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Effect of Organic Matter and Moisture Level on Extractable Soil Manganese[1]

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ABSTRACT

Studies on the optimum amounts of plant residue additives, incubation time, and moisture level for maximum release of extractable Mn were performed with four soil types using greenhouse and controlled environment facilities. Addition of decomposing ryegrass or alfalfa residues to flooded soils significantly increased extractable Mn in three of the four soil types, but no effect was obtained with any soil having a low moisture content. Organic matter decomposition and flooding tended to shift soil pH toward neutrality, lessening the effect of pH on the release of extractable Mn.

INTRODUCTION

Manganese is believed to exist in the soil in three valence states. The Mn^{+3} and Mn^{+4} forms exist primarily as highly-insoluble oxides. The divalent ion (Mn^{+2}) is much more soluble and is found in soil solutions or exchange complexes.

Soil moisture has a pronounced effect on the form of Mn which predominates in the soil at any time. Manganic oxides undergo reduction in anaerobic soils forming the more soluble manganous compounds (16). Under well-aerated conditions, the supply of oxygen is adequate to permit complete oxidation of organic materials to carbon dioxide and water, and the mineral constituents of the soil remain almost entirely in an oxidized condition (2). But when the soil is flooded, the supply of oxygen is rapidly exhausted as a consequence of the reduced rate of gas exchange with the atmosphere (16). As a result, there is an accumulation of soluble organic products of microbial metabolism and the conversion of the oxidized soil mineral constituents to their reduced counterparts (18, 19).

Conflicting reports exist regarding the effects of organic matter on the

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distribution, mobilization and availability of Mn in soils. Fujimoto and Sherman (5), and Gotoh and Yamashita (6) reported that the reduction of Mn was favored by the presence of readily-decomposable organic matter. Mulder and Gerretsen (12) indicated that at high pH values, soil organic matter may reduce higher Mn oxides to Mn^{+2}, and that this reduction may proceed either by direct reaction with organic matter or by biological processes. Leeper and Passioura (8) suggested that Mn is not held in a complex form with organic matter while Main and Schmidt (9) reported that Mn may form chelate complexes with certain components of organic matter. Misra and Mishra (11) observed that humic acid did not appreciably increase Mn retention by soils, and suggested that perhaps other fractions, such as fulvic acid might be of importance. On the other hand, Pavanasasivam (14) reported that fixed Mn is significantly and positively correlated with soil humic acid but not with fulvic acid.

The purpose of the present investigation was to gather information regarding the optimum amount of added organic residues, moisture level, and incubation time for maximum release of soil-extractable manganese.

MATERIALS AND METHODS

This study consisted of growth chamber and greenhouse experiments conducted during the period 1973–75.

GROWTH CHAMBER

An experiment was designed to determine the optimum incubation period necessary for maximum release of soil-extractable Mn under waterlogged conditions. In this study soil-extractable Mn refers to that extracted with 1 *N* ammonium acetate adjusted to pH 4.8, which includes both water-soluble and exchangeable Mn.

Ryegrass (*Lolium perenne* L.) was propagated in an Olivier silt loam soil for one month and then terminally desiccated with Paraquat[3] (0.28 kg/ha) as an aqueous foliar spray. After one week a block of soil (30 cm × 25 cm × 6 cm) with the dead sod, including the roots, was placed in a 2-gal plastic flat. Another flat was filled with adjacent soil in which no plants had been grown. The flats were then saturated with water and maintained in the growth chamber at 26.7° C for 28 days. There were two treatments and four replications in a complete randomized block design.

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[3] Trade names are used in this publication solely for the purpose of providing specific information. Mention of a trade name does not constitute a guarantee or warranty of equipment or materials by the Agricultural Experiment Station of the University of Puerto Rico or an endorsement over other equipment or materials not mentioned.

During the incubation period small portions of soil from each flat were withdrawn at 4-day intervals in the following manner: Plastic cylinders of 10 g capacity were used for this purpose. The cylinders were pushed vertically downward to a depth of 5 cm and withdrawn with the soil core. The cylinder, together with the soil sample, was immediately placed in a 250 ml Erlenmeyer flask containing 50 ml of 1 *N* ammonium acetate solution adjusted to pH 4.8 and capped with a rubber stopper in which a serum cap had been inserted. The serum cap was then punctured with a glass tube attached to a vacuum line and suction was applied to remove the air from inside the flask.

The soil samples were shaken in a mechanical shaker for 30 min and the soil extract filtered through Whatman #2 filter paper. Five ml of HCl were added to the filtered solution to prevent further oxidation of Mn in solution during storage. The Mn content in solution was determined in the Perkin-Elmer 503 atomic absorption spectrophotometer.

Four additional experiments were established in the growth chamber in which alfalfa meal, prepared as poultry feed, was added to Olivier silt loam, Sharkey clay, Commerce silt loam, and Convent sandy loam to simulate decomposing plant residues. Olivier is an Entisol of the Mississippi terrace soil area of Louisiana containing large amounts of oxidized Mn. Sharkey, Commerce, and Convent belong to the alluvial soils of the Mississippi River representing heavy, medium and light textured soils, respectively. Some characteristics of these soils are presented in table 1 and the chemical analysis of the alfalfa meal in table 2.

TABLE 1.—*Physical and chemical characteristics of the soils*

Soil property	Soil type			
	Olivier	Sharkey	Commerce	Convent
Texture	Silt loam	Clay	Silt loam	Sandy
pH	6.4	6.8	7.3	7.5
Organic matter, %	0.88	2.44	1.82	0.31
Extractable Mn (p/m)	10	18	13	8
Extractable P (p/m)	123	256	261	209
Extractable K (p/m)	157	268	196	122
Extractable Ca (p/m)	770	4000+	3160	1090
Extractable Mg (p/m)	78	1000+	711	363

TABLE 2.—*Chemical analysis of alfalfa meal*

Component	Composition
	%
Fiber	25.0
Protein	17.0
Ash	11.0
Fat	2.0
Calcium	1.5
Phosphorus	0.2

Two hundred grams of air-dried soil were mixed thoroughly with alfalfa meal at 0.1, 0.5, and 1.0% by weight and placed in plastic cups. Sufficient water was added to obtain moisture levels of 15, 30, and 60%. Samples were incubated at 26.7° C for 7 days. Soil samples were withdrawn in the manner described above and the extractable Mn content determined.

GREENHOUSE EXPERIMENTS

One greenhouse experiment for each one of the four soils was established and duplicate sets of data were obtained for 1974 and 1975. Sufficient alfalfa meal was incorporated into 250 g soil samples at 0.5, 1.0, and 2.0% levels on a dry weight basis. Water was added to bring the moisture content to 25% (field capacity) and to 60% (waterlogged). The term "field capacity" is loosely used here for greenhouse data, referring to the range of moisture required for optimum respiration of soil microflora developing in decomposing plant residues. According to Alexander (1) this range is between 60 and 80% of the soil water-holding capacity.

After a 7-day incubation period, soil samples were withdrawn for extractable Mn determination.

RESULTS AND DISCUSSION

There was a highly significant increase in soil extractable Mn by adding readily decomposable plant residues to submerged soil (table 3). The maximum amount of Mn released, 680 p/m, was obtained after 16 days incubation. However, this quantity was not significantly higher than the 642 p/m released at 8 days after incubation. Submergence per se caused significant increases in extractable Mn with time, but it took longer (20 days) to reach the maximum level (430 p/m) of Mn released in soil without plant residues.

TABLE 3.—*Soil extractable Mn as influenced by submergence with and without decomposing plant residues*[1]

Incubation time	Extractable Mn	
	With plant residues	Without plant residues
Days	*P/m*	*P/m*
0	10	9
4	521	192
88	642	171
12	648	325
16	680	319
20	644	430
24	584	407
28	550	372

[1] LSD for plant residues at the 5% level: 28.0; at the 1% level: 37.4. LSD for incubation time at the 5% level: 56.1; at the 1% level: 74.8.

The increase of extractable Mn was very rapid from the beginning of the incubation period, especially in soil containing plant residues. Thus, after 4 days of incubation, the treatment in which plant material was included contained 521 p/m Mn while the soil without plant residues contained 192 p/m Mn. These represented a 52- and a 21-fold increase, respectively, in soil extractable Mn as compared to the initial soil Mn content.

The observed increase of extractable Mn during incubation is probably a result of the reducing conditions prevailing during the decomposition and production of intermediate products in submerged soil, which are capable of maintaining Mn in a soluble and/or exchangeable form. This is a logical consequence of a stimulated microbial oxygen depletion, in turn favoring Mn^{+3} reduction. Manganic compounds were reduced to the more soluble manganous form either by serving as biological electron acceptors or by being reduced chemically by organic compounds produced during the anaerobic decomposition of organic materials. According to Mann and Quastel (10), both of these processes occur.

The observed decline in extractable Mn in the soil containing plant material after 16 days of incubation may be the result of an insoluble complex formation by soluble Mn with products of plant decomposition (4,13) after a long period required for the build-up of such decomposition products. The slower decline in extractable Mn observed in the soil without plant residues is not clearly understood, but it seems that complex formation with decomposition products of organic matter is slower because the amount of organic residues in this treatment is much less and is almost entirely dependent on the amount of native organic matter present in the soil. For Olivier silt loam the organic matter content was 0.88%.

Table 4 shows the effects of organic matter additive and moisture on extractable Mn in the four soils after 1 week of incubation. The statistical analyses show highly significant F values for the effects of both alfalfa meal concentration and moisture level, as well as a significant interaction effect between the two factors for Olivier, Sharkey and Commerce soils. Only the moisture levels produced a significant effect on the extractable Mn content of Convent soil.

Tables 5 and 6 show data from the greenhouse experiments. Raising soil moisture from 25 to 60% significantly increased extractable Mn in each of the four soils (table 5). These increases ranged from 459 to 96 p/m for the 1975 samples. The incorporation of 1% alfalfa meal further increased extractable Mn in all flooded soils except Convent.

There was a rapid decline in soil redox potentials upon flooding (table 6). The decline was more pronounced as the concentration of alfalfa meal in soil increased. Redox potential measurements in flooded soils ranged

TABLE 4.—*Ammonium acetate-soluble Mn of four soil types given variable moisture and organic matter-additive treatment in growth chamber*

Treatment			Extractable Mn		
Alfalfa meal		Moisture	Olivier	Commerce	Sharkey	Convent
%		%	*P/m*	*P/m*	*P/m*	*P/m*
0.1		15	3.9	8.8	20.3	2.2
0.5		15	2.8	17.6	27.5	3.3
1.0		15	4.4	37.4	48.4	1.1
0.1		30	102.2	109.9	16.5	44.0
0.5		30	106.1	111.0	26.4	35.2
1.0		30	103.9	124.2	56.1	34.1
0.1		60	316.9	159.4	162.8	90.2
0.5		60	461.5	220.0	255.0	94.6
1.0		60	470.8	269.5	280.4	99.0
LSD	.01		21.6	34.7	24.1	13.5
	.05		16.0	25.7	17.8	10.0

from 9 to 300 mV, indicating reduced to moderately reduced soil conditions. In the soils at 25% moisture, the redox potential measurements ranged from 370 to 622 mV, all which indicate oxidized soil conditions. However, as stated by Panamperuma (15), the narrow range of redox potential values encountered in well-aerated soils and the poor reproductivity caused primarily by a lack of poising of the oxidation-reduction systems in the oxidized range have resulted in the rejection of the redox potential measurements as a tool for characterizing aeration in well-aerated soils.

Table 7 shows that both alfalfa meal concentration and soil moisture had a highly significant effect on the soil pH. In general, there was a strong tendency for soil acidity to decrease upon flooding, except for the Convent soil. Increasing the concentration of alfalfa meal in soil further increased the pH of acid soils toward neutrality under both moisture levels. This was true for Olivier, Sharkey, and Commerce soils at both sampling dates. On the other hand, in the alkaline Convent soil, the addition of alfalfa meal did not show a definite trend. However, the observed changes in soil pH due to the treatments seem to be, generally, too small to have any significant effect on the release of extractable Mn.

In general, Olivier soil released the largest amount of extractable Mn, followed by Sharkey, Commerce, and Convent. The capacity of these soils to release Mn must be directly related to the Mn content and solubility of the parent material and secondary minerals which constituted the original components of the soil. Another important factor determining the amount of extractable Mn in soil at any given time is soil pH. In this respect the soil-extractable Mn released was inversely related to their pH (tables 5 and 7).

TABLE 5.—*Ammonium acetate-soluble Mn of four soil types given variable moisture and organic matter-additive treatments in the greenhouse. Sampled in 1974 and 1975*

Treatment		Extractable manganese, ppm							
Alfalfa meal (%)	Moisture (%)	Olivier		Sharkey		Commerce		Convent	
		1974	1975	1974	1975	1974	1975	1974	1975
0	25	13	6	6	9	4	8	6	4
0.5	25	14	6	5	17	5	11	7	4
1.0	25	20	7	7	23	7	17	9	7
2.0	25	34	5	10	32	13	38	11	10
0	60	581	465	125	270	177	133	105	100
0.5	60	691	516	139	299	219	221	104	89
1.0	60	780	647	153	292	234	259	98	97
2.0	60	729	539	145	284	221	240	91	89
LSD	Moisture (%)	34.6**	79.8**	12.6**	12.8**	10.0**	17.4**	13.7**	10.4**
	Alfalfa meal (%)	48.9**	N.S.	N.S.	18.2**	13.0**	24.6**	N.S.	N.S.

* LSD at the .05 level of probability.

** LSD at the .01 level of probability.

TABLE 6.—*Redox potential (Eh) measurements of four soil types given variable moisture and organic matter-additive treatments. Sampled in 1974 and 1975*

Treatment		Redox potential (mv)							
Alfalfa meal (%)	Moisture (%)	Olivier		Sharkey		Commerce		Convent	
		1974	1975	1974	1975	1974	1975	1974	1975
0	25	454	489	463	529	575	512	622	464
0.5	25	517	522	565	487	542	462	532	429
1.0	25	417	532	535	499	612	444	592	417
2.0	25	370	492	527	487	620	394	592	409
0	60	184	177	140	259	242	300	124	214
0.5	60	44	167	142	99	262	172	114	172
1.0	60	29	189	122	72	207	127	94	104
2.0	60	9	104	67	67	108	64	69	124
LSD	Moisture (%)	63.7**	63.9**	41.1**	43.1**	48.3**	48.0**	44.2**	37.8**
	Alfalfa meal (%)	95.2**	N.S.	42.9*	60.9**	N.S.	67.9**	N.S.	53.5**

* LSD at the .05 level of probability.

** LSD at the .01 level of probability.

TABLE 7.—*pH of four soil types given variable moisture and organic matter-additive treatments. Sampled in 1974 and 1975*

Treatment		Soil pH							
Alfalfa meal (%)	Moisture (%)	Olivier		Sharkey		Commerce		Convent	
		1974	1975	1974	1975	1974	1975	1974	1975
0	25	6.4	6.0	6.0	6.3	6.4	6.8	7.4	7.4
0.5	25	6.5	6.1	6.2	6.6	6.6	7.0	7.5	7.5
1.0	25	6.7	6.0	6.5	7.0	6.5	6.9	7.4	7.4
2.0	25	7.0	6.3	6.7	7.1	6.8	7.0	7.3	7.4
0	60	7.1	6.5	6.3	6.6	6.6	6.9	7.1	6.8
0.5	60	7.3	6.8	6.6	6.8	6.5	6.9	7.0	6.9
1.0	60	7.4	6.9	6.8	6.9	6.7	6.9	7.0	6.9
2.0	60	7.5	7.1	6.9	7.1	6.9	6.9	7.0	7.0
LSD	Moisture (%)	.11**	.15**	.08**	N.S.	.08**	.05*	.10**	.07**
	Alfalfa meal (%)	.16**	.22**	.11**	.23**	.11**	.07*	.10*	.07*

* LSD at the .05 level of probability.

** LSD at the .01 level of probability.

The observed increase in Mn mobilization with flooding is consistent with previous findings. Redman and Patrick (17) reported increases in extractable Mn after flooding which ranged from 33.6 p/m for a Commerce silt loam to 1290 p/m for Olivier silt loam. Clark and Resnicky (3) observed that the Mn level of a submerged soil was increased by a hundredfold or more.

The lack of response of soil at the lower moisture levels to applied alfalfa meal and also of the flooded Convent soil is probably due to a lack of anaerobiosis related to decomposition products of the alfalfa meal. It is known that microorganism of widely different origin are able to produce hydroxy acids from cellulose and other substances of vegetable origin, and the Mn salts of these acids are readily oxidized by oxygen from the air at pH above 7.0 (1). Therefore, it is possible that the Mn salts produced when alfalfa meal is added to a well-aerated soil (25% moisture and sandy) or alkaline soils (as the Convent) are oxidized. This explanation agrees with Heintze and Mann (7) who reported that in a saline and neutral soil, organic matter forms complexes with Mn^{++} which are dissociated to a slight extent.

RESUMEN

El efecto de la descomposición de material vegetativo y el tiempo de incubación del contenido en manganeso extractable en un suelo Olivier arcilloso lómico, ácido e inundado se investigó en una cámara de crecimiento. Se observó un marcado aumento del contenido en manganeso extractable al saturarlo con agua, el cual arrojó un máximo a los 20 días de incubación. Cuando se añadió material vegetativo al suelo inundado, se obtuvo una cantidad más elevada de manganeso extractable y a la vez se acortó el período de incubación a 8 días.

Para investigar el efecto de varias cantidades de enmiendas orgánicas (harina de alfalfa) y humedad edáfica en el contenido de manganeso extractable de cuatro tipos de suelos se usaron la técnica de incubación en cámaras de crecimiento y de invernadero. El aumentar la humedad del suelo de 25 a 60% propició un marcado aumento del contenido en manganeso extractable, especialmente en el suelo Olivier. Aumentos menos marcados se obtuvieron en los suelos Sharkey, Commerce y Convent.

La incorporación de harina de alfalfa hasta 1% en los suelos inundados aumentó aún más el contenido en manganeso extractable de los suelos Olivier, Sharkey y Commerce, pero no tuvo efecto significativo en el suelo Convent ni en ningún otro menos húmedo.

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