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Full Length Research Paper

Long-term behavior of Cu and Zn in soil and leachate of an intensive no-tillage system under swine wastewater and mineral fertilization

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The fertilization of crops with swine wastewater is a common practice and attractive for the reduction of natural resources and environmental pollution control. The feasibility of such use is due to the large volume of waste generated and the amount of nutrients that are easily mineralized when applied in soil. However, copper and zinc, added in high concentrations in swine rations, can accumulate on soil-water-plant system after successive applications. Thus, this study aimed at evaluating the effects of doses of swine wastewater associated with mineral fertilization in the levels of copper and zinc in an intensive no-tillage system (maize, black oats and soybeans) for four years. The experiments were carried out in area with twenty-four lysimeters of drainage, in typical oxisol. Swine wastewater treated in stabilization ponds and biodigester was applied in doses of 0, 100, 200 and 300 m^3 ha^{-1} associated with presence and absence of mineral fertilization, resulting in eight treatments with three repetitions each. Increases of 15.60% copper and 188% zinc in soil were found after four years of swine wastewater application. In the presence of mineral fertilization, zinc was 57% higher than in its absence. Copper and zinc levels detected were within the recommended range of mineral nutrition for maize, black oats and soybeans.

Key words: Fertilization, heavy metals, leaching, pig slurry, water reuse.

INTRODUCTION

Urban, agribusiness and animal wastewater have been used in several places in the world as a viable alternative to reduce the use of natural resources, to control the pollution of water bodies, provide water and fertilizers for crops, recycle nutrients and to increase agricultural production (Ceretta et al., 2005; Freitas et al., 2005; Hespanhol, 2003; Toze, 2006). Among these types of wastewater, swine wastewater stands out because of the significant economic and social importance of such activity, as well as because of its chemical composition, which offers a large input of nutrients that are easily mineralized when applied to soil, partly replacing the use of mineral fertilizers (Scherer et al., 2007). Many studies have been carried out to examine such properties in different crops, such as maize (Freitas et al., 2005; Prior et al., 2009; Sampaio et al., 2010; Scherer et al., 2010), beans (Doblinski et al., 2010), soybean (Dal Bosco et al., 2008; Caovilla et al., 2010; Smanhotto et al., 2010), black oats and ryegrass (Assmann et al., 2007), grassland (Queiroz et al., 2004). However, other authors have warned about the dangers of successive applications of swine wastewater, which may lead to the accumulation of heavy metals in soil and leaching to water bodies (Girotto et al., 2010). Copper and zinc stand out because pig feed have high concentrations of these elements to improve animal food converting rate (Berenguer et al., 2008; Girotto et al., 2010; Graber et al., 2005; Scherer et al.,

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Table 1. Soil chemical characterization of the experimental area before the performance of treatments.

pH	OM	CEC	Al + H	P	K	Ca	Mg	Cu	Fe	Mn	Zn
$CaCl_2$	g kg^{-1}	mmol$_c$ kg^{-1}					mg kg^{-1}				
5.47	14.00	95.70	38.80	3.00	1.50	34.10	21.40	8.62	69.20	39.26	0.82

Table 2. Description of treatments applied to the experimental area.

Treatment	SW doses (m^{3}ha^{-1})	Mineral fertilization
0 SW-A	0	Absent
0 SW-P	0	Present
100 SW-A	100	Absent
100 SW- P	100	Present
200 SW-A	200	Absent
200 SW- P	200	Present
300 SW-A	300	Absent
300 SW- P	300	Present

Table 3. History of crops managed under no-tillage in the experimental area from 2006 to 2009.

Accumulated days	Seeding	Crops
0	-	Natural soil
200	19/03/2006	Maize (*Zea mays*)
318	02/12/2006	Soybean (*Glycine max*)
418	19/07/2007	Black oats (*Avena strigosa*)
535	13/12/2007	Soybean (*Glycine max*)
594	05/07/2008	Black oats (*Avena strigosa*)
666	13/10/2008	Baby maize (*Zea mays*)
791	17/02/2009	Maize (*Zea mays*)
903	02/07/2009	Black oats (*Avena strigosa*)
1015	04/12/2009	Soybean (*Glycine max*)

2010). Therefore, high concentrations of copper and zinc in the soil are liable to be absorbed in large quantities by the crops and thus enter the food chain, or leach to underground water bodies (Berenguer et al., 2008; Queiroz et al., 2004).

The cumulative effect of heavy metals after long periods of application from domestic and industrial effluents has been studied (Dére et al., 2007; Katanda et al., 2007; Nyamangara and Mzezewa, 1999; Mapanda et al., 2005; Rattan et al., 2005; Rusan et al., 2007; Xu et al., 2010). However, research on long-term swine wastewater is still poor in the literature, mainly, associated with mineral fertilizers application.

In this context, this study aims to assess the effects of doses of swine wastewater associated with mineral fertilization on the concentrations of copper and zinc in intensive no-tillage system (maize, black oats, and soybeans) for over four years.

MATERIALS AND METHODS

The experiments were carried out in the Agricultural Engineering Experimental Center of the Western Paraná State University - Cascavel, Paraná, Brazil. The geographical coordinates 24º 54' south latitude and 53° 32' west longitude, at an altitude of 760 m. The climate, according to the classification of Köeppen, is super humid mesothermal subtropical, with average annual rainfall of 1800 mm, hot summers, infrequent frosts, and a trend of rainfall occurrence during the summer. However, there is no definite dry season. The mean temperature is 20ºC and relative humidity is 75% (Iapar, 1998).

The experimental area is composed of twenty-four drainage lysimeters, which represent experimental plots, with a volume of 1 m^3 and area of 1.60 m^2. The soil is classified as typical oxisol. Soil chemical characterization of the experimental area before treatment application was performed to determine pH, OM, CEC, Al+H, P, K, Ca, Mg, Cu, Fe, Mg and Zn by methods potentiometric, Walkley Black, extraction with Ca ethyl, ascorbic acid and espectometria (Mehlich), respectively, according to the protocols of Embrapa (1997) (Table 1).

Over four years, nine consecutive experiments were conducted with the same application doses of swine wastewater - SW (0, 100, 200 and 300 m^3 ha^{-1}) during crop cycles. In addition to the doses of application, the effects of mineral fertilization (MF) were assessed, having its presence and absence as factors. Thus, treatments applied to the experimental plots are presented in Table 2.

The succession of crops intensively managed under no-till is shown in Table 3. In all cultures, where necessary, cultivation was carried out using the recommended dosages and products. It is noteworthy that the initial characterization of the area in 2006, was identified as 0 (zero) days.

During the first three years, the collection of SW was made in the outlet of the first facultative pond; these values are presented in (Table 4). In the fourth year, in order to assess higher concentrations of elements present in the SW, collection was then made at the outlet of the biodigester (Table 5). Applications of SW were performed only once, usually seven days before the sowing of each crop.

Soil samples were collected before the seeding and after crop management, in a layer from 0 to 0.60 m depth to determine pH, OM, CEC and Cu and Zn content, according to the methods of Embrapa (1997). The collections of the leachate occurred on two occasions, after the first and last precipitation of crop cycle. For each sample, Cu and Zn were determined by methods 3111 in accordance with Apha (2005). The analyses of Cu and Zn content in plant tissue were determined according to Malavolta et al. (1997).

The experimental design was randomized blocks in factorial threefold with four doses of SW (0, 100, 200 and 300 m^3 ha^{-1}), two levels of mineral fertilization (absence and presence), and six time periods (200, 318, 418, 791, 903 and 1015 days), with three replications. The transformations of the data were carried out in order to meet the longitudinal analysis assumptions (Gomes, 2000). The effects of the treatments over time were assessed using longitudinal study (Singer et al., 2010). Once significance was proven in the longitudinal study, tests were performed to compare the means using Tukey test at 5% probability. The Pearson linear correlation and linear regression were used to assess the effects of

Table 4. Total rates of nutrient application, via MF and SW, from 2006 to 2008.

Time (days)	Treatments	MF (kg ha^{-1})			Application of SW for each element (Kg ha^{-1})							
		N	P	K	N	P	K	pH	EC	COD	Cu	Zn
200	0 SW-A	15	60	30	0	0	0	0	0	0	0	0
200	0 SW-P	22.50	90	45	0	0	0	0	0	0	0	0
200	100 SW-A	15	60	30	85	19.23	16.87	7.70	6.77	304.80	0.01	0.04
200	100 SW-P	22.50	90	45	77.50	19.23	16.87	7.70	6.77	304.80	0.01	0.04
200	200 SW-A	15	60	30	185	38.47	33.75	7.70	6.77	609.60	0.01	0.09
200	200 SW-P	22.50	90	45	177.50	38.47	33.75	7.70	6.77	609.60	0.01	0.09
200	300 SW-A	15	60	30	285	57.71	50.62	7.70	6.77	914.40	0.02	0.13
200	300 SW-P	22.50	90	45	277.50	57.17	50.62	7.70	6.77	914.40	0.02	0.13
318	0 SW-A	0	0	0	0	0	0	0	0	0	0	0
318	0 SW-P	0	50	50	0	0	0	0	0	0	0	0
318	100 SW-A	0	0	0	81.17	9.33	55.01	7.73	4.89	144.41	0.02	0.12
318	100 SW-P	0	50	50	81.17	9.33	55.01	7.73	4.89	144.41	0.02	0.12
318	200 SW-A	0	0	0	159.33	18.32	107.99	7.73	4.89	288.81	0.04	0.23
318	200 SW-P	0	50	50	159.33	18.32	107.99	7.73	4.89	288.81	0.04	0.23
318	300 SW-A	0	0	0	240.50	27.66	163	7.73	4.89	433.22	0.06	0.35
318	300 SW-P	0	50	50	240.50	27.66	163	7.73	4.89	433.22	0.06	0.35
418	0 SW-A	0	0	0	0	0	0	0	0	0	0	0
418	0 SW-P	0	0	0	0	0	0	0	0	0	0	0
418	100 SW-A	0	0	0	80.17	9.22	54.33	7.69	4.64	132	0.02	0.12
418	100 SW-P	0	0	0	80.17	9.22	54.33	7.69	4.64	132	0.02	0.12
418	200 SW-A	0	0	0	160.33	18.44	108.67	7.69	4.64	264	0.04	0.24
418	200 SW-P	0	0	0	160.33	18.44	108.67	7.69	4.64	264	0.04	0.24
418	300 SW-A	0	0	0	240.50	27.66	163	7.69	4.64	396	0.06	0.35
418	300 SW-P	0	0	0	240.50	27.66	163	7.69	4.64	396	0.06	0.35
535	0 SW-A	0	0	0	0	0	0	0	0	0	0	0
535	0 SW-P	0	80	40	0	0	0	0	0	0	0	0
535	100 SW-A	0	0	0	88.70	10.86	46.21	7.70	5.43	132.21	0.03	0.02
535	100 SW-P	0	80	40	88.70	10.86	46.21	7.70	5.43	132.21	0.03	0.02
535	200 SW-A	0	0	0	177.40	21.72	92.42	7.70	5.43	264.40	0.05	0.04
535	200 SW-P	0	80	40	177.40	21.72	92.42	7.70	5.43	264.40	0.05	0.04
535	300 SW-A	0	0	0	266.10	32.59	138.63	7.70	5.43	396.60	0.08	0.06
535	300 SW-P	0	80	40	266.10	32.59	138.63	7.70	5.43	396.60	0.08	0.06
594	0 SW-A	0	0	0	0	0	0	0	0	0	0	0
594	0 SW-P	0	0	0	0	0	0	0	0	0	0	0
594	100 SW-A	0	0	0	33.88	21.19	44	7.90	2.10	145	1.25	7.65
594	100 SW-P	0	0	0	33.88	21.19	44	7.90	2.10	145	1.25	7.65
594	200 SW-A	0	0	0	67.76	42.38	88	7.90	2.10	290	2.50	15.30
594	200 SW-P	0	0	0	67.76	42.38	88	7.90	2.10	290	2.50	15.30
594	300 SW-A	0	0	0	101.64	63.57	132	7.90	2.10	435	3.75	22.95
594	300 SW-P	0	0	0	101.64	63.57	132	7.90	2.10	435	3.75	22.95
666	0 SW-A	0	0	0	0	0	0	0	0	0	0	0
666	0 SW-P	45	0	0	0	0	0	0	0	0	0	0
666	100 SW-A	0	0	0	33.88	21.19	44	7.90	2.10	145	1.25	7.65
666	100 SW-P	45	0	0	33.88	21.19	44	7.90	2.10	145	1.25	7.65
666	200 SW-A	0	0	0	67.76	42.38	88	7.90	2.10	290	2.50	15.30
666	200 SW-P	45	0	0	67.76	42.38	88	7.90	2.10	290,00	2.50	15.30
666	300 SW-A	0	0	0	101.64	63.57	132	7.90	2.10	435	3.75	22.95
666	300 SW-P	45	0	0	101.64	63.57	132	7.90	2.10	435	3.75	22.95

Table 5. Total rates of nutrient application, via MF and SW, from 2009.

Time (days)	Treatments	MF (kg ha^{-1})			Application of SW for each element (Kg ha^{-1})							
		N	P	K	N	P	K	pH	EC	COD	Cu	Zn
791	0 SW-A	0	0	0	0	0	0	0	0	0	0	0
791	0 SW-P	120	80	90	0	0	0	0	0	0	0	0
791	100 SW-A	0	0	0	26.51	6.94	8.55	7.57	1.29	137.80	0.07	0.65
791	100 SW-P	120	80	90	26.51	6.94	8.55	7.57	1.29	137.80	0.07	0.65
791	200 SW-A	0	0	0	53.02	13.88	17.10	7.57	1.29	275.60	0.14	1.30
791	200 SW-P	120	80	90	53.02	13.88	17.10	7.57	1.29	275.60	0.14	1.30
791	300 SW-A	0	0	0	79.53	20.83	25.65	7.57	1.29	413.40	0.22	1.95
791	300 SW-P	120	80	90	79.53	20.83	25.65	7.57	1.29	413.40	0.22	1.95
903	0 SW-A	0	0	0	0	0	0	0	0	0	0	0
903	0 SW-P	0	0	0	0	0	0	0	0	0	0	0
903	100 SW-A	0	0	0	127.87	14.51	44.55	7.08	6.62	574	0.51	3.50
903	100 SW-P	0	0	0	127.87	14.51	44.55	7.08	6.62	574	0.51	3.50
903	200 SW-A	0	0	0	255.74	29.02	89.10	7.08	6.62	1148	1.01	7
903	200 SW-P	0	0	0	255.74	29.02	89.10	7.08	6.62	1148	1.01	7
903	300 SW-A	0	0	0	383.61	43.53	133.65	7.08	6.62	1722	1.52	10.50
903	300 SW-P	0	0	0	383.61	43.53	133.65	7.08	6.62	1722	1.52	10.50
1015	0 SW-A	0	0	0	0	0	0	0	0	0	0	0
1015	0 SW-P	0	50	50	0	0	0	0	0	0	0	0
1015	100 SW-A	0	0	0	60.48	10.74	22.45	7.09	3.95	576.70	0.20	1.45
1015	100 SW-P	0	50	50	60.48	10.74	22.45	7.09	3.95	576.70	0.20	1.45
1015	200 SW-A	0	0	0	120.96	21.48	44.90	7.09	3.95	1153.40	0.39	2.90
1015	200 SW-P	0	50	50	120.96	21.48	44.90	7.09	3.95	1153.40	0.39	2.90
1015	300 SW-A	0	0	0	181.44	32.22	67.35	7.09	3.95	1730.10	0.59	4.35
1015	300 SW-P	0	50	50	181.44	32.22	67.35	7.09	3.95	1730.10	0.59	4.35

SW, MF, and soil chemical properties (pH, OM, CEC) on Cu and Zn in the soil.

RESULTS AND DISCUSSION

Soil parameters

The simultaneous longitudinal study of the factors SW, MF and time of application (T) indicated that only the isolated T provided significant differences in pH, OM, CEC, Cu and Zn.

The pH increased from 5.47 to 6.77 in the soil (0 to 0.60 m) at 1015 days of SW application (Table 1 and 6). Increased pH values of soil were consistent with the high pH values of SW used, ranging from 7.08 to 7.70 (Table 4 and 5), which according to Ayers and Westcot (1991) conforms to the interval from 6.50 to 8.40 recommended for irrigation. Such increased pH in the soil is due to the alkaline characteristics of SW (Chantigny et al., 2004), and the extracts of cultures kept in the soil surface (Diehl et al., 2008). The organic matter generated by the decomposition of this material adsorbs H and Al increasing soil pH (Amaral et al., 2000; Anami et al., 2008; Miyazawa et al., 1993). The major means found for OM refer to the 318 and 1015 days after the application of SW (Table 6), and that is associated with the concentrations of biodegradable organic matter and inert something is missing here present in the wastewater of anaerobic pond and biodigester (Table 4 and 5). Increased soil OM found at 903 days can be due to a change in the collection point of SW, as well as due to the migration of organic compounds of low molecular weight over the soil profile (Novais et al., 2007). Furthermore, increases in OM with corresponding increase in depth of soil observed could be due to the presence of roots at deeper layers. Xu et al. (2010) found increases in OM in soil layer 0.10 m, at 53, 89 and 185%, in areas with applications of household sewage in periods of 3, 8 and 20 years, respectively.

The highest CEC was found at 200 days, differing from the other periods. The applications of SW increased the initial values of CEC at 200 and 318 days (Table 6) as a function of K, Ca and Mg (Smanhotto et al., 2010; Queiroz et al., 2004). After a period of 418 days, CEC showed some stabilization, with a mean value of 120 $mmol_c\ dm^{-3}$. This conforms with the findings of Katanda et al. (2007) which reported that high CEC in soils irrigated with sewage water can be attributed to the OM presence in these waters.

Table 6. Means for the parameters of the soil in the layer from 0 to 0.60 m.

Time (days)	pH ($CaCl_2$)	OM (g kg^{-1})	CEC($mmol_c$ kg^{-1})	Cu (mg kg^{-1})	Zn (mg kg^{-1})
200	6.40^{b}	23.69^{b}	165.32^{a}	5.39^{d}	0.68^{d}
318	6.46^{b}	28.17^{a}	144.25^{b}	3.98^{e}	1.29^{bc}
418	6.66^{ab}	20.28^{c}	128.15^{b}	7.95^{ab}	1.43^{bc}
791	6.68^{ab}	20.08^{c}	109.90^{c}	8.47^{a}	1.59^{bc}
903	6.89^{a}	23.99^{b}	128.16^{b}	7.02^{bc}	2.06^{b}
1015	6.77^{ab}	25.77^{ab}	116.39^{bc}	6.44^{cd}	3.29^{a}

Transformation of Johnson for CEC and Cu; Box and Cox for Zn; same letters in column indicate means equal to the 5% level of significance by Tukey test.

Cu increased from 418 to 1015 days compared to 200 and 318 days (Table 6), indicating that Cu may accumulate with successive applications of SW. At 791 days, Cu approached the initial characterization of 8.62 mg kg^{-1} (Table 1). Cu concentrations were high in the initial characterization of soil, and they significantly reduced after the first cultivation.This indicates that this micronutrient, the part extracted from the culture, becomes less available. This fact could be due to the formation of stable organo-metallic complexes of low solubility, which, in addition to complexing with organic substances, they bind to non-exchangeable fractions of the soil, such as iron and manganese oxides (Oliveira and Mattiazzo, 2001; Queiroz et al., 2004). Cu decreased significantly in periods of soybean cultivation, confirming that soybean crop is more sensitive to this micro-nutrient than maize and wheat (Lavado et al., 2001).

The highest content of Zn was found at 1015 days, statistically differing from the other periods. Increased Zn (Table 6) indicates the existence of a positive linear relationship with successive applications of SW over time, also shown in the longitudinal study. Smanhotto et al. (2010) found an increase in Zn at rates of 200 and 300 m^3 ha^{-1} in soybean and Freitas et al. (2005) also found increase in Zn in the soil with the application of raw drained SW and found concentrations ranging from 13.10 to 16.30 mg kg^{-1}. Works of Queiroz et al. (2004) and Dal Bosco et al. (2008) also reported an increase in Zn in the surface layers (0 to 0.20 m) of soil with the application of SW.

Accumulation of copper and zinc for each treatment compared to controls (0 SW-A, 0 SW-P) at 1015 days and the initial values of these metals prior to application of the treatments are shown in Table 7.

The accumulation of Cu and Zn were more significant for the treatments of 300 SW-A and 300 SW-P compared to controls (0 SW-A and 0 SW-P). The same occurred to the 100 SW-P treatments for Cu. Increases of 15.60% for Cu in the 300 SW-A treatment and 188% for Zn in the 300 SW-P treatments were found in relation to respective controls at 1015 days. Cavanagh et al. (2011) found increases of 31% for Cu and 64% for Zn in the application of sewage in relation to controls.

The national standard determined that good quality soils must have concentrations below the limits of 200 and 450 mg kg^{-1} of soil, for Cu and Zn respectively (CONAMA, 2009). Guidelines values for agricultural soils are 140 mg kg^{-1} for Cu and 300 mg kg^{-1} for Zn, according to the international standard (CEC, 1986). Although Cu and Zn (Table 7) are below the national and international recommended limits, the results may indicate possible contamination of surface and groundwater.

Berenguer et al. (2008) have assessed for over six years the effect of SW in rates of 29 and 51 m^3 ha^{-1} per year in sandy soil under maize cultivation and found increases of 32% for Cu and 11% for Zn. Girotto et al. (2010) have found concentrations of Cu and Zn, of 85.70 and 70 mg kg^{-1} respectively in the upper soil layer (0 to 0.02 m) under no-tillage when dosing maximum swine manure (80 kg ha^{-1}) for 78 months.

Mapanda et al. (2005) found much higher values of Cu in soils irrigated for more than two decades with household sewage (from 21 to 145 mg kg^{-1}) in relation to irrigated areas for a period of 5 to 15 years using household sewage and industrial wastewater (7 to 44 mg kg^{-1}). Similar results were found in the works of Nyamangara and Mzezewa (1999), Rattan et al. (2005) and Khan et al. (2008).

According to Graber et al. (2005), Cu and Zn can form complexes with humic substances that influence respective mobility in the soil. They also form complexes with phosphates, and may increase the solubility of these elements in the soil solution. Scherer et al. (2007) and Girotto et al. (2010) have reported that Cu and Zn are accumulated in the soil, especially in bioavailable forms, and the highest Cu is found in the organic and mineral soil and Zn in mineral form.

According to Novais et al. (2007), in acidic environments, Cu has great mobility, which is inversely proportional to the uptake of the element to the solid fraction. In this sense, it can be inferred, considering the increase in values of pH in this study compared with initial soil (Table 6), associated with clay soil and high concentrations of OM, that Cu has low mobility in the soil, which favors its retention in it, for a long period of time. To assess which parameters most affect the accumulation of Cu and Zn, a Pearson linear correlation was carried out (Table 8).

Strong and positive correlations were found for pH and

Table 7. Accumulation of Cu and Zn (mg kg^{-1}) in each treatment compared to controls, at 1015 days of application of SW.

Treatments	Cu	Accumulation of Cu	Zn	Accumulation of Zn
Natural soil	8.62		0.82	
0 SW-A	5.96		2	
0 SW-P	6.03		1.92	
100 SW-A	6.07	0.11	2.54	0.54
100 SW-P	6.80	0.77	3.01	1.09
200 SW-A	6.44	0.48	3.07	1.07
200 SW-P	6.56	0.53	3.91	1.99
300 SW-A	6.89	0.93	4.40	2.40
300 SW-P	6.80	0.84	5.53	3.61

Table 8. Pearson's linear correlation of soil parameters assessed for each treatment.

	Cu	Zn	pH	OM	Cu	Zn	pH	OM
	0 SW-A				**0 SW-P**			
Zn	0.15				-0.24			
pH	0.03	0.75*			-0.25	0.74**		
OM	-0.74*	0.12	0.49		-0.69**	0.46	0.67**	
CEC	-0.23	-0.14	0.07	0.56	-0.74**	-0.15	0.16	0.72**
	100 SW-A				**100 SW-P**			
Zn	0.13				0.11			
pH	-0.34	0.73*			-0.14	0.34		
OM	-0.69**	0.47	0.89*		-0.60	0.40	0.63	
CEC	-0.85*	-0.11	0.27	0.66	-0.38	-0.10	0.73**	0.28
	200 SW-A				**200 SW-P**			
Zn	0.05				0			
pH	-0.32	0.64			-0.23	0.34		
OM	-0.69**	0.34	0.87*		-0.49	0.61	0.81*	
CEC	-0.76*	-0.43	0.18	0.60	-0.52	0.03	0.64	0.65
	300 SW-A				**300 SW-P**			
Zn	-0.51				0.01			
pH	-0.30	0.44			-0.33	0.43		
OM	-0.63	0.63	0.91*		-0.58	0.43	0.94*	
CEC	-0.70**	-0.09	0.38	0.48	-0.76	-0.27	0.43	0.62

*p<0.05;**p<0.01

Zn in the 0 SW-A, 0 SW-P, and 100 SW-A treatments. Thus, Zn is more closely related to soil pH. Positive correlations were found for OM, pH and CEC, indicating that higher levels of OM improve soil buffer capacity. According to Novais et al. (2007), OM increases from 20 to 90% of CEC of the upper layers of soil minerals and virtually the entire CEC of organic soils.

Cu negatively correlated with the other soil parameters. In treatments 0 SW-A, 0 SW-P, 100 SW-A and 200 SW-A strong correlations was found for Cu and OM, and in treatments 0 SW-P, 100 SW-A, 200 SW-A and 300 SW-A also strong correlations existed for Cu and CEC. These results indicate that Cu content is inversely related to OM and CEC; higher OM and CEC, the higher the complexation and adsorption of such element in the organic and mineral fractions were obtained, and thus less available in the soil (Scherer et al., 2010).

Changes in pH and Zn over four years of study were

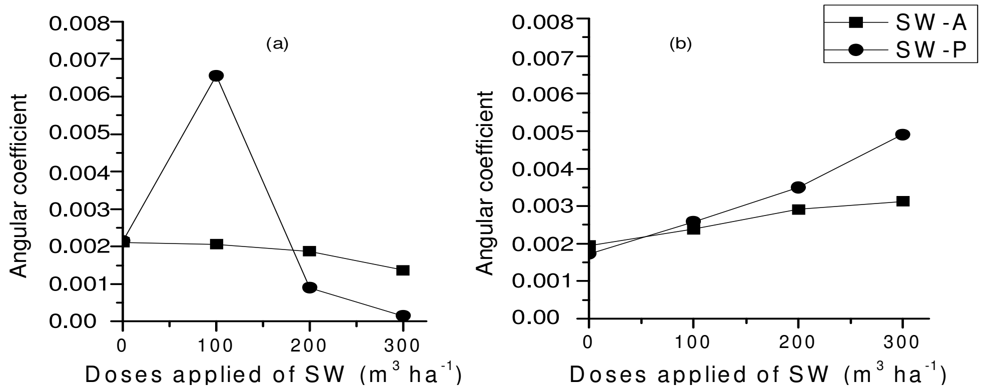

Figure 1. Angular coefficient of the linear model of pH (a) and Zn (b) as a function of the application doses of SW.

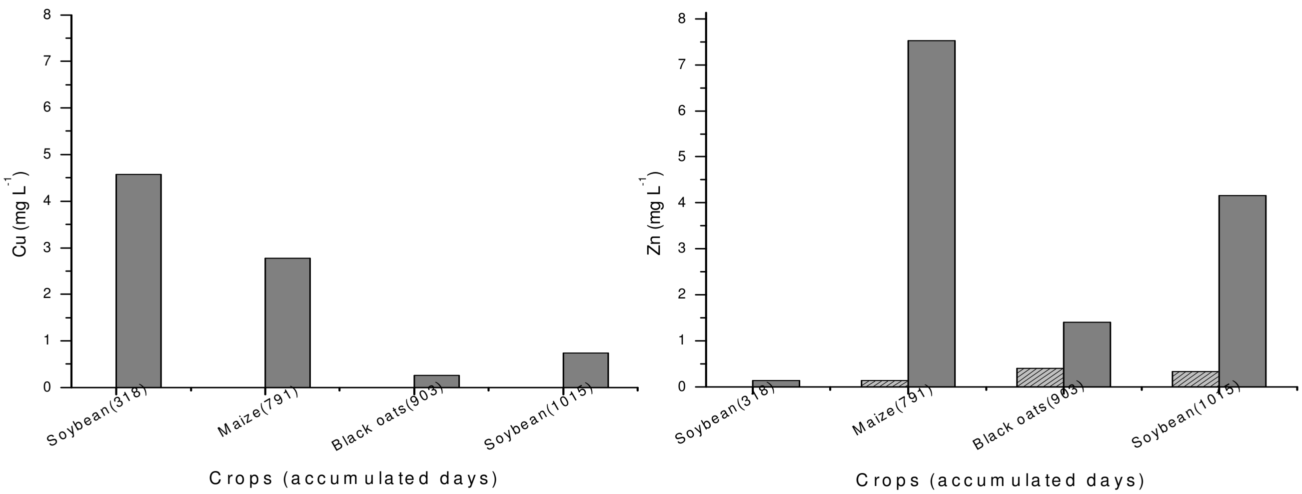

Figure 2. Minimum and maximum concentrations of Cu and Zn in leachate.

explained by simple linear models (Figure 1). For pH, an almost constant behavior is noted when MF is not used. Increased Zn trend over time is mainly influenced by application rate, and different behaviors are noted in the presence and absence of MF; in the presence of MF the slope coefficient increases significantly, that is, the daily rate of Zn accumulation in the soil. According Girotto et al. (2010) the Zn is strongly adsorbed to the functional groups, especially the mineral fraction of the soil, which explains the Zn increase with mineral fertilizer addition in our study.

Leachate parameters

Cu at 318 and 791 days is over the maximum limit of 2 mg L^{-1} for groundwater determined by Conama (2008) (Figure 2). The high value of Cu at 318 days is consistent with the lowest value found in the soil (Table 6), showing loss of the element by leaching. Zn to 791 days is also above the recommended maximum limit of 5 mg L^{-1} (Conama, 2008). Similarly to the soil, Zn indicates tendency to increase the leached over time. The amount of SW associated with mineral fertilization highlights the leaching risk of Cu and Zn in groundwater.

Agronomic parameters

Maize, black oats and soybeans crops have Cu and Zn values within the range recommended by Malavolta et al. (1997). This range recommended to maize and black oats is 6 at 20 mg Cu kg^{-1} and 10 at 30 mg Zn kg^{-1}, while, to the soybean crop is 15 at 50 mg Cu kg^{-1} and 21 to 50 mg Zn kg^{-1} (Figure 3). At 903 days, black oats culture absorbed Cu near to the maximum limit of good plant nutrition, providing low concentrations in the leachate Figure 2). In general, soybean accumulated more Cu than maize and oats, thereby reducing Cu in the soil (Table 6) and in leachate (Figure 2). Zn increasing trend

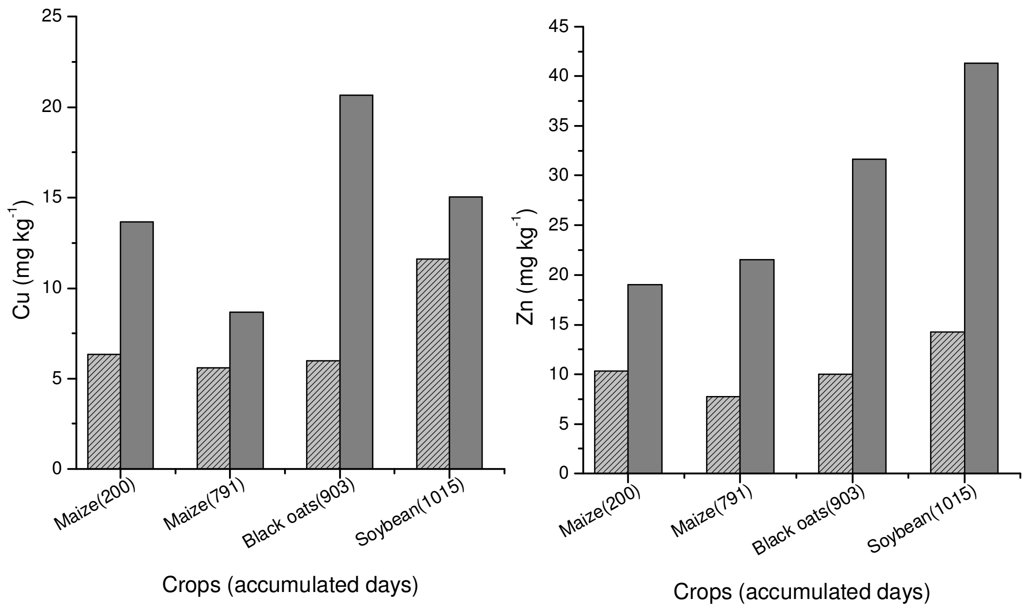

Figure 3. Minimum and maximum concentrations Cu and Zn in the plant tissue over the time of SW and MF application.

similar to that found in the soil (Table 6) was also detected in the plant tissue of cultures (Figure 3). The accumulation of Zn in soil-plant system favors higher losses of this micro-nutrient in leachate (Figure 2). Berenguer et al. (2008) have assessed Cu and Zn in maize for after six and seven years of SW application in rates of 29 and 51 m^3 ha^{-1} per year, and have found that the amounts absorbed by cultures were in accordance with the limits of phytotoxicity. The authors found at the end of the seventh year of experiment the values 2.11 and 17.5 mg kg^{-1} for Cu and Zn, respectively.

Conclusions

Finally, the applications of swine wastewater, for maize, black oats and soybeans treated with biodigester and stabilization pond, in the long term (four years), favored the accumulation of copper (15%) and zinc (188%) in the soil and therefore provides higher concentrations that standard limits determined for leachate. Considering controls as reference, zinc in the presence of mineral fertilization has shown soil accumulation potential 57% higher than in the absence of MF. In maize, black oats and soybeans, Cu and Zn are in the recommended range of good nutrition.

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ABBREVIATIONS

SW, Swine wastewater; **T,** time of application; **pH,** hydrogen potential; **OM,** organic matter; **CEC,** cation exchange capacity; **P,** phosphorus, **Al+H,** acidity; **K,** potassium, **Ca,** calcium, **Mg,** magnesium; **Cu,** copper; **Fe,** iron; **Mn,** manganese; **Zn,** zinc; **EC,** electric conductivity; **N,** nitrogen; **COD,** chemical oxygen demand; **MF,** mineral fertilization.

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