Effect of Swine Manure Amendment on Pb^{2+}, Cu^{2+}, Zn^{2+}, and Ni^{2+} Competitive Sorption onto Agricultural Soil

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Authors' contributions

This work was carried out in collaboration among all authors. Author DBR made substantial contributions to the conception and design of the study, data acquisition, analysis and interpretation of data, wrote the first draft of the manuscript and revised it critically. Authors LVC and GMCB made contributions in the experimental design, managed the analyses, and approved the submitted version. Author MJS made substantial contributions to the conception and design of the study, statistical analysis and interpretation of data, creation of new mathematical modeling, drafted the work and revised it critically for relevant intellectual content. All authors read and approved the final manuscript.

Original Research Article

ABSTRACT

Aims/Objectives: An agricultural tropical soil treated and untreated with swine manure was evaluated to Pb^{2+}, Cu^{2+}, Zn^{2+}, and Ni^{2+} competitive sorption dynamics.
Study Design: Metal ion mobility patterns were evaluated by sorption-desorption reactions with the mineral and organic matter soil phases.

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Place and Duration of Study: Agronomic Institute of Parana (IAPAR) at Londrina city, Parana State, Southern Brazil, in an experiment conducted since June 2008.

Methodology: Soybean and corn were growing up in the experimental area in summer and winter, respectively. Swine manure (SM) was applied twice a year, and the amount was calculated according each crop necessity. Experiments were in batch, varying the metal ion concentration from 1.0 to 10 meq L^{-1}. After equilibrium, the solid phase was analyzed by EDXRF and liquid phase by ICP-OES. Metal ion mobility was evaluated by applying the dual-mode Langmuir-Freundlich mathematical model, in addition to rate removal and Gibb's free energy determination.

Results: Sorption capacity increased after the SM amendment, and the retention sequence $Pb^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+}$ was observed. The sorption capacity increased in 30%, 45%, 176%, and 231% for Pb^{2+}, Cu^{2+}, Zn^{2+}, and Ni^{2+}, respectively. The relative intensity of the fluorescence emission lines showed metal ion sorption increased after the amendment, keeping the same sequence observed for the adjustable parameters from the fitting by dual-mode Langmuir-Freundlich model.

Conclusion: The possibility of a controlled release of micronutrients, considering low-affinity sorption sites, brings an excellent look to the swine manure amendment.

1 INTRODUCTION

Agricultural activities as soil tillage and fertilization may have a broad impact on the environment, modifying the availability of nutrients as well as of potentially toxic elements to the plants. Some studies have reported the effect of organic waste as manure and biosolids on agricultural soils, which may increase the concentration of some metals and cause environmental contamination [1, 2]. Since metals can accumulate in the upper layers of the soil, toxic levels to plants and animals can be reached and also impair water quality [3, 4, 5, 6].

The ample application of swine manure on Brazilian agricultural soils is due to the high organic matter content as well as nitrogen, phosphorus, zinc, and copper nutrients decreasing crop production cost and increasing profits for pig farming [7, 8, 9, 10, 11]. Although swine manure may contribute to increasing organic matter (OM) and pH changes, the increase of zinc and copper concentration may affect the availability of other nutrients for plants such as iron and manganese [12, 13, 14, 15, 16]. Additionally, lead and nickel also can be found in swine manure as contaminants from swine feed mineral supplements [17], causing environmental damage.

Metal ions find specific sorption sites on soil, binding strongly to the inorganic or organic colloids, affecting the environmental metal mobility, which depends on the interaction pattern with soil components [18, 19]. Thereby, sorption and desorption mechanisms are responsible for soil metal mobilization and are important to adequately describe their behavior and determine the environmental risk [20, 21, 22]. Among the most crucial soil ligands, clay minerals, quartz, iron oxyhydroxides as well as organic matter can form metal surface complexes and promote ion exchange [23, 24, 25, 26]. Metals can form inner-sphere complexes with layered silicates and metal oxides and outer-sphere complexes with iron and manganese oxyhydroxides, silanol, and aluminol [23, 27, 21].

Increasing productivity while preserving environmental quality is a desirable feature and can be achieved with good agricultural practices such as the organic matter amendment. Considering the environmental pressure of metal contamination from swine manure, mathematical modeling of sorption can help to describe the metal transport in soil. However, there is the hypothesis that potentially toxic ions can be retained in the soil due to the increase of specific sorption sites from the incorporated organic matter. So what will be the risk imposed

by the swine manure amendment? Hence, this study aimed to evaluate the competitive sorption dynamics of Pb^{2+}, Cu^{2+}, Zn^{2+} and Ni^{2+} onto an agricultural Oxisol (Red Latosol) in Southern Brazil amended with liquid swine manure. Mathematical modeling and X-ray fluorescence analysis were applied to verify metal ion mobilization in agricultural soil.

2 MATERIALS AND METHODS

2.1 Soil Sampling

The study was conducted for eight years in the Agronomic Institute of Parana (IAPAR), Londrina city - Parana State, Brazil (Fig. 1). The region has an average altitude of 610 m and subtropical climate (Cfa) according to Köppen classification [28]. Soybean and corn were grown in the experimental area in summer and winter, respectively. Swine manure (SM) was applied twice a year, and the amount was calculated from the needs of each crop: 150 kg ha^{-1} nitrogen (N) to corn and 300 kg ha^{-1} P_2O_5 to soybean. Soil Oxisol (Dystrophic Red Latosol

in Brazilian soil classification [29]) samples were collected at 0–10 cm layer, in plots of 50 m^2 (10 m×5 m) of SM-treated and SM-untreated areas ($23°21'58.5"S$ and $51°09'45.1"W$), using an experimental design in randomized blocks with four repetitions. The chosen region is highly productive.

2.2 Soil Characterization

Physical and chemical analyses of granulometry, phosphorus and carbon contents, pH, and cation-exchange capacity (CEC) were carried out for untreated (SN) and treated (ST) soil samples according to Embrapa [30].

The soil chemical composition was determined by energy dispersive X-ray fluorescence spectrometer (Shimadzu EDXRF-720, Japan) with Rh as an X-Ray source and Si(Li) detector. The measures were carried out ranging from Ti–U at 50 kV, 13 μA to Na–Sc at 15 kV, 202 μA for 100 seconds and 10 mm collimation incident beam, using polyester 2.5" and 63.5 mm diameter thin-film sample supports (Chemplex, Palm City, USA).
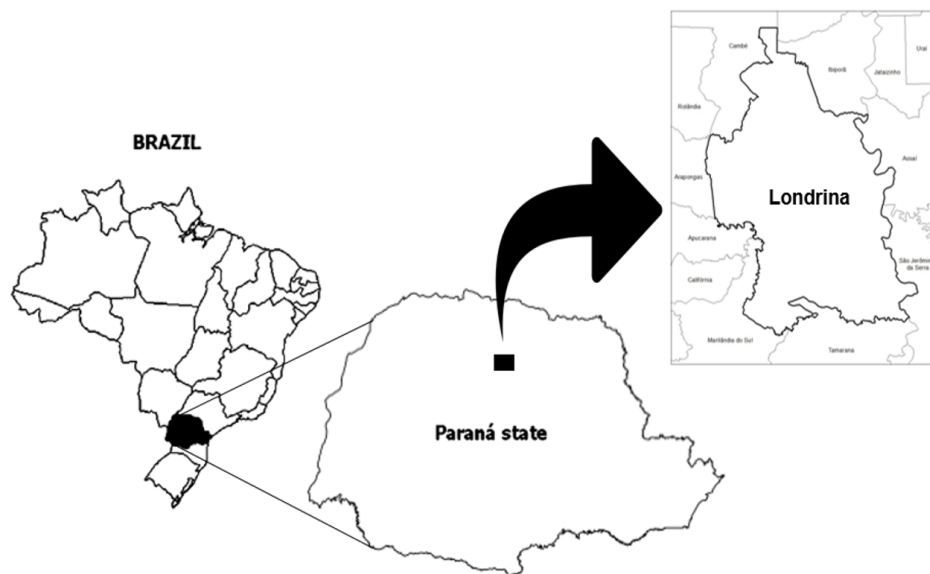
Fig. 1. Geographical location of Londrina city - Parana State ($23°21'58.5"S$ **and** $51°09'45.1"W$**), Southern Brazil**

2.3 Sorption and Desorption Experiments

The experiments were carried out in batch using a background electrolyte 2.5 meq L^{-1} $NaNO_3$ (Merck, Germany). Working solutions were prepared from the nitrate salts, (Vetec, Brazil) of Pb^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} ranging from 1.0 to 10 meq L^{-1}. Suspensions were prepared with 1:10 working solution:sample and shaken at 30 rpm for 24 h and $20\pm2°C$ in a shaking table (Edmund Buhler, SM25 model). After equilibrium of untreated soil (SNC) and treated soil (STC), the suspensions were centrifuged at $1607.9\times g$ for 10 min using a DCS-16-RV device (Presvac, Brazil) and filtered through 0.22 μm cellulose ester membrane (Millipore, USA). Supernatants were collected into polyethylene vials, and the solid was dried at 40°C (Tecnal, TE394/1 model) and analyzed by EDXRF. The pH was measured before and after equilibrium.

2.4 Isotherms

Initial (C_i, meq L^{-1}) and equilibrium (C_{eq}, meq L^{-1}) concentrations were determined by inductively coupled plasma optical emission spectrometry (ICP-OES, Perkin Elmer Optima 8300, USA). Sorbed concentration (C_{sorb}, meq kg^{-1}) was calculated by C_i and C_{eq} difference, considering the sorbent mass (in kg) and the working solution volume (in L). The rate removal or sorption efficiency (SE) of the metal ions from aqueous solution was calculated by the difference between the initial and equilibrium concentrations in relation to the initial concentration.

The dual-mode Langmuir-Freundlich model given by Eq. (2.1) was applied to explain the availability of higher-affinity and lower-affinity sites to be occupied by the metal ions [31, 22].

$$C_{sorb} = \sum_{i=1}^{J} \frac{b_i \left(K_i C_{\text{eq}}\right)^{n_i}}{1 + \left(K_i C_{\text{eq}}\right)^{n_i}} \qquad (2.1)$$

where J represents different types of sorption sites; b (meq kg^{-1}) the sorption capacity or number of available sites; K (L meq^{-1}) the affinity parameter sorbate–sorbent; n the heterogeneity of sorption sites or sorption intensity.

The Gibb's free energy ($\Delta G°$) was calculated by Eq. (2.2), according to Liu [32], to indicate thermodynamic feasibility of sorption, using the K (L mol^{-1}) parameter from Langmuir model, the universal gas constant (R) and absolute temperature (T). Negative values indicate spontaneous process [33, 34].

$$\Delta G^o = -RT \ln(55.5K) \qquad (2.2)$$

2.5 Data Analysis

The isotherms were obtained by `cftool` (Interactive Environment for Fitting Curves to One-Dimensional Data) from Matlab 7.10.0 software [35]. Fitting coefficients were constrained by positive values of $\geq$95% confidence limits and calculated by the non-linear least square method using the `Trust-region` algorithm.

3 RESULTS AND DISCUSSION

3.1 Characterization

The physical and chemical attributes for SN and ST soil samples in Table 1 are in agreement with the characteristics of a Dystrophic Red Latosol [29]. Soil chemical quality improved after the swine manure amendment (SMA), due to the phosphorus and organic matter input as well as the increase in trophic levels as K, Ca and Mg ions and decrease in trophic aluminum. Additionally, the amendment slightly increased soil pH and, therefore, the availability of nutrients to the plants, the saturation by trophic bases, and, consequently, the CEC [36].

Table 1. Physical and chemical attributes (±standard deviation) of the soil samples untreated (SN) and treated (ST) with swine manure before sorption

pH	P	OC	(H+Al)	Al	K	Ca	Mg	CEC
	(mg kg^{-1})	(mg kg^{-1})	(meq kg^{-1})					
			SN					
4.70	16.9	1.70	7.20	0.22	0.50	4.05	1.93	137
(0.05)	(2.4)	(0.28)	(0.02)	(0.07)	(0.09)	(0.73)	(0.41)	(8)
			ST					
4.90	31.3	2.27	7.20	0.06	1.08	5.00	2.55	158
(0.08)	(3.2)	(0.33)	(0.06)	(0.05)	(0.12)	(0.80)	(0.55)	(10)

P: phosphorus amount; OC: organic carbon content; CEC: cation-exchange capacity; SN: pre-sorption soil untreated with SM; ST: pre-sorption soil treated with SM

3.2 Isotherms

Competitive sorption isotherms of the metal ions on soil samples, as well as the adjustable parameters, are shown in Fig. 2 and Table 2, respectively. Both isotherm slope and shape demonstrate an increase in the sorption capacity for all the metals after the swine manure amendment (STC), indicated by (b_1+b_2) increase. Besides, the retention sequence $Pb^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+}$ could be observed. Although untreated soil (SN) has shown high affinity (K_2, b_2) to the metal ions, the amendment has changed this feature. In a general way, the sorption capacity increased in 30%, 45%, 176%, and 231%, for Pb^{2+}, Cu^{2+}, Zn^{2+} and Ni^{2+}, respectively. This change can be justified by the increase of organic matter content in the soil, which increases the metal complexation capacity. Stronger interaction affinity was observed for Pb^{2+} and Cu^{2+}, while Zn^{2+} and Ni^{2+} had their affinity decreased, although the sorption capacity increased. This statement implies a higher number of sites of lower affinity to Zn^{2+} and Ni^{2+}. The parameter n between 0 and 1 describes surface heterogeneity for values close 0 and surface homogeneity for values close to 1; above 1 sorption site cooperation is expected [37, 38, 39]. According to Do (1998), the larger n, the more nonlinear is the sorption isotherm, and as n is getting more significant, the sorption is approaching an irreversible isotherm, when concentration needs to go to an extremely low value before possible desorption. The same behavior also occurs for the dual-mode L-F model. Thus, homogeneity was observed for Pb^{2+} and Cu^{2+} and heterogeneity for Zn^{2+}

and Ni^{2+} after SMA. The dual-mode L-F model allowed a good data adjustment with $R^2 > 0.981$ and RMSE $< 5\%$. Parameters related to the soil metal sorption before (SNC) and after (STC) amendment are in Table 3. In general, higher K_d was found for Pb^{2+} followed by Cu^{2+}, Zn^{2+} and Ni^{2+}; Zn^{2+} and Ni^{2+} are predominantly retained in the soil by exchange reactions, while Pb^{2+} and Cu^{2+} form inner-sphere complexes with soil constituents [40]. Dissolved organic matter (DOM) ligands can form a bridge between the soil surface and the metals [41, 42], enhancing, therefore, the sorption capacity for metal ions as Cu^{2+} and Pb^{2+}. However, Fe-oxides in soils form the most dominant reactive sites for DOM complexation, which can result in binding sites for Cu^{2+} and Pb^{2+} blocked by organic ligand groups [43, 42, 44]. This blockage of binding sites can counteract the potentially enhanced retention of Cu^{2+} and Pb^{2+} by the mentioned mechanisms. Hence, K_d and consequently SE decreased with C_i increase. Although SE had increased after amendment, interpreted as sorption viability, a higher number of low energy sites for Cu^{2+} and Zn^{2+} (Table 2) indicates releasing of that ions to the soil solution. In addition, the post-sorption pH was always lower than the pre-sorption pH: the pre- and post-sorption pH difference decreased (0.5 to 0.1) with metal ion initial concentration increase in untreated soil (SNC) and increased (0.2 to 0.6) for treated soil (STC). The post-sorption pH was slightly higher for treated soil (STC) than for untreated soil (SNC). Firstly, the pH decreasing confirms H^+ releasing and indicates that the sorption of the metal ions actually occurred. This behavior is common in tropical soils [45, 46, 47]. The sorption with

no swine manure was favored at low metal concentration, while with manure, it was also relevant at high metal concentrations due to the greater cation sorption and H^+ leaching to the solution by the organic ligands on the surface. Furthermore, negative Gibbs free energy (Table 3) has indicated a spontaneous sorption process, except for Zn^{2+} and Ni^{2+} in STC and very low affinity sites. Similar results have been found for Pb^{2+} by Diatta [48] when studying four types of soil. The amendment promoted lower stabilization of the metal-soil complex, pointing Cu^{2+}, Zn^{2+} and Ni^{2+} mobilization capability to the soil solution.

Table 2. Adjustable parameters from dual-mode Langmuir-Freundlich model fitting for the metal sorption on soil samples; root mean square error (RMSE) and coefficient of determination (R^2) from the model fit

Metal	K_1	K_2	b_1	b_2	$b_1 + b_2$	n_1	n_2	$RMSE$	R^2
					SNC				
Pb^{2+}	0.179	2.96	15.3	50.0	65.3	2.02	0.648	1.84	0.987
Cu^{2+}	1.49	1.93	13.4	31.4	44.8	2.09	44.7	2.43	0.981
Zn^{2+}	0.268	3.47	0.268	8.74	23.5	2.20	6.99	0.593	0.995
Ni^{2+}	0.224	7.212	5.74	8.05	13.8	8.44	1.36	0.228	0.996
					STC				
Pb^{2+}	0.413	11.8	42.6	42.3	84.9	1.56	0.891	1.84	0.995
Cu^{2+}	0.273	5.38	39.3	25.9	65.1	0.952	14.1	1.74	0.996
Zn^{2+}	0.007	0.590	46.6	18.4	64.9	0.426	14.1	1.43	0.995
Ni^{2+}	0.018	0.766	14.9	30.8	45.7	0.129	2.38	0.995	0.996

K (L meq^{-1}): sorbate-sorbent affinity; b (meq kg^{-1}): number of available sorption sites; ($b_1 + b_2$): maximum sorption capacity; n: heterogeneity of sorption sites or sorption intensity; SNC: post-sorption soil untreated with swine manure, STC: post-sorption soil treated with swine manure

Table 3. Parameters after metal sorption onto soil samples ($C_{i,\min} \approx 1.0$ meq L^{-1} to $C_{i,\max} \approx 10$ meq L^{-1}): equilibrium concentration (C_{eq}), sorbed concentration (C_{sorb}), distribution coefficient ($K_d = C_{sorb}/C_{eq}$), sorption efficiency (SE) and Gibb's free energy ($\triangle G°$)

Metal	C_{eq}	C_{sorb}	K_d	SE	$\Delta G°_1;\Delta G°_2$
	(meq L^{-1})	(meq kg^{-1})	(L kg^{-1})	(%)	($\times 10^4$; kJ mol^{-1})
			SNC		
Pb^{2+}	0.040;5.38	10.8;50.5	120;9.45	92.31;48.60	$-0.40;-1.09$
Cu^{2+}	0.110;5.29	6.20;44.8	65.6;8.09	83.82;44.73	$-0.92;-0.99$
Zn^{2+}	0.460;7.31	6.20;23.5	13.5;3.21	57.41;24.33	$-0.50;-1.13$
Ni^{2+}	0.450;8.24	6.70;14.0	14.9;1.69	59.82;14.52	$-0.45;-1.31$
			STC		
Pb^{2+}	0.040;3.59	11.3;68.6	255;19.4	96.24;66.02	$-0.60;-1.43$
Cu^{2+}	0.010;2.79	6.70-68.3	67.0;2.43	98.53;70.85	$-0.50;-1.24$
Zn^{2+}	0.130;4.79	9.50;48.7	73.1;10.2	87.96;50.41	$+ 0.41;-0.69$
Ni^{2+}	0.190;5.64	9.30;40.0	48.9;7.09	83.04;41.49	$+0.17;-0.76$

SNC: post-sorption soil untreated with swine manure; STC: post-sorption soil treated with swine manure
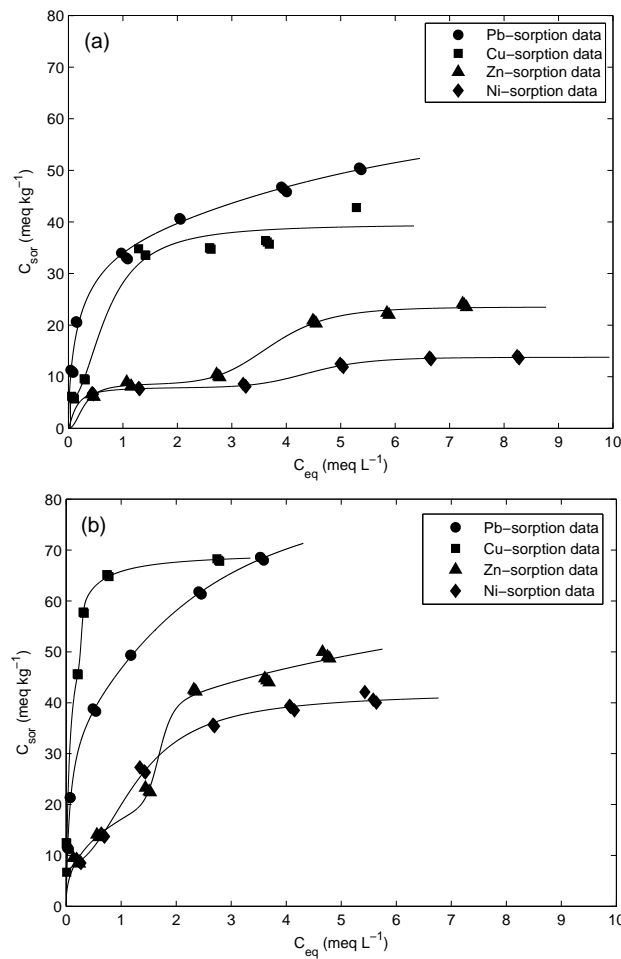
Fig. 2. Metal competitive sorption onto soil samples (a) untreated (SNC) and (b) treated with swine manure (STC)

## 3.3 Energy Dispersive X-Ray Fluorescence (EDXRF)

The treated and untreated soil with swine manure samples were analyzed to other elements by EDXRF. It should be noted here that it was not possible to detect the metals studied in the untreated pre-sorption samples (SN) (Table 4).

However, there was an increase in the target metal retention capacity post-amendment over the observed concentration in the post-sorption untreated samples, keeping the sorption sequence for SNC and STC samples.

Fluorescence emission lines for lead, copper, zinc, and nickel post-sorption are in Fig. 3. Relative intensity shows that amendment increased the sorption for the studied metal ions, with higher intensity for Pb^{2+} followed by Cu^{2+}, Zn^{2+}, and Ni^{2+}; this sequence is the same observed from the adjustable parameters in the sorption fitting by mathematical modeling.

It is worth to note results from the literature going in the same direction.
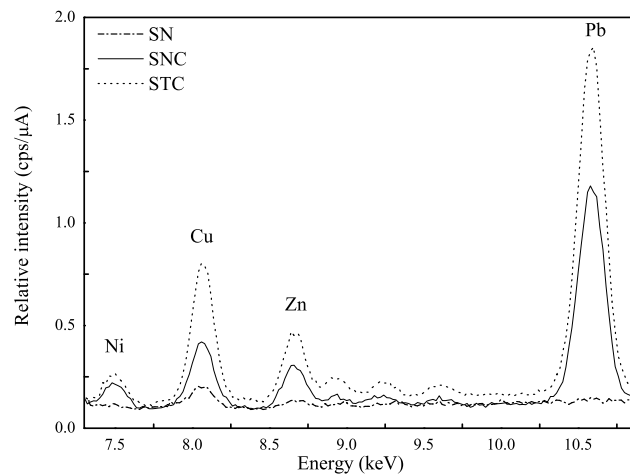
Fig. 3. EDXRF spectra of the samples: pre-sorption soil untreated with swine manure (SN-control), post-sorption soil untreated with swine manure (SNC), post-sorption soil treated with swine manure (STC). X-ray emission lines and energies related to the detection of Ni (Kα=7.46 keV), Cu (Kα=8.04 keV), Zn (Kα=8.64 keV) and Pb (Lα=10.6 keV) are indicated in the spectra

Table 4. Chemical composition by EDXRF of the soil samples. SN: pre-sorption soil untreated with swine manure (control), SNC: post-sorption soil untreated with swine manure, STC: post-sorption soil treated with swine manure

Metal	SN	SNC	STC
	($g\ kg^{-1}$)		
Fe	730	670	650
Al	120	130	100
Si	62	65	57
Ti	45	45	42
Ba	22	24	25
Mn	6.0	4.9	4.7
Ca	3.0	2.8	4.1
Pb	–	43	81
Cu	–	6.7	16
Zn	–	3.5	6.6
Ni	–	3.0	4.1

Although significantly higher potentially toxic metal input to soil was provided by adding organic fertilizer in Zaccone et al. [49], semolina from wheat plants grown in the organic farming system was poorer in Cd, Cr and Cu than those in the conventional farming system. The treatment suggests a potential for the organic system to decrease the amount of these elements in the soil solution, to limit their availability and absorption by plants, and to influence the translocation processes for grains. However, the plant samples obtained from the organic farming system showed higher concentrations of Ni, Pb, and Zn regarding those obtained from the conventional system. These differences show the opportunity to choose and relate cultivars to the adopted farming system and to the kind of metals to be preferentially accumulated or depleted,

to maintain the homeostasis of the organisms. Metal sorption evaluated in concurrence with organic matter in Refaey et al. [42] has shown strong Cu sorption by DOM and mineral phases inner-sphere complexation. In addition, Zn^{2+} and Ni^{2+} preferred outer-sphere complexation with the mineral phase. Soares et al. [50] have proposed methodology to correlate vulnerability to availability of lead for tropical soils; vulnerability indices > 0.60 imply an available fraction > 0.15. Availability herein is related to the outer-sphere complexation, although it has not explicitly been figured.

To some extent, clay minerals have influenced the mobility and consequent availability of metals in the presence of DOM. Once the mineral phase can sorb dissolved organic matter and enhance metal sorption, outer-sphere metals can mobilize while inner-sphere almost not, according to results herein obtained.

4 CONCLUSIONS

Sorption processes involved in swine manure amendment and metal ion environmental transport were useful to evaluate the toxic and micronutrient metal availability. The maximum sorption capacity for the metal ions increased with the amendment, although copper, zinc, and nickel affinity (K_1, K_2) to the soil surface have decreased, pointing out mobilization to the soil solution. Micronutrients (Cu, Zn, Ni) were, to some extent, released to the plants, while toxic ions (Pb) remained trapped in the soil solid phase. In addition to manure being an excellent soil conditioner for total phosphorus and OM, the added organic matter is capable of retaining toxic ions, as well as providing micronutrients over time. Hence, the availability of Pb^{2+} decreased while that of other ions increased, confirming the hypothesis that potentially toxic ions remain retained due to increased specific sorption sites of incorporated organic matter, although nutrients may be released. In this case, there may be a predicted environmental risk associated with the manure amendment. It is worth to note the applicability of manure from animal production in the vegetable production, closing a productive cycle. Additionally, the EDXRF technique associated with the adjustable parameters from the sorption model provided excellent applicability to the study of dynamics of metal ions and risk assessment in soils.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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