A physically-based model for dissolved pollutant transport over impervious surfaces

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Abstract:

Dissolved pollutant transport over the ground surface is one of the main contributors to water pollution in urban environment. However, existing widely applied transport models are semi-empirical and the mechanism of the dissolved pollutant runoff is still not well understood. A novel physically-based transport model for dissolved pollutant is herein proposed by adopting a “control layer” concept in the overland flow. This transport model assumes that the dissolved pollutant in the upper runoff water is completely mixed with that in the underneath control layer. To verify the proposed model, a series of laboratory experiments were conducted. It showed that the predictions made by the model are in good agreement with the experimental results. The depth of the control layer is mainly correlated with the bed slope and shows no obvious dependence on rainfall intensity. The minimum depth of the control layer is bounded by a limiting value. In addition, the maximum pollutant transport rate is found to occur at the time of concentration. The rainfall intensity, bed slope, surface roughness and catchment length are dominant factors that control the dissolved pollutant transport. The wash-off coefficient is a function of time and is found to be the reciprocal of the average water depth of the catchment area over which the equilibrium state has been reached. This study advances the understanding of the mechanism of the dissolved pollutant transport in urban environment.

Keywords: Dissolved pollutant; Rainfall simulation; Wash-off coefficient; Rainfall runoff; Transportation of pollutants.

1 Introduction

Pollutants originating from urban impervious surfaces, such as roads and squares, have been recognized as a major contributor to the deterioration of water quality (Brezonik and Stadelmann, 2002; Angela et al., 2019; Lee and Bang, 2000; Vaze and Chiew, 2002). It has been predicted that 64% of the "developing world" and 86% of the "developed world" will be urbanized by 2050 (Montgomery, 2008). The ongoing urbanization will inevitably further exacerbate the urban storm water pollution (Wang et al., 2013). In this context, understanding the mechanism of pollutant transport on impervious surfaces is essential for developing more advanced pollution management strategies (Hong et al., 2016).

Among the various substances that make up of urban stormwater pollutants, solid particles are widely considered as a major cause of contamination in receiving water (Fletcher et al., 2013). Most of the stormwater-generated pollutants are deemed to be adsorbed onto solid particles, especially the fine particles (Sartor and Boyd, 1974; Sheng et al., 2008). Therefore, most of the existing studies have focused on the particulate matter transport process by stormwater, and a number of transport models have been developed in the past (Metcalf and Eddy Inc, 1971; Sartor and Boyd, 1974; Alley, 1981; Charbeneau and Barrett, 1998; Irish et al., 1998; Osuch-Pajdzińska and Zawilski, 1998; Deletic et al., 2000; Kim et al., 2005; Shaw et al., 2006; Egodawatta et al., 2007, 2009; Massoudieh et al., 2008; Hong et al., 2016; Muthusamy et al., 2018). Many transport models were based on the assumption that the rate of pollutant transport from an effectively impervious surface is directly proportional to the mass of the remaining pollutant (Metcalf and Eddy Inc, 1971; Sartor and Boyd, 1974; Charbeneau and Barrett, 1998; Egodawatta et al., 2007, 2009; Muthusamy et al., 2018). In the earlier studies, the exponential transport model has thus been widely applied to the particulate pollutant transport process over impervious surfaces.

In practice, stormwater-borne pollutants can also appear in the dissolved phase as well as in the particulate phase (Sheng et al., 2008; Hong et al., 2017). The contribution from the dissolved pollutants to water pollution can be significant (Miguntanna et al., 2013). Goonetilleke et al. (2005) indicated that much of the pollutants transported were in the dissolved form and the common management technique of targeting particulate pollutants in urban stormwater quality control could have only limited efficiency. The difference in the transport of dissolved and particulate pollutants can be largely due to their different physical and chemical properties. Gauta et al. (2019) noted that the accuracy of the exponential transport model was clearly best for particulate pollutants, but might not be appropriate for dissolved pollutants. Xiao et al. (2016, 2017) conducted a series of experiments to investigate the transport process of dissolved pollutants over impervious surfaces, and a mathematical transport model was developed by combining the analytical equations for overland flows and the exponential equation for the pollutant wash-off. They suggested that both dissolved and particulate pollutants obey the exponential transport law. The difference in the transport of dissolved and particulate pollutants can be significant, which is reflected in the value of the wash-off coefficient k. The wash-off coefficient k, with units m^{-1}, is a key parameter for the exponential transport model (Alley, 1981; Egodawatta et al., 2007; Soonthornnonda et al., 2008). The value of k may vary with the rainfall intensity, pollutant type and the physical characteristics of the catchment (Alley, 1981; Millar, 1999). Although the exponential equation has been widely used in many water quality models, such as the SWMM model, it still belongs to a class of semi-empirical models as the wash-off coefficient k is an empirical parameter with no direct physical meaning (Egodawatta et al., 2007). However, for the dissolved pollutant, Zhang et al. (2018) suggested that the wash-off coefficient k may be related to the water depth and thus be assigned a physical meaning. Their study focused on the solute transport over vegetated impervious surfaces, and the idea of the "stationary water layer" was proposed according to the experimental results. In this study, the "stationary water layer" theory will be extended to describe the mechanism of dissolved pollutant transport over impervious surfaces.

Our objective is to develop and validate a novel physically-based model for predicting the transport process of dissolved pollutants over impervious surfaces, which may help advance our understanding of stormwater wash-off phenomena. To achieve this, the "stationary water layer" theory (Zhang et al., 2018) is coupled with the analytical equations for overland flows (Stephenson and Meadows, 1986). To validate the newly established model, a series of laboratory experiments, involving different rainfall intensities and bed slopes, have been conducted using rainfall simulators over uniform-sloped idealized rectangular catchments.

2 Mathematical model

In this study, only uniform and steady rainfall events are considered. For a uniform and steady rainfall distributed over a rectangular homogeneous impervious catchment with a uniform slope, an analytical solution to the kinematic wave equation has been derived by Stephenson and Meadows (1986). The analytical solution can be described as follows:

$$t_c = \left[L \big/ \left(\alpha I^{m-1} \right) \right]^{1/m} \tag{1}$$

$$q_t = \alpha \left(h \right)^m = \alpha \left(It \right)^m \ , \ 0 \le t \le t_c \tag{2}$$

$$q_t = \alpha \left(h \right)^m = \alpha \left(It_c \right)^m = LI \ , \ t_c \le t \le T \tag{3}$$

$$q_t = LI - I^m \alpha^{1/m} q_t^{1-1/m} \left(t - T \right) \ , \ T \le t \tag{4}$$

$$Q_t = q_t B \tag{5}$$

where, t is the time (s); t_c is the time of concentration (s); T is the rainfall duration (s); I is the rainfall intensity (m/s); L is the length of the watershed (m); B is the width of the watershed (m); q_t is the discharge per unit width which is equal to the product of velocity and water depth (m^2/s); Q_t is the flow rate (m^3/s); h is the water depth (m); α and m are two coefficients which can be derived from the Manning equation as follows.

$$\alpha = S_0^{1/2} \big/ n ; \ \ m = 5/3 \tag{6}$$

where n is the Manning roughness coefficient and S_0 is the bed slope.

The time needed to reach the equilibrium outflow rate at the end of the catchment is referred to as the time of concentration (t_c), which can be roughly taken as the time required for a raindrop to move from the top of the slope to the outlet (Liang et al., 2015). At the equilibrium stage, the constant maximum runoff rate can be calculated as:

$$Q_{\max} = LBI \tag{7}$$

where $Q_{\max}$ is the maximum or equilibrium flow rate (m^3/s).

According to Zhang et al. (2018), some logical assumptions can be made regarding the rainfall-runoff process: (a) it takes the time t_{cx} for the flow at a location x on the catchment to reach the equilibrium state, after which the flow at this location remains constant; and (b) the flow is uniform with a constant water depth, flow rate $Q(x,t)$ and velocity $v(x,t)$ downstream of the location x at time t_{cx}. Under these assumptions, the values of $v(x,t)$ and $Q(x,t)$ can be derived as:

$$v(x,t) = \frac{dx}{dt} = \frac{dQ(x,t)}{BIdt} \quad , \quad 0 \le t \le t_{cx} \tag{8}$$

$$v(x,t) = v(x,t_{cx}) \quad , \quad t_{cx} \le t \tag{9}$$

$$v(x+a,t_{cx}) = v(x,t_{cx}) \quad , \quad 0 \le a \le L-x \tag{10}$$

$$Q(x+a,t_{cx}) = Q(x,t_{cx}) = xBI \quad , \quad 0 \le a \le L-x \tag{11}$$

According to Eqs. (1) and (6), the formulation of t_{cx} can be written as:

$$t_{cx} = \left[x/\left(\alpha I^{m-1}\right)\right]^{1/m} = \left[x/\left(\alpha I^{2/3}\right)\right]^{3/5} \tag{12}$$

Combining Eqs. (2), (5), (6), and (8), we can obtain the formulation for $v(x,t)$:

$$v(x,t) = \frac{5}{3}\alpha\left(It\right)^{2/3} \quad , \quad 0 \le t \le t_{cx} \tag{13}$$

In studying the transport of solute on soil slopes, many previous researchers (Ahuja et al., 1981; Gao et al., 2004, 2005; Deng et al., 2005) suggested that a “thin layer” (the so-called mixing layer, exchange layer or active layer) near the soil surface controls the transfer of pollutants between the soil slope and the overland flow. As for vegetated surfaces, Zhang et al. (2018) suggested that the rainwater accumulates in the catchment to form a thin stationary water layer at the onset of the rainfall. Meanwhile, the pollutant begins to dissolve in this stationary water layer. After the beginning of overland flow, the pollutant in the stationary water layer gets gradually diffused into the upper runoff layer and then flows out of the catchment. Similarly, we assume that there is a thin water layer dominating the dissolved pollutant transport over impervious surfaces. We define this thin water layer as the "control layer". For an homogeneous catchment, the depth of this control layer at a location is regarded to be a constant. At the beginning of overland flow ($t = \mathbf{0}$), the depth of the control layer is defined as h_0 (m). Compared with the soil slope and vegetated surface, the impervious surface allows the more rapid mixing of the water in the control layer with the upper runoff water. Hence, the mixing layer theory (Ahuja et al., 1981) can be applied to the control layer. Applying the mixing layer theory, we assume that pollutant concentration in the upper runoff water is equal to that in the underlying water in the control layer.

As in many previous studies (Gao et al., 2004, 2005; Deng et al., 2005; Kim et al., 2005; Muthusamy et al., 2018), the dissolved pollutant is assumed to be uniformly distributed on the catchment surface before the start of rainfall. Hence, the initial pollutant concentration can be calculated to be:

$$C_0 = \frac{W_0}{BLh_0} = \frac{W_0}{Ah_0} \tag{14}$$

where C_0 is the initial runoff pollutant concentration (g/L); W_0 is the initial mass of pollutant on the surface (kg); and A is the area of catchment (m^2).

The water depth h along the catchment can be expressed as follows:

$$h\left(x, t\right) = h_0 + It \quad , \quad 0 \le t \le t_{cx} \tag{15}$$

$$h\left(x, t\right) = h_0 + It_{cx} \quad , \quad t_{cx} < t \tag{16}$$

At time t ($0 \le t \le t_c$), the raindrops move from the top edge of the catchment to location x. According to Eq. (13), the value of x can be calculated as follows:

$$x = \int_0^t v\left(x, t\right) dt = \int_0^t \frac{5}{3} \alpha \left(It\right)^{2/3} dt = \alpha I^{2/3} t^{5/3} \tag{17}$$

According to Eq. (11), the runoff rates from the top boundary of the catchment, $x = 0$, to x have reached the equilibrium state and the runoff rates from x to the bottom of the catchment $x = L$ are equal to the runoff rate at location x. From the analysis of Zhang et al. (2018), the amount of water and pollutant flowing out of the catchment at t ($0 \le t \le t_c$) depends only on the processes taking place in the catchment upstream of x. When the raindrops move from the top edge of the catchment to x, the pollutant is also transported to x. Taking into account the effect of diffusion, we assume that the pollutant concentration from 0 to x is uniform at the time of t_{cx}. The total water volume from 0 to x at time t can be calculated to be:

$$V\left(x, t\right) = \int_0^x Bh\left(x, t\right) dx = B\alpha I^{2/3} t^{5/3} \left(h_0 + \frac{5}{8} It \right) \tag{18}$$

The pollutant concentration at the outlet at time t is defined as C_t (g/L). According to the above hypothesis, the pollutant concentration from 0 to x is equal to C_t. During a tiny interval of Δt, the runoff moves forward by a small distance of

Δx:

$$\Delta x = v\left(x, t\right)\Delta t = \frac{5}{3}\alpha\left(It\right)^{2/3}\Delta t \tag{19}$$

It means that over the area from 0 to $x{+}\Delta x$ the runoff has reached an equilibrium state. We define the increase in the pollutant concentration as ΔC_t (g/L) during Δt. In this small duration of Δt, from Eq. (17), the volume of rainfall input from 0 to $x{+}\Delta x$ can be calculated by:

$$V_{rain} = \left(x + \Delta x\right) BI\Delta t = B\alpha I^{5/3}\left(t + \Delta t\right)^{5/3}\Delta t \tag{20}$$

The increase in the amount of pollutant ΔW can be expressed as follows.

$$\Delta W = \frac{\Delta x W_0}{L} = \frac{5W_0}{3L}\alpha\left(It\right)^{2/3}\Delta t \tag{21}$$

According to the law of conservation of mass of the solute, we can obtain the following equation during the period from t to $t + \Delta t$.

$$C_t V\left(x, t\right) + \Delta W = \left(C_t + \Delta C_t\right)\left(V\left(x + \Delta x, t + \Delta t\right) + V_{rain}\right) \tag{22}$$

Combining Eqs. (18), (19), (20), (21), and (22), we obtain:

$$\begin{aligned} &C_t B\alpha h_0 I^{2/3} t^{5/3} + \frac{5}{8} C_t B\alpha I^{5/3} t^{8/3} + \frac{5W_0}{3L}\alpha\left(It\right)^{2/3}\Delta t = C_t B\alpha h_0 I^{2/3}\left(t + \Delta t\right)^{5/3} + \\ &\frac{5}{8} C_t B\alpha I^{5/3}\left(t + \Delta t\right)^{8/3} + \Delta C_t B\alpha h_0 I^{2/3}\left(t + \Delta t\right)^{5/3} + \frac{5}{8}\Delta C_t B\alpha I^{5/3}\left(t + \Delta t\right)^{8/3} + \\ &\qquad C_t B\alpha I^{5/3}\left(t + \Delta t\right)^{5/3}\Delta t + \Delta C_t B\alpha I^{5/3}\left(t + \Delta t\right)^{5/3}\Delta t \end{aligned} \tag{23}$$

In the above Eq. (23), the terms of $\left(t + \Delta t\right)^{5/3}$ and $\left(t + \Delta t\right)^{8/3}$ can be approximated using the first order Taylor expansion:

$$\left(t + \Delta t\right)^{5/3} = t^{5/3} + \frac{5}{3} t^{2/3}\Delta t + R_1\left(\Delta t\right) \tag{24}$$

$$\left(t + \Delta t\right)^{8/3} = t^{8/3} + \frac{8}{3} t^{5/3} \Delta t + R_1\left(\Delta t\right) \tag{25}$$

where $R_1\left(\Delta t\right)$ represents the higher-order small terms. Combining Eqs. (23), (24), and (25) and neglecting the second order small terms, Eq. (23) can be converted into a differential equation.

$$\frac{dC_t}{dt} = -C_t \frac{5h_0 + 8It}{3t\left(h_0 + 5It/8\right)} + \frac{5W_0}{3At\left(h_0 + 5It/8\right)} \tag{26}$$

Unfortunately, there is no analytical solution to the above differential equation. Hence, the modified Euler method with second order accuracy is used to solve the above differential equation. This modified Euler method consists of a predictor step and a corrector step in each time advancement:

Predictor step: $$C^p = C_t + \Delta t \frac{dC_t}{dt} \tag{27}$$

Corrector step: $$C^c = C_t + \Delta t \frac{dC^p}{dt} \tag{28}$$

$$C_{t+\Delta t} = \frac{C^c + C^p}{2} \tag{29}$$

where p and c denote the predictor and corrector steps respectively, Δt is the time step. The initial pollutant concentration ($t = 0$) can be calculated by Eq. (14). The values of subsequent concentrations can then be obtained successively once the given number time steps is reached.

At the time of concentration t_c, the raindrops falling at the top of the catchment arrives at the outlet, which means that the flow on the whole catchment has reached an equilibrium state. After that, the whole catchment contributes to the runoff rate and pollutant discharge at the outlet. At this equilibrium state, the runoff rate at the outlet is equal to the rainfall input and the pollutant concentration is uniformly distributed over the whole catchment. Then, the total water volume V_T on the whole catchment has reached its maximum value and keeps unchanged, which can be derived by making use of Eqs. (12), (15) and (16).

$$V_T = \int_0^L Bh\left(x,t\right) dx = A\left(h_0 + \frac{5}{8}\left(IL/\alpha\right)^{3/5}\right) \tag{30}$$

During a tiny time interval of Δt, the volume of rainfall input to the whole catchment can be calculated as:

$$V_{rain} = BIL\Delta t \tag{31}$$

According to the conservation of mass of the solute, we can obtain the following relationship from t to $t + \Delta t$ ($t_c \le t$).

$$C_t V_T = \left(C_t + \Delta C_t\right)\left(V_T + V_{rain}\right) \tag{32}$$

Combining Eqs. (30), (31) and (32) and neglecting the second-order small terms, the above equation can be converted into a differential form:

$$\frac{dC_t}{C_t} = -\frac{Idt}{h_0 + \frac{5}{8}\left(IL/\alpha\right)^{3/5}} \tag{33}$$

Integrating Eq. (33) and applying the initial condition yield:

$$C_t = C_{t_c} e^{-I\left(t-t_c\right)\Big/\left(h_0 + \frac{5}{8}\left(IL/\alpha\right)^{3/5}\right)} \tag{34}$$

Here, C_{t_c} is the solute concentration at t_c, which can be obtained using the aforementioned modified Euler method.

3 Model verification

3.1 Laboratory experiments

To verify the model established in this study, a series of laboratory experiments were conducted in a rainfall-simulation hall. A large quantity of data was obtained in a relatively short period of time with the use of the rainfall simulator and a small idealized catchment. Details of the rainfall-simulation chamber can be found in previous studies (Xiao et al., 2017; Zhang et al., 2018). As mentioned before, this study focuses on the dissolved pollutant transport that accompanies the runoff flow over impervious surfaces. Similar to that in Xiao et al. (2017), a wooden board of 2.96 m in length, 1.48 m in width and 0.02 m in thickness was used to represent the impervious surface. It should be noted that the wooden board used in this study is the same as the smooth board used in Xiao et al. (2017). The main reasons for choosing the wooden boards are: (a) they are light and easy to handle and (b) they are not easy to deform. As to the dimensions of wooden board, i.e. the length and width, they are determined by the size of steel flume (3 m × 1.5 m) that accommodates the board in the rain simulation hall. The steel flume that holds the board facilitates the adjustment of the catchment slope and the collection of runoff samples. The thickness of wooden board has no effect on the experimental results, as long as the wooden board’s deformation is small in the experiment. As in the previous studies (Deng et al., 2005; Xiao et al., 2017; Zhang et al., 2018), sodium chloride (table salt) was chosen as the tracer to represent the pollutant. According to previous studies (Gao et al., 2004, 2005;

Deng et al., 2005; Kim et al., 2005; Egodawatta et al., 2007; Muthusamy et al., 2018) over small catchments, the pollutant can usually be considered as uniformly distributed. Hence, salt was uniformly spread on the catchment surface at the beginning of each experiment. The total amount of table salt in each experiment was fixed at 125 g. In contrast to the previous study (Xiao et al., 2017), a wider range of slopes and rainfall intensities were tested in this study, as listed in Table 1. Each rainfall event lasted for 28 minutes. For each experiment, the average rainfall intensity was measured, as shown in Table 1. In Table 1, S0.5-1 refers to 0.5° slope, test case 1, and similar convention applies to the names of the other test cases. The detailed information about sample collection and data recording of the runoff water and pollutant can be found in Xiao et al. (2017).

Table 1 Test cases and its measured rainfall intensity

Test case	I (mm/h)	Test case	I (mm/h)	Test case	I (mm/h)	Test case	I (mm/h)
S0.5-1	24.22	S1-7	138.96	S3-1	24.26	S4-4	79.29
S0.5-2	43.16	S2-1	20.76	S3-2	47.10	S4-5	106.93
S0.5-3	63.81	S2-2	41.72	S3-3	60.64	S4-6	117.52
S0.5-4	76.34	S2-3	62.61	S3-4	78.91	S4-7	146.61
S1-1	22.36	S2-4	83.99	S3-5	112.35	S5-1	41.92
S1-2	43.25	S2-5	99.63	S3-6	125.51	S5-2	80.75
S1-3	51.12	S2-6	110.59	S3-7	143.86	S5-3	119.83
S1-4	82.06	S2-7	119.92	S4-1	22.03	S6-1	46.61
S1-5	109.48	S2-8	139.91	S4-2	48.21	S6-2	87.76
S1-6	127.83	S2-9	149.75	S4-3	53.43	S6-3	131.55

3.2 Determination of parameters

Apart from the two parameters that define the test cases, i.e. the catchment slope and rainfall intensity, the depth of the control layer h_0 and the Manning roughness coefficient n play important roles in our model. As the transport of dissolved pollutant is closely related to the overland flow process, an accurate quantification of the overland flow process is essential for predicting the transport of dissolved pollutant. According to Eq. (2) and Eq. (6), the parameters α and n are interrelated and thus only one of them is needed for describing the rainfall-runoff process. Xiao et al. (2017) directly determined the value of α for each slope by numerically fitting the initial rising limb of the runoff hydrograph using Eq. (2). The identical boards with the same slope took the same value of α. According to Eq. (6), the values of n for different slopes can be obtained. Therefore, the values of Manning roughness coefficient n varied with the slope in their study. Xiao et al. (2017) noted that the variation may be due to the flow being not entirely hydraulically rough. From the available experimental data, it is difficult to judge whether such a conclusion is correct or not. The variation of n with the slope could also be attributed to the error in the experiment, as only a few data points were collected to plot the initial rising limb of the hydrograph, giving rise to large errors in the parameter regression. In the present study, we adopt the same value of n for all the experiments. By combining Eqs. (2) and (6), we can obtain:

$$\left(\frac{Q_t}{B\sqrt{S_0}}\right)^{3/5} \Big/ I = n^{-3/5} t \tag{35}$$

We define $Q^* = \left(\frac{Q_t}{B\sqrt{S_0}} \right)^{3/5} \Big/ I$. Hence, Q^* is proportional to t and this formulation applies to all the experiments. In order to reduce the error, we use all the experimental data about the initial rising limb of the hydrograph to determine the value of n. Fig. 1 shows the experimental results of Q^* for different test conditions. It is evident that Q^* for different conditions can be fitted well by the same linear relationship. It implies that taking the same value of n for all the experiments is reasonable. According to the linear regression, the value of Manning roughness coefficient n is determined to be 0.0457, which is very close to the average Manning roughness coefficient n of the smooth board (0.0477) in the study of Xiao et al. (2017). It indicates that the rainfall experiments have good accuracy and repeatability. This value of n obtained in this study might seem rather high if we consider that the recommended value in hydraulic manuals for a smooth wooden board surface is around 0.012 and 0.016. However, the extra roughness can be linked to the extremely small water depths in the experiments. The runoff in a thin layer is heavily affected by the effect of laminar flow in the viscous sublayer, which justifies the use of a higher bed friction coefficient. Hong et al (2016) also adopted a higher Manning coefficient value of 0.05 when reproducing the rainfall runoff process over a road surface. The time of concentration t_c for different rainfall events can be calculated using Eq. (1).

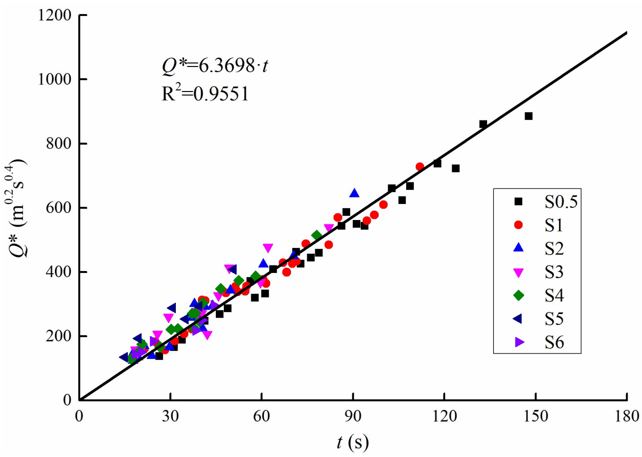

Figure 1. Q^* for different conditions

Up to this point, we have obtained the values of all free parameters except for the depth of control layer h_0. Unlike n, the value of h_0 cannot be determined by direct data fitting. A more comprehensive least-square analysis is needed. The Nash-Sutcliffe efficiency (NSE) (Nash and Sutcliffe, 1970) has often been adopted to evaluate the model performance. The formulation of NSE can be expressed as:

$$NSE = 1 - \frac{\sum_t \left(Q_{o,t} - Q_{m,t}\right)^2}{\sum_t \left(Q_{o,t} - \overline{Q_o}\right)^2} \tag{36}$$

where $Q_{o,t}$ is the observed value at time t; $Q_{m,t}$ is the modeled value at time t; $\overline{Q_o}$ is the average value of the observed data. Higher value of NSE represents a more accurate model. In this study, a Fortran program was written to determine the value of h_0 in each experiment. In the Fortran program, the value of h_0 is changed from 0.01 mm to 1.0 mm with depth step of 0.01 mm. At the end, the result with the largest NSE was selected. Therefore, the value of h_0 for each experiment can be determined independently.

3.3 Comparison of modeled and measured concentrations

Pollutant concentration is one of the most important indicators for controlling the water quality. In this study, the pollutant concentration is therefore used to determine the value of h_0 for each experiment by maximizing the Nash-Sutcliffe efficiency (NSE) of the prediction. With the selected value of h_0, the comparisons between measured and predicted pollutant concentrations in different test runs are shown in Fig. 2. In each condition, the concentration of pollutant is seen to decrease with time and finally approaches zero. In addition, the pollutant concentration is found to be affected by the rainfall intensity and the bed slope. The greater the rainfall intensity and slope, the faster is the decrease of the pollutant concentration, which is largely due to the change in the water runoff process. As described in the previous section, the pollutant concentration is closely related to the overland flow process. Overall, the pollutant concentration can be satisfactorily predicted by the proposed transport model.

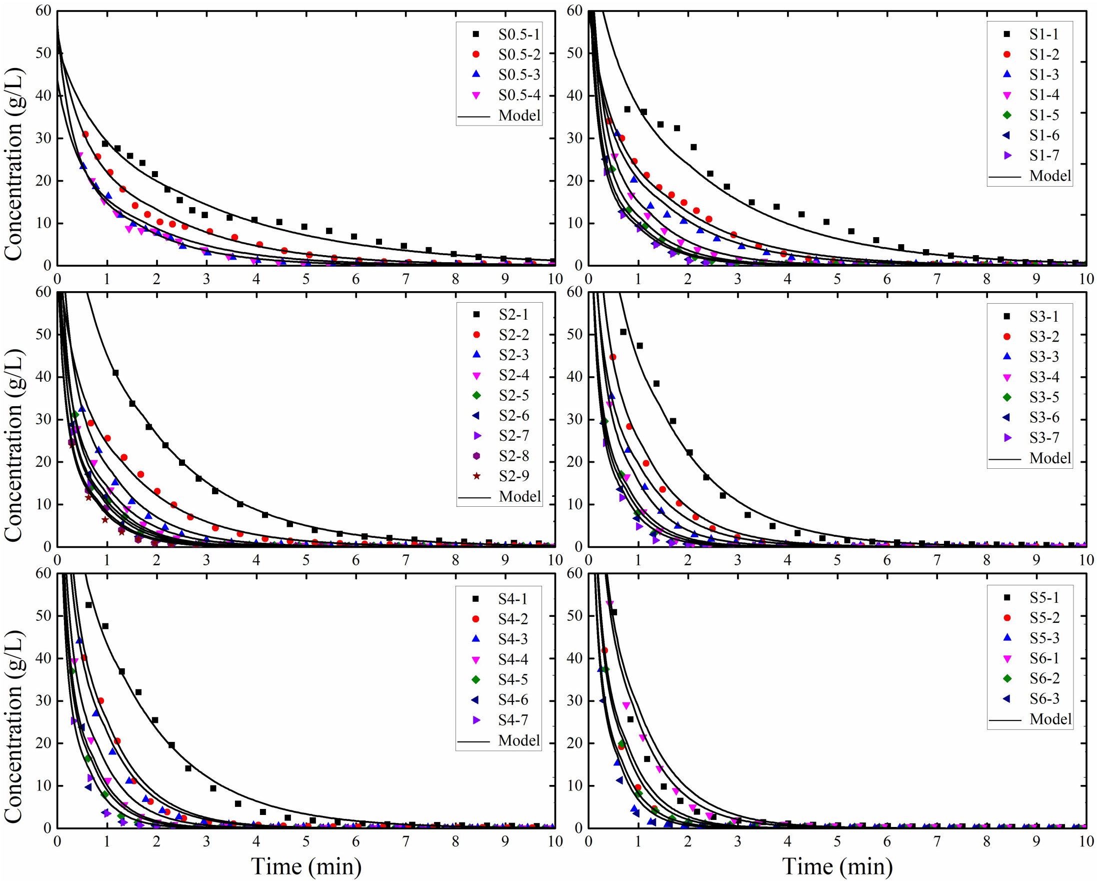

Figure 2. Measured and modeled pollutant concentrations

As mentioned before, the value of h_0 is determined in this study by fitting the experimental results of the pollutant transport. Then, the values of C_0 and t_c in each condition can be calculated from Eq. (14) and Eq. (1), respectively. Table 2 lists the estimated values of h_0, NSE, C_0 and t_c for different rainfall events. It is obvious that all the values of NSE in different conditions are very close to 1, which reaffirms the good performance of the present transport model. Fig. 3 presents the variation of h_0 in different conditions. It shows that there is no significant and consistent difference in h_0 among the rainfall intensities. To prove the above point, the Pearson's correlation analysis between h_0 and I was carried out using the SPSS statistical software (Version 25.0), and the results are presented in Table 3. It indicates that the value of h_0 shows no significant correction with the rainfall intensity. In fact, the value of h_0 for a given slope fluctuates within a small range over various rainfall intensity. Hence, it can be regarded that the value of h_0 is a constant for a given slope. Taking series S2 for example, which has been subject to many rainfall intensities, Fig. 4 illustrates the variation of NSE with different h_0. In Fig. 4, the dotted vertical line represents the average value of h_0 for different rainfall intensities. Taking the average value of h_0 as the depth of the control layer for different rainfall intensities has little effect on the performance of the transport model. It implies that the above assumption is reasonable. Figure 5 shows the average values of h_0 for different slopes. The value of h_0 decreases with the increasing slope, indicating that an increased slope can accelerate the generation of the overland flow. It may be related to the surface tension or the normal water depth along the slope. A larger slope reduces the normal water depth, and thus the water holding capacity of the catchment. In addition, the value of h_0 tends to be a constant at sufficiently large slopes. It indicates that a catchment has a limiting minimum water holding capacity, although the component of gravity along the slope keeps increasing with higher slopes.

Table 2 Estimated values of parameters for different test conditions

Test case	h_0 (mm)	NSE	C_0 (g/L)	t_c (min)	Test case	h_0 (mm)	NSE	C_0 (g/L)	t_c (min)
S0.5-1	0.551	0.9842	51.79	2.438	S3-1	0.203	0.9878	140.56	1.423
S0.5-2	0.515	0.9909	55.41	1.935	S3-2	0.227	0.9938	125.70	1.091
S0.5-3	0.652	0.9817	43.76	1.655	S3-3	0.297	0.9742	96.07	0.986
S0.5-4	0.502	0.9944	56.84	1.540	S3-4	0.226	0.9323	126.25	0.888

S1-1	0.367	0.9693	77.75	2.045	S3-5	0.278	0.9806	102.64	0.771
S1-2	0.472	0.9936	60.45	1.570	S3-6	0.264	0.9795	108.08	0.737
S1-3	0.463	0.9829	61.63	1.469	S3-7	0.231	0.9761	123.52	0.698
S1-4	0.324	0.9935	88.07	1.216	S4-1	0.258	0.9918	110.60	1.356
S1-5	0.299	0.9909	95.43	1.083	S4-2	0.194	0.9885	147.08	0.992
S1-6	0.344	0.9884	82.95	1.018	S4-3	0.216	0.9919	132.10	0.952
S1-7	0.376	0.9919	75.89	0.985	S4-4	0.222	0.9803	128.53	0.813
S2-1	0.256	0.9983	111.46	1.711	S4-5	0.206	0.9789	138.51	0.721
S2-2	0.410	0.9928	69.59	1.294	S4-6	0.205	0.8188	139.19	0.694
S2-3	0.306	0.9937	93.25	1.100	S4-7	0.195	0.9762	146.33	0.636
S2-4	0.391	0.9954	72.98	0.978	S5-1	0.197	0.9398	144.84	0.981
S2-5	0.292	0.9831	97.72	0.914	S5-2	0.204	0.9697	139.87	0.754
S2-6	0.375	0.9875	76.09	0.876	S5-3	0.206	0.9662	138.51	0.644
S2-7	0.339	0.9906	84.17	0.848	S6-1	0.190	0.9929	150.18	0.889
S2-8	0.408	0.9922	69.94	0.798	S6-2	0.198	0.9854	144.11	0.691
S2-9	0.395	0.9876	72.24	0.776	S6-3	0.184	0.9669	155.07	0.587

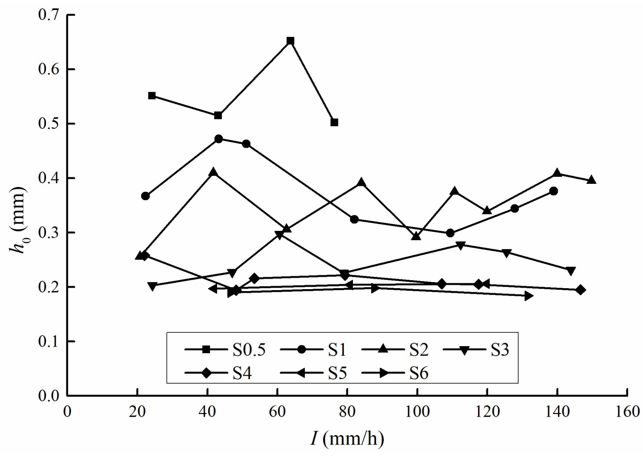

Figure 3. Estimated values of h_0 for various conditions

Table 3 Pearson's correlation coefficients for correlation between h_0 and I

Test case	S0.5	S1	S2	S3	S4	S5	S6
Number of samples	4	7	9	7	7	3	3
Pearson's correlation	0.068	-0.528	0.492	0.331	-0.652	0.952	-0.443

coefficient

**. Correlation is significant at the 0.01 level (2-tailed) *. Correlation is significant at the 0.05 level (2-tailed). According to Evans (1996), the range of absolute value of r is 0.00-0.19 "very weak"; 0.20-0.39 "weak"; 0.40-0.59 "moderate"; 0.60-0.79 "strong"; 0.80-1.0 "very strong".

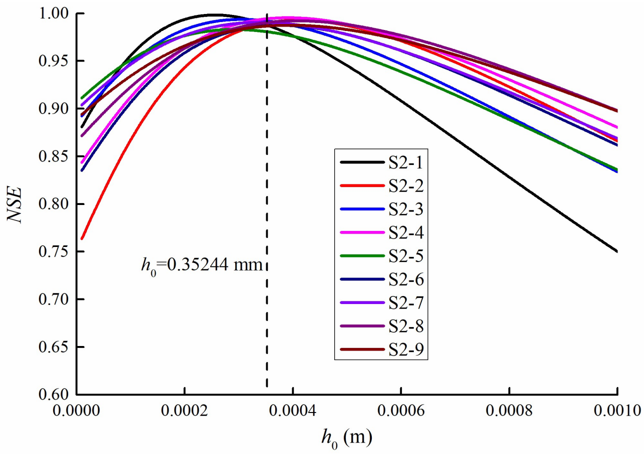

Figure 4. Variation of *NSE* for different h_0

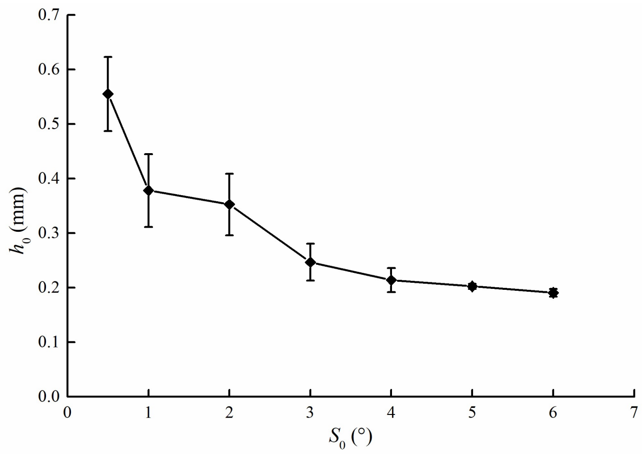

Figure 5. Average values of h_0 for different slopes

3.4 Comparison between modeled and measured transport rates

The pollutant transport rate is an important parameter, which can be defined as the flow rate of the pollutants transported out of the catchment. It can be calculated by the following equation:

$$M_t = C_t Q_t \tag{37}$$

where M_t is the pollutant transport rate at time t (g/s).

The observed and predicted pollutant transport rates under different conditions are shown in Fig. 6. Overall, the observed pollutant transport rates are in good agreement with those predicted by the transport model developed in this study. It is seen that the pollutant transport rates for different conditions show a similar single-peak shape, which consists of a steep-rising limb at the beginning and a sharp-falling limb later on. The pollutant transport rate increases from zero to a maximum and then decreases to zero. The larger the rainfall intensity and bed slope, the greater the maximum pollutant transport rate ($M_{\max}$). This may be caused by the larger flow rate and water velocity associated with the larger rainfall intensity and bed slope. Figure 6 also shows that the present model can well predict the value of the maximum transport rate $M_{\max}$.

From the modeled results, the pollutant transport rate reaches a maximum at the time of concentration t_c, *i.e.* the end of the initial rising hydrograph period under an unceasing rainfall. It implies that the pollutant transport rate increases with the runoff rate during the initial runoff period, although the pollutant concentration decreases. Xiao et al. (2017) suggested that not all the maximum pollutant transport rates occur at the time of concentration t_c. However, the time of reaching the maximum value is very close to the time of concentration. This slight discrepancy may be related to the usage of a constant Manning roughness coefficient n for different slopes in this study, while different Manning roughness coefficients were obtained for different slopes in Xiao et al. (2017).

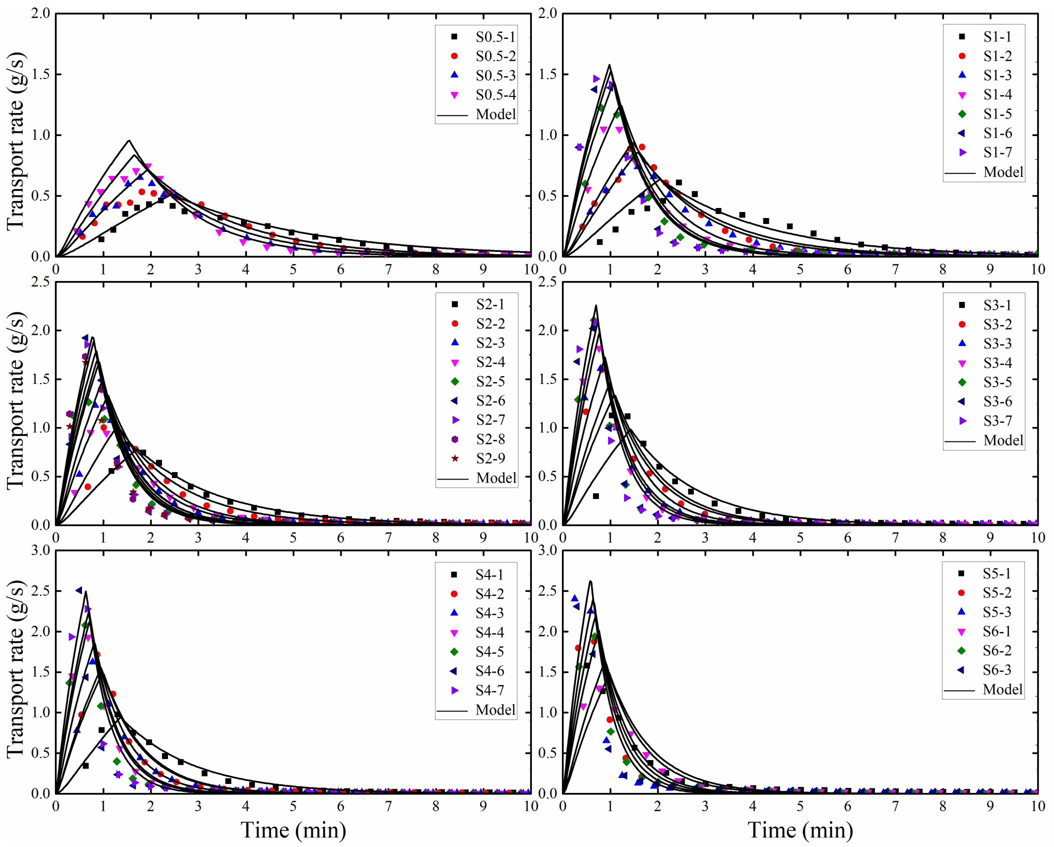

Figure 6. Measured and modeled pollutant transport rates

3.5 Sensitivity analysis

According to the developed transport model herein, it is expected that five independent parameters (L , h_0 , S_0 , n and I) affect the pollutant transport process. They all have clear physical meanings. Among these parameters, h_0 and n were determined by fitting the experimental results in this study, while the other three parameters were directly measured. Fig. 2 and Fig. 6 suggest that the rainfall intensity and bed slope have huge impacts on the pollutant transport process, especially in the initial phase. In addition, the pollutant transport process is particularly sensitive to small rain intensity and bed slope.

To investigate the influence of the other three parameters (L , h_0 and n), the pollutant transport processes for various cases are modeled, as shown in Fig. 7. It suggests that L and n exert significant effect on the pollutant concentration and transport rate, mainly in the middle period. Hence, the change in L and n will have great influence on the pollutant transport process. We can also see that a catchment with a short length leads to the faster transport of pollutant. Although the pollutant transport rate on a long catchment is large, it takes a longer time to reduce to zero. As for h_0, it shows that h_0 has an impact on the concentration mainly in the initial runoff stage, and has little influence in the later stage. This is consistent with Eq. (14), from which it is clearly seen that h_0 greatly influences the initial pollutant concentration. The difference in concentration will gradually diminish as the rainfall continues. In contrast, it is seen that h_0 has no discernable effect on the pollutant transport rate due to the small runoff rate in the initial stage. Similar results can be found with vegetated surfaces (Zhang et al., 2018). Overall, as described before, the pollutant transport process is closely related to the water runoff process. As compared with h_0, the other parameters (S_0, n and I) have direct and significant influence on the runoff process. Therefore, these parameters exert significant influence on the pollutant transport process as well.

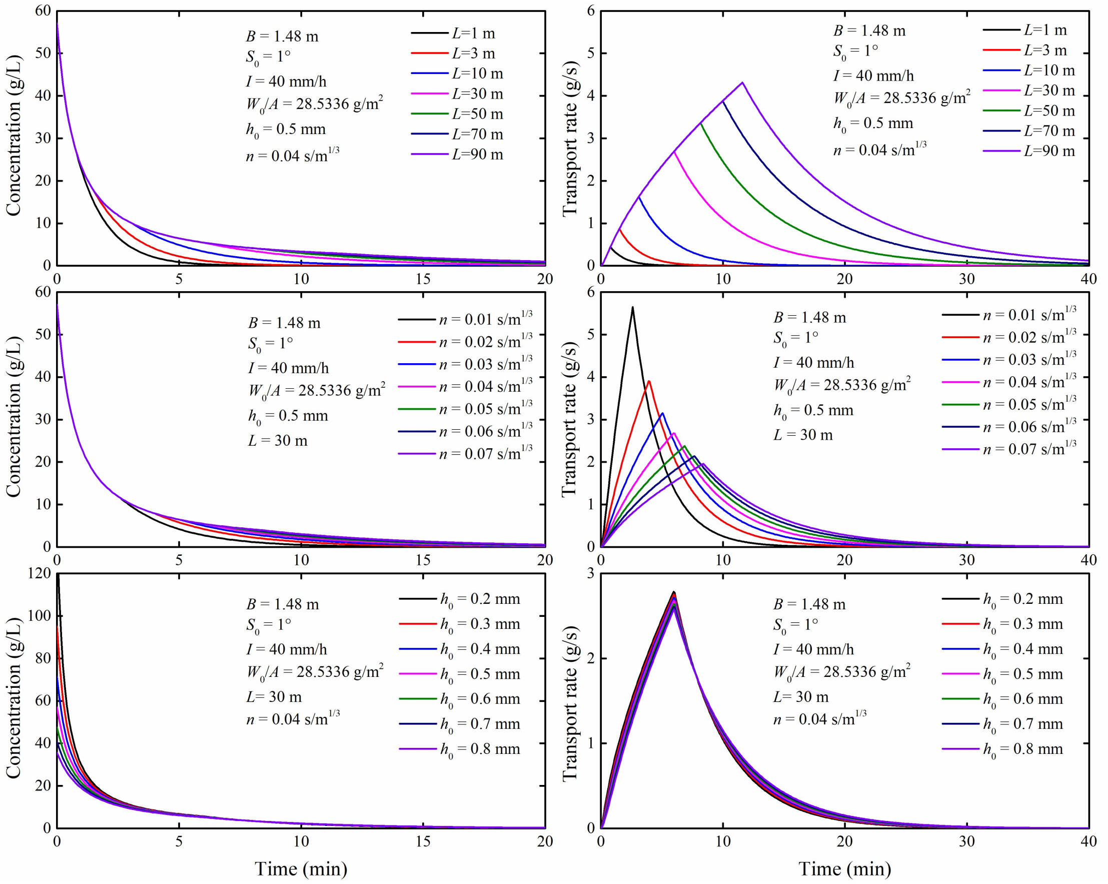

Figure 7. Pollutant concentrations and transport rates for various conditions

4 Discussions

In the present investigation, a physically-based dissolved pollutant transport model is proposed and verified. Xiao et al. (2017) also developed a semi-empirical model to describe the dissolved pollutant transport process over impervious surfaces. However, the main difference between the two models lies in the formulation of the initial runoff stage. Xiao et al. (2017)'s model suggests that the pollutant concentration conforms to an inverse S-curve, which is different from the model presented in this study. Although the dissolved pollutant transport process can be correctly described by both models, the model presented in this paper has some advantages. Most importantly, the present model is physically based.

As mentioned before, the model developed herein adopts the idea of "stationary water layer" proposed first by Zhang et al. (2018) for describing the solute transport process over vegetated surface. In this paper, we define the thin water layer underneath the overland flow as the "control layer". The naming is mainly because that the water flow over impervious surface cannot be totally stationary due to the impact of rain drops. In contrast, vegetation can effectively reduce the impact of rain drops. It is evident that runoff water and the water in the control layer will splash under the impact of raindrops. From a statistical point of view, the amount of water transported at any point on the catchment remains constant. Despite the water exchange between the control layer and the overflow runoff, the amount of water in the control layer remains constant.

According to previous studies (Xiao et al., 2017), for a constant rainfall event over impervious surfaces, the expression of the dissolved pollutant concentration at the equilibrium stage can be:

$$C_t = C_{t_c} e^{-kI(t-t_c)} \tag{38}$$

where k is the wash-off coefficient (mm^{-1}). From Eqs. (34) and (38), it is obvious that k equals to $\mathbf{1} \Big/ \left(h_0 + \frac{\mathbf{5}}{\mathbf{8}} \left(IL/\alpha \right)^{3/5} \right)$, where the term $\left(h_0 + \frac{\mathbf{5}}{\mathbf{8}} \left(IL/\alpha \right)^{3/5} \right)$ represents the average water depth of the catchment at the equilibrium stage (Eq. 30). Therefore, the wash-off coefficient k now carries a physical meaning as the reciprocal of the average water depth over the catchment at the equilibrium stage. From the expression $k = \mathbf{1} \Big/ \left(h_0 + \frac{\mathbf{5}}{\mathbf{8}} \left(IL/\alpha \right)^{3/5} \right)$, the values of k for all the experimented cases can be obtained, as shown in Fig. 8. They show that the value of k increases with the increasing bed slope and decreasing rainfall intensity. It also implies that a smaller slope and larger rainfall intensity increase the water holding capacity of the catchment. In this study, k varies from 0.56 to 1.78 mm^{-1}, which is very close to that obtained in the previous study, which varies from 0.63 to 1.93 mm^{-1} in Xiao et al. (2017). For a constant rainfall event over uniform rectangular impervious surfaces, a constant value for k has been used to describe the transport process of particulate pollutant in previous studies (Sartor and Boyd, 1974; Egodawatta et al., 2007, 2009; Muthusamy et al., 2018). As for dissolved pollutant in this study, the value of k also keeps unchanged at the equilibrium runoff stage with an expression as follows:

$$k = \mathbf{1} \Big/ \left(h_{\mathbf{0}} + \frac{\mathbf{5}}{\mathbf{8}} \left(IL/\alpha \right)^{3/5} \right) = \mathbf{1} \big/ \left(h_{\mathbf{0}} + \mathbf{0.625} I t_c \right) \tag{39}$$

However, in the initial runoff stage ($\mathbf{0} \le t \le t_c$), the value of k may vary with time as the catchment has not completely reached the equilibrium stage. Here, the wash-off coefficient k means the reciprocal of the average water depth over the upstream part of the catchment where the equilibrium stage has already been reached. The expression of k in the initial runoff stage can be easily obtained from previous sections and Eq. (39):

$$k = \mathbf{1} \big/ \left(h_{\mathbf{0}} + \mathbf{0.625} I t \right) \tag{40}$$

Figure 9 presents an example of the variation of k during a constant rainfall event. It should be noted that the physical meaning of k may not be applicable to particulate pollutants. After all, the transport mechanisms of dissolved and particulate pollutants are different.

In summary, this study proposed a novel physically-based transport model for dissolved pollutant by adopting a “control layer” concept in overland flow. The model’s underlying assumptions are: (1) the rainfall intensity is uniformly distributed and does not change with time; (2) the catchment is a single slope with constant roughness; and (3) the pollutant is initially uniformly distributed over the catchment. The concept of “control layer” has been verified to be rational by a series of experiments, which helps advance our understanding of the mechanism of the dissolved pollutant transport. After extensive comparison with experimental results, the proposed model can be regarded to accurately reflect the physical processes for the dissolved pollutant transport over impervious surfaces. Although the model is restricted to idealized scenarios only in this study, it has the potential to become the building block to develop a distributed catchment model to simulate the response of a heterogeneous real-world catchment subject to spatially and temporally varied rainfall.

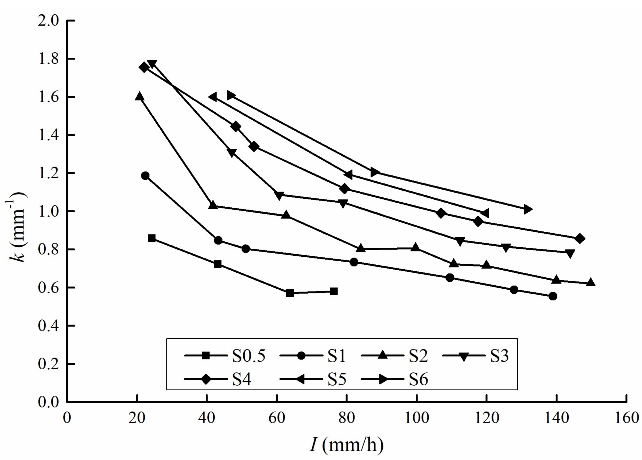

Figure 8. Values of k for various conditions

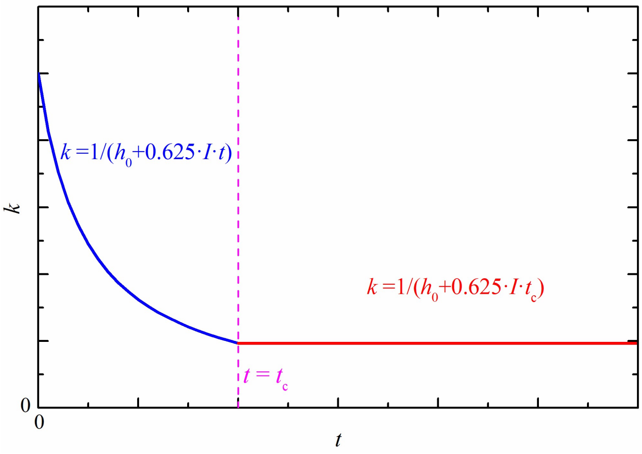

Figure 9. Values of k variation process during a constant rainfall event

5 Conclusions

This study developed a physically-based dissolved pollutant transport model over impervious surfaces. This model adopts a key assumption that a thin water layer named “control layer” is formed beneath the rapidly flowing water. The upper runoff water is completely mixed with the water in the control layer at the same horizontal position. To validate the proposed transport model, a series of simplified laboratory experiments have been conducted in a rainfall simulation hall. The results show that the pollutant concentration and pollutant transport rate can be accurately predicted by the transport model proposed in this study. The maximum pollutant transport rate takes place at the time of concentration, and is positively correlated with rainfall intensity and the bed slope. The depth of the control layer mainly depends on the bed slope and it has no noticeable dependence on the rainfall intensity. Sensitivity analysis showed that rainfall intensity, bed slope, surface roughness and the length of catchment are dominant factors in controlling the dissolved pollutant transport. In contrast, the depth of the control layer mainly influences the initial pollutant concentration, but it has no significant effect on the pollutant transport rate. The wash-off coefficient k for the dissolved pollutant carries a physical meaning as the reciprocal of the average water depth in the catchment area over which the equilibrium stage has been reached. Therefore, it is related to the water holding capacity of the catchment.

Although the physical meaning of k for dissolved pollutant has been found, further study will be needed to confirm whether the same meaning holds for the particulate pollutant transport. A real-life urban area is much more complicated, with spatially and temporally varied ground features. A robust distributed hydrological and water quality model will be needed to take into account such complicated scenarios.

Conflict of interest

The authors declare that there is no conflict of interests regarding the publication of this paper.

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