A mathematical model for the transfer of soil solutes to runoff under water scouring

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HIGHLIGHTS
• A mathematical soil solute transport model proposed with the consideration of overland flow erosion
• The mixing depth in solute transport model is a function of time.
• The comprehensive mixing coefficient (k_c) linearly correlated with Reynolds' number Re.
• Tool for water and fertilization management

GRAPHICAL ABSTRACT

ABSTRACT

The transfer of nutrients from soil to runoff often causes unexpected pollution in water bodies. In this study, a mathematical model that relates to the detachment of soil particles by water flow and the degree of mixing between overland flow and soil nutrients was proposed. The model assumes that the mixing depth is an integral of average water flow depth, and it was evaluated by experiments with three water inflow rates to bare soil surfaces and to surfaces with eight treatments of different stone coverages. The model predicted outflow rates were compared with the experimentally observed data to test the accuracy of the infiltration parameters obtained by curve fitting the models to the data. Further analysis showed that the comprehensive mixing coefficient (k_c) was linearly correlated with Reynolds’ number Re (R² > 0.9), and this relationship was verified by comparing the simulated potassium concentration and cumulative mass with observed data, respectively. The best performance with the bias error analysis (Nash Sutcliffe coefficient of efficiency (NS), relative error (RE) and the coefficient of determination (R²)) showed that the predicted data by the proposed model was in good agreement with the measured data. Thus the model can be used to guide soil-water and fertilization management to minimize nutrient runoff from cropland.

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1. Introduction

Transfer of soil nutrients and sediments along slope land to surface water can affect water quality and river health. Understanding the
mechanism of nutrients release from soil to the runoff is very important for determining the potential of both surface- and groundwater contamination (Zhang et al., 1997).

Numerous studies have been carried out to explain the mechanism of solute transport from soil to runoff (Ahuja et al., 1981; Ahuja and Lehman, 1983; Gao et al., 2004, 2005). The effective-mixing model is one of the most commonly used models describing solute transport (Ahuja et al., 1981). In this model, the degree of interaction between rainwater and soil water was maximum at the surface and decreased very rapidly with depth by using a tracer of $^{32}$P. It hypothesizes that rainwater completely mixes with soil water in the effective mixing layer (Ahuja et al., 1981), and the solute concentration in the runoff equals the concentration in the infiltrating water and in the mixing layer. Ahuja and Lehman (1983) later found that the concentration in runoff and in infiltration is not the same, solute concentration at the effective mixing depth was directly proportional to the concentrations in the infiltrating runoff water. Solute concentrations in field runoff predicted by these models typically decreased exponentially over time (Wallach et al., 1989).

Associated with effective mixing model, the “effective” parameters have been used to represent a single process dominating the system or multiple, interacting processes in the models in early studies (Frere et al., 1980; Ingram and Woolhiser, 1980; Ahuja, 1990; Steenhuis et al., 1994). Among them, the effective-mixing depth is a significant parameter in the transport of solutes from soil water to the runoff (Zhang et al., 1997).

Chemicals near the soil surface are most likely to enter the surface runoff from the mixing depth with the impact of raindrops or upslope water. Solute transport from soil to runoff is affected by the degree of mixing (Heathman et al., 1985, 1986) induced by advective flow (Wallach and Van Genuchten, 1990). The thickness of the mixing depth in the models is usually determined by calibration with experimental data (Bailey et al., 1974; Donigian, 1977; Steenhuis and Walter, 1980), and it is usually a fixed value for model simulations (Ahuja et al., 1981; Ahuja and Lehman, 1983; Wang et al., 2002). However, Havis et al. (1992) estimated mixing depth through mass balance equation, and found that the mixing depth was a linear function of rainfall intensity. Various factors can affect the mixing depth. Early studies using CaSO$_4$ in soil boxes under simulated rain showed that the mixing depth was influenced by slope gradient, rain intensity, and rain energy (Ingram and Woolhiser, 1980; Walter et al., 2007). Yang et al. (2015) proposed to use a regression equation to analyze the combined effects of various factors on the mixing depth.

An analytical solution was obtained by Wallach et al. (1989) by treating the mixing depth development as a dynamic process. The mixing depth is formed as the erosive forces of flowing water exceed the resistance of the soil to erosion (Beasley et al., 1980). Studies showed that the fine soil particles composed the main part of mixing depth (Rose and Dalal, 1988), the fine particles have much lower settling velocity, thus tending to move further and more rapidly in overland flow, so being more likely to reach waterways, and fine particles are more effective than larger particles in absorbing nutrients (Rose and Dalal, 1988). Thus, the loss of nutrients from agricultural land is very rapidly with depth by using a tracer of $^{32}$P, it hypotheses that rainwater completely mixes with soil water in the effective mixing layer (Ahuja et al., 1981), and the solute concentration in the runoff equals the concentration in the infiltrating water and in the mixing layer. Ahuja and Lehman (1983) later found that the concentration in runoff and in infiltration is not the same, solute concentration at the effective mixing depth was directly proportional to the concentrations in the infiltrating runoff water. Solute concentrations in field runoff predicted by these models typically decreased exponentially over time (Wallach et al., 1989).

Numerous studies have been carried out to explain the mechanism of nutrients release from soil to the runoff is very important for determining the potential of both surface- and groundwater contamination (Zhang et al., 1997).

The objective of this study was to propose and test a simple method to describe solute transport in overland flow. The mixing depth was assumed to be an integral of average water flow depth. The effective-mixing model together with soil detachment by overland flow was applied into the conservation of mass equation to obtain the solute concentrations into surface runoff.

2. Theory

Soil surface particles detached by water flow, leading to the release of soil solutes to overland flow. Based on the concept of the complete-mixing model (Ahuja et al., 1981), where solute concentration in runoff equals to that in the mixing depth, the solute mass conservation can be expressed as:

$$\frac{d}{dt} \left( \rho c (\theta_s + k_s) \right) = -q c,$$

where $h_m$ is mixing depth (m), $c$ is the solute concentration in the mixing depth after runoff (g m$^{-3}$), $\theta_s$ is saturated water content (m$^2$ m$^{-3}$), $\rho_s$ is soil bulk density (g m$^{-3}$), $k_s$ is the soil adsorption rate (m$^2$ g$^{-1}$), $q$ is inflow rate (m$^3$ (ms$^{-1}$)), and $t$ is time (s).

Since the soil solute in the mixing zone often interacts with the overland flow, the mixing depth can be expressed as a function of the cumulative water flow detachment capacity (Yang et al., 2016). For simplicity, the mixing depth is assumed as the same for the entire hillslopes expressed as:

$$h_m = \int_{h_0/2}^{1} k_s D_c,$$

where $h_m$ is the mixing depth (m), $k_d$ is the mass transfer coefficient between soil and runoff (m$^2$ g$^{-1}$), and $D_c$ is the rate of stream erosion due to flow per unit distance (g m$^{-1}$ s$^{-1}$).

In the case of overland flow region, the erosion occurs due to raindrop impact as well as surface shear, while in the case of channel flow erosion is caused by shear stress alone. For an overland flow area, where the effect of shear stress is dominant, the sediment erosion rate due to shear can be expressed as (Srinivasan et al., 1988; Srinivasan and Galvao, 1995):

$$D_c = k_e \tau^{1/2},$$

where $k_e$ is the soil erodibility factor (g$^{1/2}$ m$^{-1/2}$ s$^{-2}$) and $\tau$ is the shear stress (g m$^{-1}$ s$^{-2}$), which can be expressed as:

$$\tau = \rho gh,$$

where $\rho$ is the density of water (g cm$^{-3}$), $g$ is the acceleration due to gravity (m s$^{-2}$), and $h$ is the flow depth (m).

**Table 1**

<table>
<thead>
<tr>
<th>Soil sample</th>
<th>Particle-size distribution (%)</th>
<th>Organic matter (g kg$^{-1}$)</th>
<th>Total nitrate (g kg$^{-1}$)</th>
<th>Total phosphorus (g kg$^{-1}$)</th>
<th>Total potassium (g kg$^{-1}$)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shen mu</td>
<td>Clay &lt; 0.002 (mm)</td>
<td>6</td>
<td>7.84</td>
<td>0.44</td>
<td>0.97</td>
<td>27.4</td>
</tr>
<tr>
<td></td>
<td>Silt &lt; 0.002–0.05 (mm)</td>
<td>30</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sand &lt; 0.05 (mm)</td>
<td>64</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Texture</td>
<td>Sandy loam</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
where \( \rho \) is the water density (g m\(^{-3}\)), \( g \) is the gravitational acceleration (m s\(^{-2}\)), \( J \) is the hydraulic gradient, and \( h \) is the average water depth over hillslope land (m).

Water flow depth in Eq. (4) can be solved from the kinematic wave equation according to the study by Guo (1998) with the combination of the Kostiakov (1932) infiltration equation. The Kostiakov equation is usually used to describe soil infiltration rate under stone cover condition (Zhang et al., 2011; Dang et al., 2012). For simplicity, the infiltration rate (I m s\(^{-1}\)) for hillslope is described as an average of values along the entire slope and the average infiltration time is \( t_0/2 \), such as:

\[
\begin{align*}
\frac{\partial h}{\partial t} + \frac{\partial q}{\partial x} &= -i \\
q &= \alpha h^b \\
i &= a \left( t - \frac{t_0}{2} \right)^{-b}
\end{align*}
\]  

(5)

where \( q \) is overland flow rate of the unit width per second (m\(^3\) (ms\(^{-1}\)), \( \alpha \) is conveyance factor that is determined by the overland slope, \( x \) is the distance of horizontal direction (m), \( m \) is an empirical exponent that varies between 3/2 to 3 (Woolhiser and Liggett, 1967), or equals to 2 (Eagleson, 1970), \( a \) and \( b \) are infiltration parameters, \( t_0 \) is the time required for water to flow from the inlet to the outlet. The water flow depth at the outlet can be solved as:

\[
h = \frac{a}{1-b} \left( t - \frac{t_0}{2} \right)^{1-b}
\]  

(6)

Combining Eqs. (2), (3), (4) and (6), the mixing depth can be expressed as:

\[
h_m = \int_{t_0/2}^{t} k_c k_d (pg)^{3/2} \left( \frac{a l}{1-b} \right)^{3/2} \left( t - \frac{t_0}{2} \right)^{3(1-b)/2} dt.
\]  

(7)

For simplicity, defined

\[
k_c = k_c (pg)^{3/2} \left( \frac{a l}{1-b} \right)^{3/2} \frac{5 - 3b}{2}
\]  

(8)

where \( k_c \) can be considered as a comprehensive mixing coefficient. Then the mixing depth can be expressed as follows:

\[
h_m = k_c \left( t - \frac{t_0}{2} \right)^{5(1-b)/2}.
\]  

(9)

Substitute Eq. (9) into Eq. (1), solute concentration in runoff can be expressed as:

\[
c_c = c_m \exp \left( \frac{3b - 5}{2} \ln \left( t - \frac{t_0}{2} \right) - \frac{2q_l}{k_c (\theta_i + \rho_s l)} \left( t - \frac{t_0}{2} \right)^{3b - 5} \right)
\]  

(10)

where \( c_c(t) \) is solute concentration in runoff (g m\(^{-3}\)), \( c_m \) is the solute concentration in the mixing depth before runoff (g m\(^{-3}\)).

### Table 2

Parameters needed in the model for all the treatments.

<table>
<thead>
<tr>
<th>Treatments</th>
<th>( t_0 ) (min)</th>
<th>( c_m ) (g m(^{-3}))</th>
<th>( a )</th>
<th>( b )</th>
<th>( v ) (m s(^{-1}))</th>
<th>( n ) (m(^{1.5}) s)</th>
<th>Re</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inflow rates (m(^3) (ms(^{-1}))</td>
<td>0.00016</td>
<td>2.88</td>
<td>1.144</td>
<td>1.9e-05</td>
<td>0.2</td>
<td>0.093</td>
<td>0.056</td>
</tr>
<tr>
<td></td>
<td>0.00028</td>
<td>1.952</td>
<td>1.141</td>
<td>2.8e-05</td>
<td>0.2</td>
<td>0.132</td>
<td>0.046</td>
</tr>
<tr>
<td></td>
<td>0.00038</td>
<td>1.61</td>
<td>1.142</td>
<td>3.6e-05</td>
<td>0.2</td>
<td>0.163</td>
<td>0.0395</td>
</tr>
<tr>
<td>Small stone cover (%)</td>
<td>2.5</td>
<td>2.183</td>
<td>1.144</td>
<td>3.15e-05</td>
<td>0.2</td>
<td>0.12</td>
<td>0.052</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>2.649</td>
<td>1.145</td>
<td>3.35e-05</td>
<td>0.2</td>
<td>0.098</td>
<td>0.071</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>2.955</td>
<td>1.142</td>
<td>3.4e-05</td>
<td>0.2</td>
<td>0.089</td>
<td>0.083</td>
</tr>
<tr>
<td>Large stone cover (%)</td>
<td>2.5</td>
<td>2.244</td>
<td>1.143</td>
<td>3.17e-05</td>
<td>0.2</td>
<td>0.116</td>
<td>0.0537</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>3.31</td>
<td>1.144</td>
<td>3.85e-05</td>
<td>0.2</td>
<td>0.078</td>
<td>0.102</td>
</tr>
<tr>
<td>S-4.03%, M-6%</td>
<td>2.7</td>
<td>2.77</td>
<td>1.144</td>
<td>3.75e-05</td>
<td>0.2</td>
<td>0.099</td>
<td>0.073</td>
</tr>
<tr>
<td>M-6%, L-4.03%</td>
<td>2.64</td>
<td>2.17</td>
<td>1.142</td>
<td>2.75e-05</td>
<td>0.2</td>
<td>0.1</td>
<td>0.0729</td>
</tr>
<tr>
<td>S-6.45%, M-1.5%, L-2.0%</td>
<td>2.42</td>
<td>2.55</td>
<td>1.144</td>
<td>2.55e-05</td>
<td>0.2</td>
<td>0.11</td>
<td>0.0647</td>
</tr>
</tbody>
</table>

S: small stone; M: medium-sized stone; L: large stone; Inflow rate for different stones is 0.00028 m\(^3\) (ms\(^{-1}\)).
To determine the infiltration parameters $a$ and $b$ in the Eq. (5) the water balance equation for the entire hillslope becomes:

$$I_s = Q_{in} - Q_{out} = \frac{al}{1 - b} \left( t_m - t_0 \right)^{1 - b}$$

(11)

where $I_s$ is the cumulative infiltration amount of the unit width ($\text{m}^3 \text{m}^{-1}$), $Q_{in}$ and $Q_{out}$ are the volumes of inlet and outlet water ($\text{m}^3 \text{m}^{-1}$), respectively, and $t_m$ is the water stop-time at the outlet (s).

The mathematical model described above is applied to the analysis of the movement of soil solute transport with overland flow detachment. Field experiments were conducted to verify soil solute in runoff.

The kinematic wave equation was adopted to numerically obtain the outflow rate (Eq. (5)) for verifying the infiltration parameters obtained above. The values of these parameters were substituted into the equations to calculate surface runoff. Iterative method was adopted to solve the kinematic wave equation, and the initial and boundary conditions were:

$$t = 0, h = 0, q = 0$$

(12)

$$x = 0, q = C$$

(13)

where $C$ is inflow rate, which is a constant ($\text{m}^3 \text{s}^{-1}$).

Potassium transport was simulated with the proposed model using the initial soil states listed in Table 2. The three uniform inflow rates of 0.00016, 0.00028, and 0.00038 ($\text{m}^3 \text{m}^{-1} \text{s}^{-1}$) simulated water scouring during the field experiment. Parameters characterizing soil properties, such as $\theta_0$ and $\rho_s$ used the measured values, where $\theta_0$ is 0.5 $\text{m}^3 \text{m}^{-3}$, $\rho_s$ is $1.31 \times 10^6 \text{g m}^{-3}$. The non-linear adsorption of potassium was parameterized using the Freundlich-isotherm equation:

$$C_a = kC^\beta$$

(14)

where $C_a$ is the concentration in the adsorbed phase ($\text{g g}^{-1}$), $k$ is the adsorption rate ($\text{m}^3 \text{g}^{-1}$), $C$ is the solute concentration in the aqueous phase ($\text{g m}^{-3}$), and $\beta$ is the Freundlich exponent.

During simulations we varied $k$ between 0.4 and $10 \times 10^{-6} \text{ (m}^3 \text{ g}^{-1})$ within 8 steps and allow $\beta$ to vary among the three values of 0.5, 0.8, and 1. As first step we assumed that adsorption was uniform in the entire domain and the parameter set that performed best was selected. Next we characterized adsorption behavior in the soil matrix by means of averaging the parameters $k = 3.34 \times 10^{-6} \text{ (m}^3 \text{ g}^{-1})$ and $\beta = 0.8$ (Klaus and Zehe, 2011; Yang et al., 2015).

During all simulated cases, we used an average value of 10.8° representing soil slope steepness for the 11 field plots. Parameters related to soil erosion and solute transport ($k_a$) were inversely estimated from the measured data (see the ‘Results’ section).

3. Materials and methods

3.1. Site description

The field experiment was conducted on a naturally fallowed loessial slope land in the Liudaogou catchment (38°46’–38°51’N, 110°21’–110°23’E; 1094–1274 m a.s.l.), 14 km west of the Shenmu Erosion and Environment Research Station of the Institute of Soil and Water Conservation, Chinese Academy of Sciences, in Shenmu County, Shaanxi Province, China. The area has a semiarid climate with a mean annual temperature of 8.6 °C and annual precipitation of 437 mm. Rain is often brief and intense, with approximately 70% of which falls during June to August. The soil is a sandy loam with sand, silt, and clay contents of 64, 30, and 6%, respectively. The mean bulk density for the top 50 cm is 1.31 $\text{g m}^{-3}$. The physical and chemical properties of the soil are listed in Table 1.

3.2. Experimental setup

Experimental field plots (16 m × 1.25 m) were established on a slope with an average gradient of 10.8° and fallowed with alfalfa (Medicago sativa) for seven years. The plots were weeded and leveled as much as possible with a spade and then rested for approximately two weeks to allow the soil to consolidate (Fig. 1). A solution of KH2PO4 mg L⁻¹ was sprayed on the soil surface at a rate of 0.075 kg m⁻². The transfer of soil nutrients to the runoff was investigated by steady-head water-scouring experiments at inflow rates of 0.00016, 0.00028, and
0.00038 m$^3$ (ms)$^{-1}$ for bare soil surfaces and with eight treatments of stone coverage: 2.5, 10, and 20% small stones, 2.5 and 10% large stones, 4.03% small stones combined with 6% medium-sized stones, 6% medium-sized stones combined with 4.03% large stones, and 6.45% small stones combined with 1.5% medium-sized stones and 2.02% large stones. The inflow water was supplied with a pump, and the inflow rate was controlled by a valve. The duration of water scouring for each treatment was 40 min. Surface runoff (overland flow) from each plot was collected every minute in plastic containers placed underground in the center of the outlet of the plot, and the runoff volume was determined with weighing method. The concentration of potassium in the runoff was analyzed by atomic absorption spectrophotometry (Perkin-Elmer 5100ZL).

### 3.3. Measurement of flow velocity

Water-velocity distribution and its influence on the spreading of solutes in both vertical and horizontal directions are important for field-scale solute transport. The flow velocity along slope land was measured with the dye-tracer (KMnO$_4$ solution) method (Fig. 2).

Each plot was divided into five sections from the top to the bottom of the plot, each with 3.2 m in length. KMnO$_4$ solution was injected into the top section. Time was recorded when the flow reached the end unit of plot, which was used to calculate the mean surface flow velocity (Fig. 2).

The profile average velocity ($v$) can be described with the mean surface flow velocity ($v_m$) by the relation of $v = av_m$, where the coefficient $a$ increases with Reynolds number from laminar flow to turbulent flow. A theoretical study gave the coefficient $a$ value of 0.67 (Abrahams et al., 1986; Gao et al., 2010). The profile velocity on slope land was then calculated and reported in Table 2.

Water flow velocities change under different surface covers water flow input from the inlet was disturbed and dissipated with surface conditions. Soil surface features were characterized with the Manning’s roughness coefficient, and were described using the equation below:

$$ q = \left( \frac{1}{n^{1/2}} \right)^{-2/3} \frac{v^{5/2}}{J} $$

where $n$ is Manning’s roughness coefficient (m s$^{-1/3}$) and $J$ is hydraulic gradient.

The value of Manning’s roughness coefficient was calculated based on Eq. (12), results indicated that $n$ increased with stone coverage as showed in Table 2.

The values of $Re$ indicated that it increased with inflow rates and stone coverage and $Re$ is usually adopted to describe dynamic features of overland flow on soil surface:

$$ Re = \frac{v h}{\nu} $$

The values of $Re$ under different surface coverages were listed in Table 2.

### Table 3

Numerical solution of kinematic wave equation evaluated by the NS, $Re$ and $R^2$, and NS, $Re$ and $R^2$ represent the errors of outflow rates.

<table>
<thead>
<tr>
<th>Treatments</th>
<th>NS</th>
<th>Re</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare land</td>
<td>0.92</td>
<td>0.023</td>
<td>0.9</td>
</tr>
<tr>
<td>S - 20%</td>
<td>0.99</td>
<td>0.005</td>
<td>0.99</td>
</tr>
<tr>
<td>L - 2.5%</td>
<td>0.81</td>
<td>0.036</td>
<td>0.84</td>
</tr>
<tr>
<td>S - 4.03%, M - 6%</td>
<td>0.91</td>
<td>0.016</td>
<td>0.94</td>
</tr>
</tbody>
</table>

S: small stone; M: medium-sized stone; L: large stone.
3.4. Calibration and validation

For validation purposes, we compared the measured and modeled soil surface runoff \( (q) \), potassium concentration \( (c) \) at the mixing depths \( (h_m) \) of each treatment along the Loess Plateau hillslope. Literature and measured values for soil parameters were used to derive the initial values for the calibration process. We selected surface runoff for calibration. With the obtained infiltration parameters, numerical method were adopted to solve the kinematic wave equation (Eq. (5)) to calculate the surface runoff \( (q) \), and compared with the measured data.

If the calculated and measured surface runoff data were in good agreement, it means that the model can be used for prediction. After the calibration, three sets available values of stone-size combination coverage (the first one is 4.03% small-size and 6% medium-sized, second one is 6% medium-sized and 4.03% large-size, and the third one is 6.45% small-size, 1.5% medium-sized, and 2.02% large-size) were adopted to calculate potassium concentration and mass in the runoff for comparison with observed data to validate the model.

3.5. Data analysis

The Nash Sutcliffe coefficient of efficiency \( (NS) \) (Nash and Sutcliffe, 1970), relative error \( (RE) \) and the coefficient of determination \( (R^2) \) were used to evaluate the model performance:

\[
NS = 1 - \frac{\sum_{i=1}^{n} (o_i - p_i)^2}{\sum_{i=1}^{n} (o_i - \bar{o})^2}
\]
\[
RE = 1 - \frac{\sum_{i=1}^{n} |o_i - p_i|}{\sum_{i=1}^{n} |o_i|}
\]
\[
R^2 = 1 - \frac{\sum_{i=1}^{n} (o_i - p_i)^2}{\sum_{i=1}^{n} (o_i - \bar{o})^2}
\]

where \( o_i \) is the observed value at time \( i \), \( p_i \) is the predicted value at time \( i \), and \( \bar{o} \) is the mean observed value over time, \( NS \) is a descriptor of the predictive accuracy of model outputs, which ranges from \( -\infty \) to 1. The \( RE \) indicates that the model under- or over-estimates the observed data, and \( R^2 \), the square of the linear correlation coefficient, indicates the agreement between the predicted and observed values. Ideally, \( NS \) close to 1, \( RE = 0 \) and \( R^2 = 1 \). The bias was calculated as an indicator for any systematic or structural deviation of the model (Windhorst et al., 2014).

4. Results and discussion

4.1. Simulated and observed surface runoff

Fig. 3 presents the observed surface runoff with different inflow rates and stone covers. It showed that the surface runoff increased with inflow rate (Fig. 3a). The accumulative runoff water at the outlet for inflow rates of 0.00016, 0.00028, and 0.00038 m³ (ms)⁻¹ were 0.204, 0.409, and 0.575 m³ m⁻¹, accounting for 40.5, 45.9, and 48.4%, respectively, of the inflow water volume.

Surface runoff under different stone coverage was shown in Fig. 3b–c. It decreased as stone coverage and size increased (Fig. 3b–c). The total surface runoff was 0.385, 0.361, 0.342 m³ m⁻¹ (accounting for 54, 50, and 47.4% of the inflow water), respectively, for small stones at coverage of 2.5, 10, and 20%. Similarly, surface runoff was 0.384 and 0.325 m³ m⁻¹ (accounting for 54.3 and 44.7%), respectively, for the large stones at coverage of 2.5% and 10%.

Our research further indicated that at 10% coverage, a combination of 10% large stones, 6% small stones and 4% medium-sized stones could reduce surface runoff most effectively, which can be attributed to the increased depression storage and surface detention by stone covers on the soil surface, especially for large stones or the combination of stone sizes (Guo et al., 2010). Our observation showed that surface runoff developed quickly in all of the water-scouring treatments. The bare soil with an inflow rate of 0.00028 m³ (ms)⁻¹ had the quickest response to water scouring, and 10% coverage with large stones at the same inflow rate of 0.00028 m³ (ms)⁻¹ had the slowest response. The stones covers could thus delay the initiation of surface runoff.

Acknowledging the general suitability of the kinematic wave equation to delineate the prevailing flow pattern, the amount of the incoming water can be divided into main flow components: ponding water (flow depth), infiltration water and surface runoff. The infiltration parameters \( (a \) and \( b \) determined by Eq. (11) (Table 2) indicated that \( a \) increased with stone coverage. Soil infiltration thus increased with the amount of soil surface covered with stones. Parameter \( b \) was the same for all treatments.

The outflow rate were numerically obtained and compared with the experimental outflow rate for (i) bare land, (ii) 20% small stones, (iii) 2.5% large stones, and 4.03% small stones combined with 6% medium-

Fig. 5. Potassium concentration in the runoff over time: (a) different inflow rates and (b) different stone sizes, coverage (%) and (c) large stone at coverage of 10% and combinations of different stone sizes.
Fig. 6. Curve fitting of potassium transport into runoff: (a) inflow rate is 0.00016 m$^3$ (ms)$^{-1}$, (b) inflow rate is 0.00028 m$^3$ (ms)$^{-1}$, (c) inflow rate is 0.00038 m$^3$ (ms)$^{-1}$, (d) small stone coverage is 2.5%, (e) small stone coverage is 10%, (f) small stone coverage is 20%, (g) large stone coverage is 2.5%, and (h) large stone coverage is 10%.

Table 4
The values of $k_e$ for three inflow rates and five kinds of stone covers.

<table>
<thead>
<tr>
<th>Treatments</th>
<th>Inflow rates (m$^3$ (ms)$^{-1}$)</th>
<th>Small stone coverage (%)</th>
<th>Large stone coverage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.00016</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>0.00028</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>0.00038</td>
<td>20</td>
<td>20</td>
</tr>
</tbody>
</table>

$k_e$ 10.6 16 28 21 18 15 16 13
sized stones to test the accuracy of obtained parameters. The simulated surface runoff generally agreed well with the observations (Fig. 4). The linear correlations between the calculated and observed values were equally good, and are listed in Table 3.

4.2. Potassium transport under different inflow rates and stone covers

The effects of inflow rate and stone cover on potassium transport to the runoff are shown in Fig. 5. Potassium concentration in the runoff water decreased as the inflow rate increased (Fig. 5a). Potassium concentration tended to decrease with time for different stone covers (Fig. 5b–c). During the initial runoff stage, potassium concentrations decreased more rapidly with stone covers than with inflow rates. The K concentrations in the runoff were much higher for stone covers than for bare soil, even at higher inflow rates, which was attributed to the fact that stone covers decreased the surface runoff, and the higher concentrations may have been caused by the lower amount of runoff water, as well as reduced overland flow velocity due to the presence of stones on the soil surface, carrying more potassium to the runoff. The runoff rate stabilized after nearly 15 min, and potassium concentrations in the runoff reached a steady state after about 20 min in all treatments.

4.3. Comparisons between simulated and observed potassium concentrations and mass in surface runoff

Fig. 6 presents the observed potassium concentrations curve fitted with the model for different inflow rates and stone covers. The comprehensive mixing coefficient ($k_e$), which reflects the effects of surface conditions and water-flow dynamics on the transfer of soil solute, was inversely estimated through curve fitting to the observed potassium concentrations (Table 4). Stones on soil surface could decelerate flow velocity, and consequently reduce soil sediment load in the overland flow. The value of $k_e$ increased with inflow rate but decreased with stone coverage, perhaps because a higher inflow rate increased the water shear stress, detaching more surface soil and mixing it with the overland flow. The values of $Re$ increased with inflow rates and stone coverage. The variation of $k_e$ can be expressed with $Re$ which usually assess the dynamic features of overland flow under different conditions (Table 2). Under the experimental conditions of this study, $k_e$ values were a linear function of $Re$:

$$k_e = 0.172Re - 0.145$$

As depicted in Fig. 7, the value of $k_e$ can be estimated by Eq. (20) with the given of $Re$ values. Substituting $k_e$ values into Eq. (10), the potassium concentrations in runoff can then be calculated.

Three sets of stone cover combinations were used to further test the applicability and feasibility of the model by predicted potassium concentrations and cumulative mass. Comparisons between the calculated potassium concentrations and the observed data are shown in Fig. 8. It

### Table 5

Model performance assessed by the $NS$, $RE$ and $R^2$; $NS$, $RE$ and $R^2$, represent errors of potassium concentration and cumulative potassium mass in runoff, respectively.

<table>
<thead>
<tr>
<th>Treatments</th>
<th>$NS$</th>
<th>$RE$</th>
<th>$R^2$</th>
<th>$NS$</th>
<th>$RE$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-4.03%, M-6%</td>
<td>0.98</td>
<td>0.067</td>
<td>0.99</td>
<td>0.72</td>
<td>0.16</td>
<td>0.99</td>
</tr>
<tr>
<td>M-6%, L-4.03%</td>
<td>0.91</td>
<td>0.066</td>
<td>0.93</td>
<td>0.76</td>
<td>0.13</td>
<td>0.99</td>
</tr>
<tr>
<td>S-6.45%, M-1.5%, L-2.02%</td>
<td>0.97</td>
<td>0.035</td>
<td>0.98</td>
<td>0.96</td>
<td>0.07</td>
<td>0.99</td>
</tr>
</tbody>
</table>

S: small stone; M: medium-sized stone; L: large stone.
can be seen that the calculated potassium concentrations matched well with the measured data. The performance of model predictions was evaluated based on the goodness-of-fit criteria Nash Sutcliffe efficiency (NS), the coefficient of determination ($R^2$) and the relative errors (RE). The coefficients for model performance are shown in Table 5. The simulated cumulative potassium mass was also compared with the observed data. As shown in Fig. 9, predicted data slightly deviated from the 1:1 line.

The good performance of model prediction for both K concentration and mass reveals that the obtained relationship between $k_e$ and $R_e$ was reasonable, and indicates that the proposed mathematical model may be used to describe the transfer of soil nutrients to overland runoff under water scouring conditions.

4.4. Variation of mixing depth for different treatments

The mixing depth ($h_m$) is useful value for approximately estimating potential solute transport from soil to overland flow. $h_m$ increased most slowly at the inflow rate of 0.00016 m$^3$ (ms)$^{-1}$ (Fig. 10). In contrast, the mixing depth increased much faster at the inflow rate of 0.00038 m$^3$ (ms)$^{-1}$, perhaps because the higher inflow rate detached more surface soil due to the higher water-shear stress. At the inflow rate of 0.00028 m$^3$ (ms)$^{-1}$, $h_m$ was lower for stone-covered surfaces than bare land, indicating that the stones protect soil particles from becoming detached by the overland flow.

Stone coverage and stone size affected $h_m$ differently. $h_m$ was only slightly lower for the bare land than for the surface with a 2.5% coverage of small stones. Fig. 10 shows the calculated mixing depth for the bare soil and the surface with stone cover when the inflow rate was fixed at 0.00028 m$^3$ (ms)$^{-1}$. The results suggested that $h_m$ was lower for the stone covered surface than that of the bare soil, indicating that stone cover could protect soil particles from detaching by overland flow.

Both stone coverage (%) and stone size have their respective effect on $h_m$. When the soil surface was covered with small-sized stones at 2.5% coverage, $h_m$ was only slightly lower than that of the bare soil, and the difference was not significant. When large-sized stones was used at 2.5% coverage, $h_m$ was lower than that of the 2.5% small-sized stone cover. Actually $h_m$ for the 2.5% large-sized stone cover was very close to that of the 20% small-sized stone cover, as well as that of the 10% stone combination cover (6% of medium-sized stone and 4% of large-sized stone) $h_m$ started to decrease as the coverage of large stones was great as 10%. The trend was the same when the combined coverage was great as 10% (4.03% small stones and 6% of medium-sized stones), and when the small-sized stone coverage was great as 20%.

The tendency of $h_m$ to increase was less when the coverage of small stones was increased to 20%. $h_m$ has often been studied as an important variable for estimating solute transport to overland flow. At the same inflow rate in our study, increasing stone coverage decreased $h_m$.

![Fig. 9. Observed vs predicted potassium cumulative mass: (a) 4.03% small stones (S), 6% medium-sized stones (M), (b) 6% M and 4.03% large stones (L), and (c) 6.45% S, 1.5% M, and 2.02% L.](image1)

![Fig. 10. The variation of mixing depth over time at the outlet for all the treatments.](image2)
Furthermore, with the same stone coverage and a steady inflow rate, the combination of small and medium-sized stones prevented the water flow from detaching soil particles better than the other stone combinations. Our proposed the expression of $h_m$ differed from those of previous studies (Ahuja et al., 1981; Havis et al., 1992): $h_m$ varied over time rather than being constant.

5. Conclusions

In this study a simple model based on comprehensive analysis was developed to predict soil solute transport from soil to overland runoff. The model was tested using experimental data from field plots on loessial slope land under various inflow rates and stone cover conditions. Surface runoff decreased as stone coverage (%) and stone size increased. The infiltration parameters obtained from the kinematic wave equation together with experimental data were verified by numerical method. Potassium concentrations in the runoff in the treatments decreased as the inflow rate increased but as the stone coverage decreased. Model parameters such as the comprehensive mixing coefficient, $k_m$, increased linearly with the $Re$. This relationship was further verified by replacing $k_m$ with $Re$ in the proposed solute transport model. The calculated potassium concentration matched well to the predicted values by the model using $k_m$ and $Re$. The proposed method also allows the estimation of the mixing depth ($h_m$) under various treatments.

In summary the model provides means of estimating nutrient loss from soil to runoff, which can help to develop water and fertilizer management practices to efficiently minimize fertilizer loss and protect surface water quality.

Acknowledgments

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References