HEAVY METALS IN OXISOLS AMENDED WITH BIOSOLIDS AND CROPPED WITH MAIZE IN A LONG-TERM EXPERIMENT

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ABSTRACT: Biosolids comprise organic matter and plant nutrients, but are also a source of heavy metals hazardous to soils, plants and humans. The aim of this work was to evaluate accumulation, movement in the soil profile and availability to maize plants of heavy metals in two oxisols amended with biosolids for five years. The experiment was carried out in Jaboticabal, SP, Brazil, under field conditions, using a split-plot design. Biosolids were added to the soils at four different rates, 0.0 (control with mineral fertilization), 2.5; 5.0 and 10.0 t ha^{-1}, dry weight basis, annualy for three years. In the fourth and fifth years, the 2.5 t ha^{-1} treatment rate was increased to 20.0 t ha^{-1}. In the fifth year, soil samples were collected at 0-20 and 20-40 cm depths and analyzed for Cu, Ni, Mn, Pb and Zn total and extractable (Mehlich 1) contents. Biosolids increased the concentration of Ni and Zn in the Typic Eutrorthox, and of Ni, Pb, Zn and Cu in the Typic Haplorthox, but values did not exceed critical limits established by legislation. The elements generally accumulated in the 0-20 cm depth. Lead and Ni concentrations in grains were below detection limits. In general, heavy metals contents in maize plants were not affected by application of biosolids. Mehlich 1 extractant was not efficient in predicting the availability of Ni, Mn, and Pb to maize plants.
Key words: Mehlich 1, sewage sludge, maize, metal availability

METAIS PESADOS EM LATOSSOLOS TRATADOS COM BIOSSÓLIDO E CULTIVADOS COM MILHO EM EXPERIMENTO DE LONGA DURAÇÃO

RESUMO: O biossólido contém em sua composição matéria orgânica e nutrientes das plantas, mas também metais pesados danosos para solos, plantas e a saúde humana. O objetivo deste trabalho foi avaliar o acúmulo de metais pesados e sua mobilidade no perfil do solo, assim como a disponibilidade para plantas de milho cultivadas em Latossolo Vermelho distrófico (LVd) e Latossolo Vermelho eutroférrico (LVef) tratados com doses crescentes de biossólido durante cinco anos. O experimento foi conduzido em Jaboticabal, SP, Brasil, em condições de campo, utilizando-se delineamento de parcelas subdivididas com cinco repetições. Foram testadas quatro doses de biossólido: 0,0; 2,5; 5,0 e 10,0 t ha^{-1} (base seca) nos três primeiros anos. A partir do quarto ano a dose 2,5 foi substituída por 20,0 t ha^{-1}. No quinto ano de experimentação amostras de solo foram obtidas nas profundidades 0-20 e 20-40 cm e analisadas para totais e extraíveis (Mehlich 1) de Cu, Mn, Ni, Pb e Zn. O biossólido aumentou os teores de Ni e Zn no LVef e Ni, Pb, Zn e Cu no LVd, mas os valores não ultrapassaram os níveis críticos legais. Os elementos geralmente acumularam-se na profundidade 0-20 cm em ambos os solos. Os teores de Pb e Ni nos grãos ficaram abaixo do limite de detecção da metodologia empregada. As concentrações de metais pesados na planta geralmente não foram afetados pela adição de biossólido. O extrator Mehlich 1 não foi eficiente para avaliar a disponibilidade de Ni, Mn e Pb para planta de milho.
Palavras-chave: Mehlich 1, lodo de esgoto, milho, fitodisponibilidade

INTRODUCTION

Biosolids are residues from domestic and industrial wastewater treatments. Increasing costs of commercial fertilizers and large amounts of biosolids produced worldwide has made cropland application of this residue an attractive disposal option. Chemical and biological composition of biosolids depends on the wastewater composition (Melo, 2002). Usually, it is rich in organic matter and plant nutrients such as N, P and Ca (Hue, 1988), and can improve soil physical and chemical properties, such as porosity, aggregate stability, bulk density, water movement and retention (Silveira et al., 2003), and soil fertility. In the tropics, where soils are generally poor in minerals with high cation exchange capacity (CEC) and in organic matter (OM), biosolids could be an important soil amendment (Melo, 2002). On the other hand, biosolids contain hazardous constituents, such as heavy metals, and may cause soil and water pollution and toxicity to crops, animals and humans through the trophic chain (Mc Brige, 1995). Metal concentrations in biosolids vary widely, depending on the origin of the sludge and on the processes of treatment of sewage sludge (Mattigod & Page, 1983).

Total contents of heavy metals in different plants and in different plant parts vary considerably. Most vegetative parts of plants, especially leaves, have higher heavy metal contents than seeds, nuts and fruits. Even when high rates of heavy metals are added to soils by biosolids application, the uptake of such metals by plants represent less than 1.0% of the total applied to the soil (Chang et al., 1984). Many methods are used to estimate heavy metals availability to plants in biosolids-amended soils, e.g. extraction with acid solutions (0.1 mol L^{-1} HCl and Mehlich 1), with chelating agents (DTPA), or with acid and chelating agents (Mehlich 3). The objective of this work was evaluating heavy metal accumulation and movement in two soil profiles and to determine their phytoavailability to maize plants when the soils were amended with biosolids for five years.

MATERIAL AND METHODS

The experiment was carried out in a split-plot design field trial, on two soils (Typic Haplorthox (TH) and Typic Eurtrorthox (TE)), in Jaboticabal, SP, Brazil (21°15’20" S, 48°19’02" W, 579 m altitude), from 1997 to 2002. The levels of biosolids application were: 0.0 (control, no biosolids, but with mineral fertilization according to soil analysis), 2.5, 5.0 and 10 t ha^{-1}, (n = 5) dry weight basis, in the first three years. To increase the rate of heavy metals added to the soil from the fourth year the 2.5 rate was replaced by 20.0 t ha^{-1}, using the same plots. Therefore, the accumulated amounts of biosolids over five years were 0.0; 25.0; 47.5 and 50.0 t ha^{-1}. Chemical properties of the two soils during the experimental period are shown in Tables 1 and 2.

Biosolids (Table 3) were obtained from the sewage treatment plant operated by SABESP in Barueri, Great São Paulo.

Total N concentration in biosolids was determined by the micro-Kjeldhal method; organic-C by wet oxidation; K by flame photometry; P by vanado-molybdate spectrophotometric method; and Ca, Mg, Fe, Cu, Mn, Zn, Ni, Cd, Cr and Pb by digestion with HNO_3+H_2O_2+HCl (USEPA, 1986), followed by atomic absorption spectrophotometric analysis of the digest.

In the 1997/98 growing season, the area was ploughed and harrowed, and then 2.5 t ha^{-1} of dolomitic limestone were applied to raise base saturation to 70%, following recommendation of Raij et al. (1996). Thirty days after liming, plots were marked out, each with a total area of 54 m^2 (28,8 m^2 of useful area), including six, 10-m long planted lines, spaced 0.90 m. The two external lines and 1.0 m at the end of each planted line were used as plot frames; one of the two central lines was used for evaluation of grain production and the other for plant sampling.

Biosolids were spread on the soil surface and incorporated into the top 10 cm layer with a rotary hoe in the first year, and with a light harrowing in the last four years. Treatments receiving biosolids also received supplementary K and P, when necessary (Tables 4 and 5). The mineral fertilizer was applied in the plough furrow.

Table 1 - Chemical properties of a Typic Eutrorthox during five years of experimentation.

Year	pH $CaCl_2$	OM	P_{resin}	K^+	Ca^{2+}	Mg^{2+}	H+Al	SB	CEC	V
		g dm^{-3}	mg dm^{-3}	---------------------------- $mmol_c$ dm^{-3} ----------------------------						%
1997/98	5.7	34	67	4.9	42	19	22	66	87	75
1998/99	5.4	32	62	4.7	38	17	26	60	85	71
1999/00	5.3	26	60	4.2	32	18	30	54	84	63
2000/01	5.3	28	61	4.5	39	14	34	58	92	63
2001/02	5.2	24	67	4.1	41	14	38	59	82	72

Table 2 - Chemical properties of a Typic Haplorthox soil during five years of experimentation.

Year	pH $CaCl_2$	OM	P_{resin}	K^+	Ca^{2+}	Mg^{2+}	H+Al	SB	CEC	V
		g dm^{-3}	mg dm^{-3}	---------------------------- $mmol_c$ dm^{-3} ----------------------------						%
1997/98	5.7	20	44	2.2	26	11	16	39	55	71
1998/99	6.1	18	47	1.7	35	10	15	47	62	75
1999/00	5.4	16	43	1.6	20	10	19	32	51	71
2000/01	5.0	16	71	2.3	25	9	29	36	66	55
2001/02	5.1	24	54	4.8	23	10	38	38	76	50

Table 3 - Chemical composition of the biosolids used during the five years of experimentation.

Element	Unit	1997/1998	1998/1999	1999/2000	2000/2001	2001/2002
Nitrogen	g kg^{-1}	6.40	37.31	28.72	28.94	36.75
Phosphorus	g kg^{-1}	3.32	11.30	17.41	15.58	15.54
Potassium	g kg^{-1}	0.97	1.70	1.47	1.85	2.74
Manganese	mg kg^{-1}	228	294	257	263	287
Zinc	mg kg^{-1}	1800	3810	2328	1745	2354
Copper	mg kg^{-1}	664	551	660	719	627
Nickel	mg kg^{-1}	268	595	360	354	350
Lead	mg kg^{-1}	152	371	180	171	155

Table 4 - Mineral fertilizations on Typic Haplorthox soil during five years of experimentation.

Year	Treatment	N		P_2O_5		K_2O	
		Sowing	Dressed	Sowing	Dressed	Sowing	Dressed
		kg ha^{-1}					
1997/98	T	---	---	---	---	---	---
	D1	---	---	50	---	29	---
	D2	---	---	44	---	26	---
	D3	---	---	33	---	20	---
1998/99	T	16.7	60	30	---	30	---
	D1	---	---	---	---	25	---
	D2	---	---	---	---	20	---
	D3	---	---	---	---	10	---
1999/00	T	30	110	50	---	50	40
	D1	---	---	---	---	46	40
	D2	---	---	---	---	41	40
	D3	---	---	---	---	32	40
2000/01	T	30	120	50	---	50	40
	D1	---	---	---	---	5	40
	D2	---	---	32	---	39	40
	D3	---	---	2	---	28	40
2001/02	T	30	140	70	---	50	40
	D1	---	---	---	---	---	40
	D2	---	---	---	---	34	40
	D3	---	---	---	---	17	40

T-Control treatment; D1-treatment with 2.5 or 20 t ha^{-1} of biosolids; D2- treatment with 5.0 t ha^{-1} of biosolids; D3- treatment with 10.0 t ha^{-1} of biosolids.

The control treatment received mineral fertilization (Tables 4 and 5). The dressed fertilization was done 45 days after sowing on the control treatment (140 kg N ha^{-1}). The test plant in the fifth year was maize (Zea mays L.), double hybrid Agromen 3150, at 5-7 plants m^{-1} (about 55,000 plants ha^{-1}).

For the evaluation of the heavy metal concentrations in the plants, samples of five plants were taken from each plot 100 days after sowing, plants being cut just above the soil surface. The grains were harvested 120 days after sowing from all the plants in the line, dried at 65°C (forced air), then ground. An extract was prepared from nitric-perchloric acid digestion (Bataglia et al., 1983).

Soil samples (0-20 cm and 20-40 cm layers) were collected 60 days after sowing; 12 single samples in the useful area of each plot obtained at 10 cm by the side of the plants out of the line in which the mineral fertilizer was applied. Samples were air dried and sieved (2 mm). Total contents of heavy metals were determined in the extracts obtained by digestion with HNO_3+H_2O_2+HCl (USEPA, 1986). Concentrations of heavy metals (Cu, Ni, Mn, Pb, Zn) were determined in the extracts by atomic absorption spectrometry.

Tukey's test, (α = 0.05), was used for comparison of means when the F test was significant. The correlation coefficients (r) between metals extracted from soil by Mehlich 1 and amounts uptaken by maize plants (grain and shoots) were calculated.

RESULTS AND DISCUSSION

Total heavy metals content and movement in soil

Total Ni, Pb, Zn and Cu (0-20 cm) and Ni, Pb, Cu (20-40 cm) concentrations increased with increasing rates of biosolids, while Mn concentration was not affected in the TH. Martins et al. (2003) and Oliveira & Mattiazzo (2001) also observed increasing Cu and Zn concentrations with increasing rates of biosolids in the 0-20 cm depth of soil.

Increasing concentrations of Zn were observed in the two depths, Mn at 20-40 cm and Ni at 0-20 cm in TE. None of the values found for the heavy metals exceeded the critical limits permitted for agricultural use of biosolids according to CETESB (1999) and USEPA (1995). Marchiori Jr. (2002) and Oliveira (2000) recorded similar results.

Cu, Zn and Ni added to soils with biosolids tended to remain in the 0-20 cm layer (Table 6). For Pb and Mn there were differences between the depths 0-20 and 20-40 cm, suggesting low mobility of these elements when added to the soil through biosolids. Sidle et al. (1976) found that more than 93% of all heavy metals applied over a 2-yr period were accumulated in the surface soil. Parker et al. (1978) reported that more than 95% of Zn and Cu remained in the 0-25 cm layer of soil. Anderson & Nilson (1972) showed that practically all the Mn, Zn, Cu, Ni, Co, Cr, Pb, Cd, Hg, As and Se remained in the upper 0-20 cm of the soil 12 years after adding 84 t ha^{-1} of sludge. Boswel (1975) found that very little Zn moved deeper than 15 cm in a clay loam soil. The accumulation of Zn, Cu, Ni and Pb in the top layer of the soil can be attributed to the high affinity of the metals to organic matter (McGrath & Lane, 1989). The highest concentrations of metals were observed for Cu, Mn and Zn in the TE soil. Oliveira & Mattiazzo (2001) also found Cu and Zn at the highest concentrations accumulated in soil among all the analysed elements.

TE had higher metal contents than TH. This soil has higher organic matter (Table 1) and clay amounts than the TH. Heavy metals may be strongly adsorbed to the soil organic and mineral colloids such as clay, iron hydroxides and manganese oxides and to soil OM (Chaney & Giordano, 1977).

Table 5 - Mineral fertilizations on Typic Eutrorthox soil during five years of experimentation.

Year	Treatment	N		P_2O_5		K_2O	
		Sowing	Dressed	Sowing	Dressed	Sowing	Dressed
		kg ha^{-1}					
1997/98	T	---	---	---	---	---	---
	D1	---	---	50	---	29	---
	D2	---	---	44	---	26	---
	D3	---	---	33	---	20	---
1998/99	T	15	61	30	---	30	---
	D1	---	---	---	---	25	---
	D2	---	---	---	---	20	---
	D3	---	---	---	---	10	---
1999/00	T	30	110	50	---	50	40
	D1	---	---	---	---	46	40
	D2	---	---	---	---	41	40
	D3	---	---	---	---	32	40
2000/01	T	30	120	50	---	50	40
	D1	---	---	---	---	5	40
	D2	---	---	16	---	39	40
	D3	---	---	---	---	28	40
2001/02	T	30	140	50	---	50	40
	D1	---	---	---	---	---	40
	D2	---	---	---	---	34	40
	D3	---	---	---	---	17	40

T-Control treatment; D1-treatment with 2.5 or 20 t ha^{-1} of biosolids; D2- treatment with 5.0 t ha^{-1} of biosolids; D3- treatment with 10.0 t ha^{-1} of biosolids.

Table 6 - Mean contents of total heavy metals in soils after five years of biosolids application.

Biosolids	TH		TE	
	0-20 cm	20-40 cm	0-20 cm	20-40 cm
t ha^{-1}				
Copper (mg kg^{-1})				
0.0	4.78 Ca	4.73 Ba	63.55 Aa	61.87 ABa
25.0	8.56 Ba	5.52 Bb	64.60 Aa	59.09 Ba
47.5	9.78 ABa	5.89 Ab	68.12 Aa	64.57 ABa
50.0	11.94 Aa	6.71 Ab	69.37 Aa	69.87 Aa
Manganese (mg kg^{-1})				
0.0	142.20 Aa	148.67 Aa	688.95 Aa	618.15 Ab
25.0	143.08 Aa	135.54 Aa	669.40 Aa	650.80 Aa
47.5	143.58 Aa	129.86 Aa	690.60 Aa	649.60 Ab
50.0	138.35 Aa	133.35 Aa	670.05 Aa	669.70 Aa
Zinc (mg kg^{-1})				
0.0	8.22 Ba	6.54 Ca	56.17 Ba	52.79 Ba
25.0	27.58 ABa	17.74 Ab	66.24 ABa	53.45 Bb
47.5	20.53 ABa	11.26 Bb	80.36 Aa	61.94 ABb
50.0	28.98 Aa	14.22 ABb	84.07 Aa	67.53 Ab
Lead (mg kg^{-1})				
0.0	8.54 Ca	9.11 Ba	16.96 ABa	15.80 Aa
25.0	9.81 ABa	9.42 ABa	17.68 ABa	15.43 Aa
47.5	9.50 Ba	9.82 ABa	16.44 Ba	15.06 Aa
50.0	10.45 Aa	10.20 Aa	18.20 Aa	15.75 Aa
Nickel (mg kg^{-1})				
0.0	4.23 Ca	4.51 Ba	13.34 Ba	12.44 Aa
25.0	6.41 Ba	5.07 ABb	15.83 Aa	14.02 Ab
47.5	5.74 Ba	5.03 ABa	14.29 ABa	12.37 Ab
50.0	7.12 Aa	5.59 Ab	16.03 Aa	13.88 Ab

Means followed by the same letters are not different by the Tukey's test ($P < 0.05$). Capital letters compare means in the same column and for the same element and small letters compare means in the same line and for the same soil.

Heavy metal accumulation in maize plants

Metal contents were higher in shoots than in grain (Table 7). Similar results were observed by Miller et al. (1995) in an experiment with barley where the contents of Cd, Zn, Cu and Ni were higher in straw that in grain. Maize shoots and grains cropped in TH contained lower Cu, Zn and Mn concentrations than those cropped in TE. Only for Pb and Ni higher concentrations were found in plants cultivated in the TH, a sandy soil that facilitates uptake of these elements by plants.

The concentration of Pb in grain from both soils and Ni from the TE was below detection limit of the method. The transfer of Pb from soils to roots, shoots, fruits and seeds is usually low but, sometimes, can be significant (Chaney, 1989). Lead concentrations are generally much less than 1 mg kg^{-1} in fruits and grains, and 1 to 3 mg kg^{-1} in leaves (Wallace & Wallace, 1994). In general, concentration of heavy metals in maize plants was not affected by increasing rates of biosolids. Oliveira et al. (2002) showed that Cd, Cr, Ni and Pb concentrations in sugarcane leaves, stalks and juice were also below the detection limit of the methodology used, and that Cu and Zn contents in plants were not affected by successive waste compost applications. Melo et al. (2002) and Anjos & Mattiazzo (2000) corroborate those findings. Values obtained in this experiment did not exceed limits considered toxic for maize plants: 6-20 mg kg^{-1} for Cu, 225-1200 mg kg^{-1} for Mn and 15-50 mg kg^{-1} for Zn (Malavolta, 1994; Raij et al., 1996).

Mehlich 1 extractant for evaluating heavy metal availability to maize

Concentrations of Cu, Ni, Pb and Zn in the Mehlich 1 extract (Table 8) increased with increasing rates of biosolids in the TH; regarding Mn, there was no relationship between extractability and the biosolids rate.

Baxter et al (1983) observed similar results for Cu, Cr and Zn extracted with DTPA and Mehlich 3. In the TE, the Mehlich 1 extract concentrations of Ni in both depths, and of Zn, Cu and Mn in the 0-20 cm depth, increased with the increasing rates of biosolids. However, the Pb-extract concentration was not affected.

Chang et al. (1984) found that biosolids application at the rate 90 t ha^{-1} $year^{-1}$ for six years increased the concentrations of Cd, Cr, Cu, Ni and Zn extracted by 4 mol L^{-1} HNO_3 solution. Martins et al. (2003) observed that increasing sewage sludge rates induced a linear increase in the Ni, Cu and Zn concentrations of soil extracts obtained with DTPA and Mehlich 3. Balkcom et al. (2001) found that extractable Cu and Zn increased with sludge application rate, while sludge had no effect on Mn. DTPA extractor is more efficient to estimate the availability of heavy metals to plants than the Mehlich 1 extractor, and only Mn availability is efficiently estimated by DTPA in both sandy and clayey soils (Mantovani et al., 2004)

In general, the Mehlich 1 extractant was ineffective to evaluate the availability of the studied heavy metals (Cu, Ni, Mn, Pb and Zn) to maize plant in both soils (Table 9). Values of the correlation coefficients were low and not significant for Mn, Ni (r = -0.36; r = -0.27; respectively).

Table 7 - Total contents of heavy metals in maize plant in the Typic Haplorthox (TH) and in the Typic Eutrorthox (TE) in the fifth year of experimentation.

Biosolids	TH		TE	
	Shoot	Grain	Shoot	Grain
t ha^{-1}				
Copper (mg kg^{-1})				
0.0	1.85 A	1.12 A	3.35 A	1.14 A
25.0	1.81 A	1.30 A	3.06 A	1.30 A
47.5	1.65 A	0.95 A	3.68 A	1.33 A
50.0	1.63 A	1.27 A	3.00 A	1.34 A
Zinc (mg kg^{-1})				
0.0	9.69 B	11.76 B	16.09 B	16.60 A
25.0	12.06 B	16.29 AB	15.18 B	14.60 A
47.5	19.79 A	15.25 A	34.25 A	21.65 A
50.0	12.43 B	17.19 A	18.16 B	16.33 A
Manganese (mg kg^{-1})				
0.0	22.70 A	4.14 A	22.12 B	3.57 A
25.0	13.91 B	4.27 A	19.39 B	3.24 A
47.5	14.44 B	3.27 A	29.28 A	4.20 A
50.0	9.67 C	3.87 A	19.61 B	3.55 A
Lead (mg kg^{-1})				
0.0	2.17 A	< DL	0.16 A	< DL
25.0	1.93 A	< DL	0.12 A	< DL
47.5	1.87 A	< DL	0.22 A	< DL
50.0	2.06 A	< DL	0.53 A	< DL
Nickel (mg kg^{-1})				
0.0	1.15 A	0.46 A	0.65 A	< DL
25.0	1.22 A	0.18 A	0.71 A	< DL
47.5	0.97 A	0.16 A	0.93 A	< DL
50.0	1.15 A	0.27 A	0.90 A	< DL

DL = detection limit. Means followed by the same letters in the same column and for the same element are not different by the Tukey's test (*P* < 0.05).

Table 8 - Contents of heavy metals extracted by Mehlich 1 in the two soils.

Biosolids	Cu	Mn	Ni	Pb	Zn
t ha^{-1}	----------	----------	mg kg^{-3}	----------	----------
Typic Haplorthox					
0-20 cm					
0.0	1.84 c	67.69 a	0.26 c	1.14 c	0.36 b
25.0	5.12 b	73.81 a	1.73 b	1.58 b	1.71 a
47.5	5.47 b	69.72 a	2.10 b	1.48 b	2.07 a
50.0	8.41 a	76.36 a	3.04 a	2.01 a	2.78 a
20-40 cm					
0.0	1.31 b	33.06 a	0.14 b	0.94 b	0.21 c
25.0	2.10 ab	34.98 a	0.48 ab	1.11 ab	0.80 bc
47.5	2.46 ab	33.09 a	0.50 ab	1.28 a	1.10 ab
50.0	3.25 a	35.79 a	0.92 a	1.25 ab	1.61 a
Typic Eutrorthox					
0-20 cm					
0.0	12.89 b	79.13 a	0.80 b	0.27 a	1.44 b
25.0	14.75 ab	99.80 a	1.64 b	0.28 a	3.84 ab
47.5	17.64 a	99.08 a	2.97 a	0.29 a	5.56 a
50.0	18.74 a	113.84 a	3.19 a	0.43 a	5.51 a
20-40 cm					
0.0	13.38 a	49.28 a	0.37 b	0.20 a	4.53 a
25.0	12.76 a	60.93 a	0.57 b	0.25 a	4.82 a
47.5	13.98 a	53.70 a	0.98 a	0.25 a	5.84 a
50.0	15.39 a	62.58 a	1.04 a	0.22 a	6.42 a

Means followed by the same letters in the same column and for the same depth are not different by the Tukey's test (*P* < 0.05).

Table 9 - Linear correlations between heavy metals content in maize parts plant and heavy metals extracted by Mehlich 1 extractant in soil samples obtained at 0-20 cm depth.

Part of plant	Cu	Mn	Ni	Pb	Zn
Typic Haplorthox					
Plant shoot	-0.48*	-0.23	-0.07	0.03	0.43
Grain	0.20	0.36	-0.25	nd	0.39
Typic Eutrorthox					
Plant shoot	0.02	-0.17	0.36	-0.16	0.48*
Grain	-0.12	0.11	nd	nd	0.37*

*Significant at (*P* < 0.05).
nd = not determined

Abreu et al. (1994) reported that correlations between soybean Mn and soil Mn were not significant for the Mehlich 1 extractor. Abreu et al. (1995) observed, in pot experiment, that Mehlich 1, Mehlich 3 and DTPA were ineffective for evaluating availability of Pb and Ni to wheat plants, and Pb to bean plants.

Significant correlations were found only for extractable soil Zn and its concentration in grain and shoot of maize plants cropped in the TE, and for Cu in the TH soil with plant shoots. Korcak & Fenning (1978) found that the concentrations of Cd and Zn in maize plant were correlated with that extracted by Mehlich 1 and DTPA extractants in soils, when there were excessive amounts of these metals. Haq et al. (1980) tested nine extractants (aqua regia, DTPA, NTDA, EDTA, acetic acid, ammonium acetate, H_2O, hydrochloric acid, aluminium chloride) and observed that only Ni had correlation with acetic acid. The efficiency of the Mehlich 1 extractant is quite variable, depending on the metal being evaluated and on the soil type and the plant tested (Pires & Mattiazzo, 2003).

CONCLUSIONS

The concentrations of Cu, Mn, Ni, Pb and Zn in the TH and in the TE were below critical limits permitted for agricultural use of biosolids established by USEPA and CETESB. The Mehlich 1 extractant was not efficient for evaluating phytoavailability of Cu, Zn, Mn, Ni and Pb to maize plants grown on TH and TE amended for five years with biosolids. There was no movement of Mn, Ni, Cu and Pb down the soil profile and little movement of Zn.

Concentrations of heavy metals were higher in plant shoot than in grains in maize plants.

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REFERENCES

ABREU, C.A.; NOVAIS, R.F.; RAIJ, B. van; RIBEIRO, A.C. Influência da reação do solo na extração de manganês por diferentes extratores químicos. **Revista Brasileira de Ciência do Solo**, v.18, p.91-99, 1994.

ABREU, C.A.; ABREU, M.F.; RAIJ, B. van; SANTOS, W.R. Comparação de métodos de análise para avaliar a disponibilidade de metais pesados em solos. **Revista Brasileira de Ciência do Solo**, v.19, p.463-468, 1995.

ANDERSON, A.; NILSON, K.O. Enrichment of trace elements from sewage sludge fertilizer in soils and plants. **Ambio**, v.1, p.176-179, 1972.

ANJOS, A.R.M.; MATTIAZZO, M.E. Metais pesados em plantas de milho cultivadas em Latossolos repetidamente tratados com biossólido. **Scientia Agricola**, v.57, p.769-776, 2000.

BALKCOM, K.S.; ADAMS, J.F.; HARTZOG, D.L.; WOOD, C.W. Mineralization of composed municipal sludge under field condition. **Communications in Soil Science and Plant Analysis**, v.32, p.1589-1605, 2001.

BATAGLIA, O.C.; FURLANI, A.M.C.; TEIXEIRA, J.P.F.; FURLANI, P.R.; GALLO. J.R. **Métodos de análises químicas de plantas**. Campinas: Instituto Agronômico, 1983. 48p.

BAXTER, J.C.; AGUILAR, M.; BROWN, K. Heavy metals and persistent organics at sewage sludge disposal site. **Journal of Environmental Quality**, v.12, p.311-316, 1983.

BOSWEL, F.C. Municipal sewage sludge and selected element application to soil: Effect on soil and fescue. **Journal of Environmental Quality**, v.4, p.267-272, 1975.

CHANEY, R.L. Scientific analysis of proposed sludge rule. **BioCycle**, v.30, p.80-85, 1989.

CHANEY, R.L; GIORDANO, P.M. Microelements as related to plant deficiencies and toxicities. In: ELLIOT, L.F.; STEVENSON, F.J. **Soils for management of organic wastes and wastewaters**. Madison: SSSA, 1977. p.234-279.

CHANG, A.C.; WARNEKE, J.E.; PAGE, A.L.; LUND, L.J. Accumulation of heavy metals in sewage sludge-treated soils. **Journal of Environmental Quality**, v.13, p.87-91, 1984.

CETESB. **Aplicação de lodos de sistema de tratamento biológico em áreas agrícolas para projeto e operação**: manual técnico. São Paulo: ABIA, 1999. 32p. (P.4230)

HAQ, A.U.; BATES, T.E.; SOON, Y.K. Comparison of extractors for plant-available zinc, cadmium and cooper in contaminated soils. **Soil Science Society of America Journal**, v.44, p.772-777, 1980.

HUE, N.V. Residual effects of sewage sludge application on plant and soil-profile chemical composition. **Communications in Soil Science and Plant Analysis**, v.19, p.1633-1643, 1988.

KORCAK, R.F.; FENNING, D.S. Extractability of cadmium, copper, nickel and zinc by double acid levels. **Journal of Environmental Quality**, v.7, p.506-512, 1978.

MALAVOLTA, E. **Fertilizantes e seu impacto ambiental**: micronutrientes e metais pesados, mitos, mistificação e fatos. São Paulo: Produquímica, 1994. 153p.

MANTOVANI, J.R.; CRUZ, M.C.P.; EVARISTO, M.F.; ALVES, W.L. Extratores para avaliação da disponibilidade de metais pesados em solos adubados com vermicomposto de lixo urbano. **Pesquisa agropecuária brasileira**, v.39, p.371-378, 2004.

MARCHIORI Jr., M. Impacto ambiental da citricultura nos teores de metais pesados em solos do Estado de São Paulo. Jaboticabal: UNESP/FCAV, 2002. (Tese - Doutorado).

MARTINS, A.L.C.; BATAGLIA, O.C.; CAMARGO, O.A. Copper, nickel and zinc phytoavailability in an oxisol amended with sewage sludge and liming. **Scientia Agricola**, v.60., p.747-754, 2003.

MATTIGOD, S.V.; PAGE, A.L. Assessment of metal pollution in soil. In: THORNTON, I. (Ed.) **Applied environmental geochemistry**. London: Academic Press, 1983. cap.12, p.355-394.

McBRIDE, M.B. Toxic metal accumulation from agricultural use of sludge: are USEPA regulations protective? **Journal of Environmental Quality**, v.24, p.5-18, 1995.

McGRATH, S.P.; LANE, P.W. An explanation for the apparent losses of metal in long-term field experiment with sewage sludge. **Environmental Pollution**, v.60, p.235-256, 1989.

MELO, V.P. Propriedades químicas e disponibilidade de metais pesados para a cultura do milho em dois latossolos que receberam a adição de biossólido. Jaboticabal: UNESP/FCAV, 2002. (Dissertação - Mestrado).

MELO, W.J.; MARQUES, M.O.; FERREIRA, M.E.; MELO, G.M.P.; MELO, V.P. Chemical properties and enzyme activity in a sewage sludge-treated soil. **Communications in Soil Science and Plant Analysis**, v.33, p.1643-1650, 2002.

MILLER, R.W; AZZARI, D.T; GARDINER, D.T. Heavy metals in crops as affected by soil types and sewage sludge rates. **Communications in Soil Science and Plant Analysis**, v.26, p.703-711,1995.

OLIVEIRA, F.C. Disposição de lodo de esgoto e composto de lixo urbano num Latossolo Vermelho Amarelo cultivado com cana-de-açúcar. Piracicaba: USP/ESALQ, 2000. 247p. (Tese - Doutorado).

OLIVEIRA, F.C.; MATTIAZZO, M.E. Metais pesados em Latossolo tratado com lodo de esgoto e em plantas de cana-de-açúcar. **Scientia Agricola**, v.58, p.581-593, 2001.

OLIVEIRA, F.C.; MATTIAZZO, M.E.; MARCIANO, C.R.; ABREU, J.C.H. Fitodisponibilidade e teores de metais pesados em um Latossolo amarelo distrófico e em plantas de cana-de-açúcar adubadas com composto de lixo urbano. **Revista Brasileira de Ciência do Solo**, v.26, p.737-746, 2002.

PARKER, G.R.; Mc FEE, W.W.; KELLY, J.M. Metal distribution in forested ecosystem in urban and rural northwester Indiana. **Journal of Environmental Quality**, v.7, p.337-342, 1978.
PIRES, A.M.M.; MATTIAZZO, M.E. Biosolid conditioning and the availability of Cu and Zn for rice. **Scientia Agricola**, v.60, p.161-166, 2003.
RAIJ, B. van; CANTARELLA, H.; QUAGGIO, J.A.; FURLANI, A.M.C. **Recomendações de adubação e calagem para o Estado de São Paulo**. Campinas, Instituto Agronômico, 1996. 285p. (Boletim Técnico, 100).
SIDLE, R.C.; HOOK, J.E.; KARDOS, L.T. Heavy metals application and plant uptake in a land disposal system for wastewater. **Journal of Environmental Quality**, v.5, p.97-102, 1976.
SILVEIRA, M.L.A.; ALLEONI, L.R.F.; GUILHERME, L.R.G. Biosolids and heavy metals in soils. **Scientia Agricola**, v.60, p.793-806, 2003.
UNITED STATES ENVIRONMENTAL PROTECTION AGENCY. **A guide to the biosolids risk assessment for the EPA. Part 503 rules**. Cincinnati: USEPA, 1995. (EPA/832-B-93-005).
UNITED STATES ENVIRONMENTAL PROTECTION AGENCY. **Standards for the use and disposal sewage sludge**. Washington: USEPA, 1986. (Code of Federal Regulations 40 CRF Part 503).
WALLACE, G.A.; WALLACE. A. Lead and other potentially toxic heavy metals in soil. **Communications in Soil Science and Plant Analysis**, v.25, p.137-141, 1994.

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