Evaluating manure release parameters for nonpoint contaminant transport model KINEROS2/STWIR

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A B S T R A C T

Release of manure components is an important element of modeling applications in environmental water quality. The scarcity of experimental data and the multiplicity of the approaches for modeling release kinetics of the manure components introduce uncertainty and reduce reliability of overland flow and contaminant transport models. The goal of this study was to estimate release parameters for different manure components and provide input for KINEROS2/STWIR model developed for pathogen risk assessment associated with livestock operations. The objectives of this work were to evaluate reliability and robustness of the manure release parameters estimated based on individual and grouped release kinetics of soluble, particulate and combination of particulate and soluble materials from surface applied manure. The parameters of Bradford–Schijven model were evaluated from the experimental data on release of chloride, water-extractable phosphate-P, total bioactive P, organic carbon, enterococci and E. coli from surface applied manure measured in the runoff-box and runoff-plot experiments. The results showed that release of different manure components from surface applied manure can be reliably predicted with just a single set of parameters characterizing the kinetics of manure mass release. We demonstrated that the manure release parameters could be estimated more reliably when the model fit was performed using data for different manure components pooled together, while the model fit to a single release curve produced correlated parameters. The model parameters appeared to be robust and transferable from the calibration to validation datasets without any or with only minor losses of the model accuracy.

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1. Introduction

Transmission of harmful microorganisms from animal waste to humans is widespread and can be a leading cause of human diseases (McBride and Chapra, 2011). Water is an effective vector for pathogens deposited by animals on the landscape or present in applied manures, and pathogens can reach human hosts via consumption of irrigated produce, recreational activities, household water use, consumption of pathogen-contaminated farm fish and shellfish, and other water-related pathways. In particular, fresh produce and fruit consumption is implicated in a substantial portion of food-borne illness outbreaks (Mandrell, 2011). Such outbreaks result in $4.4 bn to $33 bn annual costs of illness and quality-adjusted life year losses in the United States (Hoffmann et al., 2012).

Microbial contamination of water sources by animal waste is commonly evaluated by monitoring or predicting concentrations of indicator microorganisms from the lists of primary ecological indicators (Cea et al., 2011; Rodrigues et al., 2011; Thevenon and Poté, 2012). The most often used ecological indicators are thermotolerant fecal coliforms (FC) and the bacterium Escherichia coli (Paruch and Mahlum, 2012). Based on concentrations of these organisms, fifty percent of the total 1,496,334 km of rivers and streams assessed in USA has been found impaired, and the pathogens have been the leading cause of these impairments (Pandey et al., 2012). The need for improvement of the watershed-scale E. coli fate and

Abbreviations: WEP, water-extractable phosphate; TBIOP, total bioactive P (TBIOP); CFU, colony forming units; MER, mean model error; MAE, mean absolute error; RMSE, mean root squared error; NSE, Nash–Sutcliffe efficiency index; MIA, modified index of agreement.

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transport characterization has been recently recognized and has
to be addressed via ecological modeling (Haydon and Deletic,
2009; Kim et al., 2010).

Understanding and modeling release of indicator organisms
from land-deposited animal waste is a prerequisite for quantifica-
tion of the FC and E. coli fate and transport in landscapes. Currently
there is no consensus regarding the optimal approaches to model-
ing the release of microbes and other manure components under
rainfall. In particular, the COLI model (Walker et al., 1990) uti-
izes the Universal Soil Loss Equation (MUSLE) to predict numbers
of indicator bacteria cells in runoff water as proportional to the
mass of manure eroded and the bacteria concentration in manure.
Shelton et al. (2003) uses a one-parameter exponential equation to
describe FC concentrations in the suspension released from surface
applied dairy manure as function of time. Hydrological Simulation
Program-FORTRAN (HSPF) model describes the release of FC from
storage on the land surface (Bicknell et al., 2011) as an exponential
decrease of the surface storage of FC bacteria with the total amount
of surface runoff. Vadas et al. (2004) simulated dissolves inorganic
phosphorus loss in runoff from surface-applied dairy, poultry and
swine manure using a two-parameter power equation.

KINEROS2/STWIR model has been recently developed for
pathogen risk assessment associated with livestock operations
(Guber et al., 2006, 2009). The model utilizes Bradford and Schijven
(2002) equations to simulate release of pathogen indicators from
surface applied manure. Bradford and Schijven (2002) approach has
been shown to be more accurate in predicting release of FC, chlo-
ride, organic carbon, and water-soluble phosphorus compared to
the Vadas et al. (2004) and the HSPF model in earlier study (Guber
et al., 2006).

The release model was originally developed to predict release of
Cryptosporidium and Gardia (oo)cysts from dairy calf manure into the
aqueous phase (Bradford and Schijven, 2002). It describes changes
in the manure phase density at the water-manure interface as a
result of water addition on the surface of manure. The authors
assumed (Bradford and Schijven, 2002) that no manure decay or
additions occur during the release, and that the mass transfer can
be described using a quasi steady-state approximation of Fick's
first law of diffusion (a linear driving force model, with a boundary
layer in the manure phase). Therefore they computed the aqueous
manure concentration as:

\[
C_{\text{man}}(t) = \frac{dM_{\text{man}}}{Q \, dt} = \frac{M_{\text{man}}}{Q} \left(1 + \alpha \beta t\right)^{-1(1+1/\beta)}
\]

where \(C_{\text{man}}\) is the aqueous manure concentration at time \(t\) (M L^{-3}),
\(Q\) is the average aqueous phase flow rate (L^2 T^{-1}), \(M_{\text{man}}\) is the cumu-
latve manure mass released into the aqueous phase \((M, \alpha (T^{-1})\n\text{and } \beta \text{ (dimensionless) are fitting parameters defining the shape of the}
\text{release curve, and } M_0 \text{ is the initial mass of manure } (M)\).

The value of \(\alpha\) controls the initial manure release rate, whereas
\(\beta\) determines the shape of the manure release curve in Eq. (1).
The authors also assumed that the (oo)cyst concentration in the
released manure suspension was proportional to the aqueous
manure concentration:

\[
C_m(t) = m_f E_f C_{\text{man}}(t)
\]

where \(C_m\) is the aqueous (oo)cyst concentration (MCU L^{-3}), \(m_f\)
is microorganism concentration in the applied manure (MCU M^{-1}),
\(E_f\) is microorganism release efficiency that describes the partitio-
ning behavior of (oo)cysts into water relative to that of manure, and
depends on the (oo)cyst size and charge as well as on the solution
salinity.

Therefore, in this model, the (oo)cyst release from manure is
considered as bacteria cell detachment from manure particles that
diffused from manure surface into the aqueous phase.

In spite of general recognition of the impact of soil proper-
ties, vegetation and rainfall intensity very little has been done to
account for these factors on release kinetics of manure compo-
nents in models. For instance, the bacteria release rate constant
in Shelton model has only been evaluated on results of Bradford
and Schijven (2002) experiments with Cryptosporidium and Gardia
(oo)cysts, and FC release data from bovine manure into a stony
soil (Shelton et al., 2003). In addition, even though it has been
recognized that the manure components have different physical,
chemical and biological properties such as water solubility, partic-
le size, attachment–detachment rates, that likely influence their
release rates, however, no efforts has been undertaken so far to
evaluate this parameter for different manure components and for
scales larger than laboratory setup.

The scarcity of experimental data and the multiplicity of the
approaches for modeling release kinetics of the manure com-
ponents lead to a substantial uncertainty in interpreting stream
monitoring data and identifying sources of nonpoint contaminant
transport. This study aims to fill the knowledge gap in modeling of
the release kinetics of the manure components and thus improving
the reliability and performance of the overland flow and transport
models.

We implemented the Bradford and Schijven (2002) model as a
component of KINEROS2/STWIR to simulate release of the soluble
material, the particulate material, and a combination of particulate
and soluble materials from surface applied manure.

The goal of this study was to estimate release parameters for dif-
ferent manure components and provide input for KINEROS2/STWIR
model. Our specific objectives were to: (i) evaluate reliability of
the manure release parameters estimated based on individual and
grouped release kinetics of manure components; (ii) assess applica-
ability of manure release parameters to modeling the release kinetics
of soluble, particulate and combination of particulate and soluble
materials from surface applied manure; and (iii) test the robustness
of parameter values.

2. Materials and methods

2.1. Runoff-box experiments

The bacteria release experiments in this study consisted of an
application of manure on grass-covered soil in freely drained exper-
imental boxes, followed by continual sampling of the runoff water.
Details of the rainfall simulator and runoff box setup were given in
a previous works (Guber et al., 2007; Pachepsky et al., 2009). In brief,
six runoff boxes (2.0 m × 0.41 m × 0.10 m, length/width/height)
were made from commercial lumber and were divided into five
sections lengthwise with four blades installed at 0.25, 0.50, 1.0, and
1.5 m from the top of the box. A 5-cm layer of commercial tall
fescue (F. unlnulata Schreb.) sod was placed in each box. The soil
texture of the sod was clay loam and had the saturated hydraulic
conductivity of 2.2 ± 1.1 cm h^{-1}. The top 0.25-m section of the sod
runoff boxes received dairy manure at the rate of 11.7 L m^{-2} and
had a trough mounted at its lower end to collect all the surface
runoff. In this paper, we reported only runoff data and experimen-
tal results from manure applied to this section of six soil-grass
boxes. Before initiation of the rainfall simulation, the grass was
clipped to a uniform height of 7.5 cm, and clippings were removed.
The soil-grass boxes were placed on an incline to have a 4% slope
inside the simulator frame area. Irrigation was applied at intensity
of 33.6 ± 0.4 mm h^{-1} for 1.5 h using a single TeeJetTM 1/2 HH SS
50 WSQ nozzle (Spraying Systems Co., Wheaton, IL) positioned 3 m
above the soil surface. Applied manure and runoff samples were
collected every 5 min during the experiment starting from the rain-
fall initiation and were analyzed for chloride, water-extractable
phosphate-P (WEP), total bioactive P (TBIOP), enterococci and *E. coli* contents.

Manure samples (100 g) were oven-dried at 60 °C to measure the solid:liquid ratio. Chloride content in the runoff water was measured with a model 94178 Chloride Ion-Selective Electrode (Thermo Electron Corp., Beverly, MA) with the detection range from 1.8 to 35,500 mg L⁻¹. Enterococci in water and manure samples were enumerated by plating a 50-µL exponential spiral onto culture plates containing selective membrane Enterococcus agar (Becton, Dickinson and Co., Franklin Lakes, NJ) using an Autoplate 4000 spiral-plater (Spiral Biotech, Gaithersburg, MD). Red-colored colony forming units (CFU) that developed after 48 h of incubation at 37 °C were counted with a QCount colony counter (Spiral Biotech, Gaithersburg, MD, USA). Similarly, numbers of presumptive *E. coli* CFU in manure and runoff water aliquots were determined by plating 50 µL of exponential spirals on MacConkey agar. Red-colored CFU that developed after overnight incubation at 44.5 °C were counted. Although red-colored CFU only indicated the presence of lactose-fermenting Gram-negative rods, we found that more than 99% of presumptive *E. coli* determined by this procedure were actually *E. coli* in previous studies with fresh dairy manure slurries (unpublished data). For the sake of brevity, presumptive *E. coli* was referred hereafter as *E. coli* in this study. The number of enterococci and *E. coli* in manure was determined by plating as above after dilution with sterile water (1:10, vol/vol). Each value was the average of two plates. WEP and TBIOP contents were determined according to the procedure developed by Dao (Dao et al., 2008, 2008, Green et al., 2007). In brief, four P fractions were differentiated, that is, manure WEP, ligand-exchangeable inorganic phosphate-P (EEPi), ligand-exchangeable phosphorylhydroxylase-labile P (EDTA-PHP), and the all-inclusive total bioactive P (WEP+EEPi+EDTA-PHP) in runoff, which were determined as follows. Manure WEP in runoff was measured in duplicate aliquots (7 mL) after centrifugation of the runoff samples at 10,000 × g for 15 min before phosphate-P analysis. Additional runoff aliquots (7 mL) were combined with a 5-mmol L⁻¹ solution of EDTA (1:10, wt/vol) and agitated at 250 rpm for 1 h to determine the EEPi fraction in the runoff. The supernatant phosphate-P concentrations were measured after centrifugation at 10,000 × g. Subsequently an aliquot (0.5 unit mL⁻¹) of a stock of *Aspergillus fuscum* phosphorylhydroxylases that was prepared in our laboratory (Dao and Hoang, 2008) was added to the latter suspension to replace the volume removed for the EEPi measurement. After 24-h equilibration, aliquots of the mixture were centrifuged at 10,000 × g before analysis of ligand-exchangeable and enzyme hydrolysable phosphate-P concentrations in the mixture. Acid-digest TP was determined in duplicate 15-ml aliquots of the runoff using a modified potassium persulfate-sulfuric acid digestion procedure. The mixture was brought up to a boil at 180 °C for 30 min in a heating block and at 350 °C for another 0.5 h. The digest was diluted to a final known volume for P analysis. Extracted and total P concentrations were determined using the phosphomolybdate-ascorbic acid method and a semiautomated ion-analyzer (Bran-Luebbe, Buffalo Grove, IL). Table 1 summarizes Cl⁻, WEP, TBIOP, enterococci and *E. coli* contents in the applied manure and measured irrigation rates used in the runoff-box experiments.

2.2. Runoff-box experiments

Manure release studies at small plot scale were conducted on a two-sided 20% slope lysimeter located at the Patuxent Wildlife Research Refuge (Beltsville, MD). Details on site description, experimental design and research protocols of the experiment are given in Guber et al. (2006). Briefly, eight plots 0.50 m wide and 0.30 m long were established on a sandy loam and clay loam lysimeters in the bare and vegetated areas, resulting in four treatments: bare clay loam, vegetated clay loam, bare sandy loam, and vegetated sandy loam. The dairy manure slurry collected from the dairy barn at the Dairy Research Unit of the USDA/ARS-Beltsville Agricultural Research Center, Beltsville was uniformly applied at the top of the plots at the rate of 11.7 L m⁻² and simulated rainfall was applied to study the kinetics of Cl⁻, *E. coli*, OC, and WEP release from manure to runoff. Grass was mowed prior to the experiment to maintain uniform grass height of about 5 cm. Rainfall was applied at a water pressure of 100 kPa using a rainfall simulator equipped with a TjetTM 1/4 HH SS 14 WSQ nozzle (Spraying Systems Co., Wheaton, IL) at 3 m above the soil surface. Rainfall rates were measured with rain gauges installed adjacent to each plot. Runoff was collected in troughs located at the bottom of plots for 2 min at 5-min intervals. Runoff volume, Cl⁻, *E. coli*, OC, and P concentrations were measured in each runoff sample from each plot. Chloride, *E. coli*, OC, and WEP contents measured in the applied manure along with measured irrigation rates for eight runoff plots are shown in Table 1.

2.3. Release parameters for KINEROS2/STWIR

The measured release kinetics obtained in the runoff-box and runoff-box experiments were used to compute the manure release parameters. The Levenberg–Marquardt nonlinear least-squares algorithm was applied to cumulative data of relative released mass (M/Mo) to reduce model sensitivity to the high initial concentrations. By using cumulative release curves, we increased the weights of smaller concentrations and improved model accuracy in the tailing part of the original released curves (C/Co). To do that the Bradford–Schijven model (Eqs. (1) and (2)) was integrated with respect to time:

\[
\frac{M_m(t)}{M_m(0)} = E_r(1 - (1 + a \beta t)^{-1/\beta}) \quad a = \frac{\alpha}{q}
\]

where \(M_m(t)\) is the cumulative mass of a manure component released into the aqueous phase within time \(t\) (M), \(M_m(0)\) is the initial mass of a manure component (M), \(q\) is the irrigation rate (L T⁻¹), and \(\alpha q\) term is the total head of irrigation water applied within time \(t\) (L). The fitting parameters were the manure release parameters \(\alpha\) and \(\beta\), and parameter of the release efficiency \(E_r\) specific for each manure component.

Since there are no general guidance for evaluating parameters of the release kinetics, we tested individual and grouped fits to the measured data. We first fitted Eq. (3) separately to each release curve measured in each runoff-box experiment (Fit-1). These fits provided individual sets of parameters \(\alpha\) and \(\beta\) and \(E_r\) for each measured release curve. Then new fit was performed with the values of parameter \(\alpha\) constant for all runoff-boxes and manure components, parameter \(\beta\) constant for all manure components, but individual for each runoff-box, while parameter \(E_r\) was individual for each manure component and runoff-box. This fit provided values of parameter \(E_r\) for Fit-2. The goal of Fit-2 was to evaluate uncertainty and reliability of the manure release parameters \(\alpha\) and \(\beta\) estimated based on grouped fit to data of release kinetics of the manure components. For Fit-2 the six runoff-box experiments were split into the calibration and the validation datasets. Each dataset included 3 runoff-box experiments. A total of 20 calibration/validation combinations were generated. The calibration datasets were used to compute values of \(\alpha\) and \(\beta\) parameters and the calibration errors, while the validation datasets were used to evaluate the validation errors. The parameters \(\alpha\) was constant for all runoff-boxes and parameter \(\beta\) was constant for all manure components, but individual for each runoff-box in each calibration dataset. Then fitted parameters \(\alpha\) and parameters \(\beta\) averaged for the calibration datasets were implemented for the validation datasets to test robustness of the manure release parameters.
Table 1
Selected properties of manure and irrigation time and rates used in the runoff-box and the runoff-plot experiments.

<table>
<thead>
<tr>
<th>Manure properties and irrigation rates</th>
<th>Runoff box</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid/liquid ratio (g g⁻¹)</td>
<td>0.08</td>
<td>0.08</td>
<td>0.08</td>
<td>0.08</td>
<td>0.08</td>
<td>0.08</td>
</tr>
<tr>
<td>E. coli (10⁶ CFU ml⁻¹)</td>
<td>1.49</td>
<td>0.98</td>
<td>0.76</td>
<td>2.67</td>
<td>1.52</td>
<td>1.18</td>
</tr>
<tr>
<td>Enterococci (10⁶ CFU ml⁻¹)</td>
<td>0.70</td>
<td>0.36</td>
<td>1.27</td>
<td>0.51</td>
<td>0.30</td>
<td>0.46</td>
</tr>
<tr>
<td>Cl⁻ (mg L⁻¹)</td>
<td>588.1</td>
<td>744.8</td>
<td>797.3</td>
<td>744.1</td>
<td>949.3</td>
<td>1007.3</td>
</tr>
<tr>
<td>WEP (mg L⁻¹)</td>
<td>216.40</td>
<td>172.6</td>
<td>196.2</td>
<td>117.0</td>
<td>98.8</td>
<td>145.2</td>
</tr>
<tr>
<td>TBIP (mg L⁻¹)</td>
<td>374.7</td>
<td>388.7</td>
<td>439.3</td>
<td>188.0</td>
<td>540.0</td>
<td>360.7</td>
</tr>
<tr>
<td>Irrigation time (h)</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Irrigation rate (cm h⁻¹)</td>
<td>4.23</td>
<td>3.07</td>
<td>3.26</td>
<td>3.01</td>
<td>3.21</td>
<td>3.39</td>
</tr>
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</table>

<table>
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<tr>
<th>Bare plots</th>
<th>Sandy loam</th>
<th>Clay loam</th>
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<th></th>
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</thead>
<tbody>
<tr>
<td>Solid/liquid ratio (g g⁻¹)</td>
<td>0.075</td>
<td>0.082</td>
<td>0.079</td>
<td>0.158</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl⁻ (mg L⁻¹)</td>
<td>4254</td>
<td>1595</td>
<td>2340</td>
<td>2375</td>
<td></td>
<td></td>
</tr>
<tr>
<td>WEP (mg L⁻¹)</td>
<td>15,919</td>
<td>4381</td>
<td>8794</td>
<td>4905</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Irrigation time (h)</td>
<td>1.029</td>
<td>0.95</td>
<td>1.267</td>
<td>1.217</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Irrigation rate (cm h⁻¹)</td>
<td>3.67/6.41</td>
<td>6.11/5.53</td>
<td>5.37/5.49</td>
<td>2.9/3.38</td>
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<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Vegetated plots</th>
<th>Sandy loam</th>
<th>Clay loam</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
</table>

* In irrigation rate separates two subplots.

The accuracy of the model calibration and validation were assessed using multiple performance indicators. Values of mean model error (MER), mean absolute error (MAE) and root mean squared error (RMSE), in conjunction, provided a summary of the overall model performance:

\[ \text{MER} = \frac{1}{N} \sum_{i=1}^{N} (Y_i - Y_m) \]  
(4)

\[ \text{MAE} = \frac{1}{N} \sum_{i=1}^{N} |Y_i - Y_m| \]  
(5)

\[ \text{RMSE} = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (Y_i - Y_m)^2} \]  
(6)

where \(Y_o\) and \(Y_m\) are measured and computed values of the relative cumulative mass of a manure components released into the aqueous phase \(M_m(t)/M_m(0)\), and \(N\) is number of observations.

The Nash–Sutcliffe efficiency index (NSE), the modified index of agreement (MIA), as given by Legates and McCabe (1999) and the inequality coefficient (Theil, 1966) were used as the measure of model accuracy in predicting observed concentrations:

\[ \text{NSE} = 1 - \frac{\sum_{i=1}^{N} (Y_i - Y_m)^2}{\sum_{i=1}^{N} (Y_i - \bar{Y}_o)^2} \]  
(7)

\[ \text{MIA} = 1 - \frac{\sum_{i=1}^{N} |Y_m - Y_o|}{\sum_{i=1}^{N} |Y_m - Y_o| + \sum_{i=1}^{N} |Y_m - \bar{Y}_o|} \]  
(8)

\[ U = \sqrt{\frac{\sum (\Delta Y_m - \Delta Y_o)^2}{\sum \Delta Y_o^2}} \]  
(9)

\[ \Delta Y_m = Y_m(t) - Y_m(t-1), \ \Delta Y_o = Y_o(t) - Y_o(t-1) \]

For these performance indicators the model was considered to be acceptable for NSE values within the range from 0 to 1 and for MIA > 0.75 (Köhne et al., 2005). The inequality coefficient \(U\) ranges from 0 to 1 with 0 indicating perfect model performance. Finally, the null hypothesis of dissimilarity between the observed and predicted values was evaluated using equivalence tests (Wellek, 2003; Robinson and Froese, 2004; Blanco et al., 2007). We first computed \(t_d\)-value as:

\[ t_d = \frac{\bar{X}}{S_X} \]  
(10)

where \(\bar{X}\) is average model error, and \(S_X\) is the standard error of the model error.

Then computed \(t_d\) were compared with the cutoff \(C_{0.05,N-1}(\varepsilon)\) values obtained from the non-central \(F\)-distribution for 0.05-quantile with \(1, N-1\) degrees of freedom and noncentrality parameter \(\psi = Ne^2\):

\[ C_{0.05,N-1}(\varepsilon) = [F_{1,N-1;0.05}(\psi)]^{1/2} \]  
(11)

where \(\varepsilon\) denotes the equivalence limits for the standardized model error, that was set to \(\varepsilon = 0.25\) for strict choice in this study according to guidelines in Wellek (2003).

The null hypothesis of dissimilarity between the model predictions and observations was rejected for the \(t_d\) values that were lower than the cutoff values.

Since the runoff-plot experiments were conducted at bare and vegetated plots with sandy clay and sandy loam texture it was possible to examine the effects of soil texture and vegetation on the manure release parameters of Eq. (3). The effects of soil texture and vegetation on the manure release parameters are generally unknown, therefore we used different grouping of the fitted parameters to detect those effects. That is, in Fit-1 parameter \(a\) was constant for all plots and manure components, parameters \(\beta\) were grouped for each runoff plot, so that \(\beta\) value was the same for all manure components within one plot, while \(E\) values were fitted individually to each plot and manure component. In Fit-2 parameter \(a\) was grouped according to vegetation, while parameters \(\beta\) and \(E\) were fitted similarly to Fit-1.

Two-way ANOVA was performed to evaluate effects of soil texture and vegetation on the manure release parameter \(\beta\). Three-way ANOVA was performed to evaluate effects of soil texture, vegetation, and manure components on the manure release parameter \(E\). These analyses were conducted using PROC MIXED procedure in SAS (SAS Institute, 2009). Statistical model for the data analysis consisted of soil texture, vegetation, manure component, and interactions among them as fixed factors and plots nested within soil texture and vegetation as a random factor. The plots were used
as an error term to test the main effects of soil texture and vegetation and the interaction between them. When the interactions were found to be statistically significant \( (P < 0.05) \) they were examined using slicing and cell mean plots. Since there was no data for \( \text{Cl}^- \) in the bare clay loam plot, the \( \text{Cl}^- \) data were not included in the multifactor analysis and were analyzed separately with combinations of vegetation and soil texture as three levels of a single factor. Comparisons between \( \text{Cl}^- \) levels were obtained using contrasts. Differences were declared to be statistically significant at \( P < 0.05 \) level. Assumptions of normality of the residuals and homogeneity of variances were assessed by examining normal probability plots of the residuals and residual box plots.

### 3. Results

#### 3.1. Kinetics of bacteria, chloride ion and phosphorus release

The kinetics of \( E. \text{coli} \), enterococci, \( \text{Cl}^- \) and phosphorus release are shown in Fig. 1. Relative concentrations \( C/C_0 \) expressed as a ratio of concentrations measured in the effluent to the concentrations in the applied manure differed for the manure components in the runoff-box experiments. Generally lowest \( C/C_0 \) were observed for enterococci with exemption for runoff box 2 where the \( C/C_0 \) values were smallest for \( \text{Cl}^- \). The relative concentrations of \( E. \text{coli} \) and \( \text{Cl}^- \) in the first portions of the effluent were in most cases higher than the \( C/C_0 \) values for enterococci, WEP and TBIOP. In spite of the observed difference in concentrations of the released components the release curves had similar shape. A fast decrease of the relative concentrations of the manure components \( (C/C_0) \) within first 0.6 h was followed by a gradual flattening in all release curves measured in 6 runoff-box experiments (Fig. 1).

Differences in the concentrations of the released manure components translated into the differences in the mass recovery. The recovered mass varied from 9.2% to 68% for the measured manure components in 6 runoff-box experiments (Table 2). Average percentages of mass recovery increased in the order 22%, 35%, 37%, 39% and 42% for enterococci, WEP, \( \text{Cl}^- \), TBIOP, and \( E. \text{coli} \), respectively. Due to high variability of the recovery mass for each manure component in 6 runoff-box experiments, the differences in the recovery mass between manure components were not statistically significant except for enterococci; its recovery mass was the lowest in all but one runoff box. Interestingly, there were no correlations between values of the recovered mass of the manure components except for that between WEP and TBIOP constituents. The value of Pearson correlation coefficient between the latter two forms of phosphorus released from manure was 0.86 \( (P < 0.05) \).

The release kinetics of the manure components observed in the runoff-plot experiments was similar to the results of the runoff-box experiments. Two manure release stages are well identified in Fig. 2. The first stage lasted from 0.5 to 0.6 h at the vegetated plots and from 0.1 to 0.3 h at the bare plots. Among the plots the first stage was the longest at the vegetated clay loam plot (Fig. 2a) and the shortest at the bare clay loam plot (Fig. 2b). The release kinetics differed for four manure components. At vegetated plots the WEP concentrations declined much faster than \( \text{Cl}^- \), \( E. \text{coli} \) and OC concentrations, however at bare plots these differences were not pronounced (Fig. 2b and d). The decrease in \( C/C_0 \) was the slowest for OC at the vegetated clay loam plots, where the end of the first stage of release was hard to identify (Fig. 2a).
Table 2
Percent recovery of the manure components in the runoff-box and the runoff-plot experiments.

<table>
<thead>
<tr>
<th>Manure component</th>
<th>Runoff box</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>E. coli</td>
<td>68.0</td>
<td>34.6</td>
<td>43.3</td>
<td>36.4</td>
<td>31.8</td>
</tr>
<tr>
<td>Enterococci</td>
<td>32.3</td>
<td>19.6</td>
<td>17.7</td>
<td>20.6</td>
<td>24.9</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>51.5</td>
<td>9.2</td>
<td>48.0</td>
<td>33.1</td>
<td>46.5</td>
</tr>
<tr>
<td>WEP</td>
<td>32.6</td>
<td>26.8</td>
<td>39.0</td>
<td>42.6</td>
<td>27.4</td>
</tr>
<tr>
<td>TBIOP</td>
<td>41.1</td>
<td>–</td>
<td>41.9</td>
<td>42.3</td>
<td>25.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bare runoff plots</th>
<th>Sandy loam</th>
<th>Clay loam</th>
<th>Vegetated runoff plots</th>
<th>Sandy loam</th>
<th>Clay loam</th>
</tr>
</thead>
<tbody>
<tr>
<td>E. coli</td>
<td>14.6/33.4ᵃ</td>
<td>–</td>
<td>65.7/94.1</td>
<td>56.0/63.3</td>
<td></td>
</tr>
<tr>
<td>Cl⁻</td>
<td>22.9/47.8</td>
<td>26.4/28.7</td>
<td>74.1/85.3</td>
<td>71.6/83.3</td>
<td></td>
</tr>
<tr>
<td>OC</td>
<td>15.4/19.4</td>
<td>30.5/31.8</td>
<td>69.2/89.4</td>
<td>73.6/91.3</td>
<td></td>
</tr>
<tr>
<td>WEP</td>
<td>26.4/52.5</td>
<td>15.8/22.2</td>
<td>52.5/75.8</td>
<td>39.4/40.3</td>
<td></td>
</tr>
</tbody>
</table>

ᵃ Separates two subplots.

Fig. 2. Effluent concentrations of chloride ion, organic carbon, bacteria and water-soluble P measured in the runoff-plot experiments: (a) vegetated clay loam plot, (b) bare clay loam plot, (c) vegetated sandy loam plot, (d) bare sandy loam plot.
The mass recovery computed from the release curves at the end of runoff experiments was greater at the vegetated plots compared to the bare plots (Table 2). The values of recovered mass varied greatly at all plots. They ranged from 14.6% to 52.5%, from 15.8% to 31.8%, from 52.5% to 94.1% and from 39.4% to 91.3% at bare sandy loam, bare clay loam, vegetated sandy loam and vegetated clay loam plots, respectively. The recovery of the four manure components varied with soil texture and vegetation. For example, at the bare sandy loam plots the minimum and maximum recovery mass was obtained for OC and WEP, respectively, while at the vegetated sandy loam plots the WEP recovery was the smallest and Cl\(^{--}\) the largest among other manure components. For the clay loam plots the recovery was the smallest for WEP at both bare and vegetated plots and the largest for Cl\(^{--}\) and OC at sandy loam and clay loam plots, respectively (Table 2).

Results of the model fit (Eq. (3)) to the cumulative release curves obtained in runoff-box experiments are shown in Fig. 3. Overall computed values of relative mass \(M/M_0\) and relative concentration \(C/C_0\) were very close to the measured ones in two fits. The goodness of the model fits was confirmed by examining the model performance statistics. Small values of the MER, MAE and RMSE statistics obtained in individual model fits to each release curve indicated absence of model bias and overall small model errors (Table 3). Generally, values of these statistics were the smallest for enterococci, the largest for Cl\(^{--}\) and intermediate for E. coli, WEP and TBIOP. Values of NSE and MIA statistics were very close to one, while U-value...
was close to zero for all manure components indicating high model accuracy in Fit-1. The null hypothesis of dissimilarity between the observed and predicted values has also been rejected, since $t_4$ values were smaller than the cutoff $C$ for all manure components.

Model fits with grouped parameters $\alpha$ and $\beta$ to the calibration and validation datasets (Fit-2) produced noticeably higher values of MER, MAE and RMSE statistics in the runoff-box experiments. Positive MAE values showed that the model slightly underestimated the measured data, however the RMSE values ranged from 0.45% to 8.4% of the recovery mass for the calibration datasets and varied appreciably being smaller than 10%, 15% and 20% of the recovery mass observed in the experiments in 52%, 30%, and 18% cases for the validation datasets, respectively, indicating acceptable model performance in the fits with grouped release parameters (Table 3). Values of NSE, MIA and U statistics for Fit-2 were also within the acceptable range, and the equivalence tests did not reveal dissimilarities between computed and measured values of the relative mass.

The individual fits (Fit-1) generated highly variable values of the manure release parameters. Average values of parameters $\alpha$, $\beta$ and $E_r$ for the manure components ranged from 0.279 to 0.699 cm$^{-1}$, from 0.253 to 1.774, and from 0.390 to 0.659, respectively (Table 4, runoff box: Fit-1). The variability within each manure component was also high. The largest standard deviation values were observed for parameter $\beta$, while the smallest for $E_r$ parameter. Grouping parameter $\alpha$ values for each manure component and all release curves and parameter $\beta$ for each runoff box (runoff box: Fit-2) produced the values that were close to the parameters generated in Fit-1 averaged for all manure components. However the grouping considerably reduced the uncertainty of all parameters, evaluated via the standard deviation of fitted parameters. The uncertainty still was the highest for parameter $\beta$ and the smallest for parameter $\alpha$, but the standard deviation values decreased significantly for all parameters (Table 4, runoff box: Fit-2). This decrease was less pronounced for $E_r$ and $\text{Cl}^-$ compared to the other manure components. This was likely caused by relatively high variability in the percent recovery for these components (Table 2).

The group fit of the model to data of runoff-box experiments (Fit-1) produced values of the MER, MAE and RMSE statistics that indicated minor model bias and minor deviation of computed release kinetics from observed ones (Table 5, Fit-1). The errors were somewhat higher for the vegetated plots compared to the bare ones. The goodness of the model fits was confirmed by NSE, MIA, $U$ and $t_4$ statistics. Values of NSE and MIA statistics were very close to one, while $U$-value was close to zero for all runoff plots. The $t_4$ values were smaller than the cutoff $C$ for all plots, and therefore the null hypothesis of dissimilarity between the observed and predicted values was rejected. Based on values of the model performance statistics overall fit was acceptable.

Grouping parameters according to vegetation (Fit-2) significantly improved the model performance. The values of MER, MAE and RMSE statistics in Fit-2 were substantially smaller than the values obtained in Fit-1 (Table 5, Fit-2), while the NSE and MIA values were closer to one. The equivalence test also rejected the null hypothesis of dissimilarity.

Similar to the results of the runoff-box experiments, the parameter grouping affected the values of fitted parameters. The values of parameter $\beta$ were high when a single value $\alpha$ was used for all release curves. The fitted values ranged from 4.98 to 12.6 at the bare plots and from 0.9 to 2 at the vegetated plots (Table 4, runoff plot: Fit-1). However these values became more realistic when parameter $\alpha$ was found separately for the bare and vegetated plots (Fit-2). Computed $\beta$ values were generally higher for the sandy loam plots than for the clay loam plots, and for the bare plots compared to the vegetated plots (Table 4, runoff plot: Fit-2). The value of parameter $\alpha$ for the bare plots appeared to be almost three times as high as the $\alpha$ value for the vegetated plots, indicating the effect of vegetation on the value of parameter $\alpha$. The effect of vegetation can also be seen from the fitted values of parameter $E_r$ (Fig. 4). In spite of high variability associated with manure components the $E_r$ values were consistently higher at the vegetated plots compared to the bare plots. The variability was rather random than systematic since even the $E_r$ values of the same manure component within the same runoff plot varied widely.

The statistical analysis of values obtained in the runoff-plot experiments for parameter $E_r$ showed that the three-way interaction between soil texture, vegetation, and manure components as well as the two-way interaction between soil texture and vegetation was not statistically significant. However, the two-way interactions between manure components and soil texture, and manure components and vegetation were found to be statistically significant ($P < 0.05$). Therefore comparisons between soil texture and vegetation were conducted separately for each manure component. The $E_r$ values for WEP were higher for sandy loam than for clay loam texture, however there was no difference in $E_r$ associated with soil texture for $E_{coli}$. For OC the values of parameter $E_r$ were higher for clay loam than sandy loam texture, however the difference was not statistically significant ($P = 0.11$). For all analyzed

Table 3

Performance indicators for fitting the model to the release kinetics measured in runoff-box experiments.

<table>
<thead>
<tr>
<th>Performance indicators</th>
<th>Manure components</th>
<th>Individual fit to each release curve</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_{coli}$</td>
<td>Enterococci</td>
</tr>
<tr>
<td>Fit-1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MER $&gt; 10^3$</td>
<td>$-0.330$</td>
<td>$-0.136$</td>
</tr>
<tr>
<td>MAE $&gt; 10^4$</td>
<td>$0.331$</td>
<td>0.148</td>
</tr>
<tr>
<td>RMSE $&gt; 10^2$</td>
<td>0.460</td>
<td>0.183</td>
</tr>
<tr>
<td>NSE</td>
<td>0.999</td>
<td>1.000</td>
</tr>
<tr>
<td>MIA</td>
<td>0.986</td>
<td>0.989</td>
</tr>
<tr>
<td>$U$</td>
<td>0.041</td>
<td>0.035</td>
</tr>
<tr>
<td>$t_4$ ($C = 0.437$)</td>
<td>$-0.220$</td>
<td>$-0.240$</td>
</tr>
</tbody>
</table>

Fit-2 validation

Parameters $\alpha$ and $\beta$ were the same for all calibrated curves, while values of parameter $E_r$ were individual for each release curve

<table>
<thead>
<tr>
<th>Performance indicators</th>
<th>Parameters $\alpha$ and $\beta$</th>
<th>Individual fit to each release curve</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\text{MER} &gt; 10^4$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$4.153$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$5.646$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$0.887$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$0.837$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$0.179$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$2.224$</td>
</tr>
</tbody>
</table>

Note: MER, mean model error; MAE, mean absolute error; RMSE, root mean squared error; NSE, Nash–Sutcliffe efficiency index; MIA, modified index of agreement; U, Theil’s inequality coefficient; $t_4$, equivalence $t$-value; C, equivalence cutoff. All performance indicators are dimensionless.
Table 4
Parameters of Bradford–Schiijen model fitted to the release curves measured in the runoff-box and the runoff-plot experiments.

<table>
<thead>
<tr>
<th>Parameters and RMSEs</th>
<th>Manure components</th>
<th>Performance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E. coli</td>
<td>Enterococci</td>
</tr>
<tr>
<td>Runoff box, Fit-1</td>
<td>Individual fit to each release curve</td>
<td></td>
</tr>
<tr>
<td>a (cm⁻¹)</td>
<td>0.699 ± 0.113</td>
<td>0.392 ± 0.188</td>
</tr>
<tr>
<td>β</td>
<td>0.376 ± 0.304</td>
<td>1.449 ± 2.394</td>
</tr>
<tr>
<td>Eᵢ</td>
<td>0.464 ± 0.134</td>
<td>0.390 ± 0.303</td>
</tr>
<tr>
<td>Runoff box, Fit-2</td>
<td>Parameters a and β were the same for all calibrated curves, while values of parameter Eᵢ were individual for each release curve</td>
<td></td>
</tr>
<tr>
<td>a (cm⁻¹)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>β</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eᵢ</td>
<td>0.551 ± 0.121</td>
<td>0.276 ± 0.087</td>
</tr>
</tbody>
</table>

Table 5
Performance indicators for fitting the model to the release kinetics measured in runoff-plot experiments.

<table>
<thead>
<tr>
<th>Performance indicators</th>
<th>Bare runoff plots</th>
<th>Vegetated runoff plots</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sandy loam</td>
<td>Clay loam</td>
</tr>
<tr>
<td>Fit-1 Parameter a was the same for all curves, parameters β was the same for all manure components at each runoff plot, and parameter Eᵢ was individual for each release curve</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MER × 10⁴</td>
<td>0.320</td>
<td>0.681</td>
</tr>
<tr>
<td>MAE × 10⁴</td>
<td>0.573</td>
<td>0.450</td>
</tr>
<tr>
<td>RMSE × 10²</td>
<td>0.990</td>
<td>0.682</td>
</tr>
<tr>
<td>NSE</td>
<td>0.995</td>
<td>0.994</td>
</tr>
<tr>
<td>MIA</td>
<td>0.974</td>
<td>0.968</td>
</tr>
<tr>
<td>U</td>
<td>0.121</td>
<td>0.077</td>
</tr>
<tr>
<td>τₑ</td>
<td>0.920</td>
<td>0.342</td>
</tr>
<tr>
<td>C</td>
<td>0.989</td>
<td>0.649</td>
</tr>
</tbody>
</table>

Fit-2 Parameter a was fitted separately for bare and vegetated plots, parameters β was the same for all manure components at each runoff plot, and parameter Eᵢ was individual for each release curve

<table>
<thead>
<tr>
<th>Performance indicators</th>
<th>Bare runoff plots</th>
<th>Vegetated runoff plots</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sandy loam</td>
<td>Clay loam</td>
</tr>
<tr>
<td>MER × 10⁴</td>
<td>-0.088</td>
<td>-0.070</td>
</tr>
<tr>
<td>MAE × 10⁴</td>
<td>0.203</td>
<td>0.178</td>
</tr>
<tr>
<td>RMSE × 10²</td>
<td>0.332</td>
<td>0.253</td>
</tr>
<tr>
<td>NSE</td>
<td>0.999</td>
<td>0.999</td>
</tr>
<tr>
<td>MIA</td>
<td>0.991</td>
<td>0.987</td>
</tr>
<tr>
<td>U</td>
<td>0.050</td>
<td>0.044</td>
</tr>
<tr>
<td>τₑ</td>
<td>-0.280</td>
<td>-0.254</td>
</tr>
<tr>
<td>C</td>
<td>0.989</td>
<td>0.649</td>
</tr>
</tbody>
</table>

Note: MER, mean model error; MAE, mean absolute error; RMSE, root mean squared error; NSE, Nash–Sutcliffe efficiency index; MIA, modified index of agreement; U, Theil’s inequality coefficient; τₑ, equivalence τ-value; C, equivalence cutoff. All performance indicators are dimensionless.

manure components Eᵢ values were significantly higher (P<0.05) at the vegetated plots compared to the bare plots.

4. Discussion

Two-stages release kinetics were observed in this study for all manure components for both runoff-box and runoff-plot experiments, indicating the presence of two sources of manure components with different release rates. During the first stage the manure components were primarily released with the liquid phase of the manure that constitutes the first source of manure components, and to some extent were diluted with the irrigation water. A fraction of the released material was probably adsorbed on soil surface. During the second stage the manure components were washed-off from the manure solid phase, that is the second source, which consisted primarily of incompletely decomposed bedding material, partly digested hay and grain materials, as well as material from the soil surface. Visual examination of the manure application area revealed presence of these materials on the soil surface after the irrigation experiments. It has been shown in the previous study (Guber et al., 2007) that the first and second phase of E. coli and enterococci release from the surface applied manure followed the first- and zero-order kinetic, respectively. Results of the present study demonstrated applicability of a single model for both release stages for different manure components. The model ability to capture the dynamic of both release stages implies that:
(i) there was a gradual transition in the released kinetics of the manure components from stage one to stage two in the experi-
ments; (ii) both release stages can be described adequately using a quasi-steady-state approximation of Fick’s first law; and (iii) the release parameters have the same values for both release stages.

The release kinetics of the manure components differed from those reported in earlier manure release studies. Springer et al. (1983) were probably the first who studied the release of fecal coliforms from aged manure cowpats under irrigated conditions. They observed that FC concentrations in the released suspensions increased within 15 min and were approximately constant within next 10 min of irrigation. The shape of the release kinetics was similar for the cowpats within age range from 2 days to 100 days, but the absolute values of FC concentrations in the effluent decreased following bacteria die-off in the cowpats. Contrary to the results of their study a gradual decrease of Cryptosporidium (oo)cysts and Giardia cysts from a dairy cattle manure was observed in Bradford and Schijven (2002) and Schijven et al. (2004) studies. Inconsistency of our results with these publications stems from the difference in the experiment design used in our study. In these publications the release was studied using manure enclosed into a cake pans or 5-cm diameter aluminum rings. The released suspension ran over the top of the rings filled with manure, while the volume of the manure suspension was maintained constant during the whole experiment. The decrease of the manure mass in the cited manuscripts occurred due to raindrop disturbance of the manure surface, and agitation and dilution of the resuspended material with the irrigation water. The dry surface of the aged cowpats protected FC in Springer et al. (1983) study and delayed bacteria release from the manure. The delay was not observed in Bradford and Schijven (2002) and Schijven et al. (2004) studies since they used fresh manure. The slow decrease in Cryptosporidium (oo)cysts and Giardia cysts concentrations in the effluent observed by those authors was a result of increasing effect of manure dilution and decreasing effect of disturbance and agitation with time due to manure depletion and thinning of the manure layer inside of the ring enclosure. In our study the thickness of the manure layer was less than in Bradford and Schijven (2002) study (1.2 cm vs. 1.8 cm) and the irrigation water ran off the manure surface as a result of the surface slope. Therefore the manure surface remained unprotected by the manure suspended in the irrigation water and was exposed to the raindrops during the whole experiment. This explains the relatively fast decrease in concentrations of all manure components observed in our study.

The shape of the release kinetics in our study were similar to the dissolved organic P kinetics from a dairy, poultry and swine compost presented in the Sharpley and Moyer (2000) study and the phosphorus release kinetics measured using a sequential extractions of P, Ca and Mg from a milkers, light dry and beef cattle manure with NH₄Cl solution (Nair et al., 2003). Despite different manure properties, release conditions and manure sample sizes, both phases of the release kinetics were observed in these studies.

It is unlikely that the differences in the values of the parameter α that were obtained in the runoff-box and runoff-plot experiments (Table 4) were associated with the properties of the manure used in the study or with used irrigation rates, since manure source and properties of the two experiments were similar (Table 1) and the irrigation rates were introduced into Eq. (3) explicitly. Most likely the values of parameter α reflected different vegetation conditions as indicated by the height of the grass, that was approximately 7.5 cm and 5.0 cm tall in the runoff-box and at the vegetated plots, respectively. The commercial sod had also visually higher vegetation density in runoff boxes compared to the runoff plots. Data of this study are not sufficient to derive any relationship between α values and vegetation, but a decrease of parameter α with increasing vegetation biomass implies that the vegetation alleviates the raindrop impact and to a certain extent protects the manure from erosion. This observation concurs with the result of Schijven et al. (2004) study. They reported that the values of parameters α computed from the flow rate and parameter α values were generally smaller for mist irrigation than for drip irrigation. Moreover, at flow rate of 2.89 mL.min⁻¹ for the calf manure the difference in α values between mist and drip irrigation was six-fold, indicating less raindrop impact of mist irrigation on the manure compared to drop irrigation. We surmise that parameter α reflects the erodibility which is influenced by manure properties, raindrop energy and salinity of irrigation water. The larger α values, the faster the applied manure depletes.

The values of parameter β obtained in the model calibration to the runoff-box data (Table 4, runoff-box: Fit-2) appeared to be of the same order of magnitude with the values computed for the runoff plots (Table 4, runoff plot: Fit-2). Due to high variability of β among runoff-boxes and runoff plots the differences between β values were not statistically significant. The two way analysis of variance did not reveal effects of soil texture and vegetation on the parameter β in runoff-plot experiments. Values of correlation coefficients between parameter β and irrigation rates were also statistically insignificant. The release curves measured in this study were reproduced adequately with a single value of parameter β for all manure components in each experiment. Changes in β values between the experiments indicate that this parameter characterizes the release of manure rather than the release of its components.

The physical meaning of the parameter Eᵣ in our study differed from those used by the authors of the release model (Bradford and Schijven (2002)). The authors termed parameter Eᵣ to be the microorganism release efficiency, that describes the partitioning behavior of (oo)cysts into water relative to that of manure. They reported that the values of Eᵣ were smaller than one for Cryptosporidium (oo)cysts, and both smaller and greater than one for Giardia cysts, implying that (oo)cysts can be released into the aqueous phase at different rates than manure (Schijven et al., 2004). However, the revision of Eq. (3) shows that at t → ∞ the relative release mass of the manure component is $M_m(∞)/M_m(0) → E_r$. Therefore, the $E_r$ value is the maximum possible relative mass of the manure component that can be released into the aqueous phase. Indeed we found high correlation between the recovered mass of the manure components and the parameter $E_r$ in the runoff-box and runoff-plot experiments (Fig. 5). Overall, the fitted $E_r$ values were very close to the recovered mass for small $E_r$ and larger than the recovered mass for large $E_r$ values, indicating that the length of the runoff experiments was not sufficient for complete release of the manure components with the large values of the recovered mass. Consistent with such interpretation of the parameter $E_r$, despite its high variability for the studied manure
components, its values never exceeded one, that is, 100% mass recovery, in all in the runoff-box and runoff-plot experiments.

The incomplete mass recovery observed in the runoff experiments was caused ultimately by the infiltration losses of the manure components into the soil. The results of previous study showed that values of the saturated hydraulic conductivity were 0.05 cm h$^{-1}$, 2.56 cm h$^{-1}$, 1.89 cm h$^{-1}$ and 7.12 cm h$^{-1}$ at the clay loam bare, clay loam vegetated, sandy loam bare and sandy loam vegetated plots, respectively (Guber et al., 2009). Higher saturated hydraulic conductivities resulted in higher infiltration rates in sandy loam compared to clay loam soil, and in higher infiltration rates at the vegetated plots compared to the bare plots. Therefore the largest losses of the manure components were expected at sandy loam vegetated plot, and the smallest losses at clay loam bare plot. The apparent inconsistency between our results and the infiltration loss rate can be explained by the presence of the manure components in appreciable amounts in the manure liquid phase and by the differences in the initial water contents at bare and vegetated plots. The soil in the top 5-cm layer was unsaturated and soil water content measured prior to manure application was less at the bare plots compared to the vegetation plots (Table 1). Smaller water contents at the bare plots resulted in larger amounts of manure liquid phase adsorbed by soil. Water budget computations show that the top 5-cm soil layer can absorb approximately 1.1 cm of the manure suspension at the bare plots, and 0.7 cm at the vegetated plots. The total applied manure head was 1.17 cm at each plot, therefore up to 95% and 62% of the manure could have potentially infiltrated and been adsorbed by the soil at the bare and vegetated plots, respectively. The values of $E_r$ parameter for all manure components were greater than those estimated from the water budget indicating that the actual adsorption was less than the potential one, and that the fraction of the adsorbed material was released from the soil during the second stage of release.

The Bradford–Schijven model (Eq. (3)) adequately reproduced the results of the runoff-box and runoff-plot experiments as assessed by the model performance statistics. However the parameters of Eq. (3) varied greatly among manure components and runoff-box experiments, especially in the individual fits. High correlation coefficients ($r > 0.9$) between parameters $E_r$, $a$ and $\beta$ were obtained in the individual fits indicating a structural problem in the model. This problem stems from the fact that $E_r$, $a$ and $\beta$ perform as multipliers in this equation, and an increase in one multiplier immediately results in a decrease in another one, thus producing an infinite combination of parameter values which give exactly the same output. Called by Beven (1993) equifinality, this problem, was resolved by pooling together release kinetics with different values of the recovery mass that eliminated correlations between parameter $E_r$ and parameters $a$ and $\beta$ reduced. Using single value of parameter $a$ for all runoff boxes and the same $\beta$ values for all manure components in each runoff-box experiment reduced correlation between the model parameters and improved their certainty (Table 4). The parameter uncertainty would likely be different for different number of considered manure components, replications and irrigation rates used for model fit. Therefore the number and selection of the manure components along with the experimental conditions, e.g. manure type, manure application forms and rates, irrigation rates and intensity etc., may become an interesting avenue for the future studies.

Results of the model calibrations and validations showed that the model parameters and goodness of fit were not influenced by selection of the calibration dataset in runoff-box experiments. Small values of the MER, MAE, RMSEs and $U$ statistics and closeness the NSE and MIA values to one indicated an overall good accuracy of the model calibration. Relatively high values of these performance indicators for the validated datasets can be partly attributed to slightly different vegetation conditions in runoff boxes and model sensitivity to parameter $\beta$, and partly to different chemical properties of manure used in 6 experiments (Table 1). Overall acceptable model performance as assessed using multiple indicators suggests high potential of the model in predicting release of soluble, particulate and combination of particulate and soluble materials for different soil textures and different vegetation conditions. That is, the model can be used efficiently to improve the prediction accuracy of process-based models simulating contaminant transport from surface applied manure.

The model of bacteria release from animal waste to runoff studied in this work is sufficient for the single-event modeling, but more needs to be done to model time periods covering seasons or years. Rainfall causes microorganism release not only to runoff but also microorganism release to soil with infiltrating water. Therefore, not only animal waste but also soil becomes the source of microorganisms for subsequent rainfall-runoff events. Therefore, microbial

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**Fig. 5.** Relationships between values of parameter $E_r$ and mass recovery of the manure components in runoff box (a) and runoff plot (b) experiments.
survival both in surface-applied animal waste and in soil has to be simulated to provide the information necessary to model large time periods. Such modeling efforts have just started (Oliver et al., 2010) and present a promising research avenue.

Recent attention to modeling of fate and transport of pathogen and indicator microorganisms is to substantial extent related to the fact that the design and implementation of measures to attenuate the transport of pathogens and indicator organisms from catchment source areas to points of water resource use are now legal requirements in Europe and North America (Kay et al., 2012). Models appear to be essential tools for packaging and applying the accumulated knowledge to the selection of best management practices that would alleviate pathogen load and improve the microbial water quality (Parajuli et al., 2009; McBride and Chapra, 2011; Kay et al., 2012). Sensitivity and uncertainty analysis has been applied to evaluate input and parametric sources of errors of those models (i.e. Haydon and Deleitc, 2009). Less has been done in evaluating sources of structural error to prevent the qualitative inability of model components to properly simulate the process or mechanism. Our work demonstrates that possibilities for testing and improving components of pathogen fate and transport models arise as the experimental data accumulate, and that the scale dependence of model structures and parameters has to be tested.

Manure application is known to have various and substantial ecological implications. It was noted that nonpoint inputs of nutrients are difficult to measure and regulate because they derive from activities dispersed over wide areas of land and are variable in time due to effects of weather. In aquatic ecosystems, these nutrients cause diverse problems such as toxic algal blooms, loss of oxygen, fish kills, loss of biodiversity (including species important for commerce and recreation), loss of aquatic plant beds and coral reefs, and other problems (Carpenter et al., 1998). There has been a consensus that (a) inputs of P and N to agriculture in the form of fertilizers exceed outputs in produce in the United States and many other nations; (b) nutrient flows to aquatic ecosystems are directly related to animal stocking densities, and under high livestock densities, manure production exceeds the needs of crops to which the manure is applied; (c) excess fertilization and manure production cause a surplus to accumulate in soil, some of which is transported to aquatic ecosystems; and (d) excess fertilization and manure production on agricultural lands create surplus N, which is mobile in many soils and often leaches to downstream aquatic ecosystems, and which can also volatilize to the atmosphere, redistributing elsewhere and eventually reaching aquatic ecosystems (Allan, 2004; Chambers et al., 2006). The nutrient release from land deposited manure and animal waste is the critical initial process for the nonpoint pollution. Most of knowledge about this release comes from experiments in which the cumulative release during simulated or natural rainfall is measured in the end of the event. Interpretation of this single number strongly depends on the assumed kinetics model. Pachepsky et al. (2006) demonstrated that assuming a wrong release kinetics model for manure components can lead to gross errors in extrapolation of the experimental results to events of different duration or intensity. The model developed in this work will improve both design and interpretation of experiments on release from manure of currently regulated and monitored pollutants, such as microorganisms and phosphorus, as well as emerging pollutants such as pharmaceuticals.

The wildlife animal waste also presents a source of both bacteria and nutrients that can reach water sources. The wildlife inputs may account for 15–30% of total land-deposited bacteria in a watershed with mixed agricultural and forest land use (Kim et al., 2010). The uncertainty is common in estimates of wildlife inputs to the water quality of rural creeks (Parajuli et al., 2009), and little if anything is known about the release of nutrients and microbes from wildlife animal waste. Obtaining information about the kinetics of this release presents an interesting avenue of research. Such information would be a particular interest for riparian zones that, on one hand, provide valuable water conservation service, but on the other hand create a habitat for wildlife that can generate microbial pollution of fields and water sources (Crohn and Bianchi, 2007). Wildlife is usually assumed to be the source of E. coli in water in forested watersheds (e.g. Fisher et al., 2000). However, it has been recently emphasized that freshwater sediments provide a potent reservoir of pathogenic and indicator microorganisms that modifies and to large extent controls microbial pollution of irrigation and recreation waters (Pachepsky and Shelton, 2011). Very little is known about the ecology of enteric pathogen and indicator microbes in this natural media, and evaluation of microbial inputs from wildlife animal waste to waters presents the precondition to understanding the functioning of the sediment habitat of these microbes.

5. Conclusions

The results of this study showed that release of soluble, particulate and combination of those components from surface applied manure can be reliably predicted with a single set of parameters which characterize kinetics of manure mass release. The use of a single set of parameters allows significantly reducing the number of model parameters when multicomponent transport of manure-born contaminants is considered. It appeared that the manure release parameters can be estimated more reliably when the model fit was performed using release data for different manure components pooled together. Fit to a single release curve produced correlated parameters and therefore introduce uncertainty into the model parameterization.

The parameters of the Bradford and Schijven's model appeared to be robust and transferable from the calibration to validation datasets with minor losses of the model accuracy. These parameters accounted for different physical processes. The parameter $E_r$ accounted for the manure infiltration losses and, therefore total manure mass available for the release. The parameter $a$ was influenced by the vegetation and accounted for the raindrop impact on the manure surface in the runoff-plot experiment. The physical meaning of the parameter $b$ was not revealed in this study. Functionally this parameter controls the slope of the release curve and likely controls erodibility of manure.

The results of this study provide an improvement in parameterization of KINEROS/STWIR model (Guber et al., 2006, 2009) developed for pathogen risk assessment associated with livestock operations. The ability of the Bradford and Schijven's model to describe release of soluble, particulate and combination of soluble and particulate components from surface applied manure allows to extend the KINEROS2/STWIR model to simulation of major water pollutants, i.e. organic waste, nitrate, phosphate and pathogens. Future implementations of this model for assessment of current total maximum daily loads and for development of better management practices will enhance creation of manure management strategies for mitigating risks of surface water pollution associated with increased probability of high rainfall and runoff events due to climate change.

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