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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

Effect of Organic Matter on Manganese Solubility

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ABSTRACT

The objective of this study was to re-evaluate some aspects of the relative importance of organic matter on Mn solubility in acid soil conditions. Field study showed that black oats, oil seed radish, elephant grass, lupin, leucaena, and coffee leaves serving as mulch decreased Mn solubility as compared with bare soil. The decrease in Mn solubility with plant mulch was related to increase in soil moisture content. Laboratory study showed that increasing temperature from 25 to 100^{o}C increased Mn solubility and total soil organic carbon was little changed; from 150 to 200^{o}C increased both Mn solubility and organic carbon oxidation, and up to 300^{o}C decreased Mn solubility and stoped organic carbon oxidation . Aluminum solubility always increased with increasing temperature. Organic matter exerted a control in both Mn and Al solubilities in acid soils.

Key words: Plant residue, mu lch, organic carbon, heavy metal, micronutrient

INTRODUCTION

Lowering soil pH results an increase in the level of Mn in the soil solution as illustrated by Lindsay (1979). In addition to the pH effect, Mn is also rendered soluble by redox mechanism (pH + pe = 20, see Lindsay, 1979). Thus, under acid conditions in well aerated soils Mn can become soluble and toxic to many plants. The basis for predicting Mn toxicity is less clear than that for Al toxicity because of oxi-reduction reaction and pH relationship in Mn chemistry. There are some evidences to indicate that soil preparation processes for laboratory analysis (air-dry, oven-dry, temperature, storage, etc.) changes Sherman, 1945; Pavan & Miyazawa, 1984; Miyazawa et al., 1991 and 1996). Therefore, the effectiveness of soil Mn extractants for predicting yields and Mn uptake responses can not be properly evaluated. A similar consideration may apply when the soil dries under field conditions, resulting an increase in Mn solubility and is likely to become toxic to plants. (Pavan & Miyazawa, 1984). Some useful developments have been the recognition that organic complexation of Mn is the main mechanism to control Mn solubility (Miyazawa et al., 1993), and also that Mn-organic complexes may exert a control on the Mn activity/pH relationship, which makes then potentially important controllers of Mn solubility under acid conditions. A re-examination on the relative importance of organic matter to determine Mn solubility in acid soil conditions was therefore warranted.

MATERIAL AND METHODS

Two experiments were conducted under field and laboratory conditions.
Field study with mulch - The experiment was conducted at the Instituto Agronômico do Paraná

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(IAPAR) experimental station at Londrina (23°23'S, 51°11'W, elevation 600m) in an intensively cultivated oxisol (Latossolo roxo distrófico-LRd, Brazilian soil classification or Typic Haplorthox, U.S. Soil Taxonomy). Table 1 shows the main chemical characteristics of the soil. Plant materials were: black oats (*Avena strigosa*), oil seed radish (*Raphanus sativus*), elephant grass (*Penissetum atropurpureum*), lupin (*Lupinus angustifolius*), leucaena (*Leucaena leucocephala*), and coffee leaves (*Coffea arabica*). Oats, radish, lupin, and leucaena were collected at flowering stage, and elephant grass and coffee leaves were collected at vegetable stage. Plant materials were placed on soil surface serving as mulch and allowed to dry and decompose. Oats, radish, lupin, elephant grass, leucaena, and coffee leaves were added at the following rates, respectively: 0.0 (control = bare soil) 640, 500, 560, 440, 1500 and 1300 g m^{-2}. The treatments were arranged in a randomized block design with three replications. Each plot consisted of 2m x 2m. Soil samples were collected at 49, 55, and 64 days after the beginning of the experiment for moisture and Mn determinations.

Laboratory study with soil organic matter - Soil samples were collected in a depth of 0-20 cm from cultivated areas located at Londrina (LRd), Cascavel (LRa), Ortigueira (LEa), Palotina (Tre), Ponta Grossa (Ca-1), and Curitiba (Ca-2). Table 1 shows the chemical characteristics of the soils.

Tabela 1 - Chemical characteristics of soil.

Soil Type	pH $CaCl_2$ 0.01M	Al	Ca	Mg	K	C
		-----	$cmol_c\ dm^{-3}$		-----	$g\ kg^{-1}$
LRa	4,60	0.32	6.00	2.57	0.56	47.66
Ca-2	5,20	0,00	6,71	3,54	0,25	32,87
LRd	4,20	0,87	2,40	0,92	0,23	17,01
Tre	4,90	0,09	4,12	1,48	0,56	11,45
Ca-1	4,50	0,70	4,04	2,40	0,59	49,04
LEa	5,70	0,00	7,06	1,93	0,53	26,70

Soil materials were air dried and ground to pass 1mm sieve. Five grams of soil sample were transferred to porcelain crucible and dried at 60, 100, 150, 200, 300 and 400 °C for one hour. Then, soil samples were analyzed for Mn, Al and total carbon. A control sample was carried out with moistened soil at field capacity and at room temperature (25°C).

Analytical procedures - Mn was extracted with 1mol L^{-1} NH_4AO_c (pH 7.0) solution at 1:10 soil:solution ratio, 60 min of shaking time, and centrifuged at 2500 rpm for 10 min. Aluminum was extracted with 0.1 mol L^{-1} EDTPA pH 6.8. Manganese and Al were determined by ICP (Inductively Coupled Plasma). Total carbon was determined by the Walkley-Black method.

RESULTS AND DISCUSSION

Figure 1 shows the effect of mulch treatments on Mn solubility. For control plot, soil Mn increased with time, from 31.2 to 73.2 mg kg^{-1}. Comparing with control plot (bare soil), all soil covers decreased drastically Mn solubility. After 64 days, black oats and coffee leaves were the most efficient plant materials to reduce Mn solubility.

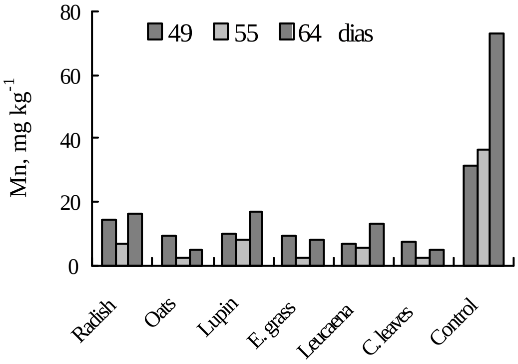

Figura 1 - The effect of mulches on Mn solubility.

The most likely explication for the effect of mulch on Mn solubility was associated with the conservation of high soil moisture (Figure 2). All plant materials increased the soil moisture content which was believed to decrease Mn solubility (Pavan & Miyazawa, 1984).

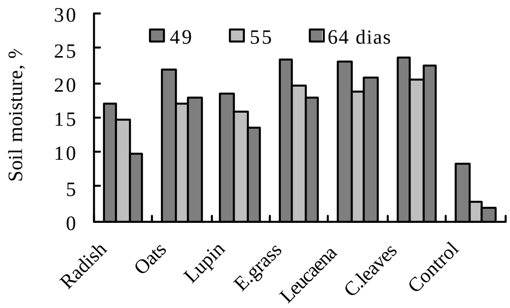

Figura 2 - The effect of plant mulches on soil moiture content.

This hypothesis can be clearly supported by the results show in Figure 3, which reveals a close relationship between soluble Mn and soil moisture content

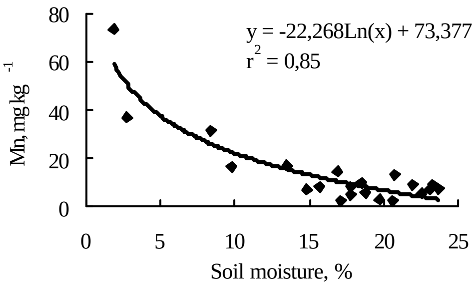

Figure 3 - The relationship between Mn solubility and soil moisture.

Second and third possibilities arose on soil temperature and sun light (data not shown) . These were not unexpected since a complex interaction between Mn solubility/soil moisture/ soil temperature/ and sunlight could be anticipated (Miyazawa et al., 1996). These authors reported that increasing soil temperature and sunlight intensity increased Mn solubility. The decrease in Mn solubility with plant mulch could be important in the reduction of Mn toxicity in well aerated acid soil. The beneficial effect of mulch reported on coffee (Medcalf, 1956; Pavan et al., 1986) could be attributed to reducing Mn toxicity since Mn level in coffee leaves under soil covers was mostly very low when compared with bare soil. The effect of temperature on Mn solubility is shown on Figure 4.

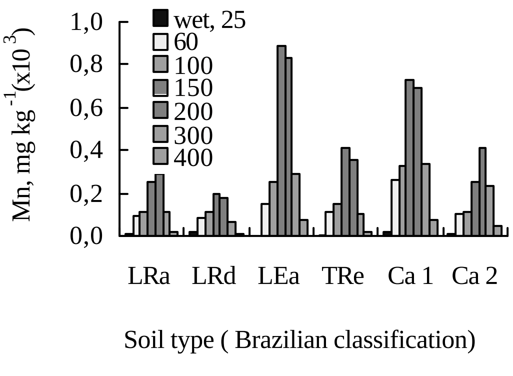

Figura 4 - Temperature (^{0}C) effect on Mn solubility.

The concentration of NH_4AO_c-Mn in soils at 25^{o}C changed from 0.4 to 22.2 mg kg^{-1} as a function of soil type. Increasing temperature to 60^{o}C, normally used in laboratory to dry soil samples for fertility purpose, increased soluble Mn from 100 to 260 mg kg^{-1} (LRa and Ca1, respectively). The highest Mn solubility was found at 150 and at 200^{o}C (885 and 827 mg kg^{-1}, respectively) in LEa. Increasing Mn solubility with increasing temperature to 150 – 200 ^{0}C has been well documented (Fujimori & Sherman, 1945; Pavan & Miyazawa, 1984; Miyazawa et al., 1991 and 1996). Increasing temperature up to 300 ^{0}C decreased drastically Mn solubility. On the other side, increasing temperature above 150^{o}C decreased total carbon and at 400^{o}C, organic carbon was totally oxidized (Figure 5).

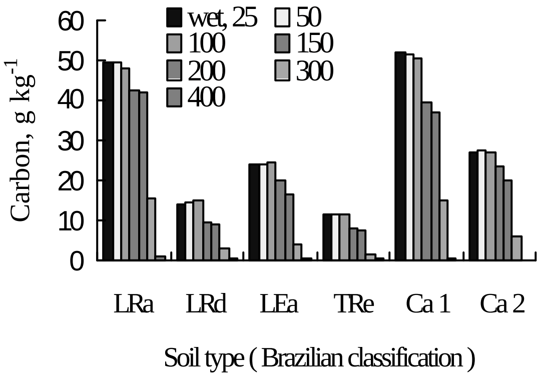

Figura 5 - Temperature (^{0}C) effect on organic carbon.

The solubility of Mn in relation to carbon oxidation showed three distinct regions. The first region (from 25 to 100^{o}C) showed an increased in Mn solubility with little change in carbon oxidation, probably as a result of thermical oxidation of Mn-organic complexes with high stability constants. The second region (from 150 to 200^{o}C), increased Mn solubility probably due to increase carbon oxidation. The third region (> 300^{o}C) decreased Mn solubility due to oxidation of Mn^{2+} released from the organic compounds to MnO_2, changing the oxidation degree from 2^+ to 7^+ rendering insoluble.

By comparing Mn solubility with other element, Figure 6 shows the effect of temperature on Al solubility. In contrast with Mn, Al solubility followed organic carbon oxidation. As the oxi-reduction did not take place in Al chemistry, its concentration increased at temperature > 300^{o}C. Thus, Al-organic complexes was probably the main controlling factor in soil solution Al activity. It may simply be fortuitous that the level of exchangeable Al often correlates well with the amount of organic carbon in Brazilian soils (Pavan, 1983). Therefore the organic matter is an important controller of Mn and Al solubilities in well aerated acid soils.

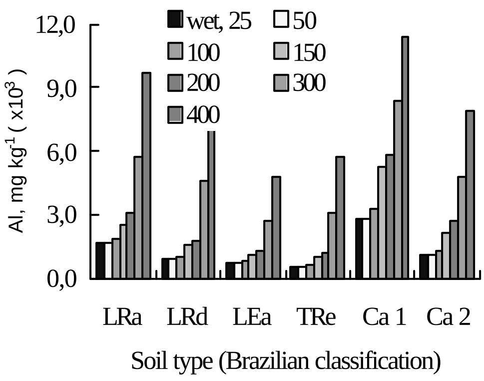

Figure 6 - Temperature (^{0}C) effect on Al soluble.

RESUMO

O estudo foi conduzido com objetivo de reavaliar alguns aspectos da importância relativa da matéria orgânica na solubilidade do Mn em solos ácidos. Em condição de campo cobertura morta com resíduos de aveia preta, nabo forrageiro, napier, tremoço, leucena e folhas de café diminuíram a solubilidade de Mn quando comparada com o solo descoberto. A redução na solubilidade do Mn em solo coberto com resíduos vegetais foi relacionada com o teor de umidade do solo. Estudos de laboratório demonstraram que o aumento da temperatura de 25 para 100°C aumentou a solubilidade do Mn com pouca alteração no teor de carbono do solo; de 150 a 200°C aumentou ambas a solubilidade do Mn e a oxidação do carbono orgânico e acima de 300°C diminuiu a solubilidade do Mn e completou a oxidação do carbono orgânico. A solubilidade do Al sempre aumentou com a elevação da temperatura. A matéria orgânica influenciou diretamente a solubilidade do Mn e do Al.

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