

Simulation of the redistribution and fate of contaminants from soil-injected animal slurry



M.G. Mostofa Amin^{a,*}, Jirka Šimůnek^b, Mette Lægdsmand^a

^a Department of Agroecology, Aarhus University, Blichers Alle 20, DK-8830 Tjele, Denmark

^b Department of Environmental Sciences, University of California, Riverside, CA 92521, USA

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ABSTRACT

Spreading of contaminants from land-applied animal slurry may create hazard for both soil and water environments. Both the leaching and persistence of the contaminants is controlled by the redistribution of the contaminants immediately after application, while the redistribution is influenced by site conditions (here different slurry dry matter content and soil texture). HYDRUS-2D was used to simulate the redistribution of water, chloride, mineral N, *Salmonella* Typhimurium Bacteriophage 28B (phage), *Escherichia coli*, and steroid hormone estrogens near the slurry injection slit over a 50-day period after slurry injection at two field sites (Silstrup and Estrup) in Denmark to estimate the controlling transport and reaction parameters based on field measurements of the contaminants. The calibrated model was thereafter used to predict the leaching potential into the subsoil. The simulations confirmed that the higher water contents measured in the slurry application slit were due to a change in the hydraulic parameters. Chloride was redistributed considerably beyond the sampled soil profile at Estrup, but not at Silstrup, which had lower hydraulic conductivities than Estrup. Average size of the microorganisms affected their mobility; the bigger the size, the higher was the effect of the site conditions. The sorption coefficient of estrogens for slurry-amended soil was remarkably lower than that for unamended soil. The study suggests that dissolved organic carbon retained in slurry can facilitate the transport of contaminants. *E. coli*, phage, and estrogens were vulnerable to leaching from the very first precipitation event after the slurry application, whereas mineral N started to leach when NO₃-N accumulated. Model predictions suggest that there are potential risks of leaching of these contaminants from the top soil to the subsoil associated with the land-injected slurry.

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1. Introduction

The spreading of pathogens, steroid hormones, and nutrients from land-applied animal slurry is a hazard for the aquatic environment (Doltra and Munoz, 2010; Guber et al., 2005; Jenkins et al., 2009; Laegdsmand et al., 2009; Lee et al., 2007). Pathogenic contamination of ready-to-eat types of crops or drinking water can cause various diseases in humans (van Overbeek et al., 2010). Estrogenic hormones are endocrine disrupters and can affect the reproductive systems of aquatic life even at a very low concentration (1–2 ng/L) (Lahnsteiner et al., 2006). Release of nutrients from agricultural land into surface water can contribute to eutrophication and have

impact on aquatic ecology. Heavy rainfall after a slurry application is the most frequent cause for the release of slurry-borne contaminants to water bodies (Jenkins et al., 2008; Kjaer et al., 2007). Pathogens from the top soil can move with both surface runoff and infiltrating water through preferential pathways, avoiding the normal filtering capacity of soils (Coffey et al., 2010; Guber et al., 2007; Jenkins et al., 2006; Lee et al., 2003). Although estrogenic hormones readily sorb to soils, they have nevertheless been found in subsurface water draining from manure-amended soils (Kjaer et al., 2007; Laegdsmand et al., 2009).

The redistribution process of contaminants depends on their chemical characteristics that can influence their leaching and persistence in soils. The redistribution and transport processes under field conditions are complex, particularly when the contaminants are reactive and degradable such as steroid hormones and pathogens. The redistribution process of water and solutes depends on the gradients of the soil water potential and solute concentrations, respectively, and attachment–detachment processes. In field conditions one frequently encounters temporal and spatial variations in water contents, flow velocities, dispersion, and dilution

* Corresponding author. Current address: Department of Irrigation and Water Management, Bangladesh Agricultural University, Mymensingh 2202, Bangladesh. Tel.: +880 91 67401x2859; fax: +880 91 61510; mobile: +880 1712 536494.

E-mail addresses: aminmgmbau@yahoo.com (M.G.M. Amin), jiri.simunek@ucr.ca (J. Šimůnek), mel@fertilitech.com (M. Lægdsmand).

(Schijven and Šimůnek, 2002). A small change in bulk density and porosity caused by the traffic of agricultural equipment can lead to considerable differences in soil hydraulic conductivities (Coquet et al., 2005). Soil column experiments with disturbed and homogeneous soils under steady-state water flow conditions may not represent field conditions properly (Kjaer et al., 2007). Furthermore, the redistribution process for contaminants applied with liquid manure can be different than when they enter the soil environment with irrigation water (Guber et al., 2005). The immobile organic matter originating from slurry can change the hydraulic properties of the soil in and around the slits through which slurry is injected (Hoorman and Shipitalo, 2006; Petersen et al., 1996; Petersen and Andersen, 1996). Presence of slurry may also alter the sorption capacity of both organic and inorganic particles of soil with alkaline pH and high carbon and salt content (Lucas and Jones, 2009). Additionally, slurry enriched with dissolved organic carbon (DOC) can enhance DOC-mediated transport of contaminants (Stumpe and Marschner, 2007). The combined effects of the chemical, physical, and microbiological changes following slurry application on the fate of contaminants are therefore important to investigate at a slurry-injected field site.

Calibration of transport parameters through simulation of the field observation data helps to understand the effect of the properties of slurry and soil on the fate of different slurry-borne contaminants. Various models are used to simulate and assess the transport and fate of contaminants in soils. A numerical model is a tool to investigate various processes intensively and elaborately in an inexpensive way. HYDRUS (2D/3D) (Šimůnek et al., 2006) is a physically based mechanistic model that solves the Richards equation for water flow and a convection–dispersion equation for solute transport (Šimůnek et al., 2008). The model has been used during the last few years to simulate the transport of soil water (Hassan et al., 2010; Kandelous and Šimůnek, 2010; Ma et al., 2010), salts (Roberts et al., 2009), nitrates (Crevoisier et al., 2008; Doltra and Munoz, 2010; Wang et al., 2010), microorganisms (Jiang et al., 2010; Schijven and Šimůnek, 2002), and organic contaminants (Cheviron and Coquet, 2009; Pang et al., 2000) in variably-saturated soil formations in a variety of soil geometries and irrigation systems. The model was chosen, as it is capable of simulating reactive and colloidal transport in two dimensions. It was hypothesized that the parameters obtained in simulating the redistribution and transport of constituents in the slurry-injected soil would be different compared to unamended soil or those observed in laboratory because of the presence of slurry organic matter, salts and altered soil hydraulic properties. The objective of the study was (a) to investigate how effectively the redistribution process of different contaminants injected into soils with animal slurry follows the general transport theory incorporated in simulation models, (b) to compare the parameters obtained in this study with those available in literature, and (c) to understand the details of the redistribution process beyond the boundary of our field experiment.

2. Materials and methods

2.1. Field experiment

This study was conducted at two experimental sites, Silstrup (56° 56' N, 8° 39' E) and Estrup (55° 30' N, 11° 45' E), of the Danish Pesticide Leaching Assessment Program. Soil properties for both sites are given in Table 1. Different types of slurry (at Silstrup: 6.38% dry matter content, 2.8% C, 2.95 g NH₄-N/L; at Estrup: 0.8% dry matter content, 0.4% C, 2.34 g NH₄-N/L) were injected at two field sites directly into pre-ploughed soil at a 25-cm spacing with an average injection depth of 9 (Silstrup) or 10 cm (Estrup). While slurry was applied at different rates, a similar N application (125 kg N/ha) was

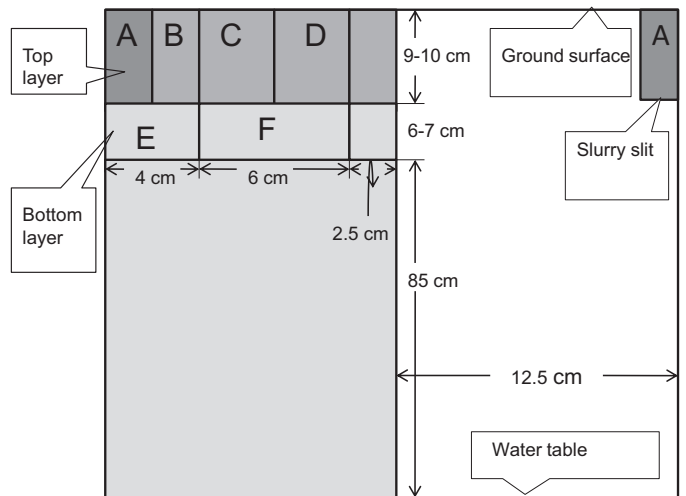


Fig. 1. Cross sectional view of the area between two neighbouring slurry slits (A). The shaded area is the modelled area and areas denoted A–F are the sampling sections.

used at both sites. All constituents used in the study were slurry-borne, except for spiked phages. In April 2009, slurry was applied during the first week, and spring barley sown in the second week, at both sites. Three slurry injection slits and five sampling positions per injection slit were randomly selected and marked with labelled flexible sticks immediately after slurry injection. Three intact soil profiles, one for each slit, with a 20 cm × 4 cm surface area, having the slurry slit in the middle and a total depth of 15 cm (Silstrup) or 17 cm (Estrup) were sampled on days 0, 1, 6, 18, and 46/49 after the application (Fig. 1). Each profile was subdivided into a top layer (a slurry injection depth) and a bottom layer (the rest of the profile depth). The top layer was again subdivided horizontally into four sections (A–D): section A (a 4 cm wide slurry slit) in the middle, and sequentially sections B (2 cm wide), C (3 cm), and D (3 cm) at both sides of section A. The bottom layer was subdivided into sections E and F. Only one side of the slurry slit is shown in Fig. 1. Samples taken from sections B at both sides of the slit were thoroughly mixed to prepare one sample. Similar mixing was done for samples from sections C, D, E, and F, assuming symmetrical distribution of all contaminants. The gravimetric soil water content in each thoroughly mixed fresh subsample was analyzed by drying (105 °C for 24 h), chloride concentrations by ion chromatography (Metrohm AG, Switzerland), NH₄-N and NO₃-N by an Auto-analyzer III Digital Colorimeter (Bran & Luebbe, Germany), viable *E. coli* by plate counting on *E. coli* Petrifilms (3 M a/s, Denmark), and phages by a double-agar layer method as described by Amin et al. (2013). Estrogens (estradiol and estrone) concentrations were determined by GC–MS/MS technique described in detail by Hansen et al. (2011). Hydrometeorological data were collected using the micrometeorological and hydrological instruments installed at both field sites. The meteorological data at two field sites during the field experiment is shown in Fig. 2.

2.2. Simulation studies

HYDRUS (2D/3D) (Šimůnek et al., 2006, 2008) was used to simulate the redistribution and persistence of slurry-borne contaminants in soils during a 50-day period following a direct injection of slurry. Only one half of the symmetrical soil profile between two adjacent slurry-injected slits (Fig. 1) was simulated to reduce calculation time. The simulated area included the entire vadose zone from the soil surface to the groundwater table situated in 1 m depth.

Table 1
Soil physico-chemical parameters at Silstrup and Estrup.

Site	Horizon	Sand (%)	Silt (%)	Clay (%)	Textural class (USDA)	OC ^a (%)	ρ_b^a (g/cm ³)	CEC ^a (cmol/kg)	pH
Silstrup	A	48	25	27	Sandy clay loam	2.1	1.34	20.7	6.7
	B	45	25	30	Sandy clay loam	0.5	1.51	19.8	6.7
Estrup	A	61	24	15	Sandy loam	2.8	1.27	15.1	7.1
	B	58	26	16	Sandy loam	0.8	1.61	10.2	6.6

^a OC, ρ_b , and CEC represent organic carbon, dry bulk density, and cation exchange capacity, respectively.

A deterministic approach, based on the numerical solution of the Richards equation by means of linear finite elements, was used to simulate soil water movement. The redistribution of all solutes was simulated by numerically solving the convection–dispersion equation. The Crank–Nicholson time weighting scheme and the Galerkin finite elements space-weighting scheme were chosen to solve the convection–dispersion equations for all contaminants. The impact of tortuosity on diffusion was also considered in the model. The general convection–dispersion equation solved by HYDRUS includes sorption, volatilization, the sink term for root solute uptake, and zero- and first-order reactions, which can have different rates in the gaseous, liquid, and/or solid phases.

2.3. Theory and equations

2.3.1. Soil water content

The redistribution of water in unsaturated soils was simulated using the Richards equation for variably saturated conditions:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x_i} \left[K(h) \left(K_{ij}^A \frac{\partial h}{\partial x_j} + K_{iz}^A \right) \right] - W_r \quad (1)$$

where θ is the water content (cm³/cm³); t is time (day); x_i is the spatial coordinate (cm), with x_1 as the vertical and x_2 as the horizontal spatial coordinate perpendicular to the injection slit (two

dimensional problem); h is the pressure head (cm); K is the hydraulic conductivity (cm/day); K_{ij}^A is a component of a dimensionless anisotropy tensor; and W_r is the root water uptake (cm³/cm³/day).

2.3.2. Chloride

Chloride is assumed to be conservative in the soil, neglecting the low sorption and the root uptake of chloride. Therefore, the retardation factor is one, the sorption and decay constants are zero and the redistribution of chloride can be described by the following convection–dispersion equation.

$$\frac{\partial \theta C}{\partial t} = \frac{\partial}{\partial x_i} \left(\theta D_{ij} \frac{\partial C}{\partial x_j} \right) - \frac{\partial q_i C}{\partial x_i} \quad (2)$$

where D_{ij} is the dispersion coefficient tensor (cm²/day) defined as (Bear, 1972):

$$\theta D_{ij} = \lambda_L |q| \delta_{ij} + (\lambda_L - \lambda_T) \frac{q_i q_j}{|q|} + \theta D_d \tau \delta_{ij} \quad (3)$$

and C represents the chloride concentration (mg/cm³), q_i is the i th component of the volumetric flux density (cm/day), D_d represents the molecular diffusion coefficient in free water (cm²/day), τ is a tortuosity factor [–], $|q|$ is the absolute value of the Darcian fluid flux density (cm/day), δ_{ij} is the Kronecker delta function, and λ_L and λ_T are the longitudinal and transverse dispersivity (cm), respectively.

2.3.3. Mineral N

The transformation of NH₄-N into nitrate was simulated by HYDRUS using a solute chain reaction option with first-order kinetic reaction parameters (Bolado-Rodriguez et al., 2010; Persicani et al., 1996). The sorption process was described using a simple instantaneous adsorption isotherm. All these processes can be described by the following equations:

$$S_{NH_4} = K_d C_{NH_4} \quad (4)$$

$$\frac{\partial \theta C_{NH_4}}{\partial t} = \frac{\partial}{\partial x_i} \left(\theta D_{ij} \frac{\partial C_{NH_4}}{\partial x_j} \right) - \frac{\partial q_i C_{NH_4}}{\partial x_i} - \rho_B \frac{\partial S_{NH_4}}{\partial t} - \mu_l \theta C_{NH_4} - \mu_s \rho_B S_{NH_4} - W_r C_{NH_4s} \quad (5)$$

where S_{NH_4} (mg/g) represents the adsorbed concentration, K_d is distribution coefficient (for linear adsorption) (cm³/g), C_{NH_4} is the NH₄-N concentration in the soil solution (mg/cm³), ρ_B is the dry bulk density (g/cm³), μ_l and μ_s are the first-order rate constants in the soil solution (day^{–1}) and in the solid phase (day^{–1}), respectively, W_r is the sink term representing root water uptake from the Richards equation, and C_{NH_4s} is the NH₄-N concentration associated with the sink term (mg/cm³).

NO₃-N dynamics in this study was simulated using the following convection–dispersion equation

$$\frac{\partial \theta C_{NO_3}}{\partial t} = \frac{\partial}{\partial x_i} \left(\theta D_{ij} \frac{\partial C_{NO_3}}{\partial x_j} \right) - \frac{\partial q_i C_{NO_3}}{\partial x_i} + \mu_s \rho_B S_{NH_4} + \mu_l \theta C_{NH_4} - \mu_{ld} \theta C_{NO_3} - W_r C_{NO_3s} \quad (6)$$

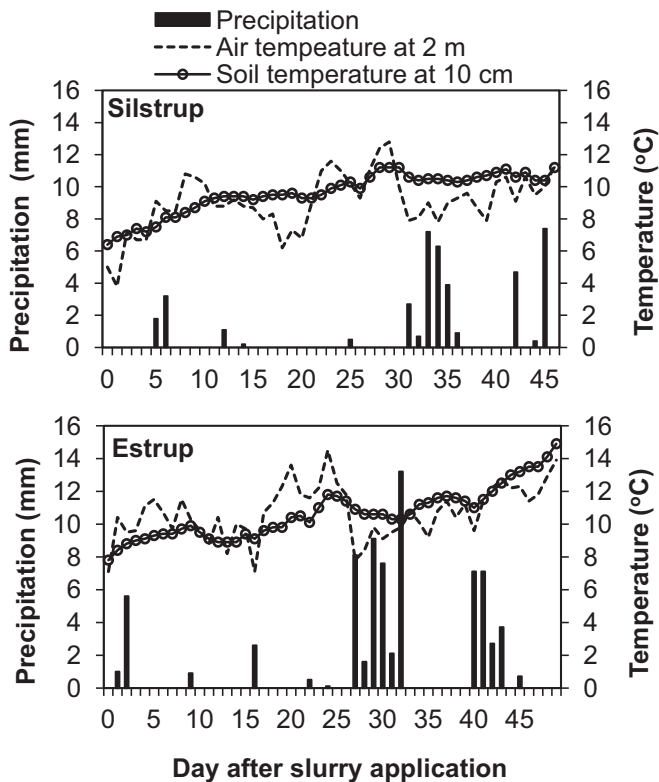


Fig. 2. Meteorological data at Silstrup and Estrup during the field experimental period.

where C_{NO_3} nitrate concentration in soil solution (mg/cm^3), μ_{1d} is the first-order rate constants in the soil solution (day^{-1}), and C_{NO_3s} is the $\text{NO}_3\text{-N}$ concentration associated with the root water uptake (mg/cm^3). The last term of Eq. (6) represents a passive uptake of $\text{NO}_3\text{-N}$. Nitrification of $\text{NH}_4\text{-N}$ is assumed to be the sole source of $\text{NO}_3\text{-N}$ in the soil, thus, all other reactive processes, such as mineralization, were neglected in our relatively short-duration experiment. The nitrification process from $\text{NH}_4\text{-N}$ to $\text{NO}_3\text{-N}$ was represented in the governing equation for $\text{NO}_3\text{-N}$ (6) as a zero-order production reaction term.

2.3.4. *E. coli* and phages

An attachment-detachment model, in which the attachment coefficient was calculated using the filtration theory, was used for simulating the transport of *E. coli* and phages. The HYDRUS model considers reversible adsorption of microorganisms to two types of kinetic sites, with one process usually representing attachment to the solid phase and the other straining (Bradford et al., 2006). The filtration theory determines the attachment coefficient based on the diameter of both soil particles and microorganisms. It is possible to assign a different blocking function for each sorption site. Sorption sites may have different sticking efficiencies and first-order entrainment rates. The code considers different first-order rates in both the liquid and solid phases representing inactivation processes. Microorganism can be removed from the liquid phase by first-order inactivation and/or attachment to the solid phase. From the solid phase they can be removed by the first-order entrainment and inactivation. The two-site attachment-detachment model is incorporated in the convection–dispersion equation as described by Hassanizadeh and Schijven (2000).

2.3.5. Estrogens

Estrogens are highly sorptive to the soil matrix and produce metabolites in the soil environment. Estradiol quickly degrades to estrone, but estrone has a lower degradation rate (Stumpe and Marschner, 2007). The instantaneous or time dependent sorption and first-order transformation reaction of estradiol into estrone can be described by solving the convective–dispersive equations as described by Casey et al. (2005).

2.4. Initial and boundary conditions

Soil hydraulic and transport parameters used as model input are shown in Table 2. Measured background values of the soil water content and different contaminants before slurry application were used as initial conditions (Table 3). The initial soil water content in the area saturated by applied slurry was specified as the water content at saturation (θ_s). Similarly, all contaminants were specified in the model using initial conditions in the slurry-applied area. A variable flux condition (calculated from precipitation and actual evapotranspiration data) was applied to the upper boundary of the

simulated zone. Actual evapotranspiration was calculated using the equation given by Allen et al. (1998). A zero flux condition was applied at the two vertical boundaries, considering the symmetrical distribution of water and slurry components and therefore no gradients over the boundaries. At the bottom boundary (the position of the groundwater table), a constant saturation condition was assumed. The depth of the water table (and the simulated zone) during the experimental period was set to 1 m, based on field observations. For solute transport, the third-type Cauchy boundary condition was chosen at the top and bottom of the soil profile. It was assumed that no contaminant was entering with precipitation and leaving with evaporation.

2.5. Calibration of parameters

The parameters of the soil water retention curves for two soil types required by the model were estimated from measured soil texture and bulk density using the Rosetta Lite software (Schaap et al., 2001) implemented in HYDRUS. Soil properties were determined by the standard methods (Amin et al., 2012). The bulk density in the top layer was lower than in the lower layer because of the breakup of soil structure during tillage and slurry injection operations. The soil hydraulic properties in slurry hotspots were different from the bulk soil, due to the added slurry organic matter. We assumed that the slurry organic matter only changed the hydraulic properties in section A after the slurry application. The inverse solution option of HYDRUS was therefore used to calculate modified soil hydraulic properties of the soil affected by the slurry application from the observed water contents. As a result, three slightly different sets of hydraulic properties were used for each field site (top soil, lower soil, and slurry hotspot). The soil hydraulic parameters of the van Genuchten–Mualem model (van Genuchten, 1980) used in HYDRUS are given in Table 2.

The longitudinal and transversal dispersivities for two soil types were manually optimized using the observed chloride redistribution data under the assumption that the ratio between longitudinal and transverse dispersivities was 10 (Pang et al., 2000). The optimized dispersivity values were then used for simulating the redistribution of other solutes. The parameters for different contaminants were estimated either from the available experimental data or from the reported values in the literature.

2.6. Statistical analysis

Agreement between predicted and observed data was evaluated by some frequently used model performance criteria, which can be expressed as (Wang et al., 2010):

Table 2
Soil hydraulic and transport parameters used as model input for HYDRUS.

Soil	θ_r^a	θ_s^a	α^b (1/cm)	n^b	K_s^c (cm/d)	l^c	λ_L^d (cm)	λ_T^d (cm)
S1 ^e	0.07	0.46	0.058	1.48	8	0.5	12	1
S2	0.11	0.46	0.055	1.48	8	0.5	12	1
S3	0.13	0.46	0.032	1.40	8	0.5	12	1
E1 ^e	0.10	0.46	0.060	1.46	62	0.5	10	1
E2	0.10	0.50	0.050	1.46	65	0.5	12	1
E3	0.10	0.48	0.030	1.30	63	0.5	10	1

^a θ_r and θ_s are the residual and saturated water contents, respectively.

^b α and n are empirical parameters determining the shape of the hydraulic functions.

^c K_s is the saturated hydraulic conductivity. l is a pore-connectivity parameter.

^d λ_L and λ_T represent longitudinal and transverse dispersivities, respectively.

^e Letters S and E in soil names refer to Silstrup and Estrup, respectively, and numbers to soil horizons: 1 for lower layer, 2 for top layer, and 3 for injection slit.

Table 3
Initial and background values of different slurry constituents used in the model.

Site ^a	SWC ^b cm ³ /cm ³	Chloride	NH ₄ -N mg/cm ³	NO ₃ -N	Phage PFU/cm ³	<i>E. coli</i> CFU/cm ³	E2 ^c ng/cm ³	E1 ^c ng/cm ³
S _S	0.46	0.69	0.98	0.008	2.0 × 10 ⁵	1.7 × 10 ⁴	16	21
S _B	0.30	0.035	0.004	0.008	0	0	0.04	0
E _S	0.48	0.28	0.80	0.007	2.0 × 10 ⁵	2 × 10 ⁴	1.2	6.3
E _B	0.30	0.025	0.004	0.007	0	0	0.03	0

^a S and E represent Silstrup and Estrup, respectively, and subscripts S and B the slurry saturated zone and the rest of the modelled area, respectively.

^b SWC, soil water content.

^c E2 and E1 represent estradiol and estrone, respectively.

(i) Root mean square error (RMSE):

$$\text{RMSE} = \sqrt{\frac{\sum_{i=1}^n (P_i - O_i)^2}{n}} \quad (7)$$

(ii) Coefficient of model determination (CD):

$$\text{CD} = \frac{\sum_{i=1}^n (O_i - \bar{O})^2}{\sum_{i=1}^n (P_i - \bar{O})^2} \quad (8)$$

(iii) Nash–Sutcliffe modelling efficiency (EF):

$$\text{EF} = 1 - \frac{\sum_{i=1}^n (O_i - P_i)^2}{\sum_{i=1}^n (O_i - \bar{O})^2} \quad (9)$$

where n is the total number of observations, O_i and P_i are the observed and predicted values of the i th data point, respectively, and \bar{O} is the observed mean.

All three indices indicate the model accuracy. The RMSE's closeness to 0 indicates the low average error in the model, however in absolute terms (same unit as variable). The CD value gives the total variance of the observed values explained by the predicted data and should be close to 1 to indicate high accuracy of the model. Modelling efficiencies (EF) can vary from $-\infty$ to 1, but the closer the model efficiency is to 1, the more accurate the model is. A zero value of EF indicates that the model predictions are no better predictors than the mean of the observed data, while a negative efficiency occurs when the observed mean is a better predictor than the model. In addition to the indices mentioned above the coefficient of determination (R^2) was calculated. Values of R^2 indicate if the precision of the model is high or low. If precision is high we will have a value of R^2 that is close to one, meaning that there is a strong correlation between the predicted and observed data, but the relation may not be 1:1 (Tedeschi, 2006). Hence, it is only relevant to discuss the precision in relation to model evaluation when accuracy is high.

3. Results and discussion

Field observation data showed that the redistribution process of aqueous and solid phase of the slurry was considerably affected by the site conditions (different slurry dry matter content and soil texture). The soil water content in slurry hotspot remained higher than that in the surrounding soil even after seven weeks of the slurry injection. The redistribution of chloride followed the similar trend of soil water content during the first two measurements due to convective transport and its nonreactive nature. On the other hand, nitrification and N balance appeared different for different conditions throughout the experimental period. Mineral N disappeared from Estrup before the last measurement after seven weeks of the slurry injection but not from Silstrup. Virus redistribution was only slightly affected, whereas *E. coli* was affected

considerably by the site conditions. The redistribution of estrogens was much more affected than that of the microorganisms. It may be due to the high estrogen sorption capacity of slurry organic matter (Amin et al., 2012). The immobile slurry dry matter sorbed estrogens and thus retarded redistribution than did for the microorganisms and mineral N. However, it was somewhat unclear what factors are more important for the redistribution processes. A simulation technique was therefore used to estimate different transport parameters such as sorption coefficient, inactivation rate of microorganisms, degradation of estrogens, nitrification and denitrification rates. The calibrated model was then used to investigate the environmental fate (leaching risks) of the slurry-borne constituents.

3.1. Parameter values

3.1.1. Chloride

Dispersivity is a sensitive parameter in estimating the leaching of contaminants through the vadose zone into groundwater (Vanderborght and Vereecken, 2007). The optimized value of longitudinal dispersivity was 12 cm at Silstrup and 10 cm at Estrup. Transverse dispersivity of 1 cm was assumed for both sites. Similar values of transverse dispersivities were reported in literature (e.g., Schijven and Šimůnek, 2002; Vanderborght and Vereecken, 2007).

3.1.2. Mineral N

The molecular diffusion of NH₄-N was set to 1.25 cm²/day. Similar values (0.85–1.65 cm²/day) for this parameter were used by Hassan et al. (2010) and Wang et al. (2010). The presence and volatilization of NH₃ was not considered individually, but it was included into the overall decay constant used in simulations to account for otherwise neglected factors. The rate coefficient of nitrification in the soil usually varies between 0.02 and 0.3 day⁻¹ depending on soil properties, water content, ammonium content, air content, and biochemical activity (Bolado-Rodriguez et al., 2010; Crevoisier et al., 2008; Hanson et al., 2006). The first-order rate constant for ammonium nitrification was assumed to be 0.05 day⁻¹ for both sites, given the low temperature during the study period (6–11 °C at Silstrup and 8–15 °C at Estrup). The K_d value for NH₄-N in the model was considered to be 1.1 cm³/g for both soils. The K_d values reported by different authors were in the range of 0.2–4 cm³/g (Hanson et al., 2006; Jellali et al., 2010). The first-order rate denitrification constant for NO₃-N was assumed to be 0.08 day⁻¹. This value was taken from the range 0.001–0.08 day⁻¹ used by Hassan et al. (2010) and Wang et al. (2010). Nitrate sorption to the soil matrix was assumed to be negligible with regards to other processes (Crevoisier et al., 2008).

3.1.3. Phage

The d_{50} for the Silstrup and Estrup soils was 0.08 mm and 0.2 mm, respectively. The average size of the phage was considered 0.1 μm (Schijven et al., 2002; Taylor et al., 2004). The first-order decay constant for both attached and free phases was assumed to be 0.05–0.07 day⁻¹, based on the experimental results. This value

could vary given different conditions, such as soil type, water content, temperature, etc. Schijven and Šimůnek (2002) optimized the value between 0.01 and 0.08 day⁻¹. The detachment coefficient was assumed to be 0.08 day⁻¹ at both sites as the centre value reported in the literature. The detachment coefficient for phage was found in the literature to be between 0.001 and 0.18 day⁻¹ (e.g., Schijven et al., 2002).

3.1.4. *E. coli*

The average size of the *E. coli* was assumed to be 1 μm (Pachepsky et al., 2006; Taylor et al., 2004). The first-order decay constant for both attached and free phase *E. coli* was found to be 0.1–0.12 day⁻¹ at both sites. Jiang et al. (2010) used this value between 0.3 and 0.8 day⁻¹. This value was a little lower in our study because of the low temperature during the whole study period. The detachment coefficient for *E. coli* was assumed 0.05 day⁻¹ at both sites.

3.1.5. Estrogens

The sorption coefficient for both estradiol and estrone was calculated as 11 ml/g for the soil at Silstrup and 14 ml/g for the soil at Estrup, based on the organic carbon content in the soil after slurry application. Since the redistribution of estrogens takes place in an environment dominated by slurry liquid the K_d value was calculated using the K_{oc} obtained for the soil-slurry environment (presence of slurry-DOC in the aqueous phase) by Amin et al. (2012). The study suggests that DOC present in slurry can facilitate transport of contaminants, and that the sorption coefficient estimated using the laboratory batch experiment can underestimate the leaching risks of slurry-borne contaminants. The same K_d value was used for both estradiol and estrone, as they have usually similar sorptivity (Caron et al., 2010). The first-order rate constant for both estrone and estradiol was assumed to be the same at both sites (0.08 day⁻¹). This value was in the lower range reported in literature, probably due to low temperatures during the study period. The value was found to be 0.007–1.8 day⁻¹ for estradiol and 0.09–0.14 day⁻¹ for estrone in literature (e.g., Das et al., 2004).

3.2. Model performance

The HYDRUS code simulated the redistribution process of different components and their persistence in soil with reasonably high model efficiency (Table 4). The EF values for the simulation of water, chloride, and mineral N were between 0.92 and 0.96 for Silstrup, and between 0.91 and 0.95 for Estrup. Redistribution and survival of both phages and *E. coli* were simulated with similar efficiency (0.86–0.94) at both sites. Transformation of estradiol to estrone, and their redistribution and persistence were predicted with higher model efficiency (EF=0.89–0.94) at Estrup, but with lower model efficiency (0.72–0.75) at Silstrup. The CD values were also close to 1, with only a few exceptions. The R^2 values between predicted and observed values for all simulations were higher than 0.89, except for estrogens at Silstrup (0.72–0.84) indicating that precision of the predictions was also high. Other users of HYDRUS achieved similar or higher ranges of model efficiency for simulating the transport/sorption processes of water and solutes (e.g., Unold et al., 2009). The relationship between the observed and predicted values of each studied component will be discussed in the following sections.

3.2.1. Soil water content

After the calibration procedure, we found good agreement between the observed and predicted soil water contents at different positions of the soil profile at both field sites (Fig. 3). Higher accuracies in simulating soil water content at field condition were also obtained using HYDRUS by Kandalous and Šimůnek (2010)

($R^2 = 0.77–0.98$) and Zhou et al. (2007) ($R^2 = 0.81–0.99$). The slurry injection slit (section A) had a higher water holding capacity due to the high content of organic matter. The simulation confirmed that the persistently increased soil water content in the injection slit could be described by the changed hydraulic parameters in this part of the soil. The short-term effect of immobile slurry organic matter on soil hydraulic parameters can considerably affect the environmental fate of contaminants in the slurry injection zone, such as the survival of microorganisms, nutrient dynamics, and degradation of organic contaminants. Although the increased water holding capacity of the slurry slit will have diminished gradually with time, the soil hydraulic parameters used in the model were time-independent, as HYDRUS does not have an option for time-variable soil hydraulic properties. Consequently, the water content in section A during the final part of the experiment was slightly overestimated (Fig. 3). Deviations between predicted and simulated values of soil water contents, observed especially in sections E and F, were likely caused by natural heterogeneity of field properties.

3.2.2. Chloride

Some observed values of chloride had a high standard error due to heterogeneous soil conditions and the likely presence of macropore flow (Fig. 3). There were some uncertainties in the uniformity of the slurry application and solid-liquid ratio along the slurry slit. However, the average values of six sampling positions probably provided a representative result. The simulated and measured chloride concentrations seem to be in agreement. However, agreements between simulated and measured values were relatively lower for most distant sections of D, E, and F. Deviations between predicted and observed values were higher at the Silstrup site because of the uncertainty caused by the preferential flow in this clay rich soil.

3.2.3. Mineral N

NH₄-N concentrations at different sampling times at both sites were simulated well when adsorption, nitrification, and dissipation processes were considered. Model predictions were close to observed values in most cases (Fig. 3). Like the soil water contents, which remained near saturation for the first three sampling times in section A at Silstrup, the NH₄-N concentrations in this section remained at high values, indicating low initial nitrification. When water contents decreased, NH₄-N concentrations started to dissipate noticeably. Moreover, the actual nitrification rate may have been different in the different sections due to different oxygen contents in the different sections. The oxygen content in section A may also have changed over time with changes in the nitrification rate. Since the nitrification rate in the model was time-independent, the model predictions deviated slightly from observed values for some sampling times at both sites (Fig. 3). Due to these reasons, the model underestimated the NH₄-N concentration in section A on day 6 at Silstrup. The model could not predict the higher NH₄-N concentration in section D on day 18 at Silstrup and in section F on day 6 at Estrup (Fig. 3). The agreements between some of the predicted and observed NO₃-N concentrations were low in the beginning of the experiments at Silstrup and at the end at Estrup.

3.2.4. Phage

It appears that the attachment coefficient calculated by the filtration theory based on the average soil particle diameter and the average phage size gave a good accuracy. Simulated phage concentrations were within the range of observed values in most cases (Fig. 4). However, there were some comparatively higher deviations between observed and predicted values in sections C–F at Silstrup. The transport of phage through the soil matrix to sections D and F was probably very low, especially in the fine-grained

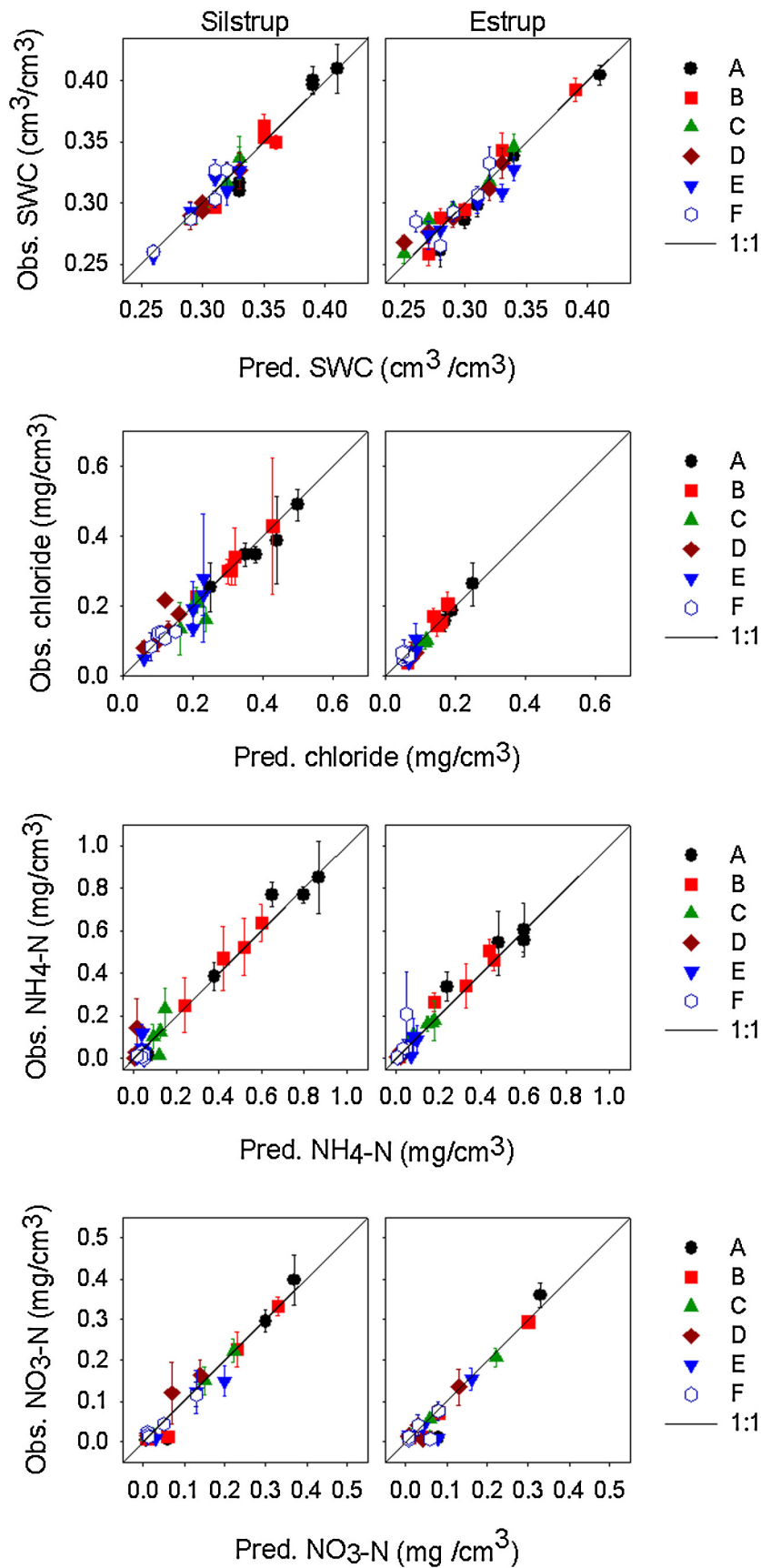


Fig. 3. Observed and predicted soil water contents, chloride, NH₄-N, and NO₃-N concentrations at Silstrup (left) and Estrup (right) (different colour symbols represent different soil sections as indicated in the legend).

Table 4
Performance indicators for the model simulating different components.

Site	Silstrup				Estrup			
	Component	R ²	RMSE ^a	CD	EF	R ²	RMSE	CD
Water (cm ³ /cm ³)	0.94	0.01	1.12	0.94	0.94	0.01	0.96	0.91
Chloride (mg/cm ³)	0.92	0.03	0.93	0.92	0.94	0.01	1.20	0.93
NH ₄ -N (mg/cm ³)	0.96	0.05	1.14	0.96	0.95	0.04	1.09	0.95
NO ₃ -N (mg/cm ³)	0.96	0.02	1.05	0.96	0.92	0.03	1.08	0.91
Phage (PFU/cm ³)	0.94	9867	0.98	0.94	0.94	16,713	1.32	0.90
<i>E. coli</i> (CFU/cm ³)	0.92	968	1.28	0.92	0.89	1305	0.98	0.86
Estradiol (ng/cm ³)	0.84	1.9	0.80	0.75	0.94	0.12	0.86	0.89
Estrone (ng/cm ³)	0.72	3.8	1.13	0.72	0.96	0.42	0.84	0.94

^a The unit of RMSE (root mean square error) is the same as the unit of the corresponding slurry constituent.

soil at Silstrup. The possibility of macropore flow was higher at Silstrup, due to the high clay content. Because of the very high concentration gradient, even insignificant macropore flow could have caused considerable variation in concentrations in sections D, E, and F. At Estrup, the model slightly underestimated the phage

concentrations in sections A–B in the beginning of the experiment, but overestimated them in sections C–F in some of the cases (Fig. 4). For simplification, the same first-order decay rate was used for all sections, although it was perhaps slightly different between the slurry slit and other sections.

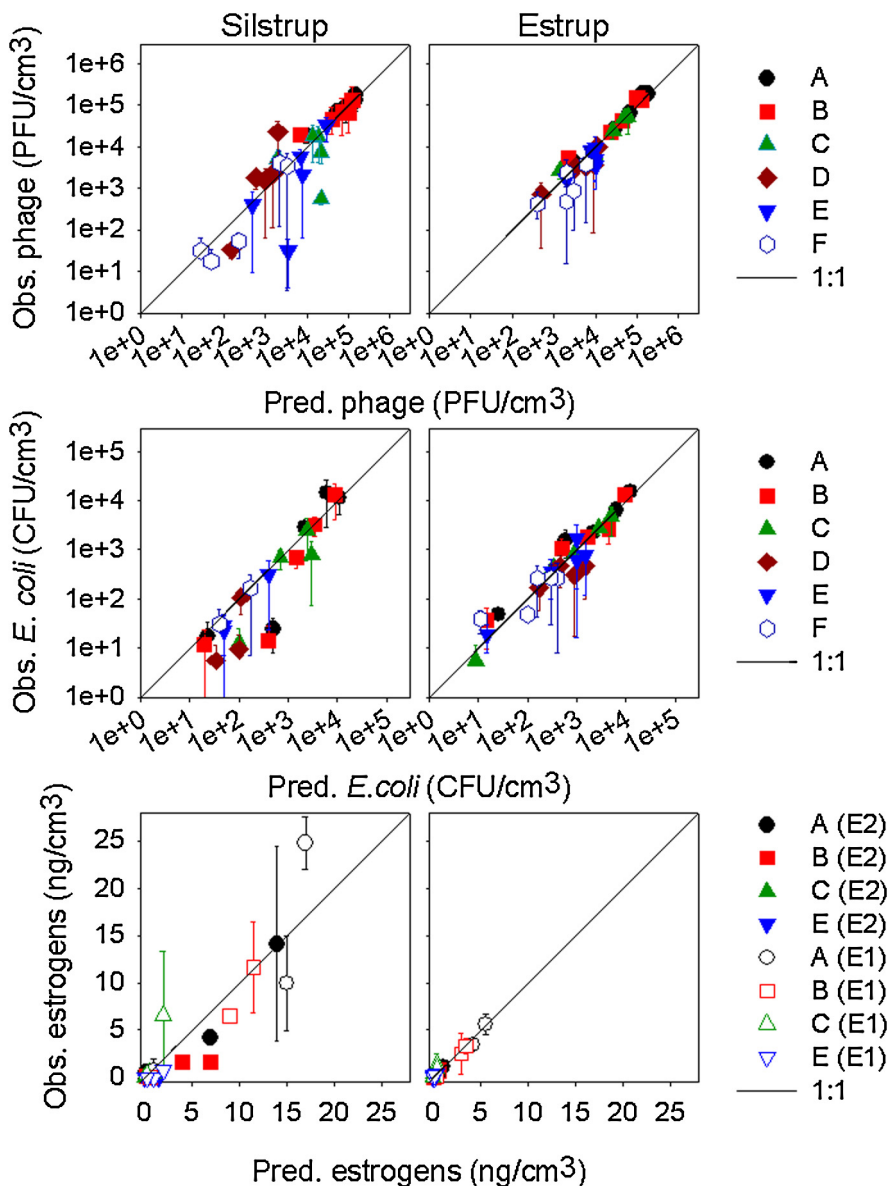


Fig. 4. Observed and predicted phages, *E. coli* and estrogens (E2 for estradiol and E1 for estrone) concentrations at Silstrup (left) and Estrup (right) (different colour symbols represent different soil sections as indicated in the legend).

3.2.5. *E. coli*

As with phages, *E. coli* concentrations in different sections and at different times were, in most cases, predicted with high accuracy (Fig. 4). The transport of *E. coli* through the soil was much lower at Silstrup, due to fine grained soil and immobile slurry dry matter. In sections D, E, and F at Silstrup, the measured concentrations were very low during the first three sampling events and under the detection limit after that. The model overestimated *E. coli* concentrations for some of these cases at Silstrup (Fig. 4). The model could not estimate concentrations as high as observed in section B on the first sampling day. Due to uncertainties in survival rates in different sections and due to preferential flow, relatively high deviations were observed at low concentration values at both sites. Although the survival rate was actually lower at Silstrup than at Estrup, because of the relatively dry conditions, an average rate was considered for both sites in order to generalize the model, and to predict the leaching potential of *E. coli* for normal weather conditions.

3.2.6. Estrogens

The redistribution and persistence of estradiol and estrone in different soil sections at Estrup were simulated well when their sorption, degradation, and transformations processes were considered. Low contact time due to the redistribution process and the presence of soluble organic matter in the slurry liquid decreased the sorption in the slurry slit. Stumpe and Marschner (2010) suggested that the presence of dissolved organic carbon in the liquid phase can decrease sorption to the solid phase. Casey et al. (2005) found a low K_{oc} value for a modelling study of a leaching experiment and argued that low contact time during transport could be responsible for the low K_{oc} value. When the K_d value specific for the slurry environment was used, we found a reasonable agreement between observations and simulations. However, there were some considerable differences between the observed and predicted values at Silstrup (Fig. 4), as is also suggested by the indices in Table 4. In a few cases, the model overestimated the estrogen concentration in section B and E, but underestimated it in section C. Concentrations in section C were quite high at only one or two times, which cannot be explained using the calculated K_d values. The increased concentration in section C was likely not due to matrix flow. Other processes, such as slurry-estrogens interactions and preferential flow, may have led to the enhanced transport (Arnon et al., 2008). The agreements between observed and predicted values were generally much lower at Silstrup compared to Estrup.

3.3. Horizontal redistribution

Simulating transport processes under field conditions is more complex than for simplified laboratory setups. For example, the high clay content of the Silstrup soil may have resulted in the development of cracks under unsaturated conditions and during tillage operations. Preferential flow through macropores, fissures, and/or voids created by crop roots is difficult to predict (e.g., Šimůnek et al., 2003). However, since the values of the statistical indices indicate that the model simulates the observed values, the simulated results were used to understand the processes that occurred in between and beyond the observation events. The temporal and spatial dynamics of different contaminants around slurry-injection slit at both sites predicted by HYDRUS is shown in Figs. 5 and 6.

Chloride transport in the horizontal direction was much slower at Silstrup than Estrup, and there was still a concentration gradient after 46 days (Figs. 5 and 6). The redistribution of slurry was slower in the sandy clay loam soil at Silstrup, due to low hydraulic conductivity, compared to conditions in the sandy loam soil at Estrup. The simulation showed that the downward flux of chloride from the observed soil profile was not considerable at Silstrup. Chloride

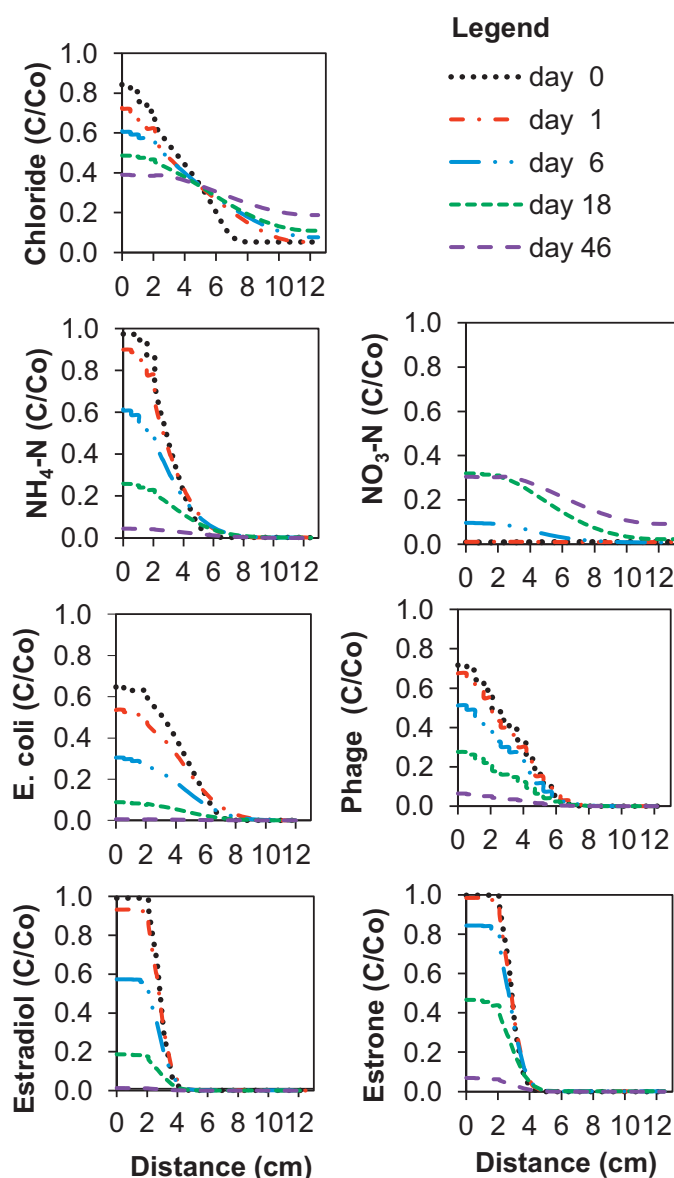


Fig. 5. Ratio of the predicted to the initial concentrations of different slurry constituents at a cross-section at a 5-cm soil depth at Silstrup.

concentrations at the end of the experiment at Estrup were close to soil background values due to the faster redistribution as well as leaching from the profile.

$\text{NH}_4\text{-N}$ redistribution was primarily within 6–7 cm at both sites due to sorption processes and nitrification (Figs. 5 and 6). On the other hand, $\text{NO}_3\text{-N}$ redistributed through the entire observed profile at both sites. The redistribution of $\text{NO}_3\text{-N}$ and chloride was not exactly the same because $\text{NO}_3\text{-N}$ took time to accumulate by nitrification and its concentrations decreased with time due to crop uptake. Denitrification was considered the same at both field sites, as they had the same crop and very similar soil moisture ($0.29\text{--}0.41\text{ cm}^3/\text{cm}^3$ at Silstrup and $0.27\text{--}0.36\text{ cm}^3/\text{cm}^3$ at Estrup) and weather conditions. At the end of the experiment the mineral nitrogen almost disappeared at Estrup, whereas the peak concentration was observed at Silstrup (Figs. 5 and 6). This suggests that the leaching of N from the sampled soil profile at Estrup was higher compared to Silstrup.

Phages primarily redistributed up to the distance of 8 cm, with only a few travelling beyond this distance in the horizontal direction (Fig. 5). At Silstrup, concentrations decreased at a rate of about

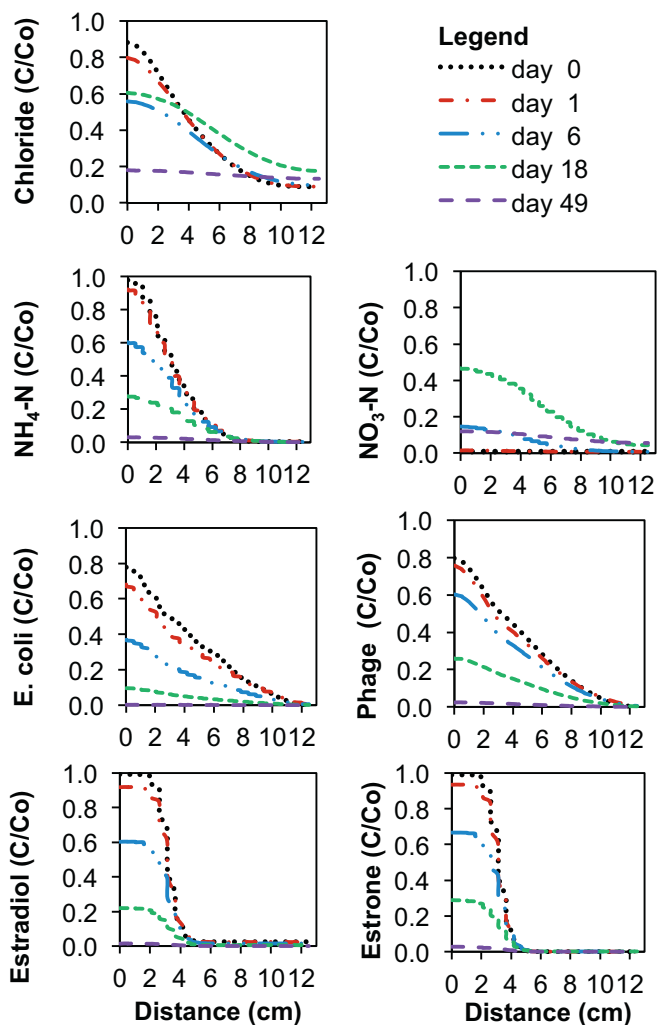


Fig. 6. Ratio of the predicted to the initial concentrations of different slurry constituents at a cross-section at a 5-cm soil depth at Estrup.

one log scale for every 2 cm travelled (data not shown). Consequently, a very low concentration was observed at a distance of 10 cm from the slurry slit at this site. On the other hand, the redistribution was higher at Estrup due to relatively larger pore sizes. Phages travelled as far as 12 cm at Estrup (Fig. 6). *E. coli* redistribution was much slower in the fine-grained soil at Silstrup. Almost all *E. coli* remained within 8 cm from the slurry slit (Fig. 5). It seems that the redistribution of *E. coli* in sandy loam soil at Estrup was much higher. They travelled up to a distance of 12 cm in the horizontal direction.

The transport of estrogens through the soil matrix was very low because of their sorptivity. They remained mainly within the distance of 5–6 cm. The values of K_d were higher at Estrup than at Silstrup, due to the higher content of the soil organic carbon at Estrup (Table 1). Estrogens can be transported in soils with the mobile DOC in the liquid phase of the injected slurry, as estrogens readily sorb to the organic carbon. However, under relatively dry conditions, the slurry-DOC can also be adsorbed to soil particles during redistribution (Stumpe and Marschner, 2010).

The simulations show that assuming a homogeneous distribution of the contaminants originating from injected-slurry when estimating the leaching or fate of these contaminants may result in errors, especially for microorganisms and estrogens.

3.4. Leaching of contaminants to the subsoil

Model predictions of the microorganism transport were supported by the analysis of the drainage leachates collected from the two field sites during the experimental period. No *E. coli* was detected in the drainage water during the entire season at Silstrup, and only a few viable *E. coli* were detected at Estrup after the rain events on days 35–38 (Bech et al., 2010). The leaching potential of mineral N, phages, *E. coli*, and estrogens from the top 20 cm of the soil profile was evaluated using HYDRUS and the parameters established above for the last 10 years of precipitation and evapotranspiration data for the respective sites (Table 5). Leached amounts varied in different years for all contaminants, but the correlation between the amount leached and the total amount of precipitation was very low. The total leaching was primarily influenced by the time and intensity of precipitation, especially for the spring application of slurry in Denmark (Fig. 7). Precipitation during the first week after the slurry application was not very effective in leaching of mineral N, as N still remained in the form of less mobile $\text{NH}_4\text{-N}$. Only after N was transformed to $\text{NO}_3\text{-N}$ by nitrification could it be leached by the infiltrating water. Hanson et al. (2006) reported that $\text{NH}_4\text{-N}$ remained concentrated around the application line at all times for all fertigation strategies, because of soil adsorption and subsequent fast nitrification and/or root uptake, whereas nitrate moved continuously downwards during the first 28-day period. The peak flux of mineral N at a 20-cm soil depth was not observed in most cases until at least 10 days after the slurry application (Fig. 7). The lowest N leaching at both sites was found in 2007, because of a very dry first 70 days at Silstrup and 40 days at Estrup. Leaching in 2005 at Silstrup was also low because of low seasonal precipitation and 15 continuous rainless days during the peak time (15–30 days after the slurry application) of $\text{NO}_3\text{-N}$ accumulation. In 2001, a continuous water flux during the peak period of $\text{NO}_3\text{-N}$ accumulation leached the highest quantity of mineral N at Silstrup. At Estrup, the highest quantity of N leached was observed in 2008 when the site received some heavy precipitation events (>30 mm/day) during the first 30 days after the slurry application. Leaching in 2003 was higher than in 2001 and 2002 at Estrup due to the timing of the high intensity precipitations (Fig. 7).

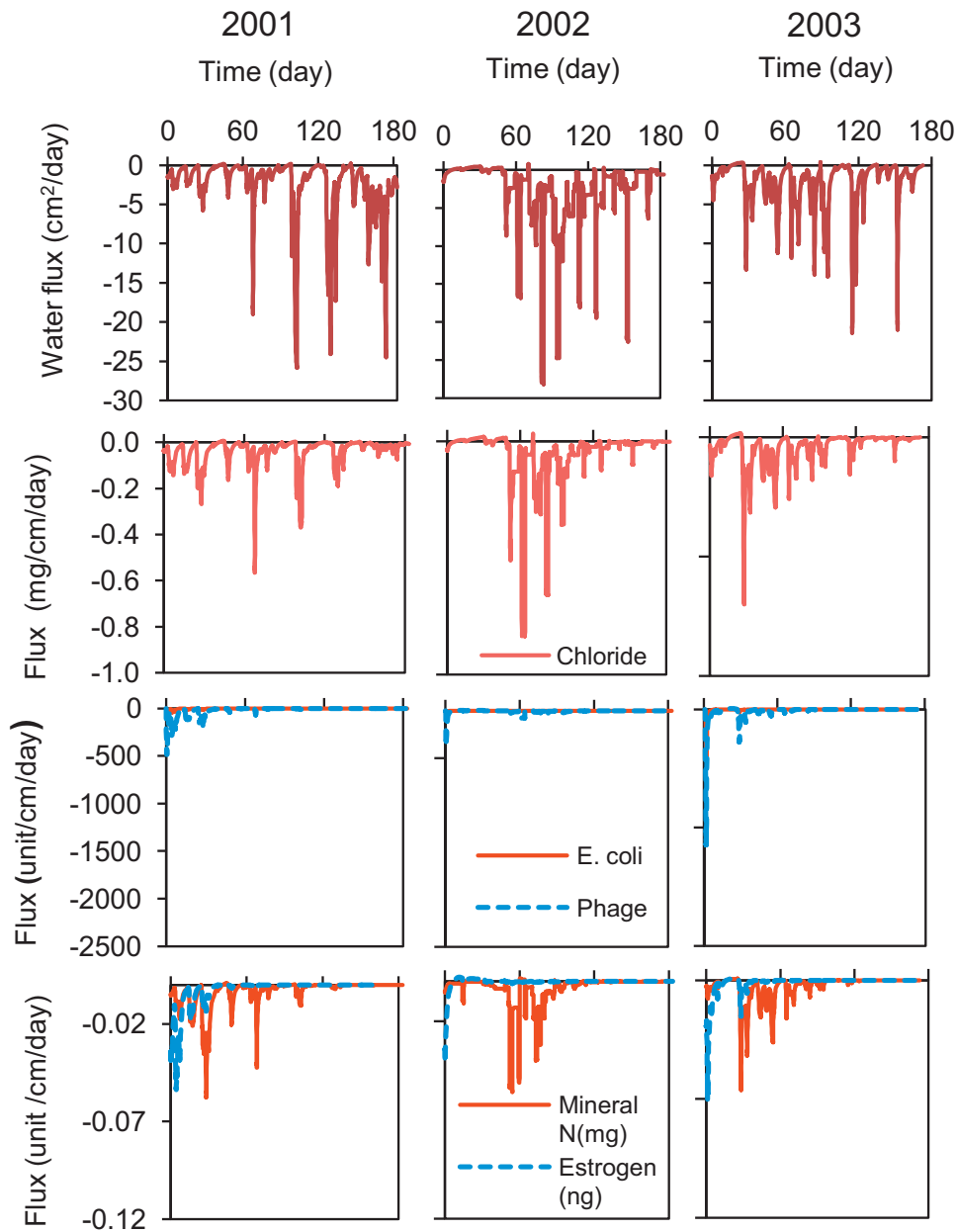
The average leaching potentials for 6 months after application from the top 20 cm of the soil for phage and *E. coli* were 12.2×10^4 PFU/m² and 2.1×10^4 CFU/m² at Silstrup and 3.3×10^6 PFU/m² and 0.58×10^6 CFU/m² at Estrup, respectively. Leaching of both phage and *E. coli* was significantly higher in the sandy loam soil at Estrup than in the sandy clay loam soil at Silstrup (Table 5). The flux of phage and *E. coli* substantially decreased with an increase in the number of rainless days just after application (Fig. 7). Phages and *E. coli* were much more susceptible to leaching for the precipitation events occurring during the first week after the slurry application. Leaching of both microorganisms at Silstrup was low in 2002, 2005, and 2007 because the 6, 3, and 7 days, respectively, after slurry application were rainless. On the other hand, the highest leaching was found in 2001 when Silstrup received considerable precipitation the very first day after slurry application. Leaching was also high at Estrup in 2003 because of high precipitation during the first 3–4 weeks after the slurry application, whereas leaching was very low in 2002 when there was no precipitation during the first several weeks (Fig. 7).

The leached mass of estrogens from the topsoil varied between 100 and 1380 ng/m² (average 0.12%) at Silstrup and 40–620 ng/m² (average 0.4%) at Estrup (Table 5). Although this seems low, it should be noted that estrogens can affect aquatic ecology at very low concentration levels (1–2 ng/L). As with phage and *E. coli*, the timing of precipitation events was very important in estrogens leaching (Fig. 7). If soils get dry after the slurry application, contaminants concentration in liquid phase becomes high which in turn

Table 5

Predicted total leaching of different contaminants below 0.20 m depth during 6 months after the slurry application using 10-year precipitation data at Silstrup and Estrup.

Year	Silstrup						Estrup					
	PPT ^a (mm)	Drainage (mm)	N ^a (10 ² mg/m ²)	Phage (10 ⁴ PFU/m ²)	<i>E. coli</i> (10 ⁴ CFU/m ²)	Es ^a (10 ² ng/m ²)	PPT (mm)	Drainage (mm)	N (10 ² mg/m ²)	Phage (10 ⁴ PFU/m ²)	<i>E. coli</i> (10 ⁴ CFU/m ²)	Es (10 ² ng/m ²)
2008	448	341	2.8	3.8	0.44	2.2	569	446	9.8	883	254	6.2
2007	427	321	1.8	4.2	0.04	1.0	594	461	3.8	94	5	0.6
2006	360	246	7.6	4.5	1.80	6.4	359	253	9.0	550	94	5.4
2005	281	189	2.4	1.5	0.24	2.6	382	265	7.8	301	26	3.6
2004	459	331	7.6	8.2	1.84	5.2	499	373	5.2	309	38	4.2
2003	417	303	10.4	20.1	1.22	4.4	419	307	7.0	442	94	3.0
2002	373	297	3.4	4.8	0.34	1.2	420	336	5.2	54	4	0.4
2001	522	396	21.6	42.6	11.66	13.8	482	374	5.0	270	28	3.4
2000	322	199	3.4	6.7	0.66	1.2	318	201	4.4	187	15	2.4
1999	548	370	13.4	25.6	2.92	7.2	444	314	4.4	197	19	2.6

^a PPT, N, and Es represent precipitation, mineral N, and total estrogens, respectively.**Fig. 7.** Simulated fluxes of different contaminants through the soil depth of 20 cm during 6 months after the slurry application at Estrup in three years (minus sign in the Y axis indicating downward flux).

increases the sorption in simulation process and also in real field condition so the effect of subsequent precipitation is less important for leaching. In these field sites in 2005–2006, estrogens were detected in sub-surface drainage water after some heavy precipitation events (Kjaer et al., 2007).

4. Conclusions

The calibrated HYDRUS 2D was capable of predicting the redistribution and persistence of slurry-borne contaminants in the soil. The simulation confirmed that the persistently increased soil water content in the injection slit could be described by the changed hydraulic parameters in this part of the soil. Comparison between simulated and observed results suggests that the N dynamics were slightly different for different sections sampled. *E. coli* redistribution was much affected by the site conditions compared to phage because of the larger size of *E. coli*. The redistribution of estrogens, assuming linear sorption and degradation and with K_d values calculated using the K_{oc} value of similar soil under similar soil-slurry environment, was simulated well at Estrup, but less so at Silstrup. Contaminants persisted for up to 4–6 months, and leached continually during this period at varying rates depending on their chemical behaviour and the intensity and frequency of precipitation events. Mineral N started to transport as soon as it was transformed from $\text{NH}_4\text{-N}$ to $\text{NO}_3\text{-N}$ and it took more than a week to accumulate a considerable amount of $\text{NO}_3\text{-N}$ in the soil. In contrast, the vulnerability to leaching of *E. coli*, phage, and estrogens decreased rapidly with time of subsequent precipitations as their concentrations decreased with time due to degradation, mineralization, and die off.

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