are expressed as mg/dm^3 of soil. However, in order to be able to reliably compare these results with the ones presented by MÄNTYLAHTI (1981), expressed as mg/kg, the present results were converted to mg/kg by dividing them by the volume weight of the soil. $Mn_{AAAc\text{-}EDTA}$ ranged from 1.8 to 158.8 mg/kg. On an average, the quantity of $Mn_{AAAc\text{-}EDTA}$ was 6.4 % of the quantity of total Mn and four times greater than the quantity of exchangeable Mn (Table 2). AAAc-EDTA extracted less Mn than did hydroxylammonium chloride and ascorbic acid but more than did hydroquinone. The present mean of $Mn_{AAAc\text{-}EDTA}$ (32.2 mg/kg or 33.3 mg/dm^3) was 40 % lower than that reported by SIPPOLA and TARES (1978) for 2 015 soil samples taken from timothy fields from various parts of Finland. However, the

Table 2. Minimum, maximum and mean values of soil Mn indices.

Mn index	Minimum, mg/kg	Maximum, mg/kg	Mean, mg/kg
AAAc-EDTA	1.8	158.8	32.2
AAAc-EDTA, pH correction 1	4.2	1097.4	131.0
AAAc-EDTA, pH correction 2	2.0	327.7	47.2
Exchangeable*	1.2	34.4	7.7
Hydroquinone-reducible*	0.3	100.9	25.5
Hydroxylammonium chloride-reducible*	0.8	186.6	47.1
Ascorbic acid-reducible*	1.1	233.3	62.6
Total Mn*	202	1296	508

* determined by MÄNTYLAHTI (1981)

ranges were practically equal in both materials.

AAAc-EDTA extractable Mn correlated most closely with hydroxylammonium chloride-reducible Mn ($r = 0.87$***) (Table 3). $Mn_{AAAc\text{-}EDTA}$ correlated more closely also with hydroquinone-reducible ($r = 0.83$***) and ascorbic acid-reducible Mn ($r = 0.82$***) than with exchangeable Mn ($r = 0.45$***) or total Mn ($r = 0.50$***).

The use of pH correction changed the original results more or less. Below pH 5.8 (coefficient 1) or pH 5.5 (coefficient 2), the original results were increased; above these pH-values they were decreased. Owing to the fact that the bulk of soil samples were acid, the quantities of Mn were usually increased by the pH correction, especially when coefficient 1 and pH($CaCl_2$) were used (Table 2). The pH correction decreased the correlation coefficients between $Mn_{AAAc\text{-}EDTA}$ and reducible Mn remarkably, but it resulted in a closer correlation with exchangeable Mn (Table 3).

There was a clear dissimilarity in the correlation of the pH-corrected and the original results of $Mn_{AAAc\text{-}EDTA}$ with the Mn content of ryegrass in the pot experiment (Table 4). The correlation between the original results of $Mn_{AAAc\text{-}EDTA}$ and plant Mn content became closer yield after yield, while the correlation between the pH-corrected indices and plant Mn became poorer. AAAc-EDTA extractable Mn explained only 3 % of the variation in the Mn content of the first yield. Instead, the pH-corrected indices explained 38 % (coefficient 1) and 34 % (coefficient 2) of the variation (Fig. 1). The original $Mn_{AAAc\text{-}EDTA}$ indices (mg/kg) and pH(H_2O) together explained only 31 % of the variation in the Mn content of the first yield (mg/kg), as follows:

$$Mn_{yield\ 1} = 267.97 + 0.41\ Mn_{AAAc\text{-}EDTA} - 38.37\ pH$$

$$F = 18.47^{***}$$
$$R^2 = 0.31$$

The equation shows that there was a negative correlation between soil pH and Mn con-

Table 3. Linear correlation coefficients between $Mn_{AAc\text{-}EDTA}$ indices and indices of exchangeable, reducible and total Mn.

	Exchangeable Mn	Reducible Mn			Total Mn
		$C_6H_4(OH)_2$	$HONH_3Cl$	$C_6H_8O_6$	
$Mn_{AAAc\text{-}EDTA}$	0.45***	0.82***	0.87***	0.82***	0.50***
$Mn_{AAAc\text{-}EDTA}$ pH correction 1	0.85***	0.60***	0.43***	0.37***	0.12^{ns}
$Mn_{AAAc\text{-}EDTA}$ pH correction 2	0.90***	0.71***	0.57***	0.51***	0.23*

Table 4. Linear correlation coefficients between soil $Mn_{AAAc\text{-}EDTA}$ indices and Mn content and uptake by ryegrass yields.

	Mn content of dry matter				Mn uptake by yields 1—4 per pot
	Yield 1	Yield 2	Yield 3	Yield 4	
$Mn_{AAAc\text{-}EDTA}$	0.17^{ns}	0.54***	0.67***	0.71***	0.66***
$Mn_{AAAc\text{-}EDTA}$ pH correction 1	0.51***	0.40***	0.41***	0.40***	0.30**
$Mn_{AAAc\text{-}EDTA}$ pH correction 2	0.51***	0.47***	0.52***	0.51***	0.41***

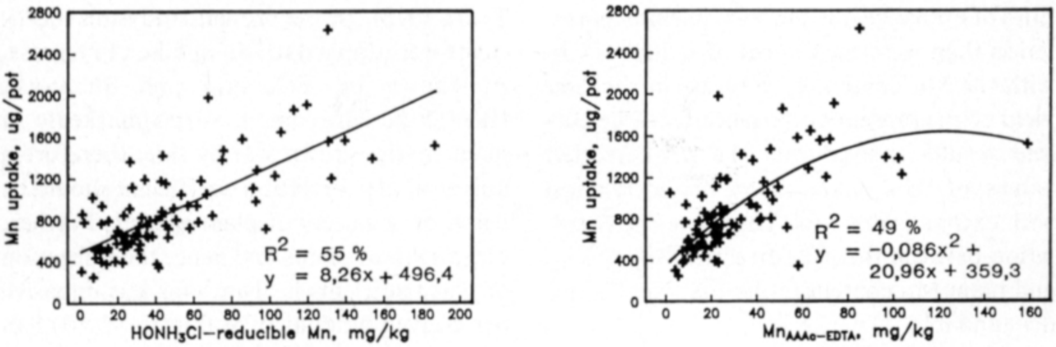

Fig. 1. The relationship between hydroxylammonium chloride-reducible Mn and Mn uptake by the four ryegrass yields as well as that between $Mn_{AAAc-EDTA}$ and Mn uptake by the yields.

tent of ryegrass. It should be pointed out that the soil $pH(H_2O)$ alone explained as much as 22 % of the variation of the Mn content of the first yield. Exchangeable Mn explained 33 % of the variation in the Mn content of the first yield (Fig. 1).

The dependence of Mn contents of the latter yields on the soil Mn indices did not support the pH correction theory. The original results of $Mn_{AAAc-EDTA}$ explained 38 %, 52 % and 55 % of the variation in the Mn content of yields 2, 3 and 4, respectively. Adding pH to the regression equation did not increase the coefficient of determination. The pH-corrected indices explained only 16—34 % of the variation in the Mn content of yields 2, 3 and 4. The $pH(H_2O)$ did not explain the variation in the Mn content of yields 2, 3 and 4 to a statistically significant degree.

The uptake of Mn by the four ryegrass yields was also studied. $Mn_{AAAc-EDTA}$ (mg/kg) explained 49 % of the variation in the total Mn uptake by the four yields (Fig. 2). However, hydroxylammonium chloride-reducible Mn gave a slightly higher coefficient of determination (55 %) than did $Mn_{AAAc-EDTA}$ (Fig. 2). The pH-corrected $Mn_{AAAc-EDTA}$ indices explained only 9 % (pH correction 1) and 17 % (pH correction 2) of the variation in Mn uptake of the yields.

Discussion

In a pot experiment, the plants are at first likely to utilize the reserves of readily available Mn. These reserves are measured upon the determination of exchangeable Mn. It was shown by Mäntylahti (1981) that the quan-

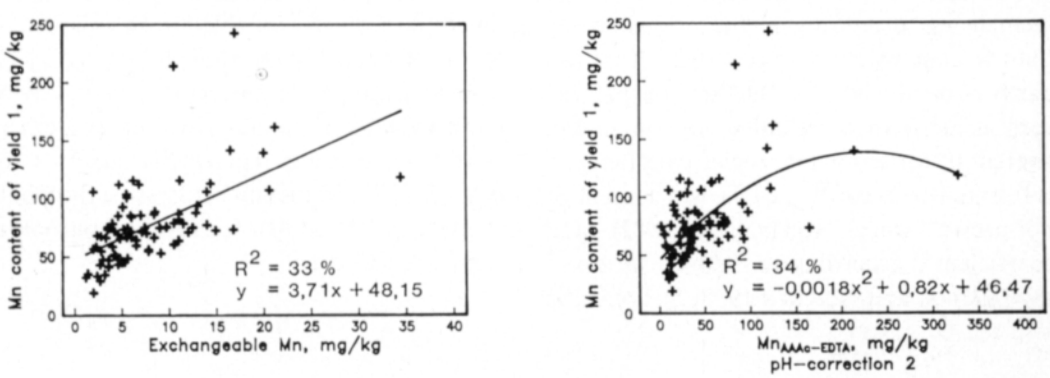

Fig. 2. The relationship between exchangeable Mn and Mn content of the first ryegrass yield as well as that between pH-corrected $Mn_{AAAc-EDTA}$ and Mn content of the first yield.

tities of exchangeable Mn were in closer correlation than were the indices of reducible Mn with the Mn content of ryegrass in the first yield of the present pot experiment. The current results showed that the pH-corrected values of $Mn_{AAAc-EDTA}$ were in correlation with exchangeable Mn. Therefore the correlation between the pH-corrected $Mn_{AAAc-EDTA}$ and plant Mn content in the first yield is understandable.

At later growth stages, ryegrass utilized the Mn reserves of soil more intensively; the Mn contents of the yields 2, 3 and 4 were twice as high as that of the first yield (MÄNTYLAHTI 1981). In a pot experiment, utilization of soil Mn can be enhanced owing to the acidification of soil in the course of the experiment, as observed e.g. by YLI-HALLA (1990), and to the production of chelating agents excreted by increasingly extensive rootsystem. The more intensive utilization of soil Mn resulted yield after yield in a closer correlation between the Mn content of plants and the indices of reducible Mn (MÄNTYLAHTI 1981), and also between the Mn content of plants and $Mn_{AAAc-EDTA}$, observed in the present study. When the close correlation between $Mn_{AAAc-EDTA}$ and reducible Mn is also taken into account, it may be assumed that the reserves of reducible Mn contribute markedly to the quantities of Mn extractable with AAAc-EDTA. Thus, $Mn_{AAAc-EDTA}$ can be given a rational interpretation as representing a considerable fraction of reducible soil Mn.

The use of pH-corrected $Mn_{AAAc-EDTA}$ seemed less promising in the present study than in that by SILLANPÄÄ (1982). This can partly be attributed to the fact that the pH correction coefficients are based only on the Mn content of certain plant species; coefficient 1 is formulated according to the Mn content of pot-grown wheat (SILLANPÄÄ 1982) and coefficient 2 according to field-grown timothy (KÄHÄRI and NISSINEN 1978, SIPPOLA and TARES 1978). In the present study the coefficients were applied to Mn uptake of ryegrass. As shown by YLÄRANTA and SILLANPÄÄ (1984), the Mn content varies markedly in plant species grown side by side; therefore a universal pH correction coefficient should be based on a variety of plant species. Further, the growth of plants and hence the utilization of plant nutrients is always far less intensive per a given amount of soil in the field than in a pot experiment (KORKMAN 1973). Owing to the decreasing correlation between the pH-corrected indices and Mn content of ryegrass in the course of the pot experiment, it may be extrapolated to the less intensive direction that the pH-corrected Mn indices would work more accurately in field conditions.

The results of the first yield of the pot experiment are likely to resemble the Mn uptake in the field more than do the ones of the subsequent yields. Consequently, for farming purposes, exchangeable Mn may be the best estimate that can be obtained by soil analysis in assessing the reserves of readily available Mn. However, other micronutrients often analyzed in soil testing (Cu, Zn) are in Finland extracted with AAAc-EDTA solution and for practical reasons also Mn is determined from the AAAc-EDTA extract. The present results showed that the pH-corrected $Mn_{AAAc-EDTA}$ indices may serve as a measure of short-term plant-availability of Mn, and $Mn_{AAAc-EDTA}$, without pH correction, may be used for estimation of the reserves of potentially available Mn. As generally known, estimation of plant-available Mn by soil analysis is difficult. Even though $Mn_{AAAc-EDTA}$, with or without pH correction, gave only a fair prediction of the plant Mn content, other extraction methods remarkably superior to AAAc-EDTA extraction in assessing the plant availability of soil Mn for farming purposes seem not to exist.

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SELOSTUS

Kasveille käyttökelpoisen mangaanin määritys maasta hapan ammoniumasetaatti-EDTA-uutolla

Oili Mohammadi[a], Markku Yli-Halla[a] ja Väinö Mäntylahti[b]

[a] *Kemira Oy Espoon tutkimuskeskus, Luoteisrinne 2, 02270 Espoo*

[b] *Viljavuuspalvelu Oy, Vellikellontie 4, 00410 Helsinki*

Eri puolilta Suomea kerätyistä 86 pintamaanäytteestä uutettiin mangaania hapan ammoniumasetaatti-EDTA-liuoksella (0.5 M CH_3COOH, 0.5 M CH_3COONH_4, 0.02 M Na_2-EDTA, pH 4.65, lyh. AAAc-EDTA). Tuloksia verrattiin maanäytteiden vaihtuvaan ja pelkistyvään mangaaniin ja mangaanin kokonaismäärään sekä astiakokeessa kasvatetun neljän peräkkäisen raiheinäsadon mangaanin ottoon. $Mn_{AAAc-EDTA}$ vaihteli 1.8—158.8 mg/kg, ollen keskimäärin 32.2 mg/kg. $Mn_{AAAc-EDTA}$:n ja pelkistyvän mangaanin väliset korrelaatiokertoimet ($r = 0.82^{***}$ – 0.87^{***}) olivat suurempia kuin $Mn_{AAAc-EDTA}$:n ja kokonaismangaanin ($r = 0.50^{***}$) tai vaihtuvan mangaanin ($r = 0.45^{***}$) väliset korrelaatiokertoimet, minkä perusteella pelkistyvän mangaanin ja AAAc-EDTA-uuttoisen mangaanin voidaan olettaa edustavan suurelta osin samaa mangaanifraktiota. Maan pH:n vaikutus AAAc-EDTA-uuttoisen mangaanin käyttökelpoisuuteen kasveille otettiin huomioon kertomalla uuttotulokset pH-

korjauskertoimella, minkä seurauksena $Mn_{AAAc\text{-}EDTA}$ korreloi paremmin vaihtuvan mangaanin ja heikommin pelkistyvän mangaanin kanssa kuin ennen pH-korjausta. Vaihtuva Mn selitti 33 % ja pH-korjatut $Mn_{AAAc\text{-}EDTA}$-luvut 34—38 % ensimmäisen raiheinäsadon mangaanipitoisuuden vaihtelusta, kun taas AAAc-EDTA-uuttoinen Mn ilman pH-korjausta selitti vain 3 % vaihtelusta. Myöhempien raiheinäsatojen kohdalla tilanne oli päinvastainen: $Mn_{AAAc\text{-}EDTA}$ selitti 38—55 % satojen mangaanipitoisuuden vaihtelusta, mutta pH korjatut $Mn_{AAAc\text{-}EDTA}$-luvut selittivät vain 16— 34 % vaihtelusta. Tämän perusteella AAAc-EDTA-uuttoista mangaania voitaneenkin pitää kasveille käyttökelpoisten mangaanivarojen kokonaismäärän mittana, kun taas pH-korjatut mangaaniluvut kuvastavat välittömästi kasvien käytettävissä olevia mangaanivaroja.