Modeling field-scale vertical movement of zinc and copper in a pig slurry-amended soil in Brazil

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HIGHLIGHTS

► We performed a model validation of Zn and Cu settings in a pig-slurry amended soil.
► A two-site model with reduced kinetic constants present the best fit with field data.
► Future 50-years scenarios related to the pig slurry applications were simulated.
► Downward Zn and Cu solute fluxes will not present risk to groundwater pollution.
► Continuous pig slurry amendments will lead to a high Cu accumulation on soil surface.

ARTICLE INFO

ABSTRACT

Organic amendments often represent a source of trace metals (TMs) in soils, which may partly leach into the groundwater. The objectives of this study were (1) to validate Hydrus-2D for modeling the transport of Zn and Cu in an Alfisol amended with pig slurry (PS) by comparing numerical simulations and experimental field data, and (2) to model the next 50 years of TM movements under scenarios of suspended or continued PS amendments. First, between 2000 and 2008, we collected detailed Zn and Cu data from a soil profile in Santa Maria, Brazil. Two hypotheses about Zn and Cu reactivity with the solid phase were tested, considering physical, hydraulic, and chemical characteristics of six soil layers. Using a two-site sorption model with a sorption kinetic rate adjusted based on laboratory EDTA extractions, Hydrus simulations of the vertical TM transport were found to satisfactorily describe the soil Zn and Cu concentration profiles. Second, the long-term fate of Zn and Cu in the soil was assessed using the validated parameterized model. Numerical simulations showed that Zn and Cu did not present risks for groundwater pollution. However, future Cu accumulation in the surface soil layer would exceed the Brazilian threshold for agricultural soils.

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1. Introduction

Soil amendment with organic waste is a common practice in agriculture worldwide. In different regions of Brazil, large-scale animal production generates large amounts of manure. These regions are often characterized by the predominance of family farming, in which each farmer has only a small land area to grow crops. The fertilizing value of organic waste, such as animal manure, is generally recognized, but its quality may vary widely. For example, pig slurry (PS) often has a relatively low nutrient content, making it uneconomical to transport over long distances. Hence, PS disposal criteria are primarily guided by a limited space, increasing risks of soil pollution by nitrate, phosphorus, and trace metals (TMs), notably zinc (Zn) and copper (Cu).

Regulatory agencies in many countries have established environmental guidelines for soil organic waste amendments [1–4]. Basically, such guidelines restrict, or ban, applications of organic waste to soils where the total TM content exceeds the maximal allowed values. Brazilian laws currently allow for the maximum TM values, which are generally higher than those adopted in the European Union. The Companhia de Tecnologia de Saneamento Ambiental (CETESB) [3], and specifically the state of Sao Paulo, authorizes 2800 and 1500 $kg\,ha^{-1}$ of Zn and Cu, respectively, as maximum loads that can be applied in a particular area. Moreover, the maximum soil TM content, when further applications of amendments to agricultural soils are prohibited, are 450

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and 200 mg kg^{-1} for Zn and Cu, respectively [5]. For comparison, the European Union [1] allows the addition of 30 kg Zn ha^{-1} and 12 kg Cu ha^{-1} based on a 10-years average. The maximum allowed soil concentrations when further amendments are restricted are 150–300 mg kg^{-1} for Zn and 50–140 mg kg^{-1} for Cu, depending on soil pH. Brazil's federal legislation was expanded in the 1990s, based on the experiences of other countries. It was recognized that the total TM levels are not good environmental indicators for making decisions, and that the type of soil management needs to be taken into consideration. For example, the maximum TM levels established by the Brazilian legislation refer to any layer of the soil profile. In southern Brazil, about 50% of agricultural operations (almost 8.5 million hectares) are managed under no-tillage practices. Consequently, the organic waste applied on the soil surface is not incorporated deeper into the soil profile, thus enhancing a rapid increase of TM concentrations in the surface layer.

Soil water movement varies in time and space and determines to a large extent the spatial distribution of TMs in soils. Mathematical modeling of the fate of metals in soils in terms of their retention and transport is helpful to assess their environmental impacts [6]. Mathematical models, simulating water flow and transport and reactions of TMs in soils, provide additional information on risks of the transfer of TMs to the groundwater. Such transfer mainly depends on the amount of water moving through a particular type of soil and on the mobility of TMs in the soil solution. On the one hand, theoretical mathematical models require many parameters to describe complex processes of TMs reactivity with functional groups of the solid phase. On the other hand, empirical models often insufficiently consider physical and chemical soil characteristics or biological activity since such models merely rely on adsorption/desorption data. However, such adsorption/desorption processes are often influenced by various soil factors, which are difficult to measure or individually control.

The Hydrus software package [7] has been widely used to simulate the fate and transport of TMs in soils [8–12]. Hydrus includes mathematical modules that simulate variably-saturated water flow and solute transport in porous media. Recently, Mallmann et al. [13] demonstrated the effectiveness of the Hydrus two-site sorption sub-model [14] by simulating changes in Zn and Pb concentration profiles in metal contaminated soils over one century. Similar modeling by Rheinheimer et al. [15] predicted that Zn and Pb concentrations in the soil solution will not exceed the reference water quality values of the Council of the European Communities (CEC) [1] during the next 50 years. Additionally, Seuntjens [16] used Hydrus to simulate two remediation scenarios for a soil contaminated with cadmium (Cd). He concluded that Cd concentrations in the soil solution were reduced after adding an organic material and/or an acidity corrector to the soil. He also predicted a decreasing Cd loss from the soil. Moradi et al. [17] simulated Cd movement in a soil amended with a sewage sludge under an arid climate. While they noted that there is little risk of groundwater contamination by leached Cd, they observed an accumulation of TM in the soil surface layer, and an increased risk for TM absorption by plant roots and/or removal by surface runoff.

Here, we use Hydrus-2D to model the past and future movements of Zn and Cu in a Brazilian Alfisol, contaminated by repetitive applications of PS, and compare the obtained results with a non-amended soil. First, we simulate changes in Zn and Cu concentration profiles in the soil using known metal inputs via PS amendments during 8 years. We consider two hypotheses for interactions between the soil solid phase and the soil solution, i.e., either a complete instantaneous equilibrium or a two-site sorption model with both equilibrium and kinetic sorption. The model's validity is assessed by comparing simulated and measured field TM distributions in 2008. Second, we predict the movement of Zn and Cu, using the adopted hypothesis, for the next 50 years under two scenarios of discontinued and continued PS applications.

2. Materials and methods

2.1. Experimental site, soil, and other characteristics

The study was conducted on experimental fields of the campus of the Federal University of Santa Maria in the state of Rio Grande do Sul in Brazil (29°42′52″S and 53°42′10″W, 90 m altitude) and involved repetitive applications of PS. Soils, classified as a Typic Hapludalf [18], are well drained, and show a strong vertical clay gradient in the profile. The parent material is upper Triassic sandstone, locally referred to as the Santa Maria Formation [19]. The soil mineralogical composition includes interstratified illite-smectite, kaolinite-smectite, hydroxy-aluminum vermiculite and kaolinite clay minerals [20]. The climate is subtropical (Cfa 2, Köppen classification), with mean annual rainfall of 1600 mm and mean annual temperature of 19 °C. The experiment lasted from May 2000 to January 2008 on plots of 4 m × 3 m. The cultivated soil was under no-tillage since 1992. Four treatments were tested with PS doses of 0, 20, 40, and 80 m^3 ha^{-1} applied on the soil surface in each cultivation cycle. Experiments involved 19 PS applications, totaling 1520 m^3 ha^{-1} for the plot with the highest dose, i.e., 70,000 kg of dry organic matter, 83.4 kg of Zn and 67.1 kg of Cu per ha. The total plant dry matter produced during the 8-year experiment was 57,870 and 147,260 kg ha^{-1} for the 0 and 80 m^3 ha^{-1} plots, respectively [21].

2.2. Soil sample collection and processing

Two plots with 0 and 80 m^3 ha^{-1} treatments were selected for this study. In January 2008, three disturbed and three undisturbed soil samples were collected from each of six layers of both plots at 0–5, 5–10, 10–25, 25–35, 35–50, and 50–60-cm depths. On disturbed samples we determined soil texture, a part of the soil water retention curve (SWRC) corresponding to the soil moisture pressures larger than 500 kPa, pH$_{H_2O}$, organic carbon content (OC), and the total concentrations and desorption curves of Zn and Cu. On undisturbed samples, we measured the saturated soil hydraulic conductivity (K_s), bulk density, and a part of the SWRC for the soil water pressure smaller than 100 kPa.

2.3. Soil physical and chemical analysis

The K_s was determined using a falling head permeameter [22]. For establishing SWRC, undisturbed samples were saturated for 48 h and then successively submitted to tensions of 1, 4, 6, and 10 kPa in a sand column [23] and to 33 and 100 kPa in a pressure cooker. Gravimetric water contents at higher tensions (500, 1000 and 1500 kPa) were determined with the dew point potentiometer on disturbed soil samples. The soil bulk density was determined on soil cylinders and the soil texture was measured following the USDA procedure [24].

Soil pH$_{H_2O}$ and OC contents were determined according to Tedesco et al. [25] and EMBRAPA [26], respectively. Total Zn and Cu concentrations were measured after total sample digestion according to Tessier et al. [27]. Desorption isotherm curves for Zn and Cu were generated using Ethylene diamine tetraacetic acid (EDTA) extractions at 0.05 mol l^{-1} (pH 6.0); soil-solution ratio 1:10 [28] at 5, 10, 15, 20, 25, 30, 60, 120, 240, 360, 480, 600, and 1440 min.

2.4. Water flow and solute transport simulations

Hydrus-2D [7] was used to simulate one-dimensional unsaturated water flow and Zn and Cu transport in a vertical rectangular domain. The analytical models of van Genuchten and of

van Genuchten–Mualem were used to describe water retention curves and unsaturated hydraulic conductivity functions, respectively [29]. Soil residual (θ_r) and saturated (θ_s) water contents, and parameters α and n for each soil layer were obtained by fitting the van Genuchten model to retention data determined in the laboratory using the SWRC software [30]. The pore connectivity/tortuosity factor (l) used in simulations was set to 0.5 for all soil layers. This value was recommended by Mualem [31] and is a default value used for soils in Hydrus modeling studies.

The initial soil and soil solution Zn and Cu concentrations within each soil layer, used in the Hydrus-2D simulations (starting on 01/01/2000), were based on values measured in the plot without PS applications. For the total TM contents we used the total concentrations measured in the laboratory. For soil solution concentrations of Zn and Cu, we used multiple regression equations proposed by Sauvé et al. [32] and tested by Mallmann et al. [13]:

$$\log Zn_{solution}(\mu g\ l^{-1}) = 3.68 - 0.55pH + 0.94 \log Zn\,(mg\ kg^{-1})$$
$$- 0.34 \log OC(\%), \tag{1}$$

$$\log Cu_{solution}(\mu g\ l^{-1}) = 1.37 - 0.21pH + 0.93 \log Cu\,(\mu g\ kg^{-1})$$
$$- 0.21 \log OC(\%), \tag{2}$$

The Freundlich nonlinear isotherm equations were developed from these total and solution TM concentrations. The Freundlich exponent n of 0.65 was used for Zn [33,34] and 0.85 for Cu [35], corresponding to average values from literature dealing with modeling studies on soils with comparable properties. Different values for Zn and Cu are based on the premise that Cu has a great binding strength with soil constituents [36] and, consequently, a low mobility in the soil profile.

Desorption Zn and Cu curves were fitted using the kinetic model of Fangueiro et al. [37]:

$$Q = Q_1(1 - e^{-kt}) + Q_2(1 - e^{-\lambda t}) \tag{3}$$

where Q (mg kg^{-1}) is TM desorbed at time t; Q_1 (mg kg^{-1}) is the easily extractable TM fraction, associated with the constant desorption kinetic rate k (h^{-1}); and Q_2 (mg kg^{-1}) is the slowly extractable TM fraction, associated with the kinetic desorption constant λ (h^{-1}). The non-extractable TM fraction by EDTA (Q_3) is calculated as the difference between the total TM (Q_T) and Q at $t = 24$ h.

In simulations of the vertical transport of Zn and Cu in the soil, the fraction Q_1 represented sorption sites with the instantaneous equilibrium sorption [37], because of the high value of k. This value led to the calculation of the β value (equation 4), which is the fraction of sorption sites with instantaneously adsorbed TMs to the functional groups (at equilibrium) and is required by Hydrus-2D:

$$\beta = \frac{Q_1}{Q_T} \tag{4}$$

The Q_2 and Q_3 TM fractions were considered to be adsorbed to functional groups according to a kinetics adsorption/desorption model [37], using the kinetic constant (λ). Since it is impossible to determine the real λ value in the field, and considering that the strong extractant character of EDTA significantly overestimate rates that occur in soils [38], we reduced the sorption rates in the Hydrus-2D simulations, following Mallmann et al. [13]. Mallmann et al. [13] reproduced the vertical distributions of Zn and Pb concentrations using Hydrus-2D after reducing EDTA-determined rates by 1:144,000 (considering that one minute of the EDTA extraction represents one day in the field and an additional reduction by a factor of 100), leading to a satisfactory fitting of observed profiles of metal concentrations in real soil situations. All physical and chemical characteristics and initial TM concentrations for the plot without

PS applications that are required to run Hydrus-2D are listed in Table 1.

Numerical solutions of the Richards equation, describing variably-saturated water flow, and the convection–dispersion equation, describing solute transport, require specification of initial and boundary conditions. The atmospheric boundary condition was considered in Hydrus-2D simulations at the soil surface. Daily precipitation data 01/01/2000–01/01/2008 were obtained from Sistema Irriga® (UFSM). Since a water loss by surface runoff was measured during 8 years of the experiment [39], rainfall was corrected by subtracting a water runoff loss. Daily evapotranspiration rates for crops cultivated on the experimental plots were obtained from the Sistema Irriga's® irrigation management program, which calculates the crop's maximum evapotranspiration (ET$_m$) using the Penman–Monteith combination equation [40]. Average amounts of annual rainfall, runoff (from the area without the PS application), and evapotranspiration were 1678, 548, and 921 mm year^{-1}, respectively.

The total amounts of Zn and Cu added to the soil via PS amendments were determined as a difference between the TM mass balance in the plot with applied PS and the one without, evaluated over a depth of 60 cm (Table 2). Furthermore, there was a significant loss of TMs from the soil profile from depths larger than 60 cm due to leaching during simulations. To maintain the balance between the results of the simulations with the plot that received PS, these quantities were also added to the amounts applied to the soil during the simulations. Thus, the total amounts of TMs added to the soil in Hydrus simulations were 76.5 and 56.5 kg ha^{-1} of Zn and Cu, respectively (Fig. 1). These quantities differ slightly from those added in field experiments during 19 PS applications (83.4 and 67.1 kg ha^{-1}, respectively). These differences are attributed mainly to the TM loss due to runoff, and to a lesser extent, the TM removal with harvested crops. The cumulative removal of TMs by harvested crops from 2001 till 2008 was very small, representing only about 0.33 and 1.13% of the total Zn mass in the 0–60-cm soil depth (Table 2) for the 0 and 80 m^3 ha^{-1} plots, respectively, and about 0.05 and 0.12% of the total Cu mass, respectively. These removed amounts were calculated based on the crop production data (for corn for years 2001, 2002, 2004, 2005, and 2007, and for beans for years 2003 and 2006) and the TM concentrations in crop grains [41,42]. The amounts of TMs added to the soil in PS applications were proportional to the measured TM contents in the amendments during the field experiment (Fig. 1). In the Hydrus-2D simulations, the Zn and Cu quantities were applied at the soil surface diluted in rainwater (assuming an instantaneous 100% solubility). This strategy was selected for two reasons: (a) to increase the downward movement of TMs since the TM transfer associated with organic or mineral particles (the so-called colloid-facilitated solute transport [43]) was not considered and (b) the kinetic approach that was used was responsible for retarding the initial sorption of the input Zn and Cu amounts to the soil sorption sites, which reproduces a non-complete solubility of the pig slurry's TMs. Using parameters listed in Table 1, we simulated the vertical transport of Zn and Cu between 01/01/2000 and 01/01/2008 while considering two hypotheses about the TM reactivity:

– hypothesis A: 100% of the total TM concentrations in each soil layer is in instantaneous chemical equilibrium with the soil solution,
– hypothesis B: the total TM concentrations in soil can be divided into an instantaneous chemical equilibrium fraction and a kinetic fraction, determined by the EDTA extraction. The kinetically adsorbed fraction reacts with the solution according to the λ rate constant, defined by the two-site kinetic sorption equation proposed by Fangueiro et al. [37]. In this equation, the kinetic
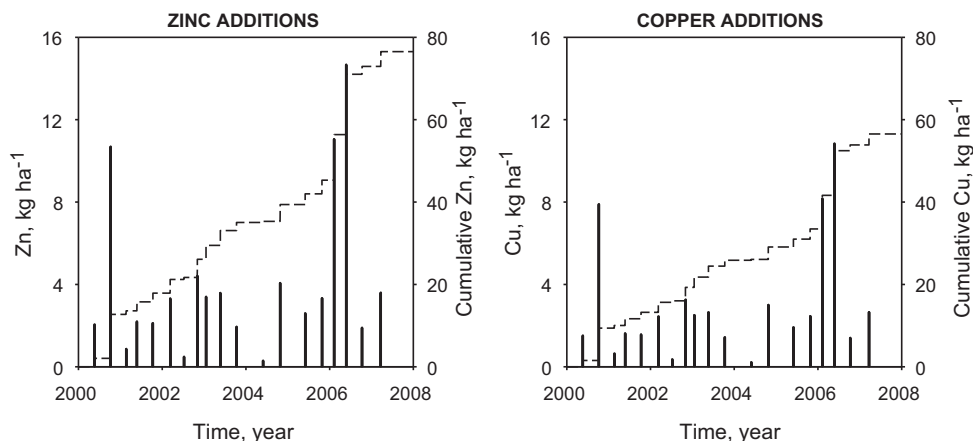
Fig. 1. Actual and cumulative zinc and copper applications used in Hydrus-2D simulations between 2000 and 2008, corresponding to 19 pig slurry applications during the experiment.

Table 1

Physical and chemical parameters of the soil in the plot without the application of pig slurry, required for simulations with Hydrus-2D.

Parameter[a]	Soil layer (cm)					
	1 (0–5)	2 (5–10)	3 (10–25)	4 (25–35)	5 (35–50)	6 (50–60)
Soil						
pH	5.29	5.34	5.50	5.50	5.42	5.42
Clay, g kg^{-1}	141	163	165	179	177	188
Silt, g kg^{-1}	365	349	347	356	368	371
Sand, g kg^{-1}	494	488	488	465	455	441
OC, g kg^{-1}	12.3	9.4	8.7	9.4	7.8	6.1
Bd, g cm^{-3}	1.53	1.61	1.69	1.49	1.46	1.41
K_s, cm d^{-1}	81.1	20.3	12.5	32.8	205.6	250.8
θ_s, cm^3 cm^{-3}	0.367	0.404	0.405	0.419	0.365	0.410
θ_r, cm^3 cm^{-3}	0.116	0.137	0.139	0.147	0.144	0.128
α_{VG}, cm^{-1}	0.0696	0.3564	0.0708	0.2716	0.1809	0.4989
n_1	1.4297	1.3249	1.4455	1.3330	1.3297	1.3603
L	0.5	0.5	0.5	0.5	0.5	0.5
LD, cm	2.5	2.5	2.5	2.5	2.5	2.5
TD, cm	0.2	0.2	0.2	0.2	0.2	0.2
Zinc						
Total, mg kg^{-1}	15.30	15.30	15.15	20.04	22.08	18.91
Solution, µg l^{-1}	71.32	73.44	61.33	77.78	100.13	93.73
β	0.56	0.29	0.14	0.04	0.04	0.02
λ, 10^{-3} d^{-1}	4.29	4.13	3.04	1.82	1.44	2.82
K_F	1.76	1.72	1.92	2.18	2.03	1.82
n	0.65	0.65	0.65	0.65	0.65	0.65
Copper						
Total, mg kg^{-1}	5.33	5.33	9.04	10.89	12.01	14.23
Solution, µg l^{-1}	9.27	9.58	15.31	18.15	21.59	26.91
β	0.61	0.46	0.21	0.13	0.07	0.06
λ, 10^{-3} d^{-1}	6.87	4.17	2.61	2.49	1.83	3.10
K_F	54.28	52.78	60.05	62.61	59.53	58.52
n	0.85	0.85	0.85	0.85	0.85	0.85

[a] OC = organic carbon; Bd = bulk density; K_s = saturated hydraulic conductivity; θ_s = saturated water content; θ_r = residual water content; α_{VG} and n_1 = retention parameters; L = pore-connectivity factor; LD and TD = longitudinal and transverse dispersivities, respectively; β = fraction of sorption sites with instantaneous sorption of the heavy metals; λ = kinetic constant for sorption sites 1-β; K_F and n = parameters of the Freundlich isotherm for the β sites, calculated with total and solution concentrations in mol g^{-1} and mol l^{-1}, respectively.

Table 2

Zinc and copper amounts measured in different soil layers of experimental plots with and without pig slurry applications.

Soil layer (cm)	Zinc, kg ha^{-1}		Copper, kg ha^{-1}	
	Plot without pig slurry	Plot with pig slurry	Plot without pig slurry	Plot with pig slurry
1 (0–5)	11.7	53.0	4.1	45.4
2 (5–10)	12.4	32.2	4.3	18.4
3 (10–25)	38.4	57.6	22.9	30.4
4 (25–35)	30.0	24.4	16.3	11.6
5 (35–50)	48.4	41.6	26.3	26.4
6 (50–60)	26.7	30.4	20.1	17.0
Total (0–60)	167.6	239.2	94.0	149.2

sorption sites react with the soil solution at a rate that is a fraction of the λ measured value, as discussed above.

After validating the model by comparing model predictions and experimental field data of Zn and Cu concentration profiles for 2000–2008, we simulated the movement of Zn and Cu for the next 50 years. These simulations included estimations of TM quantities transported to soil layers below a depth of 60 cm. To perform these simulations, precipitation, runoff, and evapotranspiration data between 2000 and 2008 were repeated successively until the completion of the desired 50-year period. Two scenarios were evaluated concerning the future applications of PS to the soil. While in Scenario I the future applications of PS were discontinued, in Scenario II the PS applications continued during 2008–2058 at doses of 80 m^3 ha^{-1} prior to cultivation, i.e., there was an additional input of 478 and 353 kg ha^{-1} of Zn and Cu, respectively.

3. Results and discussion

3.1. Simulation of Zn and Cu transport in the soil between 2000 and 2008

Simulations with hypothesis A (100% instantaneous equilibrium) produced a strong Zn and Cu retention in the soil surface layer (0–5 cm), although increasing TM contents were observed in the field down to a depth of about 25 cm (Table 3). In particular, about 97% of added Cu remained in the top 0–5 cm soil layer. Large differences between simulated and measured TM concentrations clearly indicate that the model based on hypothesis A cannot describe observed field metal concentration profiles.

Simulations with hypothesis B (a two-site sorption model with a reduced sorption rate) produced more realistic distributions of Zn and Cu when compared to measured field values ($R^2 = 0.982$ and 0.919, respectively). Simulated and observed Zn concentrations were fairly similar in the surface soil layer. Also, simulations indicated transport of Zn down to a depth of about 25 cm. In 2008, differences between measured and simulated Zn concentrations did not exceed 4.1 mg kg^{-1} in any soil layer (Table 3). The model based on hypothesis B also predicted an increased transfer of Cu in the soil. Yet, estimated and observed Cu concentrations in 2008 still diverged (Table 3). Although the transport and sorption–desorption processes considered in our simulations in general represent the main factors governing the TM movement in soils [6], other

transport mechanisms occurring in soils that were neglected in our study may be responsible for differences between simulated and measured Cu concentrations. Additional processes that may contribute to the TM transport in soil are bioturbation, mainly by earthworms [44–46], and the colloid-facilitated transport [43,47,48]. Being very difficult to parameterize, such processes were not taken into account in our simulations.

Simulated Zn concentrations fitted better the measured Zn values when hypothesis B was used, partly due to larger Zn solution concentrations throughout the simulation (Fig. 2). Consequently, the transfer of Zn to subsurface layers occurred earlier when the two-site sorption model was used. Increased Zn concentrations in the 5–10 cm soil layer were observed as early as 2001. The slower adsorption rate to the soil kinetic sorption sites, compared to the equilibrium sites, prolongs the presence of TM in the soil solution, favoring its transfer to deeper soil layers. Improved correspondence of simulated and measured concentrations when a two-site sorption model with reduced EDTA kinetic rate constants is used was recently demonstrated by Mallmann et al. [13].

Similar delay was also observed for Cu when sorption according to hypothesis B was considered (Fig. 2). Nevertheless, Cu concentrations in the soil solution during simulations were much lower than observed for Zn, explaining its limited leaching in the soil, compared to Zn. Although simple, the Freundlich sorption isotherm, describing the adsorption/desorption process in the sorption sub-model used in Hydrus-2D, was adequate to account for differences between the two TMs. Both the distribution coefficient (K_F), describing the equilibrium sorption, and the fraction of the equilibrium sorption sites (β) were higher for Cu (Table 1), indicating lower ratios of Cu in the soil solution compared to Zn and a lower susceptibility of Cu to transport via water flow. It is important to emphasize that, in our work, soil water retention and hydraulic conductivity data were all measured directly on samples collected in situ, and used to obtain parameters for the van Genuchten–Mualem model [29], describing soil hydraulic properties. Consequently, there was no need to use empirical pedotransfer functions to estimate soil hydraulic parameters.

Finally, by comparing simulated and measured Zn and Cu concentrations, the usefulness of water flow and solute transport models implemented in Hydrus for estimating the transport and distribution of TMs in soils was demonstrated. In addition to being efficient in reproducing the distribution of Zn and Pb concentrations in arable soils affected by a metallurgical fallout deposition

Table 3
Total zinc and copper concentrations in soil layers of experimental plots with pig slurry applications. Initial and final values are for 2000 and 2008, respectively. Simulated values are for 2008 (using Hydrus-2D run under hypotheses A and B.

Soil layer	Zinc					Copper				
	Initial (2000)	Final (2008)	Simulated (2008)	Difference[a]		Initial (2000)	Final (2008)	Simulated (2008)	Difference[a]	
cm	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	%	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	%
Hypothesis A: 100% equilibrium sorption model										
1 (00–05)	15.3	69.4	83.6	14.2	20.5	5.3	59.4	77.1	17.8	29.9
2 (05–10)	15.3	39.9	38.7	−1.2	−2.9	5.3	22.8	6.9	−15.9	−69.7
3 (10–25)	15.2	22.7	16.0	−6.8	−29.7	9.0	12.0	8.9	−3.1	−26.1
4 (25–35)	20.0	16.3	19.7	3.4	20.6	10.9	7.7	10.9	3.2	40.9
5 (35–50)	22.1	19.0	21.5	2.5	13.2	12.0	12.0	12.0	−0.1	−0.5
6 (50–60)	18.9	21.5	19.1	−2.4	−11.2	14.2	12.0	13.9	1.8	15.3
Hypothesis B: two-site sorption model with reduced λ values										
1 (00–05)	15.3	69.4	65.4	−4.0	−5.7	5.3	59.4	73.6	14.2	23.9
2 (05–10)	15.3	39.9	39.2	−0.7	−1.7	5.3	22.8	9.9	−12.9	−56.5
3 (10–25)	15.2	22.7	20.7	−2.1	−9.2	9.0	12.0	8.9	−3.1	−25.9
4 (25–35)	20.0	16.3	20.4	4.1	24.9	10.9	7.7	10.9	3.2	40.8
5 (35–50)	22.1	19.0	21.9	2.9	15.3	12.0	12.0	12.0	−0.1	−0.6
6 (50–60)	18.9	21.5	18.7	−2.8	−12.9	14.2	12.0	14.0	2.0	16.3

[a] Simulated (2008)–final (2008).
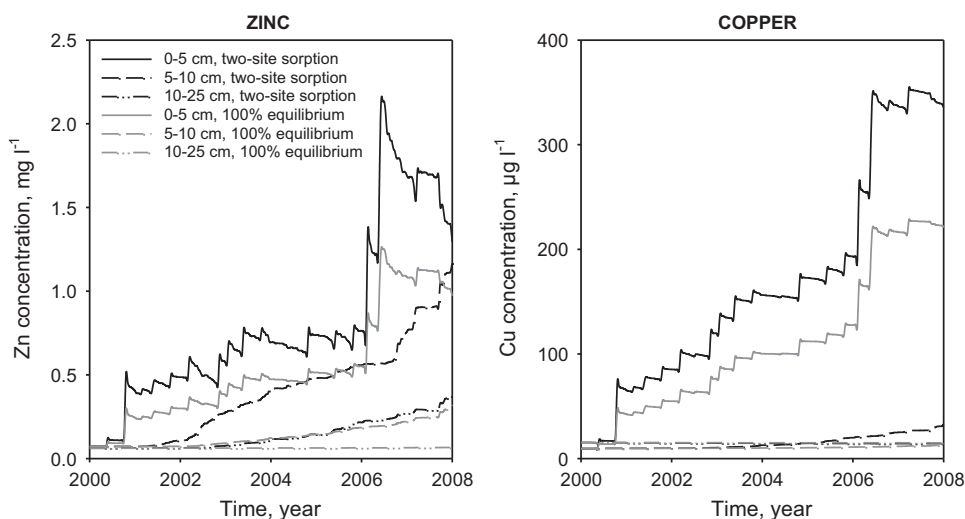
Fig. 2. Zinc and copper concentrations in the soil solution between 2000 and 2008 in the upper three soil layers, estimated with Hydrus-2D for two hypotheses: 100% chemical equilibrium and a two-site sorption with a reduced sorption rate. Note that different concentration scales are used on the *Y*-axis.

in Northern France [13], the model based on hypothesis B was also shown to be a successful tool for assessing the movement of Zn, and somewhat less of Cu, in PS amended soils in Southern Brazil, under very different pedoclimatic conditions.

3.2. Predictive simulations of Zn and Cu concentrations between 2008 and 2058

3.2.1. Scenario I: discontinued PS applications

Hydrus-2D simulations, considering hypothesis B, predicted that water flow in the soil profile was sufficient in lowering the Zn solution concentrations to levels comparable with those observed in the non-amended soil (Fig. 3). About 45% of Zn retained in the upper 25 cm of the soil profile in 2008 was desorbed and moved to depths below 25 cm. In addition, a loss of 48.4 kg Zn ha^{-1} from the upper 60 cm was estimated, representing 63% of the total Zn mass added to the soil between 2000 and 2008. Although Zn concentrations in the soil solution were similar to those observed in the non-amended soil, the observed increased retention of Zn in deeper layers of the soil was related to higher adsorption capabilities (higher K_F) and especially to a higher fraction of kinetic sorption sites $(1-\beta)$, from which desorption is very slow. Kandpal et al. [49] also highlighted the existence of the kinetic sorption sites in the soil, showing that the Zn desorption curve in the soil demonstrates the presence of a labile and another, less labile fraction. For this reason, the use of the two-site sorption model is more suitable to account for such phenomenon. Moreover, the activation energy necessary for TM desorption was reported to be higher than for adsorption [50], i.e., desorption rates are slower than adsorption rates. This indicates that, over the long-term, metal contaminants such as Zn will slowly migrate to greater soil depths and their surface concentrations will decrease.

Movement of Cu in the soil was different than movement of Zn. After suspending PS applications, the downward movement of Cu slowed, leading to a slight increase in the total Cu concentrations in the upper 25 cm, whereas Zn concentrations increased slightly in all soil layers (Fig. 3). Studying field experiments involving soil applications of sewage sludge, Han et al. [51] mentioned that at low doses, TMs were transported and repartitioned among the solid soil constituents very slowly and, with time, concentrations would return to an equilibrium state of un-amended soils. In our work, the use of EDTA extractions efficiently determined levels of Zn and Cu sorbed to kinetic sites of the soil. Labanowski et al. [38]

mentioned that the amounts of heavy metals extracted from the soil by EDTA closely coincided with the anthropogenic metal pool. Hence, EDTA extractions are indicative for long-term predictions of metal migration at different depths in soils.

3.2.2. Scenario II: continued PS applications

After an additional 50 years of PS applications, Zn concentrations in the soil solution in 2058 would increase in all soil layers compared to 2008, notably at depths below 20 cm (Fig. 3). The two-site sorption model predicted a transfer of 208 kg Zn ha^{-1} (43.6% of Zn added between 2008 and 2058) to depths below 60 cm. Such results are consistent with the findings of Abollino et al. [52], who also reported a higher TM mobility in contaminated soils than in uncontaminated soils. However, they concluded that such contaminants were potentially more environmentally damaging. Our model's estimates for 2058 indicate maximum Zn levels in the soil solution of 1.7 mg l^{-1} at a depth of 5 cm and less than 1.0 mg l^{-1} at a depth of 60 cm. Such Zn concentrations are clearly below the threshold value of 5.0 mg l^{-1} established by the Brazilian Health Ministry [53] for drinking water. In addition, although consistently larger total Zn contents were predicted for the 60-cm soil profile in 2058 (508 kg Zn ha^{-1}) than in 2008 (240 kg Zn ha^{-1}), the threshold Zn concentrations set by CETESB [5] for agricultural areas (AA) were not exceeded. The maximum Zn concentration of 97.6 mg kg^{-1} observed in the upper soil layer (Fig. 3) did not exceed either the prevention value (PV-AA: 300 mg kg^{-1}) or the intervention value (IV-AA: 450 mg kg^{-1}). Hydrus-2D simulations of the impacts of continuous PS applications did not reveal risks of groundwater pollution by Zn leaching, nor of exceeding the threshold Zn concentration in any soil layer.

Predicted variations in Cu concentrations in the soil solution of all soil layers were much smaller than for Zn. Higher Cu concentrations occurred at depths above 35 cm (Fig. 3). An estimated Cu transfer to depths below 60 cm during 50 years was low (7.0 kg ha^{-1}) and equal to the amount predicted for scenario I, representing 12.4% of the total Cu mass added to the soil between 2000 and 2008, but only 2.0% of the total Cu mass added between 2008 and 2058. This suggests that until 2058, Cu inputs from PS will not reach depths below 60 cm and that such outputs are primarily controlled by water flow through the soil and the TM solution concentration in the 50–60-cm soil layer (26.9 μg l^{-1}, Table 1). However, in 2058 the contamination plume of Cu in the soil solution would penetrate deeper in the soil profile than in 2008 (Fig. 3).
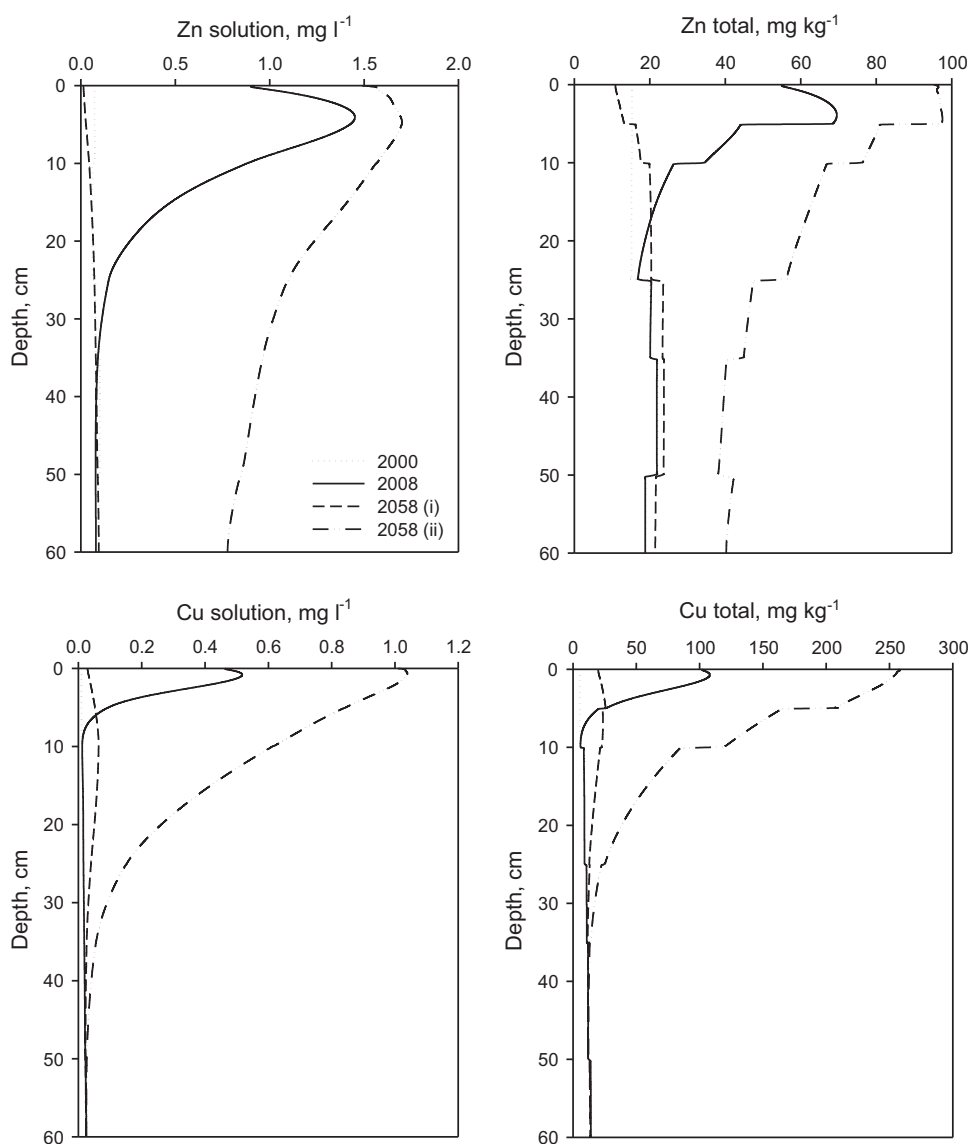
Fig. 3. Zinc (top) and copper (bottom) solution concentrations (left) and total concentrations (right) in the soil profile at 2000, 2008, and 2058 for two scenarios: (i) discontinued and (ii) continued pig slurry applications; simulated with Hydrus-2D using the hypothesis of a two-site sorption model with a reduced sorption rate. Note that different concentration scales are used on the X-axis.

Therefore, if applications of PS were maintained, the transfer of Cu to groundwater would be likely to increase significantly after 2058. Yet, the Cu concentrations remain below the threshold value for drinking water in Brazil [53] (2.0 mg l^{-1}), and 50-years of continued PS applications would not represent a risk of groundwater Cu pollution.

However, the total Cu soil concentrations are likely to represent environmental risk in case of continued PS applications. Simulated Cu concentrations in 2058 increased to 259 mg kg^{-1} at a depth of 1 cm (compared to 108 mg kg^{-1} in 2008) and to 207 mg kg^{-1} at a depth of 5 cm. According to CETESB [5], such concentrations exceed the IV-AA value of 200 mg Cu kg^{-1}. In such a case, the regulatory agency highlights direct and indirect potential risks to human health under the Agricultural Exposure Scenario. Moreover, in 2058 elevated Cu concentrations (180–100 mg kg^{-1}) were also predicted at a 5–10-cm depth (Fig. 3), representing environmental risk if PS applications were continued after 2058. At depths of 15–20 cm, simulated soil Cu concentrations remained below the Prevention Value (60 mg Cu kg^{-1}, [5]), referring to the soil's capacity to sustain its primary functions, such as protecting the ecological receptors and the quality of the groundwater. For soil depths below 25 cm, Cu

concentrations did not exceed 35.0 mg kg^{-1}, the Quality Reference Value [5], presenting no environmental risk.

Our predictive modeling of the fate of TMs revealed risks of strong Cu accumulation at the soil surface, notably in the upper 10 cm. Mechanical homogenization by mixing top soil layers and thus incorporating Cu to greater depths may represent an efficient management strategy to lower such too high surface TM concentrations. Soil management in regions where organic residues with potential hazardous impacts are disposed should be different than in regions with the traditional agricultural production under no-tillage systems. Even in unique agricultural production systems, temporary turning of soil under no-tillage is an alternative strategy not to be ignored [54]. Yet, lowering the surface TM concentration by mechanical tillage does not reduce the total accumulated metal mass.

4. Conclusion

We used Hydrus-2D with a two-site sorption model with a reduced kinetic rate constant and with measured soil hydraulic characteristics to reproduce vertical distributions of Zn and Cu

measured in an experimental plot soil profile after 8 years of repeated pig slurry applications. We considered the satisfactory correspondence between simulated and field-observed TM distributions to represent a direct model validation. We then used the validated model to predict Zn and Cu movements during the future 50 years. If PS applications are discontinued, estimated TM concentration levels, notably of Zn, would considerably decrease in surface layers. However, if PS applications continue, the model estimated a much higher Zn transfer to depths below 60 cm than for the scenario of discontinued PS applications. In addition, Cu transfer below the 60-cm depth was similar for both scenarios. Nevertheless, the transport of Zn and Cu by percolating water did not present risks in the future for polluting groundwater. Yet, a continuous application of pig slurry would lead to consistent Cu accumulation in the soil surface layer, exceeding the Brazilian threshold for copper in agricultural soils.

Acknowledgements

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