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A N I N T E R N A T I O N A L J O U R N A L

Re-evaluation of Manganese Solubility as Affected by Soil Sample Preparation in the Laboratory

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ABSTRACT

Laboratory experiments were conducted to re-evaluate the effects of drying and the time between drying and Mn analysis on soil Mn solubility using maize seedlings as test plant. Samples of five soil types were collected in the field, transferred to laboratory and submitted for the following treatments: dried in the shade at 25ºC and dried at 65ºC followed by Mn determination immediately and after 30 and 60 days. Ninety days later soil samples were rewetted at field capacity and maize seedlings were grown for 7 days. Evaluations included plant Mn content and soil Mn extracted with NH_4OAc 1 mol L^{-1} pH 7. The lowest soil and plant Mn contents were found in soil samples dried in the shade at 25ºC. Drying soil sample at 65ºC and increasing the time between drying and Mn analysis increased Mn solubility and Mn uptake by maize. Oxisols showed higher soil and plant Mn contents than other soil types. The results indicated the extreme difficulty in interpreting soil Mn results due to the great effect of soil processes in the laboratory on Mn solubility. Routine soil analysis is not recommended to evaluate plant available Mn.

Key words: Micronutrient, transition metal, soil analysis

INTRODUCTION

Oxi-reduction reaction and pH are the main factors that control soil Mn solubility (Lindsay, 1979). Thus, the physical chemistry bases to predict Mn toxicity is much more complex than that for Al toxicity, for exemplo, due to the effect of pH/pe relationship on Mn solubility. Many examples have been presented in the literature to demonstrate that soil sample preparation in the laboratory, such as drying temperature, time between drying and analysis, storage time, etc., changes Mn solubility (Fujimori and Shermam, 1945; Miyazawa et al., 1991 and 1996). Pavan and Miyazawa (1984) and Andrade et al. (2002) reported that the handling of soil sample in the field, soil moisture, temperature, sun light and organic matter content also exert great control on Mn solubity. They also reported that the efficiency of Mn extractant solution to estimate Mn bioavaliability was extremely poor due to the effects in the field and during soil sample preparation in the laboratory.

There are conflicting reports on the efficacy of Mn extractant solutions for soil fertility purpose. In same cases no correlaction between soil Mn and plant Mn was observed (Reisenawer, 1988; Smith and Peterson, 1995; Miyazawa et al., 1991 and 1996) whereas in others the relationship appeared to be quite good (Muraoka et al., 1983; Borkert et al.; 1984). There appears to be no unifying thread through these observations on which predicting plant available soil Mn level can be based. The problem with many of these observations was that the condictions under which these works were carrried out (soil handling, soil

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prepartion, etc.) were often not described in sufficient details for meaningful interpretation to be made. Because of the importance of Mn on plant nutrition, there is a need to re-evaluate the efficacy of soil Mn analysis in relation to plant responses.

MATERIAL AND METHODS

The experiment was conducted under greenhouse condictions Seven soil types were collected in the field from cultivated sites potentially used for crop production in the state of Paraná.
Table 1 presents the sites and the main soil characteristics determined according to procedures described by Pavan et al. (1992).

Table 1 - Sites and chemical characteristics of soils.

Site	Soil Type	pH $CaCl_2$ 0.01M	Al	Ca	Mg	K	C
			———	$cmol_c\ dm^{-3}$	———		$g\ kg^{-1}$
Cascavel	LVdf[1)]	4.6	0.3	6.0	2.6	0.6	48
Londrina	LVdf[2)]	4.2	0.9	2.4	0.9	0.2	17
Ortigueira	LVd	5.7	0.0	7.1	1.9	0.5	27
Palotina	NVef	4.9	0.1	4.1	1.5	0.6	12
Curitiba	CXbd[1)]	5.2	0.0	6.7	3.5	0.3	33
Ponta Grossa	CXbd[2)]	4.5	0.7	4.0	2.4	0.6	49
Guarapuava	CXdf	4.3	0.6	2.2	1.3	0.2	38

After sampling, soils were submitted for the following treatments: dried in the shade at 25ºC (TO); and at 65º C with Mn extracted immediately (T1) after 30 days (T2) and after 60 days (T3). An additional treatment was included using the soil sample dried at 65ºC, rewetted at 60 days to 0.1 MPa moisture content and Mn extracted immediately (T4) and after 30 days (T5). After each treatment, soil samples were transferred to plastic pots (3kg) and four pre-germinated maize seedlings were grown for 7 days. Each soil was considered an individual experiment and the treatments were arranged in a completely randomized block with three replicates. Aerial and root parts were collected separatedely, washed, dried at 65º C, milled to pass through 1mm sieve and digested in a concentrated HNO_3 and $HClO_4$ mixture. Soil Mn was extracted with NH_4OA_c (1mol L^{-1} pH 7.0) solution (1:10 soil: solution ratio), with 60 minutes shaking time, centrifuged at 2500 rpm during 10 minutes and Mn was determined by Inductively Coupled Plasma (ICP). Soil and plant data were analyzed using proc anova procedures (SAS Institute, 1989) and the means were compared by Tukey test (P = 0.05)

RESULTS AND DISCUSSION

Soil Mn concentrations were significantly influenced by soil sample preparation treatments in the laboratory and varied from less than 1 to 150 mg kg^{-1}, depending on soil type (Table 2).
The Oxisols (LVdf and LVd) and the alfisol (NVef) presented greater Mn content than other soil types. These differences could be attributed to the soil parental material from which the soils were developed. Similar results were reported by Catani and Gallo (1951) who made a survey of Mn content in several soils from the state of São Paulo.
In general, drying soil samples in the shade presented the lowest Mn concentration and it did not statistically differ, except for LVdf[2)], from which Mn concentration was determined 30 days after soil samples were rewetted. Drying soil samples at 65º with Mn determination immediately increased Mn solubility as compared with shade (see T1, Table 2). This result could be extremely important because the Brazilian soil laboratories, generally,dry soil samples at 65ºC for routine analysis. The process of drying soil samples increased Mn solubility which made much difficulties in interpreting Mn analytical results for soil fertility purpose.

Table 2 - Soil sample preparation effect on soil Mn content.

Treatments	LVdf[1)]	LVdf[2)]	LVd	NVef	CXbd[1)]	CXbd[2)]	CXdf
				mg kg^{-1}			
T0	5,2c	22,1e	0,4d	3,9c	0,4b	1,0c	1,1c
T1	42,6b	51,0d	58,2c	39,2b	1,2b	5,4b	3,0b
T2	46,4b	66,0c	69,6cb	49,6b	1,0b	4,6b	3,1b
T3	76,8a	97,6a	82,5b	56,2b	1,6b	6,0b	8,5a
T4	89,2a	81,2b	150,2a	115,8a	5,0a	13,0a	7,6a
T5	4,4c	3,1f	14,0d	3,4c	1,1b	1,7c	1,3c
F test	70,64**	194,63**	156,51**	49,35**	44,54**	61,52**	131,55**

Table 3 - Soil sample preparation effect on Mn content in the aerial part of maize seedlings

Treatments	LVdf[1)]	LVdf[2)]	LVd	NVef	CXbd[1)]	CXbd[2)]	CXdf
				mg kg^{-1}			
T0	75c	712c	92c	133d	27c	56c	106c
T1	237b	1550bc	322abc	708c	69a	109b	230ab
T2	443a	2720a	584a	1593a	76a	166a	294a
T3	297b	1887ab	411ab	1178b	41bc	100b	139c
T4	321b	1949ab	292abc	732c	49b	103b	215b
T5	107c	676c	139bc	288d	48b	73bc	90c
F test	64,15**	16,97**	7,86**	58,64**	25,63**	26,30**	33,17**

Table 4 - Effect of soil sample preparation on Mn content in the root part of maize seedlings

Treatments	LVdf[1)]	LVdf[2)]	LVd	NVef	CXbd[1)]	CXbd[2)]	CXdf
				mg kg^{-1}			
T0	192b	530a	540a	451c	17b	45c	93c
T1	155b	667a	412a	409c	40b	112bc	138b
T2	363a	1184a	970a	1037a	81a	259a	184a
T3	273ab	926a	761a	817b	33b	123b	75c
F test	13,44**	3,61ns	2,00ns	157,54**	13,61**	35,58**	87,59**

Increasing the time between drying soil sample and Mn analysis also increased Mn solubility, in four of seven soils studied (see T2 and T3, Table2). This result was in accordance with Pavan and Miyazawa (1984) and Miyazawa et al. (1991 and 1996), north American soils (Fujimori and Sherman, 1945; Reisenauer, 1988) and African soils (Gillier et al., 1992). This showed that the soil sample preparation in the laboratory has great effect on Mn solubility. Thus, the practical efficacy of routine soil Mn determination would be uncertain.

Tables 3 and 4 show the effects of soil sample treatments on Mn concentrations in the aerial and root parts of the maize seedlings, respectively. In a general way, the Mn concentration in the aerial plant part was higher than in the root part. Mn content in the aerial part of maize seedlings reflected the variation in the extractable Mn and showed the lowest values for soil dried under the shade and soil re-wetted and kept 30 days before sampling, except for CXbd[1)]. On the other hand, drying soil samples at 65ºC and the time between drying and Mn analysis increased Mn solubility (Table 2) and as expected, increased Mn uptake by maize seedlings (Table 3 and 4). Plants growing in Oxisols (LVdf and LVd) and alfisol (NVef) presented higher Mn concentration than those growing in other soil types. Thus, it could be expected that the Mn toxicity l was more likely to occur in these soils.

Although there were good correlation coefficients between soil Mn - NH_4AO_c pH 7.0 with plant Mn in both aereal part (r = 0.66*) and root part (r = 0.74*), it only happened because Mn ions were released by soil preparation in the laboratory and were available and readily absorbed by the maize roots in a short growing period of time (7 days). However, it could be important to note that under field condition during growing season, that type of Mn was not available and the correlation was very poor as shown by Borkert et al. (2001).

These findings emphasized the chemical complexity of Mn reactions in soil and the fact that a sound basis for estimating Mn bioavailability using routine soil analysis should be used with restriction . The fact that Brazilian laboratories dry soil samples at 65ºC is not guarantee that it would be effective for Mn diagnostic. The limitation of soil Mn analysis, therefore, could be due to the routine of soil preparation in the laboratory than anything else.

RESUMO

Avaliou-se em condições de laboratório os efeitos da secagem da amostra de solo e do tempo entre a secagem e a determinação analítica na solubilidade do Mn, utilizando-se milho como planta indicadora. Coletaram-se amostras de cinco solos agrícolas, transferiram-se para o laboratório onde foram submetidas aos seguintes tratamentos: secas a sombra a 25ºC, secas a 65ºC determinando-se o Mn imediatamente, aos 30 e 60 dias. Após 90 dias reumedeceu-se os solos e cultivou-se plantas de milho durante 7 dias. Avaliações incluem Mn-planta e Mn-solo extraído com a solução de NH_4AO_c 1mol L^{-1} pH7.0. Amostras de solo secas à sombra apresentaram os menores teores de Mn no solo e nos tecidos das plantas. A secagem do solo a 65ºC e o tempo entre a secagem e a determinação aumentaram a solubilidade de Mn no solo e a absorção de Mn pelas plantas. Os oxisolos e o alfisolo apresentaram os maiores teores de Mn. Os resultados indicaram a extrema dificuldade na interpretação analítica de Mn no solo para fins de fertilidade, devido aos efeitos do preparo da amostra no laboratório na solubilidade do Mn. Analise rotineira de solo deve ser usada com ressalvas para avaliação da disponibilidade de Mn para as plantas.

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