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Title: Modeling middle and final flush effects of urban runoff pollution in an urbanizing catchment

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Abstract:

In current literature, the first flush effect of urban runoff pollution has been studied and reported extensively. However, the effects of middle and final flushes on pollutant flushing were not given much attention. In addition, few previous studies have discussed the suitability of the widely used exponential wash-off model for describing the middle or final flush processes. In this paper, the Shiyan River catchment, a typical rapidly urbanizing catchment in China, is chosen as a study area to analyze the effects of first, middle and final flushes based on monitoring hydrographs and pollutographs. In order to simulate the middle and final flush processes observed in storm events, a new, realistically simple, parsimonious model (named as logistic wash-off model) is developed with the assumption that surface pollutant loads available for wash-off increase with cumulative runoff volume following a logistic curve. The popular exponential wash-off model and the newly developed model are used and compared in simulating the flush processes in storm events. The results indicate that all the three types of pollutant flushing are observed in the experiment; however, the first flush effect is weak, while the middle and final flush effects are substantial. The exponential model has performed well in simulating the first flush process but failed to simulate well the middle and final flush processes. However, the logistic wash-off model has effectively simulated all the three types of pollutant flush, and particularly, it has performed better in simulating the middle and final flush processes than the exponential model.

Keywords: Flush effect; Urbanization; Storm water, Runoff; Wash-off model

1 Introduction

Pollutants flushed out by surface runoff during storm events can be a large contributor to the receiving water quality problems in urban areas (Behera et al., 2006; Richardson and Tripp, 2006). The flush effects have been extensively investigated to determine whether the pollutants experience higher concentration levels in certain periods of a storm event. The first flush effect can be defined as a phenomenon in which a greater proportion of pollutant loads are washed off during the beginning of a rainfall event than in other periods (Lee et al., 2002; Sansalone and Cristina 2004). First flush phenomenon is more likely to occur in a smaller catchment with more impervious land surfaces (Kim et al. 2004; Kim et al. 2007; Lee et al., 2002; Taebi and Droste, 2004) and is highly dependent on time of concentration of a catchment, i.e., the time needed for water to flow from the most remote point in a watershed to the watershed outlet (Kang et al. 2008). A number of previous studies have been conducted to assess the occurrence and the causes of the first flush effect (e.g., Bach et al., 2010; McCarthy, 2009; Obermann et al. 2009; Sansalone and Cristina, 2004). Furthermore, with an in-depth understanding of first flush, structural measures (e.g. retention tanks and pipe networks) can be explicitly designed to intercept and treat the initial runoff and thus can minimize the impact of runoff pollution on the receiving water bodies (Deletic, 1998; Kang et al. 2008).

In addition to the first flush, previous studies have also reported that some pollutants in some storm events exhibit so-called "middle flush" or "final flush" (or "second flush", "end flush", "last flush" in the literature), which means that most of pollutant loads are washed off by the middle or the last proportion rather than the first proportion of runoff volume. Lee and Bang (2000) studied urban stormwater runoff in nine watersheds in Korea and found that the peak of pollutant concentration lagged behind that of flow rate in the watersheds with an area larger than 100 ha and a percentage imperviousness less than 50%. McCarthy et al. (2009) found that Escherichia coli (E. coli) and Total Nitrogen (TN) exhibit so-called ''end flushes'' in storm water from the urbanized catchments in Melbourne. Flint and Davis (2007) reported that the total pollutant mass load in the later 25% of the event runoff volume is greater than in the first 25% volume in at least 17% of the storm events in a commercial/residential area, indicating that a significant amount of the pollutant load can be contained in later portions of the runoff volume. Hathaway et al. (2012) found that substantial pollutant loading occurred in the latter portion of the total runoff volume of the storms from two small urban catchments in the Southeast and Mid-Atlantic USA. Lee and Bang (2000) suggested that the second flush effect is more significant in the catchment with a larger area and a higher proportion of impervious area. Zhang et al. (2012) suggested that first flush is seldom observed in the wastewater in three urban drainage systems of Beijing due to the influence of sewer sediments, sewer system characteristics, catchment characteristics and other reasons. It should be noted that there is no unified definition on quantification of first flush, second flush and third flush. In addition, compared to the number of studies on the first flush effect, there is little research on the identification, modeling, and management of middle and final flush effects.

The urbanizing process is accelerating in China and other developing countries. An urbanizing catchment is characterized by rapid economic and population growth as well as dramatic changes in land use from natural/rural to urban areas, which usually have heterogeneous land uses with a mix of residential, industrial, agricultural and natural lands. Although numerous efforts have been made to investigate the flush effect of storm runoff pollution in urban catchments, there are very few studies reporting the flush characterization in urbanizing catchments. From a recent investigation carried out in four rapidly urbanizing catchments in China (Qin et al. 2010), it was found that the first flush intensity is weak in the catchments with a low proportion of impervious areas. If first flush phenomena are not predominant and second flush phenomena are significant, the performance of urban runoff management based on the first flush theory for water quality improvement may be compromised (Flint and Davis, 2007). Hence, there is a need to characterize and examine all flush effects for the management and treatment of storm runoff pollution in urbanizing catchments.

A number of models have been developed to simulate urban runoff pollution and have been used in many computer simulation tools for pollution control analysis such as the Storage, Treatment, Overflow, Runoff Model (STORM) (USACE, 1974), FLUPOL (Bujon 1992), Stormwater Management Model (SWMM) (Rossman, 2008) and Hydroworks/InfoWorks CS (Wallingford Software, 2004). These models generally simulate surface accumulation and wash-off as well as sediment erosion and pollutant transport in sewer systems. For wash off process simulation, the most widely employed is an exponential wash-off model, in which the rate of pollutant wash-off per unit area depends linearly on the available accumulated pollutant mass, the rainfall intensity or the overland flow rate (Alley 1981; Millar et al., 1999). Avellaneda et al. (2009) used a modified exponential model that incorporates a wash-off exponent to allow nonlinear dependency on the runoff rate. The bottom shear stress of the overland flow and the energy of raindrop may also have effects on the wash-off rate, and their effects have been considered in the more refined models (Richardson and Tripp, 2006; Shaw et al., 2006; Soonthornnonda et al., 2008). Kang et al. (2006) assumed that the pollutants' mass on impervious surfaces include an easy wash-off portion and a slowly detaching pollutant portion. The two portions have different erosion rates during a rainfall event. Furthermore, Massoudieh et al. (2008) developed a model to simulate the flush behavior in highway environments, in which pollutants were assumed to be in two phases, attached to the pavement surface and mobile in the runoff water.

In theory, a complex, high resolution physically based model, which can accurately represent various processes, should have capacity to simulate any types of flush effects. However, the development of complex models is difficult in many cases due to data availability. The parsimonious models with few parameters are more applicable in practice, in particular where data are not available to develop complex models. The exponential model has been widely used due to its simplicity and ease of use. More importantly, it has been successfully used to describe the first flush effect in urban areas, particularly for impervious areas (Behera et al., 2006; Millar et al., 1999). However, few previous studies have discussed the suitability of the widely used exponential wash-off model for describing the middle or final flush processes in an urbanizing area. Thus, there is a need to improve the wash off model in order to better describe the different types of flush effects of storm runoff pollution since various flush phenomena may occur. This paper aims to 1) identify the existence of first flush, middle flush and final flush through the use of a rapidly urbanizing catchment - Shiyan river catchment, China; 2) investigate whether the conventional exponential wash-off model can be used to simulate the middle and final flush effects; and 3) extend the exponential model to simulate middle and final flushes.

2 Material and methods

2.1 Pollutant flush analysis

In this study, the pollutant flush is divided into three types: first flush, middle flush and final flush, which are defined as the respective processes in which the majority of the pollutant load is delivered in the prophase, metaphase and anaphase of a storm event.

The pollutant flush type can be visually identified by comparing the times to reach the peaks in the hydrograph and pollutograph. According to the hydrograph and pollutograph analysis, the first flush phenomenon occurs when the peak of pollutant concentration appears before that of urban runoff during a storm event (Curve a in Fig.1); the middle flush occurs when the peaks of pollutant concentration and runoff appear simultaneously (Curve b in Fig.1); the final flush occurs when the peak of pollutant concentration appears after the runoff peak (Curve c in Fig.1).

Fig.1 Hydrograph and pollutograph for different flush types

The pollutant flush type can also be identified based upon a dimensionless representation of normalized cumulative pollutant load against cumulative runoff, which are defined as below:

$$L=m\ (t)\ /\ M \quad (1)$$

$$F=v\ (t)\ /\ V \quad (2)$$

where L and F are dimensionless cumulative load and cumulative runoff flow rate, respectively; m

(t) is pollutant mass up to time t (kg); v (t) is runoff volume up to time t (m^3). M and V are the total pollutant load and total runoff volume for the entire event. A bisector *L-F* curve (45° line) represents the situation with a uniform pollutant wash off rate during a storm event (the solid line as shown in Fig.2). By referencing to the bisector line, the different characteristics of the three flush types can be reflected by the shape of *L-F* curve. A convex *L-F* curve lying above the bisector line represents a condition where the majority of the pollutant load is delivered in the prophase of the storm event, i.e., first flush (the dashed line as shown in Fig.2). Conversely, a concave *L-F* curve below the bisector line represents a condition where the majority of the pollutant load is not delivered until the anaphase of the event (the dotted line as shown in Fig.2), i.e., final flush. In addition, a "S" *L-F* curve across the bisector line describes a condition where the majority of the pollutant load is delivered in the metaphase of the event (the dot-dash line as shown in Fig. 2), i.e., middle flush.

Fig.2 Normalized cumulative curves for different flush types (Adapted from Lee and Bang 2000)

Indicators have been widely used to reflect the first flush intensity in previous studies (Bertrand-Krajewski et al., 1998; Kim et al., 2005; Wanielista et al., 1993). For example, FF20, FF25 and F30 represent the fraction of the pollution load (*L*) that is transferred in the first 20%, 25% and 30% of the total volume (*F*), respectively, in a storm event. According to the definition in the previous studies, the first flush effect is significant when FF20> 40% (FF20 criterion), FF25 > 50% (FF25 criterion), or FF30> 80% (FF30 criterion). Compared to the number of studies on the first flush, much less attention has been paid to the middle flush and final flush. In order to compare the intensities of different types of flush, *L-F* curve is divided into three phases in this study: prophase, metaphase and anaphase, corresponding to *F* ranged from 0 to 33%, 33%-67%, and 67%-100%, respectively; and, the first flush effect is considered as significant when more than 33% of cumulative mass load occurs in prophase; while the effect of middle flush and final flush is significant when more than 1/3 of pollutant load is washed off in metaphase and anaphase, respectively. In terms of these definitions, two types of flush maybe co-occur in a storm event if more than 1/3 of cumulative mass load is washed off in each of two phases, for example, "first-middle flush", "middle-final flush", or "first-final flush".

2.2 Wash-off models for flush process

2.2.1 Exponential wash-off model

In a popular exponential wash off model, the washoff load ratio (W_t) in units of mass per hour at time *t* is can be calculated as (Avellaneda et al. 2009):

$$W_t = C_1 Q_t^{C_2} (P_0 - P_{wt}) \quad (3)$$

where C_1 is washoff coefficient, C_2 is washoff exponent, Q_t is flow rate at time *t* (m^3/s), P_0 is initial pollutant buildup in the catchment before the rainfall (kg), and P_{wt} is cumulative pollutant load washed off at time *t* (kg), which can be calculated as the time integral for the washoff load ratio (W_t), i.e.,

$$P_{wt} = \int_0^t W_t dt \quad (4)$$

By solving the equations (3) and (4), the pollutant concentration in runoff can be expressed as:

$$C_t = C_1 P_0 Q_t^{C_2} e^{-C_1 \int_0^t Q_t^{C_2} dt} \quad (5)$$

where C_t represents pollutant concentration, C_t=W_t/Q_t. Thus three-parameters in the wash-off model, C_1, C_2, and P_0, are used to describe the rainfall runoff pollution processes. The equations have been used in SWMM and many other storm water quality models.

The wash-off exponent (C_2) determines the overall shape of the pollutograph. When the wash-off exponent is equal to 1, the pollutant concentration is the highest in the beginning of a rainfall event, and concentration decreases from the initial high values no matter how the runoff rate changes. When the wash-off exponent is higher than 1, the wash-off capacity is nonlinearly dependent on flow, and the shape of the pollutograph follows more closely to the hydrograph (Bai and Li, 2013). In any case, the peak of pollutant concentration simulated by the exponential washoff model appears before that of runoff during a storm event, and it can infinitely approach to, but not lag behind the runoff peak with the increase in wash-off exponent. The model can successfully simulate the first flush process; however, it fails to simulate the wash off processes characterized as “middle flush” or “final flush” due to the intrinsic limitation of the exponential model mentioned above.

2.2.2 Development of logistic wash-off model

A new wash off model is developed to simulate various types of flush phenomena in this study. Generally, the surface pollutant loads available for wash off depend on not only the initial pollutant buildup (P_0) but also the effective contributing area of runoff (S_e) in a catchment. A rapidly urbanizing catchment usually contains a mixture of agricultural, industrial and residential land uses. The pollutant wash off processes in the urbanizing catchment may be more complicated than those in the urban area dominated by impervious surfaces: in the initial period of a rainfall event, only runoff from impervious land uses (e.g. traffic, industrial and residential land) contribute to runoff pollution; however, more and more pervious lands begin to generate runoff and contribute to runoff pollution as rain continues (Qin et al. 2010). Therefore, S_e has a tendency to initially increase with an increase in rainfall amount or runoff volume, and then remain stable after all the lands begin to generate runoff. In terms of the aforementioned mechanism of the runoff pollution, it is assumed that the pollutant loads available for wash off increase with cumulative runoff volume following a logistic curve, and thus equation (3) can be modified as:

$$W_t = C_1 Q_t^{C_2}(P_0\delta_t - P_{wt}) \tag{6}$$

$$\delta_t = \frac{1}{1+B_1 e^{-B_2 V_t}} \tag{7}$$

where Q_t is flow rate at time t (m^3/s), δ_t is ratio of the pollutant loads available for wash-off at time t to P_0, B_1 and B_2 are parameters of logistic curve. V_t is cumulative runoff volume (m^3) at time t, which can be expressed as:

$$V_t = \int_0^t Q_t dt \tag{8}$$

According to equation (4),

$$W_t = dP_{wt}/dt \tag{9}$$

Further, let $r(t) = C_1 Q_t^{C_2}$, and $s(t) = C_1 Q_t^{C_2} P_0 \delta_t$, according to equation (6) and equation (9), then

$$\frac{dP_{wt}}{dt} + r(t)\cdot y = s(t) \tag{10}$$

Equation (10) is a first-order linear non-homogeneous differential equation. The equation can be solved by multiplying the integrating factor $e^{\int r(t)dt}$ throughout to obtain:

$$\frac{dP_{wt}}{dt} e^{\int r(t)dt} + r(t)\cdot P_{wt}\cdot e^{\int r(t)dt} = s(t)\cdot e^{\int r(t)dt} \tag{11}$$

The equation can be simplified using the product rule (applied backwards) to

$$\frac{d}{dt}(P_{wt}\cdot e^{\int r(t)dt}) = s(t)\cdot e^{\int r(t)dt} \tag{12}$$

On integrating both sides and solving for P_{wt} (t) gives:

$$P_{wt} = e^{-\int_0^t r(t)dt}\left(\int_0^t s(t)\cdot e^{\int r(t)dt} dt\right) \tag{13}$$

Then the pollutant concentration of runoff can be given as

$$C_t = P_{wt}/Q_t \tag{14}$$

The new model here is named as logistic wash-off model that has five parameters: C_1, C_2, P_0, B_1 and B_2. According to Equation (6), the surface pollutant loads available for wash off may rise as the rainfall continues, and the peak of pollutant concentration may appear close to or after the runoff peak. In addition, as B_1=0 or B_2=∞, δ_t=1 according to Equation (7), and the logistic wash-off model becomes the traditional exponential wash off model. Therefore, the model is expected to have more flexibility than previous models and that can be important because many storms do not show the ideal, decreasing exponential trend in concentration. The model can be used to fit a greater number of storm events, particularly when the middle and/or final flush occur.

2.3 Evaluation of model calibration

The goodness-of-fit of the exponential wash off model and the newly proposed model is assessed with data for a single storm event using the Nash-Sutcliffe (*NS*) coefficient (Nash and Sutcliffe, 1970), which is expressed as follows:

$$NS = 1 - \frac{\sum \left(X_{sim,t} - X_{obs,t} \right)^2}{\sum \left(X_{obs,t} - \overline{X}_{obs} \right)^2} \tag{15}$$

where *X* is the pollutant concentration (mg/L); the subscripts *sim* and *obs* denote the simulated and observed values, respectively. *NS* coefficient values equal to 1 indicate a perfect fit between observed and predicted data, and values equal to or less than 0 indicate that the model predictions are no better than using the average of the observed data. Generally, *NS*>0.5 indicate a satisfactory fit between the observed and predicted values (Moriasi et al., 2007). In this study, model calibration is conducted for individual storm events. For each storm event, the genetic algorithm (GA) is used to search the optimal values of the model parameters with the objective to maximize the *NS* coefficients.

3 Case study and discussion

3.1 Study area and sampling campaign

The Shiyan River catchment is located in Shenzhen city, Southeastern China (Fig.3). It has a warm, monsoon-influenced, humid subtropical climate, with an average annual rainfall of 1,933 mm. The area of the catchment is 25 km^2. Due to rapid urbanization in the last 20 years, the percentage of built-up area in the catchment increased to 32% in 2010. However, the agricultural land remains one of the main types of land use, and its area accounts for 29% of the catchment. The catchment is served by two types of drainage systems: combined sewer systems in the early developed areas and separate sewer systems in the newly developed areas. For further details of the catchment, please refer to Qin et al. (2013). It has been reported that the water quality of the river has a high rate of non-compliance with the water quality regulations and the runoff pollution is one of the major sources of pollutants in the urbanizing area (Qin et al 2010). Therefore, it is necessary to identify the pollutant flush type, evaluate the flush intensity and accurately simulate the flush process, which would be helpful in runoff pollutant loads control decision making, water quality management and drainage system design.

Fig.3 Map of the Shiyan River catchment

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Since there was no hydrological monitoring at the study area prior to this study, a temporary monitoring site was installed at the downstream section of the Shiyan River to measure streamflow and associate water quality (Fig.3). The drainage area of the section is 35 km^2, which accounts 90% of the total area of the Shiyan River catchment. The streamflow was measured at 10 min intervals by Sontek/YSI Argonaut-SW (1ASW-33000 model), which was installed at the bottom the river. The water was automatically sampled at 20 min intervals from the middle thread of the river section. In this study, runoff quality is represented by Chemical Oxygen Demand (COD) because it is one of the main pollutants in the study catchment. COD of the sample was measured by Horbi UV-COD online monitor (OPSA-150) at 20 min intervals, which was installed on the nearby river bank. The Horbi UV-COD was verified each half a month by comparing the instrument output values and manual analysis values, and the corresponding correlation coefficient is around 0.8-0.9. Rainfall data were recorded by an automated gauge (1-min interval) (Vaisala Weather Transmitter WXT510) at Shiyan reservoir rainfall monitoring station operated by Shenzhen Meteorology Bureau. A continuous measurement was conducted from April 2009 to April 2012. Due to missing values, only 26 events with complete data were extracted for analysis in this study (see in Appendix A). Table 1 summarizes the observed rainfall data. The Antecedent Dry Period (ADP), rainfall amount and rainfall duration ranged from 2.4 to 189 hours, 1.4 to 38.1mm and 0.22-8.47 hours, respectively.

Table 1 Main characteristics of observed storms

3.2 Type of pollutant flush

Fig.4(a)-(c) shows the measured flow and concentrations of COD during three storm events of October 10, 2011 (17.1 mm), June 11, 2011(15.8 mm) and July 13, 2011(7.6 mm), respectively. The COD concentration peak appeared before the flow peak and a typical first flush effect occurred during the storm event of October 10, 2011 (Fig.4 (a)). The COD concentration peak and the flow peak appeared nearly simultaneously and a typical middle flush effect occurred for the storm event of June 11, 2011 (Fig.4 (b)). In addition, the COD concentration peak appeared after the flow peak and a typical final flush effect occurred for the storm event of July 13, 2011(Fig.4 (c)). In summary, around 7, 16 and 3 of the 26 storm events have the concentration peak that appeared before, with and after the flow peak respectively. The results indicate that most of the storm events have middle flush or final flush in the study area.

Fig.4 Comparison between measured and calculated data (a) First flush; (b)Middle flush; (c) Final flush

Fig.5(a) shows the *L-F* curves of COD for all events. All the three types of curves (convex, "S" shape, concave curves) can be observed in the figure. 6, 17 and 3 of the 26 storm events have a convex curve (black line in Fig.5(a)), an "S" curve (blue line in Fig.5(a)) and a concave curve (red line in Fig.5(a)), respectively. In this study, the storm events with a convex curve are less than the storm events in which the concentration peak appears before the flow peak. This is because some storm events in which the concentration peak appears before the flow peak maybe have an "S" curve. Similar to visual inspection, the results also indicate that most of the storm events have middle flush or final flush in the study area.

Fig.5 Flush characteristics of 26 storm events. (a) Normalized cumulative pollutant load vs normalized cumulative runoff volume; (b) Variation of percentage of cumulative mass load washed off in different phases

3.3 Intensity of flush effect

In this study, the first flush intensity was evaluated by FF20, FF25 and F30 separately. As shown in Fig.5(a), FF20, FF25 and F30 ranged from 6.3%-29.2%, 5.1%-40.5%, and 10.1%-51.6%, respectively. No events have significant first flush effect according to the "FF20", "FF25" or "FF30" criteria. Overall, the occurrence of first flush was not a predominant phenomenon in the study area.

The method described in Section 2.1 provides a comprehensive assessment of the flush effect in "prophase", "metaphase" and "anaphase" of the storm events. Accordingly, it can be used to evaluate the intensity of first flush, middle flush and final flush in a storm event. Figure 5(b) shows the box-and-whisker plots of the percentage of cumulative mass load washed off in different phases. As shown in Fig.5 (b), more than 1/3 of cumulative mass load was washed off in prophase in 35% of the rainfall events, i.e., the events with first flush; more than 1/3 of cumulative mass load was washed off in metaphase in 96% of the rainfall events, implying that middle flush occurred in nearly all the rainfall events in the study; and more than 1/3 of cumulative mass load was washed off in anaphase in 12% of the rainfall events, i.e., the events with final flush. Therefore, the occurrence of middle flush was a predominant phenomenon in the study area. The reasons may be because the pollutant loads available for wash off are dependent on not only P_0 but also the area of runoff generation. Since the area of runoff generation increases with the increase of cumulative rainfall, it is possible that more pollutants are washed off in the metaphase and anaphase than that in the prophase of the storm event.

3.4 Evaluation of wash-off models

3.4.1 Model calibration

In order to compare the goodness of fit of the exponential model and the new model, the two models were calibrated for each of the 26 rainfall events and the corresponding NS coefficients were obtained. In the GA based calibration process, Q_t of the exponential wash-off model and the logistic wash-off model are input data obtained from the measured stream flow; the ranges of P_0, c_2 and c_3 used in the search for both the two models are 2000-30000 kg/km^2, 0.01-0.8, and 1-2, respectively; and the ranges of B_1 and B_2 used in the search for the logistic model are 0-50 and 0.00001-0.07m^{-3}, respectively. And we set the values of the GA parameters to 500 for population size, 90% for crossover and 1% for mutation probability. The search is terminated after 200 generations.

3.4.2 Performance of the exponential wash-off model

Fig.4 shows the pollutographs of three storm events based on the simulation using the exponential wash off model (red line). The comparison between the simulated and measured data indicates that the simulated data for the storm event of October 10, 2011 fit well with the measured data. However, the simulated data for the other two storm events failed to fit well with the measured data, particularly, there is a significant gap between the peaks of measured and simulated COD concentrations for the storm event of July 13, 2011.

Furthermore, *NS* coefficients for the 26 events of the exponential model are between -0.03 and 0.989 (Fig.6). Over 73% of the events have a *NS* coefficient higher than 0.6. Correlation analysis was made between the *NS* coefficients of the exponential model and the flush intensity indicators (e.g., FF20, FF25, FF30, and percentage of pollutant load washed off in prophase, metaphase and anaphase, respectively) (Fig.7). The results reveal that the *NS* coefficients have a positive correlation with the first flush intensity with correlation coefficients of 0.592 ($p<0.05$), 0.637 ($p<0.05$) and 0.627 ($p<0.05$) for FF20, FF25 and FF30, respectively; however, the *NS* coefficient have a negative correlation with the middle flush intensity (percentage of pollutant load washed off in metaphase), with correlation coefficients of -0.462 ($p<0.05$). The correlative analysis demonstrates that the exponential model has a good performance to simulate the first flush process but fails to simulate the middle or final flush process in the storm events.

Fig.6 Variation of NS coefficients of exponential wash-off model and logistic wash-off model

Fig.7 NS coefficient of exponential wash-off model vs flush intensity

3.4.3 Performance of the logistic wash-off model

Fig.4 also shows the pollutographs of three storm events from the logistic wash-off model (blue line). The comparison between the simulated and measured data indicates that the simulated data for all the storm events of October 10, June 11, and July 13, 2011 fit well with the corresponding measured data.

The calibrated values of P_0, C_1, C_2, B_1 and B_2 for different rainfall events are different (Table 2). This is because different events have different initial conditions prior to rainfall (e.g. initial pollutant buildup and the soil saturation degree) or the rainfall characteristics (e.g. amount, intensity). According to the results of sensitivity analysis, increasing B_1 or decreasing B_2 can delay the occurrence of the concentration peak and thus can better simulate the phenomena of middle or final flush. Furthermore, *NS* coefficients for the 26 events of the logistic wash-off model are between 0.84 and 0.99 (Fig. 6). All the events have a *NS* coefficient higher than 0.6. The results indicate that the logistic wash-off model has a good performance to simulate all the three types of pollutant flush, and particularly, it has a better performance to simulate the middle or final flush process than the exponential model. Thus the logistic wash-off model has more flexibility than the exponential wash-off model.

Table2 Model calibration for 26 individual rainfall events (logistic wash-off model)

It should be noted that the wash-off model has two more model parameters than the exponential model. Though this may slightly increase the difficulty in model calibration, it is necessary to more accurately represent the different types of flush processes and consequently the model's performance is significantly improved as demonstrated in Fig. 6.

3.4.4 Sensitivity analysis of the logistic wash-off model

A one-at-a-time sensitivity analysis was first performed to detect the effect of the new parameters (B_1 and B_2) of the logistic wash-off model on the pollutograph. The analysis was carried out by assuming a change in one parameter while others were fixed under a storm event of July 23, 2010.

Fig. 8(a) shows a set of model responses to the change in the value of B_1 (with B_2 fixed at 8.8e-5). With $\delta_t=1$ when $B_1=0$ according to equation (7), the logistic wash-off model becomes an exponential wash off model. In this case, the peak of concentration occurs earlier than that of runoff. Increasing B_1 generally delays the occurrence of the peak, and the peak of concentration appears after that of runoff when $B_1>2$.

Fig. 8(b) shows another set of model responses to the change in the value of B_2 (with B_1 fixed at 3.64). Contrary to B_1, increasing B_2 advances the occurrence of the peak, and the peak of concentration appears before that of runoff when $B_2>$5e-04. Furthermore, when $B_2=\infty$, $\delta_t=1$ according to equation (7), thus the logistic wash-off model becomes an exponential wash-off model. Therefore, both B_1 and B_2 have significant effect on the location of the peak concentration.

Fig.8 One-at-a-time sensitivity analysis for parameters of logistic wash-off model

The global sensitivity of the logistic wash-off model was further measured by Sobol's method based on variance decomposition. In the Sobol's method, the first-order index S_i measures the sensitivity from the main effect of parameter *i*; the second-order index S_{ij} measures the sensitivity from the interactions between parameter *i* and parameter *j*; and the total-order index S_{Ti} measures the main effect of parameter *i* and its interaction with all the other parameters. For further details of the Sobol's method, the reader is referred to Saltelli et al. (2010), Fu et al. (2012) and Zhang et al. (2013). The data of two rainfall events, which respectively have first flush effect and middle flush effect, are chosen as examples to evaluate the parameter sensitivity. *NS* coefficient is used as the measure of the model performance. As shown in Fig.9(a-b), P_0 and B_2 respectively have the highest level and the second highest level of sensitivity to *NS* coefficient. Except for P_0, other parameters have less individual impacts (S_i) than their interactions (S_{Ti}-S_i). In addition, the interaction between P_0 and B_1 has significant effect on the model performance, i.e., S_{ij} =0.211 and 0.114 for first flush event and middle flush event, respectively (Fig.9(b-c)) . The results indicate that B_1 and P_0 are highly correlated since they are parameters depending on the initial conditions prior to rainfall (e.g. initial pollutant buildup and the soil saturation degree). It should be noted that the high interactions cannot be revealed by the simple, one-at-a-time sensitivity analysis.

Fig.9 Sobol's sensitivity analysis for parameters of logistic wash-off model

An important use of the wash off model is to interpolate the discrete measured concentrations and calculate the even mean concentration (EMC) and mass loading (Kim et al. 2005). Compared to the exponential wash off model, the logistic wash-off model provides a better estimate of concentration, particularly for the storm event with middle or final flush effect. Another use of the model is for predicting pollutant loading and EMCs before a storm event, which will require reliable parameter estimates. Understanding of the physical implication and the impact factors of the new parameters (B_1 and B_2) can help in the parameter estimates.

According to the derivation of the new model, 1/(1+ B_1) represents the ratio of the pollutant loads available for wash-off to the total pollutant loads accumulated on the catchment (P_0) at the beginning of a rainfall event. B_1 may be affected by land use types, distribution of pollutant loads in the catchment, ADP, temperature and other weather conditions before the storm event. B_2 determines the rate of increase from 1/(1+ B_1) to 1 with the increase in V_t. B_2 may be affected by many factors, e.g., land use and soil types, rainfall amount and duration. However, further study is required to identify the factors that affect each parameter.

4 Conclusions

The paper analyzes the effects of first flush, middle flush and final flush in 26 storm events in an urbanizing catchment in China based on measured hydrographs and pollutographs. In order to simulate the middle and final flush processes observed in the storm events, a logistic wash-off model has been developed by assuming that the pollutant loads available for wash-off increase with cumulative runoff volume following a logistic curve. The results obtained are summarized below:

According to the hydrograph and pollutograph analysis, all the three types of pollutant flush occur in the study area. The first flush intensity analysis based on FF20, FF25 and F30 criteria further indicate that the first flush effect is weak in the study area. More than 1/3 of the pollutant loads were washed off during metaphase in 96% of all the storm events. More than 1/3 of the pollutant loads were washed off during anaphase in 12% of all the storm events. The results indicate the effects of middle flush and final flush are significant in the study area.

The exponential wash-off model and the logistic wash-off model were both used to simulate the flush processes in the storm events. The exponential model has a good performance to simulate the first flush process but fails to simulate the middle or final flush process in the storm event. However, the logistic wash-off model has a good performance to simulate all the three types of pollutant flush, and particularly, it has a better performance to simulate the middle or final flush process than the exponential model. Thus the logistic wash-off model has more flexibility over the exponential wash-off model. Further study is needed to better understand the mechanism of middle and final flushes and the method for reliable parameter estimation, and the logistic wash-off model should be tested on other pollutants in other urban catchments.

ACKNOWLEDGEMENTS

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Appendix A. Supplementary data

The entire monitoring data are provided as supplementary materials.

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Figure captions

Fig.1 Hydrograph and pollutograph for different flush types

Fig.2 Normalized cumulative curves for different flush types (Adapted from Lee and Bang 2000)

Fig.3 Map of the Shiyan River catchment

Fig.4 Comparison between measured and calculated data (a) First flush; (b)Middle flush; (c) Final flush

Fig.5 Flush characteristics of 26 storm events. (a) Normalized cumulative pollutant load vs normalized cumulative runoff volume; (b) Variation of percentage of cumulative mass load washed off in different phases

Fig.6 Variation of NS coefficients of exponential wash-off model and logistic wash-off model

Fig.7 NS coefficient of exponential wash-off model vs flush intensity

Fig.8 One-at-a-time sensitivity analysis for parameters of logistic wash-off model

Fig.9 Sobol's sensitivity analysis for parameters of logistic wash-off model

Table captions

Table 1 Main characteristics of observed storms

Table2 Model calibration for 26 individual rainfall events (logistic wash-off model)

Fig.1 Hydrograph and pollutograph for different flush types

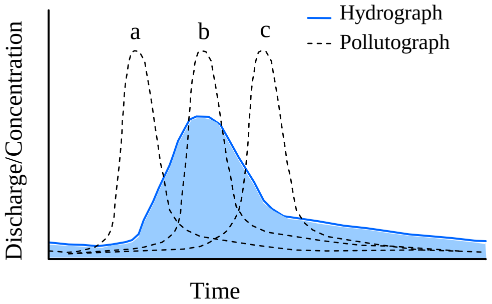

Fig.1 Hydrograph and pollutograph for different flush types

Fig.2 Normalized cumulative curves for different flush types

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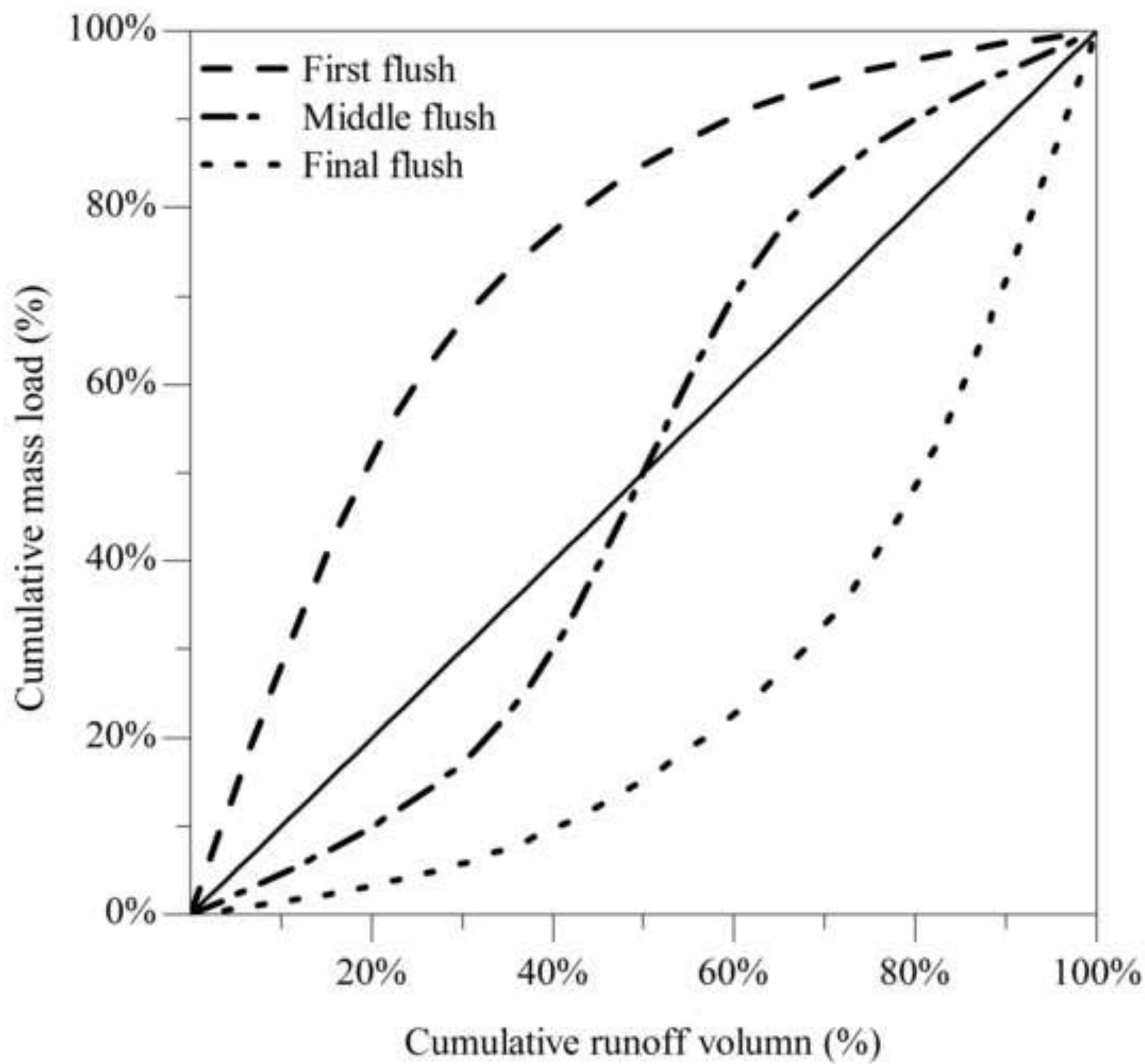

Fig.3 Map of the Shiyan River catchment

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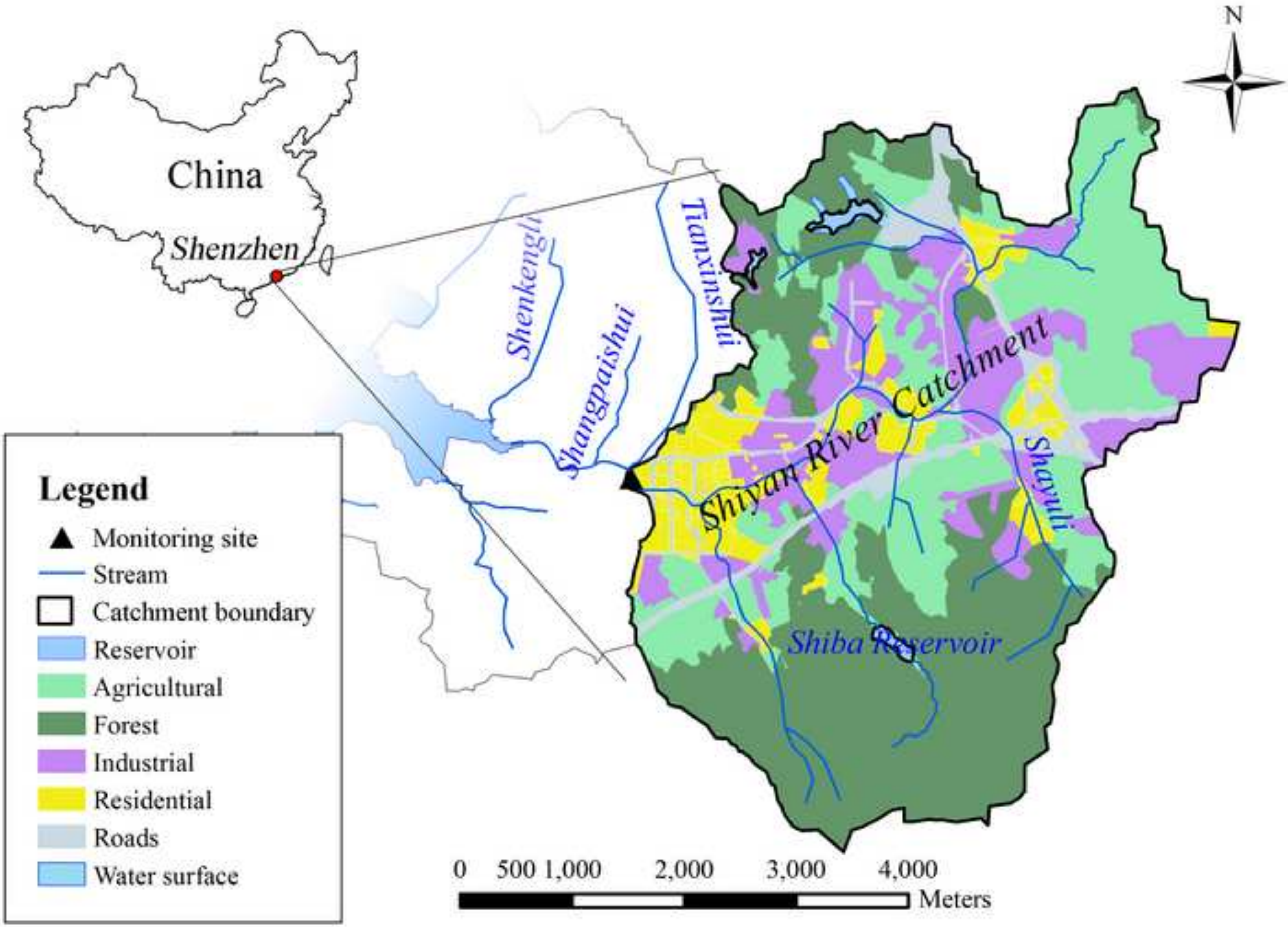

Fig.4 Comparison between measured and calculated data

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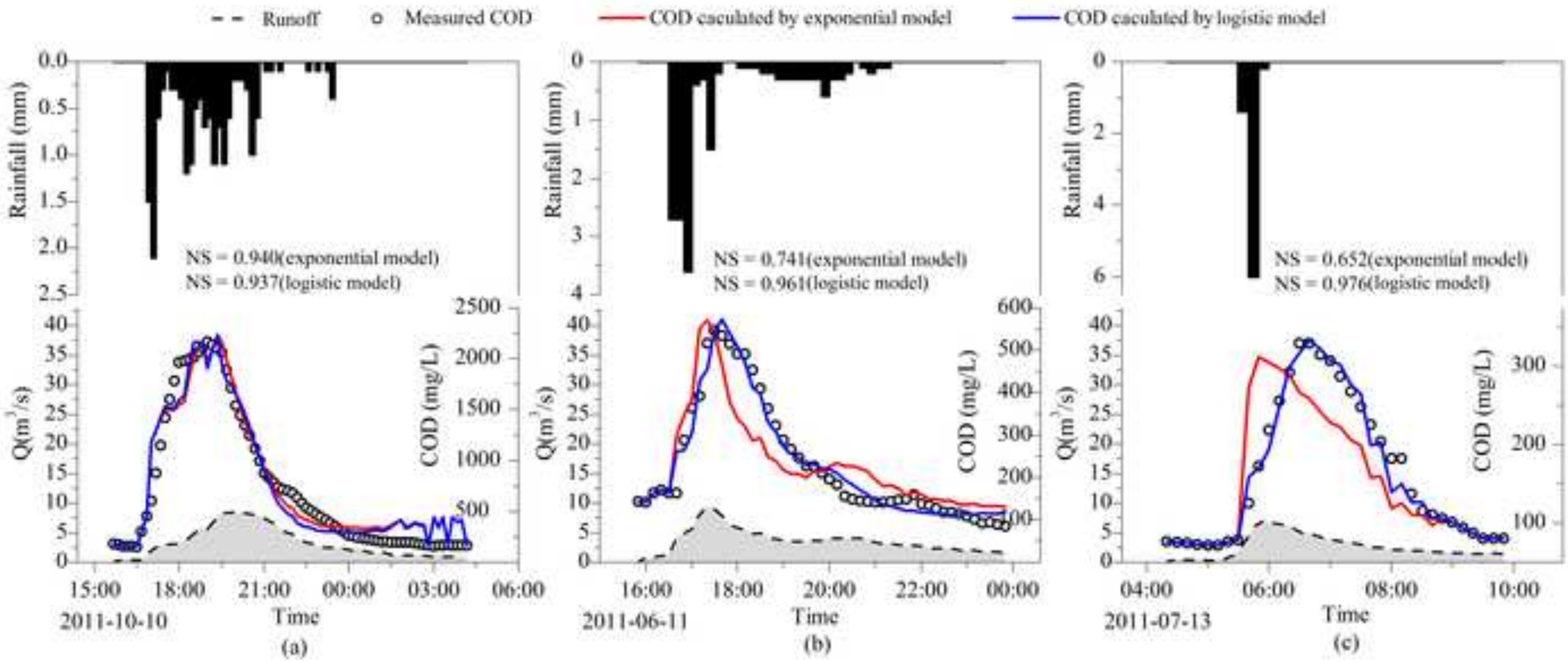

Fig.5 Flush characteristics of 26 storm events

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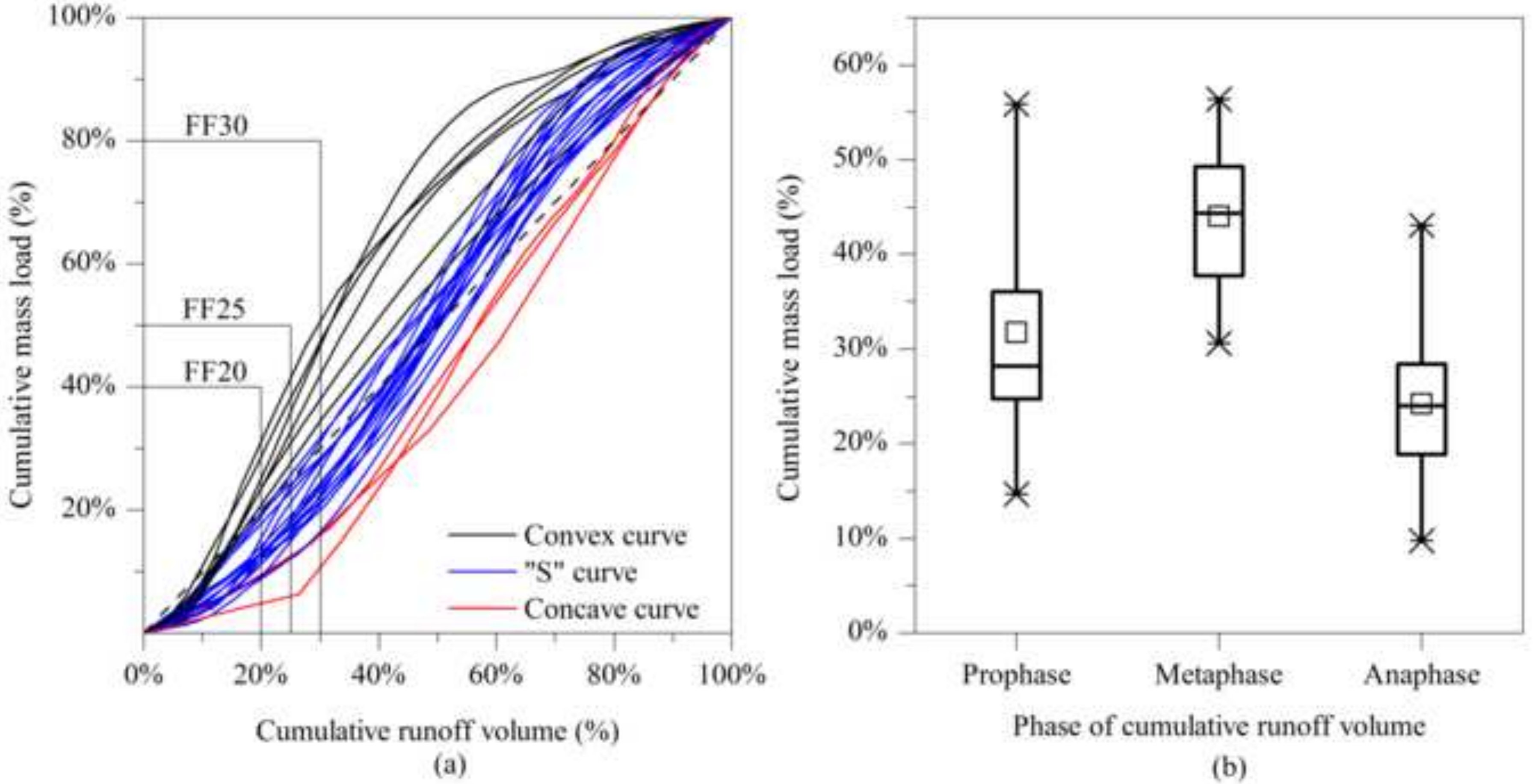

Fig.6 Variation of NS coefficients of wash-off model
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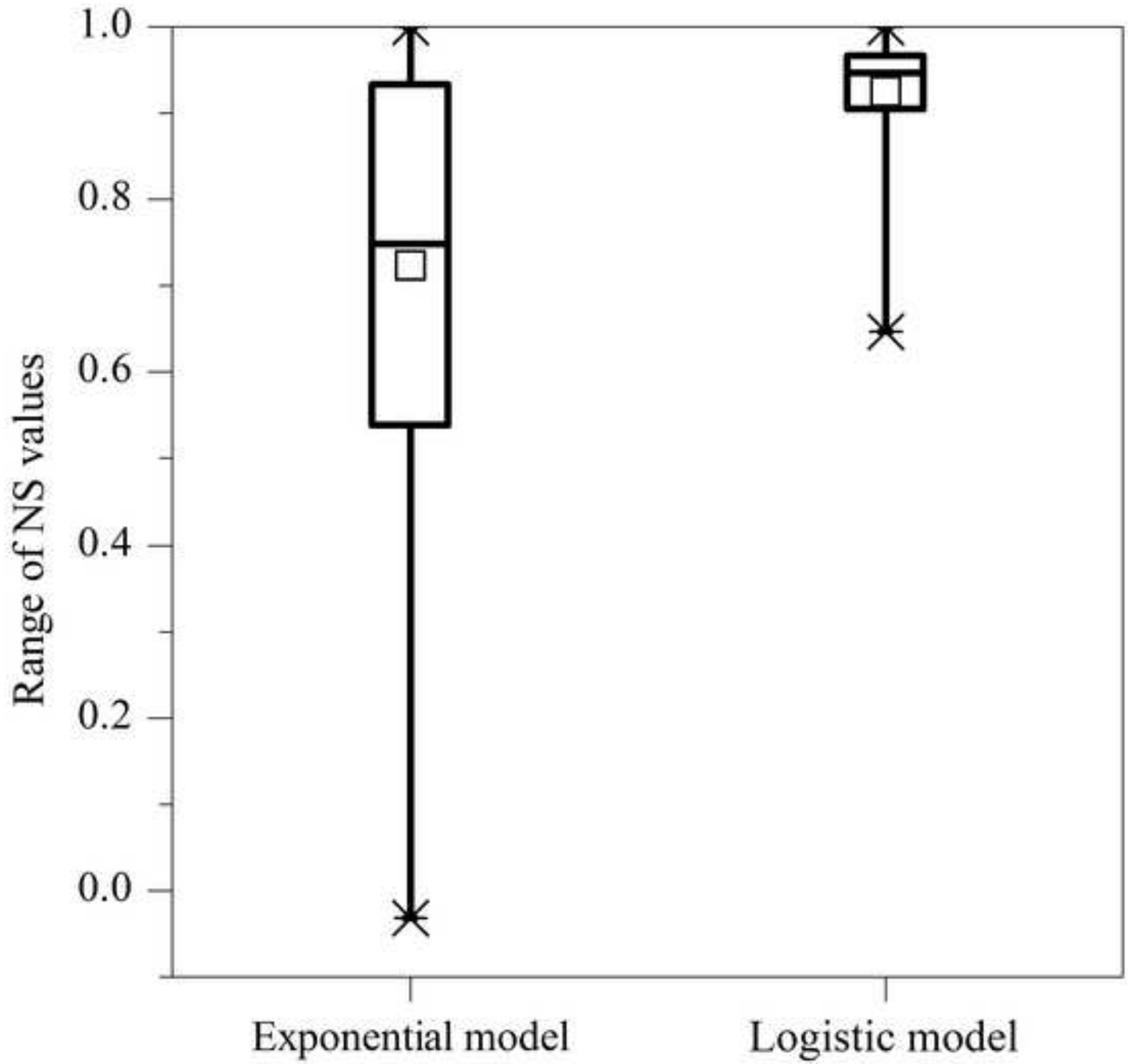

Fig.7 NS of exponential model vs flush intensity

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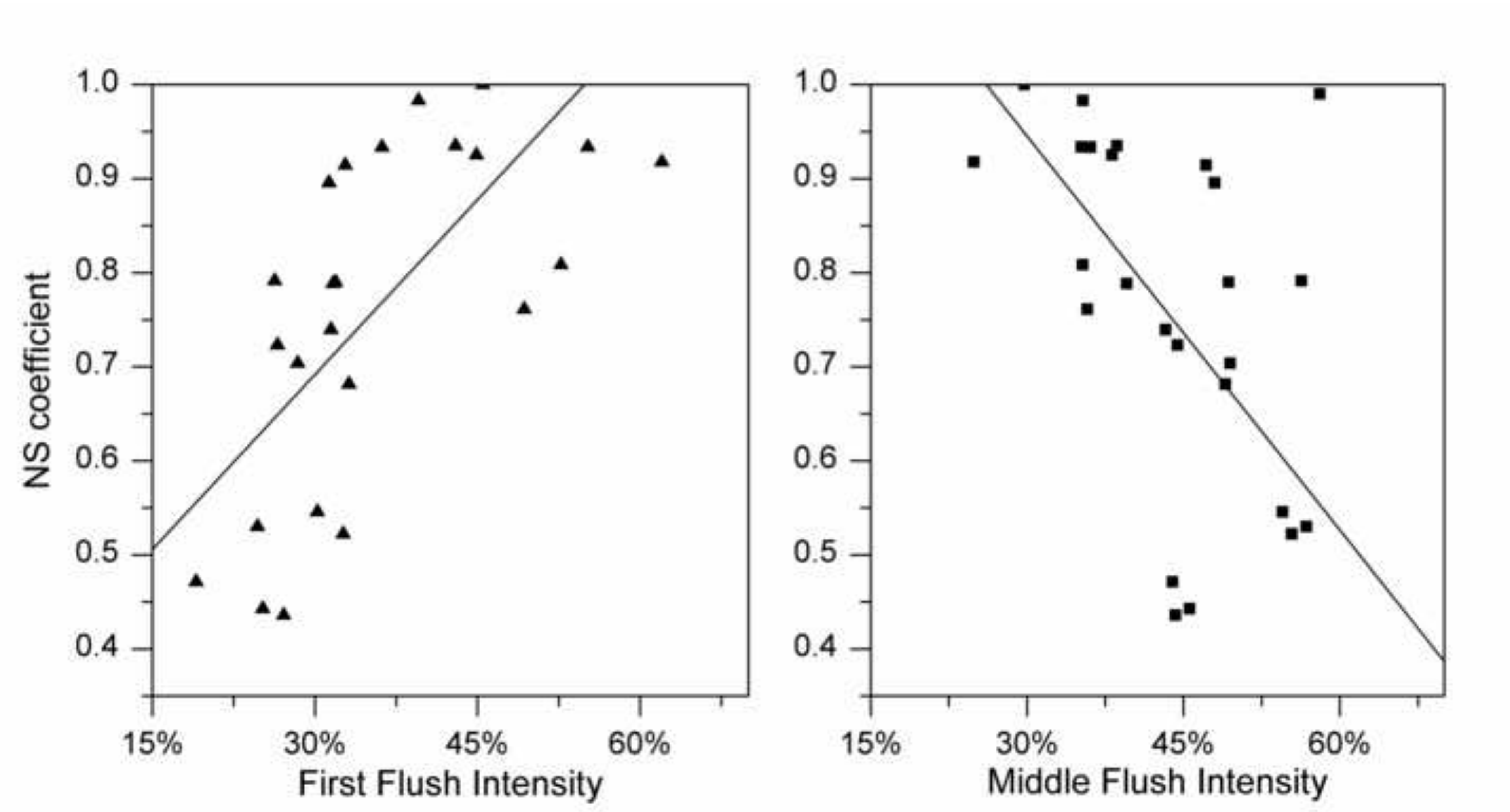

Fig.8 One-at-a-time sensitivity analysis

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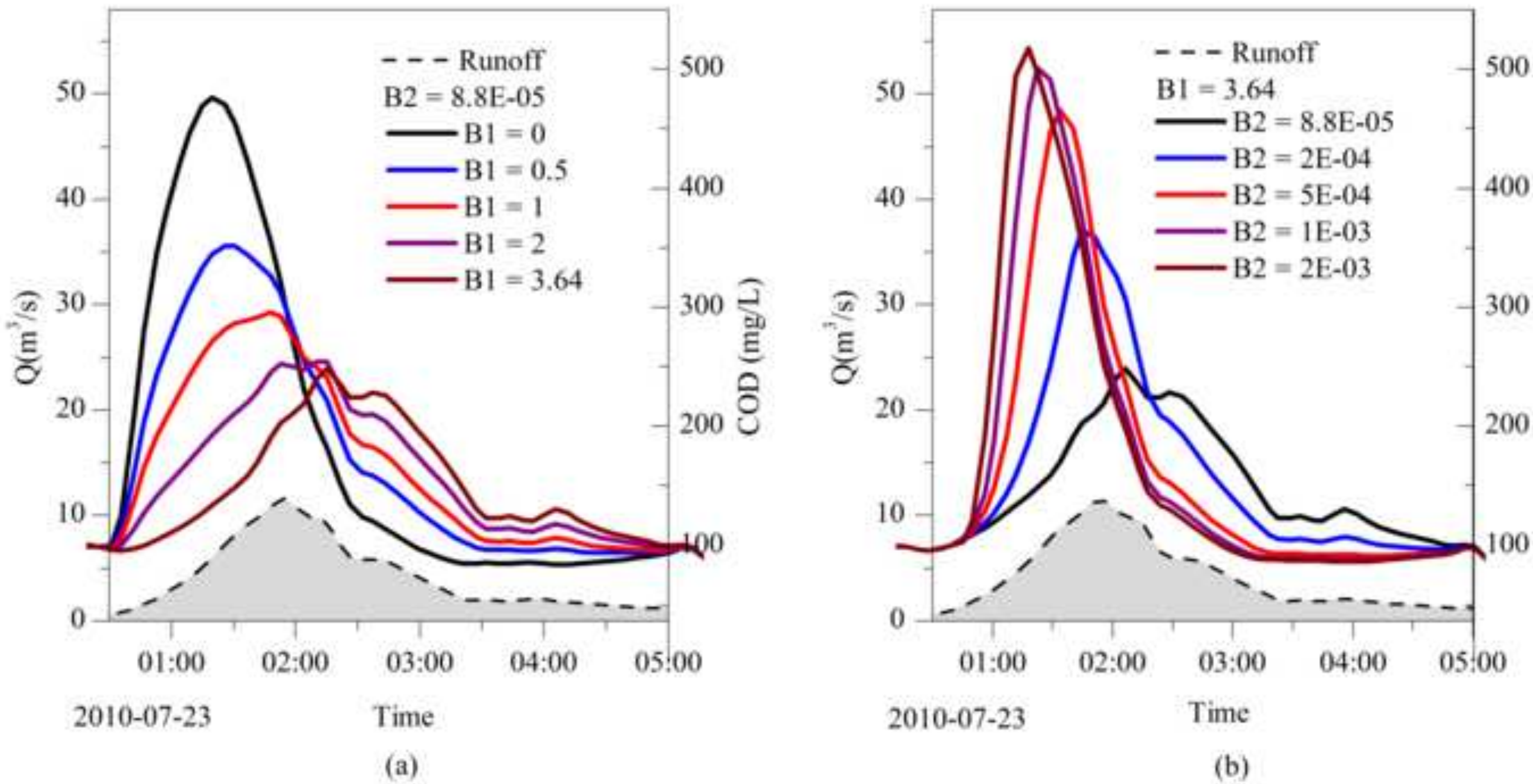

Fig.9 Sobol's sensitivity analysis for new model

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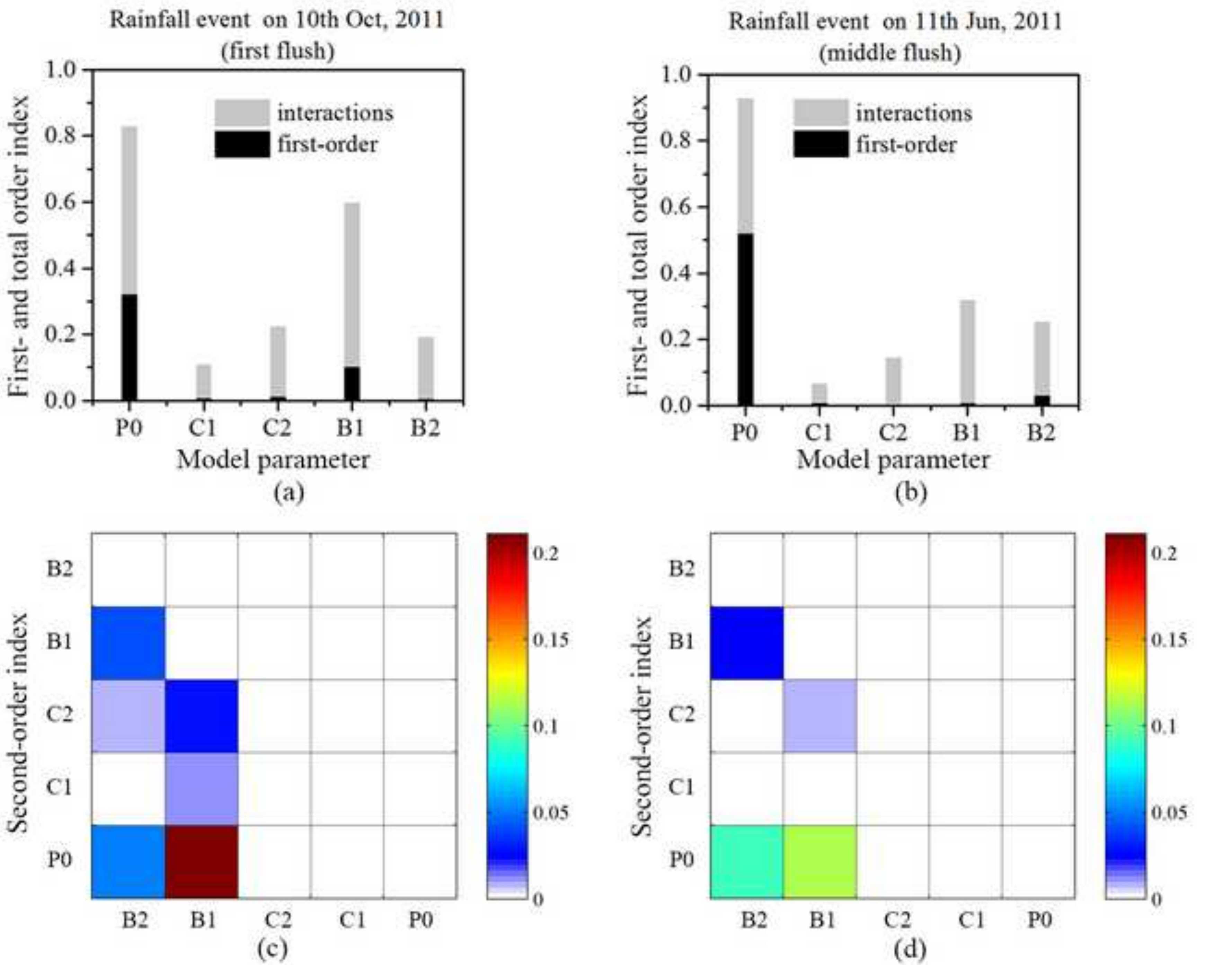

Table 1 and Table2
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Table 1 Main characteristics of observed storms

Event No.	Date [y/m/d h:m]	ADP (hr)	Rainfall amount (mm)	Rainfall duration (hr)	COD (mg/l)
1	2009/3/6 9:20	5.53	24.4	3.13	131 – 467
2	2009/4/13 14:49	20.48	6.8	1.18	84 – 358
3	2009/4/15 22:24	2.37	21.8	6.54	61 – 507
4	2009/4/16 17:00	12.08	8.7	1.12	72 – 459
5	2009/4/25 4:24	134.83	23.7	7.69	76 – 408
6	2010/4/22 11:20	8.08	22.3	3.3	111 – 347
7	2010/7/23 0:05	4.32	8.9	1.65	72 – 238
8	2011/6/11 16:25	10.45	15.8	4.55	85 – 547
9	2011/6/12 0:03	3.1	8.3	0.67	54 – 238
10	2011/6/21 15:28	46	5.8	0.4	62 – 431
11	2011/7/13 5:27	15.02	7.6	0.35	71 – 329
12	2011/7/14 11:56	24.97	14.9	5.21	63 – 205
13	2011/7/29 7:31	14.12	7.8	5.2	34 – 259
14	2011/8/8 14:24	189.25	16.2	3.12	256 – 2009
15	2011/8/9 3:02	9.53	38.1	5.25	140 – 1077
16	2011/8/10 8:19	15.78	14.5	8.47	83 – 779
17	2011/8/17 13:43	122.67	5.5	0.27	219 – 520
18	2011/8/21 13:58	96	27.9	1.08	300 – 837
19	2011/9/2 2:19	6.5	7.3	5.13	180 – 2069
20	2011/9/2 16:32	9.12	3.3	3.59	204 – 1032
21	2011/9/4 20:17	38.33	7.7	0.22	227 – 808
22	2011/9/8 14:56	58.97	4.4	1.82	201 – 1891
23	2011/10/10 16:45	157	17.1	6.6	154 – 2171
24	2011/10/12 6:07	3.4	11.8	8.31	89 – 999
25	2012/4/5 12:13	119.5	23.2	4	126 – 1452
26	2012/4/13 18:19	107.05	18.7	0.83	97 – 681

Table2 Model calibration for 26 individual rainfall events (logistic wash-off model)

	Parameters of logistic wash-off model				
	P_0 (kg)	C_1	C_2	B_1	B_2 (m^{-3})
Minimum	1.95×10^{4}	1.78×10^{-2}	1	0.911	2.30×10^{-5}
Maximum	2.14×10^{5}	3.92×10^{-1}	1.84	2.5	1.58×10^{-3}
Mean	7.70×10^{4}	1.03×10^{-1}	1.16	2.19	2.00×10^{-4}
Median	5.50×10^{4}	6.06×10^{-2}	1.11	2.46	7.80×10^{-5}
Standard deviation	5.43×10^{4}	1.00×10^{-1}	0.197	0.55	3.86×10^{-4}