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Modeling Zinc and Copper Movement in an Oxisol under Long-Term Pig Slurry Amendments

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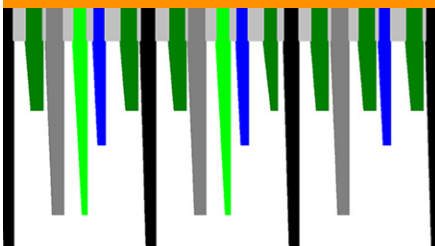
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Core Ideas

- Eleven years of Zn and Cu movement in an Oxisol amended with pig slurry (PS) was modeled.
- Root growth and water uptake effects were successfully added in HYDRUS simulations.
- Concentration profiles of Zn were described better than those of Cu.
- DOC-facilitated Cu transport needs to be considered when modeling Cu transport in soils.
- Zn concentrations will not be a problem during the next 50 yr in PS-amended soils.

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Modeling Zinc and Copper Movement in an Oxisol under Long-Term Pig Slurry Amendments

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Increases in Zn and Cu concentrations in soils amended with pig slurry (PS) can be described using numerical models. Our main objective was to validate that the HYDRUS-1D model is able to numerically describe profile concentrations and long-term vertical transport of Zn and Cu in a clay soil (Oxisol) cultivated under annual cropping in a no-till system and contaminated by successive doses of PS amendments. We first used a modeling approach that had previously been validated for an Alfisol. Then, we additionally also evaluated the effects of root growth and root water uptake on the transport of trace metals (TMs). Finally, we carried out 50-yr-long prospective simulations for different doses of PS amendments. Consideration of root growth and root water uptake processes in HYDRUS-1D simulations improved the description of measured field Zn concentrations. Although the correspondence between simulated and measured Cu concentrations was not as good as for Zn, we performed prospective simulations for both elements. Future scenarios that considered large PS doses showed large increases in concentrations of both TMs in the soil surface layer. The feasibility of using PS amendments on agricultural Oxisols will be limited by Cu because the soil Cu threshold concentration is exceeded in approximately 29 yr. Moreover, the total loads of both TMs allowed on agricultural soils are reached very fast when large rates are used, especially for Cu (19 yr), indicating that the long-term disposal of PS on agricultural soils should be done at low doses. These conclusions are probably conservative because our model did not consider potential leaching of TMs from the surface soil into deeper soil layers by dissolved organic C facilitated transport.

Abbreviations: DOC, dissolved organic carbon; HPS, high-dose pig slurry; LPS, low-dose pig slurry; PS, pig slurry; SWRC, soil water retention curve; TM, trace metal.

Applications of animal manure on soils to increase their fertility is an ancient agricultural practice. In modern agriculture, pig slurry (PS) is an important source of animal manure. Since the 1970s, an increase in intensive and confined swine commercial operations has generated huge volumes of PS. In many areas, agricultural soils have been used as PS disposal media and have received successive applications of PS, frequently at high rates.

Such amendment practices may lead to environmental contamination because PS often contains high concentrations of trace metals (TMs) such as Zn and Cu. Trace metal concentrations may vary widely, depending on the manure dry mass and the animal diet, because Zn and Cu are used as additives to improve the productivity index of swine (Li et al., 2005). Some researchers have reported total amounts of Zn and Cu in PS as high as 1225 and 528 mg kg⁻¹, respectively, on a dry-mass basis (Ogiyama et al., 2005). The continuous long-term application of PS amendments at the soil surface will promote the accumulation of TMs within the first few centimeters of the soil profile, especially in soils managed under no-till with the absence of mechanical plowing (Veiga et al., 2012;

Giroto et al., 2010a; Berenguer et al., 2008; L'Herroux et al., 1997). Moreover, the mobility of TMs, notably Cu, is low in soils (McBride, 1994). Considering that the input of animal wastes in soils can increase the organic matter content, which generally tends to decrease the TM solubility and mobility in soils (Mantovi et al., 2003), an even greater surface accumulation of Zn and Cu could be expected. Consequently, the continuous application of PS on soils raises questions about the risks of future environmental pollution of soils and surface and subsurface waters. Problems may arise due to runoff in regions with frequent high-intensity rainfall and a consequent TM transfer to surficial water bodies (Xue et al., 2003) or due to ecotoxicity of TMs for plants (Yadav, 2010) and microorganisms (Kuperman and Carreiro, 1997), with great implications for the wider environment. As mentioned by Mantovi et al. (2003), applications of animal farming manures must therefore be viewed as a controlled agronomic practice of fertilization and not as a simple way of disposal.

It is essential to study and monitor temporal increases in Zn and Cu concentrations in soils in relation to the intensity of PS applications. Depending on soil and manure conditions, the maximum TM concentration values, established by regulatory bodies for agricultural soils, may be rapidly reached and restrict the disposal of organic amendments in certain areas. Different soil properties and external factors affect the accumulation and depth redistributions of TMs in soils and their transfer to surface runoff. These factors include soil characteristics, such as pH (Gäbler, 1997), texture, organic matter and Fe oxide contents (Venditti et al., 2000), climatic conditions such as rainfall and evapotranspiration (Visser et al., 2012), land use (Fernandez et al., 2007; Baize and van Oort, 2014), and anthropogenic practices such as quality of PS amendments and their metal concentrations (Giroto et al., 2010a). Furthermore, Zn and Cu show different affinities for the charge sites of soil, which affect their mobility in soils. Trace metals form outer sphere complexes with permanent negative charges of 2:1 phyllosilicate minerals, and most of them tend to form inner sphere complexes with variable surface charges (organic matter, oxyhydroxides, and 1:1 clay minerals). Copper shows a high affinity for variable charge sites, especially of organic matter and at neutral or alkaline pH, while Zn can form inner and outer sphere complexes, the latter prevailing in acid soils (Weber et al., 1991).

Mathematical models are helpful in describing the mobility of TMs in soils (Rheinheimer et al., 2007). Many of them have been developed to simulate water flow and solute transfer processes between the soil surface and groundwater (Carrillo-González et al., 2006). The models can provide a base for designing future experiments and for interpreting and understanding trends and relationships in observed field data. They can be powerful tools in developing alternatives for soil and water management strategies (Šimůnek and de Vos, 1999). Thus, predictive simulations estimating environmental contamination risks caused by TM additions by successive PS applications in soils can help in developing better

strategies for manure management and support the adoption of public policies for swine producers.

However, a prerequisite to the use of any model and interpretation of its simulated results is model validation. For instance, Legout et al. (2009) discussed that before a model can be used, its predictive capacity and the validity of its assumptions need to be evaluated. A model needs to show that it can faithfully reproduce phenomena studied under controlled laboratory conditions or observed under natural conditions. Only after verifying the correct functionality of the model can long-term predictions be made.

Recently, Mallmann et al. (2012a, 2012b, 2014) carried out studies that involved modeling of TM migration in sandy soils. However, they did not consider the effects of plant roots in their simulations. Schoups and Hopmans (2002) discussed the effects of roots on solute movement in soils, highlighting the importance of considering this factor in modeling studies. Roots may form macropores, which can enhance the downward movement of TMs due to preferential flow. On the other hand, among many other rhizosphere processes important for TM mobility in soils, root water uptake may reduce water fluxes and TM leaching through the soil profile (Robinson et al., 2009). Moreover, roots may stabilize TMs in the soil and affect the soil pH, redox potential, and biomass, activity, and diversity of microorganisms, and influence the speciation of TMs. Therefore, changes in the downward movement of TMs within the root zone are expected when roots are considered in simulations.

It is also well known that the soil's clay and oxide contents, among other factors, affect its hydro-physical and chemical characteristics and consequently the potential for TM adsorption (Lang Burak et al., 2013). In clayey soils, such as Oxisols, the adsorption capacity for TMs is higher than in sandy soils (Mattias, 2006). Soil texture governs to a large extent the soil's water retention capacity and hydraulic conductivity, which are larger and smaller, respectively, in clay soils than in sandy soils (Reichert et al., 2009; Tindall and Kunkel, 1999). Consequently, although less TM leaching is expected in clay soils, the quantification and better understanding of these processes is necessary. Therefore, it is important to validate solute transport models for different types of soils, to verify the influence of plant roots on simulation results, and to increase the range of model applicability for estimating TM movement in contaminated soils.

Our main objective was to validate that the HYDRUS-1D model is able to numerically describe profile concentrations and long-term vertical transport of Zn and Cu in a clay soil (Oxisol) cultivated under annual cropping in a no-till system contaminated by successive doses of PS amendments. For the model validation, we first tested the transport model previously used by Mallmann et al. (2012b) for an Alfisol and then additionally also considered the effects of roots on TM transport in the soil. Finally, we performed

50-yr-long simulations to predict the accumulation of Zn and Cu in the soil surface layers and their downward movement in the soil profile toward the groundwater for different PS application rates.

Materials and Methods

Experimental Site, Soil, and Other Characteristics

The study was conducted at the demonstration field of the Cooperativa Regional Agropecuária de Campos Novos (Copercampos), in Campos Novos, Santa Catarina State, Brazil (27°21'56" S, 51°15'33" W, 896 m altitude), with periodical PS applications. The soil, developed from the intermediate effusive rock saprolites of the Serra Geral Formation, is classified as a Rhodic Hapludox (Soil Survey Staff, 2003) or a Rhodic Ferralsol (IUSS Working Group WRB, 2014) and referred to as Latossolo Vermelho Distroférico típico in the Brazilian System of Soil Classification (Empresa Brasileira de Pesquisa Agropecuária, 2004). At the beginning of the experiment, the 0- to 20-cm soil layer had the following chemical characteristics: 5.8 pH in water (1:1 v/v); 45 g kg⁻¹ organic matter; 0.0, 5.0, 47.0, and 29.0 mol_c m⁻³ of exchangeable Al, K, Ca, and Mg, respectively; and 10.0, 1.7, and 10.5 g m⁻³ of extractable P, Zn, and Cu, respectively (Veiga et al., 2012). Exchangeable Al, Ca, and Mg were extracted with 1.0 M KCl solution; K and P were extracted using Mehlich-1 solution (0.0125 M H₂SO₄ + 0.05 M HCl); and Cu and Zn were extracted with 0.1 M HCl solution (Tedesco et al., 1995). The climate is humid mesothermal with mild summers, the Cfb type according to the Köppen classification, with annual precipitation ranging from 1460 to 1820 mm and annual average temperatures from 15.8 to 17.9°C (Pandolfo et al., 2002).

The experiment started in 2000, on a field previously managed with a crop rotation and no-till system for >10 yr. Treatments consisted of four different annual PS doses: 0, 50, 100, and 200 m³ ha⁻¹, divided into two surface applications: half before winter crop sowing and the other half before summer crop sowing. These treatments were applied to three field replicates in a randomized block design, with plots measuring 6 by 5 m. More details can be found in Veiga et al. (2012). During 11 yr of the experiment, 22 PS applications were applied, using manure obtained from an anaerobic lagoon reservoir at a pig finishing farm, with the dry mass content ranging from 0.40 to 10.27% and an average of 2.62%.

The number of crop cultivations during the 11 yr of the experiment was the same as the number of PS applications. Seeding was performed by direct drilling and followed a 3-yr crop rotation scheme: black oat (*Avena strigosa* Schreb.) + common vetch (*Vicia sativa* L.)–corn (*Zea mays* L.), black oat–soybean [*Glycine max* (L.) Merr.], and black oat–common bean (*Phaseolus vulgaris* L.). The average production for the 0, 50, 100, and 200 m³ ha⁻¹ treatments was 5188, 6908, 7025, and 7046 kg ha⁻¹, respectively, of the dry

mass for the winter crops and 4919, 5729, 5789, and 6024 kg ha⁻¹, respectively, for the summer crops.

Soil and Solution Sample Collection

The soil and solution samples were collected in June of 2011. Disturbed soil samples were collected from 10 layers, at depths of 0 to 5, 5 to 10, 10 to 15, 15 to 20, 20 to 25, 25 to 30, 30 to 35, 35 to 40, and 40 to 60 cm, for the treatments with PS doses of 0, 50, and 200 m³ ha⁻¹ yr⁻¹, hereafter referred to as the 0-, 50-, and 200-m³ treatments, respectively. The soil samples were dried, sieved at 2.0 mm, and stored in plastic pots prior to chemical analyses. In the control plots (the 0-m³ treatment), soil solution samples were collected using tension lysimeters at three depths: 20, 40, and 80 cm.

For the determination of the soil hydro-physical characteristics, soil samples were collected in two different places located between the experimental blocks from six soil layers: depths of 0 to 5, 5 to 10, 10 to 20, 20 to 30, 30 to 40, and 40 to 60 cm. These locations had the same soil characteristics and received the same management as the control plot (the 0-m³ treatment). First, 10 undisturbed soil samples were collected from each soil layer for each type of analysis: the saturated hydraulic conductivity (K_s), the bulk density (B_d), and the soil water retention curve (SWRC) for soil water tensions <100 kPa. Second, disturbed bulk samples were collected for the measurement of soil texture and the SWRC for soil water tensions >500 kPa.

Soil Hydro-Physical Analysis

The saturated hydraulic conductivity, K_s , was measured on undisturbed soil samples, fully saturated with water for 48 h, using a falling-head permeameter linked to the Ksat computer software (Gubiani et al., 2010). This procedure consists of measuring the time needed for a specific volume of water, contained between the upper and lower limits of a water supply tube, to pass through the soil sample. The K_s was then calculated as suggested by Hillel (1998).

Undisturbed soil samples, also fully saturated for 48 h, were used for SWRC measurements. These samples were subjected to successive tensions of 1, 6, and 10 kPa in a sand tank (Reinert and Reichert, 2006) and to 33 and 100 kPa in a Richards chamber. Gravimetric water contents at higher tensions (500, 1000, and 1500 kPa) were determined using the dew point potentiometer method on disturbed soil samples. The paired tension and water content values of the SWRC were used to fit the α , n_1 , and m parameters of the van Genuchten model (van Genuchten, 1980). The soil B_d was calculated by dividing the dry mass of soil contained in the cylinder (dried in a stove at 105°C to constant weight) by the cylinder volume. The soil texture was measured following the Soil Conservation Service (1972) procedure.

Soil Chemical Analysis

All chemical analyses were performed on disturbed soil samples collected in the experimental plots. Soil pH (in water, 1:1 v/v) was

determined following the methodology described by Tedesco et al. (1995), and the organic C with an elemental CHNS autoanalyzer.

Total soil concentrations of Zn and Cu were measured using an atomic absorption spectrometer after sample digestion according to the USEPA (2007) procedure. Solution concentrations of TMs were determined directly using an inductively coupled plasma optical emission spectrometer on samples collected in the field.

Soil desorption isotherm curves for Zn and Cu were determined using ethylenediaminetetraacetic acid (EDTA) extractions at 0.05 mol L^{-1} (pH 6.0), with a soil/solution ratio of 1:10 (Bermond et al., 1998). The contact times between the soil and EDTA solution were 1, 5, 15, 30, 60, 120, 300, 660, 1020, and 1440 min. The amounts of TMs extracted from the soil by EDTA are similar to the anthropogenic metal additions (Labanowski et al., 2008). Labanowski et al. (2008) also suggest that EDTA extractions are indicative of long-term predictions of TM migration to different soil depths, which meets the goals of this work.

The adsorption isotherm curves of TMs were determined using the procedure described by Mattias (2006), adding 10 mL of a $0.0025 \text{ mol L}^{-1}$ $\text{Ca}(\text{NO}_3)_2$ solution containing different concentrations of Zn or Cu (0, 2.5, 5, 10, 20, 40, 60, 80, 120, 160, 200, 240, 280, 320, and 360 mg L^{-1}) to 0.5 g of soil. These solution

concentrations were set to reach the maximum adsorption capacity of the soil.

Climate Data

Daily meteorological data from May 2000 to June 2011, i.e., precipitation, air temperature, air relative humidity, wind speed, and radiation, were obtained from the Meteorological Station of EPAGRI (Empresa de Pesquisa Agropecuária e Extensão Rural de Santa Catarina), in Campos Novos, SC. The data, except for precipitation, were used to calculate the daily potential evapotranspiration of the crops (ET_p) cultivated during the experiment using the Penman–Monteith equation (Allen et al., 1998).

Daily and cumulative values of measured precipitation and calculated transpiration and evaporation between the beginning of the experiment and soil sampling (1 May 2000 and 15 June 2011, respectively) are shown in Fig. 1. Cumulative precipitation and evapotranspiration (transpiration + evaporation) were 23,267 and 8649 mm, respectively, corresponding to average annual values of 2090 and 777 mm yr^{-1} , respectively.

Solute Transport Simulations

Model and Parameterization Details

HYDRUS-1D (Šimůnek et al., 2016) was used to simulate unsaturated water flow and the transport of Zn and Cu in a vertical soil

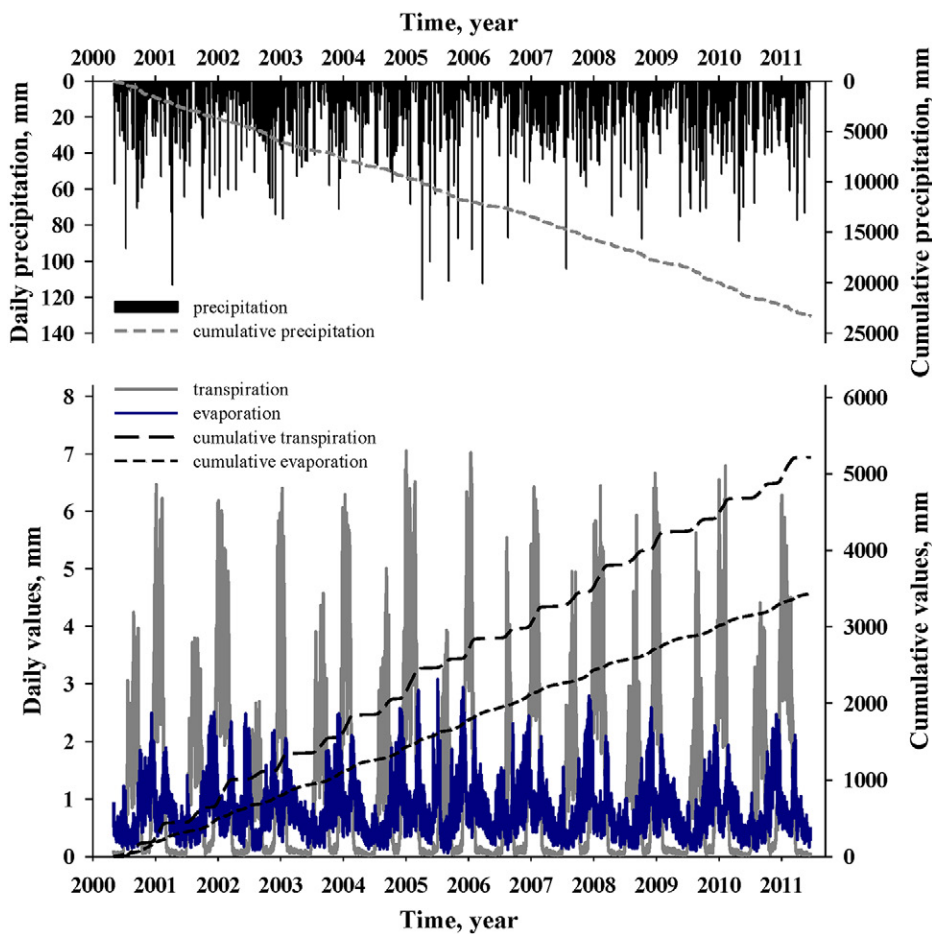


Fig. 1. Daily and cumulative values of precipitation, transpiration, and evaporation from 1 May 2000 to 15 June 2011 used in simulations with HYDRUS-1D for an experiment with different pig slurry doses conducted on an Oxisol in Campos Novos, SC, Brazil.

profile. The van Genuchten–Mualem analytical models were used to describe soil water retention curves and unsaturated hydraulic conductivity functions (van Genuchten, 1980). The soil residual (θ_r) and saturated (θ_s) water contents and parameters α and n_1 for each soil layer were obtained by fitting the van Genuchten model to retention data determined in the laboratory using the SWRC software (Dourado Neto et al., 2000). The pore connectivity–tortuosity factor (l) was set in all simulations and for all soil layers to 0.5, as recommended by Mualem (1976).

The initial total and solution concentrations of Zn and Cu of each soil layer used in HYDRUS-1D (1 May 2000) were set according to measured values in the control plot. Based on these values and on the average value of the n parameter determined from the adsorption curves fitted with the Freundlich nonlinear isotherm, the K_F values for both TMs for each soil layer were calculated. The Freundlich sorption isotherm was used rather

than the Langmuir isotherm because it better fit the adsorption data, reaching R^2 values >0.98 when comparing estimated and measured concentrations.

From the Zn and Cu desorption curves, the β and λ parameters of the Fangueiro kinetic model (Fangueiro et al., 2005) were determined. The β parameter is the fraction of soil sorption sites that instantaneously adsorb TMs to the functional groups (at equilibrium), and the λ parameter is the kinetic desorption constant of the nonequilibrium sites ($1 - \beta$) of the soil, both calculated according to Mallmann et al. (2012b). The values of the parameters used in the HYDRUS-1D simulations are listed in Table 1.

Trace Metal Inputs

During model validation simulations, the total amounts of Zn and Cu added to the soil surface via PS amendments were determined as the difference between the TM mass of a particular

Table 1. Hydro-physical and chemical soil parameters at 10 depths of the control plot in the pig slurry experiment located in Campos Novos, Santa Catarina State, Brazil, and initial values required for simulations with HYDRUS-1D.

Parameter†	0–5 cm	5–10 cm	10–15 cm	15–20 cm	20–25 cm	25–30 cm	30–35 cm	35–40 cm	40–50 cm	50–60 cm
<u>Soil</u>										
pH	4.94	4.81	4.72	4.57	4.48	4.47	4.50	4.52	4.61	4.70
OC, g kg ⁻¹	39.4	34.6	32.3	31.4	30.7	29.2	27.7	27.4	25.8	23.6
Clay, g kg ⁻¹	662	679	686	684	671	689	711	735	762	786
Silt, g kg ⁻¹	318	307	303	305	319	302	281	258	231	207
Sand, g kg ⁻¹	20	14	11	11	10	9	8	7	7	7
B_d , g cm ⁻³	1.03	1.06	1.08	1.08	1.06	1.06	1.04	1.04	1.02	1.02
K_s , cm dia ⁻¹	117.3	79.1	91.4	91.4	117.3	117.3	127.0	127.0	77.9	77.9
θ_s , cm ³ cm ⁻³	0.60	0.59	0.58	0.58	0.59	0.59	0.60	0.60	0.61	0.61
θ_r , cm ³ cm ⁻³	0.26	0.27	0.28	0.28	0.27	0.27	0.24	0.24	0.25	0.25
α_{VG} , cm ⁻¹	0.251	0.296	0.489	0.489	0.412	0.412	0.326	0.326	0.415	0.415
n_1	1.335	1.340	1.299	1.299	1.308	1.308	1.344	1.344	1.322	1.322
l	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
<u>Zinc</u>										
Total, mg kg ⁻¹	101.5	99.1	95.6	99.6	100.3	98.5	99.1	101.3	108.3	109.5
Solution, mg L ⁻¹	0.036	0.036	0.036	0.036	0.032	0.032	0.032	0.032	0.035	0.035
β	0.233	0.110	0.057	0.025	0.013	0.007	0.007	0.005	0.010	0.014
λ , 10 ⁻⁵ d ⁻¹	5.623	4.374	3.159	2.160	1.257	1.407	0.759	0.810	0.992	2.078
K_F	11.78	11.51	11.11	11.58	12.53	12.31	12.39	12.67	12.81	12.95
n	0.62	0.62	0.62	0.62	0.62	0.62	0.62	0.62	0.62	0.62
<u>Copper</u>										
Total, mg kg ⁻¹	113.2	110.3	110.3	113.1	115.9	118.7	118.7	118.7	124.2	125.6
Solution, mg L ⁻¹	0.0037	0.0037	0.0037	0.0037	0.0036	0.0036	0.0036	0.0036	0.0051	0.0051
β	0.181	0.128	0.096	0.075	0.070	0.063	0.059	0.053	0.053	0.057
λ , 10 ⁻⁵ d ⁻¹	4.888	4.783	4.552	4.272	4.128	4.030	4.068	3.983	3.984	4.385
K_F	0.51	0.50	0.50	0.51	0.53	0.54	0.54	0.54	0.51	0.51
n	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34	0.34

† OC, organic carbon; B_d , 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; β , fraction of sorption sites with instantaneous sorption of heavy metals; λ , kinetic constant for sorption sites $1 - \beta$; 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).

treatment and a corresponding mass of the 0-m³ treatment evaluated across the 60-cm depth using the soil bulk density (Table 1) and the TM total concentration. These amounts accounted for 43.0 and 27.3 kg ha⁻¹ of Zn and Cu, respectively, in the 50-m³ treatment and for 120.9 and 71.7 kg ha⁻¹ of Zn and Cu, respectively, in the 200-m³ treatment (Fig. 2). Temporal distributions of TM additions to the soil are shown in Fig. 2. The amounts of Zn and Cu added to the soil in each application were proportional to the dry mass content of the manure used in 22 amendments.

Model Validation

First, the Zn and Cu vertical transport was simulated in the PS-amended soil profiles for two different doses (50 and 200 m³ ha⁻¹ yr⁻¹) during 4063 d (1 May 2000–15 June 2011, between the beginning of the experiment and the soil sampling date, respectively), testing the modeling approach used and validated by Mallmann et al. (2012a, 2012b). The model is based on a two-site nonequilibrium solute transport model. In this solute transport model, the sorption on the equilibrium fraction of sorption sites (the β parameter) follows the Freundlich isotherm and on the kinetic fraction of sorption sites ($1 - \beta$) the first-order kinetic reaction (with a kinetic rate constant λ). The kinetic rate constant λ was derived from the EDTA-determined rates and was validated by Mallmann et al. (2012a, 2012b). In this modeling approach, water uptake by plant roots and corresponding transpiration were not considered. Consequently, all water losses through the soil surface to the atmosphere occurred only via evaporation. This modeling approach is hereafter referred to as Model I.

Second, root water uptake and root growth modules, available in HYDRUS-1D (Šimůnek et al., 2012a), were used in simulations. The modeling approach that considers root water uptake and root growth is hereafter referred to as Model II. In this second modeling approach, root water uptake was simulated using the model of Feddes et al. (1978). Root growth data for all crops cultivated during the experiment, i.e., the rooting depths on each day (Fig. 3), were set to average values for different phenological stages of particular crops. These data were obtained from other experiments and agricultural areas cultivated under similar pedoclimatic conditions. Additionally, the solute uptake of TMs by plant roots was neglected because the amounts of Zn and Cu absorbed by plants is usually very small. For example, Mallmann et al. (2012b) showed that cumulative removals of TMs by harvested crops in an 8-yr pig slurry amendment experiment represented only 0.33 to 1.13 and 0.05 to 0.12% of the total Zn and Cu masses, respectively, in the 0- to 60-cm soil depth. Furthermore, calculated potential evapotranspiration rates (ET_p) were divided into potential evaporation (E_p) and transpiration (T_p) rates using Beer's law, as suggested by Šimůnek et al. (2012a), based on the soil cover fraction (SCF):

$$E_p = ET_p (1 - SCF) \quad [1]$$

$$T_p = ET_p \times SCF \quad [2]$$

This resulted in cumulative evaporation and transpiration of 3434 and 5215 mm, respectively, and annual averages of 308.5 and 468.5 mm yr⁻¹ (0.85 and 1.28 mm d⁻¹), respectively (Fig. 1).

The modeling results for both Models I and II were evaluated using the coefficient of determination (R^2). The regression lines for simulated and measured concentrations were forced to pass through the origin so that the set of values from the simulations was equal to the measured ones and not just proportional.

Future Scenarios

The HYDRUS-1D model that best fit the experimental data, i.e., the model that considered root water uptake and root growth (Model II), was then extended to simulate an additional 50 yr of pig slurry applications (until 15 June 2061). This prospective modeling, which considered the same PS doses of 50 and 200 m³ ha⁻¹ yr⁻¹ used in the experiment, represented the low-dose (LPS) and high-dose (HPS) scenarios.

For the simulations of future scenarios with HYDRUS-1D, the same parameters as in the validation simulations were used. The data set of precipitation, evaporation, transpiration, root growth, and Zn and Cu additions from the first 10 yr of the model validation simulations were sequentially used five times. During the 50-yr simulations, the total amount of

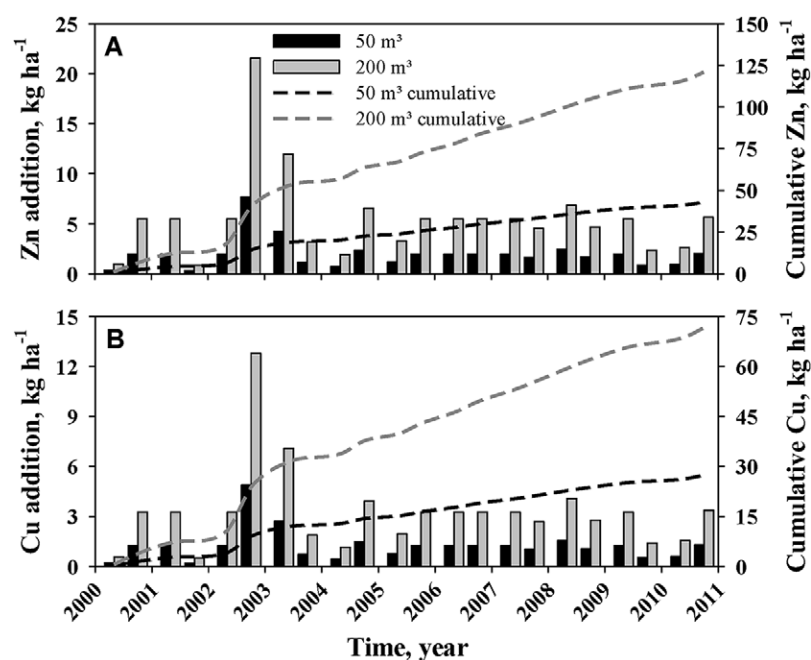


Fig. 2. (A) Zinc and (B) Cu amounts (bars are applications and lines are cumulative values) applied at the soil surface via pig slurry in two treatments (50 and 200 m³ ha⁻¹ yr⁻¹) in the experiment conducted on an Oxisol in Campos Novos, SC, Brazil.

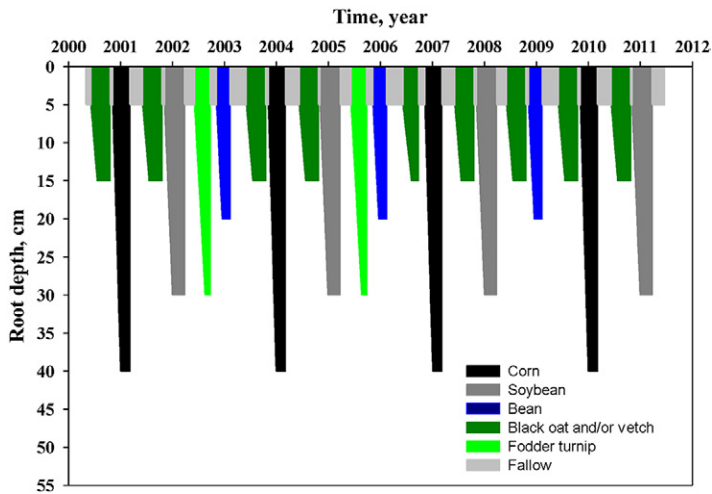


Fig. 3. Daily values of the rooting depth for different crops cultivated in an experiment from 1 May 2000 to 15 June 2011 with different pig slurry doses conducted on an Oxisol in Campos Novos, SC, Brazil. These values were used in the simulations with HYDRUS-1D.

precipitation was 105,201 mm, the total amounts of added Zn and Cu were 196 and 129 kg ha⁻¹, respectively, for the LPS scenario and 560 and 342 kg ha⁻¹, respectively, for the HPS scenario, whereas cumulative evaporation and transpiration were 15,619 and 23,390 mm, respectively.

Results

Simulations for Model Validation

Model I without Root Water Uptake

Concentrations of Zn estimated using Model I were found to be very similar to the measured ones. In the soil's surface layer (0–5 cm), the simulated Zn concentrations were 147.3 mg kg⁻¹ for

the 50-m³ treatment and 223.6 mg kg⁻¹ for the 200-m³ treatment, differing only by –6.2 and 4.1%, respectively, from the concentrations measured at sampling (Table 2). For the other nine soil layers, the differences between simulated and measured concentrations of Zn were even smaller in the 50-m³ treatment, with differences less than 3.3% (the 35–40-cm layer). For the 200-m³ treatment, these differences did not exceed 4.4% (the 5–10-cm layer; Table 2). When comparing simulated and measured concentrations for both treatments, the *R*² values were 0.942 and 0.988 for the 50- and 200-m³ treatments, respectively (Fig. 4).

The simulated Cu concentrations in the soil profile after 22 PS amendments fitted measured concentrations less well. Table 2 shows that the simulated Cu concentrations in the 0- to 5-cm layer were 15.1 and 17.0% higher than the measured concentrations for the 50- and 200-m³ treatments, respectively. The *R*² values of 0.674 for the 50-m³ treatment and 0.839 for the 200-m³ treatment (Fig. 4) were much lower than for Zn, especially for the LPS scenario.

Model II with Root Water Uptake and Root Growth

When root water uptake and root growth were considered in the HYDRUS-1D simulations, soil concentrations of Zn and Cu differed slightly from the results obtained by Model I. The largest differences were observed in the surface soil layer (0–5 cm), where concentrations of Zn and Cu reached values of 144.9 and 156.1 mg kg⁻¹, respectively, for the 50-m³ treatment and 217.8 and 201.1 mg kg⁻¹, respectively, for the 200-m³ treatment at the end of simulations. When compared with the measured concentrations, the simulated Zn concentrations differed by –7.7 and 1.4% for the 50- and 200-m³ treatments, respectively, while for Cu the simulated and measured concentrations differed by 14.6 and 15.7%, respectively (Table 3).

Table 2. Zinc and Cu concentrations measured (Mea) in soil profiles after 11 yr of pig slurry amendments and treatments with annual doses of 50 and 200 m³ ha⁻¹ and the corresponding concentrations simulated using HYDRUS-1D and the chemical modeling approach of Mallmann et al. (2012a) (SM). Also shown is the percentage difference between simulated and measured concentrations (Dif).

Soil layer	Zinc						Copper					
	Dose 50 m ³ ha ⁻¹			Dose 200 m ³ ha ⁻¹			Dose 50 m ³ ha ⁻¹			Dose 200 m ³ ha ⁻¹		
	Mea	SM	Dif	Mea	SM	Dif	Mea	SM	Dif	Mea	SM	Dif
cm	— mg kg ⁻¹ —			— mg kg ⁻¹ —			— mg kg ⁻¹ —			— mg kg ⁻¹ —		
0–5	157.0	147.3	–6.2	214.7	223.6	4.1	136.2	156.8	15.1	173.8	203.3	17.0
5–10	117.2	115.3	–1.7	146.0	152.4	4.4	123.4	116.9	–5.2	145.3	149.9	3.2
10–15	99.9	100.3	0.4	115.5	116.9	1.2	114.8	110.3	–3.9	125.6	115.4	–8.1
15–20	98.8	101.0	2.3	108.2	108.0	–0.1	116.3	113.1	–2.7	122.8	113.1	–7.9
20–25	100.5	101.0	0.6	107.0	104.3	–2.5	117.7	115.9	–1.5	120.0	115.9	–3.4
25–30	98.2	98.9	0.7	103.7	101.0	–2.6	119.1	118.7	–0.4	121.4	118.7	–2.2
30–35	99.9	99.3	–0.6	104.8	100.5	–4.1	119.1	118.7	–0.3	121.4	118.7	–2.2
35–40	98.2	101.5	3.3	105.3	102.4	–2.8	120.5	118.8	–1.4	120.7	118.8	–1.5
40–50	106.2	108.4	2.0	109.9	109.3	–0.5	124.8	123.9	–0.7	124.9	123.9	–0.8
50–60	109.1	109.5	0.4	111.6	110.1	–1.3	126.2	125.6	–0.5	126.3	125.6	–0.5

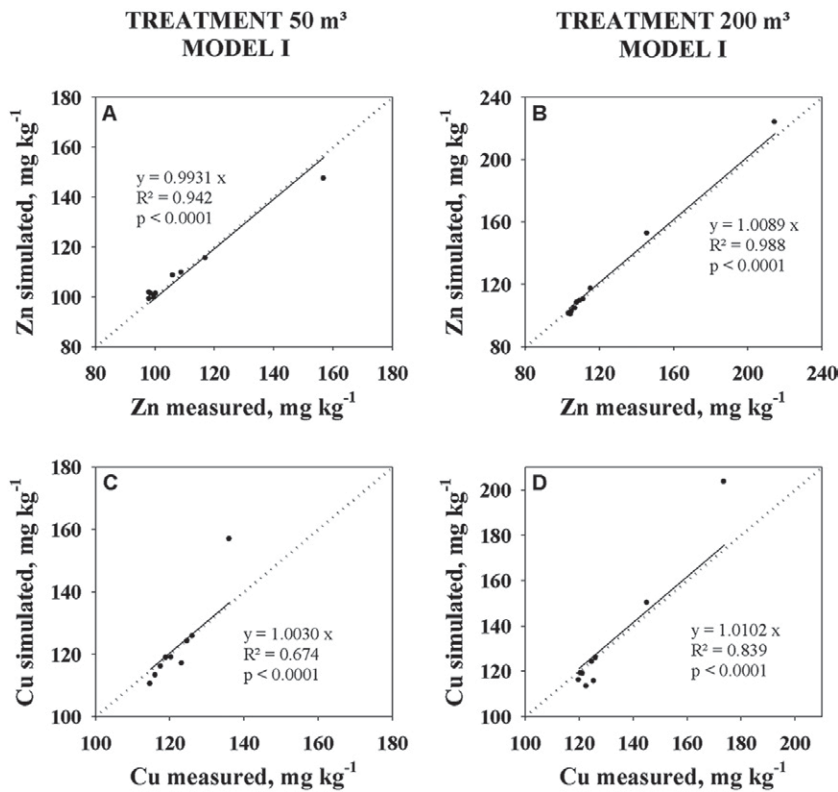


Fig. 4. The regression analysis for measured and simulated (A,B) Zn and (C,D) Cu concentrations in soils (an Oxisol located in Campos Novos, SC, Brazil) amended with pig slurry at rates of (A,C) 50 and (B,D) 200 m³ ha⁻¹ yr⁻¹. Measured values are the total concentrations obtained using the USEPA (2007) procedure. Simulated values were obtained using the Model I parameterization. Dotted line is the 1:1 line.

When comparing the Zn and Cu concentrations simulated using Model II (Table 3) with the corresponding initial concentrations (Table 1), no considerable increase in Zn concentrations (>2.0 mg kg⁻¹) was observed in soil layers deeper than 15 and

87, 52, and 30%, respectively. For Cu, the simulated concentrations reached 201, 149, and 122 mg kg⁻¹ (Fig. 7), corresponding to Cu mass increases of 82, 35, and 8%, respectively. Considerable increases (>10%) in Cu concentrations in the profile amended with

30 cm for the 50- and 200-m³ treatments, respectively. For Cu, a considerable increase was observed only in the upper soil profile depths of 0 to 10 and 0 to 15 cm, respectively.

The consideration of processes of root water uptake and root growth in the HYDRUS-1D simulations (Model II) resulted in simulated profile concentrations of Zn and Cu that generally better fit the measured TM concentrations than the results obtained by Model I (without root processes). The R² values obtained by Model II were 0.905 and 0.993 for Zn and 0.685 and 0.853 for Cu for the 50- and 200-m³ treatments, respectively (Fig. 5).

Simulations of Future Scenarios Pig Slurry Applications at Low Doses

Simulations of the LPS scenario predicted that additions of Zn and Cu during the 61 yr resulted in an increase in the TM mass in the 0- to 60-cm profile by 30 and 20%, respectively. Total Zn and Cu concentrations at the soil surface (0–5 cm) increased by 127 and 132%, reaching 231 (Fig. 6) and 262 mg kg⁻¹ (Fig. 7), respectively. Within the top 20 cm of the cultivated layer, the total Zn concentrations reached 185, 146, and 129 mg kg⁻¹ in soil layers of 5 to 10, 10 to 15, and 15 to 20 cm (Fig. 6), respectively, corresponding to mass increases of

Table 3. Zinc and Cu concentrations measured (Mea) in soil profiles after 11 yr of pig slurry amendments and treatments with annual doses of 50 and 200 m³ ha⁻¹ and the corresponding concentrations simulated using HYDRUS-1D and the chemical modeling approach of Mallmann et al. (2012a), while additionally considering root water uptake and root growth modules (SMR). Also shown is the percentage difference between simulated and measured concentrations (Dif).

Soil layer	Zinc						Copper					
	Dose 50 m ³ ha ⁻¹			Dose 200 m ³ ha ⁻¹			Dose 50 m ³ ha ⁻¹			Dose 200 m ³ ha ⁻¹		
	Mea	SMR	Dif	Mea	SMR	Dif	Mea	SMR	Dif	Mea	SMR	Dif
cm	— mg kg ⁻¹ —			— mg kg ⁻¹ —			— mg kg ⁻¹ —			— mg kg ⁻¹ —		
0–5	157.0	144.9	-7.7	214.7	217.8	1.4	136.2	156.1	14.6	173.8	201.1	15.7
5–10	117.2	115.6	-1.4	146.0	152.3	4.4	123.4	117.6	-4.7	145.3	150.7	3.7
10–15	99.9	101.0	1.1	115.5	118.0	2.1	114.8	110.4	-3.9	125.6	116.7	-7.1
15–20	98.8	101.4	2.6	108.2	108.9	0.7	116.3	113.1	-2.7	122.8	113.1	-7.9
20–25	100.5	101.3	0.8	107.0	105.0	-1.9	117.7	115.9	-1.5	120.0	115.9	-3.4
25–30	98.2	99.1	0.9	103.7	101.6	-2.0	119.1	118.7	-0.4	121.4	118.7	-2.2
30–35	99.9	99.4	-0.5	104.8	100.9	-3.7	119.1	118.7	-0.3	121.4	118.7	-2.2
35–40	98.2	101.6	3.4	105.3	102.7	-2.5	120.5	118.9	-1.4	120.7	118.9	-1.5
40–50	106.2	108.4	2.1	109.9	109.7	-0.1	124.8	123.9	-0.7	124.9	123.9	-0.8
50–60	109.1	109.5	0.4	111.6	110.5	-1.0	126.2	125.6	-0.5	126.3	125.6	-0.5

low PS doses were observed only in the top 15 cm, accompanied by variations smaller than 1% in soil layers below 20 cm. For Zn, considerable mass increases in the LPS scenario were observed in the upper 30 cm of the soil, while in the 30- to 60-cm soil layer increases were in the range of 6 to 8%.

Solution concentrations of Zn increased in all soil layers during the LPS scenario simulation, reaching a maximum value of 0.22 mg L^{-1} in the surface layer (Fig. 6). However, at the bottom of the soil profile (a depth of 60 cm), the Zn concentrations remained below 0.06 mg L^{-1} during the entire simulated period (Fig. 8). Simulations also showed that the highest Cu solution concentrations appeared in the 0- to 5-cm layer (0.11 mg L^{-1}), while increasing Cu concentrations were predicted only in the four upper layers (Fig. 7 and 8). Simulations predicted losses of 46.4 kg ha^{-1} of Zn and 5.4 kg ha^{-1} of Cu for depths below 60 cm during the simulated 61 yr.

Pig Slurry Applications at High Doses

The initial mass of Zn and Cu in the 60-cm soil profile increased by 91 and 54%, respectively, during the 61 yr simulated in the HPS scenario. Total Zn concentrations reached 419, 331, 244, and 196 mg kg^{-1} at the end of simulations in soil layers of 0 to 5, 5 to 10, 10 to 15, and 15 to 20 cm, respectively (Fig. 6). Such concentrations imply 313, 234, 155, and 96% increases, respectively. Estimated Zn concentrations in deeper soil layers also showed consistent increases, with the 40- to 50-cm layer showing the smallest gain of 28%.

For Cu, the HPS scenario resulted in total concentrations of 372, 317, 257, and 204 mg kg^{-1} in 2061 in the upper four soil layers, respectively (Fig. 7), which corresponded to 228, 188, 133, and 80% more Cu than at the beginning in 2000. Moreover, the deepest soil layer with a consistent increase (11%) in the total concentration of Cu was the 25- to 30-cm depth, while deeper soil layers showed only very small variations (<2%).

In the HPS scenario, the soil solution concentrations were highest in the surface layer, reaching maximum concentrations of 0.65 mg L^{-1} for Zn (Fig. 6) and 0.37 mg L^{-1} for Cu (Fig. 7). All soil layers in the 60-cm profile showed increases in the Zn soil solution concentration after 61 yr, including at the profile bottom (60 cm deep), where it increased from 0.035 mg L^{-1} in 2000 to 0.169 mg L^{-1} in 2061 (Fig. 8). Such concentrations predicted a total Zn loss of 100.4 kg ha^{-1} from the soil profile to layers below the depth of 60 cm. On the other hand, the Cu solution concentrations did not change below the depth of 30 cm. Thus, solution concentrations of this TM remained constant at the profile bottom

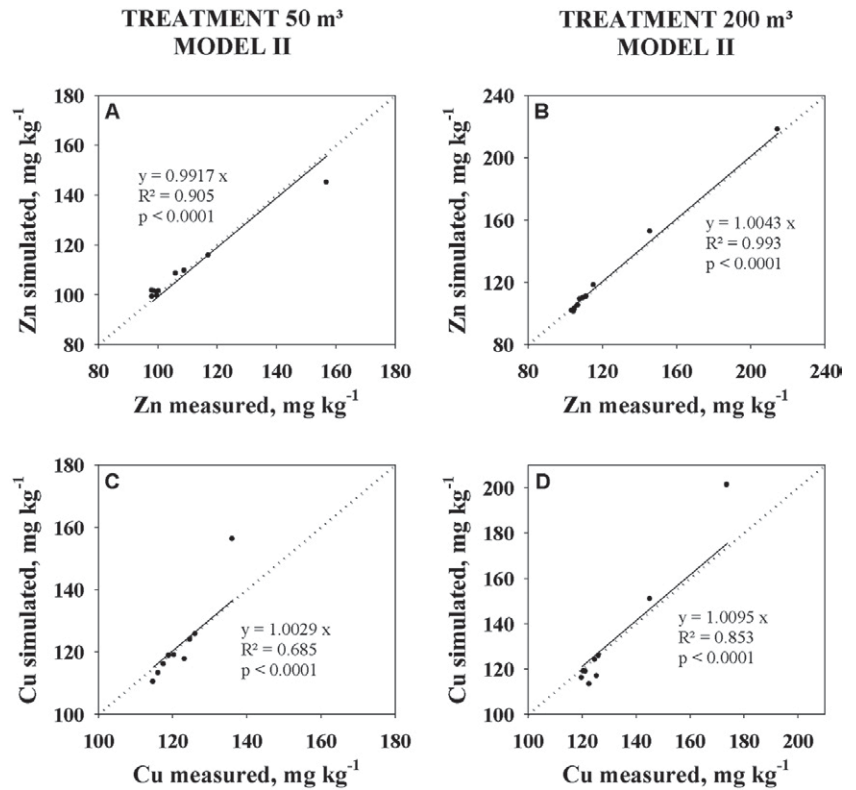


Fig. 5. The regression analysis for measured and simulated (A,B) Zn and (C,D) Cu concentrations in soils (an Oxisol located in Campos Novos, SC, Brazil) amended with pig slurry at rates of (A,C) 50 and (B,D) 200 $\text{m}^3 \text{ ha}^{-1} \text{ yr}^{-1}$. Measured values are the total concentrations obtained using the USEPA (2007) procedure. Simulated values were obtained using the Model II (with root water uptake and root growth) parameterization. Dotted line is the 1:1 line.

during the entire simulated period, leading to a Cu transfer of only 5.5 kg ha^{-1} to soil layers below 60 cm (Fig. 8).

Discussion

Model Validation and Effect of Roots on Trace Metal Movements in Soil

The HYDRUS-1D simulations using Model I, which neglected the effects of roots on TM movement, produced results that were in very good agreement with the measured Zn concentrations in the PS field experiment for both evaluated treatments. Tables 1 and 2 indicate that simulated Zn concentrations were comparable to concentrations observed under field conditions. However, simulated results using Model I were less good for Cu than for Zn. Simulated Cu concentrations in deeper soil layers were notably lower than measured under field conditions. Therefore, we are able to validate Model I only for Zn for this PS-amended soil.

It is important to mention that Model I was already validated under other conditions, where the type of TM contaminants, the soil type, and climate characteristics were different. One of the validation studies (Mallmann et al., 2012a) was done for Zn and

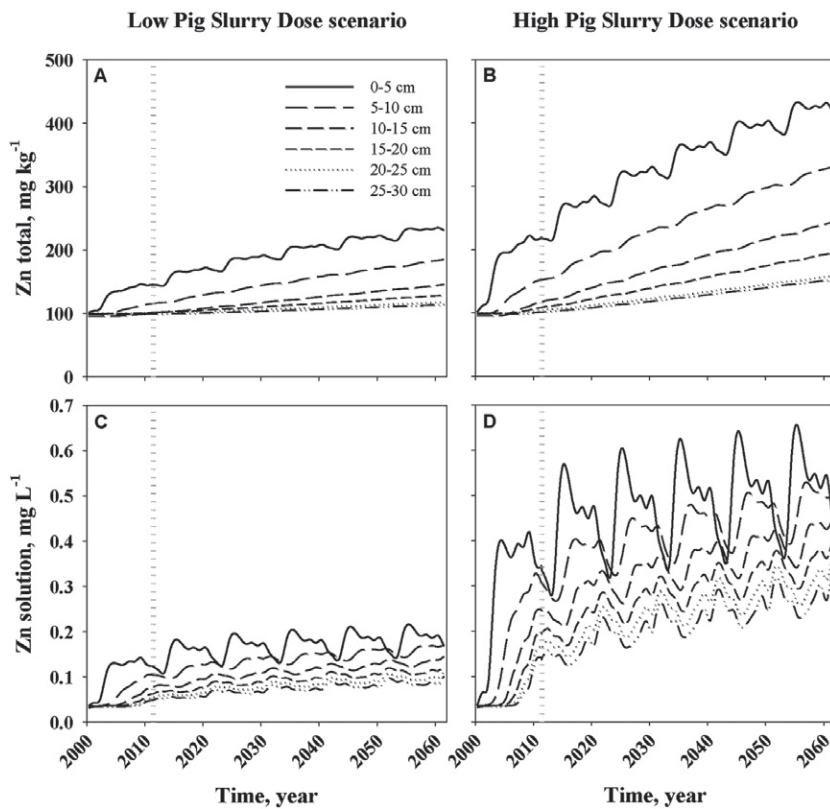


Fig. 6. Zinc (A,B) total and (C,D) solution concentrations in six soil layers simulated from 2000 to 2061 using HYDRUS-1D for future scenarios under (A,C) low and (B,D) high rates of pig slurry amendments applied at the soil surface of an Oxisol located in Campos Novos, SC, Brazil. The vertical dotted gray line indicates the time of soil sampling.

Pb in a 50-yr simulation for two agricultural arable soils located in northern France, classified as Eutric Cambisols, with an average clay content of 110 g kg^{-1} , receiving atmospheric fallout of Zn and Pb from a metal smelter complex during the past century. The second validation study was performed for Zn and Cu in an agricultural Alfisol in southern Brazil, with approximately 150 g kg^{-1} of clay in the A and E horizons, submitted to successive PS amendments for 8 yr (Mallmann et al., 2012b). In this latter work, simulated Cu inputs were similarly less incorporated into deeper soil layers and estimated Cu concentration profiles fitted less well the measured Cu field concentrations than was observed for Zn. However, these differences were smaller than our findings in this study for a clayey Oxisol. It is likely that in an Oxisol other processes, besides the TM sorption-desorption processes that are considered in the Model I approach, play a significant and important role in Cu transport in the soil.

In order to better describe field conditions, the processes of root water uptake and root growth were considered in the second set of simulations with HYDRUS-1D, denoted as Model II. Thus, the HYDRUS-1D projects for Model I served as a basis for Model II, which required additional information about root processes. Results of these simulations with Model II produced a better correspondence with measured Zn and Cu field concentrations (Fig.

4 and 5). In comparison to Model I, the main effect of considering root processes in Model II on TM transport was to increase the amounts of Zn and Cu transferred from the upper soil layer (0–5 cm) to the two underlying layers (5–10 and 10–15 cm) and to reduce surface accumulation.

Considering that all water that flows through the soil contains solutes to some extent, the reduction of TM accumulation at the soil's surface is mainly due to a different way in which water is returned to the atmosphere. While in Model I the water transfer to the atmosphere all occurred through the soil surface via evaporation, in Model II approximately 60% of water was transferred via transpiration. In this case, water did not flow all the way to the soil surface before being transferred to the atmosphere but was partly absorbed by roots in the soil rooting zone (ranging from 5–40-cm depth, depending on the crop). The upward movement of Zn and Cu from lower depths to the 0- to 5-cm soil layer decreased, while water absorption by roots in deeper layers forced downward flow of water and solutes. This hypothesis is consistent with the study of Schoups and Hopmans (2002), in which the important effects of water uptake by plants on root zone concentrations and fluxes and travel times of water and solutes in soil were discussed.

The surface accumulation of TMs in simulations that considered root water uptake and growth was smaller than in simulations that did not consider these processes. The differences in Zn mass were 1.2 and 3.0 kg ha^{-1} and in Cu mass were 0.3 and 1.2 kg ha^{-1} in the 50- and 200- m^3 treatments, respectively. This is equivalent to 2.8 and 2.5% of Zn and to 1.1 and 1.7% of Cu, respectively, added to the soil during simulations. Because Model II improved modeling results for Zn compared with Model I, we consider it to be validated for Zn. However, the improvements in predicting Cu concentrations by Model II were not sufficient to consider the model to be validated. Therefore, in order to obtain better results for Cu transport in the PS-amended soil, more parameters need to be adjusted or additional processes need to be considered in the HYDRUS-1D simulations.

The movement of TMs in the soil profile associated with solid particles, i.e., colloidal or colloid-facilitated transport, is of varying importance depending on the chemistry of the metals (notably Cu and Pb) and the pedo-geochemical conditions (van Oort et al., 2006; Citeau et al., 2003). Failure to account for such colloidal processes during solute transport simulations may lead to a severe underestimation of the transport and the potential risk assessment for considered TMs (Šimůnek et al., 2006). Considering the findings of Girotto et al. (2010b) that Cu in water leached

from a PS-amended soil occurred predominantly (approximately 75%) in particulate forms, the colloid-facilitated transport probably represents a process that is not well described by the validation simulations for Cu movement in the case of the PS-amended Oxisol studied here. Such particulate movement is less relevant in simulations of Zn transport in the soil profile because Zn movement in soils is considered to occur mainly ($\geq 85\%$) in a dissolved, free ion form (Citeau et al., 2003).

Pig slurry amendments also add organic matter (OM) to soils, which can be an important factor involved in TM movement in the soil profile, especially for Cu (as discussed above). Organic matter may not be completely humified (Moral et al., 2005) and may be subject to microbial degradation that could cause a release of dissolved organic C (DOC) into the soil solution. Because DOC has a high affinity with Cu, it may form soluble Cu-DOC complexes that can enhance the Cu concentration in solution (Díaz-Barrientos, 2003) and the leaching and transfer into deeper soil layers (Madrid; Díaz-Barrientos, 1998). Accounting for the presence of OM and DOC in the model could improve the correspondence between simulated and observed Cu concentrations in the soil profiles. Using adsorption isotherms measured on disturbed soil samples is another factor that may affect the results of transport models. Soil disturbance increases exposure of its functional groups and the contact between soil mineral particles and equilibrium solutions, favoring Zn and Cu adsorption and overestimating the accumulation of TMs on the soil surface in the simulations.

According to Šimůnek et al. (2006), models that can simulate various mechanisms controlling colloid and solute transport, as well their mutual interactions and interactions with the solid phase, are essential for improving the predictions of colloid-facilitated transport of solutes in variably saturated porous media. Therefore, it is likely that prediction of Cu concentrations in the PS-amended Oxisol could be improved using the C-Ride module (Šimůnek et al., 2012b), available for both HYDRUS-1D and HYDRUS (2D/3D) software packages, that incorporates various processes associated with colloid and colloid-facilitated solute transport in variably saturated porous media. However, this module requires a significant number of additional parameters, e.g., Cu sorption to DOC and the fraction of total C in DOC forms, which are currently unknown and which would require new studies for their correct estimation.

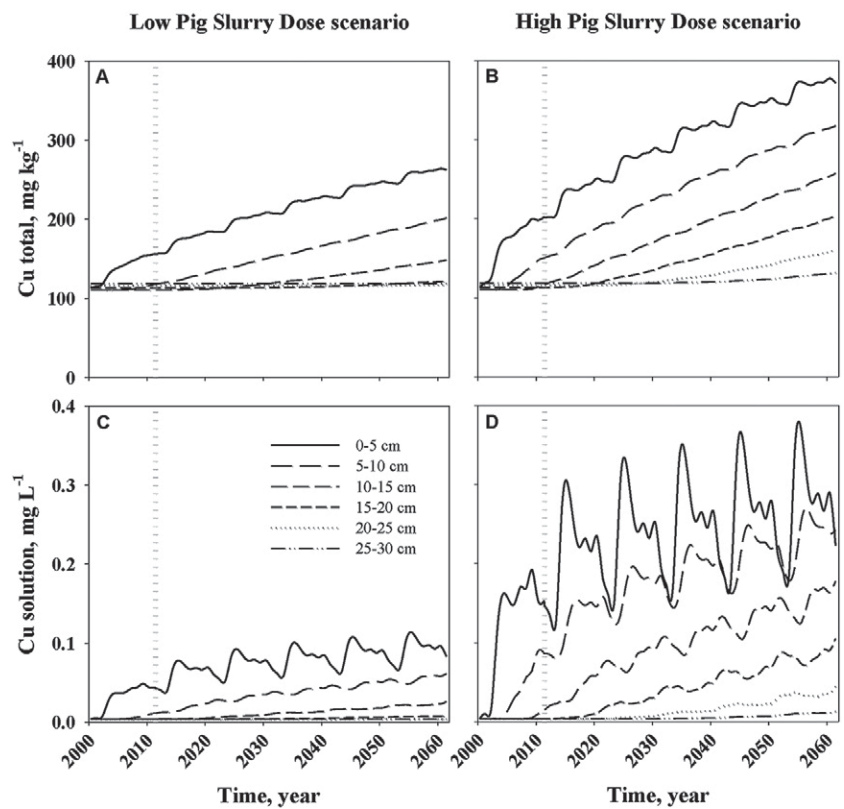


Fig. 7. Copper (A,B) total and (C,D) solution concentrations in six soil layers simulated from 2000 to 2061 using HYDRUS-1D for future scenarios under (A,C) low and (B,D) high rates of pig slurry amendments applied at the soil surface of an Oxisol located in Campos Novos, SC, Brazil. The vertical dotted gray line indicates the time of soil sampling.

Short- and Long-Term Feasibility of Pig Slurry Amendments

Future scenarios simulated for estimating Zn transport in the PS-amended Oxisol showed that in the short term, e.g., 10 yr after soil sampling (June 2011), the total concentrations of this TM reached

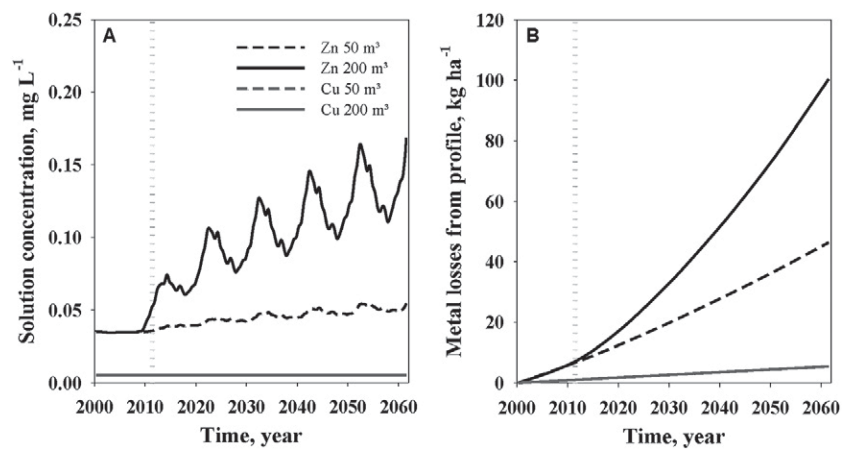


Fig. 8. (A) Soil solution concentrations of Zn and Cu at the bottom of the soil profile and (B) the metal losses from the soil profile. The HYDRUS-1D simulations were carried out for a 61-yr period and for scenarios with amendments of low and high (50 and 200 m³ ha⁻¹ yr⁻¹, respectively) pig slurry rates on an Oxisol in Campos Novos, SC, Brazil. The vertical dotted gray line indicates the time of soil sampling.

170 and 275 mg kg⁻¹, respectively, in the 0- to 5-cm soil layer (Fig. 6) and 129 and 184 mg kg⁻¹, respectively, in the 0- to 20-cm soil layer (Fig. 7) for the LPS and HPS scenarios. The Zn concentrations thus remained far below 450 mg kg⁻¹, which is the Zn threshold value established by the Conselho Nacional do Meio Ambiente (CONAMA), the Brazilian council for investigation in agricultural soils (Conselho Nacional do Meio Ambiente, 2009). At the same time, the long-term scenarios predicted a great increase in the Zn surface accumulation, especially for the HPS scenario. Total concentrations in the 0- to 5-cm soil layer during the last 5 yr were very high and led to a concentration in the 0- to 20-cm layer of 297 mg kg⁻¹. In this way, no potential risks related to Zn environmental problems were predicted during the simulated scenarios. However, this also means that if PS additions were done at the same HPS rate after 2061, and the Zn concentration in the 0- to 20-cm layer increased at the same rate, the soil would exceed its Zn threshold concentration in about an additional 50 yr. Besides, if we consider the Brazilian law that establishes the amounts of TMs that can be added to agricultural soils via sewage sludge, the maximum addition of Zn of 445 kg ha⁻¹ (Conselho Nacional do Meio Ambiente, 2006) from PS would be reached in the HPS scenario in 2038, i.e., 27 yr after the beginning of the future 50-yr simulation. Therefore, this law can limit the feasibility of PS amendments to agricultural soils when added at high rates, whereas in the LPS scenario the maximum addition of Zn was not reached.

Considering Zn concentrations in the soil solution, neither scenario presented significant problems to the environment or to the related Brazilian limits for groundwater (1.05 mg L⁻¹; Conselho Nacional do Meio Ambiente, 2009) in both the short and long term. However, the amounts of Zn transferred to layers below a depth of 60 cm during the simulated 61 yr were equivalent to approximately 15% (LPS) and 19% (HPS) of the total amounts of this TM added to the soil via PS. This was a consequence of increases in the soil solution concentrations at the profile bottom (Fig. 8), which indicates a transport of the exogenous Zn throughout the entire 0- to 60-cm soil profile.

Significant accumulation of Zn on the soil surface, albeit at lower concentrations than in this Oxisol, was also detected by Mallmann et al. (2012b) in simulations predicting future scenarios for an Alfisol amended with high doses of PS. Moreover, the Zn losses below the depth of 60 cm were higher in the Alfisol than the Oxisol. These differences between the two soil types are ascribed mainly to the lower clay and oxide contents and, consequently, the more coarse-grained texture of the Alfisol, which exhibited a lower tendency for heavy metal adsorption than fine-grained soils (Bradl, 2004).

Although the chemical model was not validated for Cu transport in the Oxisol because it

overestimated Cu soil surface accumulation, we still performed simulations of the movement of this TM for future scenarios. These results may help to guide the establishment of management strategies for PS amendments. Simulations for the HPS scenario indicated that in 18 yr after 2011 the Cu concentrations in the 0- to 20-cm soil surface layer would exceed the Brazilian threshold for Cu concentration in agricultural soils, which is 200 mg kg⁻¹ (Conselho Nacional do Meio Ambiente, 2009) (Fig. 9). If the manure doses are applied to the soil at low rates (LPS scenario), the concentration of Cu in this soil layer will remain below the threshold value for at least another 50 yr, extending the feasibility of this Oxisol receiving successive disposals of PS on the soil surface (Fig. 9). Indeed, the maximum load of Cu of 137 kg ha⁻¹ (Conselho Nacional do Meio Ambiente, 2006) that is allowed to be added to agricultural soils was not reached in the LPS scenario, while in the HPS scenario this limit was reached already in 2019. Therefore, when the goal is long-term availability of agricultural soils for PS disposal, the applications should be done at low doses.

The HYDRUS-1D simulations also estimated very low concentrations of Cu in the soil solution during 61 yr in both scenarios. As shown in Fig. 8, the solution concentration at the profile bottom did not change during this period. This indicates that Cu introduced on the soil surface with PS amendments was not transferred to the deepest layers of the soil profile. These results agree with the findings of Mallmann et al. (2012b) for an Alfisol and confirm again the higher soil affinity for adsorption of Cu than Zn, independently if the soil has high (Nascimento and Fontes, 2004) or low (Arias et al., 2005) clay contents.

Considering only the soil contamination caused by TMs, the long-term feasibility of PS amendments in the clayey Oxisol of Campos Novos is viable only if PS amendments are done at low rates. However, even then the successive applications of the manure

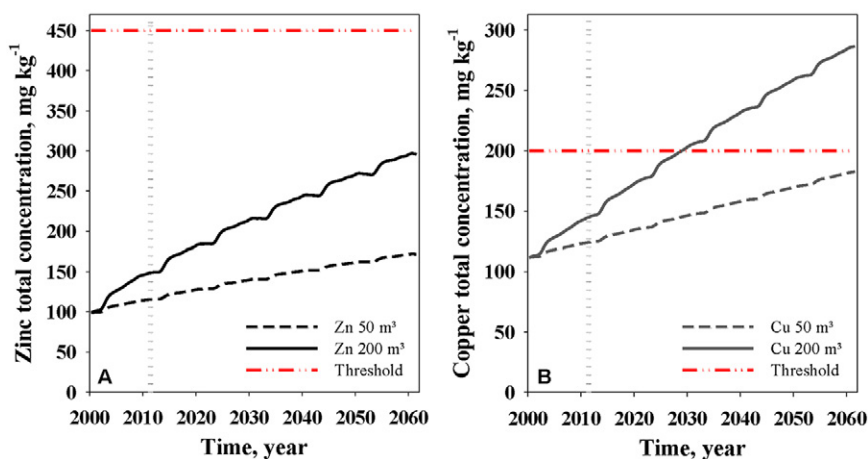


Fig. 9. (A) Zinc and (B) Cu total concentrations in the upper 0- to 20-cm soil layer simulated using HYDRUS-1D during a 61-yr period for scenarios with amendments of low and high (50 and 200 m³ ha⁻¹ yr⁻¹, respectively) pig slurry rates on an Oxisol in Campos Novos, SC. The red line corresponds to the threshold value for agricultural soils. The vertical dotted gray line indicates the time of soil sampling.

at the soil surface will increase soil concentrations of Cu until they reach the threshold value established by Conselho Nacional do Meio Ambiente (2009), making the Oxisol unusable for agricultural production. Therefore, after validating the transport model for Cu transport in an Oxisol, future studies should be carried out about the effect of soil tillage on reducing the TM accumulation on the soil surface and thus on extending the time suitable for PS amendments of agricultural soils, similarly to those performed by Mallmann et al. (2014) for an Alfisol.

Conclusion

A transport model (Model I) constructed in HYDRUS-1D, and already validated by Mallmann et al (2012b) for a coarse textured Alfisol, was evaluated in this study to simulate the vertical movement of Zn and Cu in a clayey Oxisol subjected to PS amendments with low and high doses for 11 yr. The simulated total Zn concentrations throughout the soil profile provided a good fit with the corresponding measured values for both treatments, leading to the validation of this transport model also for the clayey Oxisol and increasing its applicability to a larger range of soil types. However, estimated concentrations of Cu were found to be less satisfactory, overestimating surface Cu accumulation. Therefore, the transport model was not validated for Cu transport in a clayey Oxisol.

Consideration of root water uptake and root growth processes in the original transport model (Model II) improved the correspondence between both simulated and measured Zn and Cu concentrations. However, the improvement was not sufficient to allow the validation of this solute transport model for Cu. Thus, we recommend in future studies to additionally also account for the colloid-facilitated movement of TMs, increasing the range of transport processes considered in the simulations. However, models that consider such processes, such as the C-Ride module of HYDRUS-1D, require many additional parameters, such as those characterizing sorption of TMs on particulate matter and/or DOC, which will need to be measured experimentally.

Simulations of future scenarios that considered continued PS amendments of the Oxisol during the next 50 yr do not indicate that Zn accumulation in the soil or Zn leaching to groundwater would exceed the threshold values of the Brazilian law under either low or high application rates. However, these simulations also indicate that the feasibility of PS amendments to the agricultural Oxisol will be limited due to Cu. Although the transport model was not validated for Cu, several trends could be extracted from simulations of the fate of this TM in the soil. First, the threshold value can be reached approximately after 29 yr when high doses of PS amendments are applied to the unamended Oxisol. Second, no problems were observed during the next 50 yr when the PS amendments were made at low rates. Moreover, the total loads of both TMs allowed by the law on agricultural soils were reached very fast when high rates were used, especially for Cu (19 yr). Therefore, for the long-term feasibility of PS disposal to

agricultural soils, such as this Oxisol, the manure applications should be done at low doses. These conclusions are probably conservative because our model did not consider potential leaching of TMs from the surface soil into deeper soil layers by DOC-facilitated transport.

Acknowledgments

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References

- Allen, R.G., L.S. Pereira, D. Raes, and M. Smith. 1998. Crop evapotranspiration: Guidelines for computing crop water requirements. Irrig. Drain. Pap. 56. FAO, Rome.
- Arias, M., C. Pérez-Novo, F. Osorio, E. López, and B. Soto. 2005. Adsorption and desorption of copper and zinc in the surface layer of acid soils. *J. Colloid Interface Sci.* 288:21–29. doi:10.1016/j.jcis.2005.02.053
- Baize, D., and F. van Oort. 2014. Potentially harmful elements in forest soils: A pedological viewpoint. In: C. Bini and J. Bech, editors, PHEs, environment and human health. Springer, Dordrecht, the Netherlands. p. 151–198.
- Berenguer, P., S. Cela, F. Santiveri, J. Boixadera, and J. Lloveras. 2008. Copper and zinc soil accumulation and plant concentration in irrigated maize fertilized with liquid swine manure. *Agron. J.* 100:1056–1061. doi:10.2134/agronj2007.0321
- Bermond, A., I. Yousfi, and J.P. Ghestem. 1998. Kinetic approach to the chemical speciation of trace metals in soils. *Analyst* 123:785–789. doi:10.1039/a707776i
- Bradl, H.B. 2004. Adsorption of heavy metal ions on soils and soil constituents. *J. Colloid Interface Sci.* 277:1–18. doi:10.1016/j.jcis.2004.04.005
- Carrillo-González, R., J. Šimůnek, S. Sauvé, and D. Adriano. 2006. Mechanisms and pathways of trace element mobility in soils. *Adv. Agron.* 91:111–178. doi:10.1016/S0065-2113(06)91003-7
- Citeau, L., I. Lamy, F. van Oort, and F. Elsass. 2003. Colloidal facilitated transfer of metals in soils under different land use. *Colloids Surf. A* 217:11–19. doi:10.1016/S0927-7757(02)00554-X
- Conselho Nacional do Meio Ambiente. 2006. Resolução no 375, de 29 de agosto de 2006. Define critérios e procedimentos, para o uso agrícola de lodos de esgoto gerados em estações de tratamento de esgoto sanitário e seus produtos derivados, e dá outras providências. CONAMA, Brasília.
- Conselho Nacional do Meio Ambiente. 2009. Resolução no 420/2009, de 28/12/2009. Dispõe sobre critérios e valores orientadores de qualidade do solo quanto à presença de substâncias químicas e estabelece diretrizes para o gerenciamento ambiental de áreas contaminadas por essas substâncias em decorrência de atividades antrópicas. CONAMA, Brasília.
- Díaz-Barrientos, E. 2003. Copper and zinc retention by an organically amended soil. *Chemosphere* 50:911–917. doi:10.1016/S0045-6535(02)00695-1
- Dourado Neto, D., D.R. Nielsen, J.W. Hopmans, K. Reichardt, and O.O.S. Bacchi. 2000. Software to model soil water retention curves (SWRC, version 2.00). *Sci. Agric.* 57:191–192. doi:10.1590/S0103-9016200000100031
- Empresa Brasileira de Pesquisa Agropecuária. 2004. Solos do Estado de Santa Catarina. Boletim de Pesquisa e Desenvolvimento 46. EMBRAPA, Centro Nacional de Pesquisa de Solos, Rio de Janeiro.
- Fangueiro, D., A. Bermond, E. Santos, H. Carapuça, and A. Duarte. 2005. Kinetic approach to heavy metal mobilization assessment in sediments: Choose of kinetic equations and models to achieve maximum information. *Talanta* 66:844–857. doi:10.1016/j.talanta.2004.12.036
- Feddes, R.A., P.J. Kowalik, and H. Zaradny. 1978. Simulation of field water use and crop yield. John Wiley & Sons, New York.
- Fernandez, C., J. Labanowski, P. Cambier, A.G. Jongmans, and F. van Oort. 2007. Fate of airborne metal pollution in soils as related to agricultural management: 1. Zn and Pb distributions in soil profiles. *Eur. J. Soil Sci.* 58:547–559. doi:10.1111/j.1365-2389.2006.00827.x
- Gäbler, H.E. 1997. Mobility of heavy metals as a function of pH of samples from an overbank sediment profile contaminated by mining activities. *J. Geochem. Explor.* 58:185–194. doi:10.1016/S0375-6742(96)00061-1
- Giroto, E., C.A. Ceretta, G. Brunetto, D.S. Rheinheimer, L.S. Silva, C.R. Lourenzi, et al. 2010a. Copper and zinc forms and accumulation in soil after successive pig slurry applications. (In Portuguese, with English abstract.) *Rev. Bras. Cienc. Solo* 34:955–965. doi:10.1590/S0100-06832010000300037

- Giroto, E., C.A. Ceretta, D.S. Rheinheimer, G. Brunetto, J.G. Andrade, and J. Zalamea. 2010b. Forms of losses of copper and phosphorus in water of runoff and percolation in soil with successive pig slurry application. (In Portuguese, with English abstract.) *Cienc. Rural* 40:1948–1954. doi:10.1590/S0103-84782010005000141
- Gubiani, P.I., D.J. Reinert, J.M. Reichert, N.S. Gelain, and J.P.G. Minella. 2010. Falling head permeameter and software to determine the hydraulic conductivity of saturated soil. (In Portuguese, with English abstract.) *Rev. Bras. Cienc. Solo* 34:993–997. doi:10.1590/S0100-06832010000300041
- Hillel, D. 1998. *Environmental soil physics*. Academic Press, San Diego.
- IUSS Working Group WRB. 2014. World reference base for soil resources. International soil classification system for naming soils and creating legends for soil maps. World Soil Resour. Rep. 106. FAO, Rome.
- Kuperman, R.G., and M.M. Carreiro. 1997. Soil heavy metal concentrations, microbial biomass and enzyme activities in a contaminated grassland ecosystem. *Soil Biol. Biochem.* 29:179–190. doi:10.1016/S0038-0717(96)00297-0
- Labanowski, J., F. Monna, A. Bermond, P. Cambier, C. Fernandez, I. Lamy, and F. van Oort. 2008. Kinetic extractions to assess mobilization of Zn, Pb, Cu, and Cd in a metal-contaminated soil: EDTA vs. citrate. *Environ. Pollut.* 152:693–701. doi:10.1016/j.envpol.2007.06.054
- Lang Burak, D., F. van Oort, T. Becquer, E. Foy, and M.P. Ferreira Fontes. 2013. Unraveling zinc and lead distributions in dolomitic and metapelitic soils of the Brazilian Central Plateau: Insight from physical fractionation, optical microscopy and X-ray micro-fluorescence. *Eur. J. Soil Sci.* 64:131–144. doi:10.1111/ejss.12006
- Legout, C., J. Molenat, and Y. Hamon. 2009. Experimental and modeling investigation of unsaturated solute transport with water-table fluctuation. *Vadose Zone J.* 8:21–31. doi:10.2136/vzj2007.0182
- L'Herroux, L., S. Le Roux, P. Appriou, and J. Martinez. 1997. Behaviour of metals following intensive pig slurry applications to a natural field treatment process in Brittany (France). *Environ. Pollut.* 97:119–130. doi:10.1016/S0269-7491(97)00072-9
- Li, Y., D.F. McCrory, J.M. Powell, H. Saam, and D. Jackson-Smith. 2005. A survey of selected heavy metal concentrations in Wisconsin dairy feeds. *J. Dairy Sci.* 88:2911–2922. doi:10.3168/jds.S0022-0302(05)72972-6
- Madrid, L., and E. Díaz-Barrientos. 1998. Release of metals from homogeneous soil columns by wastewater from an agricultural industry. *Environ. Pollut.* 101:43–48. doi:10.1016/S0269-7491(98)00032-3
- Mallmann, F.J.K., D.S. Rheinheimer, P. Cambier, J. Labanowski, I. Lamy, M.A. Santanna, et al. 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. doi:10.1016/j.envpol.2011.11.039
- Mallmann, F.J.K., D.S. Rheinheimer, C.A. Ceretta, C. Cella, J.P.G. Minella, R.L. Guma, et al. 2014. Soil tillage to reduce surface metal contamination: Model development and simulations of zinc and copper concentration profiles in a pig slurry-amended soil. *Agric. Ecosyst. Environ.* 196:59–68. doi:10.1016/j.agee.2014.06.024
- Mallmann, F.J.K., D.S. Rheinheimer, C.A. Ceretta, C. Cella, J. Šimůnek, and F. van Oort. 2012b. Modeling field-scale vertical movement of zinc and copper in a pig slurry-amended soil in Brazil. *J. Hazard. Mater.* 243:223–231. doi:10.1016/j.jhazmat.2012.10.022
- Mantovi, P., G. Bonazzi, E. Maestri, and N. Marmiroli. 2003. Accumulation of copper and zinc from liquid manure in agricultural soils and crop plants. *Plant Soil* 250:249–257. doi:10.1023/A:1022848131043
- Mattias, J.L. 2006. *Metais pesados em solos sob aplicação de dejetos líquidos de suínos em duas microbacias hidrográficas de Santa Catarina*. Ph.D. diss. Univ. Federal de Santa Maria, Santa Maria, RS, Brazil.
- McBride, M.B. 1994. *Environmental chemistry of soils*. Oxford University Press, New York.
- Moral, R., J. Moreno-Caselles, M.D. Perez-Murcia, A. Perez-Espinosa, B. Rufete, and C. Paredes. 2005. Characterisation of the organic matter pool in manures. *Bioresour. Technol.* 96:153–158. doi:10.1016/j.biortech.2004.05.003
- Mualem, Y. 1976. A new model for predicting the hydraulic conductivity of unsaturated porous media. *Water Resour. Res.* 12:513–522. doi:10.1029/WR012i003p00513
- Nascimento, C.W.A., and R.L.F. Fontes. 2004. Correlation between characteristics of latosols from Minas Gerais State, Brazil, and parameters of adsorption equations of copper and zinc. (In Portuguese, with English abstract.) *Rev. Bras. Cienc. Solo* 28:965–971. doi:10.1590/S0100-06832004000600004
- Ogiyama, S., K. Sakamoto, H. Suzuki, S. Ushio, T. Anzai, and K. Inubushi. 2005. Accumulation of zinc and copper in an arable field after animal manure application. *Soil Sci. Plant Nutr.* 51:801–808. doi:10.1111/j.1747-0765.2005.tb00114.x
- Pandolfo, C., H.J. Braga, V.P. Silva, Jr., A.M. Massignam, E.S. Pereira, and V.M.R. Thomé. 2002. *Atlas climatológico digital do Estado de Santa Catarina*. EPAGRI, Florianópolis, SC, Brazil.
- Reichert, J.M., J.A. Albuquerque, D.R. Kaiser, D.J. Reinert, F.L. Urach, and R. Carlesso. 2009. Estimation of water retention and availability in soils of Rio Grande do Sul. *Rev. Bras. Cienc. Solo* 33:1547–1560. doi:10.1590/S0100-06832009000600004
- Reinert, D.J., and J.M. Reichert. 2006. Use of sand column to measure soil water retention: Prototypes and test. (In Portuguese, with English abstract.) *Cienc. Rural* 36:1931–1935. doi:10.1590/S0103-84782006000600044
- Rheinheimer, D.S., J. Labanowski, F. Elsass, P. Cambier, M.A. Santanna, and D. Tessier. 2007. Heavy metal transport modelling in soil: Sorption/desorption phenomena, water fluxes and contaminant fate. *Top. Cienc. Solo* 5:135–180.
- Robinson, B.H., G. Bañuelos, H.M. Conesa, M.W.H. Evangelou, and R. Schulin. 2009. The phytomanagement of trace elements in soil. *Crit. Rev. Plant Sci.* 28:240–266. doi:10.1080/07352680903035424
- Schoups, G., and J.W. Hopmans. 2002. Analytical model for vadose zone solute transport with root water and solute uptake. *Vadose Zone J.* 1:158–171. doi:10.2136/vzj2002.1580
- Šimůnek, J., and J.A. de Vos. 1999. Inverse optimization, calibration, and validation of simulation models at the field scale. In: J. Feyen and K. Wiyono, editors. *Modelling of transport process in soils at various scales in time and space*. Wageningen Pers, Wageningen, the Netherlands. p. 431–445.
- Šimůnek, J., C. He, L. Pang, and S.A. Bradford. 2006. Colloid-facilitated solute transport in variably saturated porous media: Numerical model and experimental verification. *Vadose Zone J.* 5:1035–1047. doi:10.2136/vzj2005.0151
- Šimůnek, J., M. Šejna, H. Saito, M. Sakai, and M.Th. van Genuchten. 2012a. The HYDRUS-1D software package for simulating the movement of water, heat, and multiple solutes in variably saturated media, version 4.15. HYDRUS Softw. Ser. 3. Dep. of Environ. Sci., Univ. of California, Riverside.
- Šimůnek, J., M. Šejna, and M.Th. van Genuchten. 2012b. The C-Ride module for HYDRUS (2D/3D) simulating two-dimensional colloid-facilitated solute transport in variably-saturated porous media, Version 1.0. PC Progress, Prague.
- Šimůnek, J., M.Th. van Genuchten, and M. Šejna. 2016. Recent developments and applications of the HYDRUS computer software packages. *Vadose Zone J.* 15(7). doi:10.2136/vzj2016.04.0033
- Soil Conservation Service. 1972. *Procedures for collecting soil samples and methods of analysis for soil survey*. Soil Surv. Invest. Rep. 1. USDA, Washington, DC.
- Soil Survey Staff. 2003. *Keys to Soil Taxonomy*. 9th ed. Natl. Soil Surv. Ctr., Lincoln, NE.
- Tedesco, M.J., C. Gianello, C.A. Bissani, H. Bohnen, and S.J. Volkenweiss. 1995. *Análise de solo, plantas e outros materiais*. Dep. de Solos, Federal Univ. of Rio Grande do Sul, Porto Alegre, RS, Brazil.
- Tindall, J.A., and J.R. Kunkel. 1999. *Unsaturated zone hydrology for scientists and engineers*. Prentice-Hall, Englewood Cliffs, NJ.
- USEPA. 2007. Method 3051A: microwave assisted acid digestion of sediments, sludges, soils, and oils. In: SW-846: Test methods for evaluation solid waste physical and chemical methods. USEPA, Washington, DC.
- 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. doi:10.2136/sssaj1980.03615995004400050002x
- van Oort, F., A.G. Jongmans, L. Citeau, I. Lamy, and P. Chevallier. 2006. Metal transport dynamics in soils as revealed by microscale zinc and lead distribution patterns in subsurface horizons. *Eur. J. Soil Sci.* 57:154–166. doi:10.1111/j.1365-2389.2005.00725.x
- Veiga, M., C.M. Pandolfo, A.A. Balbinot, Jr., and E. Spagnollo. 2012. Chemical attributes of a Hapludox soil after nine years of pig slurry application. *Pesq. Agropecu. Bras.* 47:1766–1773. doi:10.1590/S0100-204X2012001200013
- Venditti, D., S. Durécu, and J. Berthelin. 2000. A multidisciplinary approach to assess history, environmental risks, and remediation feasibility of soils contaminated by metallurgical activities: A. Chemical and physical properties of metals and leaching ability. *Arch. Environ. Contam. Toxicol.* 38:411–420. doi:10.1007/s002449910055
- Visser, A., J. Kroes, M.T.H. van Vliet, S. Blenkinsop, H.J. Fowler, and H.P. Broers. 2012. Climate change impacts on the leaching of a heavy metal contamination in a small lowland catchment. *J. Contam. Hydrol.* 127:47–64. doi:10.1016/j.jconhyd.2011.04.007
- Weber, W.J., Jr., P.M. McGinley, and L.E. Katz. 1991. Sorption phenomena in subsurface systems: Concepts, models and effects on contaminant fate and transport. *Water Res.* 25:499–528. doi:10.1016/0043-1354(91)90125-A
- Xue, H., P.H. Nhat, R. Gächter, and P.S. Hooda. 2003. The transport of Cu and Zn from agricultural soils to surface water in a small catchment. *Adv. Environ. Res.* 8:69–76. doi:10.1016/S1093-0191(02)00136-3
- Yadav, S.K. 2010. Heavy metals toxicity in plants: An overview on the role of glutathione and phytochelatin in heavy metal stress tolerance of plants. *S. Afr. J. Bot.* 76:167–179. doi:10.1016/j.sajb.2009.10.007