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Soil tillage to reduce surface metal contamination – model development and simulations of zinc and copper concentration profiles in a pig slurry-amended soil



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ARTICLE INFO

Article history:

Received 18 September 2013

Received in revised form 23 June 2014

Accepted 25 June 2014

Available online xxx

Keywords:

Hydrus-1D

Trace metals

Organic waste

Solute movement

Groundwater pollution

Surface accumulation

ABSTRACT

Long-term applications of organic amendments, such as pig slurry (PS), may represent environmental risk of soil and water pollution by trace metals (TM). Our objective was to examine different soil and manure management scenarios that enhance the long-term agricultural use of soils under repetitive PS applications while avoiding environmental risk. Firstly, we developed a new module for simulating the impacts of soil tillage frequencies in Hydrus-1D. Secondly, we used a previously validated modeling approach to predict the surface accumulation and movement of the TM during the next 100-year in the soil under different PS doses (80 and 40 m³ ha⁻¹ cultivation⁻¹) and tillage frequencies (no-tillage and 20, 10, and 5-year tillage). No-tillage simulations revealed consistent TM surface accumulations, reaching the soil threshold value for Cu in the 0–20 cm layer after 86 years of PS amendments at high doses, but in layers 0–5, 0–10, and 5–10 cm, this concentration was already reached after 17, 38, and 75 years, respectively. While soil tillage reduced TM concentrations over the top 20 cm of the soil profile, it increased their transfer to deeper layers. Periodical soil tillage each 5, 10, and 20 years was found to allow PS applications without reaching the Cu threshold value in soil during 100 years. However, soil solution concentrations of Zn reached the threshold values for groundwater. Therefore, the best manure management practice for the long-term PS disposal with respect to Zn and Cu concentrations in soil is the application of moderate PS rates.

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1. Introduction

Long-term applications of organic waste amendments on soils may lead to a notable accumulation of mineral and organic micropollutants in the soil's surface layer. Hence, such practices potentially represent environmental risk of soil and groundwater pollution. Recently, we have carried out validating and prospective modeling work, using the Hydrus software package, to simulate the movements of trace metals (TM) zinc (Zn) and lead (Pb), derived from past industrial metallurgical activities, in agricultural

soils under different long-term land uses in northern France (Rheinheimer et al., 2013; Mallmann et al., 2012a). Then we have successfully applied the same modeling approach to simulate the movement of Zn and copper (Cu) in an Alfisol in Southern Brazil, managed under repetitive applications of pig slurry (PS) (Mallmann et al., 2012b). In addition to major nutrients such as phosphorus (P), nitrogen (N), and potassium (K) (Lourenzi et al., 2013), PS contains consistent amounts of oligo-nutrient elements such as Zn and Cu that at high concentrations become contaminants (Giroto et al., 2010; Berenguer et al., 2008; L'Herroux et al., 1997). Both Zn and Cu are consistently present in pigs' diet, representing mineral supplements or growing elements, aiming to increase the productivity index of these animals (Li et al., 2005). A large fraction of Zn and Cu, however, is not absorbed by the animal

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gastrointestinal tract and is released via pig manure (Nicholson et al., 2003). In the work of Mallmann et al. (2012b), we showed how a continuous application of PS on the Alfisol for 50 years would lead to large Zn and Cu contents in the 0–5 cm soil layer. Particularly for Cu, the simulated soil concentrations in this layer exceeded the Brazilian guideline intervention value for agricultural areas of 200 mg kg^{-1} , established by the Conselho Nacional do Meio Ambiente (CONAMA, 2009).

Such strong accumulation of TMs at the soil's surface is directly related to agricultural land management practices of no-tillage, currently widely used in Brazil. More than 60% of cultivated land (23.6 million hectares) is farmed as a no-till system, maintaining the soil covered and unplowed, sowing is performed directly on the soil surface without its previous preparation and crop rotation is used (Mello and van Raij, 2006). Therefore, no-tillage practices in agricultural lands under long-term PS amendments will favor the accumulation of Zn and Cu within the first few centimeters of the soil profile, and reduce the movement of these TMs to layers below the depth of 20 cm. In this view, the no-tillage management represent a disadvantage in comparison to the conventional tillage management, where the surface layer is annually mixed by plowing and, consequently, the concentrations of added micro-pollutants are mechanically homogenized over the entire plow-depth (about 20 cm). Therefore, introducing periodical soil tillage, as a sustainable land management practice, represents an original solution for reducing the strong surface accumulation of the TMs by mixing them over a greater depth. It also represents a solution to comply with Brazilian environmental guidelines on maximum TM values (CONAMA, 2009), which may be restrictive for long-term organic amendments on no-tillage farming systems.

Soil tillage practices, however, by homogenizing the plow layer and thus reducing the soil solution metal concentrations in the uppermost soil layer and increasing them at the bottom of the tilled layer, favor the downward movement of the TMs via the soil solution to depths below the plow layer. They may then propagate down to the bottom of the soil profile and require a more detailed examination, especially at depths close to the groundwater table. Therefore, the threshold values for groundwater established by the Brazilian legislation (CONAMA, 2009), i.e. 1.05 and 2.0 mg L^{-1} for Zn and Cu, respectively, should not be reached at deeper soil depths to avoid risks of groundwater pollution.

The aims of the present work were to examine current and adapted soil and manure management practices for a sustainable agricultural land use of soils under repetitive PS applications, while avoiding environmental pollution risks. For that, we used Hydrus-1D to model the future movement of Zn and Cu in an Alfisol contaminated by repetitive applications of PS. First, we developed a new module that simulates the effects of soil tillage at different time intervals and implemented it in Hydrus-1D. Second, we used the validated modeling approach of Mallmann et al. (2012a,b) to predict the surface accumulation, soils solution concentrations, and redistribution of TMs in the Alfisol profile for different PS doses and varying soil tillage frequencies during the next 100 years. Simulated soil and solution concentrations of Zn and Cu were then compared with current Brazilian guideline values.

2. Materials and methods

2.1. General and site characteristics, soil sampling and analysis

The studied soil profile, a typic Hapludalf (USDA, 2003), is located at the experimental fields of Federal University of Santa Maria, Rio Grande do Sul State, Brazil ($29^{\circ}42'52''\text{S}$ and $53^{\circ}42'10''\text{W}$, 90 m altitude). An experiment that was conducted during eight years (01/2000–01/2008) under the no-tillage management and

that received applications of different PS doses (0, 20, 40, and $80 \text{ m}^3 \text{ ha}^{-1}$) serves as the basis of this study. The PS doses were applied at the soil's surface before each cultivation; one time in 2007, two times in 2000, 2004, and 2005, and three times in 2001–2003, and 2006.

Soil samples from a plot with the $80 \text{ m}^3 \text{ ha}^{-1}$ PS treatment were collected in January 2008 from soil layers of 0–5, 5–10, 10–25, 25–35, 35–50, and 50–60 cm depths, with three subsamples per layer. We determined the soil's particle density, water retention curve (SWRC), particle size distribution, saturated soil hydraulic conductivity (K_s), bulk density, total porosity, $\text{pH}_{\text{H}_2\text{O}}$, total content and desorption curves of Zn and Cu, and organic carbon. Analytical methods and procedures used for the determination of these parameters are extensively described in Mallmann et al. (2012b). The results are shown in Table 1.

2.2. Model parameterization and solute transport simulations

Hydrus-1D (Šimůnek et al., 2008) was used to simulate one-dimensional unsaturated water flow and Zn and Cu transport in a vertical domain for a one century period. The analytical models of van Genuchten and van Genuchten–Mualem were used to describe water retention curves and unsaturated hydraulic conductivity functions (van Genuchten, 1980), respectively. This software also requires additional hydro-physical and chemical parameters to run all desired simulations. For Brazilian climatic conditions with high intensity rainfalls, the most important physical parameter is the saturated hydraulic conductivity (K_s), since it determines water infiltration and percolation through the soil profile, the transport of dissolved solutes, and their transfer to greater depths. Additional key parameters include the soil residual (θ_r) and saturated (θ_s) water contents, the shape parameters α_{VG} and n_1 obtained from SWRC, and the pore connectivity/tortuosity factor (L).

Mallmann et al. (2012a,b) and Rheinheimer et al. (2013) used the TM profile concentrations collected in field experiments to show that the two-site sorption model reproduced better the TM movement in the soil compared to the equilibrium sorption model. Similar conclusions were obtained by many other researchers who collected metal breakthrough curves from soil column studies. For example, Chotpanarat et al. (2012) showed that the two-site sorption model fitted both rising and declining branches of breakthrough curves of heavy metals much better than the equilibrium sorption model. Pang et al. (2002) showed that metal interactions with the soil indicate the presence of chemical non-equilibrium in the system, due to the presence of long tailing in breakthrough curves. Moreover, according to Pang and Close (1999), non-equilibrium sorption models describe better the transport of heavy metals and provide better explanations for the spreading and asymmetry of breakthrough curves.

In this way, the chemical parameters required by the two-site model include the initial Zn and Cu solution concentrations, and the Freundlich's n and K_F parameters, describing the equilibrium adsorption/desorption process. The most important parameters characterizing the sorption kinetics are β and λ . The β parameter defines the amounts of sorption sites in chemical equilibrium with the soil solution. In our conditions, this parameter decreases with depth. The lower the value of this parameter, the more important are the sorption sites that react slower with the dissolved heavy metals. These sites are sometimes called kinetic sorption sites. As the fraction of kinetic sorption sites increases, the λ parameter, describing the sorption rate, becomes more important. The lower its value, the slower the adsorption to the soil sorption sites, and, consequently, the higher the solute concentration in the soil solution and the faster the transport to deeper layers. However, during the desorption phase, the low value of the λ parameter

Table 1

Hydro-physical and chemical soil parameters, and initial values required for simulations with Hydrus-1D.

Parameter ^a	Soil layer (cm)						
	1 (0–5)	2 (5–10)	3 (10–25)	4 (25–35)	5 (35–50)	6 (50–60)	Mixed (0–20)
Soil							
pH	5.51	5.43	5.41	5.12	5.01	5.06	5.44
Clay, g kg ⁻¹	158	174	182	188	176	173	174
Silt, g kg ⁻¹	376	354	350	322	345	393	357
Sand, g kg ⁻¹	466	472	468	490	478	434	469
OC, g kg ⁻¹	24.5	12.4	9.3	8.6	7.8	6.3	13.9
Bd, g cm ⁻³	1.33	1.51	1.56	1.46	1.46	1.41	1.49
K _s , cm dia ⁻¹	190.49	93.85	65.93	58.78	216.8	301.8	104.05
θ _s , cm ³ cm ⁻³	0.386	0.393	0.406	0.380	0.322	0.324	0.398
θ _r , cm ³ cm ⁻³	0.142	0.139	0.142	0.122	0.109	0.117	0.141
α _{VC} , cm ⁻¹	0.1834	0.1248	0.2834	0.127	0.092	0.1564	0.2168
n ₁	1.3696	1.4095	1.367	1.4092	1.4891	1.3632	1.3714
L	0.5	0.5	0.5	0.5	0.5	0.5	0.5
D, cm	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Zinc							
Total, mg kg ⁻¹	69.36	39.91	22.74	16.33	18.97	21.47	38.69
Solution, μg L ⁻¹	177.02	146.71	98.11	106.95	145.78	164.56	129.99
β	0.56	0.29	0.14	0.04	0.04	0.02	0.36
λ, 10 ⁻⁵ day ⁻¹	4.29	4.13	3.04	1.82	1.44	2.82	3.97
K _F	4.41	2.87	2.12	1.44	1.37	1.43	2.88
n	0.65	0.65	0.65	0.65	0.65	0.65	0.65
Copper							
Total, mg kg ⁻¹	59.38	22.77	12.02	7.73	12.02	12.02	26.55
Solution, μg L ⁻¹	80.34	36.92	20.93	15.77	26.35	26.85	39.78
β	0.61	0.46	0.21	0.13	0.07	0.06	0.49
λ, 10 ⁻⁵ day ⁻¹	6.87	4.17	2.61	2.49	1.83	3.10	5.33
K _F	96.38	71.57	61.22	50.07	50.34	49.53	72.60
n	0.85	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_{VC} and n₁: retention parameters; L: pore-connectivity factor; D: longitudinal dispersivity; 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.

produces a slow rate of desorption from the soil sorption sites to the soil solution and, consequently, the slower transport of the heavy metals to deeper soil layers.

As shown in Table 1, the β values vary significantly between different soil layers. This is because these values do not depend only on soil texture, which is very similar throughout the soil profile. Both Zn and Cu total concentrations in the soil affect significantly the value of this parameter. As their concentrations increase, the saturation of soil sorption sites increases as well, resulting in weaker bonds between the soil functional groups and the chemical, and higher amounts of the early extractable metal (in percentage value). Consequently, the fraction of easily extractable metals tends to be much higher in soil layers with higher metal concentrations (i.e., in the surface soil layer). Other soil characteristics that can strongly affect the β values are the organic carbon contents and soil pH (Carrillo-González et al., 2006). The organic carbon in the soil can bond to Cu or Zn and increase or decrease their solubility, depending on the type and amount of the compound. With respect to soil pH, the higher its value, the weaker the metal binding, which favors the desorption from the soil. It is also important to emphasize that the β parameter is related to Q₁/Q_{total}, where Q₁ is the fraction of the metal easily extractable with EDTA and Q_{total} is the total content of the metal in soil (Mallmann et al., 2012a,b). As the natural content of Zn and Cu in our soil is low (and has very low desorbed values with EDTA) and the concentration of metal in the surface layer of the soil under PS applications is high (exogenous contents of metals have high desorption when extracted with EDTA), the β parameter tends to be high at the surface and very low at deeper layers, especially in places with low downward movement of metals, as in our study.

Hydro-physical and chemical parameters were determined for all soil layers from the experiment with the 80 m³ ha⁻¹ PS dose, following the procedure described by Mallmann et al. (2012b), and are presented in Table 1.

Numerical solutions of the Richards equation describing variably-saturated water flow, and the convection–dispersion equation describing solute transport, require the specification of initial and boundary conditions. The initial concentration profiles of Zn and Cu were defined based on the analysis of soil samples collected at the experimental site, as described in Section 2.1. The atmospheric and free drainage boundary conditions were considered in Hydrus-1D simulations at the soil surface and bottom, respectively. Daily precipitation and evapotranspiration data from 01/01/2000–01/01/2008 used by Mallmann et al. (2012b) (Fig. 1) were used repeatedly 12.5 times to cover the entire simulated period of one century. Average annual rainfall and evapotranspiration were 1678 and 921 mm, respectively.

The total amounts of TMs added to the soil during the simulated 100-year period, considering a PS dose of 80 m³ ha⁻¹ cultivation⁻¹, were 954 and 704 kg ha⁻¹ of Zn and Cu, respectively. For simulations that considered the 40 m³ ha⁻¹ doses, corresponding amounts were half, i.e., 477 and 352 kg ha⁻¹, respectively. More details about the temporal distribution of TMs during the simulation and their amounts added to the soil at each time can be found in Mallmann et al. (2012b). This dataset was also repeated 12.5 times and formed our base plan for the TMs introduction at the soil surface.

We simulated the vertical movement of Zn and Cu in soil using Hydrus-1D, for 100 years (2008–2108), using a two-site sorption chemical model validated by Mallmann et al. (2012a,b), which considers that the total TM concentration in the soil is partitioned

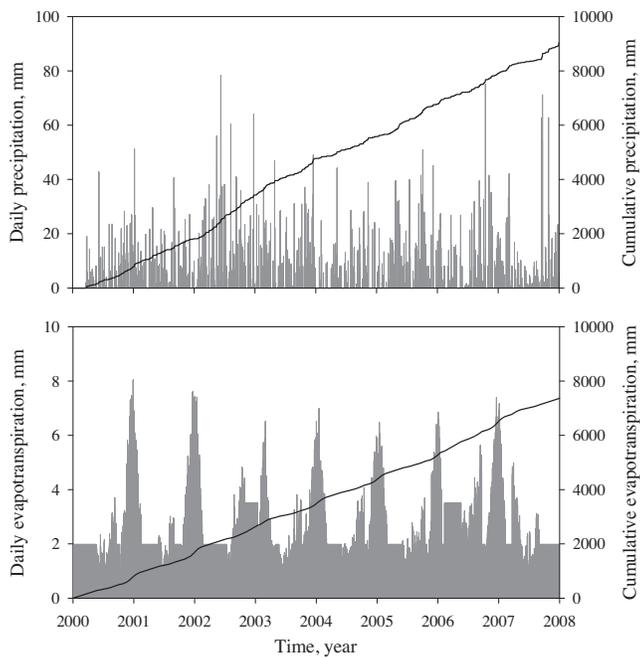


Fig. 1. Daily (bars) and cumulative (line) precipitation (top) and crop evapotranspiration (bottom) at the experimental site in Santa Maria, Rio Grande do Sul State, Brazil, from 2000 to 2008. Constant evapotranspiration values of 1.98 mm day^{-1} correspond to fallow periods and represent average values from places close to the experimental site. Source: Sistema Irriga[®]–UFSM.

between soil water and instantaneous and kinetic sorption sites. Our simulations included estimations of TM quantities transported to soil layers below a depth of 60 cm. Eight tested scenarios included different PS doses applied on the soil's surface before each cultivation and different frequencies of soil tillage. Scenarios A through D were ran for $80 \text{ m}^3 \text{ ha}^{-1}$ PS doses (a high dose) and soil management practices with no-tillage (A) or tillage of the upper 0–20 cm layer every 20 (B), 10 (C), and 5 (D) years. These scenarios are hereafter referred to as 80 m^3 no-till, 80 m^3 20y-till, 80 m^3 10y-till, and 80 m^3 5y-till, respectively. Scenarios E through H involved $40 \text{ m}^3 \text{ ha}^{-1}$ PS doses (a moderate dose) and the same sequence of soil tillage frequencies, hereafter referred to as 40 m^3 no-till, 40 m^3 20y-till, 40 m^3 10y-till, and 40 m^3 5y-till, respectively. Scenarios in which soil tillage was considered every year are not presented here, because they did not show any significant differences compared to scenarios with soil tillage every 5 years. Moreover, such a one-year tillage frequency would be in contradiction with the actual no-tillage conservative soil management policies promoted in Brazil, a concept we kept in mind in our work since it is of great interest for practical agricultural applications.

For simulations of scenarios that used periodical soil tillage (B–D and F–H), we changed the soil characteristics for the upper 20 cm. This 0–20 cm layer was referred to as a mixed layer, for which we used weighted average values of soil characteristics from the layers 1, 2, and 3 (Table 1). Indeed, the first soil tillage in the simulations was performed on the first day, and then repeated according to particular frequencies of each scenario.

2.3. Development of a soil tillage module for Hydrus-1D

To be able to perform simulations for scenarios with periodical soil tillage, we have developed a new module for Hydrus-1D. This module allowed us to select different depths and frequencies (dates) of soil tillage. At the time of specified tillage, Hydrus-1D

simply homogenizes the surface layer subject to tillage. It first integrates water over the tillage depth and then assigns the average water content to this entire soil layer as follows:

$$\bar{\theta} = \frac{\int \theta(z) dz}{L_{\text{tillage}}} \quad (1)$$

where $\theta(z)$ is the water content ($\text{cm}^3 \text{ cm}^{-3}$) at a depth z at time of tillage, L_{tillage} is the depth (cm) of tillage, and $\bar{\theta}$ is the average water content ($\text{cm}^3 \text{ cm}^{-3}$) over the tillage depth after tillage.

Similar homogenization (averaging) is done for solutes. For a nonreactive solute, the averaging would be done as follows:

$$\bar{c} = \frac{\int \theta(z)c(z) dz}{\bar{\theta} L_{\text{tillage}}} \quad (2)$$

where $c(z)$ is the liquid phase concentration (mmol cm^{-3}) at a depth z at time of tillage and \bar{c} is the average liquid phase concentration (mmol cm^{-3}) over the tillage depth after tillage.

Since the solute transport model adopted in this study considers a reactive solute, which is present in the liquid phase as well as instantaneously and kinetically sorbed to the solid phase, the tillage routine of Hydrus-1D needs to consider all these phases. The code first integrates the solute mass, which is present in the equilibrium and nonequilibrium states as follows:

$$s_e = \int [\theta(z)c(z) + f\rho s_e(z)] dz \quad (3)$$

$$s_k = \int [(1-f)\rho s_k(z)] dz \quad (4)$$

where s_e and s_k are solid phase concentrations at equilibrium (mmol cm^{-3}) and kinetic sorption sites (mmol g^{-1}), respectively, and S_e and S_k are solute masses in equilibrium (mmol cm^{-2}) and nonequilibrium (mmol cm^{-2}) states over the tillage depth, respectively. The average solid phase concentration in the nonequilibrium state is calculated similarly as shown above for a nonreactive solute:

$$\bar{s}_k = \frac{S_k}{(1-f)\rho L_{\text{tillage}}} = \frac{\int [(1-f)\rho s_k(z)] dz}{(1-f)\rho L_{\text{tillage}}} \quad (5)$$

However, since the solid phase concentration at equilibrium sites is calculated using the Freundlich isotherm, which is a nonlinear equation, a root finding routine needs to be adopted to calculate the average liquid phase concentration from the solute mass in equilibrium state in the tillage depth, S_e .

The two main input parameters into the tillage module, apart from water content and concentration distributions in the tillage soil layer, are the frequency of tillage (e.g., no-tillage and/or tillage each 5, 10, and 20 years) and the thickness of the tilled soil layer. It is one of the objectives of this study to evaluate the effects of the frequency of tillage on the transport of heavy metals.

There are several limitations of this new tillage module. The module neglects any possible changes in soil hydraulic properties, which are likely to occur during tillage. In our simulations, we assumed that as a result of tillage, the soil hydraulic properties in the tilled layer were constant over time and equal to average properties of the top three layers (Table 1).

Another source of uncertainty is the extent of mixing during tillage. Limiting examples of mixing may be defined as (a) no mixing, (b) complete mixing, and (c) a complete turnover of the tilled soil layer, when material (including moisture and solutes) from the top will be moved to the bottom and vice versa. Since the new tillage module assumes complete mixing, in simulations presented in this study we account for scenarios without mixing (no-tillage scenario) and with complete mixing (scenarios with tillage each 5, 10 and 20 years).

3. Results

3.1. Water mass balance in soil

Simulations of scenarios without soil tillage displayed an average water storage in the soil profile (60 cm deep) of 14.5 cm. Moreover, during these 100-year simulations, water evapotranspiration and drainage reached cumulative amounts of 5364 and 5944 cm, respectively. Scenarios with periodical soil tillage, compared to the no-tilled soil, had a similar average water storage of 14.7 cm. However, evapotranspiration was 16.7% lower and drainage was 15.2% higher. The frequency of soil tillage did not change noticeably the water balance among different tilled scenarios. The differences among various scenarios did not result from the soil tillage practices simulated by the new module, but from different soil hydraulic parameters used for the tilled layer (0–20 cm) in scenarios with soil tillage (Table 1), as explained in Section 2.2.

3.2. Prospective modeling of 100 years of Zn and Cu movement without tillage

Simulations of scenarios without soil tillage produced a high TM retention in the soil surface layer (0–5 cm). After 100 years, the total Zn concentration in the first soil layer increased from an initial value of 69.4 to 247.0 mg kg⁻¹ in scenario A (80 m³ no-till) (Fig. 2A) and to 160.0 mg kg⁻¹ in scenario E (40 m³ no-till) (Fig. 2E). For the same scenarios, the Cu increases were even higher, i.e., from an initial value of 59.4 to 445.0 and to 246.0 mg kg⁻¹, respectively (Fig. 3A and 3E). Moreover, continuous PS applications with both doses increased Zn concentrations in the entire soil profile (up to 60 cm depth). At the soil bottom, the initial Zn concentration (21.5 mg kg⁻¹) increased substantially and reached 47.9 and 32.9 mg kg⁻¹ after one century for PS doses of 80 and 40 m³ ha⁻¹, respectively (Fig. 4). On the other hand, the Cu concentrations at the 60 cm depth almost did not change during the simulation

period, and the Cu concentration profile showed a consistent increase only in the 0–40 cm soil layer in scenario A and in the 0–30 cm soil layer in scenario E (Fig. 5).

No-tillage scenarios also showed a great increase of TM solution concentrations in the soil profile. The Zn concentration in the soil solution increased in the entire soil profile, and the maximum values at the end of simulations were observed approximately at depths of 7–10 cm, reaching 1.50 and 0.75 mg L⁻¹ for PS doses of 80 and 40 m³ ha⁻¹, respectively (Fig. 4). Furthermore, Zn solution concentrations at the bottom of the soil profile were 1.20 and 0.60 mg L⁻¹ in scenarios A and E, respectively. These concentrations slowly increased during the simulations, leading to an increase in Zn transfer to soil layers deeper than 60 cm, reaching up to 473.0 kg ha⁻¹ (scenario A) and 231.0 kg ha⁻¹ (scenario E) after 100 years (Fig. 6). The Cu solution concentrations also increased in the whole profile, but more consistently in the upper 30 cm of the soil. The maximum (at the 1–3 cm depth) and bottom solution concentrations at the end of the 100-year simulation period were 0.97 and 0.08 mg L⁻¹ for scenario A, and 0.48 and 0.05 mg L⁻¹ for scenario E, respectively. These small bottom solution concentrations explain small transfers of Cu to soil depths below 60 cm: 21.4 and 17.3 kg ha⁻¹ for scenarios with 80 and 40 m³ ha⁻¹ PS doses, respectively.

3.3. Future Zn and Cu movement under different scenarios of soil tillage

The introduction of soil tillage data in simulations of Hydrus-1D showed that after 100 years, scenarios with soil tillage each 20, 10, and 5 years with PS doses of 80 m³ ha⁻¹ (scenarios B, C, and D) had Zn surface concentrations in the 0–5 cm soil layer of 132.9, 131.6, and 127.7 mg kg⁻¹, respectively. For scenarios with 40 m³ ha⁻¹ doses (scenarios F, G, and H), these concentrations were 87.3, 86.0, and 83.4 mg kg⁻¹, respectively (Fig. 2). For Cu, the surface concentrations reached 230.5, 210.6, and 189.4 mg kg⁻¹ when using 80 m³ ha⁻¹ PS doses (scenarios B, C and D), and 128.3, 116.3, and 107.2 mg kg⁻¹

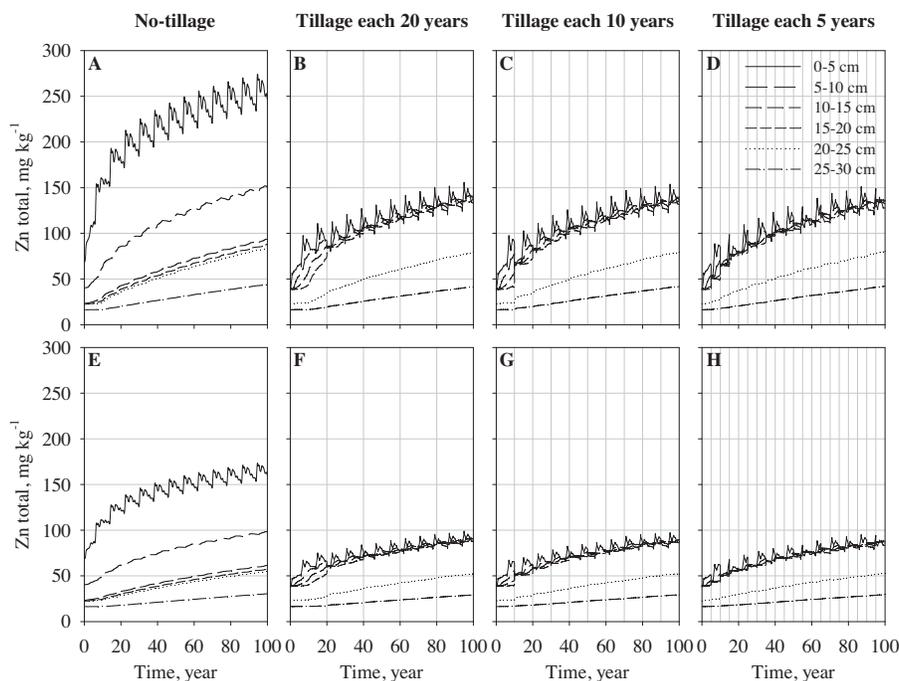


Fig. 2. Total zinc concentrations in six layers of the soil profile during one century simulations, considering scenarios with different pig slurry doses and soil tillage frequencies. Upper and lower graphs were simulated under 80 and 40 m³ ha⁻¹ cultivation⁻¹ doses, respectively. Letters A and E represent scenarios under no-tillage soil management. Vertical lines indicate soil tillage, performed with frequencies of each 20 (B and F), 10 (C and G), and 5 (D and H) years.

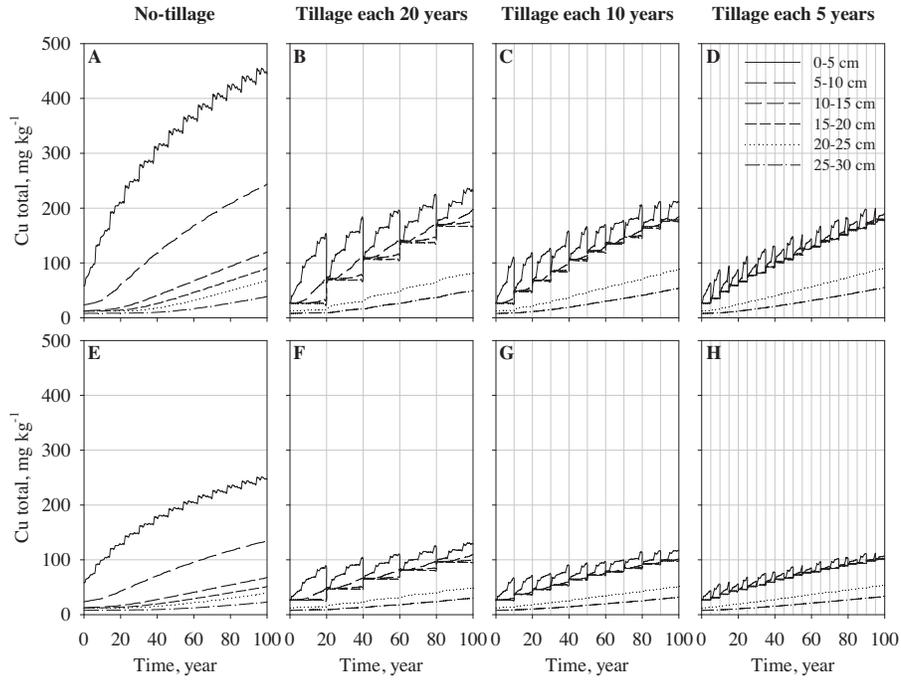


Fig. 3. Total copper concentrations in six layers of the soil profile during one century simulations, considering scenarios with different pig slurry doses and soil tillage frequencies. Upper and lower graphs were simulated under 80 and $40 \text{ m}^3 \text{ ha}^{-1}$ cultivation⁻¹ doses, respectively. Letters A and E represent scenarios under no-tillage soil management. Vertical lines indicate soil tillage, performed with frequencies of each 20 (B and F), 10 (C and G), and 5 (D and H) years.

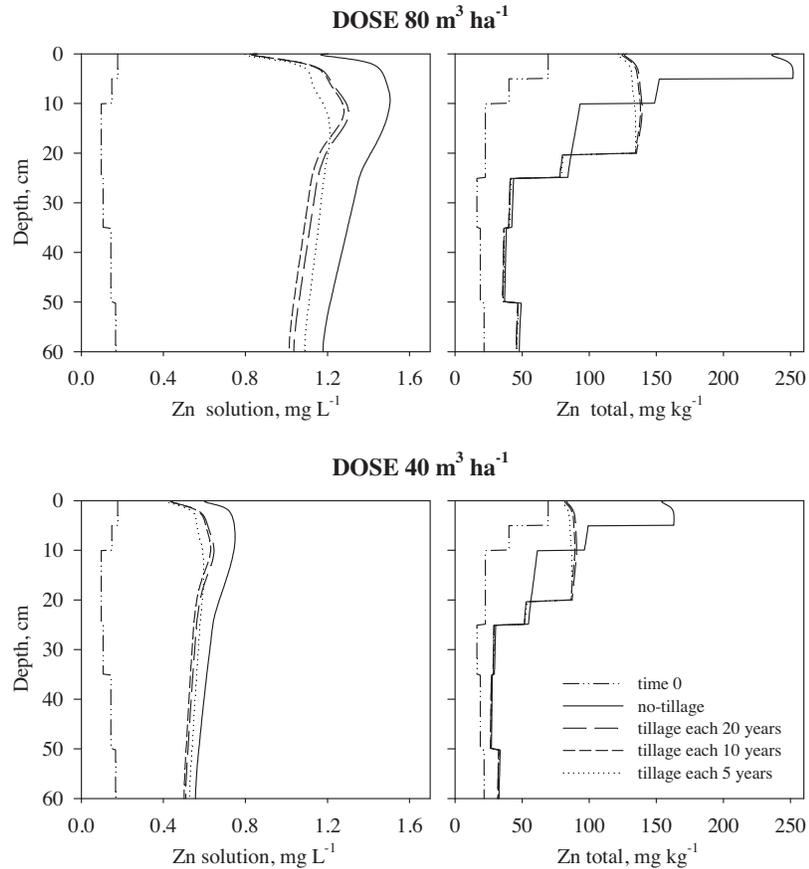


Fig. 4. Solution (left) and total (right) zinc concentrations in the soil profile under continued pig slurry applications after 100 years, considering scenarios involving two manure doses (80 and $40 \text{ m}^3 \text{ ha}^{-1}$ cultivation⁻¹) and different soil tillage frequencies (no-tillage and tillage every 20, 10, and 5 years).

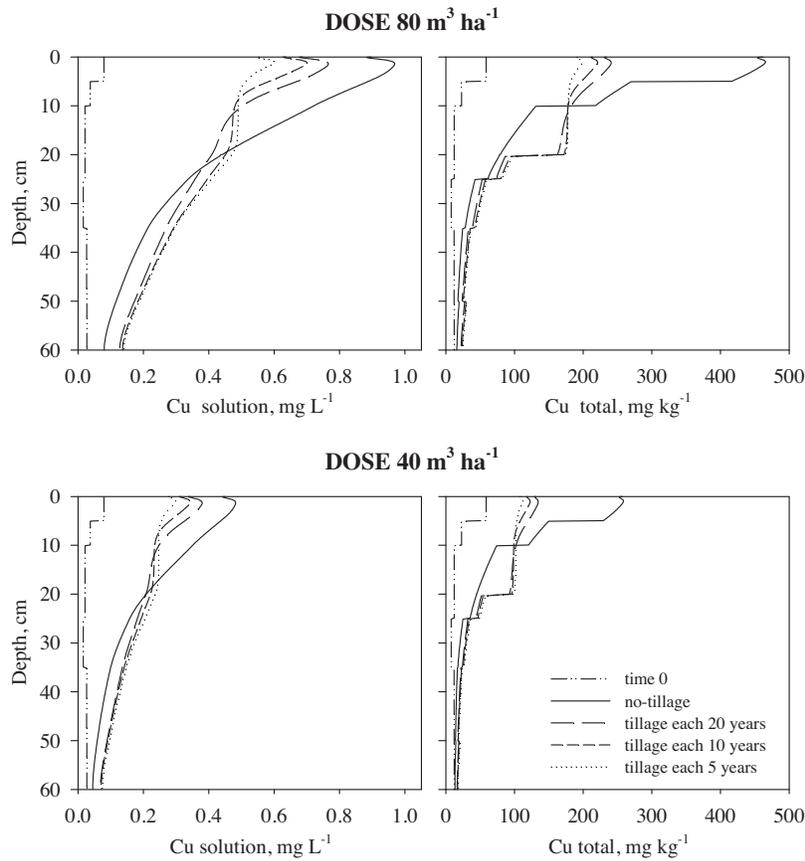


Fig. 5. Solution (left) and total (right) copper concentrations in the soil profile under continued pig slurry applications after 100 years, considering scenarios involving two manure doses (80 and $40\text{ m}^3\text{ ha}^{-1}$ cultivation $^{-1}$) and different soil tillage frequencies (no-tillage and tillage each 20, 10, and 5 years).

when using $40\text{ m}^3\text{ ha}^{-1}$ PS doses (scenarios F, G and H, Fig. 3). Although surface accumulation of Zn and Cu decreased when soil tillage was used, their concentrations in the 10–20 cm layer increased substantially, and independently of the tillage frequency. For scenarios B and F, the concentrations in this soil layer increased after 100 years to approximately 139 and 89 mg kg^{-1} for Zn (Fig. 4) and to 172 and 97 mg kg^{-1} for Cu (Fig. 5), respectively.

After 100 years, the Zn solution concentrations simulated for scenarios with periodical soil tillage were lower than for no-tillage scenarios at all soil depths. For $80\text{ m}^3\text{ ha}^{-1}$ PS doses, the maximum values reached were 1.30 , 1.28 , and 1.21 mg L^{-1} for scenarios B, C,

and D, respectively, and bottom values (60 cm depth) were 1.04 , 1.01 , and 1.09 mg L^{-1} (Fig. 4). For moderate PS doses ($40\text{ m}^3\text{ ha}^{-1}$), the Zn maximum and bottom solution concentrations were lower and equal to 0.65 and 0.51 mg L^{-1} , respectively, for scenario B, 0.63 and 0.50 mg L^{-1} for scenario C, and 0.60 and 0.53 mg L^{-1} for scenario D (Fig. 4). The transfers of Zn to depths below 60 cm were slightly higher at all times in scenarios with soil tillage than without tillage. The total amounts of transferred Zn reached 498 , 506 , and 513 kg ha^{-1} for the high PS dose scenarios B, C, and D, respectively, and 250 , 252 , and 256 kg ha^{-1} for scenarios F, G, and H with $40\text{ m}^3\text{ ha}^{-1}$ PS doses, respectively (Fig. 6).

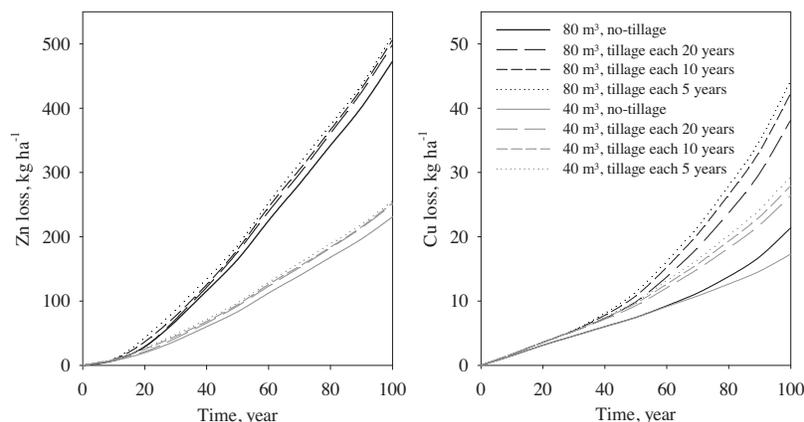


Fig. 6. Zinc (left) and copper (right) amounts transferred in the soil profile under continued pig slurry applications to depths greater than 60 cm, during future one century simulations using different manure doses (80 and $40\text{ m}^3\text{ ha}^{-1}$ cultivation $^{-1}$) and soil tillage frequencies (no-tillage and tillage each 20, 10, and 5 years).

The final Cu solution concentrations in scenarios considering periodical soil tillage were lower than in the no-tillage scenarios only in the plow layer (0–20 cm), reaching maximum values at a 1–2 cm depth of 0.77, 0.70, 0.60, 0.38, 0.34, and 0.30 mg L⁻¹ in scenarios B, C, D, F, G, and H, respectively (Fig. 5). Below the plow layer, the Cu solution concentrations in soil tillage scenarios were higher than in scenarios without tillage (A and E). The bottom values of Cu solution concentrations were 0.128, 0.136, 0.141, 0.068, 0.071, and 0.075 mg L⁻¹, respectively, for scenarios B, C, D, F, G, and H (Fig. 5). Thus, the cumulative amounts of Cu loss to depths below 60 cm when using PS doses of 80 m³ ha⁻¹ were 38.1, 42.3, and 44.3 kg ha⁻¹ for scenarios B, C, and D, respectively, and using PS doses of 40 m³ ha⁻¹, they were 26.4, 27.9, and 29.4 kg ha⁻¹ for scenarios F, G and H, respectively (Fig. 6).

4. Discussion

4.1. Effects of soil tillage on Zn and Cu in the top soil

The assessment of risks related to Zn and Cu accumulations in soils requires a comparison between measured or simulated TM concentrations and those established by regulatory bodies (Mantovi et al., 2003). Considering no-tillage scenarios, the Zn and Cu concentrations in the soil surface layer increased significantly during 100 years, especially for the 80 m³ ha⁻¹ PS dose applications. For this scenario, the Cu concentration in the

0–5 cm surface layer exceeded 200 mg kg⁻¹ after 17 years (Fig. 3), in the 0–10 cm layer after 38 years, in the 5–10 cm layer after 75 years, and in the entire 0–20 cm layer after 86 years (Fig. 7). This Cu concentration (i.e., 200 mg kg⁻¹) refers to the Brazilian threshold value, also defined as an intervention value for agricultural soils (CONAMA, 2009). However, the law establishes that the entire 0–20 cm layer needs to be considered to evaluate the concentration limits of a soil. In this way, the threshold value for Cu in scenario A was reached only after 86 years and even at the end of the simulation the Cu concentration was only slightly higher, i.e., 216 mg kg⁻¹ (Fig. 7).

When the PS doses of 40 m³ ha⁻¹ were used, the average Cu concentration in the surface 0–5 cm layer exceeded 200 mg kg⁻¹ 38 years later than when the 80 m³ ha⁻¹ PS doses were used (Fig. 3). In this case (in scenario E), the soil threshold value of CONAMA (2009) (200 mg kg⁻¹ in the 0–20 cm soil layer) was not reached during the 100-year simulation. The final average Cu concentration in the 0–20 cm soil layer reached only 120 mg kg⁻¹ (Fig. 7). For Zn, although its surface concentrations under no-tillage scenarios also strongly increased, they did not exceed the maximum guideline concentrations (450 mg kg⁻¹) of CONAMA (2009) in either of PS doses scenarios.

The main effect of considering soil tillage was related to a reduction of the surface accumulation of TMs. This effect was more pronounced for Cu; the scenarios with a 20, 10, and 5-year soil tillage frequencies lowered the surface Cu concentrations below

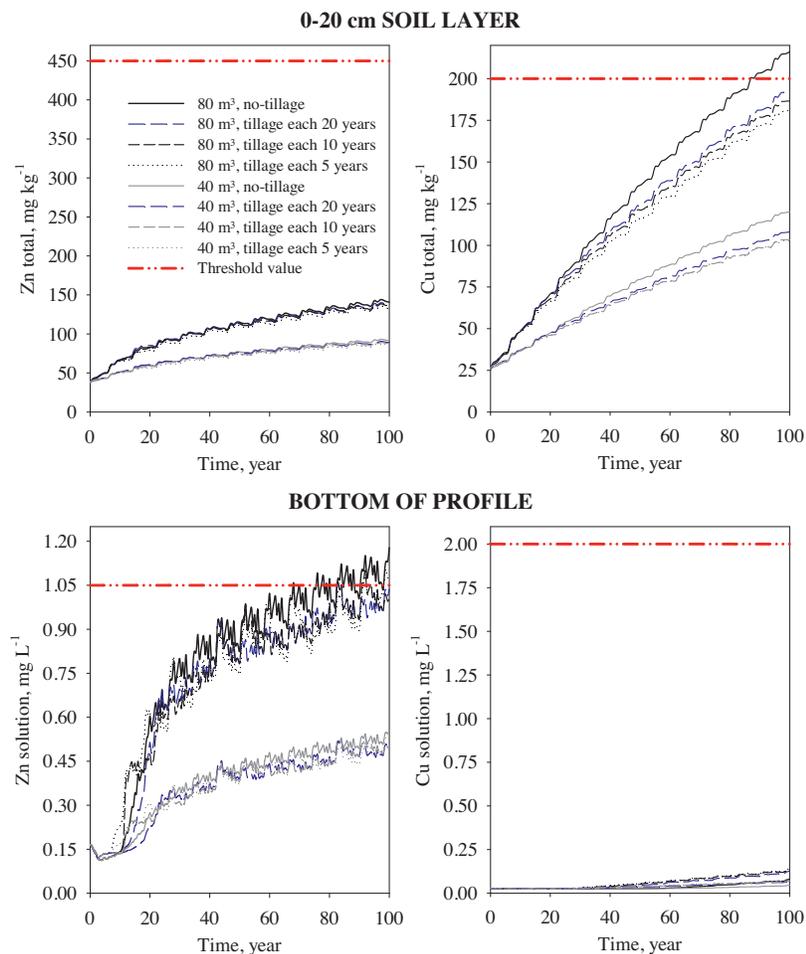


Fig. 7. Zinc (left) and copper (right) total concentrations at the top 0–20 cm soil layer and solution concentrations at the bottom of the soil profile (60 cm depth) under continued pig slurry applications during future one century simulations using different manure doses (80 and 40 m³ ha⁻¹ cultivation⁻¹) and soil tillage frequencies (no-tillage and tillage each 20, 10, and 5 years).

the Brazilian threshold value for agricultural soils when the $80 \text{ m}^3 \text{ ha}^{-1}$ PS doses were used (scenarios B, C, and D). However, for soil tillage to be effective, it needs to be done down to a depth of 20 cm, and not only its shallow version for the upper 5 or 10 cm. As shown in Scenario A, the high Cu concentrations of 0–5 and 5–10 cm layers need to be distributed over the entire 0–20 cm layer. Lowering of Cu surface concentrations by soil tillage not only allows for the continuous use of PS applications in conformity with national regulations, but also reduces potential risks of TM transfers by surface runoff to surface waters, such as rivers or lakes, as related by Xue et al. (2003).

Soil tillage also resulted in an increase of Zn and Cu concentrations in the 10–20 cm soil layer, promoting a larger transfer of these TMs below the plow layer. In scenario D, 70.6% of Zn and 34.5% of Cu added to the soil during the one-century simulation period were moved from the upper 20 cm to deeper soil layers, while in scenario A (no-tillage), these amounts were 67.7 and 19.2%, respectively.

Our simulations of Zn and Cu movements in the soil profile were in good agreement with the general biogeochemical cycling dynamics of these two TMs in soil, with Zn showing higher mobility than Cu (McBride, 1994) and, consequently, generally observed higher transfers of Zn to deeper layers. Moreover, when TM additions to soil are accompanied by organic compost amendments, the difference between Zn and Cu mobility is even greater, due to the higher affinity of Cu to sorption sites in the organic matter (Díaz-Barrientos, 2003).

After one century of PS applications on soils, the soil solution concentrations of Zn and Cu in the 0–20 cm layer were lower in scenarios that considered periodical tillage than in corresponding no-tillage scenarios. One of the soil chemistry laws of Barrow (1999) indicates that the adsorption process between chemicals and soil functional groups depends to a large extent on the accessibility of these sites. Accordingly, soil tillage and corresponding breaking of soil aggregates may facilitate the access of TMs to adsorption sites in the plow layer, and thus reduce their solution concentrations.

4.2. Effects of tillage on Zn and Cu distribution at depth

Contrary to the effects observed in the upper 20 cm of the soil profile, the one century simulations did not show great differences in TM concentrations in soil layers deeper than 20 cm between scenarios with and without soil tillage. The quantities of Zn and Cu in the 20–60 cm layers at the end of simulations with comparable PS doses were very similar in all scenarios. Indeed, the total TM concentrations in these subsurface layers remained much lower than the Brazilian threshold values (CONAMA, 2009) during the 100-year simulations. Similar findings were mentioned by Seuntjens (2002) for 100-year simulations of TM movements in soil, with mean Cd concentrations in the subsoil of the plowed scenario being not significantly greater than in the “no-action” scenario, and remaining close to the background value.

The higher TM transfers from the plow layer (0–20 cm) in scenarios with soil tillage coincide with greater transfers of Zn and Cu to soil layers below 60 cm. The results presented in Fig. 6 indicate a greater loss of Zn and Cu from the upper 60 cm soil profile when soil tillage is performed. For Zn when PS doses of $80 \text{ m}^3 \text{ ha}^{-1}$ were used, such losses were 5.4, 7.0, and 8.5% greater in scenarios B, C, and D, respectively, than in no-tillage scenario A. For Cu, these percentages were much greater than for Zn, reaching 78.3, 97.7, and 107.3%, respectively, although the absolute amounts were smaller. Obviously, the 20–60 cm soil layer acts as a bypass layer for the excess TMs coming from the top soil due to soil tillage, probably because its lower Zn and Cu K_F values indicate lower adsorption capabilities when compared to the surface or mixed layers (Table 1).

4.3. Risks of Zn and Cu output from soil

Soil tillage did not lead to significant changes in the Zn and Cu solution concentrations at greater depths, as shown in Fig. 7. The TM solution concentrations at the bottom of the soil profile (60 cm depth) varied only little during the entire simulation period for scenarios with the same PS dose (Fig. 7). However, the continued PS disposal at the soil's surface notably increased TM solution concentrations in the entire soil profile, especially when applying doses of $80 \text{ m}^3 \text{ ha}^{-1}$. This increase was so high that the Zn solution concentrations at the bottom of the soil profile at the end of simulations in scenarios A and D reached values higher than the Brazilian threshold value for groundwater (1.05 mg L^{-1}) (CONAMA, 2009), and were not very different in comparison to scenarios B and C (Fig. 4). For Cu solution concentrations, a similar effect was observed, but the increase at the profile's bottom did not reach in any simulation the threshold value, which is higher for Cu (2.0 mg L^{-1}) than for Zn (CONAMA, 2009).

Comparing simulated results of the solution Zn concentrations with a threshold value of the Brazilian Health Ministry, that is higher than that of CONAMA (2009), the profile bottom concentrations, as well as those in the whole profile, remained below 5.0 mg L^{-1} , the maximum value of Zn for drinking water (BRAZIL, 2004). Although these solution concentrations were not exceeding guideline values with respect to human health, we need to consider the environmental guidelines that indicate reference values for groundwater, and that are directly linked to effects induced by a long-term PS disposal on soils.

In the view of the goal of keeping the TM solution concentrations below the threshold values, the best strategy for managing soils during one century of PS applications is to adopt the use of moderate doses, i.e., $40 \text{ m}^3 \text{ ha}^{-1}$ cultivation⁻¹. In that case, the solution concentrations at the profile's bottom after 100 years are approximately half of those found for high dose PS applications, independently of whether the soil was frequently plowed or not (Fig. 7). Reduction of PS doses implies a reduction of TM inputs and consequently, lowering of the surface TM accumulation. This was also discussed by Novak et al. (2004); who showed a positive impact of reducing manure application rates on declining topsoil total Zn and Cu accumulation.

Moreover, if soils are used for a PS disposal during a shorter time, i.e., 50 years, as previously studied by Mallmann et al. (2012b); Zn solution concentrations will not reach the threshold value. Consequently, $80 \text{ m}^3 \text{ ha}^{-1}$ PS doses will not present risk for environment if PS amendments are combined with periodical soil tillage, thus solving the problem of excessive surface accumulation of Cu, as previously highlighted by Mallmann et al. (2012b).

According to Carrillo-González et al. (2006) and Koo et al. (2005) the presence of plant roots may modify the soil environment in the rhizosphere. Plants may utilize various strategies to mobilize nutrients, such as modification of the chemical composition or association of roots with micro-organisms (Neumann and Romheld, 2002). Consequently, plant roots may play an important role in the transformation and chemical speciation of TMs in soils, which may affect their accumulation and solubility in the soil (especially in the upper layers). Additionally, plant roots can also act as biosorbents. However, it was not possible to consider these effects in our simulations with Hydrus-1D, which does not account for these processes. However, since Hydrus-1D was calibrated using experimental field data, the effects of these “non-accounted” processes should be reflected in the calibrated model, and thus the simulated results should not be significantly different, if these processes were considered directly.

Finally, it is important to emphasize that, if soil tillage is applied in the field, other soil conservation practices such as soil cover with crops and residues, and appropriate terracing must be more

carefully used. These latter practices reduce the losses of soil and chemicals due to erosion, which may be induced by soil tillage, and therefore reduce the loss of TMs by surface runoff and consequent transfer to, and contamination of, surface water bodies (Avalos et al., 2009; Blanco and Lal, 2008; Bertol et al., 2003).

5. Conclusion

We used Hydrus-1D to predict vertical movements of Zn and Cu over a period of 100 years in a pig slurry amended soil. We used a two-site sorption and transport model, previously validated by Mallmann et al. (2012a,b) and complemented it in this work with a new soil tillage module. Simulations that did not consider tillage showed a great surface accumulation of TMs, especially for Cu and for PS doses of $80 \text{ m}^3 \text{ ha}^{-1}$ cultivation⁻¹. In this scenario, the total Cu concentrations in the 0–20 cm soil layer reached the Brazilian maximum threshold value after 86 years. When PS doses of $40 \text{ m}^3 \text{ ha}^{-1}$ cultivation⁻¹ were considered, the Cu threshold limit for agricultural soils was not reached during 100 years, similarly as predicted for Zn under both PS doses in no-tillage scenarios.

We also simulated scenarios considering soil tillage of the 0–20 cm soil layer every 20, 10, and 5 years for the two PS application doses. Soil tillage promoted dilution of TMs over the first 20 cm depth, but increased the amounts of Zn and Cu transferred to deeper layers. If prolonged PS applications to soil should remain in conformity with Brazilian regulations, the slowest increases on TMs concentrations in the 0–20 cm soil layer were obtained using the scenario with tillage every 5 years. Indeed, scenarios with applications of $80 \text{ m}^3 \text{ ha}^{-1}$ PS doses indicated that the total Cu concentrations in soil remained under the threshold value during the 100-year simulation period for the 20, 10, and 5-year tillage frequencies. However, soil tillage was found less effective in reducing surface accumulation of TMs in areas with high PS doses than reducing the PS dose by half.

Moreover, in addition to decreasing the TM concentrations at the soil's surface, soil tillage also affected TM concentrations in the soil solution. Soil tillage slightly increased the transfer of Zn and Cu in the soil profile to depths larger than 60 cm. For the PS dose of $80 \text{ m}^3 \text{ ha}^{-1}$, the Zn solution concentrations at the soil depth of 60 cm were close, or exceeded, the threshold value after 100 years, presenting risk for groundwater pollution. Yet when the considered duration of PS applications was shortened, or when PS doses were reduced, the Zn solution concentrations at larger depths were no longer an environmental problem with regards to guideline values.

Hydrus-1D proved to be a very useful tool for supporting the agricultural and environmental planning, and in evaluating the impacts of modifying soil and manure management practices. Periodical soil tillage may be an efficient practice to reduce TM surface concentrations in PS-contaminated soils and to extend their agricultural use when under manure applications. However, depending on desired duration of PS disposal and requirement to meet environmental guidelines related to Zn and Cu, soil tillage must be accompanied by a reduction in PS doses applied to soil.

Acknowledgements

F.J.K. Mallmann acknowledges CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brazil) and CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico – Brazil) for postgraduate scholarships.

References

Avalos, J.M.M., Bertol, I., Fouz, P.S., Díaz, C.C., Vázquez, E.V., Gonzalez, A.P., 2009. The effects of applied crop residues on losses of Fe, Mn, Cu and Zn in run-off from a soil prone to crusting. *Soil Use Manag.* 25, 193–200.

- Barrow, N.J., 1999. The four laws of soil chemistry: the Leeper lecture. *Aust. J. Soil Res.* 37, 787–829.
- Berenguer, P., Cela, S., Santiveri, F., Boixadera, J., Lloveras, J., 2008. Copper and zinc soil accumulation and plant concentration in irrigated maize fertilized with liquid swine manure. *Agron. J.* 100, 1056–1061.
- Bertol, I., Mello, E.L., Guadagnin, J.C., Zaparolli, A.L.V., Carrafa, M.R., 2003. Nutrient losses by water erosion. *Sci. Agric.* 60, 581–586.
- Blanco, H., Lal, R., 2008. *Principles of Soil Conservation and Management*. Springer, Berlin.
- BRAZIL, 2004. Portaria n° 518/GM de 25 de março de 2004. Controle e Vigilância da Qualidade da Água Para Consumo Humano e seu Padrão de Potabilidade. Ministério da Saúde.
- Carrillo-González, R., Šimunek, J., Sauve, S., Adriano, D., 2006. Mechanisms and pathways of trace element mobility in soils. *Adv. Agron.* 91, 111–178.
- Chotopantarat, S., Ong, S.K., Sutthirath, C., Osathaphan, K., 2012. Competitive modeling of sorption and transport of Pb^{2+} , Ni^{2+} , Mn^{2+} and Zn^{2+} under binary and multi-metal systems in lateritic soil columns. *Geoderma* 189–190, 278–287.
- CONAMA – Conselho Nacional do Meio Ambiente, 2009. Resolução n° 420/2009, de 28.12.09.
- Díaz-Barrientos, E., 2003. Copper and zinc retention by an organically amended soil. *Chemosphere* 50, 911–917.
- Giroto, E., Ceretta, C.A., Brunetto, G., Rheinheimer, D.S., Silva, L.S., Lourenzi, C.R., Lorensini, F., Vieira, R.C.B., Schmatz, R., 2010. Acúmulo e formas de cobre e zinco no solo após aplicações sucessivas de dejetos líquido de suínos. *Rev. Bras. Ciênc. Solo* 34, 955–965.
- Koo, B.J., Adriano, D.C., Bolan, N.S., Barton, C., 2005. Plant root exudates. In: Hillel, D., Hillel, D. (Eds.), *Encyclopedia of Soils in the Environment*. Elsevier, Amsterdam, pp. 421–428.
- L'Herroux, L., Le Roux, S., Appriou, P., Martinez, J., 1997. Behaviour of metals following intensive pig slurry applications to a natural field treatment process in Brittany (France). *Environ. Pollut.* 97, 119–130.
- Li, Y., Mccrory, D.F., Powell, J.M., Saam, H., Smith, D.J., 2005. A survey of selected heavy metal concentrations in Wisconsin dairy feeds. *J. Dairy Sci.* 88, 2911–2922.
- Lourenzi, C.R., Ceretta, C.A., Silva, L.S., Giroto, E., Lorensini, F., Tiecher, T.L., De Conti, L., Trentin, G., Brunetto, G., 2013. Nutrients in layers of soil under no-tillage treated with successive applications of pig slurry. *Rev. Bras. Ciênc. Solo* 37, 157–167.
- Mallmann, F.J.K., Rheinheimer, D.S., Cambier, P., Labanowski, J., Lamy, I., Santanna, M.A., Tessier, D., van Oort, F., 2012a. Using a two site-reactive model for simulating one century changes of Zn and Pb concentration profiles in soils affected by metallurgical fallout. *Environ. Pollut.* 162, 294–302.
- Mallmann, F.J.K., Rheinheimer, D.S., Ceretta, C.A., Cella, C., Šimunek, J., van Oort, F., 2012b. Modeling field-scale vertical movement of zinc and copper in a pig slurry-amended soil in Brazil. *J. Hazard. Mater.* 243, 223–231.
- Mantovi, P., Bonazzi, G., Maestri, E., Marmiroli, N., 2003. Accumulation of copper and zinc from liquid manure in agricultural soils and crop plants. *Plant Soil* 250, 249–257.
- McBride, M.B., 1994. *Environmental Chemistry of Soils*. Oxford University Press, New York.
- Mello, I., van Raij, B., 2006. No-till for sustainable agriculture in Brazil. *Proceedings of World Association of Soil and Water Conservation* P1-06 49–57.
- Nicholson, F.A., Smith, S.R., Alloway, B.J., Smith, C.C., Chambers, B.J., 2003. An inventory of heavy metals inputs to agricultural soils in England and Wales. *Sci. Total Environ.* 311, 205–219.
- Neumann, G., Romheld, V., 2002. Root-induced changes in the availability of nutrients in the rhizosphere. In: Waisel, Y., Waisel, Y., Eshel, A., Eshel, A., Kafkafi, U., Kafkafi, U. (Eds.), *Plant Roots: the Hidden Half*. Marcel Dekker, Inc., New York pp. 617–649 (chapter 36).
- Novak, J.M., Watts, D.W., Stone, K.C., 2004. Copper and zinc accumulation, profile distribution, and crop removal in coastal plain soils receiving long-term, intensive applications of swine manure. *Trans. ASAE* 47, 1513–1522.
- Pang, L., Close, M., 1999. Non-equilibrium transport of Cd in alluvial gravels. *J. Contam. Hydrol.* 36, 185–206.
- Pang, L., Close, M., Schneider, D., Stanton, G., 2002. Effect of pore-water velocity on chemical nonequilibrium transport of Cd, Zn, and Pb in alluvial gravel columns. *J. Contam. Hydrol.* 57, 241–258.
- Rheinheimer, D.S., Cambier, P., Mallmann, F.J.K., Labanowski, J., Lamy, I., Tessier, D., van Oort, F., 2013. Prospective modeling with Hydrus-2D of 50 years Zn and Pb movement in metal contaminated agricultural soils. *J. Contam. Hydrol.* 145, 54–66.
- Seuntjens, P., 2002. Field-scale cadmium transport in a heterogeneous layered soil. *Water Air Soil Pollut.* 140, 401–423.
- Šimunek, J., van Genuchten, M.Th., Šejna, M., 2008. Development and applications of the HYDRUS and STANMOD software packages, and related codes. *Vadose Zone J.* 7, 587–600.
- USDA – United States Department of Agriculture, 2003. *Soil Survey Staff. Keys to Soil Taxonomy*, ninth ed., Natural Resources Conservation Service, USDA, Washington.
- van Genuchten, M.Th., 1980. A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. *Soil Sci. Soc. Am. J.* 44, 892–898.
- Xue, H., Nhat, P.H., Gächter, R., Hooda, P.S., 2003. The transport of Cu and Zn from agricultural soils to surface water in a small catchment. *Adv. Environ. Res.* 8, 69–76.