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MODELAGEM DA TRANSFERÊNCIA DE COBRE E ZINCO EM SOLOS CONTAMINADOS POR DEJETO LÍQUIDO DE SUÍNOS

TESE DE DOUTORADO

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Santa Maria, RS, Brasil

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MODELAGEM DA TRANSFERÊNCIA DE COBRE E ZINCO EM SOLOS CONTAMINADOS POR DEJETO LÍQUIDO DE SUÍNOS

Fábio Joel Kochem Mallmann

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Orientador: Prof. Danilo Rheinheimer dos Santos

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Universidade Federal de Santa Maria
Centro de Ciências Rurais
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MODELAGEM DA TRANSFERÊNCIA DE COBRE E ZINCO EM SOLOS CONTAMINADOS POR DEJETO LÍQUIDO DE SUÍNOS

elaborada por
Fábio Joel Kochem Mallmann

como requisito parcial para obtenção do grau de
Doutor em Ciência do Solo

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RESUMO

Tese de Doutorado
Programa de Pós-Graduação em Ciência do Solo
Universidade Federal de Santa Maria

MODELAGEM DA TRANSFERÊNCIA DE COBRE E ZINCO EM SOLOS CONTAMINADOS POR DEJETO LÍQUIDO DE SUÍNOS

AUTOR: FÁBIO JOEL KOCHEM MALLMANN
ORIENTADOR: DANILO RHEINHEIMER DOS SANTOS
LOCAL E DATA DA DEFESA: SANTA MARIA, 07 DE JUNHO DE 2013.

Solos submetidos a sucessivas aplicações de dejeto líquido de suínos (DLS) apresentam incrementos nos seus teores de zinco (Zn) e cobre (Cu), principalmente na camada superficial. A continuidade dessa prática faz com que esses metais pesados (MP) se acumulem no solo, aumentando o potencial de contaminação do ambiente. Dessa forma, o desenvolvimento de métodos que estimem o acúmulo superficial e o movimento de Zn e Cu no solo é de extrema importância no planejamento do manejo dos DLS e dos solos agrícolas que recebem esses resíduos. O trabalho objetivou modelar o transporte vertical de Zn e Cu no perfil de solos agrícolas contaminados por aplicações sucessivas de altas, moderadas e baixas doses de DLS, avaliando o efeito do revolvimento do solo e da absorção de água pelas raízes no movimento desses MP, prevendo, no longo prazo, seus acúmulos na camada superficial do solo e suas transferências rumo ao lençol freático, confrontando os resultados estimados com os respectivos limites de concentração para solos agrícolas e águas subterrâneas estabelecidos pelo Conselho Nacional do Meio Ambiente (CONAMA). Foram realizados dois estudos em experimentos de campo com diferentes doses de DLS, o primeiro localizado sobre um Argissolo, em Santa Maria – RS, e o segundo sobre um Latossolo, em Campos Novos – SC. Diversas características físico-hídricas e químicas foram determinadas nesses solos para, juntamente com os dados atmosféricos e do histórico de aplicação de DLS nessas áreas, serem introduzidos no HYDRUS-1D para parametrização do modelo químico de dois sítios utilizado. No primeiro estudo foram realizadas simulações para os próximos 100 anos, considerando cenários combinando duas doses de DLS e quatro intervalos de tempo entre revolvimentos periódicos da camada arável do solo. O modelo de transporte de solutos utilizado nessas simulações já havia sido validado para o solo deste local em outro trabalho. No segundo estudo foi feita a validação de um modelo de transporte de solutos, seguindo as mesmas premissas do modelo utilizado no Argissolo. Posteriormente, módulos de absorção de água e crescimento de raízes foram incorporados ao modelo. Realizaram-se então simulações futuras de cenários considerando aplicações de diferentes doses de DLS durante os próximos 50 anos. O modelo de transporte de solutos validado previamente no Argissolo foi validado também no Latossolo, apresentando resultados ainda melhores quando os módulos de raízes foram introduzidos no HYDRUS-1D. Isso aumenta a abrangência desse modelo para simular o transporte de Zn e Cu em outros solos contaminados. Os cenários futuros mostram que ocorre grande acúmulo desses MP na camada superficial do solo durante os períodos simulados. Além disso, quando os solos são submetidos a altas doses anuais de DLS, as suas concentrações de Cu atingem os valores máximos estipulados pelo CONAMA, para solos agrícolas, em aproximadamente 94 anos no Argissolo e 29 anos no Latossolo. Reduzir as doses de DLS e revolver o solo esporadicamente são alternativas que retardam o aumento da concentração desses MP na camada superficial do solo, diminuindo o potencial de impacto ao ambiente e tornando a adição de DLS em áreas agrícolas viável por mais tempo.

Palavras-chave: Dejeto líquido de suínos. Zinco. Cobre. HYDRUS-1D. Contaminação ambiental.

ABSTRACT

Doctor Science Thesis
Graduate Program in Soil Science
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MODELING OF COPPER AND ZINC TRANSFERENCE IN SOILS CONTAMINATED BY PIG SLURRY

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ADVISOR: DANILO RHEINHEIMER DOS SANTOS
PLACE AND DATE OF DEFENSE: SANTA MARIA, JUNE 07th, 2013.

Soils subjected to successive pig slurry (PS) amendments present zinc (Zn) and copper (Cu) increases, mostly on soil surface layer. The continuous application of PS causes accumulation of these heavy metals (HM) in soil, increasing risks for environmental contamination. Therefore, development of methods to estimate Zn and Cu accumulation in surface layer and their movement in soil is very important for the management planning of PS and of the agricultural soils amended with these residues. The main objective of this work was to model the vertical transport of Zn and Cu in profile of agricultural soils receiving successive application of PS at high, moderate and low doses, evaluating the effects of soil tillage and water absorption by roots on the movement of these HM. We also aimed to predict the long-term accumulation of HM in soil surface and their transport into groundwater, comparing estimated results with the threshold values established for agricultural soils and groundwater by the Conselho Nacional do Meio Ambiente (CONAMA). Two studies were performed on field experiments composed by different PS doses, the first located on an Alfisol in Santa Maria – RS, and the second on an Oxisol in Campos Novos – SC. Hydro-physical and chemical characteristics of these soils were measured and, accompanied by atmospheric and PS application data sets, were introduced into HYDRUS-1D for parameterization of the two-site model used. In the first study, simulations for next 100 years were performed under scenarios combining two PS doses and four time intervals between soil tillage of the arable layer. The solute transport model used on these simulations was already validated for this local soil in another study. In the second study, the validation of a solute transport model was carried out primarily, following the same approaches used for the Alfisol. Afterwards, root water uptake and root growth modules were introduced to the model. The future scenarios were simulated using applications of different PS doses during the next 50 years. The solute transport model previously validated for the Alfisol was also validated for the Oxisol, and the introduction of the root modules in HYDRUS-1D produced even better results. This increased the usefulness of the model for its use in simulations related to Zn and Cu transport on other contaminated soils. Future scenarios exhibit a great accumulation of these two HM in soil surface layer during the simulated times. Moreover, when soils are submitted to high PS annual doses, its Cu concentrations reached the maximum values established by CONAMA for agricultural soils in approximately 94 years on the Alfisol and in 29 years on the Oxisol. Reduction in PS doses and sporadic soil tillage are strategies that slow the increase of these HM concentrations in soil surface layer, decreasing so the environmental risks and making PS additions on agricultural soils viable for longer time.

Key words: Pig slurry. Zinc. Copper. HYDRUS-1D. Environmental contamination.

LISTA DE TABELAS

ARTIGO I

ARTIGO II

LISTA DE FIGURAS

ARTIGO I

ARTIGO II

DISCUSSÃO GERAL

LISTA DE APÊNDICES

SUMÁRIO

1 INTRODUÇÃO GERAL

A atividade agrícola altera as características originais dos locais onde é introduzida e desenvolvida. Isso ocorre por causa da substituição de espécies, alteração do manejo do solo, utilização de fertilizantes (minerais ou orgânicos) e biocidas (inseticidas, fungicidas, herbicidas). A aplicação intensiva e em longo prazo de produtos nos cultivos agrícolas pode contaminar o solo e as águas pela introdução de várias substâncias ou elementos químicos. Entre os principais estão o fósforo (P), o nitrogênio (N), os pesticidas e os metais pesados.

Os metais pesados são constituintes naturais das rochas e dos solos. Normalmente, esses elementos se encontram em baixas concentrações, não representando assim riscos para o homem, animais e plantas (COSTA et al., 2004). A sua concentração natural no solo, também chamada de fundo geoquímico local, é derivada principalmente do material de origem associado aos processos e fatores que atuaram na sua formação (BURNOL et al., 2004). Entretanto, o emprego prolongado de fungicidas, fertilizantes, esterco de animais, lixo urbano ou lodos de esgoto, pode elevar as concentrações de metais pesados até níveis potencialmente tóxicos às plantas, resultando em uma possível contaminação da cadeia trófica (MATTIAS, 2006), e/ou aos corpos de água superficiais e subsuperficiais.

Na região Sul do Brasil, em especial nos estados do Rio Grande do Sul (RS) e de Santa Catarina (SC), destaca-se uma prática agrícola que introduz quantidades elevadas de metais pesados ao solo, que é a aplicação de dejeto líquido de suínos (DLS) com o intuito de adubar o solo ou descartar este resíduo. Os DLS são os resíduos orgânicos gerados pela suinocultura, caracterizados pela sua propriedade fertilizante por conter vários nutrientes, principalmente de P, K e N (CQFS-RS/SC, 2004). Além de macronutrientes, os DLS também possui na sua composição alguns metais pesados, principalmente Zn e Cu, que, segundo Jondreville et al. (2003), são oriundos das rações fornecidas aos suínos, adicionados a elas em altas concentrações como suplemento alimentar, geralmente em quantidades que excedem o requerimento fisiológico desses animais. Também chamados de aditivos, o Zn e o Cu exercem efeitos farmacológicos benéficos aos animais, podendo aumentar sua eficiência alimentar e produtividade (MANTOVI et al., 2003). Do total desses dois elementos químicos adicionado às rações dos suínos, Bonazzi et al. (1994) estimam que de 92 a 96 % do Zn e de 72 a 80 % do Cu são eliminados nos seus dejetos. A adição de Zn e Cu ao solo via aplicações sucessivas de DLS ocorre em quantidades muito maiores que aquelas necessárias ao bom

desenvolvimento das culturas (LEGROS et al., 2013). A partir disso e em função da mobilidade limitada destes elementos no solo, ocorre aumento nos teores totais desses dois metais pesados no solo que, ao longo do tempo, atingem concentrações elevadas principalmente na camada superficial. Pelo risco de transporte por erosão, há grande preocupação com o alto potencial contaminante desses resíduos ao ambiente.

O acúmulo excessivo de Zn e Cu em solos submetidos à aplicação de DLS e os seus problemas ao ambiente já foram relatados em vários trabalhos científicos no mundo. Como exemplos temos os trabalhos de L'Herroux et al. (1997) na França, citando que o incremento de Zn e Cu na camada superficial do solo ocorre nas frações mais disponíveis às plantas ou aptas a deixar o solo por escoamento superficial ou lixiviação; de Mantovi et al. (2003) na Itália, que constataram que as concentrações destes metais pesados no solo após 15 anos de aplicação de DLS podem afetar o crescimento de plantas; e de Ogiyama et al. (2005) no Japão, relatando o alto potencial contaminante destes metais pesados aos solos aráveis, podendo ultrapassar o nível regulatório em apenas 5 anos.

Além da influência do clima no potencial de risco dos contaminantes ao ambiente e apesar do solo ser considerado um filtro natural, cada tipo de solo apresenta capacidade definida de adsorver determinado elemento. Por serem elementos altamente reativos com os grupos funcionais, tendem a se ligar às partículas do solo e apresentar baixa mobilidade no perfil. Porém, cada tipo de solo apresenta uma capacidade de adsorção limitada e, a partir do momento em que esta for atingida, os metais pesados serão transportados com maior velocidade para as camadas mais profundas do perfil do solo. As características do solo que interferem na sua capacidade de adsorver metais pesados são, principalmente, o pH, o teor de matéria orgânica e a presença de óxidos de ferro, alumínio e manganês (COSTA et al., 2004). É importante destacar, também, que o processo de adsorção dos elementos químicos aos mais variados grupos funcionais de partículas reativas do solo são dependentes do tempo. Nesse sentido, Barrow (1999) relata que, com a adição de determinado elemento ao solo, ocorre inicialmente uma reação de adsorção relativamente rápida na superfície da partícula do solo, que atinge o equilíbrio em poucas horas, seguida então por outras reações muito mais lentas. Isso também confere ao solo certa capacidade de adsorção temporal para determinado elemento ou substância. Em função desses aspectos é necessário quantificar a capacidade do solo em reter os contaminantes sem causar prejuízos ao ambiente. Para isso, devemos saber, também, como ocorre a dinâmica e a velocidade de adsorção dos metais pesados oriundos das mais variadas fontes, entre elas os DLS, nos diferentes tipos de solo. Isso possibilita verificar se determinada atividade apresenta riscos ao ambiente no curto e longo prazo.

Atualmente a demanda social e ambiental de estudos sobre a contaminação do solo, da água, enfim, dos recursos naturais em geral, é grande, pois a elevação dos níveis de contaminação acima de concentrações suportadas pela biota gera a poluição, que irá afetar o crescimento e desenvolvimento dos seres vivos no entorno. Para tentar controlar os níveis de contaminação e manter a qualidade do ambiente, os órgãos reguladores, como o Conselho Nacional do Meio Ambiente, estabelecem limites de concentração para cada elemento, tanto no solo como na água (CONAMA, 2009). Porém, muitas vezes não se sabe qual é a capacidade que determinado solo tem de receber a adição de contaminantes sem ultrapassar esses limites.

Além disso, há também a demanda científica por informações. Segundo Carrillo-González et al. (2006), nos últimos anos tem aumentado muito o uso de modelos matemáticos no estudo do movimento de contaminantes desde a superfície do solo até o lençol freático. Porém, esses estudos são quase que exclusivamente desenvolvidos no exterior. No Brasil, estudos sobre a modelagem de fluxo de água e de solutos no solo ainda são escassos.

Entretanto, o uso de modelos matemáticos para simular determinado fenômeno requer, primeiramente, uma base de dados com grande número de variáveis e com resultados de qualidade (HAAN et al., 1994). Quanto maior for o conjunto de dados disponíveis, maior o potencial de uso de modelos matemáticos mais complexos. Cabe ressaltar então que a etapa de campo e/ou laboratorial de um estudo é muito importante, pois é ela quem fornecerá sustentação para viabilizar a aplicação de um modelo matemático.

Dependendo do propósito do trabalho e do modelo matemático a ser utilizado, há a necessidade de se fazer um monitoramento das características do local de estudo por longos períodos. Isso aumenta a dificuldade para a obtenção das amostras, pois requer muito trabalho, recurso financeiro e disponibilidade de mão-de-obra. A obtenção de amostras que sejam realmente representativas do local ou situação amostrada, além do uso de metodologias laboratoriais não apropriadas para mensurar determinadas características dos parâmetros requeridos pelos modelos, também são problemas que precisam ser superados. Šimůnek e van Genuchten (1999) comentam que a dificuldade de se obter medidas precisas das propriedades hidráulicas do solo se deve à alta não-linearidade destas propriedades, às limitações instrumentais e à alta heterogeneidade do ambiente subsuperficial.

Atualmente estão sendo desenvolvidos modelos computacionais cada vez mais complexos para simular fluxos subsuperficiais e processos de transporte. A qualidade dessas simulações numéricas depende largamente da acurácia com que vários parâmetros do modelo podem ser estimados (Šimůnek; van Genuchten, 1999), reforçando novamente a necessidade

de se obter medições precisas das propriedades do solo. Entre elas, Inoue et al. (2000) destaca os parâmetros hidráulicos do solo, que caracterizam a retenção da água e a permeabilidade do solo, bem como os parâmetros químicos e de transporte, que afetam a taxa de propagação dos elementos químicos e a sua distribuição entre as fases sólida e líquida, afirmando que elas são as variáveis de entrada mais importantes para tais modelos.

Modelos de fluxo e transporte para a zona insaturada geralmente são baseados nas soluções numéricas da equação de Richards (equação 1). Essa equação requer conhecimento das funções hidráulicas do solo não saturado, como a curva de retenção de água e a condutividade hidráulica não saturada. Elas são representadas pelas funções $\theta(h)$, que descreve a relação entre o conteúdo e a tensão de água no solo (equação 3), e $K(h)$, que define a condutividade hidráulica em função da tensão da água no solo (equação 5), respectivamente (Šimůnek; van Genuchten, 1999). Essas equações serão brevemente descritas a seguir.

Equação de Richards:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x}\left[K(\theta)_x \frac{\partial h}{\partial x}\right] \tag{1}$$

dada para uma dimensão, onde: θ é a umidade do solo; t é o tempo; x é a posição; $K(\theta)$ é a condutividade hidráulica não-saturada; e h é a pressão no solo.

A equação de Richards deriva da equação da continuidade, que para apenas uma dimensão é assim descrita:

$$\frac{\partial \theta}{\partial t} = -\frac{\partial q_x}{\partial x} \tag{2}$$

onde: q_x é a densidade de fluxo de água.

A equação de van Genuchten (1980) descreve as características da adsorção de água no solo:

$$\theta(h) = \theta_r + \frac{(\theta_s - \theta_r)}{[1+(\alpha h)^n]^m} \tag{3}$$

onde: θ é o conteúdo volumétrico de água no solo ($cm^3\ cm^{-3}$); θ_r é a umidade volumétrica residual ($cm^3\ cm^{-3}$); θ_s é a umidade volumétrica do solo saturado ($cm^3\ cm^{-3}$); h é a pressão de água no solo (cm H_2O); e α, n e m são os coeficientes empíricos, sendo que m é obtido através da equação 4:

$$m = 1 - \frac{1}{n} \tag{4}$$

A função $K(h)$, dada na equação 5, é descrita pela combinação da equação 3 com o modelo de distribuição de poros para a condutividade hidráulica não-saturada de Mualem (1976):

$$K(h) = K_s \frac{|1-(\alpha|h|)^{mn}\,(1+(\alpha|h|)^n)^{-m}|^2}{[1+(\alpha\,h)^n]^{ml}} \quad (5)$$

onde: K_s é a condutividade hidráulica saturada; e l é o fator tortuosidade e conectividade entre poros.

Já os modelos utilizados para simulação do transporte de solutos no solo geralmente são empíricos, baseados em hipóteses de equilíbrio termodinâmico local e sem identificar os mecanismos envolvidos na reação. Eles não consideram toda a complexidade envolvida no fenômeno, mas se foram calibrados e validados adequadamente para as situações e locais onde forem aplicados, apresentarão resultados satisfatórios (RHEINHEIMER et al., 2007). Por isso, antes de se fazer inferências sobre o comportamento de determinado elemento no solo do local em questão, deve-se validar os modelos químicos a serem utilizados.

Os modelos empíricos utilizados nas simulações do transporte de solutos, entre eles os metais pesados, estão associados ao uso de isotermas de adsorção (FONTES; ALLEONI, 2006). Uma forma simplificada de representar o grau de associação ou dissociação de um metal pesado na fase sólida é o seu simples particionamento, que é a razão entre a quantidade de metal adsorvido na fase sólida e de metal dessorvido na solução, representada pela expressão:

$$K_d = \frac{metal_{adsorvido}}{metal_{dessorvido}} \quad (6)$$

Quanto maior o valor do coeficiente de partição (K_d), maior a adsorção na fase sólida e menor a dessortividade do metal, mantendo assim menor quantidade do elemento em solução (SILVEIRA et al., 2003). Esse parâmetro é muito útil na comparação da capacidade de adsorção de diferentes solos ou materiais para qualquer íon, desde que medidos nas mesmas condições (ALLOWAY, 1990).

Rheinheimer et al. (2007) também destacam a possibilidade da utilização de outras isotermas de adsorção/dessorção, que descrevem melhor o fenômeno da reatividade dos metais pesados entre as fases líquida e sólida do solo, em função da introdução de novos parâmetros. Entre as principais, estão as equações de Langmuir (7) e de Freundlich (8).

$$M_{ads} = \frac{(K\,C\,b)}{(1+K\,C)} \quad (7)$$

onde: M_{ads} é a quantidade de metal adsorvido; K é uma constante relacionada à energia de ligação (parâmetro ajustável); C é a concentração de equilíbrio; e b é a quantidade máxima de metal adsorvido.

$$M_{ads} = k\,C^n \quad (8)$$

onde: k e n são parâmetros de regressão.

A principal desvantagem do uso deste modelo é que ele não inclui um máximo de adsorção como o modelo anterior (SILVEIRA et al., 2003). Porém, a equação de Freundlich já foi utilizada e validada em trabalhos simulando o transporte vertical de Zn e Cu (MALLMANN et al., 2012a) e de Zn e Pb (MALLMANN et al., 2012b) no perfil de solos contaminados.

Existem várias outras equações que simulam a reatividade química dos elementos com a fração sólida do solo, com graus de complexidade variados (GOLDBERG et al., 2007; RHEINHEIMER et al., 2007). Entretanto, a escolha de uma delas irá depender da disponibilidade e qualidade de dados para a realização do trabalho. Ainda nesse sentido, Goldberg et al. (2007) afirmam que, para ser aplicado num modelo de transporte de solutos e nas aplicações de avaliação de risco, a complexidade do modelo de adsorção precisa ser balanceada com o objetivo de se utilizar, entre aqueles que se apresentarem consistentes com os dados observados, o modelo mais simples possível.

Nas últimas décadas houve grande progresso na compreensão e descrição dos processos matemáticos que regem o movimento da água e o transporte de solutos em solos não saturados (VAN GENUCHTEN; ŠIMŮNEK, 2004). A partir disso, muitos modelos foram desenvolvidos para quantificar os processos físicos e químicos que interferem no transporte da maioria dos íons. Primeiramente, os modelos hidrológicos, de transporte de solutos e de equilíbrio químico com a água eram desenvolvidos independentemente e somente mais tarde, com a evolução dos processos computacionais, é que esses três modelos foram acoplados (SUAREZ; ŠIMŮNEK, 1997). Tais modelos geralmente são baseados nas soluções numéricas da equação de Richards para o fluxo saturado/não saturado da água no solo e da equação de convecção-dispersão de Fickianbased para o transporte de solutos (GONÇALVES et al., 2006).

Entre os modelos computacionais que simulam o transporte de solutos, os mais utilizados, segundo Gonçalves et al. (2007), tem sido o LEACHM (WAGENET; HUTSON, 1987) e o UNSATCHEM (ŠIMŮNEK et al., 1996). Mais recentemente o UNSATCHEM foi incorporado ao HYDRUS-1D, originando as versões 3.0 e 4.0 deste último (ŠIMŮNEK et al., 2012), tornando-o uma poderosa ferramenta para simular o fluxo vertical de água e o transporte de solutos em solo com saturação variável. Além do UNSATCHEM e do HYDRUS-1D, Šimůnek et al. (1999) desenvolveram o HYDRUS-2D, capaz de simular os mesmos processos do HYDRUS-1D em duas dimensões. Recentemente, baseado nos dois softwares anteriores e introduzindo vários processos novos, Šimůnek et al. (2006) também desenvolveram o HYDRUS-2D/3D, que realiza simulações em duas ou três dimensões.

Atualmente, os softwares HYDRUS-1D e HYDRUS-2D/3D são constantemente avaliados por pesquisadores em todo o mundo, muitas vezes gerando novas demandas que fazem com que eles sejam continuamente aprimorados (ŠIMŮNEK et al., 2008). Segundo Yu e Zheng (2010), o HYDRUS é estável, eficiente e fácil de usar, destacando também que ele é uma boa escolha para qualquer pesquisador ou engenheiro ambiental interessado em fluxo subterrâneo, transporte ou remediação onde condições de saturação variável precisam ser consideradas.

O HYDRUS utiliza a equação de Richards (1) para o fluxo de água em ambiente com saturação variável e a equação para o transporte não reativo de solutos (*J*) do tipo convecção-dispersão (9) (ŠIMŮNEK et al., 1999):

$$J = -C\left[K(\theta)\frac{\partial H}{\partial ds}\right] - \theta D\frac{\partial C}{\partial s} \tag{9}$$

onde: *C* é a massa de solução dissolvida; *K(θ)* é a condutividade hidráulica não saturada; *H* é o potencial hidráulico da água; *D* é o fluxo hidrodinâmico dispersivo; e *s* é a distância transportada.

Ainda em relação à reatividade química, para um modelo químico de dois sítios o modelo de reatividade do metal pesado com o solo, que está acoplado ao modelo não reativo de transporte de solutos, é dado pelas equações que compõem o balanço de massas (10):

$$S_T = S_{eq} + S_{non} \tag{10}$$

onde: S_T são os sítios totais do solo; S_{eq} é a fração do metal pesado que reage rapidamente com a fase sólida do solo, controlada pelo equilíbrio químico instantâneo; e S_{non} é a fração do metal pesado que reage mais lentamente com a fase sólida do solo, seguindo uma cinética de reação lenta, que é controlada principalmente pela difusão.

O balanço de massas também pode ser descrito assim:

$$S_T = \beta S_T + (1-\beta)S_T \tag{11}$$

em que β é o coeficiente de partição entre os sítios em equilíbrio e os sítios cinéticos.

As duas frações que compõem os sítios totais são demonstradas nas equações 12 e 13:

$$S_{eq} = \frac{K\,C^n}{1+m\,C^n} \tag{12}$$

onde: *C* é a concentração do metal pesado na solução do solo; e *K*, *m* e *n* são parâmetros ajustáveis que variam com o tipo e concentração do metal pesado e com a natureza dos constituintes do solo.

$$\rho\frac{\partial S_{non}}{\partial t} = \alpha\,C\,\theta - \lambda\,\rho\,S_{non} \tag{13}$$

onde: ρ é a densidade do solo; θ é a umidade do solo; α é uma constante cinética dianteira; λ é uma constante cinética retrógrada; e *t* é o tempo.

Além das equações acima apresentadas, o HYDRUS possibilita ao usuário escolher diversas outras equações e modelos disponíveis na plataforma do programa. Isso lhe confere alta versatilidade e capacidade de adaptação às mais diversas condições. Mundialmente já foram realizados vários trabalhos utilizando este software como ferramenta para estimar o fluxo de água e/ou o transporte de solutos, como por exemplo os de Jacques et al. (2002) na Bélgica, Coquet et al. (2005) na França, Köhne et al. (2006) nos Estados Unidos, Pang e Šimůnek (2006) na Nova Zelândia, Rajmohan e Elango (2007) na Índia e Yoon et al. (2007) na Coréia.

Se adequadamente utilizado, o software HYDRUS possibilita aprofundar o conhecimento das zonas de saturação variável do solo que, segundo Yu e Zheng (2010), são fundamentais para entender vários aspectos da hidrologia, entre elas a infiltração, o armazenamento de água no solo, a evaporação, a absorção de água, a recarga das águas subterrâneas, o escoamento superficial e a erosão. Além disso, cresce cada vez mais a demanda por estudos focados no ciclo integrado da água, que consideram as trocas de água e solutos entre a superfície e as águas subterrâneas, incluindo as zonas saturadas e não saturadas do solo, como é o caso dos estudos de Mallmann et al. (2012a) e Rheinheimer et al. (2013) sobre a predição do movimento de Zn, Cu e Pb em solos contaminados e o potencial de contaminação da água subterrânea, ambos utilizando o software HYDRUS. Portanto, em função da descrição, da flexibilidade, da importância e do impacto do HYDRUS no meio científico, ele será muito útil no desenvolvimento dos estudos propostos nesta tese e ajudará a alcançar os objetivos traçados.

2 HIPÓTESES

Os modelos matemáticos de transporte de solutos envolvem o acoplamento de modelos de fluxo hidráulico e de modelos de reatividade dos solutos com a fase sólida do solo. Antes de realizar previsões com esses modelos, os mesmos necessitam ser validados. Nesse sentido, um modelo de transporte de solutos que utilize equações relativamente simples, como as de dois-sítios (uma fração dos grupos funcionais do solo reage imediatamente com os solutos, chamados de sítios ao equilíbrio, e outra fração dos grupos funcionais que reage com menor velocidade, os chamados sítios cinéticos), e suprido por características do solo, atmosféricas e dos contaminantes, e por parâmetros das equações determinados diretamente nas amostras de solo dos locais de estudo, é suficiente para simular o transporte vertical de zinco e cobre em solos agrícolas contaminados pelo uso de diferentes doses de dejeto líquido de suínos, sejam eles revolvidos periodicamente ou não.

A alteração do código do HYDRUS, com a introdução de novas ferramentas ou ajuste daquelas já disponíveis, permite sua adaptação às condições específicas dos trabalhos realizados neste estudo e viabiliza sua aplicação no estabelecimento de estratégias de manejo do solo, como o revolvimento periódico do solo, e do dejeto líquido de suínos, como a aplicação sucessiva de baixas ou altas doses, visando o prolongamento da atividade agrícola associado à diminuição da contaminação ambiental por ela gerada.

As sucessivas aplicações de altas doses de dejeto líquido de suínos em áreas agrícolas no longo prazo elevam os teores de zinco e cobre na camada superficial do solo para níveis acima dos permitidos pela legislação brasileira, principalmente quando não for revolvido.

A prática de revolvimento do solo, quando realizada esporadicamente na camada superficial de 0–20 cm, prolonga o uso de solos agrícolas para o descarte de dejeto líquido de suínos, pois eleva os teores de zinco e cobre na camada inferior da camada arável, aumentado assim suas transferências para as camadas de solo abaixo de 20 cm de profundidade. Além disso, essa prática favorece que os teores de zinco e cobre sejam mantidos, no longo prazo, abaixo dos limites estabelecidos pela legislação brasileira, principalmente quando associada à aplicação de baixas doses desse resíduo.

Os teores naturais de zinco e cobre do solo influenciam no tempo máximo que ele pode suportar, no âmbito da lei, a aplicação periódica das respectivas doses de dejeto líquido de suínos, sem ultrapassar os limites estabelecidos pela legislação brasileira.

3 OBJETIVO GERAL

O trabalho objetivou modelar o transporte vertical de zinco e cobre no perfil de solos agrícolas contaminados por aplicações sucessivas de altas, moderadas e baixas doses de dejeto líquido de suínos, avaliando o efeito do revolvimento do solo e da absorção de água pelas raízes no movimento desses metais pesados, prevendo, no longo prazo, seus acúmulos na camada superficial do solo e suas transferências rumo ao lençol freático, confrontando os resultados estimados com os respectivos limites de concentração para solos agrícolas e águas subterrâneas estabelecidos pelo Conselho Nacional do Meio Ambiente (CONAMA).

4 ESTRATÉGIA DE ESTUDO

Procurando responder às hipóteses e atender ao objetivo proposto por esta tese, foi adotada como estratégia a divisão do trabalho em dois capítulos, os quais estão escritos com formatação de artigo científico. Esses artigos foram elaborados seguindo as normas do periódico internacional Agriculture, Ecosystems & Environment.

O primeiro estudo consiste na continuação de parte do trabalho realizado pelo autor em sua dissertação de mestrado (MALLMANN, 2009; MALLMANN et al., 2012a), que validou um modelo químico para simulação do transporte de Zn e Cu no perfil de um Argissolo Vermelho distrófico típico, localizado em Santa Maria (RS), submetido a sucessivas aplicações de dejeto líquido de suínos. Neste capítulo foram realizadas simulações futuras, de 100 anos, prevendo o acúmulo desses dois metais pesados na camada superficial do solo e as suas transferências para camadas mais profundas. Para tal, foram criados diversos cenários em função das doses de dejeto a serem aplicadas a cada cultivo e de diferentes intervalos de tempo entre as operações de revolvimento da camada arável do solo (0–20 cm). Para realizar as previsões contendo as operações de revolvimento do solo, necessitou-se primeiramente criar um novo módulo que simulasse essa prática. Este módulo foi desenvolvido, testado e acoplado ao HYDRUS-1D durante o período de doutorado sanduíche (bolsa SWE do CNPq) realizado entre 01 de setembro e 30 de novembro de 2012, sob orientação do professor Ph.D. Jirka Šimůnek, na University of California Riverside (UCR), localizada em Riverside, Califórnia, Estados Unidos. Verificou-se, no longo prazo, o efeito de altas e baixas doses de dejeto líquido de suínos e das operações de revolvimento do solo sobre o movimento vertical de Zn e Cu no perfil. Também foi estimado o período de tempo em que o solo poderá ser submetido às sucessivas aplicações desse resíduo sem elevar os teores dos dois metais pesados para acima dos valores máximos estipulados pela legislação brasileira.

No segundo estudo buscou-se validar o mesmo modelo químico de transporte de solutos do capítulo anterior, usando o HYDRUS-1D, num Latossolo Vermelho distroférrico típico, visando aumentar a abrangência do uso deste tipo de modelo. Também foi simulada a influência da absorção de água pelas raízes, e consequente transferência para a atmosfera via transpiração, no movimento de Zn e Cu no perfil do solo, bem como realizadas simulações prospectivas para um período futuro de 50 anos. Este estudo foi realizado utilizando-se um experimento com aplicação de diferentes doses de dejeto líquido de suínos, localizado na área

experimental da Cooperativa Regional Agropecuária de Campos Novos (Copercampos) e conduzido pela Empresa de Pesquisa Agropecuária e Extensão Rural de Santa Catarina (Epagri) de Campos Novos, SC. Durante a condução deste experimento, entre os anos de 2000 e 2011, foram realizadas 22 aplicações de dejetos, aumentando consideravelmente os teores de Zn e Cu no perfil do solo. Os parâmetros relacionados ao fluxo de água e ao transporte de solutos exigidos pelo HYDRUS-1D foram medidos e extraídos das amostras de solo coletadas no experimento. Os dados atmosféricos de precipitação e evapotranspiração referentes ao período de condução do experimento, e que foram usados nas simulações, foram obtidos e calculados a partir dos dados diários da estação meteorológica da Epagri de Campos Novos. Já as quantidades de Zn e Cu aportadas ao solo foram estimadas pela diferença entre os estoques no solo dos tratamentos com adição de dejeto (50 ou 200 m^3 ha^{-1} ano^{-1}) e o tratamento testemunha, sendo que sua distribuição nas simulações seguiu o histórico de aplicações de dejetos no experimento. Neste estudo, o período de doutorado sanduíche na UCR contribuiu no desenvolvimento das estratégias de simulação, bem como no aprendizado das ferramentas relacionadas ao crescimento radicular e à absorção de água pelas raízes, disponíveis no HYDRUS-1D. Utilizando o conjunto de dados anteriormente citado, realizaram-se as simulações para a validação do modelo químico e, posteriormente, as simulações dos cenários futuros, verificando o efeito das doses de dejeto líquido de suínos no aumento dos teores de Zn e Cu nas camadas superficiais do Latossolo e no movimento destes metais pesados para camadas mais profundas do perfil. Tais estimativas nos fornecem indícios sobre o período viável da aplicação de dejeto líquido de suínos em solos agrícolas de textura argilosa e com elevados teores de óxidos.

5 ARTIGO I – Revolvimento do solo para redução da contaminação superficial de metais – desenvolvimento de um modelo e simulações futuras das concentrações de zinco e cobre no perfil de um Argissolo do sul do Brasil submetido a aplicações de dejeto líquido de suínos por longo período

Soil tillage to reduce surface metal contamination – model development and prospective simulations of zinc and copper concentration profiles in a long-term pig slurry-amended Alfisol in Southern Brazil[1]

Abstract

Long term applications of organic amendments, such as pig slurry (PS), may represent environmental risk of soil and water pollution by heavy metals (HM). Our objective was to examine different soil and manure management scenarios enhancing 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. Second, we used a previously validated modeling approach to predict the next 100-year surface HM accumulation and movement in the soil under different PS doses (80 and 40 m^3 ha^{-1} $cultivation^{-1}$) and tillage frequencies (no-tillage, and 20, 10, and 5-year tillage). No-tillage simulations revealed consistent HM surface accumulations, reaching the soil threshold value for Cu in the layer 0–20 cm 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 HM 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

[1] Artigo elaborado de acordo com as normas da revista Agriculture, Ecosystems & Environment.

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.

Keywords: HYDRUS-1D; heavy metals; organic waste; solute movement; groundwater pollution; surface accumulation.

5.1. 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 and, hence, represent environmental risk for soil and groundwater pollution. Recently, we have carried out validating and prospective modeling work, using the HYDRUS software package, to simulate the movements of heavy metals (HM) 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). After that, we have successfully applied the same modeling approach to simulate the movement of Zn and copper (Cu) in an Alfisol in Southern Brazil, receiving repetitive applications of pig slurry (PS) (Mallmann et al., 2012b). In addition to containing major nutrients such as phosphorus (P), nitrogen (N), and potassium (K) (Lourenzi et al., 2013), PS includes certain amounts of oligo-nutrient elements such as Zn and Cu that at high concentrations become contaminants (Girotto et al., 2010; Berenguer et al., 2008; L'Herroux et al., 1997). 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 part of Zn and Cu is not absorbed by the animal 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 investigation value for agricultural areas of 200 mg kg^{-1}, established by the Conselho Nacional do Meio Ambiente (CONAMA, 2009).

Such strong accumulation of HMs 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 directly on the soil surface without its previous preparation and using crop rotation (Mello and van Raij, 2006). Therefore, no-tillage practices in agricultural lands under long-term PS amendments lead to the accumulation of Zn and Cu within the first few centimeters of the soil profile, and reduce the movement of these HMs to layers below the depth of 20 cm. In this view, soils under the no-tillage management have disadvantage in comparison to soils under the conventional tillage management where the surface layer is annually mixed by plowing and, consequently, the concentrations of possible added micropollutants are mechanically homogenized over the entire plow-depth (about 20 cm). Hence, introducing periodical soil tillage, as a sustainable land management practice, represents an original solution for reducing the rapid accumulation of HMs at the soil's surface by mixing them over a greater depth and promoting their transfer to depths below 20 cm. It also represents a solution to comply with Brazilian environmental guidelines on maximum HM values (CONAMA, 2009), which may be restrictive for long-term organic amendments on no-tillage farming systems.

Soil tillage practices, however, by favoring the downward movement of HMs to depths below the plow layer, lead to an increase of their concentrations in the soil solution. Such effect may propagate down to the bottom of the soil profile and requires 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 can simulate 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, 2012b) to predict the surface accumulation, soils solution concentrations, and redistribution of HMs 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.

5.2. Materials and Methods

5.2.1. 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°42'52"S and 53°42'10"W, 90 m altitude). An experiment, receiving applications of different PS doses (0, 20, 40, and 80 m^3 ha^{-1}) applied at the soil's surface before each cultivation, two to three times per year, conducted during eight years (2000 – 2008) under no-tillage management, serves as the basis of this study.

Soil samples from a plot with the 80 m^3 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, pH_{H2O}, 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 on Table 1.

5.2.2. 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.

HYDRUS-1D requires additional hydro-physical and chemical parameters to run all desired simulations. The hydro-physical parameters include the saturated hydraulic conductivity (K_s), the soil residual (θ_r) and saturated (θ_s) water contents, parameters α and n obtained from SWRC, and pore connectivity/tortuosity factor (L). The chemical parameters include the initial Zn and Cu solution concentrations; the Freundlich's n and K_F parameters, related to adsorption/desorption process; and the β (the fraction of sorption sites with instantaneous HM adsorption to the functional groups - at equilibrium) and λ (a kinetic

desorption constant) parameters. The latter two parameters describe the HM partitioning between the soil and solution and the adsorption/desorption rate for soil's kinetic sites, respectively. These hydro-physical and chemical parameters were determined for all soil layers from the experiment with the 80 m^3 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 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) (Figure 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 HMs added to the soil during the simulated 100-year period, considering a PS dose of 80 m^3 ha^{-1} $cultivation^{-1}$, were 954 and 704 kg ha^{-1} of Zn and Cu, respectively. For simulations that considered the 40 m^3 ha^{-1} doses, corresponding amounts were half, *i.e.*, 477 and 352 kg ha^{-1}, respectively. More details about the temporal distribution of HMs 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 HMs 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, 2012b), which considers that the total HM concentration in the soil is partitioned between soil water and instantaneous and kinetic sorption sites. Our simulations included estimations of HM 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 m^3 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 80m^3 no-till, 80m^3 20y-till, 80m^3 10y-till, and 80m^3 5y-till, respectively. Scenarios E through H involved 40 m^3 ha^{-1} PS doses (a moderate dose) and the same sequence of soil tillage frequencies, hereafter referred to as 40m^3 no-till, 40m^3 20y-till, 40m^3 10y-till, and 40m^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.

5.2.3. 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:

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

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

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

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

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

Since the solute transport model adopted in this study considers a nonreactive 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:

$$S_e = \int [\theta(z)c(z) + f\rho s_e(z)]dz \tag{3}$$

$$S_k = \int [(1-f)\rho s_k(z)]dz \tag{4}$$

where s_e and s_k are solid phase concentrations at equilibrium and kinetic sorption sites, respectively, and S_e and S_k are solute masses in equilibrium and nonequilibrium 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:

$$\overline{s_k} = \frac{S_k}{(1-f)\rho L_{tillage}} = \frac{\int [(1-f)\rho s_k(z)]dz}{(1-f)\rho L_{tillage}} \tag{5}$$

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.

5.3. Results

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

Simulations of scenarios without soil tillage produced a high HM 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 (80m^3 no-till) (Figure 2A) and to 160.0 mg kg^{-1} in scenario E (40m^3 no-till) (Figure 2E). For the same scenarios, the Cu increases were even higher, *i.e.*, from an initial value of 59.4 to 445.0 and 246.0 mg kg^{-1}, respectively (Figure 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 m^3 ha^{-1}, respectively (Figure 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 (Figure 5).

No-tillage scenarios also showed a great increase of HM 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 m^3 ha^{-1}, respectively (Figure 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 (Figure 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 m^3 ha^{-1} PS doses, respectively.

5.3.2. 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 m^3 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 m^3 ha^{-1} doses (scenarios F, G, and H), these concentrations were 87.3, 86.0, and 83.4 mg kg^{-1}, respectively (Figure 2). For Cu, the surface concentrations reached 230.5, 210.6, and 189.4 mg kg^{-1} when using 80 m^3 ha^{-1} PS doses (scenarios B, C and D), and 128.3, 116.3, and 107.2 mg kg^{-1} when using 40 m^3 ha^{-1} PS doses (scenarios F, G and H, Figure 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 (Figure 4) and to 172 and 97 mg kg^{-1} for Cu (Figure 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 m^3 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} (Figure 4). For moderate PS doses (40 m^3 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 (Figure 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 m^3 ha^{-1} PS doses, respectively (Figure 6).

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 (Figure 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 (Figure 5). Thus, the cumulative amounts of Cu loss to depths below 60 cm when using PS doses of 80 m^3 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 m^3 ha^{-1}, they were 26.4, 27.9, and 29.4 for scenarios F, G and H, respectively (Figure 6).

5.4. Discussion

5.4.1. 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 HM 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 m^3 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 (Figure 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 (Figure 7). This Cu concentration (*i.e.*, 200 mg kg^{-1}) refers to the Brazilian threshold value, also defined as an investigation 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} (Figure 7).

When the PS doses of 40 m^3 ha^{-1} were used, the Cu concentrations in the surface 0–5 cm layer exceeded 200 mg kg^{-1} 38 years later than for the 80 m^3 ha^{-1} PS doses. In this case, scenario E, the soil threshold value of CONAMA (2009) was not reached during the 100-year simulation. The final Cu concentration in the 0–20 cm soil layer reached only 120 mg kg^{-1}. 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 HMs. 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 the Brazilian threshold value for agricultural soils when the 80 m^3 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 HM 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 HMs 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 HMs in soil, with Zn showing higher mobility than Cu (McBride, 1994) and, consequently, generally observed higher transfers of Zn to deeper layers. Moreover, when HM 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 HMs to adsorption sites in the plow layer, and thus reduce their solution concentrations.

5.4.2. Effects of tillage on Zn and Cu distribution at deeper layers

Contrary to the effects observed in the upper 20 cm of the soil profile, the one century simulations did not show great differences in HM 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 HM 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 HM 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 HM 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 Figure 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 m^3 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 HMs 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).

5.4.3. 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 Figure 7. The HM 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 (Figure 7). However, the continued PS disposal at the soil's surface

notably increased HM solution concentrations in the entire soil profile, especially when applying doses of 80 m^3 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 (Figure 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 HM 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 m^3 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 (Figure 7). Reduction of PS doses implies a reduction of HM inputs and consequently, lowering of the surface HM 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 m^3 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).

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 HMs 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).

5.5. 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, 2012b), and complemented it in this work with a new soil tillage module. Simulations that did not consider tillage showed a great surface accumulation of HMs, especially for Cu and for PS doses of 80 m^3 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 m^3 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 HMs 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 HMs concentrations in the 0–20 cm soil layer were obtained using the scenario with tillage every 5 years. Indeed, scenarios with applications of 80 m^3 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 HMs in areas with high PS doses than reducing the PS dose by half.

Moreover, in addition to decreasing the HM concentrations at the soil's surface, soil tillage also affected HM 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 m^3 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 HM 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.

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5.6. 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 Manage. 25, 193–200.

Barrow, N.J., 1999. The four laws of soil chemistry: the Leeper lecture 1998. 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. Agronomy 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. Agr. 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.

CONAMA – Conselho Nacional do Meio Ambiente, 2009. Resolução n° 420/2009, de 28/12/2009.

Díaz-Barrientos, E., 2003. Copper and zinc retention by an organically amended soil. Chemosphere 50, 911−917.

Girotto, E., Ceretta, C.A., Brunetto, G., Rheinheimer, D.S., Silva, L.S., Lourenzi, C.R., Lorensini, F., Vieira, R.C.B., Schmatz, R., 2010a. Acúmulo e formas de cobre e zinco no solo após aplicações sucessivas de dejeto líquido de suínos. Rev. Bras. Ciênc. Solo 34, 955–965.

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. of Dairy Sci. 88, 2911–2922.

Lourenzi, C.R., Ceretta, C.A., Silva, L.S., Girotto, 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., Šimůnek, 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.

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.

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. Cont. Hydr. 145, 54–66.

Seuntjens, P., 2002. Field-scale cadmium transport in a heterogeneous layered soil. Water Air Soil Pollut. 140, 401–423.

Šimůnek, 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.

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

Parameter*	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_{VG}, 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

* *OC* = organic carbon; *Bd* = bulk density; K_s = saturated hydraulic conductivity; θ_s = saturated water content; θ_r = residual water content; α_{VG} and n_1 = retention parameters; *l* = pore-connectivity factor; *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.

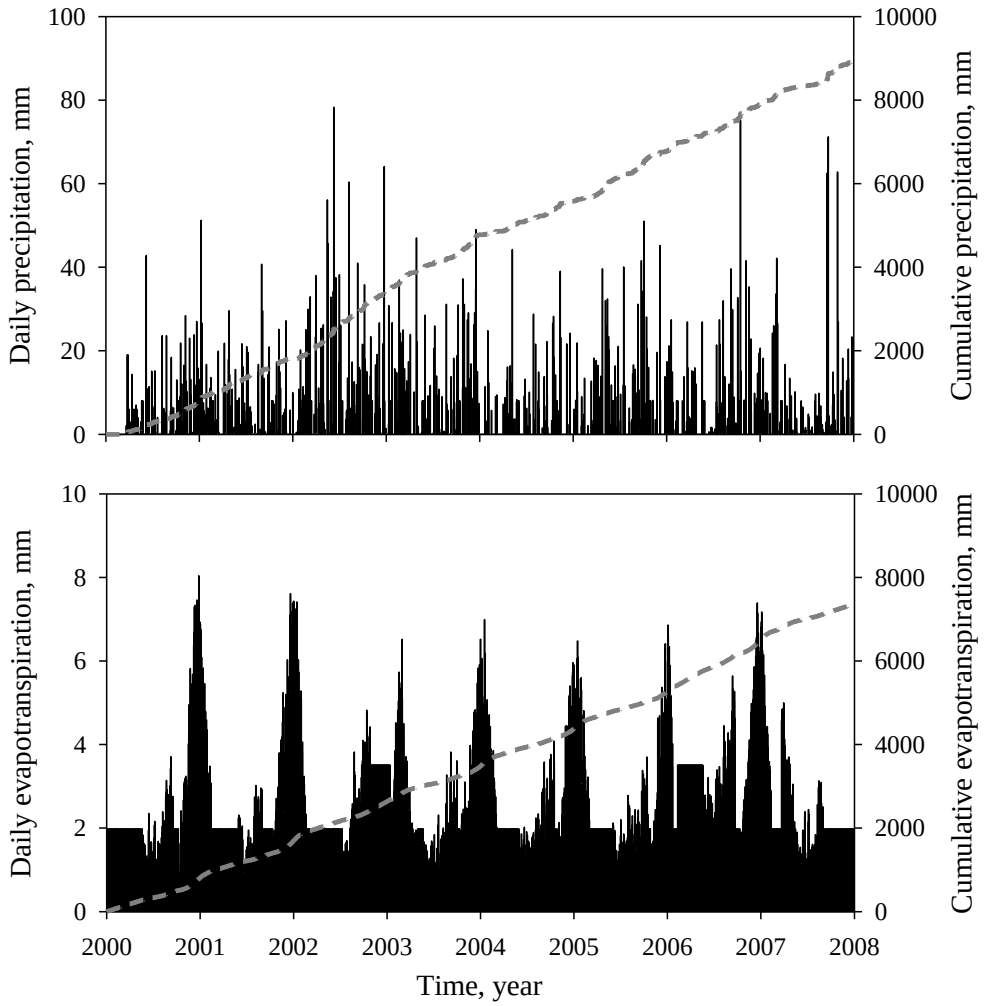

Figure 1 – Daily (bars) and cumulative (line) precipitation (upper) and crop evapotranspiration (lower) at the experimental site in Santa Maria, Rio Grande do Sul State, Brazil, from 2000 to 2008. Source: Sistema Irriga® – UFSM.

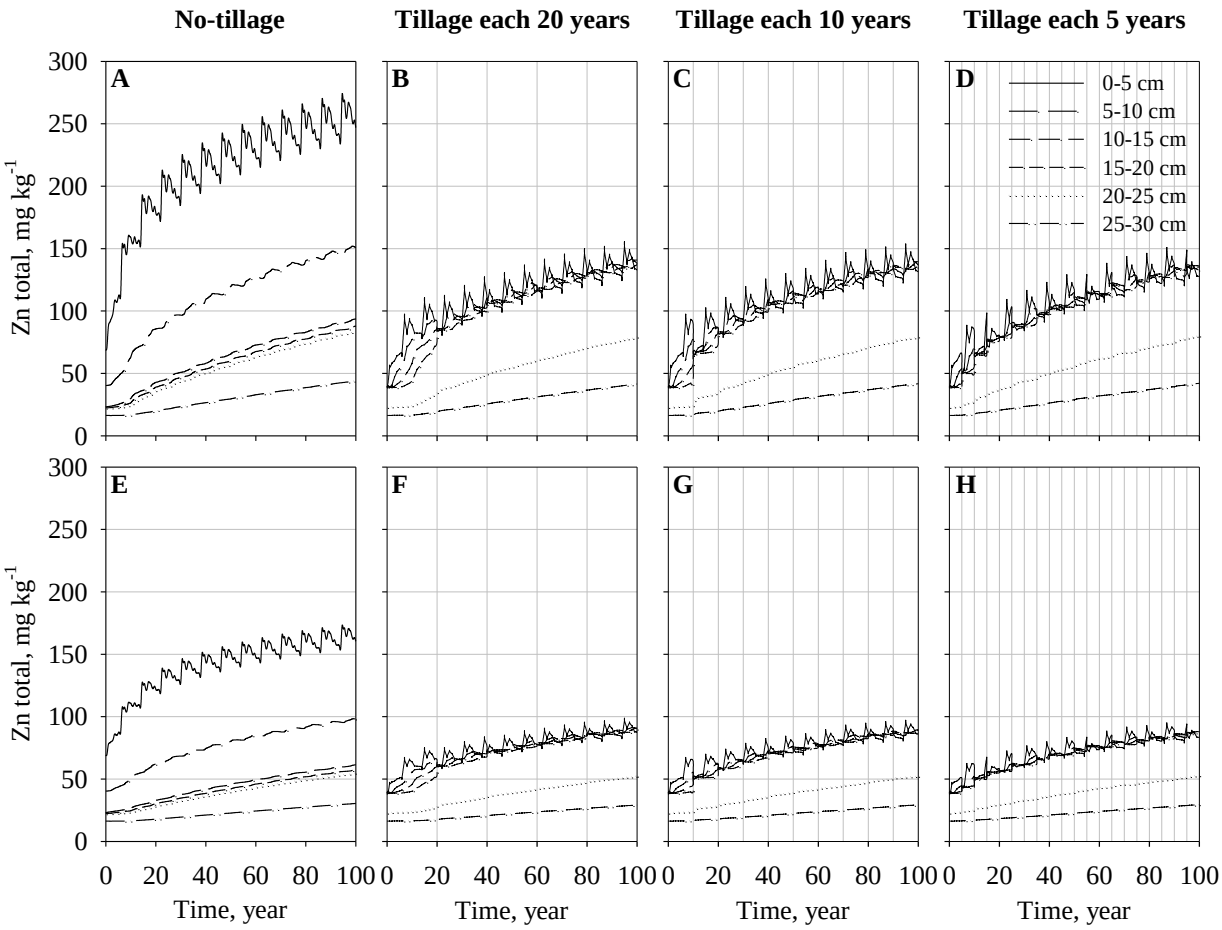

Figure 2 – Total zinc concentrations in six layers of the soil profile during one century simulations, considering scenarios with different pig slurry doses and soil tillage frequencies. Upper and lower graphs were simulated under 80 and 40 m^3 ha^{-1} $cultivation^{-1}$ doses, respectively. Letters 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.

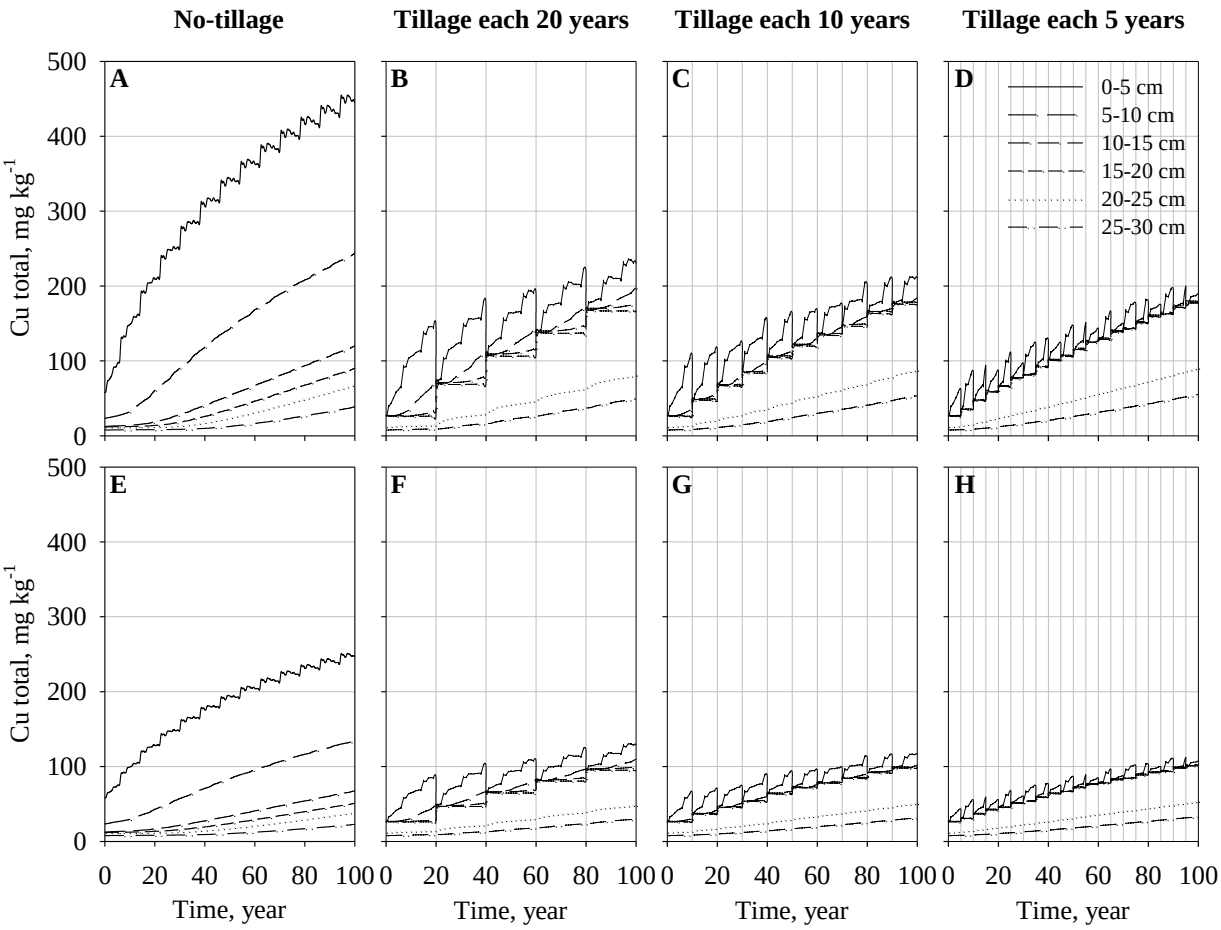

Figure 3 – Total copper concentrations in six layers of the soil profile during one century simulations, considering scenarios with different pig slurry doses and soil tillage frequencies. Upper and lower graphs were simulated under 80 and 40 m^3 ha^{-1} $cultivation^{-1}$ doses, respectively. Letters 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.

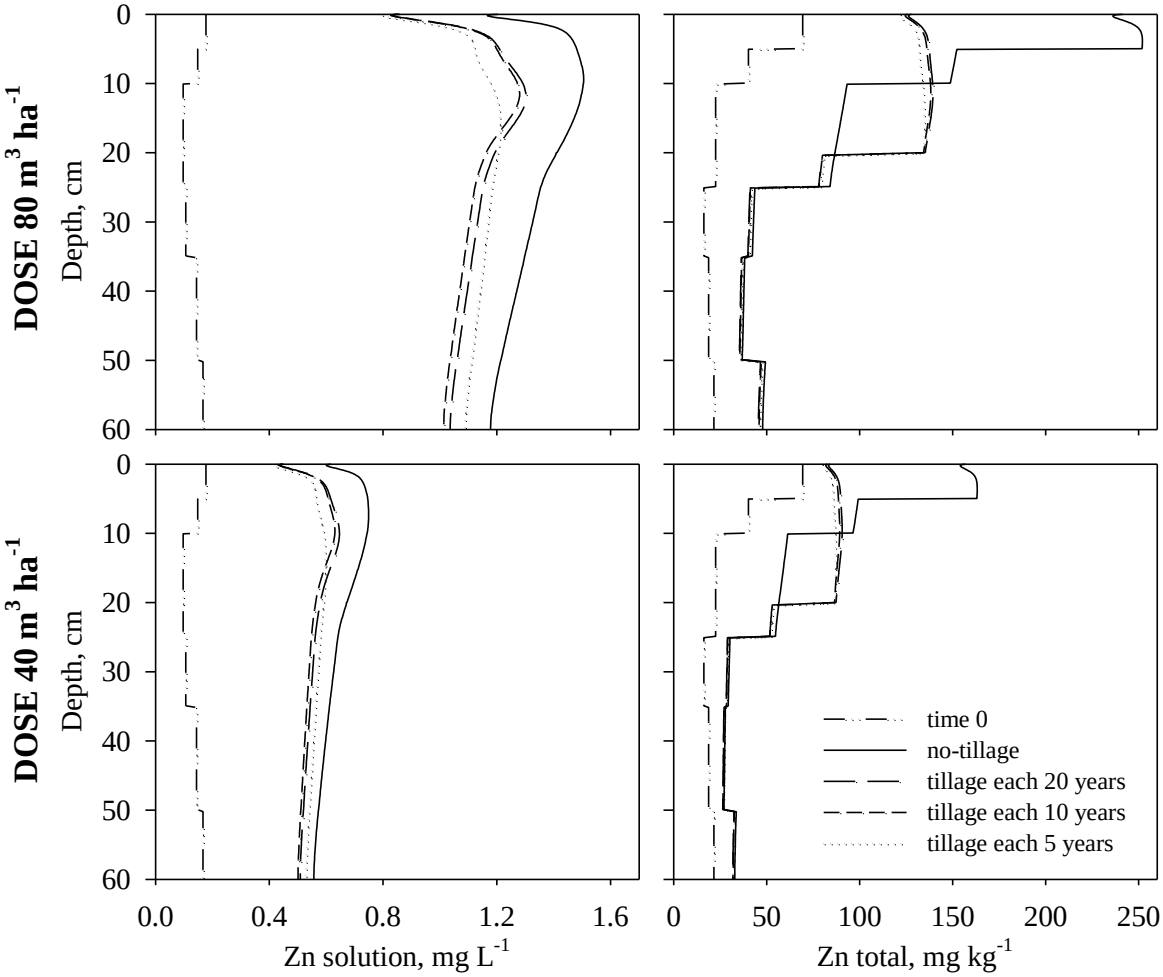

Figure 4 – Solution (left) and total (right) zinc concentrations in the soil profile under continued pig slurry applications after 100 years, considering scenarios involving two manure doses (80 and 40 m^3 ha^{-1} $cultivation^{-1}$) and different soil tillage frequencies (no-tillage and tillage each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

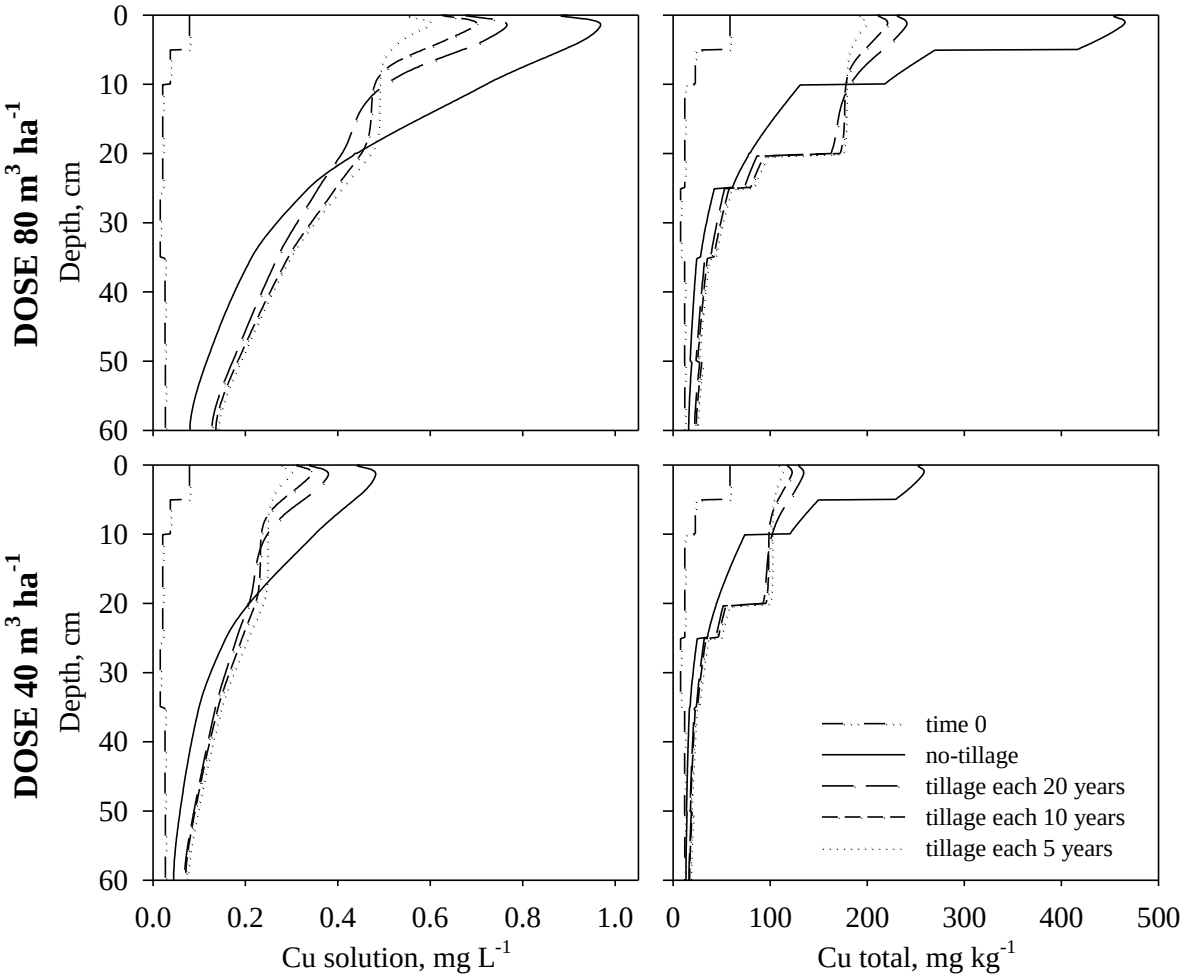

Figure 5 – Solution (left) and total (right) copper concentrations in the soil profile under continued pig slurry applications after 100 years, considering scenarios involving two manure doses (80 and 40 m^3 ha^{-1} $cultivation^{-1}$) and different soil tillage frequencies (no-tillage and tillage each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

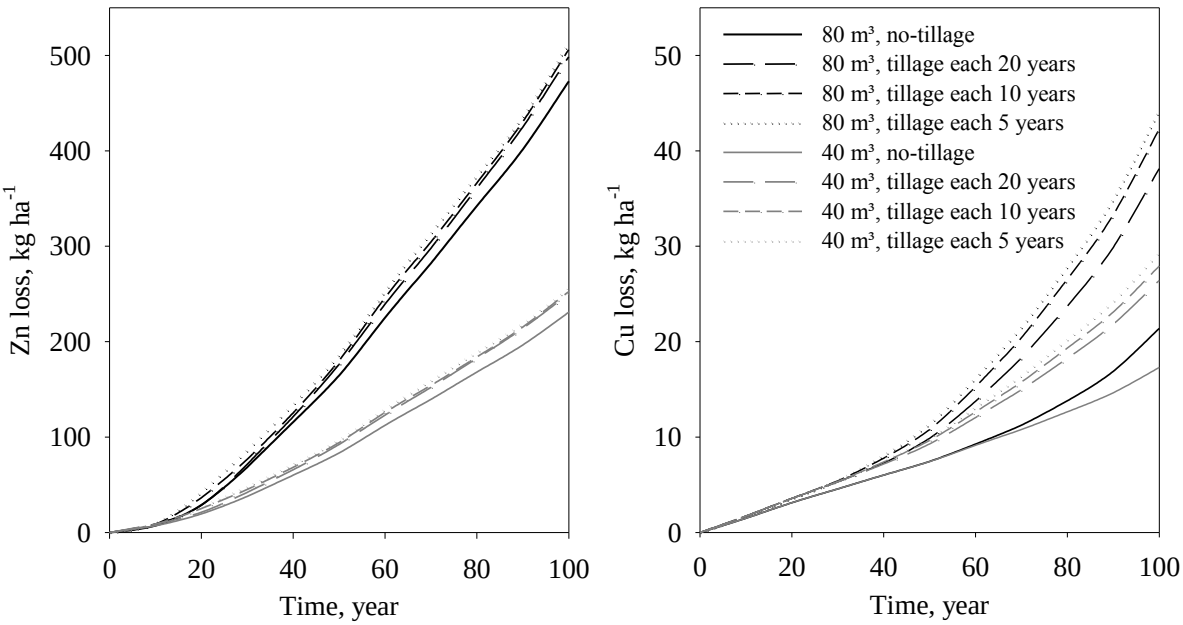

Figure 6 – Zinc (left) and copper (right) amounts transferred in the soil profile under continued pig slurry applications to depths greater than 60 cm, during future one century simulations using different manure doses (80 and 40 m^3 ha^{-1} $cultivation^{-1}$) and soil tillage frequencies (no-tillage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

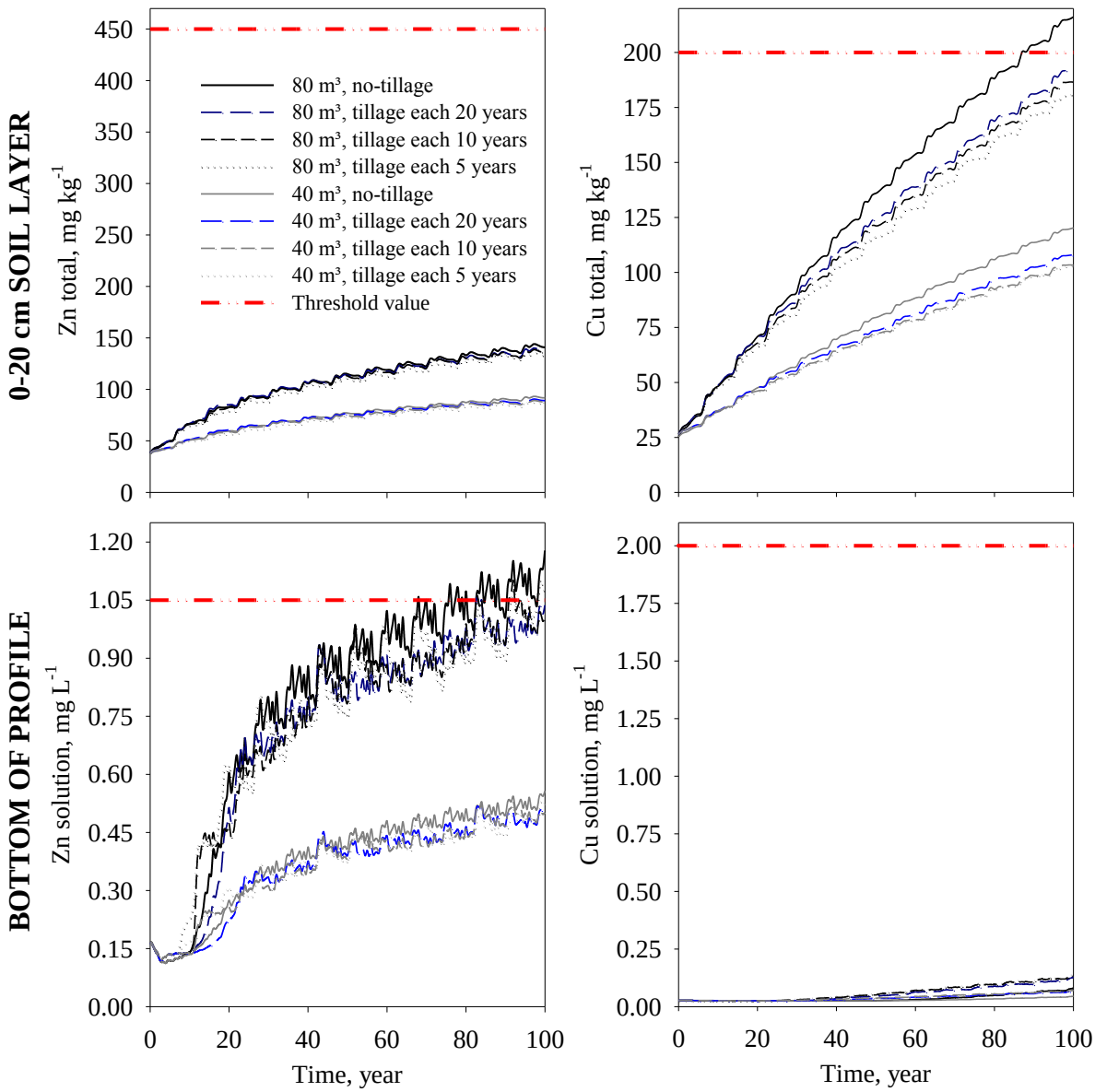

Figure 7 – Zinc (left) and copper (right) total concentrations at the top 0–20-cm soil layer and solution concentrations at the bottom of the soil profile (60 cm depth) under continued pig slurry applications during future one century simulations using different manure doses (80 and 40 m^3 ha^{-1} $cultivation^{-1}$) and soil tillage frequencies (no-tillage and tillage each 20, 10, and 5 years).

6 ARTIGO II – Modelagem do movimento de zinco e cobre num Latossolo argiloso brasileiro contaminado por aplicações de dejeto líquido de suínos em longo prazo

Modeling zinc and copper movement in a Brazilian clayey Oxisol contaminated by long-term pig slurry amendments[2]

Abstract

Increases on zinc (Zn) and copper (Cu) concentrations in soils amended with pig slurry (PS) can be predicted using numerical models. Our main objective was to simulate the vertical transport of Zn and Cu, using HYDRUS-1D, in a clayey soil (Oxisol) cultivated under annual cropping in a no-tillage system and contaminated by successive PS amendments. For the model validation, we tested simulations using a chemical model approach previously validated for an Alfisol, and later we also introduced root water uptake and root growth modules to improve this approach. Then we performed 50-years prospective scenarios for PS amendments using different doses. Introduction of root modules into HYDRUS-1D model improved the fitting of simulated results to measured field concentrations, leading to the validation of a transport model for Zn. Although Cu simulated results were not as good as for Zn, we performed prospective simulations for both elements. Future scenarios using high PS doses showed a strong increase of both heavy metals (HM) at soil surface layer. However, feasibility of PS amendment on the agricultural Oxisol will be limited by Cu, because of exceeding the soil threshold concentration in approximately 29 years. Moreover, total loads of both HM allowed on agricultural soils are reached very fast when high rates are used, especially of Cu (19 years). Therefore, long-term feasibility of PS disposal on agricultural soils requires applications of the manure at low doses.

Keywords: HYDRUS-1D; model validation; prospective simulation; heavy metal; root water uptake and growth modules.

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[2] Artigo elaborado de acordo com as normas da revista Agriculture, Ecosystems & Environment.

6.1. Introduction

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

Such amending practices may lead to environmental damage, because PS often presents large concentrations of heavy metals (HM) such as Zn and Cu. Still, their concentrations may widely vary, depending on the manure dry mass and the animal diet, since Zn and Cu are used as additives to improve the productivity index of the swine (Li et al., 2005). Some authors have mentioned total Zn and Cu amounts as high as 1225 and 528 mg kg^{-1}, respectively (Ogiyama et al., 2005). Particularly for soils managed under no-tillage, in the absence of mechanical plowing, continuous long-term PS amendments at soil surface will promote the accumulation of these HM within the first centimeters of the soil profile (Veiga et al., 2012; Girotto et al., 2010a; Berenguer et al., 2008; L'Herroux et al., 1997). Moreover, the mobility of HM is low in soil, notably of Cu (McBride, 1994). Considering that input of animal wastes in soils can increase the organic matter content, which generally tend to decrease the HM solubility and mobility in soils (Mantovi et al., 2003), could promote an even greater surface accumulation of Zn and Cu. Consequently, the continuous application of PS on soils raises questions about risks for future environmental pollution of soils and surface water. Problems may arise with respect to runoff in regions with frequent high intensity rains and consequent HM transfer to superficial water bodies (Xue et al., 2003), or ecotoxicity of HM for plants (Yadav, 2010) and microorganism (Kuperman and Carreiro, 1997), with great implications for the wider environment. As mentioned by Mantovi et al. (2003), application of animal farming manures must therefore be viewed as a controlled agronomical practice of fertilization, and not as a simple way of disposal.

It is essential to study and monitor the time span of increase of Zn and Cu concentrations in soils in relation to the intensity of PS applications. Depending on soil and manure conditions, maximum HM 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 intrinsic and external factors are implied in the accumulation,

redistributions and transfer to depth or by surface runoff of HM in soils, *i.e.*, soil characteristics, such as pH (Gäbler, 1997), texture, organic matter and iron oxide contents (Venditti et al., 2000), climatic conditions as rainfall and evapotranspiration (Visser et al., 2012), land use (Fernandez et al., 2007) and anthropogenic practices such as PS amendments and its metal contents (Girotto et al., 2010a). Mathematical models are helpful to predict the mobility and transfer of HM in soils (Rheinheimer et al., 2007). They provide a base for interpreting experimental results and understanding trends and relationships in observed field data. Besides, they are powerful tools to assist in developing alternatives for soil and water management strategies (Šimůnek and de Vos, 1999).

Nowadays, studies on soil pollution risks related to anthropic activities in the view of land use sustainability are abundant, and mathematical models based on numerical solutions are being used in a wide range of applications for research and the management of natural resources (Šimůnek et al., 2008). Many numerical models have been developed for simulations of HM movements in soil to predict the water and solute transfer process between the soil's surface and the groundwater (Carrillo-González et al., 2006). Moreover, a prerequisite to interpret the results of simulations is the model validation. For instance, Legout et al. (2009) defend that whatever the model used, one needs to evaluate its predictive capacity and the validity of its assumptions, using controlled laboratorial experiments that faithfully reproduce the phenomena observed under natural conditions. So, we will be able to predict about a phenomena at long-term only after verifying the correct functionality of the model.

HYDRUS-1D is a free software package for simulating the movement of water, heat and solutes in one-dimensional variably saturated porous media under a wide range of complex boundary conditions and irregular transport domains and soil heterogeneities (Šimůnek et al., 2012a). HYDRUS-1D sub-models, as in HYDRUS-2D and HYDRUS-2D/3D, may consider specific hydro-physical and chemical characteristics for multiple soil layers, daily atmospheric characteristics such as precipitation and evapotranspiration (according to different land use and cultivated crops), as well as geochemical characteristics of contaminants added to soils over time (Mallmann et al., 2012a). Recently, some studies on modeling the migration of metal contaminants using HYDRUS software were carried out to validate the model for different sources of HM and under different pedoclimatic conditions, by fitting simulated HM profile concentrations to field measured values after respective metal inputs over considered time. Satisfactory predicted changes in Zn and Pb concentration profiles, for two arable soils in northern France contaminated by atmospheric fallout, were

reported by Mallmann et al. (2012b), where metal stocks entering in the soils were inferred from historic industrial activity of a metallurgical plant. In Brazil, HYDRUS simulations for Zn and Cu concentrations in a soil profile under PS amendments during eight years were well adjusted to field data, using input HM amounts derived from Zn and Cu concentrations of known PS doses (Mallmann et al., 2012a). However, the soil of this latter work was classified as a Typic Hapludalf, which has different soil characteristics with respect to soils widely used for PS disposal in the Southern Brazil States of Rio Grande do Sul and Santa Catarina. It is well known that the soil's clay and oxide contents affect its hydric-physical characteristics and potential for HM adsorption. In clayey soils, as Oxisols, the adsorption capacity of HM is higher than in sandy soils (Mattias, 2006). Soil texture to a large extent governs the soil's water retention capacity and hydraulic conductivity, which in clay soils are smaller than in sandy soils (Reichert et al., 2009; Tindall and Kunkel, 1999). Therefore, it is very important to validate a solute transport model for different types of soils, increasing the range of model applicability for estimating HM movement in contaminated soils.

Prospective simulations are frequently the main goal of the mathematical models. Such simulations should be made after the model calibration and validation (Šimůnek et al., 2012b). Rheinheimer et al. (2013), for example, simulated the future 50 years of Zn and Pb vertical movements in French contaminated soils, supported by the model validation performed by Mallmann et al. (2012b). With these models it is also possible to make prospective simulations under different scenarios of land management, *i.e.*, considering different PS amendments rates (Mallmann et al., 2012a). In this way, simulations estimate possible environmental contamination risks caused by HM additions in some place, help to develop better strategies for PS management and may support the adoption of public politics toward swine producers and the entire related chain.

Our main objective was to simulate the vertical transport of Zn and Cu using HYDRUS-1D in a clay soil cultivated under annual cropping in a no-tillage system, contaminated by successive PS amendments. For the model validation, we first tested simulations using the chemical model approach previously validated by Mallmann et al. (2012a) for an Alfisol. Second, we introduced root water uptake and root growth modules in this HYDRUS-1D model approach to detect the influence of roots on the HM movements in soil. Third, we performed different 50-years prospective scenarios to predict Zn and Cu accumulation in soil surface layers and their movements in the soil profile towards the groundwater, accordingly to the PS application rate.

6.2. Materials and Methods

6.2.1. Experimental site, soil, and other characteristics

The study was conducted on a field experiment with periodical PS applications, located at the demonstrative field of the Cooperativa Regional Agropecuária de Campos Novos (Copercampos), in Campos Novos, Santa Catarina State, Brazil (27°21’56’’S and 51°15’33’’W, 896 m altitude). The soil, developed from intermediate effusive rock saprolites of Serra Geral Formation, is classified as Rhodic Hapludox (USDA, 2003), referred as Latossolo Vermelho distroférrico típico in the Brazilian System of Soil Classification (EMBRAPA, 2004). At the beginning of the experiment, the 0–20 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, 0.5, 4.7 and 2.9 cmol$_c$ dm^{-3} of exchangeable Al, K, Ca and Mg, respectively; and 10.0, 1.7 and 10.5 mg dm^{-3} of extractable P, Zn and Cu, respectively (Veiga et al., 2012). The climate is humid mesothermal with mild summers, Cfb type according Köppen classification, showing annual precipitation ranging from 1460 to 1820 mm, and annual average temperatures from 15.8 to 17.9^{o}C (Pandolfo et al., 2002).

The experiment started in 2000, on a field previously managed with crop rotation and no-tillage system for more than 10 years. Treatments were composed by four different annual PS doses: 0, 50, 100 and 200 m^3 ha^{-1}, divided in two superficial applications: half before winter crops sowing and other half before summer crops sowing. These treatments were applied in three field replicates on a randomized block design, with plots measuring 6 x 5 m. More details can be found in Veiga et al. (2012). During the eleven years of the experiment, 22 PS applications were carried out, using manure obtained from an anaerobic lagoon reservoir at a pig finishing farm, which presented dry mass content ranging from 0.40 to 10.27%, and average of 2.62%.

The number of crop cultivations for the eleven years of experiment was the same as the number of PS applications. Seeding was performed by direct drilling and followed a three year 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 productions on treatments 0, 50, 100 and 200 m^3 ha^{-1} were, respectively, 5188, 6908, 7025 and 7046 kg ha^{-1} of dry mass by the winter crops, and 4919, 5729, 5789 and 6024 kg ha^{-1} of grains by the summer crops.

6.2.2. Soil and solution sample collection

The soil and solution samples collection was performed in June of 2011.We collected disturbed soil samples from ten layers: 0–5, 5–10, 10–15, 15–20, 20–25, 25–30, 30–35, 35–40 and 40–60 cm depth, on the treatments with PS doses of 0, 50 and 200 m^3 ha^{-1} $year^{-1}$, hereafter referred to as $0m^3$, $50m^3$ and $200m^3$, respectively. The soil samples were dried, sieved at 2.0 mm and stored in plastic pots prior to chemical analysis. In the control plots (treatment $0m^3$) we also collected soil solution samples with tension lysimeters at three profile depths: 20, 40 and 80 cm.

For determination of soil hydro-physical characteristics, soil samples sets were collected from six soil layers: 0–5, 5–10, 10–20, 20–30, 30–40 and 40–60 cm depth, in two different places located between the experimental blocks. These areas have the same soil characteristics and received the same management of the control plot (treatment $0m^3$). Firstly, we collected undisturbed soil samples using metallic rings, totalizing 10 samples per layer for each type of analysis: saturated hydraulic conductivity (K_s), bulk density (B_d), and a part of the soil water retention curve (SWRC) for the soil water tensions < 100 kPa. After that, we collected disturbed bulk samples for measurement of soil texture and the second part of the SWRC, corresponding to the soil moisture tensions > 500 kPa.

6.2.3. Soil hydro-physical analysis

The K_s was measured on undisturbed soil samples, already completely saturated with water 48 hour before, using a falling head permeameter linked to specific computer software (Gubiani et al., 2010). This procedure consists on measurements of the time needed for a specific water volume contained between the upper and lower limits of a tube to cross the soil sample, defined accordingly the interval of hydraulic loads considered. So, K_s was calculated as suggested by Hillel (1998):

$$K_s = \left(2{,}3\ a\ \frac{L}{A}\ \Delta t\right)\ (\log H_n - \log H_{n+1}) \qquad (1)$$

where: H_n and H_{n+1} are the initial and final hydraulic loads, respectively; Δt is the time for hydraulic load decreasing from H_n to H_{n+1}; A is the cross sectional area of the soil sample; L is the length of soil sample; and a is the internal cross sectional area of the tube containing the water column.

We also used undisturbed soil samples, previously saturated for 48 hour, for SWRC measurements. These samples were submitted to successive tensions of 1, 6 and 10 kPa in a sand column (Reinert and Reichert, 2006), and to 33 and 100 kPa in a pressure cooker. Gravimetric water contents at higher tensions (500, 1000 and 1500 kPa) were determined with the dew point potentiometer on disturbed soil samples. The paired tension and water content values of SWRC were used to fit α, n and m parameters of van Genucthen's model (van Genuchten, 1980). The soil B_d was calculated by dividing the dry mass of soil contained in the cylinder (stove at 105°C till constant weight) by the cylinder volume, and the soil texture was measured following the USDA (1972) procedure.

6.2.4. Soil chemical analysis

All chemical analyses were performed on the disturbed soil samples collected in the experimental plots. Soil pH (in water, relation 1:1 v/v) was determined following methodology described in Tedesco et al. (1995), and organic carbon (OC) with an elementary CHNS auto-analyzer.

Total soil concentrations of Zn and Cu were measured with an atomic absorption spectrometer after sample digestion according EPA 3051A procedure (USEPA, 2007). Solution concentrations of these HM were determined with an inductively coupled plasma optical emission spectrometer (ICP-OES), directly on the samples collected in the field.

Soil desorption isotherm curves for Zn and Cu were determined using ethylene diamine tetraacetic acid (EDTA) extractions at 0.05 mol L^{-1} (pH 6.0), with soil-solution ratio of 1:10 (Bermond et al., 1998) and contact times of 1, 5, 15, 30, 60, 120, 300, 660, 1020 and 1440 min. Adsorption isotherm curves of these HM to the soil followed procedure described by Mattias (2006), adding 10 ml of a 0.0025 mol L^{-1} $Ca(NO_3)_2$ solution containing different Zn or Cu concentrations (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.

6.2.5. 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. These data, except precipitation, were used for calculations of daily evapotranspiration of crops cultivated during the experiment, following the equation for potential crop evapotranspiration (ET_p) of Penman-Monteith (Allen et al., 1998), as follows:

$$ET_p = ET_o \; x \; K_c \tag{2}$$

where: ET_o is the reference evapotranspiration, estimated by Penman-Monteith equation presented below; and K_c is the crop coefficient, also obtained from Allen et al. (1998).

$$ET_o = \frac{0.408\,\Delta\,(R_n - G) + \gamma\,\frac{900}{T+273}\,u_2\,(e_s - e_a)}{\Delta + \gamma(1 + 0.34\,u_2)} \tag{3}$$

where: Rn is the net radiation at the crop surface; G is the soil heat flux density; T is the air temperature at 2 m height; u_2 is the wind speed at 2 m height; e_s is the saturation vapor pressure; e_a is the actual vapor pressure; $e_s - e_a$ is the saturation vapor pressure deficit; Δ is the slope vapor pressure curve; and γ is the psychrometric constant.

The total measured precipitation and calculated evapotranspiration for the time between experiment beginning and soil sampling reached 23267 and 8649 mm, respectively, corresponding to average values of 2090 and 777 mm year^{-1} (5.73 and 2.13 mm day^{-1}), respectively.

6.2.6. Solute transport simulations

6.2.6.1. Software and parameterization details

HYDRUS-1D (Šimůnek et al., 2012a) was used to simulate unsaturated water flow associated to Zn and Cu transport in a vertical plane. Van Genuchten and van Genuchten-Mualem analytical models were used to describe respectively the soil water retention curve and unsaturated hydraulic conductivity (van Genuchten, 1980).

Soil residual (θ_r) and saturated (θ_s) water contents and parameters α and n_{VG} 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) used in simulations was set to 0.5 for all soil layers, as recommended by Mualem (1976).

The Zn and Cu total and solution concentrations used in HYDRUS-1D at initial time of simulations (May 1st, 2000) for each soil layer were those measured in the control plot.

Based on these values and on the average value of the *n* parameter adjusted from the adsorption curves with Freundlich nonlinear isotherm, we calculated the K_F value of both HM for each soil layer, as follows:

$$K_F = \frac{total}{solution^{\,n}} \tag{4}$$

For Zn and Cu desorption curves we adjusted the β and λ parameters of Fangueiro kinetic model (Fangueiro et al., 2005). These parameters match for the fraction of soil sorption sites in instantaneous equilibrium with HM in solution, and for the kinetic desorption constant of the nonequilibrium sites (1–β), respectively, calculated according to Mallmann et al. (2012a). The values of the used parameter data set are listed in table 1.

6.2.6.2. Heavy metal inputs

During simulations for model validation, the total amounts of Zn and Cu added to the soil surface via PS amendments were determined as a difference between the HM stock of the respective treatment and the stock of the treatment 0m^3, evaluated over 60 cm depth and based on the soil bulk density (Table 1) and on the HM total concentration. These amounts accounted respectively for 43.0 and 27.3 kg ha^{-1} of Zn and Cu on treatment 50m^3 and for 120.9 and 71.7 kg ha^{-1} on treatment 200m^3 (Figure 1). Temporal distribution of the HM additions over the soil, also shown in figure 1, followed the historic of PS amendments on field. Moreover, the amounts of Zn and Cu added to the soil in each application were proportional to the dry mass content of the respective manure used along the 22 amendments.

6.2.6.3. Model validation

Firstly, we simulated the Zn and Cu vertical transport in the PS amended soil profiles for two different doses (50 and 200 m^3 ha^{-1} year^{-1}) during 4063 days (01/05/2000 to 15/06/2011, corresponding to the experiment beginning and the soil sampling dates, respectively), testing the chemical model approach used and validated by Mallmann et al. (2012a, 2012b). This chemical model is based on the time weighting scheme of Crank-Nicholson and the Galerkin Finite Elements for space weighting scheme, associated to a two-site nonequilibrium solute transport model. In this solute transport model, the reaction of the equilibrium fraction (β parameter) between soil and solution follows the Freundlich isotherm and the kinetic fraction (1–β) reacts according the kinetic constant (λ), using reduced EDTA-determined rates (1:144000) as validated in the two former works. Moreover, water uptake by roots and consequent transpiration was not considered. Consequently, all water losses through

evapotranspiration, calculated for the crops during the experiment conduction, were transferred during these simulations from soil to atmosphere only via evaporation. This model approach is hereafter also named as first assumption model.

Second, root water uptake and root growth modules, available in HYDRUS-1D (Šimůnek et al., 2012a), were introduced in simulations, representing our second assumption model. For this second model approach, we used the water absorption model of Feddes (1978), and the roots growth data for all crops cultivated during the experiment, *i.e.*, root depth for each day, were detailed according their phenological stages. Additionally, the solute stress by roots was neglected in this model, because the amounts of Zn and Cu absorbed by these plants are very small (Mallmann et al., 2012a) when compared to the total HM amounts present in the profiles of this experiment. Furthermore, the calculated evapotranspiration (ET_p) data set was divided in evaporation (E_p) and transpiration (T_p) using Beer's law, as suggested by Šimůnek et al. (2012a), based on the soil cover fraction (*SCF*):

$$E_p = ET_p \; x \; (1 - SCF) \tag{5}$$

$$T_p = ET_p \; x \; SCF \tag{6}$$

Calculation gave total evaporation and transpirations amounts of 3434 and 5215 mm, and averages of 308.5 and 468.5 mm year^{-1} (0.85 and 1.28 mm day^{-1}), respectively.

To evaluate the fitting of the model results based on these two assumptions, adjusting coefficients were estimated using coefficient of determination (R^2). The regression lines for simulated and measured concentrations were forced to pass through origin, so that the set of values from simulations were equal to the measured ones, and not just proportional.

6.2.6.4. Future scenarios

After adjusting of simulations for model validation, we used the best HYDRUS-1D projects including root water uptake and root growth modules (second assumption model) and extended them for the forthcoming 50 years (until 15/06/2061). This prospective modeling considered the same PS doses used in the experiment: 50 and 200 m^3 ha^{-1} year^{-1}, thus representing a low dose (LPSD) and a high dose (HPSD) scenario.

For the simulations of future scenarios with HYDRUS-1D, we adopted the same parameters of the validation simulations, and we used five times the data set of precipitation, evaporation, transpiration, root growth, and Zn and Cu additions, from the first ten years of the model validation projects. During the future 50 years simulations, these data totalized inputs of 105201 mm of water by rain and respectively 196 and 129 kg ha^{-1} of Zn and Cu for

the LPSD scenario, and 560 and 342 kg ha^{-1} for the HPSD scenario, whereas the evaporation and transpiration outflows during these scenarios reached 15619 and 23390 mm, respectively.

6.3. Results

6.3.1. Simulations for model validation

6.3.1.1. Using the first assumption model

With the first assumption model, which followed the same approach validated by Mallmann et al. (2012a, 2012b), the estimated concentrations of Zn were found 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 $50m^3$ treatment and 223.6 mg kg^{-1} for $200m^3$ treatment, differing only by –6.2 and 4.1% from the concentrations measured at the sampling time, respectively (Table 2). For the other nine soil layers, the differences between simulated and measured concentrations of Zn were even smaller in $50m^3$ treatment, with differences ≤ 3.3% (layer 35–40 cm). For $200m^3$ treatment these differences did not exceed 4.4% (layer 5–10 cm – Table 2). When adjusting simulated to measured concentrations for both treatments, the R^2 values reached 0.942 and 0.988 for $50m^3$ and $200m^3$, respectively (Figure 2).

The simulated Cu concentrations in the soil profile after 22 PS amendments fitted less well. Table 2 shows that simulated Cu concentrations in the 0–5 cm layer were 15.1 and 17.0% higher than the measured concentrations for $50m^3$ and $200m^3$ treatments, respectively. The R^2 values reached 0.674 for $50m^3$ and 0.839 for $200m^3$ treatments (Figure 2), much lower than for Zn, especially for the low PS dose one.

6.3.1.2. Coupling of root water uptake and root growth modules to HYDRUS-1D simulations

When including the root water uptake and root growth modules in HYDRUS-1D, for model validation, Zn and Cu soil concentrations slightly differed from the previous model approach. The highest differences were observed for the surface soil layer (0–5 cm), where concentrations of Zn and Cu reached respectively 144.9 and 156.1 mg kg^{-1} for treatment $50m^3$, and 217.8 and 201.1 mg kg^{-1} for treatment $200m^3$ at the end of simulations. When compared to the measured concentrations in the experiment, these Zn results differed by –

7.7% and 1.4% for $50m^3$ and $200m^3$ treatments, respectively, while for Cu these results diverged by 14.6 and 15.7%, respectively (Table 3).

When comparing the Zn and Cu results obtained with these validation simulations using the root modules (Table 3) with the respective initial concentrations (Table 1), the $50m^3$ and $200m^3$ treatments have not presented considerable Zn increase (> 2.0 mg kg^{-1}) for soil layers deeper than 15 and 30 cm, respectively. For Cu, a considerable increase was observed only in the upper 0–10 and 0–15 cm profile depth, respectively.

Finally, the introduction of the root modules in HYDRUS-1D projects resulted on simulated profile concentrations of Zn and Cu that generally fitted rather better to the measured concentrations than the first model assumption. The R^2 values obtained from regression curves for these data were 0.905 and 0.993 for Zn and 0.685 and 0.853 for Cu, on $50m^3$ and $200m^3$ treatments, respectively (Figure 3).

6.3.2. Simulations of future scenarios

6.3.2.1. Pig slurry applications at low doses (LPSD)

During the 61 years simulated period, the LPSD scenario estimated additions of Zn and Cu that increased the HM stocks in the 0–60 cm profile by 30 and 20%, respectively. Total Zn and Cu concentrations at soil surface (0–5 cm) increased by 127 and 132%, reaching 231 (Figure 4) and 262 mg kg^{-1} (Figure 5), respectively. Within the upper 20 cm of the cultivated layer, total Zn concentrations reached respectively 185, 146 and 129 mg kg^{-1} in layers 5–10, 10–15 and 15–20 cm (Figure 4), corresponding to stock increases of 87, 52 and 30%. For Cu, the simulated concentrations reached 201, 149 and 122 mg kg^{-1} (Figure 5), corresponding to Cu stock increases of 82, 35 and 8%, respectively. Considerable increases (> 10%) of Cu in the profile amended with low PS doses were observed only in the top 15 cm, accompanied by a variation smaller than 1% in the layers below 20 cm. For Zn, considerable stock increases with the LPSD scenario were expected for the upper 30 cm of soil, and for 30–60 cm layer the increases varied from 6 to 8%.

Solution concentrations of Zn increased in all soil layers during the LPSD scenario simulation, reaching a maximum value of 0.22 mg L^{-1} in the surface layer (Figure 4), but at the profile bottom (60 cm deep), these Zn concentrations remained below 0.06 mg L^{-1} during the simulation period (Figure 6). Estimations also showed that the highest Cu solution concentrations appeared in the 0–5 cm layer (0.11 mg L^{-1}), but increasing Cu concentrations

were predicted only in the four upper layers (Figures 5 and 6). Such simulated solute concentrations, especially those at the profile bottom, 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 years.

6.3.2.2. Pig slurry applications at high doses (HPSD)

The initial stocks of Zn and Cu in the 60 cm soil profile increased by 91% and 54%, respectively, during the 61 years simulations under HPSD scenario. Total Zn concentrations reached 419, 331, 244 and 196 mg kg^{-1} at the end of simulations in soil layers of 0–5, 5–10, 10–15 and 15–20 cm, respectively (Figure 4). Such concentrations imply a 313, 234, 155 and 96% of increasing, respectively. Considering the estimated Zn concentrations in deeper soil layers, they all showed consistent increases (> 10%), with the 40–50 cm layer showing the smallest gain, of 28%.

For Cu, the HPSD scenario estimated total concentrations of 372, 317, 257 and 204 mg kg^{-1} for year 2061 in the upper four soil layers, respectively (Figure 5), which correspond to 228, 188, 133 and 80% more Cu than those of year 2000. Moreover, the deepest soil layer with consistent increase on total concentration of Cu was at 25–30 cm depth, which increased 11%, while the soil layers below it showed only very small variations (< 2%).

In this HPSD scenario, soil solution concentrations were highest in the surface layer, reaching maximum concentration of 0.65 mg L^{-1} for Zn (Figure 4) and 0.37 mg L^{-1} for Cu (Figure 5). All soil layers of the 60 cm profile presented increases on Zn soil solution after 61 years of simulations, including the profile bottom (60 cm deep), which increased from 0.035 mg L^{-1} in 2000 to 0.169 mg L^{-1} in 2061 (Figure 6). Such concentrations predicted a total Zn loss of 100.4 kg ha^{-1} from soil profile to layers below 60 cm depth. Otherwise, Cu solution concentrations did not change below 30 cm depth. Thus, solution concentration of this HM at profile bottom remained constant during whole simulated period, leading to a Cu transfer of only 5.5 kg ha^{-1} for soil layers deeper than 60 cm (Figure 6).

6.4. Discussion

6.4.1. Model validation and effect of roots on heavy metal movements in soil

The simulations on HYDRUS-1D using the first assumption model presented results in a very good agreement to the Zn concentrations measured in the PS field experiment for both evaluated treatments. Tables 1 and 2 indicate that the simulations introduced Zn to soil depths in comparable concentrations than observed in field conditions. However, the results estimated by this model assumption for Cu showed a poorer fitting to the field soil concentrations than for Zn. Deep incorporation of Cu derived from PS was notably lower than on field conditions, overestimating the surface accumulation. In this way, for this PS amended soil we are able to validate the first assumption of chemical model only for Zn.

It is important to mention that this assumption approach for the chemical model was already validated for other conditions, where the type of HM contaminants and the soil and climate characteristics were different. One of the validation studies (Mallmann et al., 2012b) was done for Zn and Pb on a 50-years 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. A second validation work was performed for Zn and Cu in an agricultural Alfisol at Southern Brazil, with approximately 150 g kg^{-1} of clay in the A and E horizons, and submitted to successive PS amendments during eight years (Mallmann et al., 2012a). In this latter work, simulated Cu inputs were less incorporated to deeper layers and estimated Cu concentration profiles fitted less well with the measured Cu field concentrations than was observed for Zn. However, such differences were smaller than our findings for this clayey Oxisol. Probably in the Oxisol other processes, besides HM sorption/desorption processes considered in the chemical model approach, have also a significant and important role on Cu transport in soil.

In order to run simulations closer to the field conditions and aiming the model validation, we introduced modules of root water uptake and root growth in the projects of HYDRUS-1D. Thus, the projects of the first assumption served as basis for the second assumption, receiving the root modules and data set necessary to perform these simulations. Results of these simulations showed better fittings for Zn and improved the adjustment of Cu data to field concentrations (Figures 2 and 3). In comparison to the first assumption simulations, the main effect of the root modules on HM transport was to increase the amounts

of Zn and Cu transferred from upper soil layer (0–5 cm) to the two layers below (5–10 and 10–15 cm), reducing surface accumulation.

Considering that all water that flows in throughout soil contains chemical solute to some extent, the reduction of HM accumulation at the soil's surface is mainly due to a difference of the way that water outflowed to the atmosphere. While for the first assumption model the water transference to the atmosphere occurred all through the soil surface via evaporation, in the second assumption model approximately 60% of water was transferred via transpiration. In this case, water did not necessary flow until the soil surface before transfer to the atmosphere, but was partly absorbed by roots in the soil rooting zone (ranging from 5 to 40 cm depth, depending on the crop). So, upward movement of Zn and Cu from depth to the 0–5 cm soil layer decreased, while water absorption by roots at 40 cm depth, for example, forced downward flow of water and solutes. Such hypothesis is consistent with the study of Schoups and Hopmans (2002), mentioning the important effect of water uptake by plants on the root zone concentration, affecting the flux and travel time of water and solutes in soil.

The reduction on surface accumulation of HM with simulations considering root water uptake and growth, in relation to simulations without root modules, was not so much in this study. It corresponds to 1.2 and 3.0 kg ha^{-1} of Zn and 0.3 and 1.2 kg ha^{-1} for Cu on $50m^3$ and $200m^3$ treatments, respectively, being equivalent to 2.8 and 2.5% of Zn and to 1.1 and 1.7% of Cu added to soil during simulations, respectively. As the second assumption improved modeling results for Zn and Cu, it is also considered validated for Zn, but the little change in Cu simulated concentrations was not enough to consider it also validated. Therefore, for obtaining better results of Cu transport in this PS amended soil, more parameters need to be adjusted or other tools that consider different processes could be introduced into the HYDRUS-1D chemical model.

The movement of HM in soil profile associate to solid particles, colloidal or colloid-facilitated transport, is of varying importance depending on the chemistry of metals (notably Cu and Pb) and pedogeochemical conditions (van Oort et al., 2006; Citeau et al., 2003). Failure to account for such colloidal processes during solute transport simulations may lead to severe underestimation of the transport and potential risk assessment of the considered HM (Šimůnek et al., 2006). Considering findings of Girotto et al. (2010b), that the Cu amounts in percolation water from a PS amended soil occurred predominantly (approximately 75%) as particulate forms, the colloid-facilitated transport probably represents a process not well covered by the validation simulations for Cu movement in the case of the PS amended Oxisol here studied. Such particulate movement process is less relevant for simulations of Zn

transport in soil profile, since Zn movement in soils is considered to occur mainly (≥ 85%) in a dissolved free ion form (Citeau et al., 2003).

According to Šimůnek et al. (2006), models that can simulate the 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, a way for validating Cu simulations in the PS amended Oxisol is to use the C-Ride module (Šimůnek et al., 2012c), already developed for HYDRUS-2D/3D software package, that incorporates various processes associated with colloid and Colloid-Facilitated Solute Transport (CFSTr) in variably-saturated porous media. However, for that, an important limitation is the parameterization of the correct values for the variable set considered in the equations of this module, which requires new studies for their correct adjustment.

6.4.2. Short and long-term feasibility of pig slurry amendments

Future scenarios simulated for estimating Zn transport in the PS amended Oxisol showed that for a short term period, *i.e.*, 10 years after soil sampling (June 2011), total concentrations of this HM in 0–5 cm soil layer, of 170 and 275 mg kg^{-1} for LPSD and HPSD scenarios, respectively (Figure 4), remained below and far from 450 mg kg^{-1}. Consequently, the 0–20 cm soil layer on both scenarios, with estimated concentrations of 129 and 184 mg kg^{-1}, respectively (Fig. 7), did not reach the Zn threshold value established by the Conselho Nacional do Meio Ambiente (CONAMA), the Brazilian parameter for investigation in agricultural soils, which is 450 mg kg^{-1} (CONAMA, 2009). At the same time, the long-term scenarios for PS amendments on the Oxisol estimated a great increase on Zn surface accumulation, especially for the HPSD scenario, where the total concentrations at 0–5 cm soil layer during the last five years of simulations were very high, and lead to a concentration in the 0–20 cm layer of 297 mg kg^{-1}. It means that if PS additions are done at same HPSD rate after 2061, and the Zn concentration in the 0–20 cm layer increases at same velocity, the soil would exceed its Zn threshold concentration in about more 50 years. In this way, no potential risks related to Zn environmental problems were predicted during these simulated scenarios. However, if we consider the Brazilian law that establishes the amounts of HM added to agricultural soils via sewage sludge also for PS, the maximum addition of Zn, of 445 kg ha^{-1} (CONAMA, 2006), is reached on HPSD scenario in 2039, *i.e.*, 28 years after beginning of the

future 50-years simulations. Therefore, this law can limit the feasibility of PS amendments to agricultural soils when added at high rates, whereas in LPSD scenario the maximum addition of Zn was not reached.

Considering the Zn concentration in soil solution, both scenarios did not present significant problems to environment or related to Brazilian limits for groundwater, of 1.05 mg L^{-1} (CONAMA, 2009), in short- and long-term periods of PS amendments. But, during the 61-years simulated period, the amounts of Zn transferred for layers below 60 cm depth were equivalent to approximately 15% (LPSD) and 19% (HPSD) of total amounts of this HM added to soil via PS. This was a consequence of its increases on soil solution concentration at profile bottom (60 cm deep) along the simulation previews (Figure 6), which indicate a transport of the exogenous Zn through whole 0–60 cm soil profile here considered.

Important Zn accumulation on soil surface, but at lower concentration than in this Oxisol, was also detected by Mallmann et al. (2012a) on simulations predicting future scenarios for an Alfisol amended with high doses of PS. Moreover, the Zn losses for soil depths below 60 cm were higher in that Alfisol than in the Oxisol. These differences among 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 exhibit lower tendency for heavy metal adsorption than fine-grained soils (Bradl, 2004).

Although the chemical model was not validated for Cu transport in this soil, because overestimation on its soil surface accumulation, we also showed here the results of future scenarios about movement of this HM in soil. These results may help to guide the establishment of management strategies for PS amendments. Thus, the forecasting simulated under HPSD indicates that, in 18 years after 2011, the 0–20 cm soil surface layer will exceed the Brazilian threshold for Cu concentration in agricultural soils, of 200 mg kg^{-1} (CONAMA, 2009) (Figure 7). If the manure doses are applied to soil at low rates (LPSD scenario), the concentration of Cu in this soil layer will remain below the threshold value for, at least, more 50 years, extending the feasibility of this Oxisol for receiving successive disposal of PS on soil surface (Figure 7). Indeed, the maximum load of Cu allowed to be added on agricultural soils, of 137 kg ha^{-1}(CONAMA, 2006), was reached in year 2053 with LPSD scenario, while on HPSD scenario this limit was reached already in year 2020. Therefore, when we aim a long-term feasibility for PS amendments on agricultural soils, the applications should be done at low doses.

The HYDRUS-1D simulations also estimated very low concentrations of Cu in soil solution during the 61 years in both scenarios and, as showed in figure 6, the solution

concentration at profile bottom did not change during this period. With these information, and associated to the fact that Cu losses for soil layers below 60 cm were the same for the LPSD and HPSD scenarios, it is possible to deduce that Cu introduced on soil surface with PS amendments was not transferred to the deepest layers of the soil profile here considered, agreeing with findings of Mallmann et al. (2012a) in the Alfisol. These results confirm again the usual 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.

In this way, considering only the soil contamination caused by HM, the long-term feasibility of PS amendments in the clayey Oxisol of Campos Novos is viable only if PS amendments will be done at low rates. Even so, the successive applications of this manure at soil surface, without other interference, will increase soil concentrations of Cu until reach the threshold value established by CONAMA (2009) immediately after the simulation period, making this Oxisol unusable for agricultural production. Therefore, after validate the chemical model for Cu transport in this soil, future studies about the effect of soil tillage on reducing the HM accumulation in the surface and consequent time extending for PS amendments in agricultural soils, as performed by Mallmann et al. (Unpublished results) in an Alfisol, should be done also for this Oxisol.

6.5. Conclusion

A chemical model approach constructed in HYDRUS-1D, and already validated by Mallmann et al (2012a) for a coarse textured Alfisol, was examined here to simulate the Zn and Cu vertical movements in a clayey Oxisol, submitted to PS amendments with low and high doses during 11 years. Simulated results for total concentrations of Zn along the profile showed a good fitting to measured values on both treatments, leading to the validation of the chemical model also in this clayey soil. However, estimated concentrations of Cu were found less satisfactory, overestimating surface accumulation on soil profile. Therefore, the chemical model tested was not validated for Cu transport in this clayey Oxisol.

Introduction of root water uptake and root growth modules to the previous chemical model increased both Zn and Cu adjusting of simulated to measured concentrations. However, the improvement was not enough to allow the validation of this solute transport model for Cu. Thus, we recommend the introduction of a module that account for colloid-facilitated

movement in the used chemical model approach, increasing the range of transport processes considered in the simulations.

Future scenarios, estimating continued PS amendments during the next 50 years in the Oxisol, do not indicate Zn accumulation on soil or flow to groundwater that exceed threshold values of Brazilian law under both low or high doses application rates. According prospective simulations, feasibility of PS amendments to the agricultural Oxisol will be limited, among the two tested HM, by Cu. Although the chemical model was not validated for Cu, some trends related to this HM could be extracted from the estimative. One is that threshold value can be reached approximately after 29 years when HPSD are applied to the same non-amended Oxisol. Second, no problems are observed during the next 50 years when the PS amendments are made with low doses. Moreover, the total loads of both HM allowed on agricultural soils are reached very fast when high rates are used, especially of Cu (19 years). Therefore, for long-term feasibility on PS disposal to agricultural soils, such as this Oxisol, the manure applications should be done at low doses.

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6.6. References

Allen, R.G., Pereira, L.S., Raes, D., Smith, M., 1998. Crop evapotranspiration: guidelines for computing crop water requirements. FAO, Rome.

Arias, M., Pérez-Novo, C., Osorio, F., López, E., Soto, B., 2005. Adsorption and desorption of copper and zinc in the surface layer of acid soils. J. Colloid Interf. Sci. 288, 21–29.

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.

Bermond, A., Yousfi, I., Ghestem, J.P., 1998. Kinetic approach to the chemical speciation of trace metals in soils. Analyst 123, 785–789.

Bradl, H.B., 2004. Adsorption of heavy metal ions on soils and soil constituints. J. Colloid Interf. Sci. 277, 1–18.

Carrillo-Gonzáles, R., Šimůnek, J., Sauvé, S., Adriano, D, 2006. Mechanisms and pathways of trace element mobility in soils. Adv. Agron. 91, 111–178.

Citeau, L., Lamy, I., van Oort, F., Elsass, F., 2003. Colloidal facilitated transfer of metals in soils under different land use. Colloids Surf. A 217, 11–19.

CONAMA – Conselho Nacional do Meio Ambiente, 2006. Resolução no 375, de 29 de agosto de 2006.

CONAMA – Conselho Nacional do Meio Ambiente, 2009. Resolução no 420/2009, de 28/12/2009.

Dourado Neto, D., Nielsen, D.R., Hopmans, J.W., Reichardt, K., Bacchi, O.O.S., 2000. Programa computacional para modelagem de curvas de retenção de água no solo (SWRC, versão 2.00). Scientia Agric. 57, 191–192.

EMBRAPA – Empresa Brasileira de Pesquisa Agropecuária, 2004. Centro Nacional de Pesquisa de Solos. Solos do Estado de Santa Catarina. EMBRAPA/CNPS, Rio de Janeiro. (Boletim de Pesquisa e Desenvolvimento, n. 46).

Fangueiro, D., Bermond, A., Santos, E., Carapuça, H., Duarte, A., 2005. Kinetic approach to heavy metal mobilization assessment in sediments: choose of kinetic equations and models to achieve maximum information. Talanta 66, 844–857.

Feddes, R.A., Kowalik, P.J., Zaradny, H., 1978. Simulation of field water use and crop yield. John Wiley & Sons, New York.

Fernandez, C., Labanowski, J., Cambier, P., Jongmans, A.G., van Oort, F., 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.

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.

Girotto, E., Ceretta, C.A., Brunetto, G., Rheinheimer, D.S., Silva, L.S., Lourenzi, C.R., Lorensini, F., Vieira, R.C.B., Schmatz, R., 2010a. Acúmulo e formas de cobre e zinco no

solo após aplicações sucessivas de dejeto líquido de suínos. Rev. Bras. Ciênc. Solo 34, 955–965.

Girotto, E., Ceretta, C.A., Rheinheimer, D.S., Brunetto, G., Andrade, J.G., Zalamena, J., 2010b. Formas de perdas de cobre e fósforo em água de escoamento superficial e percolação em solo sob aplicações sucessivas de dejeto líquido de suínos. Cienc. Rural 40, 1948–1954.

Gubiani, P.I., Reinert, D.J., Reichert, J.M., Gelain, N.S, Minella, J.P.G., 2010. Permeâmetro de carga decrescente associado a programa computacional para a determinação da condutividade hidráulica do solo saturado. Rev. Bras. Ciênc. Solo 34, 993–997.

Hillel, D, 1998. Environmental soil physics. Academic Press, San Diego.

Kuperman, R.G., Carreiro, M.M., 1997. Soil heavy metal concentrations, microbial biomass and enzyme activities in a contaminated grassland ecosystem. Soil Biol. Biochem. 29, 179–190.

Legout, C., Molenat, J., Hamon, Y, 2009. Experimental and modeling investigation of unsaturated solute transport with water-table fluctuation. Vadose Zone J. 8, 21–31.

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. of Dairy Sci. 88, 2911–2922.

Mallmann, F.J.K., Rheinheimer, D.S., Ceretta, C.A., Cella, C., Minella, J.P.G., Guma, R.L., Filipović, V., van Oort, F., Šimůnek, J., Unpublished results. Soil tillage to reduce surface metal contamination – model development and prospective simulation of Zn and Cu concentration profiles in a long-term pig slurry-amended Alfisol in Southern Brazil.

Mallmann, F.J.K., Rheinheimer, D.S., Ceretta, C.A., Cella, C., Šimůnek, J., van Oort, F., 2012a. Modeling field-scale vertical movement of zinc and copper in a pig slurry-amended soil in Brazil. J. Hazard. Mater. 243, 223– 231.

Mallmann, F.J.K., Rheinheimer, D.S., Cambier, P., Labanowski, J., Lamy, I., Santanna, M.A., Tessier, D., van Oort, F., 2012b. 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.

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.

Mattias, J.L., 2006. Metais pesados em solos sob aplicação de dejetos líquidos de suínos em duas microbacias hidrográficas de Santa Catarina. 164 f. Dissertation (Doctorate on Soil Science) – Universidade Federal de Santa Maria, Santa Maria.

McBride, M.B., 1994. Environmental Chemistry of Soils. Oxford University Press, New York.

Mualem, Y., 1976. A new model for predicting the hydraulic conductivity of unsaturated porous media. Water Resour. Res. 12, 513–522.

Nascimento, C.W.A., Fontes, R.L.F., 2004. Correlação entre características de Latossolos e parâmetros de equações de adsorção de cobre e zinco. R. Bras. Ci. Solo 28, 965–971.

Ogiyama, S., Sakamoto, K., Suzuki, H., Ushio, S., Anzai, T., Inubushi, K., 2005. Accumulation of zinc and copper in an arable field after animal manure application. Soil Sci. Plant Nutr. 51, 801–808.

Pandolfo, C., Braga, H.J., Silva Júnior, V.P., Massignam, A.M., Pereira, E.S., Thomé, V.M.R., 2002. Atlas climatológico digital do Estado de Santa Catarina. EPAGRI, Florianópolis.

Reichert, J.M., Albuquerque, J.A., Kaiser, D.R., Reinert, D.J., Urach, F.L., Carlesso, R., 2009. Estimation of water retention and availability in soils of Rio Grande do Sul. R. Bras. Ci. Solo 33, 1547–1560.

Reinert, D.J., Reichert, J.M., 2006. Coluna de areia para medir a retenção de água no solo: protótipos e teste. Ciênc. Rural 36, 931–1935.

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. Cont. Hydr. 145, 54–66.

Rheinheimer, D.S., Labanowski, J., Elsass, F., Cambier, P., Santanna, M.A., Tessier, D., 2007. Heavy metal transport modelling in soil: sorption/desorption phenomena, water fluxes and contaminant fate. Topicos Cienc. Solo 5, 135–180.

Schoups, G., Hopmans, J. W., 2002. Analytical model for vadose zone solute transport with root water and solute uptake. Vadoze Zone J. 1, 158–171.

Šimůnek, J., Šejna, M., Saito, H., Sakai, M., van Genuchten, M.Th., 2012a. The HYDRUS-1D software package for simulating the movement of water, heat, and multiple solutes in variably saturated media, version 4.15, HYDRUS Software Series 3. Department of Environmental Sciences, University of California Riverside, Riverside.

Šimůnek, J., van Genuchten, M.Th., Šejna, M., 2012b. HYDRUS: Model use, calibration and validation. Special issue on Standard/Engineering Procedures for Model Calibration and Validation. Transactions of the ASABE 55, 1261–1274.

Šimůnek, J., Šejna, M., van Genuchten, M. Th., 2012c. 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., Köhne, J.M., Kodesová, R., Sejna, M., 2008. Simulating nonequilibrium movement of water, solutes and particles using HYDRUS – A review of recent applications. Soil & Water Res. 3, S42–S51.

Šimůnek, J., He, C., Pang, L., Bradford, S.A., 2006. Colloid-facilitated solute transport in variably saturated porous media: numerical model and experimental verification. Vadose Zone J. 5, 1035–1047.

Šimůnek, J., de Vos, J.A., 1999. Inverse optimization, calibration, and validation of simulation models at the field scale, in: Feyen, J., Wiyo, K. (Eds.), Modelling of transport process in soils at various scales in time and space. Wageningen Pers, Wageningen, pp. 431–445.

Tedesco, M.J., Gianello, C., Bissani, C.A., Bohnen, H., Volkenweiss, S.J., 1995. Análise de solo, plantas e outros materiais. Dep. de Solos, UFRGS, Porto Alegre.

Tindall, J.A., Kunkel, J.R., 1999. Unsaturated zone hydrology for scientists and engineers. Prentice-Hall, New Jersey.

USDA – United States Department of Agriculture, 2003. Soil Survey Staff, Keys to Soil Taxonomy, ninth ed., Natural Resources Conservation Service, USDA, Washington.

USDA – United States Department of Agriculture, 1972. Soil Conservation Service. Soil Survey Investigations, Whashington. (Report, n.1).

USEPA – United States Environmental Protection Agency, 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.

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.

Van Oort, F., Jongmans, A.G., Citeau, L., Lamy, I., Chevallier, P., 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.

Veiga, M., Pandolfo, C.M., Junior, A.A.B., Spagnollo, E., 2012. Chemical attributes of a Hapludox soil after nine years of pig slurry application. Pesq. Agropec. Bras. 47, 1766–1773.

Venditti, D., Durécu, S., Berthelin, J., 2000. A multidisciplinary approach to assess history, environmental risks, and remediation feasability of soils contaminated by metallurgical activities. Part A: chemical and physical properties of metals and leaching ability. Arch. Environ. Contam. Toxicol. 38, 411–420.

Visser, A., Kroes, J., van Vliet, M.Th., Blenkinsop, S., Fowler, H.J., Broers, H.P., 2012. Climate change impacts on the leaching of a heavy metal contamination in a small lowland catchment. J. Contam. Hydrol. 127, 47–64.

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.

Yadav, S.K., 2010. Heavy metals toxicity in plants: An overview on the role of glutathione and phytochelatins in heavy metal stress tolerance of plants. S. Afr. J. Bot. 76, 167–179.

Table 1 – Hydro-physical and chemical soil parameters of the control plot in the pig slurry experiment located in Campos Novos, SC, and initial values required for simulations with HYDRUS-1D.

Parameter*	**Soil layer, cm**									
	0–5	5–10	10–15	15–20	20–25	25–30	30–35	35–40	40–50	50–60
Soil:										
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
Zinc:										
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}	0.0036	0.0036	0.0036	0.0036	0.0032	0.0032	0.0032	0.0032	0.0035	0.0035
β	0.233	0.110	0.057	0.025	0.013	0.007	0.007	0.005	0.010	0.014
λ, 10^{-5} day^{-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
Copper:										
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} day^{-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; *Bd* = bulk density; K_s = saturated hydraulic conductivity; θ_s = saturated water content; θ_r = residual water content; α_{VG} and n_1 = retention parameters; l = pore-connectivity factor; β = fraction of sorption sites with instantaneous sorption of the heavy metals; λ = kinetic constant for sorption sites 1-β; K_F and n = parameters of the Freundlich isotherm for the β sites, calculated with total and solution concentrations in mol g^{-1} and mol L^{-1}, respectively.

Table 2 – Zinc and copper concentrations measured in soil profile after eleven years of pig slurry amendments on treatments with annual doses of 50 and 200 m^3 ha^{-1} (Mea), the respective simulated concentrations with HYDRUS-1D using chemical model approach of Mallmann et al. (2012a) (SM), and 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

Table 3 – Zinc and copper concentrations measured in soil profile after eleven years of pig slurry amendments on treatments with annual doses of 50 and 200 m^3 ha^{-1} (Mea), the respective simulated concentrations with HYDRUS-1D using chemical model approach of Mallmann et al. (2012a) with coupling of root water uptake and growth modules (SMR), and 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

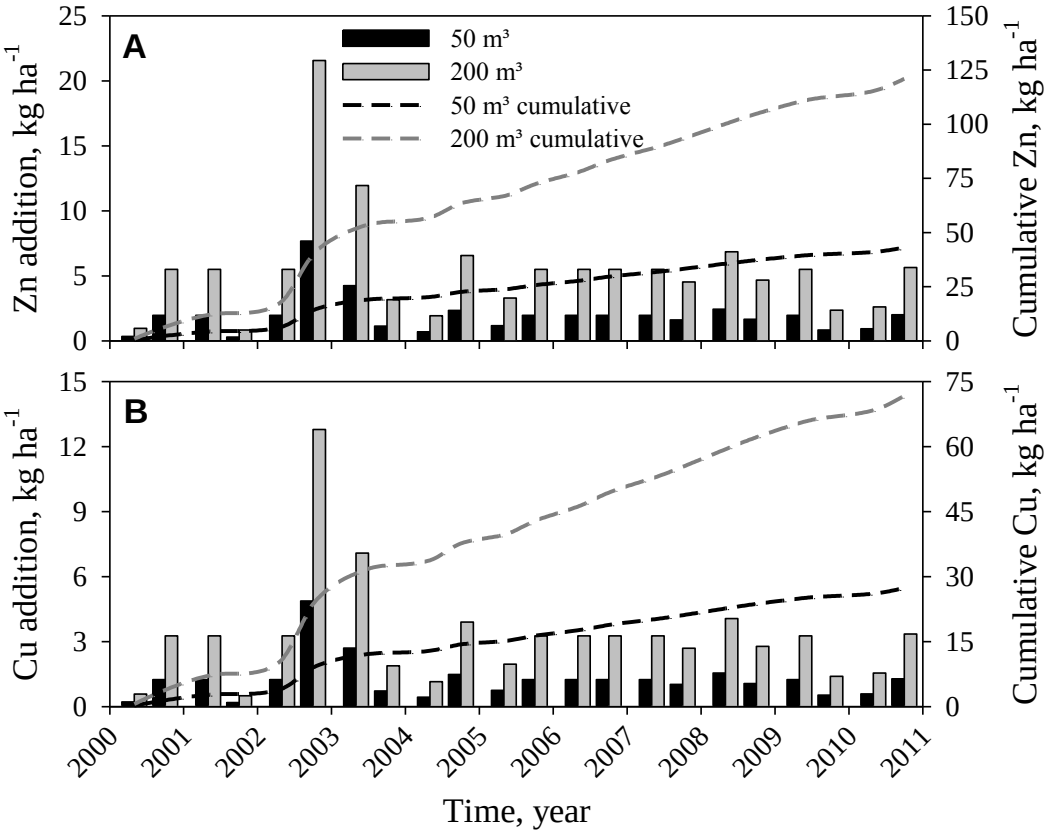


Figure 1 – Zinc (A) and copper (B) amounts applied to soil surface via pig slurry, by application (bars) and cumulative (lines), in the two evaluated treatments (50 and 200 m^3 ha^{-1} $year^{-1}$) during simulations with HYDRUS-1D, related to an experiment conducted on an Oxisol in Campos Novos, SC, Brazil.

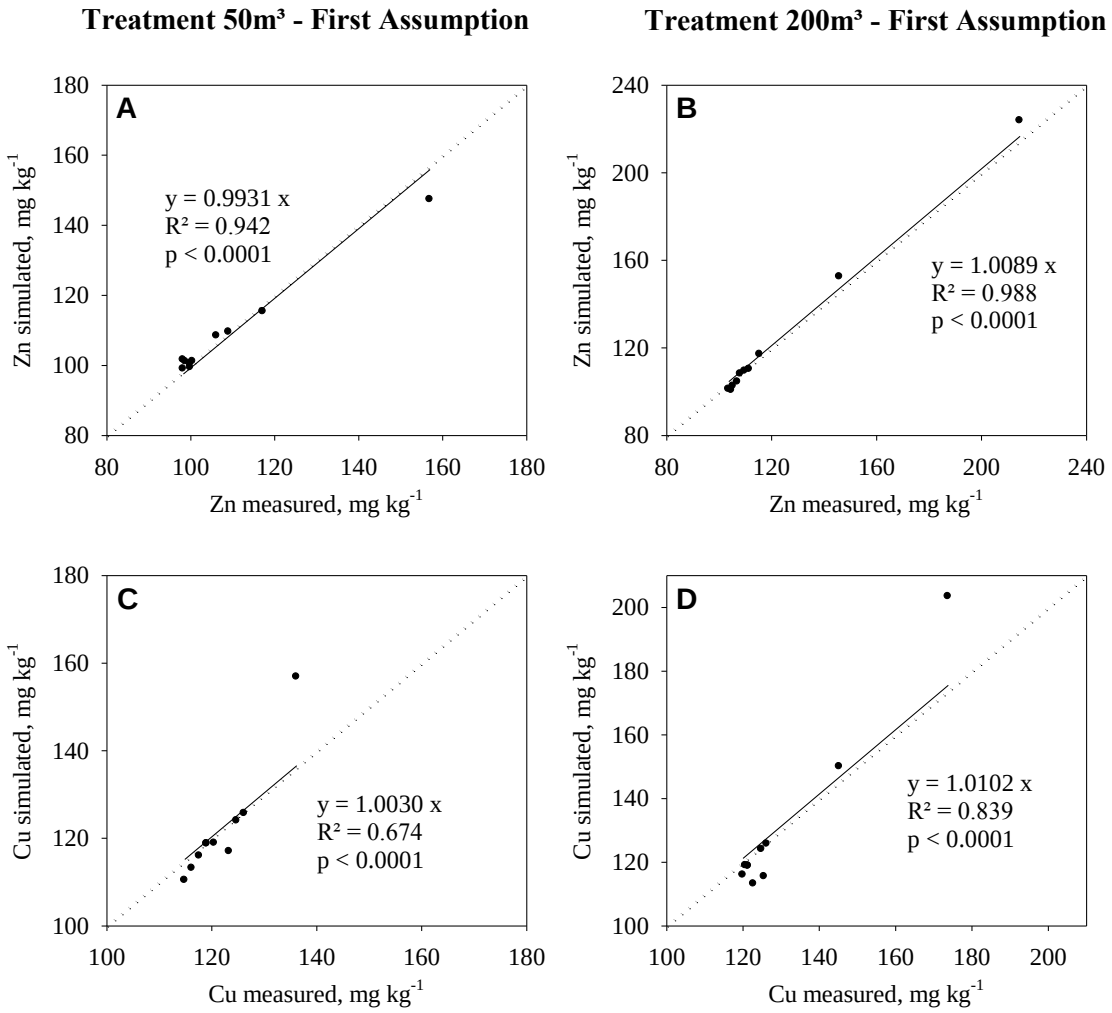


Figure 2 – Regression analysis for measured and simulated zinc (A and B) and copper (C and D) concentrations in a pig slurry amended soil under treatments of 50 m^3 (A and C) and 200 m^3 (B and D) ha^{-1} $year^{-1}$, for an Oxisol located in Campos Novos, SC, Brazil. Simulated values were obtained using the first assumption for model parameterization. Dotted line is the data proportion of 1:1.

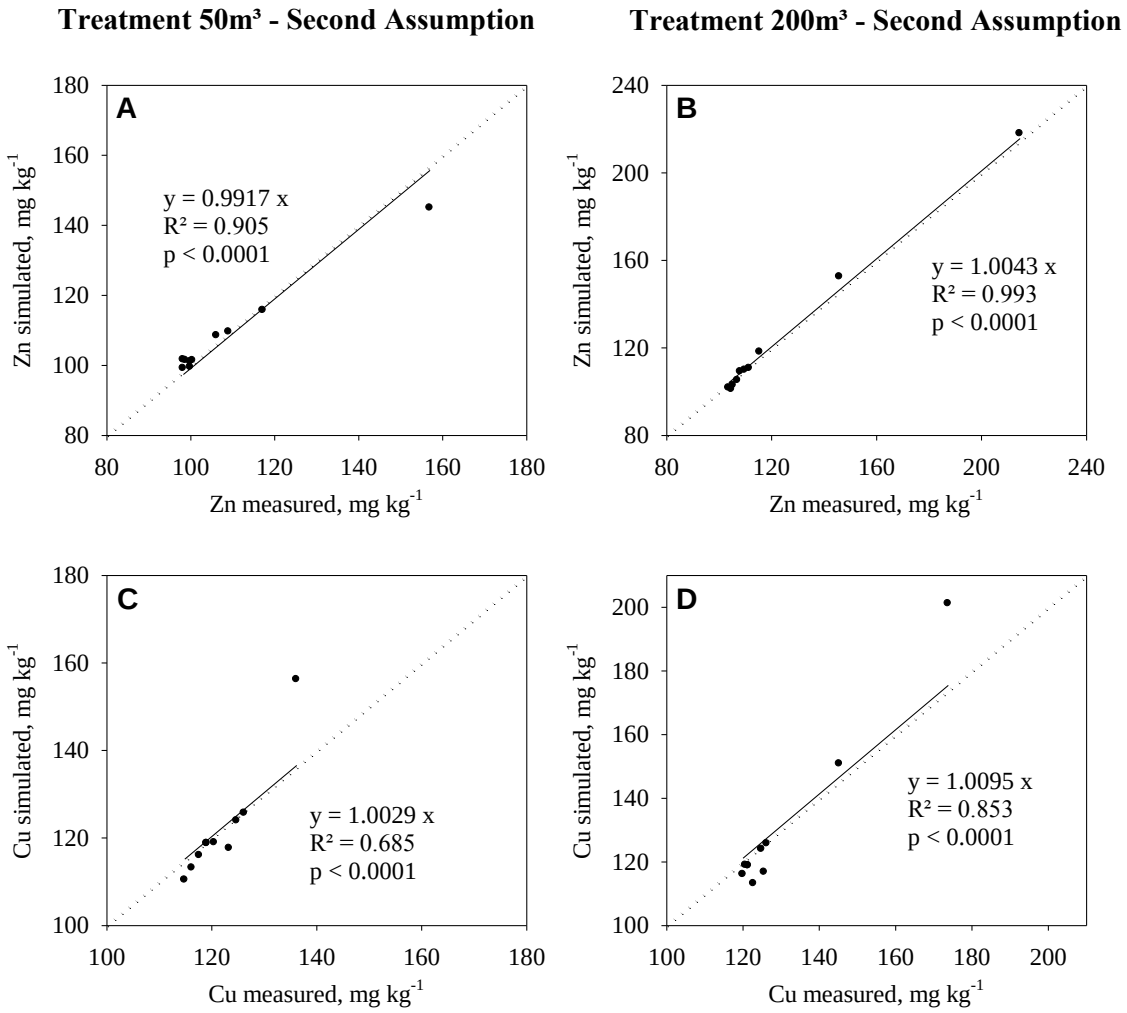


Figure 3 – Regression analysis for measured and simulated zinc (A and B) and copper (C and D) concentrations in a pig slurry amended soil under treatments of 50 m^3 (A and C) and 200 m^3 (B and D) ha^{-1} $year^{-1}$, for an Oxisol located in Campos Novos, SC, Brazil. Simulated values were obtained using the second assumption – introduction of root water uptake and root growth modules – for model parameterization. Dotted line is the data proportion of 1:1.

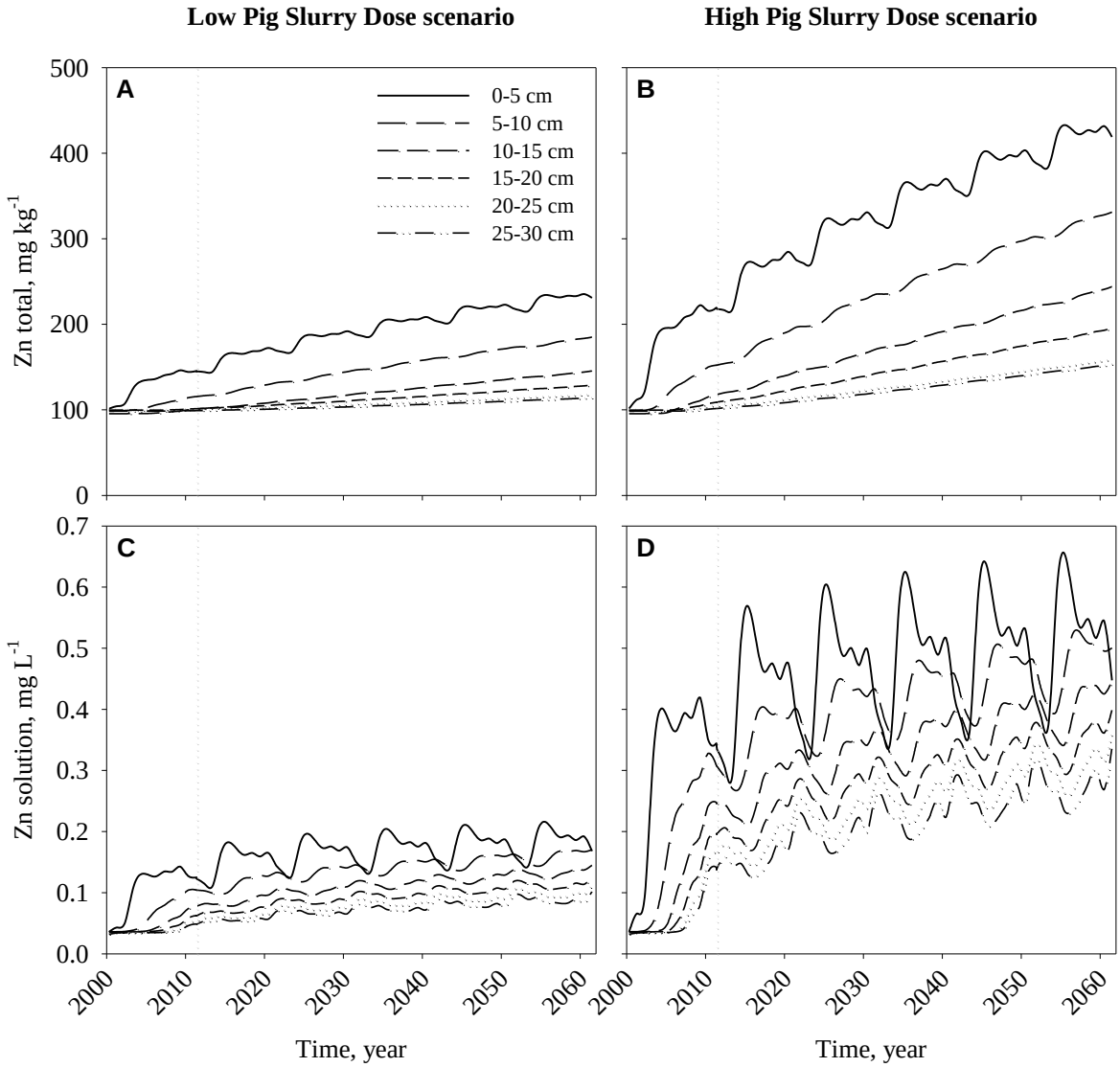


Figure 4 – Zinc total (A and B) and solution (C and D) concentrations at six soil layers simulated from 2000 to 2061 with HYDRUS-1D for future scenarios using low (A and C) and high (B and D) doses of pig slurry amendments applied at soil surface of an Oxisol located in Campos Novos, SC. Vertical dotted gray line indicates the time of soil sampling.

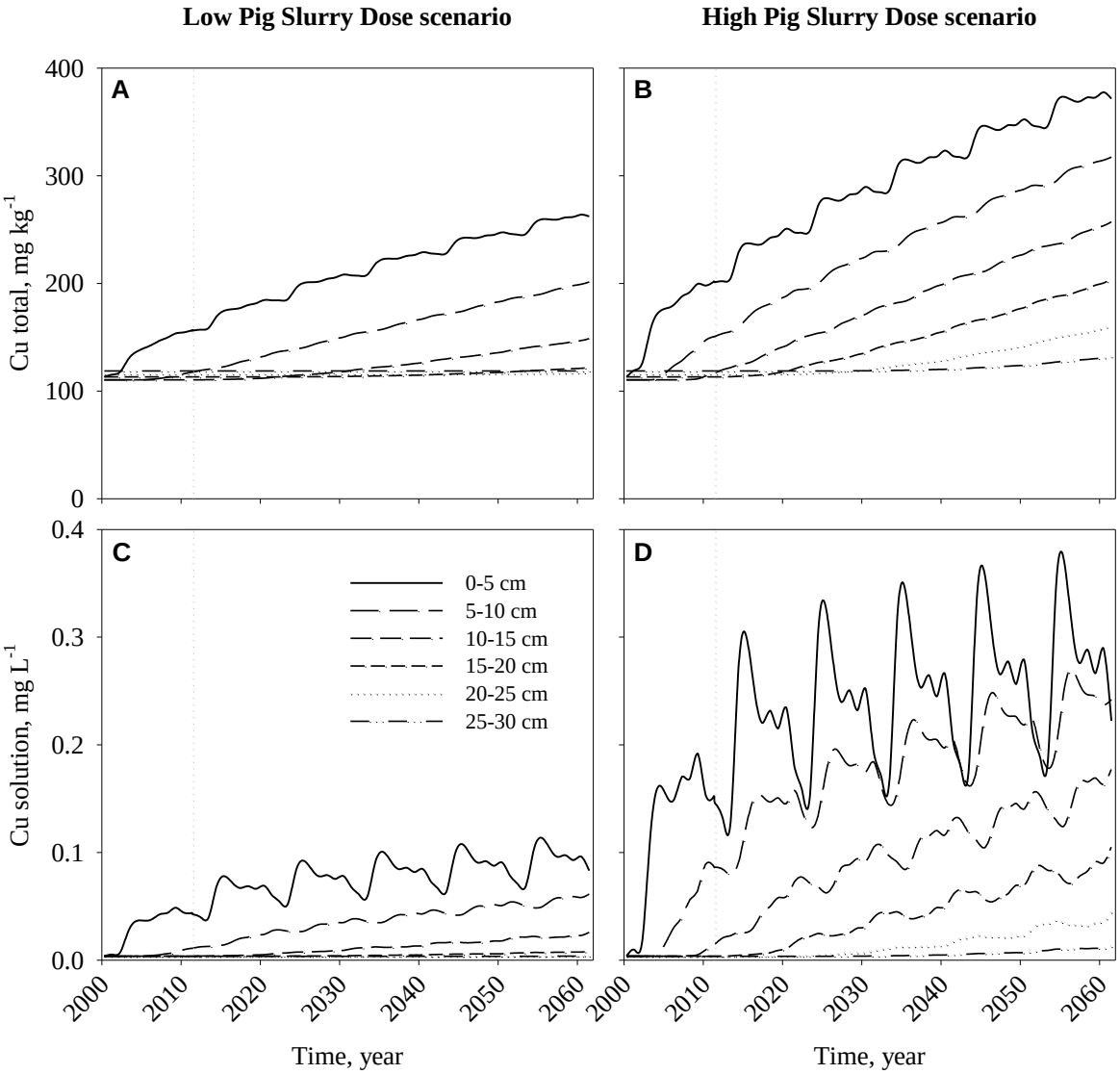


Figure 5 – Copper total (A and B) and solution (C and D) concentrations at six soil layers simulated from 2000 to 2061 with HYDRUS-1D for future scenarios using low (A and C) and high (B and D) doses of pig slurry amendments applied at soil surface of an Oxisol located in Campos Novos, SC. Vertical dotted gray line indicates the time of soil sampling.

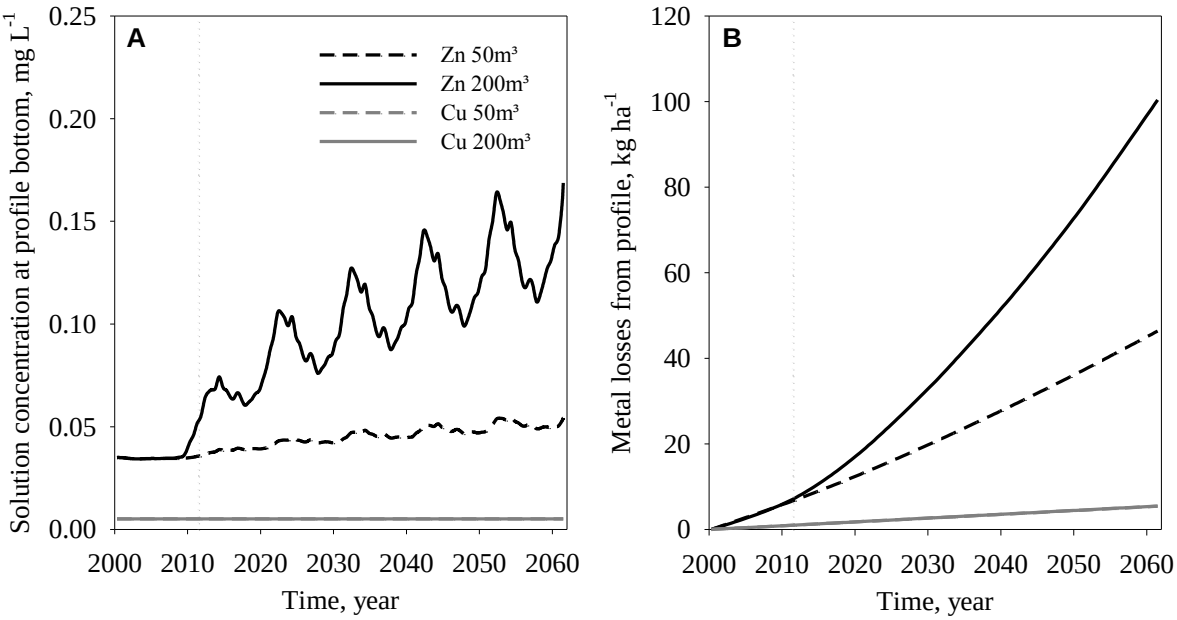


Figure 6 – Soil solution concentrations of zinc and copper at profile bottom (A) and respective metal losses from profile (B) estimated with HYDRUS-1D during a 61-years simulated period under scenarios with amendments of low ($50m^3$) and high ($200m^3$) pig slurry doses on an Oxisol in Campos Novos, SC. Vertical dotted gray line indicates the time of soil sampling.

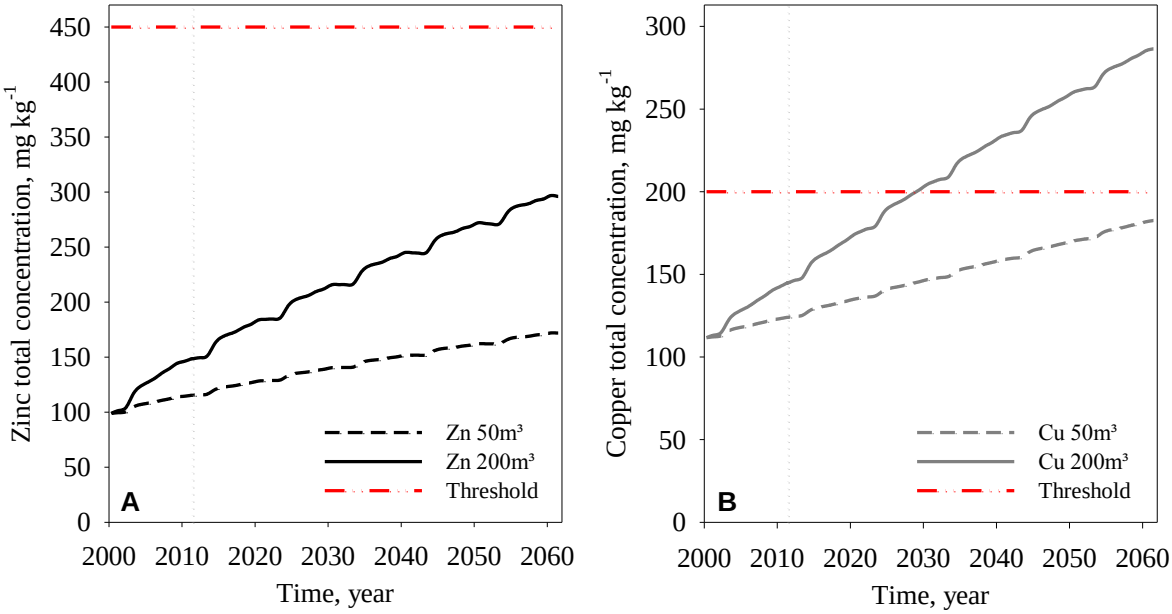


Figure 7 – Zinc (A) and copper (B) total concentrations at the upper 0–20-cm soil layer, estimated with HYDRUS-1D during a 61-years simulated period under scenarios with amendments of low (50m^3) and high (200m^3) pig slurry doses on an Oxisol in Campos Novos, SC. The red line corresponds to the threshold value for agricultural soils. Vertical dotted gray line is the time of soil sampling.

7 DISCUSSÃO GERAL

No trabalho buscou-se estimar o movimento futuro de Cu e Zn no perfil de um Argissolo e de um Latossolo, ambos submetidos a sucessivas aplicações de DLS, utilizando o software HYDRUS-1D (ŠIMŮNEK et al., 2012). Para tal, foi simulando o efeito da adição de diferentes doses deste resíduo na superfície do solo, em longo prazo. No Artigo I foi verificado também o efeito do revolvimento periódico do solo no transporte destes metais pesados (MP) no perfil. Já no Artigo II, antes de proceder com as simulações futuras, foram testadas diferentes suposições para o modelo químico de transporte de solutos no solo com o intuito de validá-lo, verificando ainda a influência das raízes no movimento dos dois MP no perfil. Os resultados das simulações preditivas realizadas nos dois artigos foram também confrontados com os valores de investigação estabelecidos para áreas agrícolas na resolução no. 420 do Conselho Nacional do Meio Ambiente, o CONAMA, de 28 de dezembro de 2009, que "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, 2009). Isso porque, conforme ressaltado por Mantovi et al. (2003), a avaliação dos riscos relacionados com o acúmulo de Cu e Zn no solo requer comparações entre as concentrações medidas e estimadas com aquelas estabelecidas pelas agências reguladoras.

O software HYDRUS-1D mostrou-se uma boa ferramenta para estimar os movimentos de Cu e Zn nos solos contaminados, pois permitiu a validação de um modelo químico de dois sítios para o Latossolo no Artigo II, usando as mesmas premissas utilizadas anteriormente para a validação realizada no Argissolo sob aplicação de DLS utilizado nas simulações do Artigo I (MALLMANN et al., 2012a). Além disso, este mesmo modelo também já foi validado para solos agrícolas franceses contaminados pela deposição atmosférica de Zn e chumbo (MALLMANN et al., 2012b). Isso aumenta a abrangência de uso desse modelo para diversos locais com características de solo semelhantes, podendo ser muito útil no estabelecimento de estratégias de manejo dos DLS e até mesmo do solo, como no caso do primeiro artigo, que utilizou práticas de revolvimentos periódicos do solo nos cenários futuros para verificar o efeito dessa intervenção mecânica no movimento de Cu e Zn no perfil.

Dentre os principais resultados obtidos nas simulações desses dois estudos (Artigos I e II) temos aqueles que se referem à viabilidade na continuidade da aplicação de DLS no solo

por longos períodos, em função dos teores máximos de Cu e Zn no solo de áreas agrícolas estabelecidos pela norma do CONAMA (2009). Dessa forma, e considerando os respectivos solos não cultivados como pontos de partida, o Argissolo suportaria a aplicação de altas doses anuais (aproximadamente 200 m^3 ha^{-1}) de DLS por aproximadamente 94 anos, compostos pelos oito anos iniciais do trabalho de validação do modelo (MALLMANN et al., 2012a) e pelos 86 anos relatados no Artigo I deste trabalho, até atingir o valor de investigação de Cu no solo, enquanto que para o Latossolo esse período se limitaria a 29 anos (Figura 1).

O valor de investigação, segundo a norma do CONAMA (2009), "é a concentração de determinada substância no solo ou na água subterrânea acima da qual existem riscos potenciais, diretos ou indiretos, à saúde humana, considerando um cenário de exposição padronizado". Vale lembrar também que esse valor de investigação, relativo à camada 0–20 cm de profundidade, foi determinado primeiramente pela Companhia de Tecnologia de Saneamento Ambiental do estado de São Paulo (CETESB, 2005) e estabelecido com base na avaliação de risco, considerando o perigo inerente às características químicas do elemento associado à exposição, direta ou indireta, e a capacidade dos organismos em absorver o elemento diariamente, sem comprometer a saúde (NASCIMENTO; BIONDI, 2013). Diante dessa legislação, pode-se verificar, portanto, que dos dois solos avaliados neste trabalho, o Latossolo teria menor tempo viável para receber as sucessivas aplicações de DLS do que o Argissolo.

Isso vai de desencontro ao fato dos solos argilosos geralmente apresentarem maior capacidade de adsorção de MP do que os solos com textura mais arenosa, em função da reatividade da argila, pela composição maior em óxidos de ferro e alumínio e até mesmo pela presença de maiores teores de matéria orgânica, como foi comprovado por Mattias (2006) ao determinar isotermas de adsorção para vários MP em diferentes classes de solo do estado de Santa Catarina. Dessa forma, considerando os solos aqui estudados, o Latossolo constituído por aproximadamente 70% de argila (Artigo II – Tabela 1) deveria ter capacidade de suportar maiores doses de Cu e Zn do que o Argissolo, que tem em média apenas 17% de argila (Artigo I – Tabela 1). Contudo, as simulações aqui realizadas não apontaram isso porque os teores naturais de Cu e Zn total no perfil do Latossolo, de 110 a 125 e de 95 a 109 mg kg^{-1}, respectivamente (Artigo II – Tabela 1), são muito maiores que os do Argissolo, de 5 a 14 e de 15 a 22 mg kg^{-1}, respectivamente (MALLMANN et al., 2012a). Essa diferença na concentração natural dos MP entre os dois solos fez com que o Latossolo atingisse mais rapidamente a concentração de 200 mg kg^{-1} de Cu durante as simulações, que é o valor de

investigação estabelecido pelo CONAMA (2009) para áreas agrícolas, e que entre os dois MP estudados foi o que limitou as aplicações de DLS ao solo.

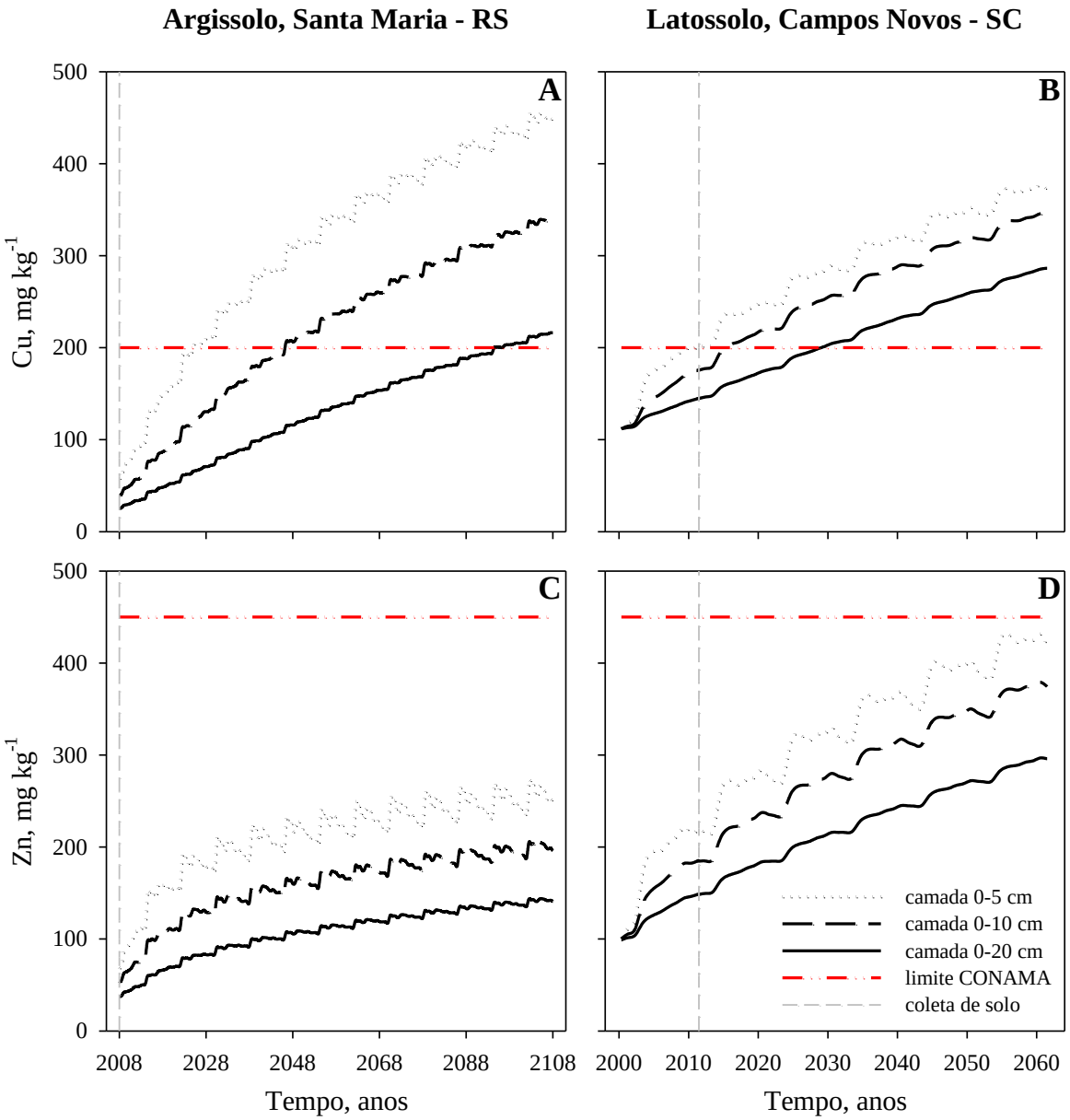


Figura 1 – Teores totais de cobre (A e B) e zinco (C e D) no solo das camadas 0–5, 0–10 e 0–20 cm de profundidade, simulados com o HYDRUS-1D para cenários futuros sob sucessivas aplicações de altas doses de dejeto líquido de suínos na superfície de um Argissolo Vermelho em Santa Maria, RS (A e C) e de um Latossolo Vermelho em Campos Novos, SC (B e D).

Nesse sentido, convém ressaltar que os diversos solos encontrados no ambiente apresentam concentrações naturais de Cu e Zn, entre outros elementos, muito variáveis. Isso

ocorre tanto em solos classificados numa mesma ordem, como os Latossolos brasileiros caracterizados no trabalho de Campos et al. (2003), quanto em solos de diferentes ordens localizados em territórios relativamente menores, neste caso tomando por exemplo os resultados da caracterização dos solos do estado do Pernambuco (BIONDI et al, 2011). Consequentemente, solos com teores naturais de Cu e Zn elevados acabam sendo prejudicados quanto à sua viabilidade legal para receber aplicações de resíduos que contenham quantidade expressiva desses dois MP, como foi o caso do Latossolo utilizado neste trabalho.

Embora os valores de investigação do CONAMA (2009) sejam confrontados com os resultados da camada de solo de 0–20 cm de profundidade, em áreas cultivadas sob sistema de plantio direto, como é o caso dos dois experimentos com aplicação de DLS utilizados neste trabalho, o acúmulo de Cu e Zn na superfície do solo gera um alto gradiente nas suas concentrações dentro dessa camada (Artigo I – Figuras 2, 3, 4 e 5; Artigo II – Figuras 4 e 5). Nos cenários simulados sob aplicação de altas doses de DLS foi estimado que a concentração de 200 mg kg^{-1} de Cu nas camadas de solo 0–5 e 0–10 cm no Argissolo será atingida em 2025 e 2046, respectivamente, e que no Latossolo isso ocorreria em 2011 e 2015, respectivamente (Figura 1).

Além disso, quando a concentração de Cu no solo atingir o valor de investigação, em 2094 no Argissolo e em 2029 no Latossolo, a concentração deste MP no solo da camada 0–5 cm já será de 439 e 283 mg kg^{-1}, respectivamente. Considerando que o valor de investigação é determinado com base na análise de risco à exposição humana, e que o solo que entra em contato com as pessoas usualmente é aquele da superfície, seja via inalação da poeira e/ou ingestão de partículas aderidas aos alimentos e/ou contato direto com a pele, sugere-se que os órgãos regulamentadores, especialmente o CONAMA, estabeleçam valores orientadores para os solos agrícolas considerando os diferentes sistemas de manejo agrícolas. Isso porque os solos manejados no sistema plantio direto costumam apresentar gradientes de concentração de elementos químicos dentro da camada arável (0–20 cm de profundidade) maiores do que os solos manejados no sistema convencional (LIMOUSIN; TESSIER, 2007; LÓPEZ-FANDO; PARDO, 2009). Vale destacar que a importância do sistema plantio direto no Brasil pode ser verificada pela sua abrangência, que segundo dados da safra 2011/2012 apresentados pela Federação Brasileira de Plantio Direto e Irrigação, este sistema de cultivo é adotado em 31,8 milhões de hectares, o que representa mais de 62% de toda área cultivada no país (FEBRAPDP, 2013).

Outra forma de verificar a viabilidade legal que os solos possuem em receber a adição de Cu e Zn via DLS é comparar o histórico das quantidades destes MP aplicadas no solo às quantidades máximas permitidas pela Resolução 375 do CONAMA (CONAMA, 2006), que para Cu e Zn são 137 e 445 kg ha^{-1}, respectivamente. Embora esta resolução defina critérios e procedimentos para o uso agrícola de lodos de esgoto, ela será aqui utilizada como parâmetro também para o uso de DLS, visto que ambos compostos são resíduos orgânicos de natureza semelhante e que passam por processos de fermentação e depósito similares. Assim, estimou-se que no Argissolo as aplicações sucessivas de altas doses de DLS atingirão as quantidades máximas de Cu e Zn permitidas por essa legislação nos anos de 2019 e 2046, respectivamente, enquanto que no Latossolo isso ocorrerá em 2020 e 2039. Essa pequena diferença entre os dois solos no tempo de aplicação de DLS permissível pelo CONAMA (2006) deve-se basicamente às diferenças nas concentrações de Cu e Zn nos dejetos utilizados nos dois locais, visto que os experimentos iniciaram no mesmo ano e que as doses anuais consideradas são semelhantes: 190 m^3 ha^{-1} no Argissolo e 200 m^3 ha^{-1} no Latossolo. Se considerado o cenário que utiliza doses moderadas de DLS no Argissolo, verificou-se que as aplicações de DLS atingirão as quantidades máximas de Cu e Zn nos anos de 2030 e 2086, respectivamente. Já no cenário submetido a doses baixas de DLS no Latossolo, a quantidade máxima de Cu será atingida em 2053, enquanto que a de Zn não atingirá o limite durante o período simulado (2000 a 2061). Dessa forma, para aumentar o tempo viável dos solos em receber adições de Cu e Zn segundo as quantidades máximas estabelecidas pela norma do CONAMA (2006), recomenda-se que as doses de DLS utilizadas nas aplicações periódicas ao solo sejam de baixas a moderadas (50 a 100 m^3 ha^{-1} ano^{-1}).

A abordagem considerando as cargas máximas de Cu e Zn permissíveis de serem aplicadas em solo que recebe adições sucessivas de DLS foi também utilizada por Girotto et al. (2010), mas os autores ressaltam que a sua adoção isolada não assegura a utilização adequada dos DLS a longo prazo, pois as especificidades do local não são levadas em consideração. Isso é reforçado pelos resultados das simulações deste trabalho, onde foi estimado que ao aplicar 137 kg ha^{-1} de Cu e 445 kg ha^{-1} de Zn, via altas doses de DLS, as concentrações totais desses dois MP na camada 0–20 cm do Argissolo serão, respectivamente, de 52 e 104 mg kg^{-1}, enquanto no Latossolo serão de 175 e 243 mg kg^{-1} (Figura 2). Dessa forma, quando atingidas as quantidades máximas de Cu e Zn aplicadas ao solo permitidas pelo CONAMA (2006), as concentrações destes MP serão diferentes nos dois solos estudados, sendo que em nenhum deles será atingido o valor de investigação (limite de concentração no solo) estabelecido pela norma do CONAMA (2009).

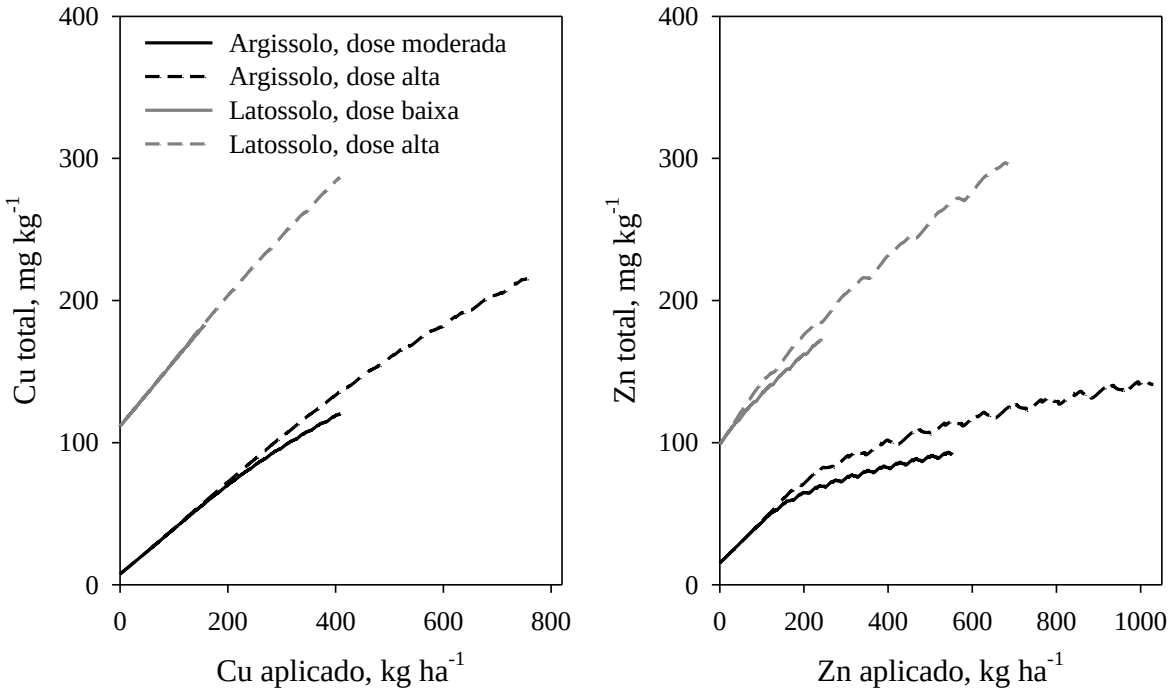


Figura 2 – Teores totais de cobre e zinco no solo da camada 0–20 cm de um Argissolo Vermelho e de um Latossolo Vermelho, localizados respectivamente em Santa Maria – RS e Campos Novos – SC, estimados com o HYDRUS-1D em função das quantidades desses metais pesados aplicadas ao solo via diferentes doses de dejeto líquido de suínos.

Foi estimado também que no Latossolo a concentração total de Cu e Zn no solo em função da dose desses MP adicionados via DLS aumenta mais rapidamente do que no Argissolo (Figura 2), demonstrando novamente que solos compostos por maiores teores de argila e óxidos possuem maior capacidade de adsorção por estes elementos (MATTIAS, 2006). Isso é um reflexo dos teores de Cu e Zn na solução do solo estimados durante o período simulado, muito maiores no Argissolo (Artigo I – Figuras 4 e 5) que no Latossolo (Artigo II – Figuras 4 e 5), considerando que o modelo utilizado no HYDRUS-1D para simular o transporte de MP no solo foi regido apenas pelo processo de adsorção/dessorção entre os elementos presentes na solução e aqueles da fase sólida do solo (ŠIMŮNEK et al., 2012).

Consequentemente, as transferências de Cu e Zn para camadas de solo abaixo de 20 cm de profundidade, inclusive as suas perdas para abaixo do perfil considerado nos dois locais (até 60 cm de profundidade), também foram maiores no Argissolo do que no Latossolo. Enquanto no Argissolo as transferências de Cu e Zn para abaixo de 60 cm de profundidade até o ano de 2061 (53 anos de simulação futura) foram estimadas em aproximadamente 8 e 165 kg ha^{-1} (Artigo I – Figura 6) sob aplicação de altas doses de DLS, no Latossolo foram de

apenas 5 e 100 kg ha^{-1} (Artigo II – Figura 6). A transferência de Zn para camadas de solo abaixo de 60 cm de profundidade estimada no Argissolo foi ainda maior após os 100 anos simulados, atingindo quantidades aproximadas de 500 kg ha^{-1} nos cenários futuros submetidos a aplicações de altas doses de DLS. Tais quantidades são decorrentes da alta concentração deste MP na solução do solo no limite inferior do perfil, principalmente após 40 anos de simulação, que chegou a ultrapassar o limite de concentração máximo para águas subterrâneas estabelecido pelo CONAMA (2009), de 1,05 mg L^{-1}, depois de 80 anos de simulação. Essa situação pode ser prejudicial aos mananciais de água subterrânea pelo fato do nível do lençol freático neste solo de Santa Maria (RS) oscilar em torno de 1,0 m de profundidade e, consequentemente, estar suscetível a receber esta carga de Zn transportada para profundidades mais profundas do perfil. Assim, recomenda-se novamente que as doses de DLS a serem utilizadas nas aplicações periódicas deste resíduo ao solo devem ser de baixas a moderadas, para assim evitar a contaminação excessiva do solo e da água e a consequente inutilização dessas áreas agrícolas.

8 CONCLUSÃO

A determinação de todos os parâmetros físicos e químicos necessários às equações utilizadas no HYDRUS-1D a partir das amostras de solo coletadas nos solos estudados constitui-se numa estratégia segura e eficiente para simular o movimento de zinco e cobre no solo. Seguindo essa lógica, um modelo químico de dois sítios foi validado para estimar o movimento de zinco e cobre num Argissolo e num Latossolo, ambos contaminados por sucessivas aplicações de dejeto líquido de suínos. Entretanto, para simular o transporte de cobre em solos argilosos aconselha-se introduzir também, neste modelo, um módulo que considere o movimento particulado deste elemento.

A introdução dos módulos de crescimento radicular e de absorção de água pelas raízes nas simulações com o HYDRUS-1D resultou em maior incorporação de zinco e cobre no perfil do solo, melhorando o ajuste dos dados simulados aos medidos. Entretanto, a diferença em relação às simulações sem a presença desses módulos foi pequena.

As aplicações sucessivas de altas doses de dejeto líquido de suínos aos solos elevam os teores de zinco e cobre na superfície, de modo que o limite de concentração de cobre estabelecido pela legislação para áreas agrícolas seja atingido, a partir de um solo sem histórico de aplicação, em aproximadamente 29 anos no Latossolo e 94 anos no Argissolo. Tal fato inviabiliza a continuidade da atividade agrícola e da adição dos dejetos nessas áreas.

Em áreas agrícolas que recebem sucessivas aplicações de dejeto líquido de suínos na superfície do solo, o uso de doses baixas a moderadas, de 50 a 100 m^3 ha^{-1} ano^{-1}, visando diminuir a entrada de zinco e cobre, e o revolvimento periódico da camada arável do solo, que dilui a concentração destes metais pesados da camada superficial e acelera o movimento para camadas mais profundas, a cada 20 anos, para evitar os problemas relacionados ao potencial de erosão do solo causado por esta prática, são estratégias que prolongam o período que os solos agrícolas podem ser usados também como meio para descarte desse tipo de resíduo.

O HYDRUS-1D mostra-se, portanto, uma ótima ferramenta para auxiliar na previsão do acúmulo e movimento vertical de zinco e cobre em solos submetidos a sucessivas aplicações de dejeto líquido de suínos, tanto em Argissolo quanto em Latossolo. Assim, previsões sob os mais diversos cenários podem alertar para a necessidade de alterações no manejo do solo ou dos resíduos, direcionando os gestores ou responsáveis nas suas tomadas de decisão.

9 PERSPECTIVAS DE ESTUDOS FUTUROS

Esta tese gerou resultados importantes para o avanço nos estudos envolvendo a modelagem de metais pesados em solos submetidos a aplicações de dejeto líquido de suínos. Esses avanços servem de estímulo para a realização de novos estudos que visem aprimorar ainda mais esse campo do conhecimento. Alguns dos itens que merecem atenção neste avanço e que poderão servir de base para estudos futuros estão brevemente listados a seguir:

a) Parametrizar e acoplar o módulo C-Ride ao modelo químico utilizado no HYDRUS-1D para simular o transporte particulado de contaminantes no solo. Com isso será possível melhorar os resultados das estimativas da concentração de cobre, principalmente, nos solos contaminados, especialmente naqueles mais argilosos como o de Campos Novos, SC.

b) Simular cenários futuros considerando revolvimentos periódicos do solo da camada arável associados ao uso de diferentes doses de dejeto líquido de suínos em solos argilosos.

c) Parametrizar o HYDRUS-1D para realizar simulações com outros elementos/compostos adicionados via dejeto líquido de suínos ao solo e que apresentam potencial de contaminação ambiental, como antibióticos, fósforo e nitrogênio.

d) Usar o software HYDRUS na modelagem do movimento de metais pesados, ou de outros contaminantes, em outros solos, agrícolas ou não, e que estejam submetidos à adição de quantidades consideráveis de contaminantes, como é o caso dos lixões, dos solos com cultivo de videira e consequente adição de calda bordalesa, áreas submetidas ao depósito ou descarte dos rejeitos de mineração, entre outros.

e) Verificar junto aos órgão ambientais a viabilidade da utilização de modelos, como o HYDRUS, para a realização de estudos necessários à avaliação da viabilidade ambiental de determinada atividade, bem como no planejamento do manejo mais adequado para ela.

10 REFERÊNCIAS BIBLIOGRÁFICAS

ALLOWAY, B. J. **Heavy metals in soils**. New York: John Wiley & Sons, 1990. 339 p.

BARROW, N. J. The four laws of soil chemistry: the Leeper lecture 1998. **Australian Journal of Soil Research**, Melbourne, v. 37, n. 5, p. 787-829, Sept./Oct. 1999.

BIONDI, C. M.; NASCIMENTO, C. W. A.; NETA, A. B. F.; RIBEIRO, M. R. Teores de Fe, Mn, Zn, Cu, Ni e Co em solos de referência de Pernambuco. **Revista Brasileira de Ciência do Solo**, Viçosa, v. 35, n. 3, p. 1057-1066, maio/jun. 2011.

BONAZZI, G.; CORTELLINI, L.; PICCININI, S. Presenza di rame e zinco nei liquami suinicoli e rischio di contaminazione dei suoli. **L'Informatore Agrario**, v. 36, p. 55-59, 1994.

BURNOL, A.; BLANC, P.; GUYONNET, D. **Recommandations pour la modélisation des transferts métalliques dans les eaux souterraines**. 2004. 73 p. (Rapport final).

CAMPOS, M. L.; PIERANGELI, M. A. P.; GUILHERME, L. R. G.; MARQUES, J. J.; CURI, N. Baseline Concentration of Heavy Metals in Brazilian Latosols. **Communications in Soil Science and Plant Analysis**, Philadelphia, v. 34, n. 3/4, p. 547-557, Feb. 2003.

CARRILLO-GONZÁLEZ, R. et al. Mechanisms and pathways of trace element mobility in soils. **Advances in Agronomy**, San Diego, v. 91, n. 3, p. 111-178, Sept./Dec. 2006.

CETESB – Companhia de Tecnologia de Saneamento Ambiental. **Decisão de diretoria Nº 195-2005-E, de 23 de novembro de 2005**. Disponível em: <http://www.cetesb.sp.gov.br/Solo/relatorios/tabela_valores_2005.pdf>. Acessado em: 05 de fev. 2013.

CQFS-RS/SC – Comissão de Química e Fertilidade do Solo RS/SC. **Manual de adubação e decalagem para os estados do RS e SC**. 10. ed. Porto Alegre: Sociedade Brasileira de Ciência do Solo - Núcleo Regional Sul, 2004. 394 p.

CONAMA – Conselho Nacional do Meio Ambiente. 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.

Diário Oficial [da] República Federativa do Brasil, Brasília, DF, nº 167, 30 ago. 2006. p. 141-146.

CONAMA – Conselho Nacional do Meio Ambiente. Resolução no 420, de 28 de dezembro de 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. **Diário Oficial [da] República Federativa do Brasil**, Brasília, DF, nº 249, 30 dez. 2009. p. 81-84.

COQUET, Y. et al. Water and solute transport in a cultivated silt loam soil: 2. numerical analysis. **Vadose Zone Journal**, Madison, v. 4, n. 3, p. 587-601, July/Sept. 2005.

COSTA, C. N. et al. Contaminantes e poluentes do solo e do ambiente. In: MEURER, E. J. **Fundamentos de Química do Solo.** Porto Alegre: Gênesis, 2004. p. 239-281.

FEBRAPDP – FEDERAÇÃO BRASILEIRA DE PLANTIO DIRETO E IRRIGAÇÃO. **Evolução da área cultivada no sistema de plantio direto na palha – Brasil.** Disponível em: <http://www.febrapdp.org.br/download/PD_Brasil_2013.pdf>. Acessado em: 25 de mar. 2013.

FONTES, M. P. F.; ALLEONI, F. R. F. Electrochemical attributes and availability of nutrients, toxic elements, and heavy metals in tropical soils. **Scientia Agricola**, Piracicaba, v. 63, n. 6, p. 589-608, nov./dez. 2006.

GIROTTO, E. et al. Acúmulo e formas de cobre e zinco no solo após aplicações sucessivas de dejeto líquido de suínos. **Revista Brasileira de Ciência do Solo**, Viçosa, v. 34, n. 3, p. 955-965, maio/jun. 2010.

GOLDBERG, S. et al. Adsorption–desorption processes in subsurface reactive transport modeling. **Vadose Zone Journal**, Madison, v. 6, n. 3, p. 407-435, July/Sept. 2007.

GONÇALVES, M. C. et al. Multicomponent solute transport in soil lysimeters irrigated with waters of different quality. **Water Resources Research**, Washington, v. 42, n. 1, p. 1-17, Jan. 2006.

GONÇALVES, M. C. et al. Modelação da dinâmica da água e dos sais num Aluviossolo regado com águas de diferente qualidade: ensaio de validação do modelo HYDRUS-1D com observações em monólitos. **Revista de Ciências Agrárias**, Lisboa, v. 30, n. 2, p. 38-52, jul./dez. 2007.

HAAN, C. T.; BARFIELD, B. J.; HAYES, J. C. **Design hydrology and sedimentology for small catchments**. California: Academic Press, 1994. 588 p.

INOUE, M. et al. Simultaneous estimation of soil hydraulic and solute transport parameters from transient infiltration experiments. **Advances in Water Resources**, Oxford, v. 23, n. 7, p. 677-688, June 2000.

JACQUES, D. et al. Calibration of Richards' and convection-dispersion equations to field-scale water flow and solute transport under rainfall conditions. **Journal of Hydrology**, Amsterdam, v. 259, n. 1, p. 15-31, Mar. 2002.

JONDREVILLE, C.; REVY, P. S.; DOURMAD, J. Y. Dietary means to better control the environmental impact of copper and zinc by pigs from weaning to slaughter. **Livestock Production Science**, Amsterdam, v. 84, n. 2, p. 147-156, Dec. 2003.

KÖHNE, J. M.; MOHANTY, B. P.; ŠIMŮNEK, J. Inverse dual-permeability modeling of preferential water flow in a soil column and implications for field-scale solute transport. **Vadose Zone Journal**, Madison, v. 5, n. 1, p. 59-76, Jan./Apr. 2006.

L'HERROUX, L. et al. Behaviour of metals following intensive pig slurry applications to a natural field treatment process in Brittany (France). **Environmental Pollution**, Barking, v. 97, n. 1, p. 119-130, Jan./Apr. 1997.

LEGROS, S. et al. Fate and behaviour of Cu and Zn from pig slurry spreading in a tropical water–soil–plant system. **Agriculture, Ecosystems and Environment**, Amsterdam, v. 164, n. 1, p. 70-79, Jan. 2013.

LIMOUSIN, G.; TESSIER, D. Effects of no-tillage on chemical gradients and topsoil acidification. **Soil & Tillage Research**, Amsterdam, v. 92, n. 1, p. 167-174, Jan. 2007.

LÓPEZ-FANDO, C.; PARDO, M.T. Changes in soil chemical characteristics with different tillage practices in a semi-arid environment. **Soil & Tillage Research**, Amsterdam, v. 104, n. 2, p. 278-284, July 2009.

MALLMANN, F. J. K. **Simulação do transporte vertical de zinco, chumbo e cobre em solos contaminados**. 2009. 147 f. Dissertação (Mestrado em Ciência do Solo) – Universidade Federal de Santa Maria, Santa Maria, 2009.

MALLMANN, F. J. K. et al. Modeling field-scale vertical movement of zinc and copper in a pig slurry-amended soil in Brazil. **Journal of Hazardous Materials**, Amsterdam, v. 243, n. 1, 223-231, Dec. 2012a.

MALLMANN, F. J. K. et al. Using a two site-reactive model for simulating one century changes of Zn and Pb concentration profiles in soils affected by metallurgical fallout. **Environmental Pollution**, Barking, v. 162, n. 1, p. 294-302, Mar. 2012b.

MANTOVI, P. et al. Accumulation of copper and zinc from liquid manure in agricultural soils and crop plants. **Plant and Soil**, Dordrecht, v. 250, n. 2, p. 249-257, Mar. 2003.

MATTIAS, J. L. **Metais pesados em solos sob aplicação de dejetos líquidos de suínos em duas microbacias hidrográficas de Santa Catarina**. 2006. 164 f. Tese (Doutorado em Ciência do Solo) – Universidade Federal de Santa Maria, Santa Maria, 2006.

MUALEM, Y. A new model for predicting the hydraulic conductivity of unsaturated porous media. **Water Resources Research**, Washington, v. 12, n. 3, p. 513-522, May/June 1976.

NASCIMENTO, C. W. A.; BIONDI, C. M. Teores orientadores de qualidade do solo em estados do nordeste. **Sociedade Brasileira de Ciência do Solo**, Boletim informativo, v. 38, n. 1, p. 29-32, jan./abr. 2013.

OGIYAMA, S. et al. Accumulation of zinc and copper in an arable field after animal manure application. **Soil Science Plant Nutrition**, Malden, v. 51, n. 6, p. 801-808, Oct. 2005.

PANG, L.; ŠIMŮNEK, J. Evaluation of bacteria-facilitated cadmium transport in gravel columns using the HYDRUS colloid-facilitated solute transport model. **Water Resource Research**, Washington, v. 42, n. 12, p. W12-S10, Dec. 2006.

RAJMOHAN, N.; ELANGO, L. Mobility of major ions and nutrients in the unsaturated zone during paddy cultivation: a field study and solute transport modelling approach. **Hydrological Processes**, Malden, v. 21, n. 20, p. 2698-2712, Sept. 2007.

RHEINHEIMER, D. S. et al. Heavy metal transport modelling in soil: sorption/desorption phenomena, water fluxes and contaminant fate. **Tópicos em Ciência do Solo**, Viçosa, v. 5, p. 135-180, 2007.

RHEINHEIMER, D. S. et al. Prospective modeling with Hydrus-2D of 50 years Zn and Pb movements in low and moderately metal-contaminated agricultural soils. **Journal of Contaminant Hydrology**, Amsterdam, v. 145, n. 1, p. 54-66, Feb. 2013.

SILVEIRA, M. L. A.; ALLEONI, L. R. F.; GUILHERME, L. R. G. Biosolids and heavy metals in soils. **Scientia Agricola**, Piracicaba, v. 60, n. 4, p. 793-806, jul./ago. 2003.

ŠIMŮNEK, J.; SUAREZ, D. L.; ŠEJNA, M. **The UNSATCHEM software package for simulating one-dimensional variably saturated water flow, heat transport, carbon dioxide production and transport, and multicomponent solute transport with major ion equilibrium and kinetic chemistry**. Versão 2.0, Research Report No. 141. Riverside: U.S. Salinity Laboratory, 1996, 186 p.

ŠIMŮNEK, J.; VAN GENUCHTEN, M. Th. Using the Hydrus-1D and Hydrus-2D codes for estimating unsaturated soil hydraulic and solute transport parameters. In: VAN GENUCHTEN, M. Th.; LEIJ, F. J.; WU, L. (Org.) **Characterization and measurement of the hydraulic properties of Unsaturated Porous Media**. Riverside: University of California Riverside, 1999. p. 1523-1536.

ŠIMŮNEK, J.; ŠEJNA, M.; van GENUCHTEN, M. Th. **The HYDRUS-2D software package for simulating the two-dimensional movement of water, heat, and multiple solutes in variably-saturated media**. Reverside: International Ground Water Modeling Center, Colorado School of Mines, Golden-CO, 1999. 225 p.

ŠIMŮNEK, J.; VAN GENUCHTEN, M. Th.; ŠEJNA, M. **The HYDRUS software package for simulating two- and three-dimensional movement of water, heat, and multiple solutes in variably-saturated media: Technical manual**. Version 1.0. Prague: PC-Progress, 2006. 213 p.

ŠIMŮNEK, J. et al. Simulating nonequilibrium movement of water, solutes and particles using HYDRUS – A review of recent applications. **Soil & Water Research**, Prague, v. 3, n. 2, p. S42–S51, Apr./June 2008.

ŠIMŮNEK, J. et al. The HYDRUS-1D software package for simulating the movement of water, heat, and multiple solutes in variably saturated media. version 4.15. HYDRUS Software Series 3. Riverside: Department of Environmental Sciences, University of California Riverside, 2012. 303 p.

SUAREZ, D. L.; ŠIMŮNEK, J. UNSATCHEM: unsaturated water and solute transport model with equilibrium and kinetic chemistry. **Soil Science Society of America Journal**, Madison, v. 61, n. 6, p. 1633-1646, Nov./Dec. 1997.

VAN GENUCHTEN, M. Th.; ŠIMŮNEK, J. Integrated modeling of vadose zone flow and transport processes. In: FEDDES, R. A.; ROOIJ, G. H.; VAN DAM, J. C. (Org.) **Unsaturated zone modelling: progress, challenges and applications**. Dordrecht: Kluwer Academic Publishers, 2004. p. 37-69.

VAN GENUCHTEN, M. Th. A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. **Soil Science Society of America Journal**, Madison, v. 44, n. 5, p. 892-898, Sept./Oct. 1980.

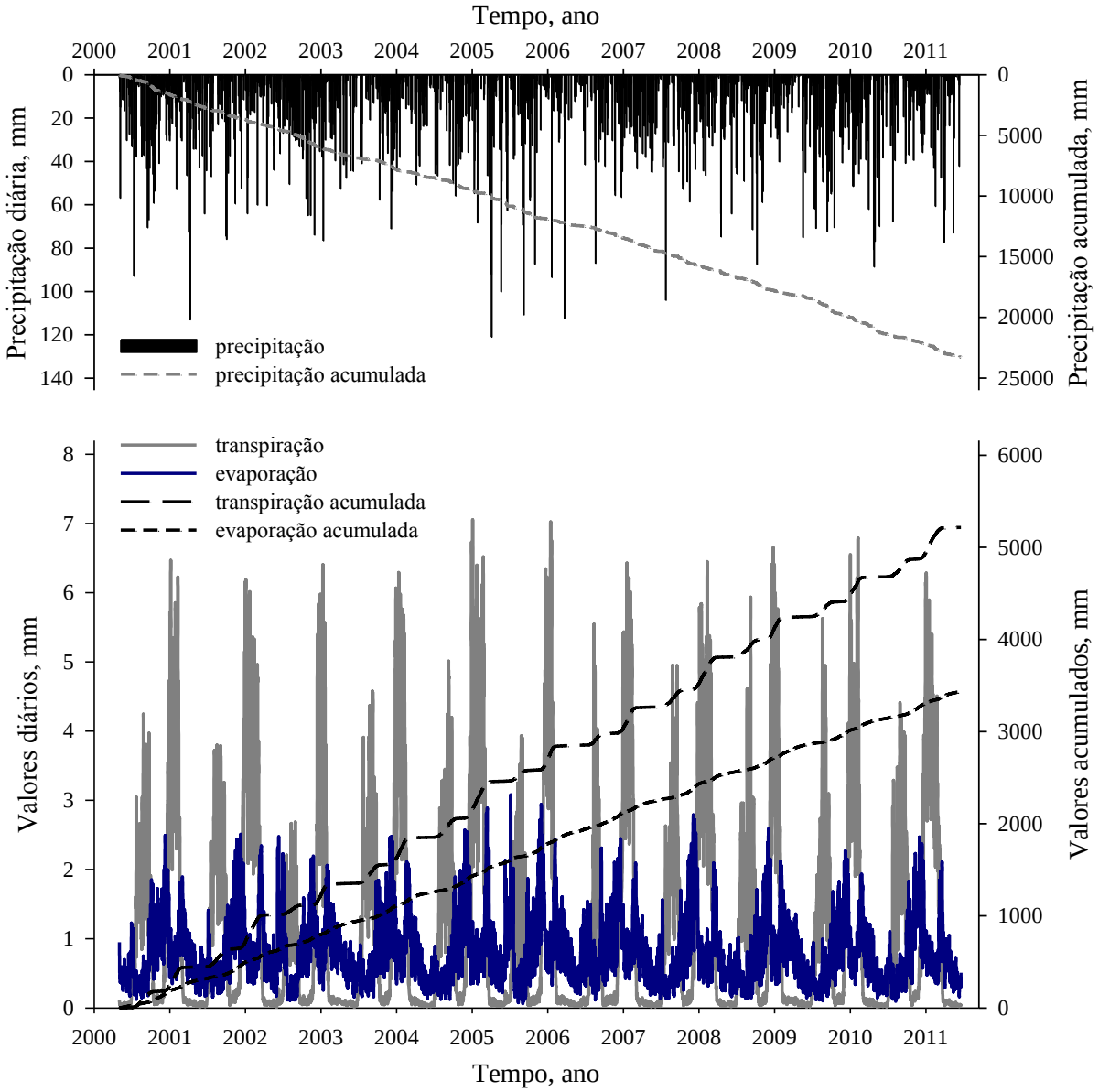
WAGENET, R. J.; HUTSON, J. L. **LEACHM: Leaching Estimation and Chemistry Model, a process-based model of water and solute movement, transformations, plant uptake and chemical reactions in the unsaturated zone**. Continuum 2. Ithaca: Water Resour. Inst., Cornell University, 1987. 148 p.

YOON, H.; HYUN, Y.; LEE, K. K. Forecasting solute breakthrough curves through the unsaturated zone using artificial neural networks. **Journal of Hydrology**, Amsterdam, v. 335, n. 1/2, p. 68-77, Jan./June 2007.

YU, C.; ZHENG, C. HYDRUS: software for flow and transport modeling in variably saturated media. **Ground Water**, Malden, v. 48, n. 6, p. 787-791, Nov./Dec. 2010.

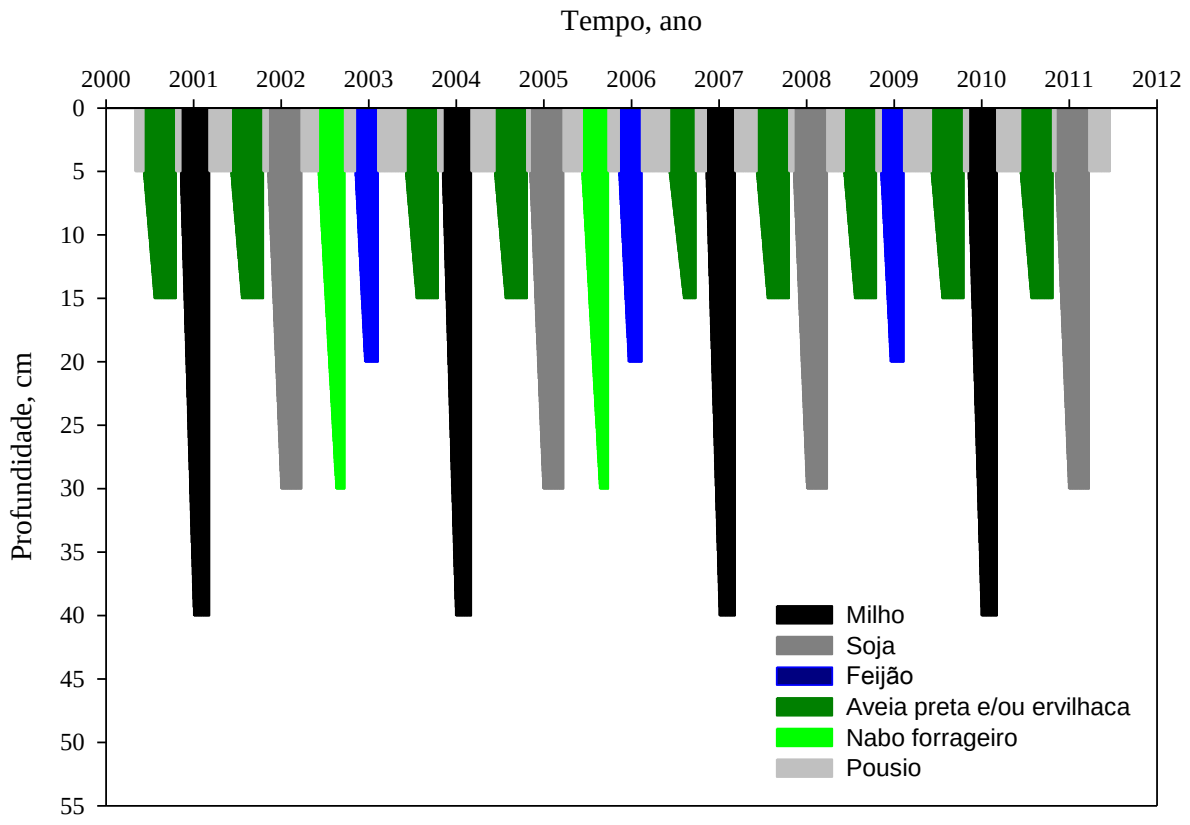
11 APÊNDICES

Apêndice A – Precipitação, transpiração e evaporação em Campos Novos, SC.



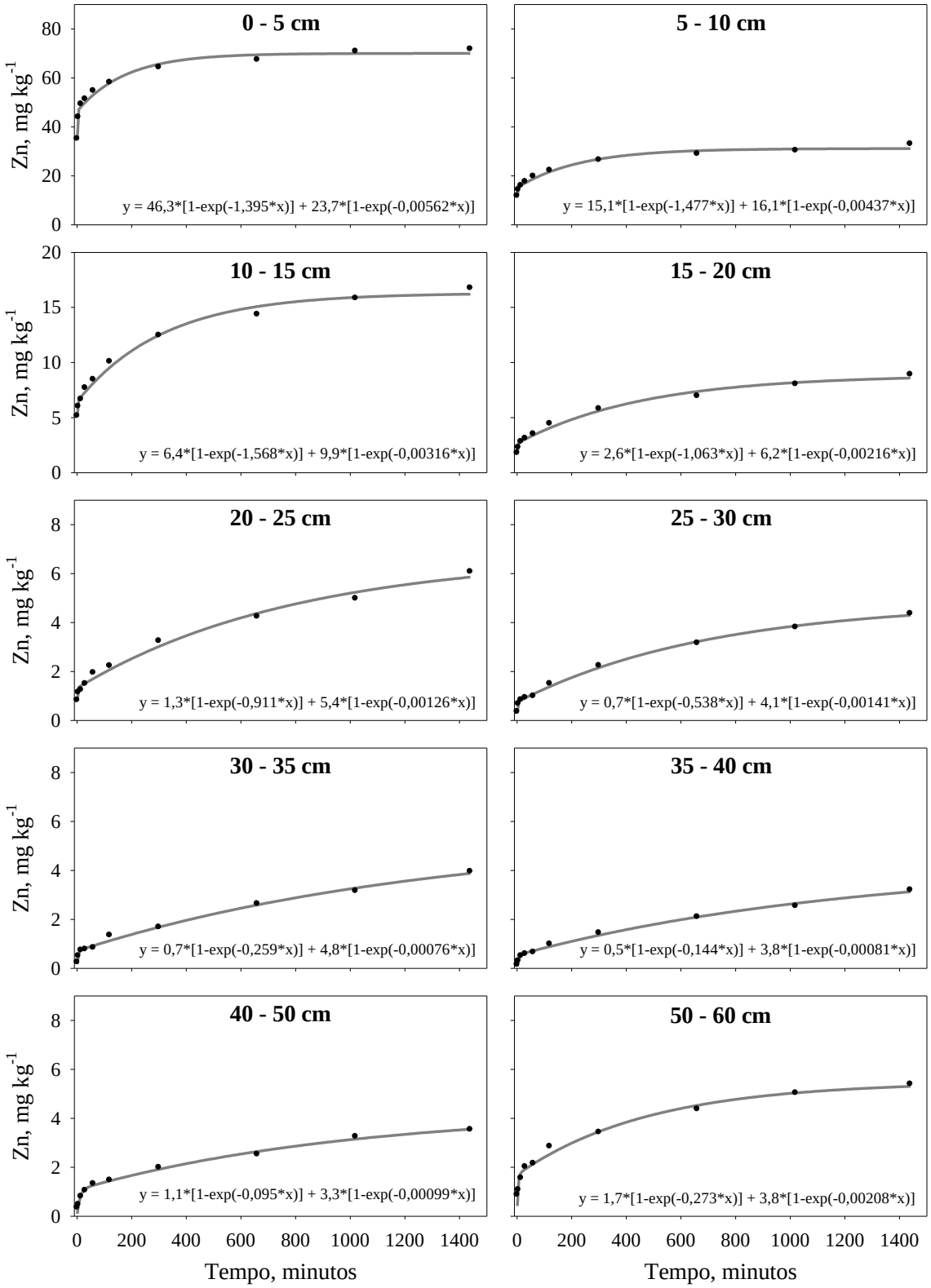
Valores diários e acumulados de precipitação, transpiração e evaporação entre 01/05/2000 e 15/06/2011 utilizados nas simulações do HYDRUS-1D no Artigo II, referentes ao período de condução e às culturas cultivadas no experimento com diferentes doses de dejeto líquido de suínos de Campos Novos – SC.

Apêndice B – Profundidade de raízes nas simulações do HYDRUS-1D.



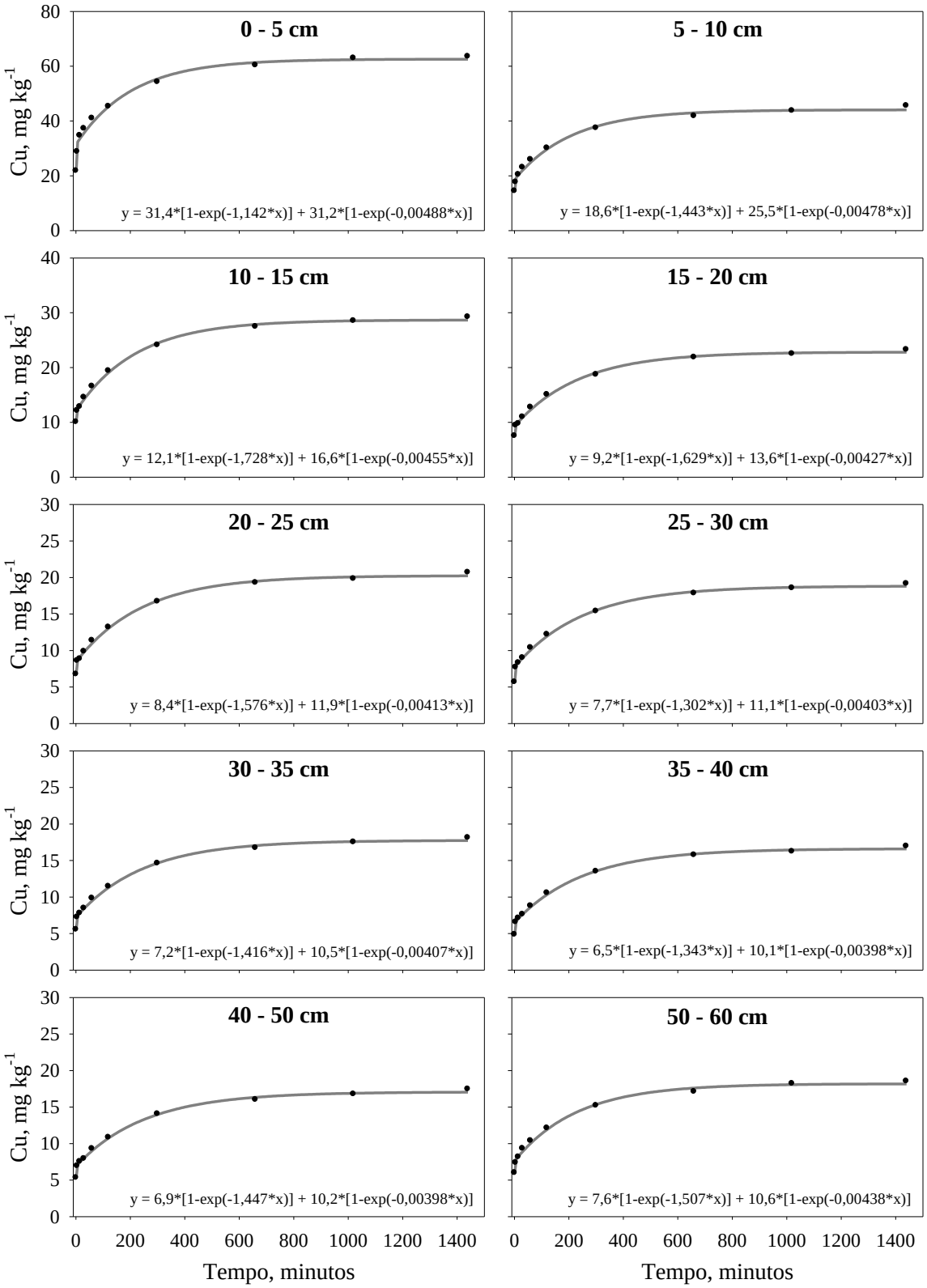
Valores diários da profundidade de raízes das culturas cultivadas entre 01/05/2000 e 15/06/2011 no experimento com diferentes doses de dejeto líquido de suínos de Campos Novos – SC, utilizados nas simulações do HYDRUS-1D no Artigo II. Dados estimados com base na literatura.

Apêndice C – Dessorção de zinco no solo do experimento de Campos Novos, SC.



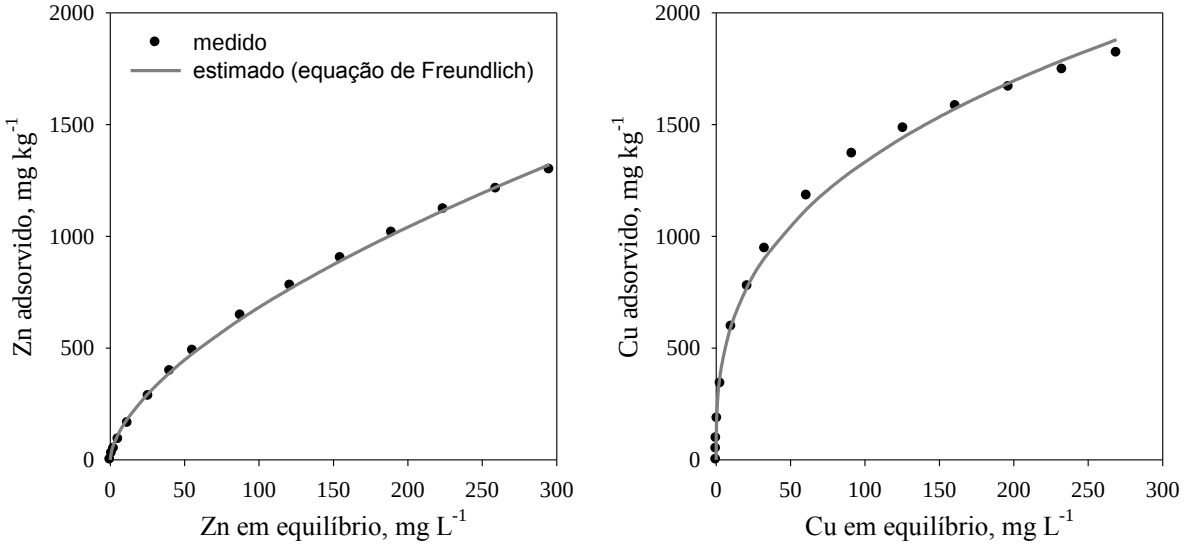
Curvas de dessorção de zinco no solo de dez camadas do tratamento sob aplicação anual de 200 m^3 ha^{-1} de dejeto líquido de suínos, experimento de Campos Novos – SC. As equações (linhas) foram ajustadas aos dados (pontos) seguindo o modelo $y = a*(1–e^{(-b*x)}) + c*(1–e^{(-d*x)})$.

Apêndice D – Dessorção de cobre no solo do experimento de Campos Novos, SC.

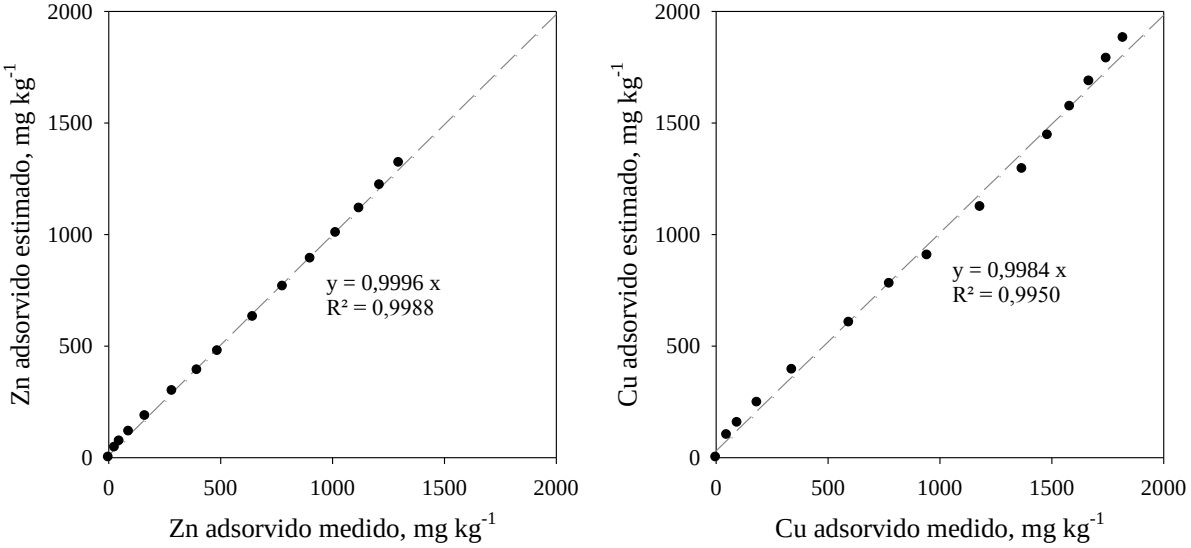


Curvas de dessorção de cobre no solo de dez camadas do tratamento sob aplicação anual de 200 m^3 ha^{-1} de dejeto líquido de suínos, experimento de Campos Novos – SC. As equações (linhas) foram ajustadas aos dados (pontos) seguindo o modelo $y = a*(1–e^{(-b*x)}) + c*(1–e^{(-d*x)})$.

Apêndice E – Adsorção de zinco e cobre no solo do experimento de Campos Novos, SC.



Curvas de adsorção de zinco e cobre no solo do experimento com diferentes doses de dejeto líquido de suínos de Campos Novos – SC. Os pontos correspondem aos valores médios do perfil de solo do tratamento testemunha, até 60 cm de profundidade, e as linhas representam as estimativas geradas pelo ajuste do modelo de Freundlich aos dados.



Correlação entre os teores medidos e os estimados pelo modelo de Freundlich para as curvas de adsorção de zinco e cobre no solo do tratamento testemunha do experimento com diferentes doses de dejeto líquido de suínos de Campos Novos – SC. As linhas pontilhadas correspondem à proporção 1:1.