A mathematical model for soil solute transfer into surface runoff as influenced by rainfall detachment

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HIGHLIGHTS
• Mixing depth is the function of time.
• Mechanisms of nutrients (K, P, N) transferred into runoff were revealed and simulated.
• The values of mixing extent of soil solute with rainwater (m) and the detachment and mixing coefficient (km) for different nutrients were determined.

GRAPHICAL ABSTRACT

ABSTRACT

Nutrients transport is a main source of water pollution. Several models describing transport of soil nutrients such as potassium, phosphate and nitrate in runoff water have been developed. The objectives of this research were to describe the nutrients transport processes by considering the effect of rainfall detachment, and to evaluate the factors that have greatest influence on nutrients transport into runoff. In this study, an existing mass-conservation equation and rainfall detachment process were combined and augmented to predict runoff of nutrients in surface water in a Loess Plateau soil in Northwestern Yangling, China. The mixing depth is a function of time as a result of rainfall impact, not a constant as described in previous models. The new model was tested using two different sub-models of complete-mixing and incomplete-mixing. The complete-mixing model is more popular to use for its simplicity. It captured the runoff trends of those high adsorption nutrients, and of nutrients transport along steep slopes. While the incomplete-mixing model predicted well for the highest observed concentrations of the test nutrients. Parameters inversely estimated by the models were applied to simulate nutrients transport, results suggested that both models can be adopted to describe nutrients transport in runoff under the impact of rainfall.

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KEYWORDS:
Nutrients transport
Rainfall
Detachment
Model
Mixing depth

1. Introduction

Nitrate, phosphate and potassium are necessary nutrients for agriculture crops. However, their loading from agricultural land threatens...
the quality and ecosystem of surface waters (Destouni et al., 2010). Even being considered rather immobile in many soils (Marconi and Nelson, 1984), phosphate can interact with soil particles in its changeable form known as orthophosphate (McBride, 1994; Sims et al., 1998). The soil acts as a sink that traps \( PO_4^{3-} \) from the soil solution (Sharpley et al., 1981, 1984; Sharpley, 1995; Mahananda et al., 2010).

Excess phosphate (P), nitrate (N), and potassium (K) in water can affect aquatic life, plant growth and quality, and human health (Downing et al., 2001; Camargo and Alonso, 2006; U.S. Environmental Protection Agency, 1982). A better understanding of nitrate, phosphate and potassium processes will aid environmental policy- and decision-makers in the development of scientifically sound, equitable standards for agricultural nutrient use (Sims et al., 1998).

Soil nutrients transport with surface runoff is recognized as complicated physical, chemical, and biological processes, which are affected by many factors such as raindrop properties, soil structure and texture, slope and length, soil coverage, and chemical properties. To describe soil solute transport into runoff water impacted by rainfall, several models that conceptualize the transport process in different ways have been presented.

The mixing-layer concept is the most commonly used model to describe chemical transport from soil to runoff water (Steenhuis and Walter, 1980; Ahuja et al., 1981; Ahuja and Lehman, 1983; Ahuja, 1986; Wallach et al., 1988; Wallach and Van Genuchten, 1990; Steenhuis and Walter, 1980; Steenhuis et al., 1994; Zhang et al., 1997; Gao et al., 2004, 2005; Walter et al., 2007; Dong et al., 2013). Soil solute transfer into surface runoff is usually via the mixing layer, the depth and degree of which is primarily influenced by raindrop and overland flow. However, few studies in the past considered this relationship between rainfall characters and mixing depth.

This study aimed at investigating the runoff of soil nutrients under the effect of raindrop impact and to test the applicability of a proposed physically based model in predicting soil nutrients transport from soil surface into runoff. The experimental study included (1) investigating the transport processes of different nutrients into runoff under different rainfall intensities, slopes and initial water contents by considering soil erosion, (2) evaluating the effect of rainfall intensity on the degree of mixing depth, and (3) comparing the measured data with model predictions through inverse estimate of model parameters from experimental data in combination with specific local hydraulic parameters and adsorption parameters from direct measurement.

2. Theory

Under rainfall impact, the solute in the mixing layer partially transfers into runoff and partially to infiltration as runoff forms, and the remaining stays in the mixing layer. The rainwater is assumed to mix completely and uniformly with soil water in the mixing layer (Ahuja et al., 1981), and the mass conservation equation is:

\[
\frac{dD_mc(\theta_i + \rho_s k)}{dt} = -rc
\]

(1)

where \( D_m \) is mixing depth (m), \( c \) is solute concentration in the mixing depth (g m\(^{-3}\)), \( \theta_i \) is the saturated water content (m\(^3\) m\(^{-3}\)), \( \rho_s \) is the soil bulk density (g m\(^{-3}\)), \( k \) is solute adsorption coefficient (m\(^3\) g\(^{-1}\)), \( r \) is the rainfall intensity (m s\(^{-1}\)).

On the other hand, if the soil water only partially mixes with soil solute, the solute concentrations of the soil water and of the infiltration water are then different. The mass conservation equation of incomplete-mixing can be expressed as:

\[
\frac{d(D_mc(\theta_i + \rho_s k))}{dt} = -a(r-i)c-bic
\]

(2)

where \( i \) is infiltration rate (m s\(^{-1}\)), \( a \) is the ratio of solute concentrations between runoff water and mixing-layer soil water, \( b \) is the ratio of solute concentration between infiltration water and mixing-layer soil water.

The mixing depth is dependent on time and related to the inter-rill sediment delivery rate from soil \((D_i, \text{kg s}^{-1} \text{ m}^{-2})\):

\[
D_m = k_cD_it^n
\]

(3)

where \( D_i \) is the inter-rill sediment delivery rate from soil (kg s\(^{-1}\) m\(^{-2}\)), \( k_c \) is mixing coefficient, \( m \) is the mixing extent of soil solute with rainwater.

Several factors can affect the inter-rill erosion rate. Using rainfall simulation data, Meyer and Harmon (1984) found that for a given slope, the inter-rill sediment could be described by Sharma et al. (1993):

\[
D_i = K_n r^n
\]

(4)

where \( K_n \) is an experimentally derived soil detachability coefficient (g m\(^{-3}\)), \( n \) is an exponent.

When rainfall intensity is a constant, Eq. (3) can be expressed as (Sharma et al., 1993):

\[
D_m = k_m r^m
\]

(5)

where \( k_m \) is the detachment and mixing coefficient.

Soil solute absorption can be considered as a linear process, thus it can be expressed as (Wang and Wang, 2010):

\[
C_i = k_D_c c
\]

(6)

where \( C_i \) is the amount of solute absorbed on soil particle.

The Philip's infiltration (1957) equation is usually adopted to describe the infiltration process under surface ponding condition. For both ponding and non-ponding conditions, the soil infiltration rate

<table>
<thead>
<tr>
<th>Treatments</th>
<th>60 (mm h(^{-1}))</th>
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<th>100 (mm h(^{-1}))</th>
<th>120 (mm h(^{-1}))</th>
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</tbody>
</table>

*✓* presents the experiment was conducted, ‘-‘ indicate none experiment was conducted.
during a rainfall event can be expressed as (Yang et al., 2016):

\[
\begin{align*}
    i & = \frac{r t}{\ln (1 - \frac{t}{t_p})} \quad & t \leq t_p \\
    i & = \frac{1}{2} S (t - t_0)^{-0.5} \quad & t > t_p
\end{align*}
\]  

(7)

where \( S \) is soil sorptivity and \( t_0 \) is the difference time between ponding infiltration and infiltration under rainfall condition (s).

Substitute Eq. (5) into Eq. (1), and integrating Eq. (1), the complete-mixing equation is:

\[
c(t) = c_m \exp \left( - \frac{r (t^{1-m} - t_p^{1-m})}{(1-m) k_m (t_p + \rho_b k)} + m \ln \frac{t}{t_p} \right)
\]

(8)

\( c_m \) is the concentration of solute in the mixing layer before runoff defined as (Wang and Wang, 2010):

\[
c_m = \frac{\theta_i + \rho_b k}{(t_p + \rho_b k)} c_i
\]

(9)

where \( c_i \) is the initial solute concentration (g m\(^{-3}\)), and \( \theta_i \) is the initial water content (m\(^3\) m\(^{-3}\)).

Integrating Eq. (2):

\[
c = c_m \exp \left( - \frac{a \int_{t_p}^{t} \frac{(r-i)dt}{t} + b \int_{t_p}^{t} \frac{i dt}{t} + \int_{t_p}^{t} \frac{k_m (t_p + \rho_b k) dt}{t} }{k_m (t_p + \rho_b k)} \right)
\]

(10)

where \( t_p \) is runoff time (min).

Combining Eq. (7) with Eq. (10), the solute concentration in the runoff can be approximately expressed as:

\[
c = c_m \exp \left( - \frac{(2ar - (a-b)S)}{2(1-m)} \left( t^{1-m} - t_p^{1-m} \right) + \frac{t_p S (a-2b)}{4m} \left( t^{1-m} - t_p \right) \right)
\]

(11)

The proposed mathematical model can be applied to predict soil solute transport into surface runoff by considering rainfall impact. The schematic representing soil solute transport of the model was depicted in Fig. 1.

3. Materials and methods

3.1. Study site description

The study area is located in Yangling demonstration zone, at the middle of Guanzhong Plains, Shaanxi Province (E107°59′–108°08′, N34°14′–34°20′). The main crops included grain and oil crops, vegetables, flowers and nursery plants, edible fungi and economical forestry and orchard. The area has an arid-humid monsoon climate. The annual mean precipitation and evapotranspiration are 637.6 mm and 884.0 mm, respectively (Huang et al., 2013). It belongs to a part of Loess Plateau area of China (E100°54′–114°33′, N33°43′–41°16′), which is famous for its intense soil erosion (1000–15,000 t km\(^{-2}\) a\(^{-1}\)). Serious soil erosion has instigated a series of environmental problems (Shi and Shao, 2000) in the region. Soil samples were taken from croplands in this area. Soil particle size distribution was determined by sieving in combination with the pipette method.

Fig. 2. The variation of runoff coefficient, sediment concentration and infiltration in total under different rain intensities, slopes and initial water contents.
The test soil was a loam with 10% sand (>0.050 mm), 57% silt (0.050–0.002 mm) and 33% clay (<0.002 mm).

3.2. Experimental equipment

The experiments were performed in the rainfall simulation hall at the Key Laboratory of Soil Erosion and Dryland Farming on the Loess Plateau, Yangling. The rainfall simulation system was composed by a rain simulator, a computer to control both rainfall intensity and water pressure, a pump, a water tank, and a rainfall intensity meter. The nozzles were placed 15 m above the ground to simulate the natural rainfall conditions. Pressure was controlled by the computer to obtain different rainfall intensities ranging from 40 to 120 mm h\(^{-1}\). Desirable rainfall intensity was determined by the computer that was connected to the rainfall intensity meter.

3.3. Soil sample collection and preparation

Soil samples used for conducting runoff experiments were collected from the fallowed cropland in Yangling, Shaanxi Province. Soil was taken at the depth of 5–30 cm along the soil profile. This sampling depth was supposed to be most vulnerable to the impact of rainfall and tillage. The collected soils were air-dried, and sieving through 5 mm mesh. The soils were uniformly spiked with 500 mg potassium and nitrate (KNO\(_3\)), and 500 mg phosphorus (KH\(_2\)PO\(_4\)) dissolved with different quantitative water (the amount designed levels of initial water content) per kg of dry soil to simulate the typical local N-P-K fertilization level. The spiked soil samples in covered containers were allowed to equilibrate for 24 h before packing. Soils were then filled and packed in the flumes (1 m in length by 0.4 m in width by 0.5 m in height) every 5 cm layer by layer (bulk density of 1.35 g cm\(^{-3}\)) with a 10 cm sand layer placing at the bottom to form a boundary permeable to air and water. The angle of the flume (slope) was adjustable from 0° to 30°. Along each side of a flume, a 15 cm exclusive zone was left to prevent raindrop splashed to outside of the flume.

3.4. Experimental setup and analysis

Variations in rainfall intensities, slopes and initial water contents can contribute to soil surface erosion to certain extent. Four rainfall intensities (60, 80, 100, 120 mm h\(^{-1}\)), 4 slopes (10°, 15°, 20°, 30° (degree)), and 4 initial water contents (9.2, 13.6, 17.4, and 21.2%) were tested in

Fig. 3. Nutrients concentrations in runoff such as potassium, phosphate and nitrate under different rain intensities, slopes, initial water contents conditions.
4 Results and discussion

4.1 Runoff coefficient, sediment concentration and infiltration

Runoff coefficients, sediment and nutrient concentrations, and infiltration rates for the 0.4 m² plots under simulated rainfalls with rainfall intensities ranging from 60 to 120 mm h⁻¹, slope steepness ranging from 10° to 30°, and initial water contents ranging from 9.2 to 21.2% were shown in Fig. 2. The runoff coefficients expressed as a percentage of the applied rain are presented to allow comparison between results for different rainfall intensities (Chaplot and Bissonnais, 2000). As shown in Fig. 2a–b, runoff coefficients increased with increases of initial soil water content, rainfall intensity and slope. Since higher rainfall intensity, greater slope steepness, and higher initial water content can promote surface flow but decrease infiltrability and runoff time (Walter et al., 2007), which result in the increase of runoff coefficient.

Sediment concentration for the experiments under simulated rainfall was depicted in Fig. 2a, c. Initial water content affected sediment concentrations (Cs). It decreased slightly when initial water content increased, soil water content, rainfall intensity and slope. Since higher rainfall intensity made the soil surface easier to be saturated as well as compacted, which promoted surface runoff, especially shortened the start of runoff time and reduced the soil infiltration rate. On the other hand, the increase in soil slope greatly accelerated the velocity of overland flow, which increased the surface runoff in a unit time, furthermore, the increase in flow velocity reduce the standing time of surface water infiltrate into deep soil.

4.2 Transport of potassium, phosphate and nitrate to the runoff

By analyzing the experimental data, we observed that the solution concentration in the runoff was controlled mainly by the rainfall and the solution concentration in the mixing zone in the beginning several minutes after runoff takes place. Greater mixing promoted solute runoff, but when the solution concentration in the runoff got stabilized, the solution concentration in the runoff was controlled mainly by the diffusion between the mixing zone and the soil under the mixing zone (Yang et al., 2015). The potassium, phosphate and nitrate concentrations in the runoff over time for different treatments are summarized in Fig. 3. As rainfall intensity increased, nutrients concentrations in the runoff increased. However, changes of concentrations for the three nutrients in the runoff were different due to their respective chemical properties.

Potassium concentration decreased sharply with time at the initial runoff stage, and then decreased slowly to nearly a constant level after about 20 min (Fig. 3a). Phosphate fluctuated over time by a large margin influenced by rainfall intensity (Fig. 3b). For example, when rainfall intensity was lower than 80 mm h⁻¹, phosphate concentration peaked further increased from 13.6 to 21.2%, at which the initial water content was in the range of optimal soil compaction (Walter et al., 2007).

Sediment concentration increased as rainfall intensity increased, which agrees with the observations by Chaplot and Bissonnais (2000). Slope also had significant effect on sediment concentrations, with slope increased from 10° to 30°, sediment concentrations increased nearly about 1.5 times for all the test rainfall intensities.

Fig. 2a, d showed the infiltration under rainfall simulation for the plots. As the initial soil water content, rainfall intensity and slope increased, soil infiltration rate decreased. Higher initial water contents may lead to a greater swelling of the clay particles in the soil and reduce the size of the pores, consequently reducing the hydraulic gradient and thus infiltrability (Liu et al., 2011).

Increase in rainfall intensity made the soil surface easier to be saturated as well as compacted, which promoted surface runoff, especially shortened the start of runoff time and reduced the soil infiltration rate. On the other hand, the increase in soil slope greatly accelerated the velocity of overland flow, which increased the surface runoff in a unit time, furthermore, the increase in flow velocity reduce the standing time of surface water infiltrate into deep soil.

Table 2

<table>
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<th>Rain intensity (mm h⁻¹)</th>
<th>Slope</th>
<th>Initial water content (%)</th>
<th>tₚ (min)</th>
<th>ρₛ (g m⁻³)</th>
<th>cₛ (g m⁻³)</th>
<th>K⁺</th>
<th>PO₄⁻</th>
<th>NO₃⁻</th>
<th>a</th>
<th>b</th>
<th>θₛ (m² m⁻¹)</th>
<th>S (m s⁻¹/²)</th>
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The results of the research. The 16 flumes were filled with soil that had a fixed initial water content of 13.6% for the first set of experiment, and every four of the 16 flumes were adjusted to the slope from 10°, 15°, 20°, to 30°, resulting in 4 groups of flumes that had the same initial water content, but different slopes. Details were listed in Table 1.
around 3 min at the initial runoff stage and then decreased over time. When rainfall intensity was higher than 80 mm h\(^{-1}\), phosphate concentration decreased sharply at the beginning of 20 min, and then slightly decreased over time. Nitrate concentrations in runoff distributed with scatter points, and slightly decrease trends were observed (Fig. 3c).

Fig. 3d–f shows the influence of slope on runoff of the three soil nutrients. As slope increased to 30\(^{\circ}\), potassium concentration was much higher, and then declined sharply with time (Fig. 3d).

Compared with potassium transport, phosphate concentration in the runoff decreased in a more gradual manner (Fig. 3e). Due to stronger soil adsorption, phosphate did not mix completely with rain water, but was eroded and transported with sediments in the runoff water down the slopes.

Nitrate concentrations in the runoff were very low (Fig. 3f), which agrees with the observations by Shuman (2002). The impact of slope on nitrate transport is not obvious similar to that of rainfall intensity. In this study nitrate concentration was lower than 3 mg L\(^{-1}\) below the 10 mg L\(^{-1}\) drinking water standard (Raymond-Whish et al., 2007), when the local fertilizer application rate was used.

Concentrations of the nutrients in runoff water varied with initial water contents (Fig. 3g–i). More potassium was transferred to runoff as initial water content increased, as showed in Fig. 3g. But for phosphate, initial water contents had insignificant effect on P runoff (Fig. 3h).

Nitrate concentration in runoff over time did not change much under different rainfall intensities and slopes (Fig. 3c, f), which may be attributed to the uniform distribution of nitrate by the initial water content.
4.3. Modeling of nutrient concentrations in runoff

4.3.1. Parameters estimation

Parameters in the proposed mathematical models can be obtained with different ways. As many parameters as possible were set at independently observed values (e.g. $\theta_s$ and $\rho_s$) in both of the complete- and incomplete-mixing models. $\theta_s$ at the effective mixing depth was assumed to be saturated after the generation of runoff, i.e. $0.491 \text{ m}^3 \text{ m}^{-3}$, and $\rho_s$ was $1.35 \text{ g m}^{-3}$. $\theta_i$ is the initial soil water content preset before the experiment. The experimental runoff time, $t_{p}$, was measured directly. The coefficient of adsorption, $k$, was measured directly based on the isothermal linear adsorption method, and $3.34 \text{ m}^3 \text{ g}^{-1}$ for potassium (Yang et al., 2015), and $35.6 \text{ m}^3 \text{ g}^{-1}$ for phosphate, and $13.9 \text{ m}^3 \text{ g}^{-1}$ for nitrate. The initial concentration $c_i$, measured directly from the prepared soil samples. Details were listed in Table 2.

For the parameters that cannot be directly measured, such as $k_m$ and $m$ in the complete-mixing model, and $k_m$, $m$, $a$, $b$ and $S$ are needed for predicting nutrient transport by the incomplete-mixing model. In this study parameters $a = 0.3$, $b = 0.01$ were obtained with the method similar to the study by Yang et al. (2016), $S$ values were determined by curve fitting to Philip’s infiltration equation (Yang et al., 2016) (Table 2). For the parameters $m$ and $k_m$, they were inversely estimated by curve fitting to the experimental data.

4.3.2. Model prediction of the nutrient runoff

By assuming nutrient concentrations are at equilibrium between infiltration and runoff water, the effect of rainfall on soil detachment and

![Fig. 6](image_url). The concentrations of nutrients into runoff affected with initial water contents were fitted by complete- and incomplete-mixing model.
nutrients transport are described for the complete- and incomplete-mixing model. Experimental data for the three different rainfall intensities, slopes and initial water contents were curve fitted (Figs. 4–6, respectively).

The complete-mixing model fit potassium concentration data well at the initial runoff stage, but failed to describe the potassium runoff 10 min after the runoff started (Fig. 4a). Nevertheless, the incomplete-mixing model predicted the decrease of K concentrations with time much better than the complete-mixing model did (Fig. 4a). As the rainfall intensity increased from 60 to 120 mm h⁻¹, the fitted curves of the complete-mixing model decreased sharply at the later runoff stage (Table 3). For phosphate, the models captured the concentration change of the entire runoff process reasonably well, especially for the post-event recession (Fig. 4b).

For nitrate, the complete-mixing model fitted well with the experimental data at the later runoff stage, but underestimated the initial concentration (Fig. 4c). On the other hand, the incomplete-mixing model better predicted the initial runoff concentration and the decrease trend over time, but there appeared to be some bias during the middle runoff stage (Fig. 4b).

Fig. 5 shows the slope effect on K concentrations predicted by the two models. When slope was >30°, the decreasing trend of potassium concentrations was well-predicted with the incomplete-mixing model (Fig. 5a). Fig. 5b shows the observed phosphate concentrations could be well predicted well with the two models. For nitrate, the two models could capture the initial N concentrations in runoff, and it successfully captured the trend of N concentration in runoff (Fig. 5c).

Fig. 6 shows the effect of initial water content on nutrient runoff. The complete- and incomplete-mixing model fitted well with the experimentally observed potassium concentrations in the runoff, especially at the initial runoff stage (Fig. 6a). For phosphate concentrations, the two models captured the variation trends well (Fig. 6b). The complete-mixing underestimated the observed nitrate concentrations, especially at the initial stage of runoff (Fig. 6c), while the incomplete-mixing model over-predicted the initial nitrate concentration for the higher initial water content treatment (Fig. 6c).

The parameters in the two models, such as m and km, obtained from curve fittings are listed in Table 3. For the complete-mixing model, the m values were different for each nutrient, with m = 0.5 for potassium, m = 0.22 for phosphate, and m = 0.1 for nitrate. The m values in the complete-mixing model were affected by the type of nutrients, not by rainfall intensity, slope and initial water content.

A greater m value for potassium than those of phosphate and nitrate indicated that larger amount of soil potassium mixed with surface water under the rainfall impact, resulting in more potassium transport to runoff (overland flow). Since more P was adsorbed (retained) by soil particles, less P was transferred into mixing layer, and consequently, less P was observed in runoff. Lower m value for nitrate indicated less N transferred into mixing layer from deep soil.

The values of km in the complete-mixing model varied with rainfall intensity, slope, initial water content, as well as nutrients type. It can be seen from Table 3 that km decreased with the increase of rainfall intensity, and slightly increased with slope, but had no obvious change with initial water content. Generally, the order of km for nutrients were potassium > phosphate > nitrate. The relationship between km and rainfall intensity, slope, initial water content and nutrient types was further analyzed by regression:

\[
km(K) = 1.238r^{-0.59}e^{0.007k} \quad R^2 = 0.96
\]

\[
km(P) = 0.067r^{-0.59}e^{0.007k} \quad R^2 = 0.93
\]

\[
km(N) = 0.13r^{-0.59}e^{0.007k} \quad R^2 = 0.97
\]

where s is slope. According to the above equations, km for the three nutrients decreased with rainfall intensity (r), and exponentially and linearly increased with slope (s) and adsorption rate (k), respectively.

Meanwhile, m values obtained from the incomplete-mixing model showed that it was correlated with nutrient type: with m = 0.25 for potassium, m = 0.22 for phosphate, and m = 0.9 for nitrate. It indicates that more nitrate was transferred to the mixing layer from deep soil than potassium and phosphate, which was attributed to nitrate higher mobility. The obtained value of km values in the incomplete-mixing model decreased with rainfall intensity, increased with slope, and was not affected by the initial water contents (Table 3). The km values for nitrate were greater than those for potassium, and km for phosphate were the smallest. It can be concluded that rainfall intensity, slope and nutrient type all affected the km values, and their relationships can be expressed as:

\[
km(K) = 0.637r^{-0.59}e^{0.00643k} \quad R^2 = 0.82
\]
It indicated that both slope and adsorption rate have positive effect on $k_m$, however, rainfall intensity has a negative effect in the incomplete-mixing model, and the trend is the same as in the complete mixing model.

$$k_m(P) = 0.083r^{-0.596}e^{0.00643k} \quad R^2 = 0.6$$

$$k_m(N) = 0.678r^{-0.596}e^{0.00643k} \quad R^2 = 0.6.$$
4.4. Comparison between complete- and incomplete-mixing model

The observed nutrient concentrations and cumulative mass under the experimental conditions of rainfall intensity of 80 mm h⁻¹, slope of 15°, and initial water content of 13.6% were used to compare the complete- and incomplete-mixing models (Figs. 7–8).

Fig. 7 shows that the complete-mixing model failed to capture the decreasing trend of K concentrations in the runoff water: it overestimated the initial concentration in runoff but under-predicted the concentration in later runoff stage. The predictions by the complete-mixing model were not better than those of the incomplete-mixing model (Fig. 7a). Different from predicting the K concentrations, both models predicted phosphate concentrations well (Fig. 7b). Our study showed that both models can be used to simulate phosphate transport. The simulated nitrate concentrations are shown in Fig. 7c. It can be seen that the complete-mixing model captured the decreasing trend of nitrate concentrations very well, with the exception that it predicted the initial nitrate concentration.

In contrast, the fitted results with incomplete-mixing model matched the experimental data well, especially for the nitrate concentrations in the runoff. The success of the incomplete-mixing model in predicting the initial concentrations and the decreasing trend is encouraging and supports the postulated transport process of partial displacement of solute from a relatively small volume of “mobile” pore water in the near surface layer of the soil. The displaced water is mixed with “new” water from rainfall (Pearce et al., 1986), which is assumed to bypass the soil matrix completely.

Besides, it is also important to evaluate the accuracy of the model predictions in terms of cumulative nutrient loss from soil to runoff. Comparison between the measured and simulated data showed that both the complete and incomplete mixing models predicted the total nutrient (mass) loss well (Fig. 8), while the incomplete-mixing model performed even better than the complete-mixing model for predicting cumulative potassium and nitrate losses (Fig. 8a, c). Fitting results implies that both models can be used to predict inert ions such as phosphate (Fig. 8b). But for non- or less adsorptive nutrients, the incomplete-mixing model should be given the priority.

The Nash-Sutcliffe Efficiency (NS) (Nash and Sutcliffe, 1970) was adopted to evaluate the accuracy of the model predictions. Results indicated that the incomplete-mixing model performed slightly better in predicting nutrient concentration in runoff than the complete-mixing model did (Table 4). The NS values for both models were >0.9 when the models were used to predict the cumulative nutrient losses (Table 5).

The root mean square error (RMSE) was calculated to compare the errors between the measured data and the simulated data for both models. Based on the RMSE values, the incomplete-mixing model predicted K and P concentrations and the cumulative losses of all three nutrients better than the complete-mixing model did (Table 5).

The correlation coefficient was also calculated to determine correlations and cumulative mass between observed and simulated nutrient concentrations. It showed that the models performed well in some cases while not so well in others. For example, correlations between observed and simulated phosphate concentrations were significant for both models, but positive correlation was weak between the observed and the predicted nitrate concentrations, especially for the complete-mixing model (Table 4). Positive correlations between the measured cumulative mass and model predictions by both models were observed (Table 5).

5. Conclusion

On the basis of the results obtained from the present study it can be concluded that the proposed models described the measured experimental data well. Both the complete- and incomplete-mixing models consider a mixing layer under rainfall impact and erosion, and nutrient runoff is affected by the factors (rainfall intensity, initial water content, and slope) related to soil erosion. Our study indicated that the incomplete-mixing model predicted the measured concentrations of the three nutrients (Nitrate, P, and K) better than that the complete-mixing model did.

The parameters obtained by fitting the experimental data to the models provide a way to assess the effects of different experimental conditions such as soil type, rainfall intensity, slope, initial water content (and others) on nutrient runoff. In the meantime, the parameter values for different nutrients also reflect the mobility of the nutrients in soil, runoff, and leachate. The complete-mixing model could better predict runoff of nutrients with high adsorption (such as phosphate) or under steeper slope condition. But underestimate potassium concentration in runoff under lower slope steepness (≤20°), as well as the initial high concentration of nitrate at the earlier runoff stage.

The models mentioned above were verified with experimental data from loess area. Further experiments from different area are needed to test the model’s applicability, more experiments should focus on the effect of kinetic energy of rain on detachment of soil nutrients, which may provide additional information concerning the soil-nutrient interactions and nutrient runoff to surface water.

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References


