DYNAMICS OF MN AVAILABILITY OF AERATED SOILS BY ENVIRONMENTAL CONDITION

https://doi.org/10.56238/sevened2024.031-055

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ABSTRACT

Manganese is a micronutrient absorbed by the plant in the form of Mn2+, the available content of soils is between 1 and 10 $mg.kg^{-1}$, but it is the only element that undergoes major changes with climate changes (temperature, humidity, solar radiation) of tropical soils. The other nutrients do not change with climatic conditions. There is still no consensus on the mechanism of the dynamics of Mn solubilization in aerated soil. The known reactions are neutralization of Mn2+ toxicity by liming, forming $Mn(OH)_2$ and the other is increased solubilization by reducing MnO2 to Mn2+ by anaerobic microorganism.

This article presents the results of research on the dynamics of Mn2+, Mn-disp, availability of aerated soils. The soil temperature below 20 ºC remains unchanged for a long time. But when the soil is heated and dried by solar radiation, a temperature > 50 ºC, the Mn-disp increases from 5 to 70 $mg.kg^{-1}$. However, when the soil is moistened with rainwater, after a few days, the Mn-disp content returns to the initial value, 5$mg.kg^{-1}$. Showing that, in order to remain stable Mn-disp content, it requires soil cover with vegetables, keeps it moist and keeps temperature fluctuations minimal to favor the development of microorganisms.

The complementary research of the study of the dynamics of Mn-disp in soils, no reduction of MnO2 to Mn2+ or oxidation of Mn2+ to MnO2 was observed. That is, the increase or decrease in the availability of Mn does not alter the total levels of Mn2+ or MnO2 in the soils.

Keywords: Mn toxicity. Soil microorganisms. Soil management. Chemical analysis of soils. Soil micronutrient.

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INTRODUCTION

Manganese is a micronutrient that belongs to the class of transition metals Cr, Mn, Fe, Co, Ni and Cu, it has oxidation states: Mn0, Mn2+, Mn3+, Mn4+, Mn5+ and Mn7+, but in the soil it is predominantly Mn2+ and Mn4+. Mn2+ is found in the soil in different forms: free Mn2+, organic complexes, precipitates of OH^-, CO32-, S2-, and others, and Mn4+ is found in the soil in the form of insoluble MnO2. The total Mn content in the soil ranges from 100 to 3000 mg/kg and the bioavailable content ranges from 2 to 50 mg/kg (extractable in NH4OAc 1.0M). Most of the soil Mn is found in the form of insoluble MnO2 and a smaller fraction in the form of Mn2+ (Miyazawa et al. 1993).

The chemical analysis of the soil for fertility purposes follows the protocol of the procedure described in the "Manual of Soil Analysis Methods" (Pavan et al, 1996; Raij et al., 1987; Silva, 2009). The chemical fertility analysis of soils determines the levels of nutrients available or absorbable by the plants, so they are not absolute values.

For soil fertility analysis, samples are collected in the field, dried in the shade or in the greenhouse at 60 ºC, passed through a 2.0 mm sieve (fine air-dried earth, TFSA). The samples are dried in the oven for 24 to 72 hours and analyzed after one to 30 days, according to sample demand.

They were observed in the laboratory of the Agronomic Institute of Paraná, IAPAR, in the results of Cu, Zn, Mn and Fe of the soils, when repeated analyses, the values of Cu, Zn and Fe showed few changes, less than 5%, but the values of Mn of some soils increased more than 200%. To verify these differences, analyses of some soil samples from the IAPAR Soil Laboratory were repeated. The results confirmed, the longer the storage time, the higher the manganese values, some exceeded 100 $^{mg.kg-1}$ (> 300% increase), but the contents of other metals, Cu, Zn and Fe with minimal changes. To understand this increase in Mn, a literature review and some experiments on the dynamics of Mn availability in aerated soils were carried out.

Some Mn reactions in the soils are agreed upon by all, they are: decrease in Mn toxicity by the application of CaCO3 by the formation of $Mn(OH)_2$ of low solubility and another reaction to increase the availability of Mn by reduction of MnO2 in anaerobic medium to Mn2+ by reducing microorganisms (Ponnamperuma, 1972).

But there are still contradictions about the increase in the availability of Mn from aerated soil, some attribute to the microbiological reduction of MnO2 after high-intensity rain (Jackson, 2019). Others attribute it by the breakdown of organic substances in the release of Mn2+ from the compounds (Christensen et al. 1950).

Analysis of available Mn from the soil - Most laboratories in Brazil use Mehlich 1 solution for Mn extraction for convenience, because this solution is also used in the extraction of P, Cu, Zn and Fe, but NH4OAc 1.0 M pH 7.0 solution is also used. The Mn content extracted by Mehlich 1 can find values higher than 100 $^{mg.kg-1}$, equivalent values macro nutrients, P and K. On the other hand, the NH4OAc 1.0 M pH 7.0 solution extracts smaller amounts, between 1 and 10 $^{mg.kg-1}$ of available Mn from agricultural soils. Therefore, in these studies of the dynamics of Mn availability from soils, they were extracted with NH4OAc 1.0 M pH 7.0.

The analytical procedure was: 2.0 g of sample was transferred to a 50.0 mL Falcon tube, 20 mL of solution was added and stirred for one hour. The suspension was centrifuged and the Mn was determined by atomic absorption, EAA.

In this work we present our long-term results, since 1980, and completed with some results that have not yet been published to understand the mechanism of the dynamics of Mn availability in aerated soils of tropical climate.

Some terms used in this text:

Mn-available (Mn-disp)- Mn extracted with NH4OAc solution 1.0 M pH 7.0.

Moist soil-soil with moisture field capacity, 1/3 MPa.

DRYING TEMPERATURE AND STORAGE TIME OF SOILS

Different environmental conditions and storage time of soil samples in Mn-disp were evaluated. Soil samples of Dystrophic Dark Red Latosol, LEd and Terra Roxa, TR, were collected at the depth of 0 to 20 cm. The samples were dried under the following conditions: TFSA (60 oC); dry at room temperature (25 oC); humid 10 oC (refrigerator); and humid at -5 oC (refrigerator). The Mn-disp was determined monthly for six months.

The Mn-disp levels of LEd stored in the refrigerator for 6 months at -5 oC and 10 oC remained unchanged, around 1.0 mg.kg-1. And the soil dried in the shade, 25 oC showed a slight increase at the end of 6 months, 1.3 mg.kg-1. However, in the TFSA, dry at 60 oC caused an increase to 8.0 mg.kg-1 at the beginning of the evaluation (month 0) and a gradual increase until the end of 6 months, 18.0 mgkg-1 (Table 1).

The Mn-disp contents of the wet RT also did not show changes in the two storage conditions, refrigerator at -5 oC and 10 oC, around 1.8 mg.kg-1. And the sample dried in the shade at 25 oC also caused only a slight increase at the end of 6 months, from 2.2 mg.kg-1 to 4.5 mg.kg-1. Dry soil at 60 oC (TFSA) increased to 10.0 mg.kg-1 over time, 0 months, and gradually increased until the end of 6 months, 58.8 mg.kg-1.

Table 1. Soils stored under the following conditions, wet, dry at 25 °C and 60 oC (TFSA) and determined Mn-disp for 6 months (unpublished data).

Soil	Drying	0 month	1 month	2 months	4 months	6 months
		---------- Mn, mg^{-1} ----------				
Led	agel. - 5 °C	1,0	0,9	0,9	1,0	1,0
	bgel. 10 °C	1,0	1,0	0,9	1,0	0,9
	cseco 25 °C	1,0	0,9	1,0	1,2	1,3
	TFSA	8,0	10,1	13,0	15,5	18,0
TR	agel. - 5 °C	1,8	1,9	1,7	1,9	1,7
	bgel. 10 °C	1,9	1,7	1,6	1,8	1,7
	cseco 25 °C	2,2	2,3	2,2	3,5	4,5
	TFSA	10,1	20,1	40,5	52,1	58,8

a) refrigerator at -5 °C; b) refrigerator at 10 oC; c) dried in a laboratory environment.

Samples of moist soils stored in the refrigerator at -5 oC to 10 oC did not alter Mn-disp contents and those dried in the shade (25 oC) may cause a slight increase after 4 months of storage. The Mn-disp contents of the TFSA samples (dried at 60 oC) cause constant increases during the entire storage period, from the beginning to 6 months, causing increases of 18 to 30 times of the original moist soil.

The Mn-disp contents of the soils stored moist in the refrigerator or environmental condition, remained stable. The TFSA samples stored in the ambient condition, the Mn-disp contents increase continuously. Confirming the results in the repetitions of the samples made at the IAPAR Laboratory, in 1980. Webb et al. (1993) also observed an increase in Mn in the dry soil of Australia in four years stored.

These results show that the Mn analyses of the producers' soils do not represent real plant conditions in the field, for the following reasons: soil sample preparation process (time from collection to analysis, drying) and soil environment with plants (soil moisture and temperature.

MN-AVAILABLE MONITORING IN THE FIELD

The objective of this study was to evaluate the effect of climate on the dynamics of the Mn-disp of the bare soil. The Mn-disp content of the aerated soil (Dystrophic Purple Latosol) was monitored for one year at the IAPAR Experimental Station, Londrina - PR, Brazil, at the depths of 0 to 5 cm, 5 to 10 cm and 10 to 20 cm, collected monthly. The following parameters were determined: humidity, temperature and Mn-disp extracted with NH4OAn 1.0 M, pH 7.0.

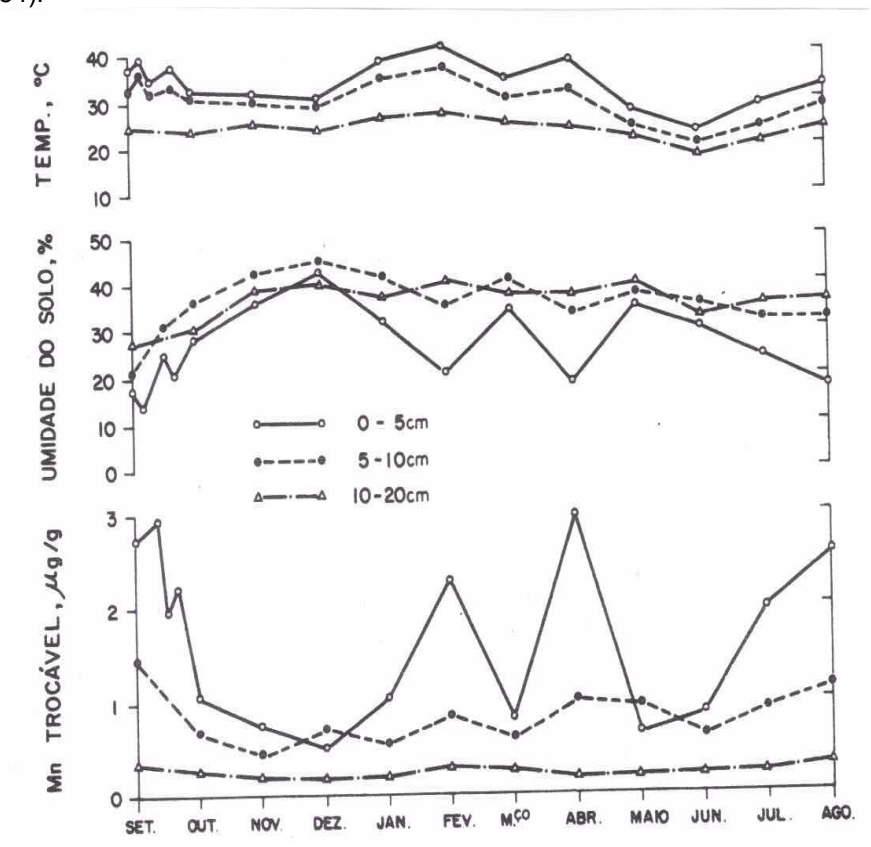
The Mn-disp contents of the 0 to 5 cm layer showed greater variations during the year, from 0.3 to 3.0 $mg.kg^{-1}$ and the moisture contents were 40% and 19%, these were the samples collected in Dec/82 and Apr/83, respectively. In the other periods, they presented intermediate values (Figure 1). And in the samples of the 10 to 20 cm layer, they showed

smaller variations in: temperatures, humidity and Mn-disp contents during the evaluated period.

The Mn-disp contents increased in the superficial layer of the soil, 0 to 5 cm, in the dry season (dry period) and decreased after wetting with rain. In the 10 to 20 cm layer, there were minimal changes in Mn-disp, because the temperature and humidity oscillations were minimal.

Fujimoto and Sherman (1945) observed in the soil of the Island of Hawaii an increase in Mn toxicity to plants in the hot and dry summer period, but it may disappear in the rainy spring and low temperature. Therefore, they concluded that the Mn oxidation/reduction reaction does not explain the increase and decrease of available soil Mn. Khan and Soltanpour (1978) evaluated 5 mMol DTPA-soluble Mn, pH 7.3, in soils of Colorado, USA, the 1st was immediately after 7 days of incubation and the 2nd was 7 days after drying at 110 oC for 48 hours. The soluble Mn content of the moist soil was 1.9 mg.kg-1 and of the dry soil at 110 oC was 4.4 mg.kg-1, an increase of 130%. They concluded that the solubility of Mn increases with soil warming to 110 oC. And the alfalfa plant showed severe Mn toxicity grown during hot summers and prolonged droughts (Leeper, 1970; Conyers, et al, 1997).

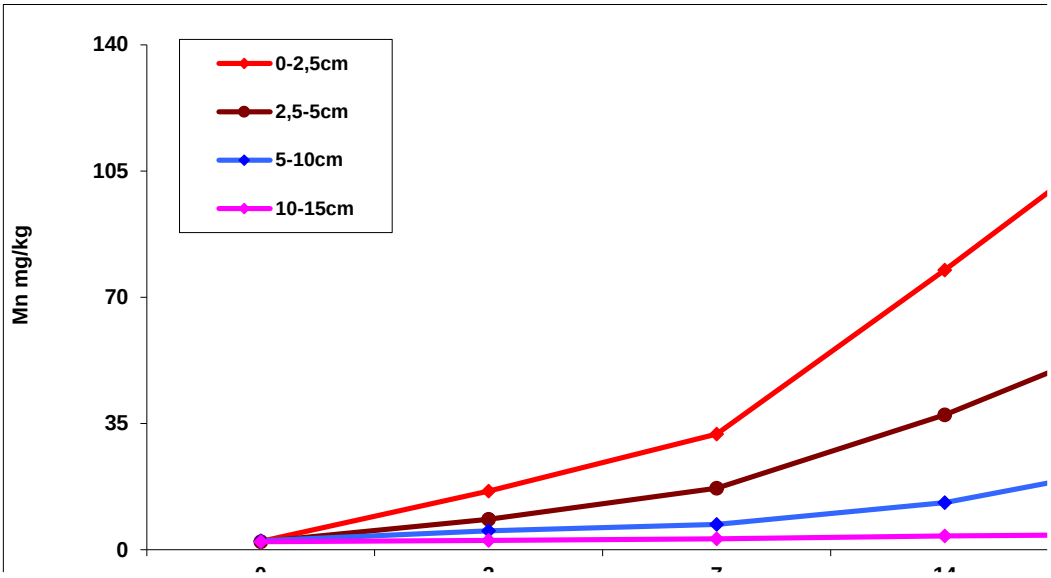
Figure 1. Monthly soil temperature, humidity and Mn-disp data monitored from Sept/1982 to Aug/1983 (Pavan and Miyazawa, 1984).



SOIL WITHOUT VEGETATION COVER IN MN-DISP IN THE SOIL PROFILE

The effect of direct solar radiation on the soil without vegetation cover in Mn-disp was evaluated, simulating dry conditions in conventional tillage (Miyazawa et al. 1993). Dystrophic Purple Latosol, LEd, was collected in the 0 to 20 cm layer, dried in the shade, sieved through a 2.0 mm sieve and homogenized. The soil was transferred to a plastic box with a depth of 25 cm and maintains the moisture field capacity. The soil was exposed to solar radiation and was covered with transparent plastic tarpaulin on rainy days. The following were determined: Mn-disp at 0, 3, 7, 14 and 21 days at depths from 0 to 2.5; 2.5 to 5.0; 5.0 to 10 and 10 to 15 cm, soil moisture and surface layer temperature at 14; 00 hours.

Figure 2. Contents of Mn-disp, $^{mg.kg-1}$, in the soil profile under solar radiation for 21 days (Miyazawa et al. 1993).



The concentrations of Mn-disp increased with the time of exposure to solar radiation, the greatest change was in the layer from 0.0 to 2.5 cm, from 3.0 $^{mg.kg-1}$ at the beginning to 121.0 $^{mg.kg-1}$ (21 days) and the smallest change was in the layer from 10.0 to 15.0 cm, from 3.0 to 3.2 $^{mg.kg-1}$. Soil moisture in the 1st layer decreased from 33% to 12% at 21 days of radiation, and in the layer from 10.0 to 15.0 cm the decrease was almost nil. And the soil surface temperature at the beginning of the experiment (0 day) was 39 ^{o}C and on the last day (21 day) it was 67 oC, this temperature increase was due to a decrease in subsoil moisture (figure 2).

The Mn-disp content of the soil, without cover, increases on the surface with the heating and decrease of soil moisture by solar radiation, on the other hand, in the lower layers the effect of solar radiation is minimal. This result shows the importance of vegetation cover in the chemical and microbiological property of soils. Makino et al. (2000) evaluated

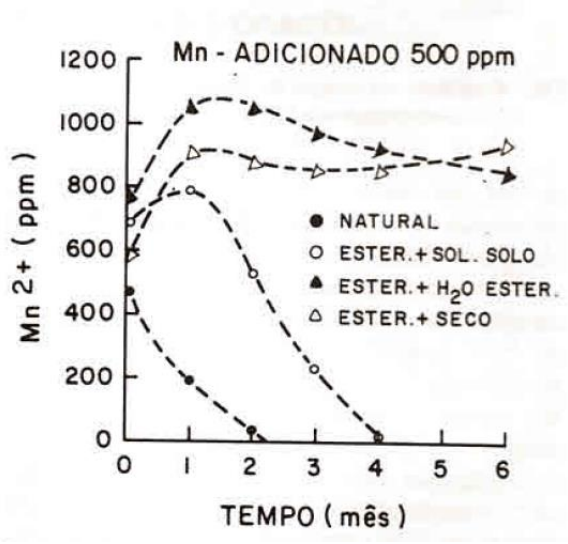
exchangeable Mn in four soil layers of Yawara – Japan, on three occasions: beginning, during and end of the 25-day summer. The exchangeable Mn content in the 0.0 to 1.0 cm layer, at the beginning of the summer it was 7 $^{mg.kg-1}$ and at 25 days of the dry spell (period without rain) it increased to 75 $^{mg.kg-1}$, but after four days of rain, the exchangeable Mn content returned to the value close to the beginning and in the 10.0 to 20 cm layer there were no changes in the Mn and in the other layers, 1.0 to 5.0 cm and 5.0 to 10.0 cm, the changes were minimal.

INCUBATION OF STERILIZED SOIL WITH DIFFERENT CONDITIONS IN THE MN-AVAILABLE

Autoclaved soil incubation with the addition of Mn2+ in the dynamics in Mn-available was evaluated. The sample of Dystrophic Purple Latosol, LRd, was collected from about 10 kg of soil at the depth of 0 to 20 cm, dried in the shade and passed through a 2.0 mm sieve. The soil had a pH of 4.2; sum of bases 2.87 $^{cmol.kg-1}$ and Al 1.62 $^{cmol.kg-1}$.

It was added on the basis of 500 $^{mg.kg-1}$ of Mn (MnSO4) in 5.00 kg of dry soil in the shade and separated into: a) 1.00 kg of natural soil was incubated with distilled water; and the remaining 3.00 kg of soil was autoclaved (120 ^{o}C) one hour, twice with an interval of one day, dried in the shade and separated into three parts of 1.00 kg each; b) kept dry; c) autoclaved + sterilized water; d) autoclaved + native soil solution; and were incubated for 6 months with moisture field capacity. The Mn-disp was determined at: 0 (immediate), 1, 2, 4 and 6 months.

Figure 3. Available Mn-content of soil with the addition of 500 $^{mg.kg-1}$ Mn2+ and incubated for 6 months with different environments (Miyazawa et al. 1993).



The Mn-disp content of the original soil was 7.0 $^{mg.kg-1}$. Natural soil incubation with a dition of 500 $^{mg.kg-1}$ of Mn2+, at the beginning the value of Mn-disp was 405 $^{mg.kg-1}$ (t = 0 month) and after two months of incubation it decreased to < 10 $^{mg.kg-1}$.

The Mn-disp content of autoclaved soil, incubated with natural soil solution, at the beginning was 700 $^{mg.kg-1}$ (t = 0 month), after one month, it increased to 800 $^{mg.kg-1}$ and after 4 months of incubation, it returned to the natural soil value, < 10 mgkg-1.

In autoclaved soils, kept dry and incubated with sterilized water, the average Mn-available content at the beginning (t = 0 month) was around 700 $^{mg.kg-1}$ and at 2 month it increased to around 1,000 $^{mg.kg-1}$ and maintained until the end of the experiment, 6 months (figure 4). Showing that simple soil wetting (sterilized water) does not decrease Mn-disp content, showing that the decrease of Mn-disp in the soil is not a simple chemical reaction. Showing that the possible chemical reactions of Mn2+ in the soil, for example: precipitation (OH-, CO32-, PO43-), oxidation (MnO2) and complexation (humic acid, fulvic) did not occur. The increase in Mn-disp of autoclaved soils up to two months of incubation suggests the solubilization of MnO.nH2O and Mn(OH)2.nH2O hydration.

By adding 500 $^{mg.kg-1}$ of Mn2+ to the natural soil, after 4 months of incubation, the Mn-disp value decreased to near the control soil, < 10 $^{mg.kg-1}$. But in the soil autoclaved and incubated with natural soil solution, it took six months of incubation to decrease to < 10 $^{mg.kg-1}$. The longest time spent to decrease Mn-disp of this treatment was the time needed for repopulation of microorganisms.

This soil, Dystrophic Purple Latosol, LRd, contains more than 1,500 $^{mg.kg-1}$ of total Mn, even addition of 500 $^{mg.kg-1}$ in natural or autoclaved soil + natural soil solution, after an incubation time, decreases to value less than 10 $^{mg.kg-1}$ of Mn-disp, is the value of a normal soil, which develops most plants.

These results show that in sterilized soil, absence of microorganism activities (autoclaved soil, sterilized water) increases Mn-disp and does not decrease with incubation. On the other hand, reactivation of microorganisms (or inoculation with soil microorganisms), the Mn-disp value, returns to the normal value of the natural soil.

DRYING AND INCINERATION TEMPERATURE OF SOILS IN MN-AVAILABLE

Heating temperature between 25 ^{o}C and 800 oC of the soils was evaluated in Mn solubility in NH4OAc 1.0 M, pH 7.0 and EDTA 0.1M. Two samples of agricultural soils from Paraná were collected, at the depth of 0 to 20 cm, dried in the shade and passed through a 2.0 mm sieve, the soils were: Londrina (LEd) and Irati (PVAd). The soils were heated from 25 oC to 800 oC and soluble Mn contents in NH4OAc 1.0 M and EDTA 0.1 M were

evaluated. The drying temperatures in the greenhouse for 24 hours were: 25 oC; 60 oC and 105 oC; and incinerated for two hours at temperatures of: 220 oC; 400 oC; 600 oC; and 800 oC . The soluble Mn was extracted with NH4OAc 1.0 M, pH 7.0 (Mn-OAc), the same procedure used in the available Mn and the weights were corrected for dry soil at 60 oC.

The EDTA-soluble Mn2+ was determined with three successive extractions with 0.1 M EDTA solution (Mn-EDTA). The procedure was: 1.0 g of soil + 20 mL of 0.1M EDTA in a 50 mL Falcon tube, stirred for one hour at 150 rpm, centrifuged for 15 min at 3,000 rpm. The supernatant was transferred to a 200 mL vial and the three extracts were combined, homogenized and the Mn determined by AAS.

The Mn-OAc contents of the soils increased with the increase in temperature from 25 ºC to 105 ºC, the smallest increase was in Londrina, from 2.5 $^{mg.kg-1}$ to 131 $^{mg.kg-1}$ and the largest increase was in Irati, from 6.0 $^{mg.kg-1}$ to 296 $^{mg.kg-1}$. However, in all soils, temperatures above 220 ºC gradually decreased to 800 ºC, the smallest change was from Londrina 73 $^{mg.kg-1}$ to 26 $^{mg.kg-1}$ and the greatest decrease was in Irati, from 267.0 $^{mg.kg-1}$ to 8.6 $^{mg.kg-1}$ (Table 2).

The Mn-EDTA values of all soils were higher than Mn-OAc, but the contents of dry soils from 25 ºC to 105 oC did not increase with the increase in temperature, as observed in Mn-OAc, i.e., the values were almost constant. However, for temperatures between 220 °C and 800 °C of all soils, the Mn-EDTA contents decreased with the increase in temperature, the lowest values were in Londrina, 281 $^{mg.kg-1}$ and 50 $^{mg.kg-1}$, respectively, and the highest values were in Irati, 359 $^{mg.kg-1}$ and 56 $^{mg.kg-1}$, respectively.

Table 2. Teores of MnOAc and Mn-EDTA of heated soils between 25 ºC to 800 oC (Miyazawa et al. 2014).

	Mn-OAc, $mg.kg^{-1}$						
Soil	25 oC	60 oC	105 oC	220 oC	400 oC	600 oC	800 oC
	---------- $mg.kg^{-1}$ ----------						
Londrina, LEd	2,5	43	131	73	14	24	26
Irati, PVAd	6,0	49	296	267	41	22	8,6
	Mn-EDTA, $mg.kg^{-1}$						
Londrina, LEd	315	301	328	281	262	85	50
Irati, PVAd	426	417	447	359	415	162	56

The Mn-OAc contents at temperatures between 25 oC and 105 oC increased with increasing temperatures and between 220 oC and 800 oC decreased with increasing temperature. On the other hand, the Mn-EDTA contents between 25 oC and 105 oC remained almost constant and at temperatures between 220 oC and 800 oC decreased, as observed in Mn-OAc.

The Mn-EDTA contents for temperature above 220 oC gradually decreased up to 800 oC, in relation to room temperature, there was a decrease of 13 to 30%. As EDTA is a

ligand they form complexes of high stability with cations of the soils Fe3+, Al3+, Mn2+, Zn2+, Cu2+, Co2+ and Ni2+. But they do not solubilize precipitates of low solubility: oxides, hydroxides, sulfides, silicates, carbonates and others.

As there were no differences in the concentrations of Mn-EDTA of the dry soils from 25 oC to 105 oC, they show that there was no oxidation or reduction of Mn. On the other hand, the values from 220 oC to 800 oC showed a gradual decrease in Mn with the increase in temperature, showing that there was oxidation of Mn2+ to insoluble MnO2 with an increase in temperature.

According to Gibbs' free energy diagram, Mn2+ has lower energy and Mn4+ (MnO2) is higher energy, that is, to oxidize Mn2+ to MnO2 requires energy supply, it does not occur spontaneously. On the other hand, since the free energy of MnO2 is greater than Mn2+, reduction can occur without external energy supply (Mackay and Mackay, 1974). Therefore, the reduction reaction occurs spontaneously in the area of soil flooded by anaerobic microorganisms, reduces MnO2 to Mn2+ and uses released energy.

On the other hand, the 1.0 M NH4OAc solution is a neutral salt, it extracts only weakly adsorbed ions by van der Walls force on the surfaces of the clay particles, so it extracts forms of Mn readily absorbable by plants. But, EDTA forms very stable complexes with polyvalent metals, capable of displacing metals from other complexes.

Therefore, the increase in Mn-disp of soils by warming from 25 ^{o}C to 120 oC is not by the reduction of MnO^{2}, but by the destabilization of organic Mn-by warming.

CONCLUSIONS

* The levels of available Mn of tropical soils increase with the dry spell when there is little vegetation cover, due to the direct incidence of solar radiation, causing heating and drying mainly in the surface layer.

* The increase in temperature and storage time of dry soils continuously increases the availability of soil Mn.

* Improper environmental conditions (heating by solar radiation - T > 30 ^{o}C, low humidity) such as summer, for the development of microorganisms, increase the availability of Mn in the soils. However, when a favorable environment for soil microbiota returns, the Mn-disp levels also return to values < 10 mg.kg-1.

* The Mn content of autoclaved soil can exceed 1,000 $^{mg.kg-1}$ and remains unchanged indefinitely. And incubation with sterile water also does not decrease Mn-disp. But incubation of autoclaved soil by inoculating with natural soil microorganisms, the Mn-disp content returns to the original soil value, < 10 $^{mg.kg-1}$.

* The increase in Mn availability by heating and drying and the decrease by wetting with rainwater do not alter the total levels of Mn2+ and MnO2 of aerated soils.

* The dynamics of soil Mn availability is a function of the activities of soil microorganisms.

* It is unlikely that microorganisms from soils capable of absorbing (accumulating in the body) more than 1,000 $^{mg.kg-1}$ amount of Mn2+ from soils.

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