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Zinc, copper and manganese availability in soils treated with alkaline sewage sludge from Paraná state (Brazil)

Disponibilidade de Zn, Cu e Mn em solos tratados com lodo de esgoto alcalinizado do estado do Paraná (Brasil)

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ABSTRACT

In Paraná, most of the sludge generated in sewage treatment plants is subjected to the prolonged alkaline stabilization process. Although it is known that the alkaline sewage sludge contains micronutrients such as Zn, Cu and Mn, little is known about the availability of these elements in soils treated with this type of sewage sludge. Thus, the objective of the study was to evaluate the influence of alkaline sewage sludge from Paraná on Zn, Cu and Mn availability in soils. Twenty sewage treatment plants were selected throughout Paraná, where alkaline sewage sludge and the most representative agricultural soil of the each region were collected. Each soil was incubated for 60 days with alkaline sewage sludge rates (0, 10, 20, 40, and 80 Mg ha^{-1}) from their region. Subsequently, Zn, Cu and Mn availability was determined using the Mehlich-1 extractant. The alkaline sewage sludge increased Zn availability and decreased Mn availability in most soils. Cu showed intermediate results, with increased availability, primarily in medium texture soils and decrease in most of the clayey soils. In soils with pH close to ideal for the plant growth, the alkaline sewage sludge rate should be carefully calculated so that there is no excessive increase in the pH and Zn, Cu and Mn imbalance.

Index terms: Acid soils; organic residues; recycling; micronutrients.

RESUMO

No Paraná, a maioria do lodo de esgoto gerado em estações de tratamento é submetida ao processo de estabilização alcalina prolongada. Embora seja conhecido que o lodo de esgoto alcalinizado contém micronutrientes como Zn, Cu e Mn, pouco se conhece sobre a disponibilidade desses elementos em solos tratados com esse tipo de lodo de esgoto. Assim, o objetivo do estudo foi avaliar a influência de lodos de esgoto alcalinizados do estado do Paraná sobre a disponibilidade de Zn, Cu e Mn no solo. Foram selecionadas vinte estações de tratamento de esgoto ao longo do Paraná, onde foram coletadas amostras de lodo de esgoto alcalinizado e amostras do solo agrícola mais representativo da região. Cada solo foi incubado por 60 dias com doses de lodo de esgoto (0, 10, 20, 40, e 80 Mg ha^{-1}) da sua região. Posteriormente, foi determinada a disponibilidade de Zn, Cu e Mn no solo usando o extrator Mehlich-1. A aplicação de lodo de esgoto alcalinizado ao solo aumentou a disponibilidade de Zn e diminuiu a disponibilidade de Mn na maioria dos solos. Já o Cu apresentou resultados intermediários, com aumento de disponibilidade basicamente em solos de textura média e com diminuição para a maioria dos solos muito argilosos. Em solos com pH próximo ao ideal para o cultivo agrícola, a dose de lodo de esgoto alcalinizado deve ser cuidadosamente calculada para que não ocorra o aumento excessivo do pH e desbalanço nos teores de Zn, Cu e Mn.

Termos para indexação: Solos ácidos; resíduos orgânicos; reciclagem; micronutrientes.

INTRODUCTION

Among the micronutrients, Zn is the most deficient in the natural condition of Brazilian soils, requiring supplementation in new areas via fertilization to allow plant cultivation. Although less common, Cu deficiency occurs mainly in sandy or organic soils (Motta et al., 2007). The specific adsorption is one of the most important mechanisms for controlling Zn and Cu availability in soil. The Zn and Cu adsorption capacity varies depending on the texture, mineralogy, organic matter and pH (Arias et al., 2006; Casagrande; Soares; Mouta, 2008; Smolders et al., 2012), thus, the availability of these nutrients may vary from soil to soil. On the other hand, under natural acid soil condition the Mn usually has high availability, which may promote plants toxicity (Millaleo et al., 2010).

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The use of organic residues on agricultural land has been increasingly common (Barcellos et al., 2015; Mondal et al., 2015). In Brazil, the states that most use sewage sludge for agricultural purposes are: Paraná, São Paulo and Rio Grande do Sul (Sampaio, 2010). Between 2007 and 2010 the sewage treatment plants in the Curitiba metropolitan region allocated 33,404 Mg (dry basis) of sanitized sewage sludge for use on 2,288 hectares of agricultural areas (Bittencourt et al., 2014). Studies have found that the sewage sludge have significant amounts of some elements essential to plants, such as Zn and Cu (Fia; Matos; Aguirre, 2005; Yada et al., 2015), and which can improve physical and biological soil properties (Bonini; Alves; Montanari, 2015; Mondal et al., 2015).

The chemical composition of sewage sludge varies with origin, collection time and type of treatment to which it was submitted (Healy et al., 2016). In Paraná, most of the sewage sludge is subjected to sanitization by a prolonged alkaline stabilization process (addition of lime aimed at raising the pH of the mixture to 12 and a curing period of 30 days) (Paraná, 2009). Thus, when applied to agricultural land, the alkaline sewage sludge has double action, it increases the soil pH (Berton; Nogueira, 2010; Poggere et al., 2012) and can be a micronutrients source (Smolders et al., 2012; Bittencourt et al., 2014). However, unlike mineral fertilizer, the chemical composition of sewage sludge is quite variable, which results in a high degree of uncertainty regarding the micronutrient supply. Thus, the objective of this study was to evaluate the influence of alkaline sewage sludge from Paraná as to Zn, Cu and Mn availability in soils.

MATERIAL AND METHODS

The Sanitation Company of Paraná (SANEPAR) is divided into twenty sectors throughout the Paraná State (Brazil); and in each sector there are several sewage treatment plants (STPs). In this study, for each of the twenty SANEPAR sectors, the STP from sector municipal headquarters was selected, where the sludge was generated by anaerobic treatment. The samples of sewage sludge were collected between March 2009 and August 2010, and consisted of raw sludge recently dewatered in a drying bed. The sludge was sanitized by prolonged the alkaline stabilization process with the addition of lime (calcium oxide; total neutralizing power [TNP] 105.1) at 50% total solids and 30 days of curing. The total content of Zn, Cu and Mn present in the alkaline sewage sludge were determined according to the methodology described in Martins and Reissmann (2007).

For each municipality where the sewage sludge was collected, we also selected the type of agricultural soil most representative of the region. For each soil samples were taken from the 0-20 cm layer [point known by the use of global position system (GPS)] in area without having added lime for at least five years. The samples were air dried, ground, homogenized, passed through a 2 mm sieve, and analyzed as to physical and chemical attributes. With the help of location points provided by GPS, soil classes were allocated according to Bhering and Santos (2008). The results of the soil and soil class analyses are shown in Table 1. Detailed information concerning these soils and sludges has been previously reported (Poggere et al., 2012).

Each soil was incubated with increasing rates of alkaline sewage sludge from their respective sector. The incubation assay was employed according to the official methodology described in Brasil (2006). Each soil was incubated with five rates of alkaline sewage sludge (0, 10, 20, 40, and 80 Mg ha^{-1} of total solids), with three replications. After 60 days of incubation, soil samples were: collected; air dried; ground; homogenized; passed through a 2 mm sieve. The pH of the samples was determined ($CaCl_2$ 0.01 mol L^{-1}; soil:solution 1:2.5) (Table 2). To analyze the Zn, Cu and Mn availability, 10 cm^3 of soil sample were transferred into glass flasks (150 ml) and then added to 100 mL of Mehlich-1 (0.05 mol L^{-1} HCl + 0.0125 mol L^{-1} H_2SO_4). The flasks remained in a horizontal shaker for 5 minutes and then at rest for one night. The Zn, Cu and Mn concentrations were then determined in the equilibrium solution by atomic absorption spectrometry (Varian, AA240FS).

For each soil, data on Zn, Cu and Mn availability were subjected to analysis of variance (ANOVA), following a completely randomized design with three replications. When ANOVA was significant ($p < 0.05$), the data were subjected to regression analysis, choosing the model with the highest coefficient of determination (R^2) and significance ($p < 0.05$ or $p < 0.01$). To determine the Zn, Cu and Mn recovery efficiency (by Mehlich-1 extraction) as a function of the amount of these elements added to the alkaline sewage sludge application, the following formula was used:

$$ER = \frac{\left(\left(\text{Czero} - \text{Css}\right) * 2\right)}{\text{EASS}} * 100$$

where: ER, element recovery (%); Czero, element content in soil without alkaline sewage sludge aplication (mg kg^{-1}); Css, element content in soil with alkaline sewage sludge application (mg kg^{-1}); EASS, element addition with sewage sludge (kg ha^{-1}).

Table 1: Class and physical and chemical properties of the soil used in the incubation process with alkalized sewage sludge in Paraná, Brazil.

Sector	Soil class [1]	Sand [3]	Silt	Clay	Al^{3+}	$H+Al^{3+}$	Ca^{2+}	Mg^{2+}	K^+	P	OC
		----- g kg^{-1} -----			----------- cmol^c dm^{-3} -----------					mg dm^{-3}	g dm^{-3}
Apucarana	NVef	58	191	750	0.1	5.4	4.2	2.3	0.5	2.2	24.3
Cascavel	LVdf	45	103	850	1.3	10.5	3.6	1.2	0.3	3.6	30.7
Campo Mourão	LVdf	70	129	800	0.9	7.2	1.5	0.8	0.2	3.4	35.1
Francisco Beltrão	LVdf	31	268	700	5.3	17.6	2.5	1.4	0.4	3.6	19.2
Foz do Iguaçu	NVef	24	326	650	0.1	4.3	4.5	2.1	0.3	2.5	31.8
Guarapuava	LBd	35	215	750	1.3	12.1	1.9	1.2	0.3	2.7	38.6
Londrina	LVdf	40	234	725	0.0	4.0	2.6	1.1	0.1	2.7	15.3
Maringá	NVef	51	198	750	0.3	6.7	4.8	1.8	0.3	3.6	45.7
Pato Branco	LVdf	19	131	850	2.9	14.1	0.5	0.1	0.1	1.3	46.9
Pinhais	LBw	221	129	650	3.7	15.8	3.1	1.6	0.1	1.3	65.4
Toledo	LVdf	67	132	800	1.5	7.8	2.0	0.9	0.5	3.7	31.8
Cornélio Procópio	NVef	110	439	450	0.2	7.9	4.0	1.4	0.6	3.8	25.3
Santo Antônio da Platina	LVef	300	274	425	0.3	6.3	3.2	1.5	0.2	3.8	17.2
Arapongas [2]	LVd	701	49	250	1.2	7.2	1.3	0.5	0.3	4.2	23.2
Matinhos	CXbd	488	211	300	2.3	7.8	0.1	0.2	0.1	3.2	28.5
Ponta Grossa	LV	646	78	275	0.3	4.3	1.2	0.6	0.1	2.4	13.3
Rio Negro	RRdh	446	328	225	2.7	9.0	0.2	0.2	0.1	5.9	30.7
Telêmaco Borba	PVAd	391	384	225	2.4	9.7	0.5	0.1	0.1	2.2	18.2
Paranavaí	PVd	803	47	150	0.2	2.5	0.7	0.4	0.1	1.4	5.1
Umuarama	LVd	767	33	200	0.7	5.8	1.2	0.4	0.1	3.1	13.3

[1] Predominant soil type in the mapping unit corresponding to the soil sample collection local, according to Brazilian classification (Bhering; Santos, 2008); LVdf: LATOSSOLO VERMELHO Distroférrico; LBw: LATOSSOLO BRUNO Ácrico; LBd: LATOSSOLO BRUNO Distrófico; Nvef: NITOSSOLO VERMELHO Eutroférrico; RRdh: NEOSSOLO REGOLÍTICO Distro-húmbrico; CXbd = CAMBISSOLO HÁPLICO tb Distrófico; PVAd: ARGISSOLO VERMELHO-AMARELO Distrófico; LVd: LATOSSOLO VERMELHO Distrófico; LV: LATOSSOLO VERMELHO; [2] Soil collected in the municipality of Maringá, representative of Arapongas sector. [3] Soil analysis: granulometry by hidrometer method; Ca^{2+}, Mg^{2+}, Al^{3+} (extracted with KCl 1mol L^{-1}); $H+Al^{3+}$ (Estimated by pH-SMP); organic carbon (OC) (volumetric method by potassium dichromate); K^+ and P (Mehlich-1 extraction).

RESULTS AND DISCUSSION

The total Zn, Cu and Mn contents in the alkaline sewage sludge were varied greatly (Table 3). All Zn values observed are below the average value of 369 mg kg^{-1}, observed by Bittencourt et al. (2014) for 99 batches of alkaline sewage sludge, intended for agricultural use, from 2007 to 2010 in the metropolitan region of Curitiba. For Cu values, nine alkaline sewages sludges were higher than the average 96.8 mg kg^{-1} obtained by Bittencourt et al. (2014). However, both elements were below the total values of 3,176 mg kg^{-1} for Zn and 1,019 mg kg^{-1} for Cu, obtained by Rangel et al. (2006), who studied sludge coming from the wastewater treatment plant of Barueri, São Paulo, which deals with domestic and industrial sewage.

The values comply with the current legislation for maximum state (Sema 021/09) (Paraná, 2009) and federal levels permitted (Conama 375/06) (Brazil, 2006), with no limitation as to use. These low values are due mainly to low or no presence of industrial dumping in the sewage disposal system, since the policy is to treat industrial sludge before its release into the collection network and Sanepar has restrictive policies regarding reception of industrial wastewater in the sewage system (Paraná, 2013).

Table 2: pH-$CaCl_2$ values obtained in soil corresponding to each sector after incubation with increasing rates of the respective alkaline sewage sludge of Paraná State, Brazil.

Sector	Sewage sludge (Mg ha^{-1})				
	0	10	20	40	80
Apucarana	5.1	5.8	6.2	6.8	7.6
Cascavel	4.0	4.5	4.9	5.7	6.6
Campo Mourão	4.0	5.0	5.7	6.5	7.5
Francisco Beltrão	4.0	4.3	4.5	5.1	6.3
Foz do Iguaçu	5.1	6.0	6.7	7.6	8.1
Guarapuava	4.4	4.5	5.2	6.2	7.3
Londrina	5.0	5.9	6.5	7.2	7.9
Maringá	4.3	5.4	6.4	7.2	7.6
Pato Branco	3.8	4.2	4.6	5.4	6.4
Pinhais	4.2	4.6	4.9	5.5	6.5
Toledo	3.9	4.7	5.5	6.5	7.3
Cornélio Procópio	4.9	6.3	7.2	7.7	8.2
Santo Antônio da Platina	5.3	5.9	7.1	7.8	8.2
Arapongas [1]	3.8	5.1	6.6	7.6	8.2
Matinhos	5.6	6.3	6.8	7.2	7.7
Ponta Grossa	4.5	6.7	7.8	8.2	8.6
Rio Negro	5.7	6.2	6.6	7.4	8.2
Telêmaco Borba	3.8	4.9	5.7	7.2	7.8
Paranavaí	4.5	7.0	7.1	8.2	8.5
Umuarama	4.2	6.0	7.3	7.8	8.4
Mean	4.5	5.5	6. 2	6.9	7.6

[1] Soil collected in the municipality of Maringá, representative of Arapongas sector.

Table 3: Total content and added amounts of Zn, Cu and Mn in 20 alkaline sewage sludges from Paraná state (Brazil) and maximum values established by Sema and Conama regulations.

Sector	Total content (mg kg^{-1})			Zn ------ (kg ha^{-1}) ------				Cu ------ (kg ha^{-1}) ------				Mn ------ (kg ha^{-1}) ------			
	Zn	Cu	Mn	10	20	40	80	10	20	40	80	10	20	40	80
Apucarana	212	36	88	2.1	4.2	8.4	16.9	0.3	0.7	1.4	2.8	0.8	1.7	3.5	7.0
Cascavel	307	163	105	3.0	6.1	12.2	24.5	1.6	3.2	6.5	13.0	1.0	2.1	4.2	8.4
Campo Mourão	258	79	135	2.5	5.1	10.3	20.6	0.7	1.5	3.1	6.3	1.3	2.7	5.4	10.8
Francisco Beltrão	265	70	107	2.6	5.3	10.6	21.2	0.7	1.4	2.8	5.6	1.0	2.1	4.2	8.5
Foz do Iguaçu	51	42	63	0.5	1.0	2.0	4.0	0.4	0.8	1.6	3.3	0.6	1.2	2.5	5.0
Guarapuava	226	49	190	2.2	4.5	9.0	18.0	0.4	0.9	1.9	3.9	1.9	3.8	7.6	15.2
Londrina	304	635	148	3.0	6.0	12.1	24.3	6.3	12.7	25.4	50.8	1.4	2.9	5.9	11.8
Maringá	260	189	68	2.6	5.2	10.4	20.8	1.8	3.7	7.5	15.1	0.6	1.3	2.7	5.4

Continue...

Table 3: Continuation.

Sector	Total content (mg kg^{-1})			Zn ------ (kg ha^{-1}) ------				Cu ------ (kg ha^{-1}) ------				Mn ------ (kg ha^{-1}) ------			
	Zn	Cu	Mn	10	20	40	80	10	20	40	80	10	20	40	80
Pato Branco	254	101	87	2.5	5.0	10.1	20.3	1.0	2.0	4.0	8.0	0.8	1.7	3.4	6.9
Pinhais (CMR) [1]	319	81	117	3.1	6.3	12.7	25.5	0.8	1.6	3.2	6.4	1.1	2.3	4.6	9.3
Toledo	302	126	94	3.0	6.0	12.0	24.1	1.2	2.5	5.0	10.0	0.9	1.8	3.7	7.5
Cornélio Procópio	96	108	77	0.9	1.9	3.8	7.6	1.0	2.1	4.3	8.6	0.7	1.5	3.0	6.1
Santo Antônio da Platina	271	78	127	2.7	5.4	10.8	21.6	0.7	1.5	3.1	6.2	1.2	2.5	5.0	10.1
Arapongas [2]	289	104	107	2.8	5.7	11.5	23.1	1.0	2.0	4.1	8.3	1.0	2.1	4.2	8.5
Matinhos	288	81	126	2.8	5.7	11.5	23.0	0.8	1.6	3.2	6.4	1.2	2.5	5.0	10.0
Ponta Grossa	249	48	147	2.4	4.9	9.9	19.9	0.4	0.9	1.9	3.8	1.4	2.9	5.8	11.7
Rio Negro	256	53	158	2.5	5.1	10.2	20.4	0.5	1.0	2.1	4.2	1.5	3.1	6.3	12.6
Telêmaco Borba	284	68	112	2.8	5.6	11.3	22.7	0.6	1.3	2.7	5.4	1.1	2.2	4.4	8.9
Paranavaí	295	238	120	2.9	5.9	11.8	23.6	2.3	4.7	9.5	19.0	1.2	2.4	4.8	9.6
Umuarama	298	137	103	2.9	5.9	11.9	23.8	1.3	2.7	5.4	10.9	1.0	2.0	4.1	8.2
Sema 021/09 [2]	2,500	1,000	nd												
Conama 375/06 [3]	2,800	1,500	nd												

[1]CMR: Curitiba metropolitan region; [2]Paraná (2009); [3]Brasil (2006). nd: not available.

The results presented in Table 4 indicate a linear increase of Zn in 17 of the 20 analyzed soils after application of alkaline sewage sludge. The increase occurred despite an increase in pH, that at a rate of 80 Mg ha^{-1}, promoted pH-CaCl$_2$ increases to values above 7 in most soils, with an average of 7.6 (Table 2). As a result, the availability of the elements can be affected, with their liberation into the soil solution or with retention/precipitation (Berton & Nogueira, 2010). Decreased Zn availability with increasing pH is well known and, according to Nachtigall, Nogueirol and Alleoni (2009), this fact is related to the transition of exchangeable Zn to no-exchangeble forms, resulting in precipitation of insoluble forms, such as oxides and organic complex.

However, the acid solution of Mehlich-1 can extract insoluble soil Zn forms, not satisfactorily discriminating the pH effect on Zn availability for plants (Abreu; Lopes; Santos, 2007). This is due to a greater extraction ability of Mehlich-1 compared to other extractors (such as DTPA, for example), a capacity assigned to less weakening of the acid solution in more buffered conditions (Oliveira et al., 1999). This fact indicates an increase in critical Zn level in soils with high pH for plant growth. In this direction, Reszel, Reszel and Glowacka (2007) evaluated the influence of sewage sludge and a mixture (sewage sludge, sugar beet residue and ash) on available soil Zn and Cu content (1 mol L^{-1} HCl extractant) and in corn plants and observed that: in soil, the application of sewage sludge or sludge + waste, increased the levels of these micronutrients; in plants, the two micronutrients decreased. However, it is important to note that the Zn availability in soil, evaluated by Mehlich-1, shows good correlation with the amount of this nutrient in the plant shoots (Borges; Coutinho, 2004; Sobral et al., 2013). However, Pontoni (2012) found an increase or maintenance of Zn content in plants in soil amended with alkaline sewage sludge, contrasting with a decrease of Zn with the isolated application of lime.

Of the three soils that showed no increase in Zn content after the addition of alkaline sewage sludge (Table 4), the only soil in which this result may have a plausible explanation is that from Foz do Iguaçu, as it received sludge with the lowest Zn level (51 mg kg^{-1}) (Table 3). The sludges from Guarapuava and Santo Antonio da Platina showed levels of 226 and 271 mg kg^{-1}. The lack of change in Zn availability with the addition of alkaline sewage sludge may be due to the Zn release (which may have been low) from the sludge itself and/or transformation of Zn into forms that the extractant was unable to extract in solid phase. Thus, for a minority of cases, the alkaline sewage sludge will bring no Zn availability benefits, and more studies are needed to identify the factors related to the Zn increase absence.

Table 4: Available Zn in soils of Paraná state (Brazil) as a function of increasing sludge rates from their respective sector and the best regression equations.

TC[1]	Sector	Alkaline sewage sludge (Mg ha^{-1})					Sig	Equation	R^2	CV
		0	10	20	40	80				
		-------- Available Zn (mg dm^{-3}) --------								%
	Apucarana	4.7 §	6.4	7.7	9.6	15.5 §	**	$y = 4.869 + 0.131x$	0.99	3.2
	Cascavel	3.5 §	5.2	7.2	11.3	17.3 §	**	$y = 3.673 + 0.174x$	0.99	4.8
	Campo Mourão	1.6 /	1.4	1.6	2.3	4.3 §	**	$y = 1.106 + 0.038x$	0.94	10.3
	Francisco Beltrão	1.2 †	1.4	1.9	2.9	5.1 §	**	$y = 0.976 + 0.051x$	0.99	11.3
Very clayey	Foz do Iguaçu	3.0 §	2.6	2.9	3.2	2.9 §	ns	---	---	14.1
	Guarapuava	2.9 §	4.0	3.0	3.1	5.1 §	ns	---	---	3.1
	Londrina	1.6 /	3.2	6.0	10.1	15.6 §	**	$y = 1.960 + 0.178x$	0.98	4.5
	Maringá	4.1 §	4.2	5.8	8.8	10.3 §	**	$y = 4.094 + 0.085x$	0.91	5.8
	Pato Branco	1.2 †	3.4	2.3	3.1	5.9 §	**	$y = 1.687 + 0.050x$	0.81	33.6
	Pinhais (CMR)[2]	3.6 §	4.6	6.0	4.8	6.8 §	*	$y = 4.179 + 0.032x$	0.67	27.9
	Toledo	1.7 /	3.5	5.6	8.8	14.5 §	**	$y = 2.035 + 0.159x$	0.99	5.5
Clayey	Cornélio Procópio	3.5 §	3.8	4.2	5.4	6.9 §	**	$0.0435x + 3.455$	0.99	8.3
	St Ant da Platina	2.5 /	3.0	8.5	5.5	3.5 §	ns	---	---	6.4
	Arapongas	3.6 §	3.4	5.6	11.0	18.3 §	**	$y = 2.447 + 0.197x$	0.97	10.8
	Matinhos	1.7 /	2.3	3.7	5.0	6.4 §	**	$y = 2.080 + 0.058x$	0.93	14.5
	Ponta Grossa	2.4 §	2.8	3.5	5.8	7.6 §	**	$y = 2.381 + 0.068x$	0.97	4.1
Medium texture	Rio Negro	1.5 †	2.4	2.5	2.7	6.2 §	**	$y = 1.400 + 0.055x$	0.91	23.7
	Telêmaco Borba	1.2 †	3.3	2.9	6.3	10.4 §	**	$y = 1.440 + 0.113x$	0.97	17.8
	Paranavaí	0.7 ‡	6.6	9.5	12.5	17.8 §	**	$y = 3.676 + 0.191x$	0.89	9.9
	Umuarama	1.8 /	3.3	5.5	8.0	12.3 §	**	$y = 2.276 + 0.130x$	0.98	5.3

[1] TC = textural class; [2] CMR = Curitiba metropolitan region; Costa and Oliveira (1998), § = high available Zn in soil; / = good available Zn in soil; † = mean available Zn in soil; ‡ = low available Zn in soil; ns = not significant; * and **significant at 5 and 1%, respectively; cv = coeficient of variation.

The magnitude of Zn increase due to alkaline sewage sludge varied between soil and sludge. Alkaline sewage sludge from Pinhais was that with the highest total Zn content (319 mg kg^{-1}), but the increase in available Zn in the soil was 0.032 mg Mg^{-1} of sludge, reaching values of 1.8 times higher at the maximum rate (80 Mg ha^{-1}) in comparison to soil without sludge application. For Cascavel, Toledo and Londrina, which showed total Zn content in sludge similar to Pinhais, increases in the Zn availability were 4.9; 8.5 and 9.7 fold, following the additions of 0.174; 0.154 and 0.178 mg Mg^{-1} of sludge, respectively. This result was probably due to higher organic carbon (65 g dm^{-3}) present in Pinhais soil. According to Alloway (1995), the humic substances present a high degree of selectivity for micronutrients; in this case, greater affinity for Cu and lower for Zn, but forming the inner sphere complexes with both elements. Studies with Zn fractionation in soil have reported that with increasing pH, exchangeable Zn decreases, but Zn associated with organic fraction and mineral fraction of the soil present increases (Melo et al., 2008; Torri; Lavado, 2008).

In all soils, Zn available content reached appropriate or high levels from the second rate applied (Table 4), but did not reach levels above 30 mg dm^{-3}, considered excessive (Costa; Oliveira, 1998). However, the total amount of Zn applied to the maximum sludge rate (80 Mg ha^{-1} x Zn content in the sludge), ranged from 4.1 kg ha^{-1} (Foz do Iguaçu) to 25.5 kg ha^{-1} (Pinhais), being higher than those usually recommended. According to Raij et al. (1996), for São Paulo state, the recommended Zn rates range from 1 to 6 kg ha^{-1} for different crops. The Commission of Chemistry and Soil Fertility (CQFS-RS/SC, 2004), cites that micronutrient deficiency is unlikely in Rio Grande do Sul and Santa Catarina states. However, Motta et al. (2007) report that the Zn appears frequently at critical levels in Paraná soils.

In general, the Zn recovery by the Mehlich-1 extractor ranged from -154% to 399% (Figure 1), and in only three soils were negative recovery values observed (Campo Mourão, Foz do Iguaçu and Arapongas). Negative values indicate a decrease in soil native Zn with alkaline sewage sludge, overlaps the Zn applied. On the other hand, values above 100% suggest that the alkaline sewage sludge, besides making Zn available, intensified the release Zn from low availability forms to available forms.

In very clayey and clayey soils Zn recovery for the highest rate (80 Mg ha^{-1}) ranged from -5 to 127% (Figure 1). The highest values were observed in Apucarana (127%), Londrina (115%), Cascavel (112%) and Toledo (106%) soils, that received sludge with Zn levels above 212 mg kg^{-1} (Table 3). Despite the high clay content and probably higher oxide contents, which could promote high adsorption specific Zn (Birth; Supplies, 2004; Motta et al., 2007), the results for the four above-mentioned soils (higher recovery Zn) indicate that the Zn availability varied with the soil attributes and nutrient content of each sludge. These results emphasize that in this study, the effect of soil pH, after alkaline sewage sludge application, had little influence on the availability of Zn by the Mehlich-1 extractor.

The medium texture soils presented Zn recovery varying between 41 and 144% in application of 80 Mg ha^{-1} (Figure 1), and the Paranavaí soil presented the higher rate (144%) of Zn recovery. However, it is noteworthy that this soil has a clay content of 150 g kg^{-1}, near the lower limit for sandy soils, and in soils like this, the maximum application rate of alkaline sewage sludge (Poggere et al., 2012) is much less than the highest rate (80 Mg ha^{-1}) used in this study. Similar results was observed in Arapongas and Umuarama soils, with clay contents of 250 and 200 g kg^{-1}, and 127 and 88% recovery rates, respectively, for the rate of 80 Mg ha^{-1}. In this condition, due to the smaller amount of clay, Zn released from sludge probably had low adsorption on the soil solid phase (Abreu; Lopes; Santos, 2007), allowing high recovery values.

Similar to that observed for Zn, Cu availability after addition of alkaline sewage sludge varied depending on the soil (Table 5). But unlike Zn, responses ranged from a Cu decrease to increase. This can be explained by the lower Cu content in the sludge, compared to Zn, except for Londrina sludge. A direct relationship between sludge rate and available Cu was observed; with linear and quadratic equations for 9 soils and 1 soil. However, an inverse relationship was observed with linear and quadratic equations for 8 soils and 1 soil. That is, only one soil did not present a change resulting from the alkaline sewage sludge application.

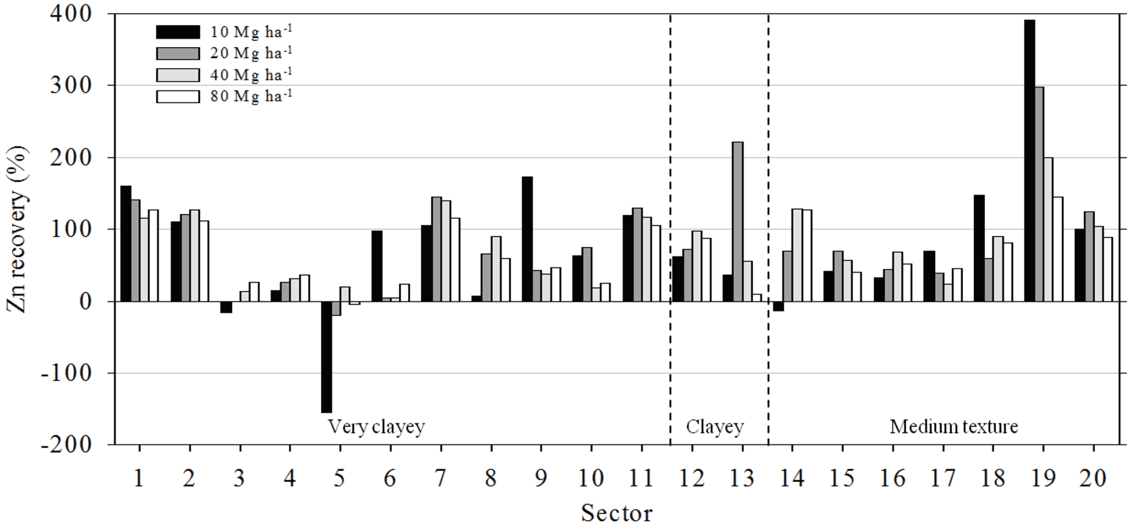

Figure 1: Zinc recovery (%) (Mehlich-1 extractor) from soils treated with alkaline sewage sludge from Paraná, Brazil. Sector: 1 - Apucarana; 2 - Cascavel; 3 - Campo Mourão; 4 - Francisco Beltrão; 5 - Foz do Iguaçu; 6 - Guarapuava; 7 - Londrina; 8 - Maringá; 9 - Pato Branco; 10 - Pinhais; 11 - Toledo; 12 - Cornélio Procópio; 13 - Santo Antônio da Platina; 14 - Arapongas; 15 - Matinhos; 16 - Ponta Grossa; 17 - Rio Negro; 18 - Telêmaco Borba; 19 - Paranavaí; 20 - Umuarama.

Table 5: Available Cu in soils of Paraná state (Brazil) as a function of increasing sludge rates from their respective sector and the best regression equations.

TC[1]	Sector	Alkaline sewage sludge (Mg ha^{-1})					Sig	Equation	R^2	CV
		0	10	20	40	80				
		------- Available Cu (mg dm^{-3}) ------								%
Very clayey	Apucarana	10.6 ¥	8.9	8.9	8.7	6.6 §	*	$y = 10.002 - 0.041x$	0.86	5.2
	Cascavel	7.6 §	8.2	8.4	8.5	9.1 ¥	**	$y = 7.890 + 0.016x$	0.85	3.5
	Campo Mourão	5.9 §	5.3	4.9	4.5	4.4 §	**	$y = 5.512 - 0.017x$	0.76	4.2
	Francisco Beltrão	12.4 ¥	11.0	10.1	9.9	11.3 ¥	**	$y = 12.2 - 0.116x + 0.001x^2$	0.94	5.3
	Foz do Iguaçu	10.5 ¥	8.6	8.5	8.3	7.5 §	**	$y = 9.536 - 0.029x$	0.67	5.1
	Guarapuava	2.8 §	2.8	2.6	2.2	2.1 §	**	$y = 2.800 - 0.010x$	0.89	22.8
	Londrina	13.0 ¥	16.1	18.6	21.1	20.7 ¥	**	$y = 15.317 + 0.086x$	0.65	5.6
	Maringá	3.5 §	2.9	3.2	3.0	1.8 /	**	$y = 3.437 - 0.018x$	0.83	6.1
	Pato Branco	3.8 §	3.6	3.7	3.3	3.1 /	**	$y = 3.747 - 0.008x$	0.81	33.6
	Pinhais (RMC)2	2.9 §	2.7	2.5	2.5	1.4 †	**	$y = 2.905 - 0.017x$	0.91	17.9
	Toledo	8.0 ¥	8.3	8.4	8.7	8.1 ¥	ns	---	---	5.6
Clayey	Cornélio Procópio	9.3 ¥	9.6	8.9	8.4	6.8 §	**	$y = 9.631 - 0.034x$	0.96	3.7
	St. Ant. da Platina	8.9 ¥	9.5	11.8	11.2	9.9 ¥	**	$y = 8.9 + 0.125x - 0.001x^2$	0.75	5.8
Medium texture	Arapongas	1.0 †	1.2	1.3	1.6	1.6 /	**	$y = 1.089 + 0.007x$	0.77	13.4
	Matinhos	2.2 §	2.1	2.3	2.6	2.7 §	**	$y = 2.158 + 0.007x$	0.84	8.1
	Ponta Grossa	1.9 /	1.9	2.1	2.2	2.2 §	**	$y = 1.931 + 0.004x$	0.72	11.2
	Rio Negro	1.7 /	1.8	2.0	1.9	2.1 §	**	$y = 1.775 + 0.004x$	0.86	3.6
	Telêmaco Borba	0.9 †	1.4	1.3	1.5	1.8 /	**	$y = 1.084 + 0.010x$	0.82	6.2
	Paranavaí	1.2 †	2.0	2.9	4.7	7.4 §	**	$y = 1.289 + 0.077x$	0.99	14.7
	Umuarama	2.1 §	2.3	2.7	2.9	3.1 §	**	$y = 2.295 + 0.011x$	0.81	4.9

[1] TC = textural class; [2] CMR = Curitiba metropolitan region; Costa and Oliveira (1998), ¥ = very high available Cu in soil; § = high available Cu in soil; / = good available Cu in soil; † = mean available Cu in soil; ‡ = low available Cu in soil; ns = not significant; * and **significant at 5 e 1%, respectively; cv = coeficient of variation.

The Cu availability decreases with the use of alkaline sewage sludge were observed in 9 of 13 clayey and very clayey soils (Table 5). In addition to the higher clay content, this group of soils showed high organic carbon content. Thus, smaller increases in Cu compared to Zn are evident, as well as the importance of the texture in the Cu response due to sludge.

The lowest Mehlich-1 Cu extraction ability, compared to Zn was observed; and is possibly related to at least three reasons: 1) Cu has a lower hydrolysis constant than Zn, which is related to the formation of complexes with higher binding energy (Sparks, 2003); 2) Cu has a higher electronegativity than Zn, being more strongly bound by the mineral constituents of the soil (Arias et al, 2006); 3) Cu has a higher affinity for organic matter in comparison to Zn (Souza et al., 2012).

Corroborating the Cu availability decrease results, Fan et al. (2011) observed reduction in exchangeable content (readily available) and increase in content in the oxides and the residual fraction after application of alkaline sludge. The authors explain the reduction of Cu exchangeable by its precipitation in the form of carbonates. On the other hand, the increase in Cu availability in soil with very clayey texture (Table 5) can be justified by the high Cu content in Londrina sludge (635 mg kg^{-1}), well above the levels the other sludges (mean 97 mg kg^{-1}, range: 36-238 mg kg^{-1}) (Table 3). For Cascavel soil this result was not expected, which has a quarter of Londrina sludge content and high carbon (30.7 g dm^{-3}) and clay content (850 g kg^{-1}), which would provide a high adsorption capacity to the soil.

Of the other soils that showed an increase in the Cu availability in response to the sludge addition, all have a medium texture (300-150 g kg^{-1}). As a result, buffering capacity of these soils is low, which reduces the capacity of the solid phase to adsorb Cu added via sludge. Another consequence of the low buffering capacity of medium texture soils is that there was no effect on the extraction capacity of the Mehlich-1, even with increasing pH values above 7 in the higher sludge rate. This effect is evident when one carefully examines the soil characteristics. The increase in the available Cu in Paranavaí soil at a high sludge rate (80 Mg ha^{-1}) was 6.1 fold, in comparison to the soil that did not received sludge, while in the remaining medium texture soils, increases were between 1.1 and 2.0 fold. This result is a consequence of the low clay (150 g kg^{-1}) and organic carbon content (5.1 g dm^{-3}) of Paranavaí soil and higher Cu content in the sludge (137 mg kg^{-1}), compared to sludge applied to medium texture soils.

In general, the Cu recovery by Mehlich-1 extractor was negative for seven very clayey soils (Figure 2). There was Cu retention in these soils and the addition of sludge acts more like a drain than as a source, due to the influence of the pH increase on the increase of the Cu adsorption capacity for the mineral or organic soil fraction (Arias et al., 2006; Souza et al., 2012). But, the Cu recovery was positive for two very clayey, one clayey and six medium texture soils (Figure 2). Thus, besides the soil ability to adsorb Cu, other factors affect the recovery (e.g., amount of Cu added via sludge, sludge decomposition and mineralization of Cu).

The amount of total Cu applied per hectare to the soil with the sludge at the largest sludge rate (80 Mg ha^{-1} x Cu content in the sludge), ranged from 3 to 51 kg ha^{-1}. These Cu values are higher than generally recommended. According to Raij et al. (1996), for São Paulo state, the recommended Cu rates range from 1 to 5 kg ha^{-1} for different cultures. But, Cu and Zn have long residual effect in the soil, according to Fan et al. (2011), this residual effect is due to the prevalence of specific adsorption to soil mineral and organic colloids. Thus, monitoring Cu content in the soil is necessary to avoid high sludge applications rates causing Cu toxicity in plants, especially in soils with low buffering capacity.

Unlike Zn, the Mn availability after the addition of alkaline sewage sludge decreased in 15 soils, increased in two soils and did not change in three (Table 6). The amount of Mn applied, generally, is near that applied to Cu, which indicates that not only the amount should be considered. Thus, decreasing levels of available Mn in these soils is directly linked to increased sensitivity of the element to the pH change (Abreu; Lopes; Santos, 2007). With the increase of the soil pH, the Mn^{2+} cationic form is converted into manganic oxides (Hue; May, 2002) or strongly bound to organic matter (Moreira et al., 2016; Nachtigall; Nogueirol; Alleonni, 2009).

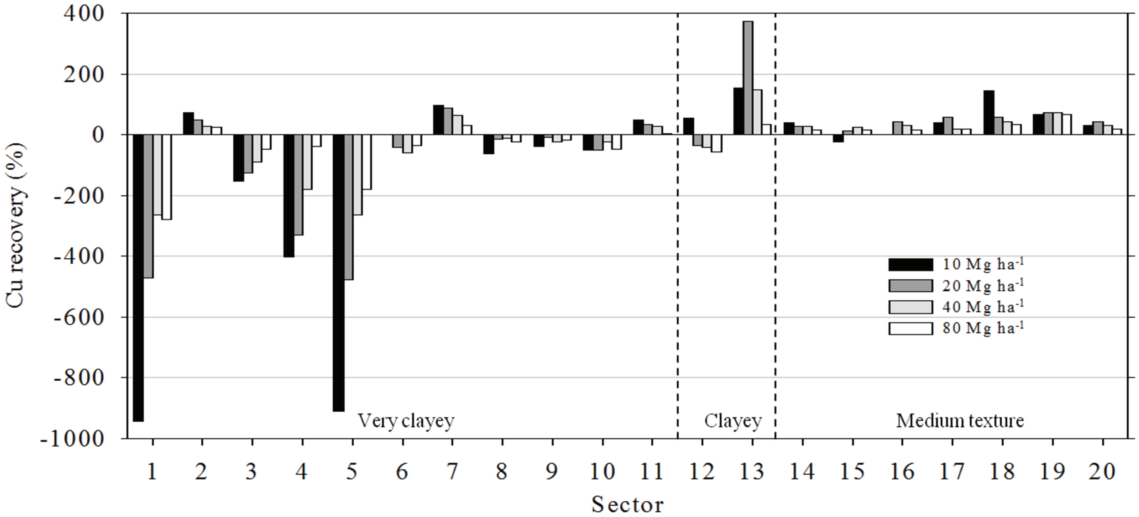

Figure 2: Copper recovery (%) (Mehlich-1 extractor) from soils treated with alkaline sewage sludge from Paraná, Brazil. Sector: 1 - Apucarana; 2 - Cascavel; 3 - Campo Mourão; 4 - Francisco Beltrão; 5 - Foz do Iguaçu; 6 - Guarapuava; 7 - Londrina; 8 - Maringá; 9 - Pato Branco; 10 - Pinhais; 11 - Toledo; 12 - Cornélio Procópio; 13 - Santo Antônio da Platina; 14 - Arapongas; 15 - Matinhos; 16 - Ponta Grossa; 17 - Rio Negro; 18 - Telêmaco Borba; 19 - Paranavaí; 20 - Umuarama.

On the other hand, Matinhos and Telêmaco Borba, who obtained an increase in Mn availability, showed behavior contrary to other soils with similar clay and organic matter content. Borges and Coutinho (2004) applied sewage sludge with and without lime in two soils, and observed an increase in available Mn extracted by Mehlich-1. Abreu et al. (2004) point out that higher values of Mn extracted by Mehlich-1 solution (acidic solution) and Mehlich-3 (mixed solution) may be due to greater capacity for solubilizing Mn in some soils, particularly when linked to iron oxides.

The Mn recovery by Mehlich-1 extractor was negative in 18 soils, with very low levels, reaching -8571% (Foz do Iguaçu soil, at a rate of 10 Mg ha^{-1}) (Figure 3). The extremely low recovery values demonstrate how Mn is influenced by pH values and Mn content in sewage sludge. In practical terms, the decrease in Mn may be a positive aspect, since it is the second most likely element to cause toxicity in acid soils (Millaleo et al., 2010). Therefore, the pH increase and decrease in Mn availability can mean its toxicity decrease and a benefit to plants. Corroborating the results of this study, Pontoni (2012) found a large decrease in Mn content in leaf tissue as a result of the alkaline sewage sludge application in soil. However, we found that despite the decrease in the Mn availability in most soils, there was virtually no change in the interpretation of Mn level in the soil (Table 6).

Table 6: Available Mn in soils of Paraná state (Brazil) as a function of increasing sludge rates from their respective sector and the best regression equations.

TC[1]	Sector	Alkaline sewage sludge (Mg ha^{-1})					Sig	Equation	R^2	CV
		0	10	20	40	80				
		------ Available Mn (mg dm^{-3}) ------								%
Very clayey	Apucarana	195 ¥	179	174	153	160 ¥	**	$y = 89.434 - 0.182x$	0.65	7.8
	Cascavel	149 §	142	136	134	137 §	ns	---	---	6.3
	Campo Mourão	42 §	36	31	27	26 §	**	$y = 38.308 - 0.185x$	0.72	10.9
	Francisco Beltrão	104 §	93	90	79	78 §	**	$y = 98.439 - 0.303x$	0.76	8.1
	Foz do Iguaçu	192 ¥	165	148	133	135 §	**	$y = 173.530 - 0.609x$	0.62	4.5
	Guarapuava	67 §	59	52	43	44 §	**	$y = 61.468 - 0.264x$	0.69	8.1
	Londrina	221 ¥	208	200	192	165 ¥	**	$y = 217.200 - 0.658x$	0.98	3.8
	Maringá	186 ¥	160	155	123	83 §	**	$y = 178.820 - 1.228x$	0.98	6.2
	Pato Branco	43 §	32	31	32	28 §	**	$y = 37.593 - 0.133x$	0.53	10.6
	Pinhais (RMC)[2]	35 §	23	13	11	9 /	**	$Y = 26.573 - 0.267x$	0.60	12.0
Clayey	Toledo	95 §	83	83	81	76 §	**	$y = 89.434 - 0.182x$	0.65	7.9
	Cornélio Procópio	188 ¥	176	159	147	167 ¥	**	$y = 175.030 - 0.239x$	0.23	4.7
	St Ant da Platina	182 ¥	180	160	169	166 ¥	*	$y = 176.530 - 0.158x$	0.31	5.5
Medium texture	Arapongas	47 §	39	41	36	39 §	*	$y = 43.158 - 0.073x$	0.34	9.7
	Matinhos	1.7 ‡	2.0	3.2	3.4	3.5 ‡	**	$y = 2.145 + 0.021x$	0.64	19.5
	Ponta Grossa	12 /	10	10	10	11 /	**	$y = 11.6 - 0.079x + 0.001x^2$	0.68	7.8
	Rio Negro	11 /	10	10	9.9	11 /	*	$y = 11.5 - 0.081x + 0.001x^2$	0.40	8.7
	Telêmaco Borba	11 /	13	14	17	17 §	**	$y = 12.361 + 0.082x$	0.82	9.3
	Paranavaí	66 §	48	54	62	67 §	*	$y = 59.6 - 0.249x + 0.004x^2$	0.38	12.3
	Umuarama	87 §	65	74	54	50 §	*	$y = 78.721 - 0.408x$	0.70	27.0

[1] TC = textural class; [2]CMR = Curitiba metropolitan region; Costa and Oliveira (1998), ¥ = very high available Mn in soil; § = high available Mn in soil; / = good available Mn in soil; † = mean available Mn in soil; ‡ = low available Mn in soil; ns = not significant; * and **significant at 5 e 1%, respectively; cv = coeficient of variation.

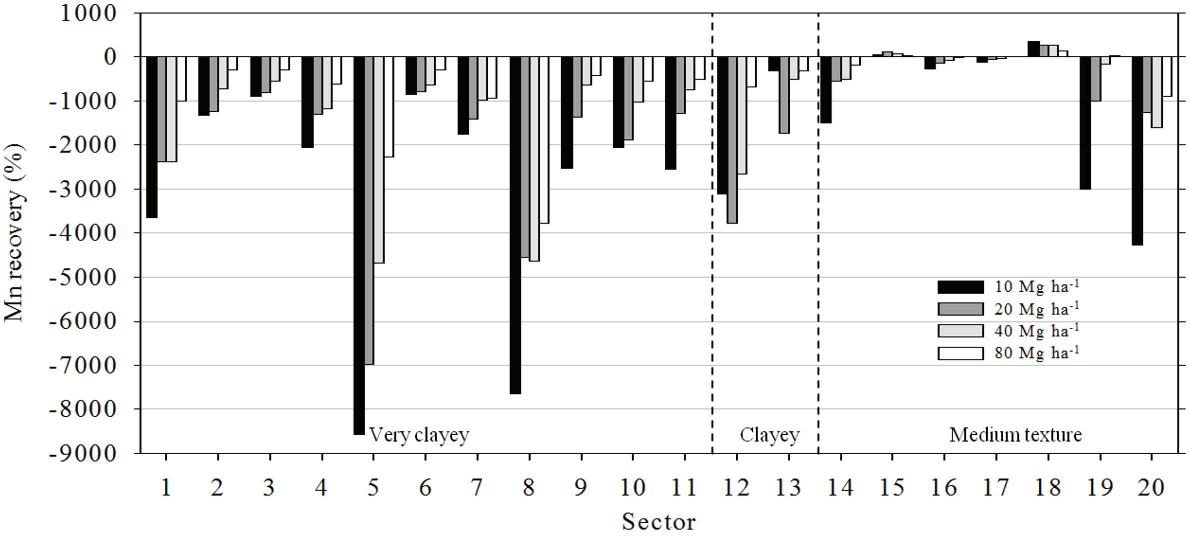

Figure 3: Manganese recovery (%) (Mehlich-1 extractor) from soils treated with alkaline sewage sludge from Paraná, Brazil. Sector: 1 - Apucarana; 2 - Cascavel; 3 - Campo Mourão; 4 - Francisco Beltrão; 5 - Foz do Iguaçu; 6 - Guarapuava; 7 - Londrina; 8 - Maringá; 9 - Pato Branco; 10 - Pinhais; 11 - Toledo; 12 - Cornélio Procópio; 13 - Santo Antônio da Platina; 14 - Arapongas; 15 - Matinhos; 16 - Ponta Grossa; 17 - Rio Negro; 18 - Telêmaco Borba; 19 - Paranavaí; 20 - Umuarama.

The positive Mn recovery occurred in two soils (Matinhos and Telêmaco Borba) (Figure 3), and these soils showed good Mn content and low availability, respectively (Table 6). However, the level of interpretation changed (high) only for Telêmaco Borba soil. Thus, in these two soils, applications of alkaline sewage sludge had no significant impact as a Mn source. It is worth noting that the Mn deficiency has been observed especially in soils receiving excessive liming (Tanaka; Mascarenhas; Bulisani, 1993) or in systems that favor the accumulation of organic matter, such as the no-tillage system (Moreira et al., 2016).

CONCLUSIONS

The alkaline sewage sludge from Paraná state had a distinct effect on the three micronutrients. There was an increase in Zn availability for most soils, especially sandy soils. Available Cu presented a decrease with alkaline sewage sludge application in very clayey soil, suggesting that the increase in the adsorption/precipitation overlaps via the sludge addition. However, in soils with lower adsorption capacity, the opposite occurs. Therefore, two attributes were keys in the effect of the alkaline sewage sludge Cu availability, texture and Cu content in the sludge. The high sensitivity of Mn to pH elevation resulted in a decrease in availability. Thus, regardless of the Mn content in the sludge, raising the pH decreased the Mn availability.

REFERENCES

ABREU, C. A. et al. Avaliação da disponibilidade de manganês e ferro em solos pelo uso do método modificado da resina de troca iônica. **Revista Brasileira de Ciência do solo**. 28(3):579-584, 2004.

ABREU, C. A.; LOPES, A. S.; SANTOS, G. C. G. Micronutrientes. In: NOVAIS, R. F. et al. (eds.). **Fertilidade do solo**. Viçosa, SBCS, 2007. p.645-736.

ALLOWAY, B. J. **Heavy metals in soils**. 2.ed. London, Blackie Academic & Professional, 1995, 368p.

ARIAS, M. et al. Competitive adsorption and desorption of copper and zinc in acid soils. **Geoderma**. 133:151-159, 2006.

BARCELLOS, M. et al. Atributos químicos de Latossolo sob plantio direto adubado com esterco de bovinos e fertilizantes minerais. **Comunicata Scientiae**. 6:263-273, 2015.

BERTON, R. S.; NOGUEIRA, T. A. R. Uso do lodo de esgoto na agricultura. In: COSCIONE, A. R.; NOGUEIRA, T. A. R., PIRES, A. M. M. (eds.). **Uso agrícola de lodo de esgoto**. Botucatu, FEPAF, 2010. p.31-50.

BHERING, S. B.; SANTOS, H. G. **Mapa de solos do Estado do Paraná: legenda atualizada**. Rio de Janeiro, EMBRAPA-IAPAR, 2008. 74p.

BITTENCOURT, S. et al. Sewage sludge usage in agriculture: A case Study of its destination in the Curitiba Metropolitan Region, Paraná, Brazil. **Water, Air and Soil Pollution**. 225:2-8, 2014.

BONINI, C. S. B.; ALVES, M. C.; MONTANARI, R. Recuperação da estrutura de um Latossolo Vermelho degradado utilizando lodo de esgoto. **Revista Brasileira de Ciências Agrárias**. 10(1):34-42, 2015.

BORGES, M. R.; COUTINHO, E. L. M. Metais pesados do solo após aplicação de biossólido. II – Disponibilidade. **Revista Brasileira de Ciência do Solo**. 28:557-568, 2004.

BRASIL. Ministério do Meio Ambiente. Conselho Nacional do Meio Ambiente. **Resolução CONAMA nº 375**, de 29 de agosto de 2006. Define critérios e procedimentos, para o uso agrícola de lodos de esgoto gerados em estações de tratamento de esgoto sanitário. 2006. Available in: <www.mma.gov.br/port/conama/res/res06/res37506.pdf>. Access in Jun 9, 2016.

CASAGRANDE, J. C.; SOARES, M. R.; MOUTA, E. R. Zinc adsorption in highly weathered soils. **Pesquisa Agropecuária Brasileira**. 43(1):131-139, 2008.

COSTA, J. M.; OLIVEIRA, E. F. **Fertilidade do solo e nutrição de plantas**. Cascavel, Campo Mourão: COAMO/COODETC, 1998. 89p.

COMISSÃO DE QUÍMICA E FERTILIDADE DO SOLO - CQFSRS/SC. **Manual de adubação e calagem para os Estados do Rio Grande do Sul e de Santa Catarina**. 10. ed. Porto Alegre, SBCS - Núcleo Regional Sul/UFRGS, 2004. 400p.

FAN, J. et al. Immobilization of copper in contaminated sandy soils using calcium water treatment residue. **Journal of Hazardous Materials**. 189(3):710-718, 2011.

FIA, R.; MATOS, A. T.; AGUIRRE, C. I. Características químicas de solo adubado com doses crescentes de lodo de esgoto caleado. **Engenharia na Agricultura**. 13:287-299, 2005.

HEALY, M. G. et al. Metal concentrations in lime stabilized, thermally dried and anaerobically digested sewage sludges. **Waste Management**. 48:404-408, 2016.

HUE, N. V.; MAI, Y. Manganese toxicity in watermelon as affected by lime and compost amended to a Hawaiian acid Oxisol. **HortScience**. 37(4):656-661, 2002.

MARTINS, A. P. L.; REISSMANN, C. B. Material vegetal e as rotinas laboratoriais nos procedimentos químico-analíticos. **Scientia Agraria**. 8:1-17, 2007.

MELO, E. E. C. et al. Disponibilidade e fracionamento de Cd, Pb, Cu e Zn em função do pH e tempo de incubação com o solo. **Ciência e Agrotecnologia**. 32:776-784, 2008.

MILLALEO, R. et al. Manganese as essential and toxic element for plants: Transport, accumulation and resistance mechanisms. **Journal of Soil Science and Plant Nutrition**. 10(4):470-481, 2010.

MONDAL, S. et al. Changes in soil quality in response to short-term application of municipal sewage sludge in a typic haplustept under cowpea-wheat cropping system. **Environmental Nanotechnology, Monitoring and Management**. 4:37-41, 2015.

MOREIRA, S. G. et al. Chemical forms in soil and availability of manganese and zinc to soybean in soil under different tillage systems. **Soil and Tillage Research**. 163:41-53, 2016.

MOTTA, A. C. V. et al. **Micronutrientes na Rocha, Solo e na Planta**. 1. ed. Curitiba, Edição do Autor, 2007. 246p.

NACHTIGALL, G. R.; NOGUEIROL, R. C.; ALLEONI, L. R. Extração seqüencial de Mn e Zn em solos em função do pH e adição de cama-de-frango. **Revista Brasileira de Engenharia Agrícola e Ambiental**. 13(3):240-249, 2009.

OLIVEIRA, M. F. G. et al. Relação entre o zinco "disponível", por diferentes extratores, e as frações de zinco em amostras de solos. **Revista Brasileira de Ciência do Solo**. 23(4):827-836, 1999.

PARANÁ. Secretaria de Estado de Meio Ambiente e Recursos Hídricos. **Resolução Sema 021/09**. Dispõe sobre licenciamento ambiental, estabelece condições e padrões ambientais e dá outras providências, para empreendimentos de saneamento. Diário Oficial do Estado do Paraná, Curitiba, n. 7962, p.13-16. 2009.

PARANÁ. Instituto Ambiental do Paraná. **Portaria IAP 256/2013**. Aprova e estabelece os critérios e exigências para a apresentação da declaração de carga poluidora, através do sistema de automonitoramento de Atividades Poluidoras no Paraná e determina seu cumprimento. Diário Oficial do Estado do Paraná, Curitiba, 23 de setembro de 2013. Available in: <http://celepar7.pr.gov.br/sia/atosnormativos/form_cons_ato1.asp?Codigo=2760>. Access in: Jun 10, 2016.

POGGERE, G. C. et al. Lodos de esgoto alcalinizados em solos do estado do Paraná: Taxa de aplicação máxima anual e comparação entre métodos para recomendação agrícola. **Revista Brasileira de Engenharia Agrícola Ambiental**. 17:429-438, 2012.

PONTONI, D. R. **Nutrição e crescimento do feijoeiro (*Phaseolus vulgaris* L.) em função de lodo de esgoto e calcário para solos subtropicais**. Curitiba, PR, 2012. Available in: <http://acervodigital.ufpr.br/handle/1884/26258>. Access in: November, 08, 2016.

VAN RAIJ, B. et al. **Recomendações de adubação e calagem para o estado de São Paulo**. 2. ed. Campinas: IAC, Boletim técnico, 1996. 285p.

RANGEL, O. J. P. et al. Efeito de aplicações de lodos de esgoto sobre os teores de metais pesados em folhas e grãos de milho. **Revista Brasileira de Ciência do Solo**. 30(3):583-594, 2006.

RESZEL, R.; RESZEL, H.; GLOWACKA, A. Phytoavailability of copper and zinc from soil reclaimed by lime-treated sewage sludge and other waste. **Environment Protection Engineering**. 33(2):205, 2007.

SAMPAIO, A. O. Adequação das estações de tratamento de esgotos sanitários à resolução número 375 do CONAMA. In: COSCIONE, A. R.; NOGUEIRA, T. A. R.; PIRES, A. M. M. **Uso agrícola de lodo de esgoto**. Botucatu, FEPAF, 2010. p.256-280.

SOBRAL, L. F. et al. Comparison of copper, manganese, and zinc extraction with Mehlich 1, Mehlich 3, and DTPA solutions for soils of the Brazilian coastal tablelands. **Communications in Soil Science and Plant Analysis**. 44(17):2507-2513, 2013.

SOUZA, R. A. S. et al. Extração sequencial de zinco e cobre em solos tratados com lodo de esgoto e composto de lixo. **Química Nova**. 35:308-314, 2012.

SPARKS, D. L. **Environmental soil chemistry**. San Diego, Elsevier, 2003. 345p.

SMOLDERS, E. et al. The availability of copper in soils historically amended with sewage sludge, manure, and compost. **Journal of Environmental Quality**. 41(2):506-514, 2012.

TANAKA, R. T.; MASCARENHAS, H. A. A.; BULISANI, E. A. Manganese deficiency in soybean induced by excess lime. **Better Crops International**. 9:1-7, 1993.

TORRI, S. I.; LAVADO, R. Zinc distribution in soils amended with different kinds of sewage sludge. **Journal of Environmental Management**. 88(4):1571-1579, 2008.

YADA, M. M. et al. Chemical and biochemical properties of oxisols after sewage sluge application for 16 years. **Revista Brasileira de Ciência do Solo**. 39:1302-1310, 2015.