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Essential title page information

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

Hua-peng Qin^{a*}, Kang-mao He^a, Guangtao Fu^b

^aKey Laboratory for Urban Habitat Environmental Science and Technology, School of Environment and Energy, Peking University Shenzhen Graduate School, 518055, Shenzhen, China;

^bCentre for Water Systems, College of Engineering, Mathematics and Physical Sciences, University of Exeter, Exeter EX4 4QF, UK

*Corresponding author.

Tel: +86 755 26035291; Fax: +86 755 26035291

Email: qinhp@pkusz.edu.cn

Postal address:

Room 414, E Building,
Peking University Shenzhen Graduate School,
Lishui Road, Xili, Nanshan District
Shenzhen 518055, China

21 **Abstract:**

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

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

40

41 **1 Introduction**

42 Pollutants flushed out by surface runoff during storm events can be a large contributor to the
43 receiving water quality problems in urban areas (Behera et al., 2006; Richardson and Tripp, 2006). The
44 flush effects have been extensively investigated to determine whether the pollutants experience higher
45 concentration levels in certain periods of a storm event. The first flush effect can be defined as a
46 phenomenon in which a greater proportion of pollutant loads are washed off during the beginning of a
47 rainfall event than in other periods (Lee et al., 2002; Sansalone and Cristina 2004). First flush
48 phenomenon is more likely to occur in a smaller catchment with more impervious land surfaces (Kim
49 et al. 2004; Kim et al. 2007; Lee et al., 2002; Taebi and Droste, 2004) and is highly dependent on time
50 of concentration of a catchment, i.e., the time needed for water to flow from the most remote point in a

51 watershed to the watershed outlet (Kang et al. 2008). A number of previous studies have been
52 conducted to assess the occurrence and the causes of the first flush effect (e.g., Bach et al., 2010;
53 McCarthy, 2009; Obermann et al. 2009; Sansalone and Cristina, 2004). Furthermore, with an in-depth
54 understanding of first flush, structural measures (e.g. retention tanks and pipe networks) can be
55 explicitly designed to intercept and treat the initial runoff and thus can minimize the impact of runoff
56 pollution on the receiving water bodies (Deletic, 1998; Kang et al. 2008).

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

78 The urbanizing process is accelerating in China and other developing countries. An urbanizing
79 catchment is characterized by rapid economic and population growth as well as dramatic changes in
80 land use from natural/rural to urban areas, which usually have heterogeneous land uses with a mix of

81 residential, industrial, agricultural and natural lands. Although numerous efforts have been made to
82 investigate the flush effect of storm runoff pollution in urban catchments, there are very few studies
83 reporting the flush characterization in urbanizing catchments. From a recent investigation carried out in
84 four rapidly urbanizing catchments in China (Qin et al. 2010), it was found that the first flush intensity
85 is weak in the catchments with a low proportion of impervious areas. If first flush phenomena are not
86 predominant and second flush phenomena are significant, the performance of urban runoff
87 management based on the first flush theory for water quality improvement may be compromised (Flint
88 and Davis, 2007). Hence, there is a need to characterize and examine all flush effects for the
89 management and treatment of storm runoff pollution in urbanizing catchments.

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

107 In theory, a complex, high resolution physically based model, which can accurately represent
108 various processes, should have capacity to simulate any types of flush effects. However, the
109 development of complex models is difficult in many cases due to data availability. The parsimonious
110 models with few parameters are more applicable in practice, in particular where data are not available

111 to develop complex models. The exponential model has been widely used due to its simplicity and ease
112 of use. More importantly, it has been successfully used to describe the first flush effect in urban areas,
113 particularly for impervious areas (Behera et al., 2006; Millar et al., 1999). However, few previous
114 studies have discussed the suitability of the widely used exponential wash-off model for describing the
115 middle or final flush processes in an urbanizing area. Thus, there is a need to improve the wash off
116 model in order to better describe the different types of flush effects of storm runoff pollution since
117 various flush phenomena may occur. This paper aims to 1) identify the existence of first flush, middle
118 flush and final flush through the use of a rapidly urbanizing catchment - Shiyao river catchment, China;
119 2) investigate whether the conventional exponential wash-off model can be used to simulate the middle
120 and final flush effects; and 3) extend the exponential model to simulate middle and final flushes.

121

122 **2 Material and methods**

123 **2.1 Pollutant flush analysis**

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

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

133

134 **Fig.1 Hydrograph and pollutograph for different flush types**

135

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

$$138 \quad L = m(t) / M \quad (1)$$

$$139 \quad F = v(t) / V \quad (2)$$

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

141 (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
142 pollutant load and total runoff volume for the entire event. A bisector $L-F$ curve (45° line) represents
143 the situation with a uniform pollutant wash off rate during a storm event (the solid line as shown in
144 Fig.2). By referencing to the bisector line, the different characteristics of the three flush types can be
145 reflected by the shape of $L-F$ curve. A convex $L-F$ curve lying above the bisector line represents a
146 condition where the majority of the pollutant load is delivered in the prophase of the storm event, i.e.,
147 first flush (the dashed line as shown in Fig.2). Conversely, a concave $L-F$ curve below the bisector line
148 represents a condition where the majority of the pollutant load is not delivered until the anaphase of the
149 event (the dotted line as shown in Fig.2), i.e., final flush. In addition, a “S” $L-F$ curve across the
150 bisector line describes a condition where the majority of the pollutant load is delivered in the
151 metaphase of the event (the dot-dash line as shown in Fig. 2), i.e., middle flush.

152

153 **Fig.2 Normalized cumulative curves for different flush types** (Adapted from [Lee and Bang 2000](#))

154

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

169

170 **2.2 Wash-off models for flush process**

171 2.2.1 Exponential wash-off model

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

$$174 W_t = C_1 Q_t^{C_2} (P_0 - P_{wt}) \quad (3)$$

175 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
176 pollutant buildup in the catchment before the rainfall (kg), and P_{wt} is cumulative pollutant load washed
177 off at time t (kg), which can be calculated as the time integral for the washoff load ratio (W_t), i.e.,

$$178 P_{wt} = \int_0^t W_t dt \quad (4)$$

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

$$180 C_t = C_1 P_0 Q_t^{C_2} e^{-C_1 \int_0^t Q_t^{C_2} dt} \quad (5)$$

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

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

194

195 2.2.2 Development of logistic wash-off model

196 A new wash off model is developed to simulate various types of flush phenomena in this study.
197 Generally, the surface pollutant loads available for wash off depend on not only the initial pollutant
198 buildup (P_0) but also the effective contributing area of runoff (S_e) in a catchment. A rapidly urbanizing
199 catchment usually contains a mixture of agricultural, industrial and residential land uses. The pollutant
200 wash off processes in the urbanizing catchment may be more complicated than those in the urban area

201 dominated by impervious surfaces: in the initial period of a rainfall event, only runoff from impervious
 202 land uses (e.g. traffic, industrial and residential land) contribute to runoff pollution; however, more and
 203 more pervious lands begin to generate runoff and contribute to runoff pollution as rain continues (Qin
 204 et al. 2010). Therefore, S_e has a tendency to initially increase with an increase in rainfall amount or
 205 runoff volume, and then remain stable after all the lands begin to generate runoff. In terms of the
 206 aforementioned mechanism of the runoff pollution, it is assumed that the pollutant loads available for
 207 wash off increase with cumulative runoff volume following a logistic curve, and thus equation (3) can
 208 be modified as:

$$209 \quad W_t = C_1 Q_t^{C_2} (P_0 \delta_t - P_{wt}) \quad (6)$$

$$210 \quad \delta_t = \frac{1}{1+B_1 e^{-B_2 V_t}} \quad (7)$$

211 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
 212 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 ,
 213 which can be expressed as:

$$214 \quad V_t = \int_0^t Q_t dt \quad (8)$$

215 According to equation (4),

$$216 \quad W_t = dP_{wt}/dt \quad (9)$$

217 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),

218 then

$$219 \quad \frac{dP_{wt}}{dt} + r(t) \cdot y = s(t) \quad (10)$$

220 Equation (10) is a first-order linear non-homogeneous differential equation. The equation can be

221 solved by multiplying the integrating factor $e^{\int r(t)dt}$ throughout to obtain:

$$222 \quad \frac{dP_{wt}}{dt} e^{\int r(t)dt} + r(t) \cdot P_{wt} \cdot e^{\int r(t)dt} = s(t) \cdot e^{\int r(t)dt} \quad (11)$$

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

$$224 \quad \frac{d}{dt} (P_{wt} \cdot e^{\int r(t)dt}) = s(t) \cdot e^{\int r(t)dt} \quad (12)$$

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

$$226 \quad P_{wt} = e^{-\int_0^t r(t)dt} \left(\int_0^t s(t) \cdot e^{\int r(t)dt} dt \right) \quad (13)$$

227 Then the pollutant concentration of runoff can be given as

$$228 \quad C_t = P_{wt}/Q_t \quad (14)$$

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

237

238 **2.3 Evaluation of model calibration**

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

$$242 \quad NS = 1 - \frac{\sum (X_{sim,t} - X_{obs,t})^2}{\sum (X_{obs,t} - \overline{X_{obs}})^2} \quad (15)$$

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

250

251 **3 Case study and discussion**

252 **3.1 Study area and sampling campaign**

253 The Shiyan River catchment is located in Shenzhen city, Southeastern China (Fig.3). It has a
 254 warm, monsoon-influenced, humid subtropical climate, with an average annual rainfall of 1,933 mm.
 255 The area of the catchment is 25 km². Due to rapid urbanization in the last 20 years, the percentage of
 256 built-up area in the catchment increased to 32% in 2010. However, the agricultural land remains one of

257 the main types of land use, and its area accounts for 29% of the catchment. The catchment is served by
258 two types of drainage systems: combined sewer systems in the early developed areas and separate
259 sewer systems in the newly developed areas. For further details of the catchment, please refer to [Qin et
260 al. \(2013\)](#). It has been reported that the water quality of the river has a high rate of non-compliance
261 with the water quality regulations and the runoff pollution is one of the major sources of pollutants in
262 the urbanizing area ([Qin et al 2010](#)). Therefore, it is necessary to identify the pollutant flush type,
263 evaluate the flush intensity and accurately simulate the flush process, which would be helpful in runoff
264 pollutant loads control decision making, water quality management and drainage system design.

265

266 **Fig.3 Map of the Shiyang River catchment**

267 .

268 Since there was no hydrological monitoring at the study area prior to this study, a temporary
269 monitoring site was installed at the downstream section of the Shiyang River to measure streamflow and
270 associate water quality (Fig.3). The drainage area of the section is 35 km², which accounts 90% of the
271 total area of the Shiyang River catchment. The streamflow was measured at 10 min intervals by
272 Sontek/YSI Argonaut-SW (1ASW-33000 model), which was installed at the bottom the river. The
273 water was automatically sampled at 20 min intervals from the middle thread of the river section. In this
274 study, runoff quality is represented by Chemical Oxygen Demand (COD) because it is one of the main
275 pollutants in the study catchment. COD of the sample was measured by Horbi UV-COD online monitor
276 (OPSA-150) at 20 min intervals, which was installed on the nearby river bank. The Horbi UV-COD
277 was verified each half a month by comparing the instrument output values and manual analysis values,
278 and the corresponding correlation coefficient is around 0.8-0.9. Rainfall data were recorded by an
279 automated gauge (1-min interval) (Vaisala Weather Transmitter WXT510) at Shiyang reservoir rainfall
280 monitoring station operated by Shenzhen Meteorology Bureau. A continuous measurement was
281 conducted from April 2009 to April 2012. Due to missing values, only 26 events with complete data
282 were extracted for analysis in this study (see in Appendix A). Table 1 summarizes the observed rainfall
283 data. The Antecedent Dry Period (ADP), rainfall amount and rainfall duration ranged from 2.4 to 189
284 hours, 1.4 to 38.1mm and 0.22-8.47 hours, respectively.

285

286 **Table 1 Main characteristics of observed storms**

287 **3.2 Type of pollutant flush**

288 Fig.4(a)-(c) shows the measured flow and concentrations of COD during three storm events of
289 October 10, 2011 (17.1 mm), June 11, 2011(15.8 mm) and July 13, 2011(7.6 mm), respectively. The
290 COD concentration peak appeared before the flow peak and a typical first flush effect occurred during
291 the storm event of October 10, 2011 (Fig.4 (a)). The COD concentration peak and the flow peak
292 appeared nearly simultaneously and a typical middle flush effect occurred for the storm event of June
293 11, 2011 (Fig.4 (b)). In addition, the COD concentration peak appeared after the flow peak and a
294 typical final flush effect occurred for the storm event of July 13, 2011(Fig.4 (c)). In summary, around 7,
295 16 and 3 of the 26 storm events have the concentration peak that appeared before, with and after the
296 flow peak respectively. The results indicate that most of the storm events have middle flush or final
297 flush in the study area.

298

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

300

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

309

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

312

313 **3.3 Intensity of flush effect**

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

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

331

332 **3.4 Evaluation of wash-off models**

333 **3.4.1 Model calibration**

334 In order to compare the goodness of fit of the exponential model and the new model, the two
335 models were calibrated for each of the 26 rainfall events and the corresponding NS coefficients
336 were obtained. In the GA based calibration process, Q_i of the exponential wash-off model and the
337 logistic wash-off model are input data obtained from the measured stream flow; the ranges of P_0 , c_2
338 and c_3 used in the search for both the two models are 2000-30000 kg/km², 0.01-0.8, and 1-2,
339 respectively; and the ranges of B_1 and B_2 used in the search for the logistic model are 0-50 and
340 0.00001-0.07m⁻³, respectively. And we set the values of the GA parameters to 500 for population
341 size, 90% for crossover and 1% for mutation probability. The search is terminated after 200
342 generations.

343 **3.4.2 Performance of the exponential wash-off model**

344 Fig.4 shows the pollutographs of three storm events based on the simulation using the exponential
345 wash off model (red line). The comparison between the simulated and measured data indicates that the
346 simulated data for the storm event of October 10, 2011 fit well with the measured data. However, the
347 simulated data for the other two storm events failed to fit well with the measured data, particularly,

348 there is a significant gap between the peaks of measured and simulated COD concentrations for the
349 storm event of July 13, 2011.

350 Furthermore, *NS* coefficients for the 26 events of the exponential model are between -0.03 and
351 0.989 (Fig.6). Over 73% of the events have a *NS* coefficient higher than 0.6. Correlation analysis was
352 made between the *NS* coefficients of the exponential model and the flush intensity indicators (e.g.,
353 FF20, FF25, FF30, and percentage of pollutant load washed off in prophase, metaphase and anaphase,
354 respectively) (Fig.7). The results reveal that the *NS* coefficients have a positive correlation with the first
355 flush intensity with correlation coefficients of 0.592 ($p<0.05$), 0.637 ($p<0.05$) and 0.627 ($p<0.05$) for
356 FF20, FF25 and FF30, respectively; however, the *NS* coefficient have a negative correlation with the
357 middle flush intensity (percentage of pollutant load washed off in metaphase), with correlation
358 coefficients of -0.462 ($p<0.05$). The correlative analysis demonstrates that the exponential model has a
359 good performance to simulate the first flush process but fails to simulate the middle or final flush
360 process in the storm events.

361

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

363

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

365

366 **3.4.3 Performance of the logistic wash-off model**

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

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

378 has a good performance to simulate all the three types of pollutant flush, and particularly, it has a better
379 performance to simulate the middle or final flush process than the exponential model. Thus the logistic
380 wash-off model has more flexibility than the exponential wash-off model.

381

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

383

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

388

389 **3.4.4 Sensitivity analysis of the logistic wash-off model**

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

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

398 Fig. 8(b) shows another set of model responses to the change in the value of B_2 (with B_1 fixed at
399 3.64). Contrary to B_1 , increasing B_2 advances the occurrence of the peak, and the peak of concentration
400 appears before that of runoff when $B_2 > 5e-04$. Furthermore, when $B_2 = \infty$, $\delta_t = 1$ according to equation
401 (7), thus the logistic wash-off model becomes an exponential wash-off model. Therefore, both B_1 and
402 B_2 have significant effect on the location of the peak concentration.

403

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

405

406 The global sensitivity of the logistic wash-off model was further measured by Sobol's method

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

422

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

424

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

432 According to the derivation of the new model, $1/(1+ B_1)$ represents the ratio of the pollutant loads
433 available for wash-off to the total pollutant loads accumulated on the catchment (P_0) at the beginning
434 of a rainfall event. B_1 may be affected by land use types, distribution of pollutant loads in the
435 catchment, ADP, temperature and other weather conditions before the storm event. B_2 determines the
436 rate of increase from $1/(1+ B_1)$ to 1 with the increase in V_r . B_2 may be affected by many factors, e.g.,

437 land use and soil types, rainfall amount and duration. However, further study is required to identify the
438 factors that affect each parameter.

439

440 **4 Conclusions**

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

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

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

461

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467 substantially improved this article.

468

469 **Appendix A. Supplementary data**

470 The entire monitoring data are provided as supplementary materials.

471

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550 **Figure captions**

551

552 **Fig.1 Hydrograph and pollutograph for different flush types**

553

554 **Fig.2 Normalized cumulative curves for different flush types** (Adapted from [Lee and Bang](#)
555 [2000](#))

556

557 **Fig.3 Map of the Shiyang River catchment**

558

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

561

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

565

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

567

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

569

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

571

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

573

574 **Table captions**

575

576 **Table 1 Main characteristics of observed storms**

577

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

Fig.1 Hydrograph and pollutograph for different flush types

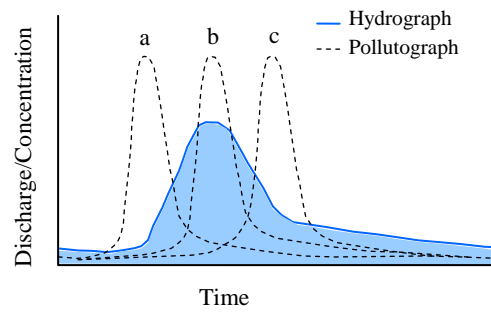


Fig.1 Hydrograph and pollutograph for different flush types

Fig.2 Normalized cumulative curves for different flush types
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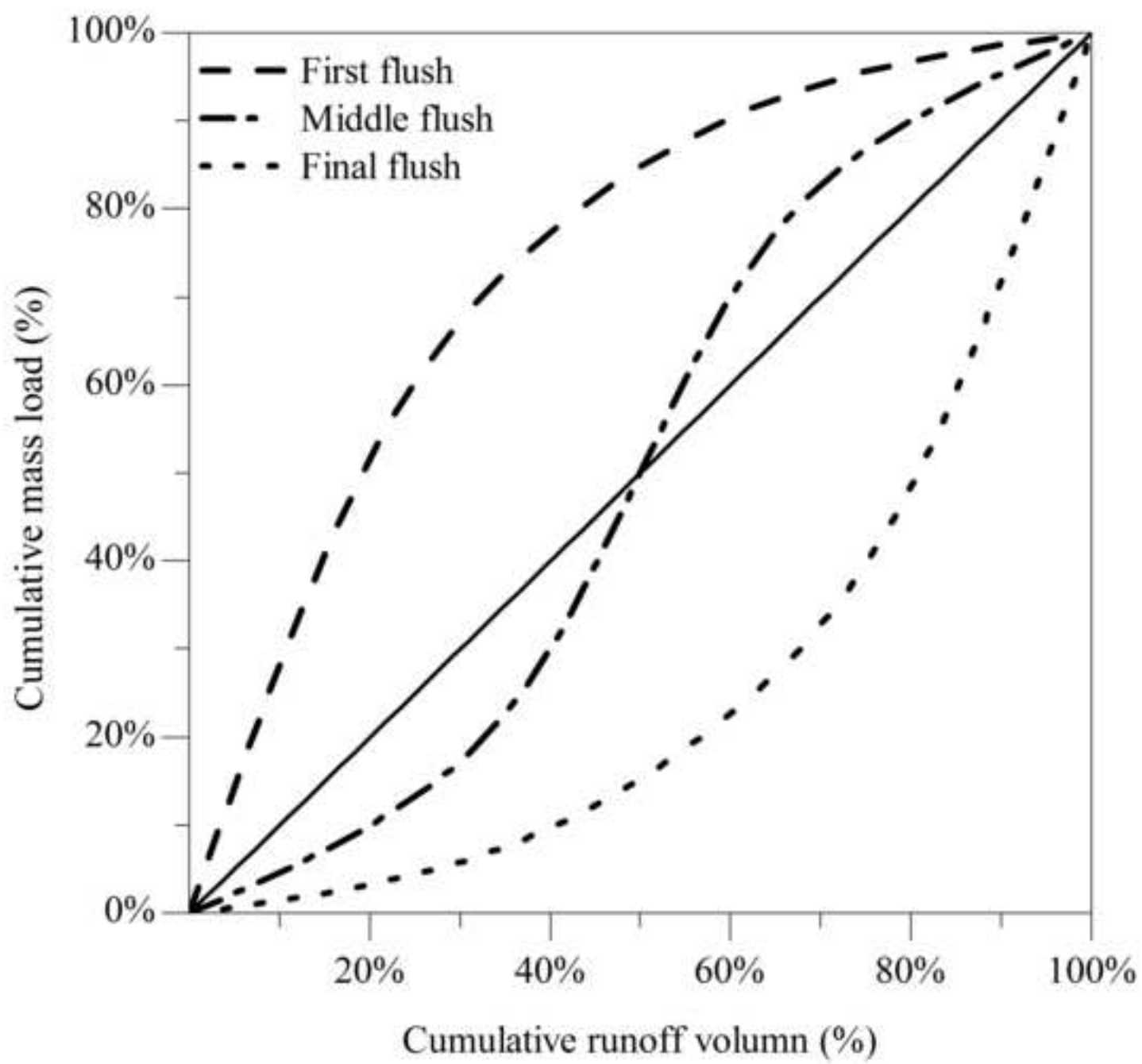


Fig.3 Map of the Shiyao River catchment
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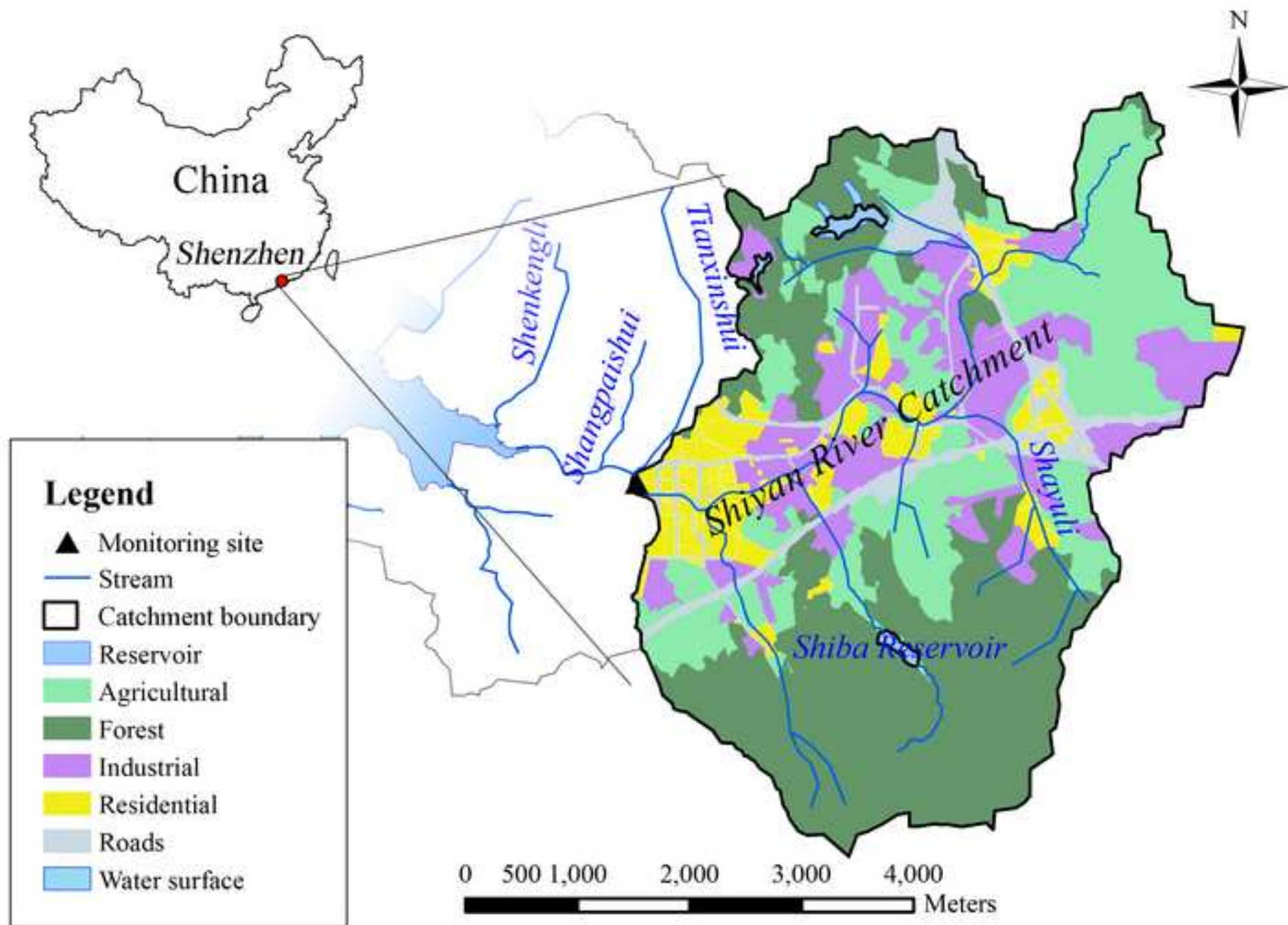


Fig.4 Comparison between measured and calculated data
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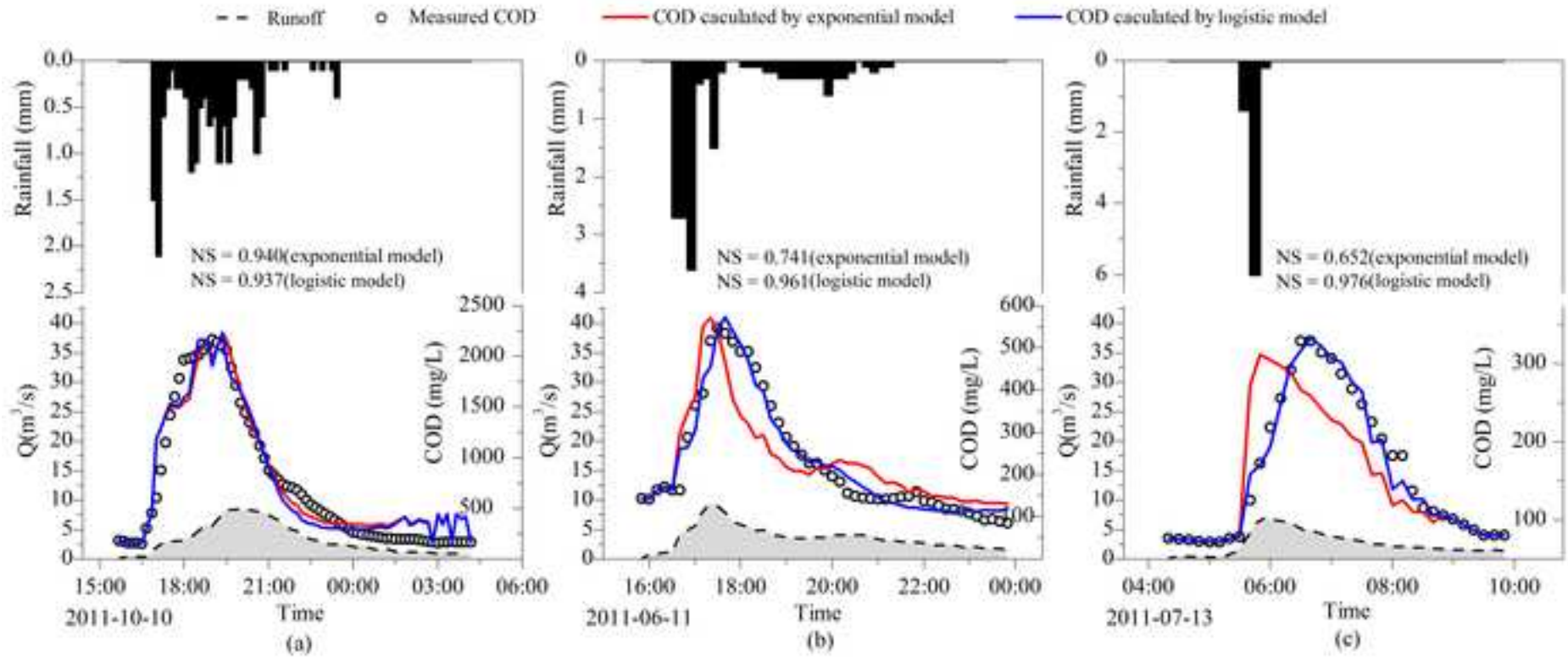


Fig.5 Flush characteristics of 26 storm events
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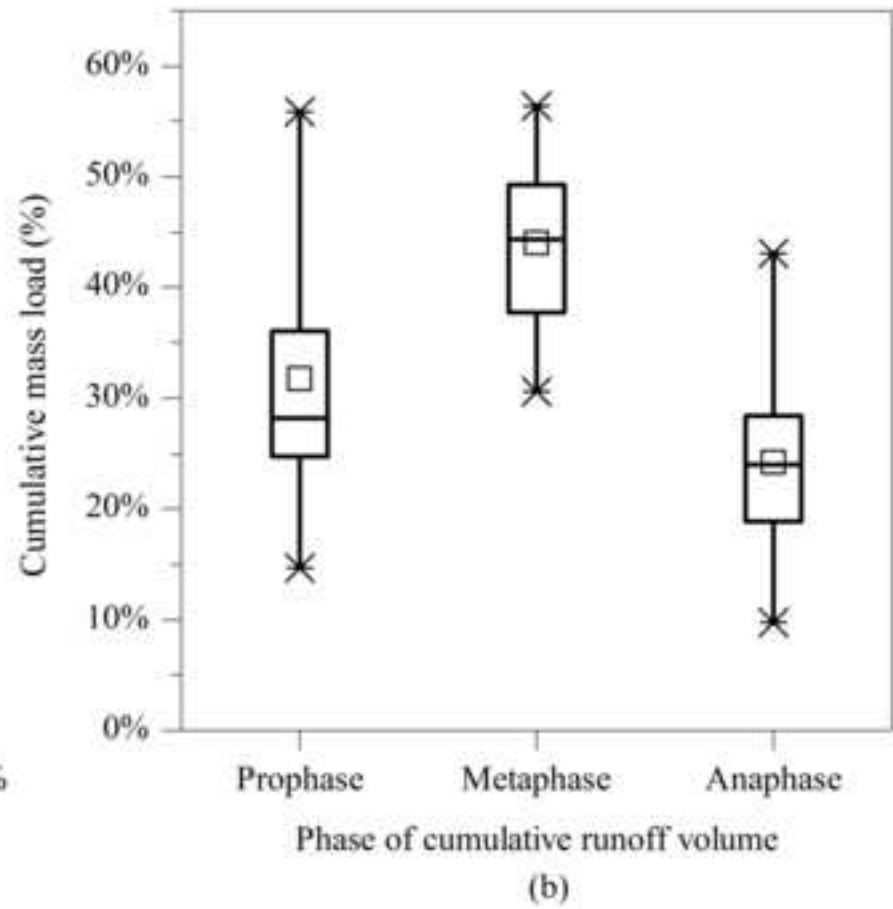
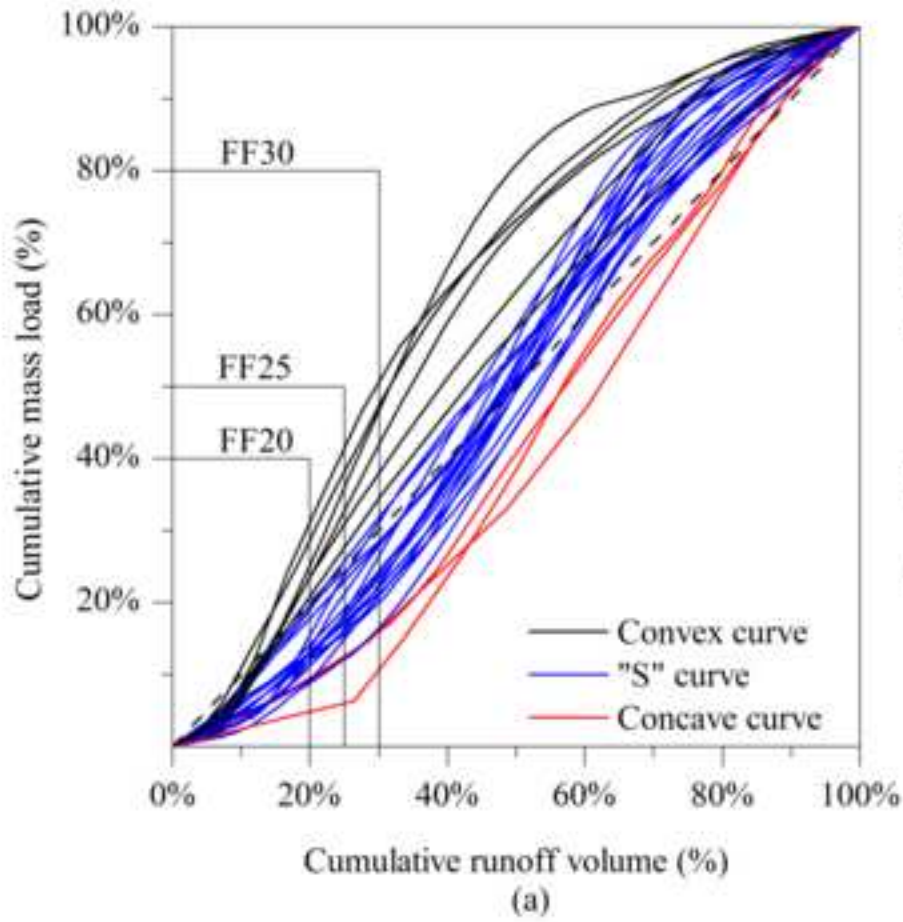


Fig.6 Variation of NS coefficients of wash-off model
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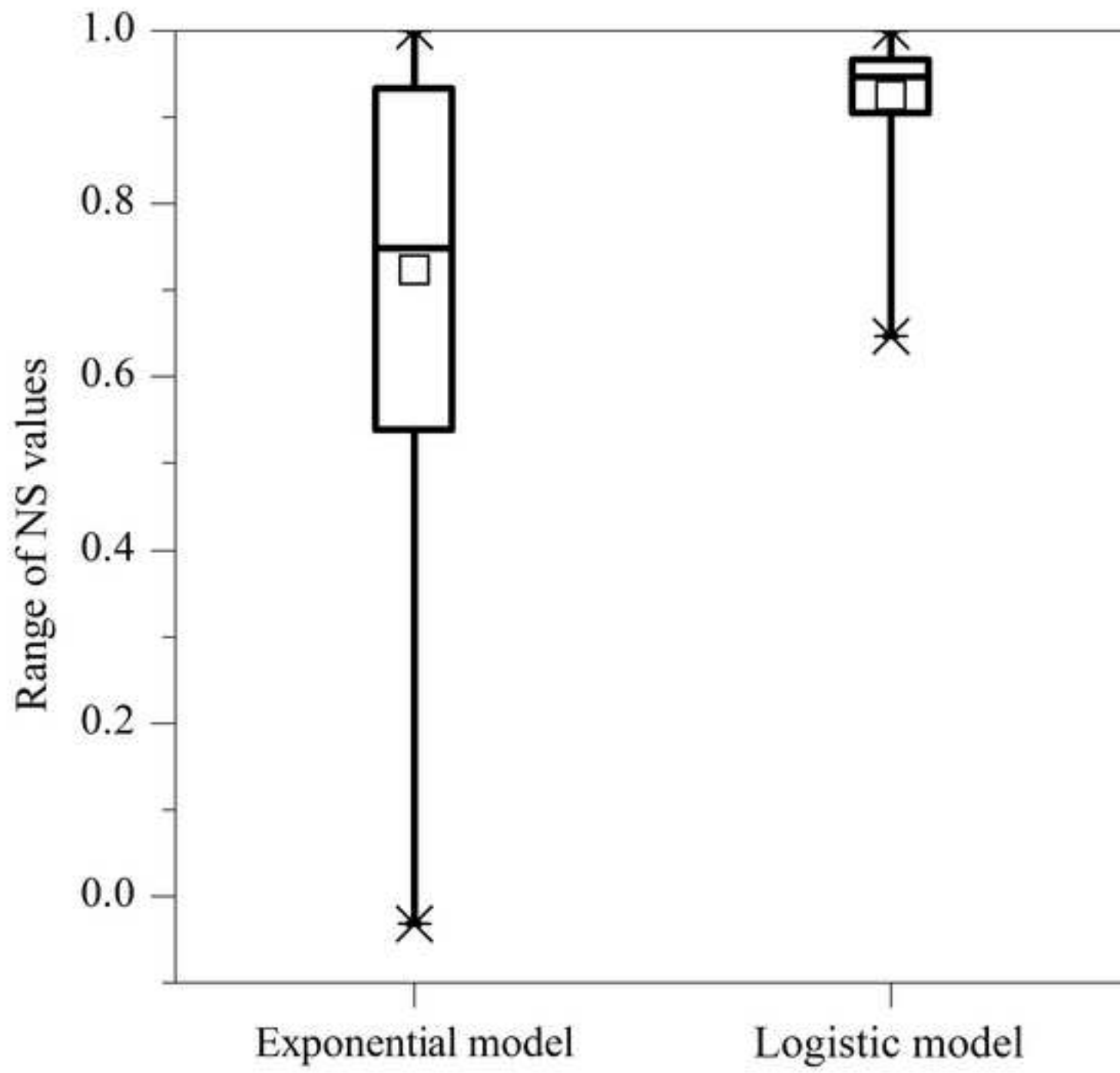


Fig.7 NS of exponential model vs flush intensity
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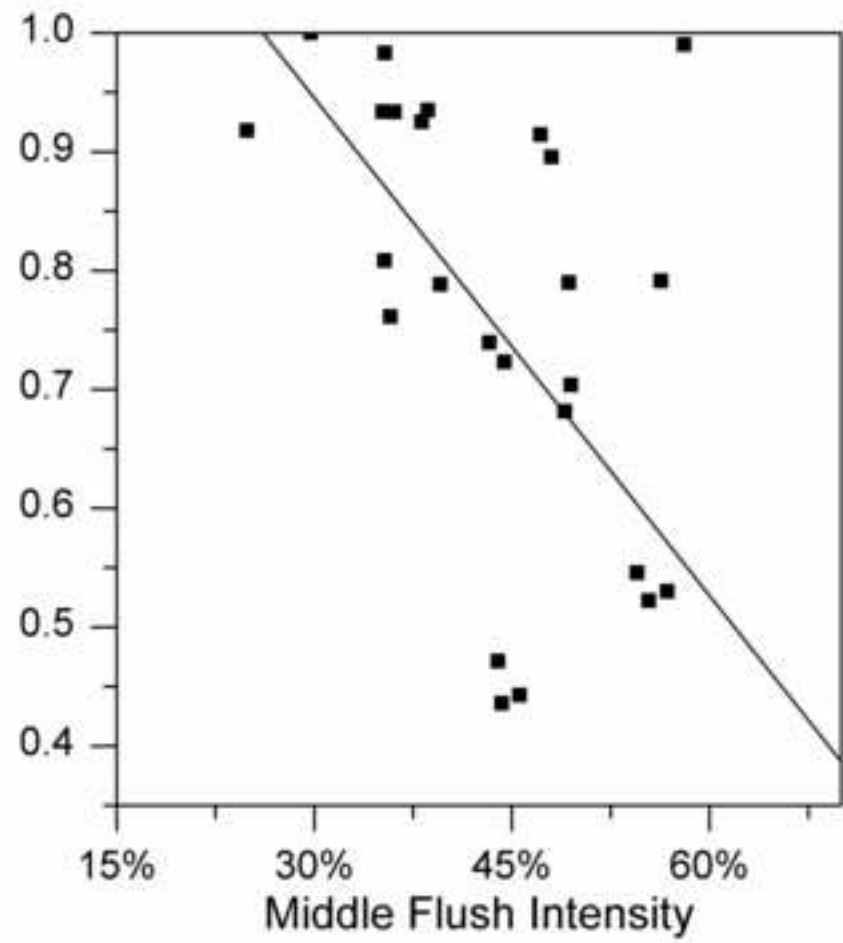
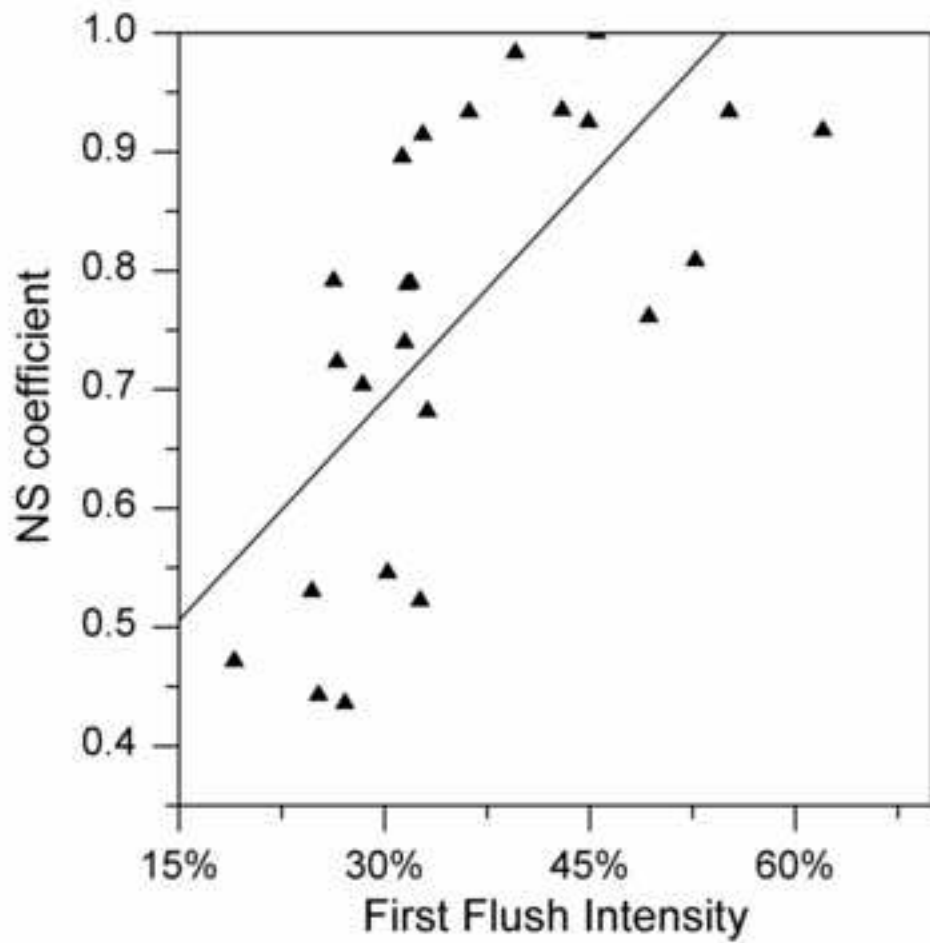
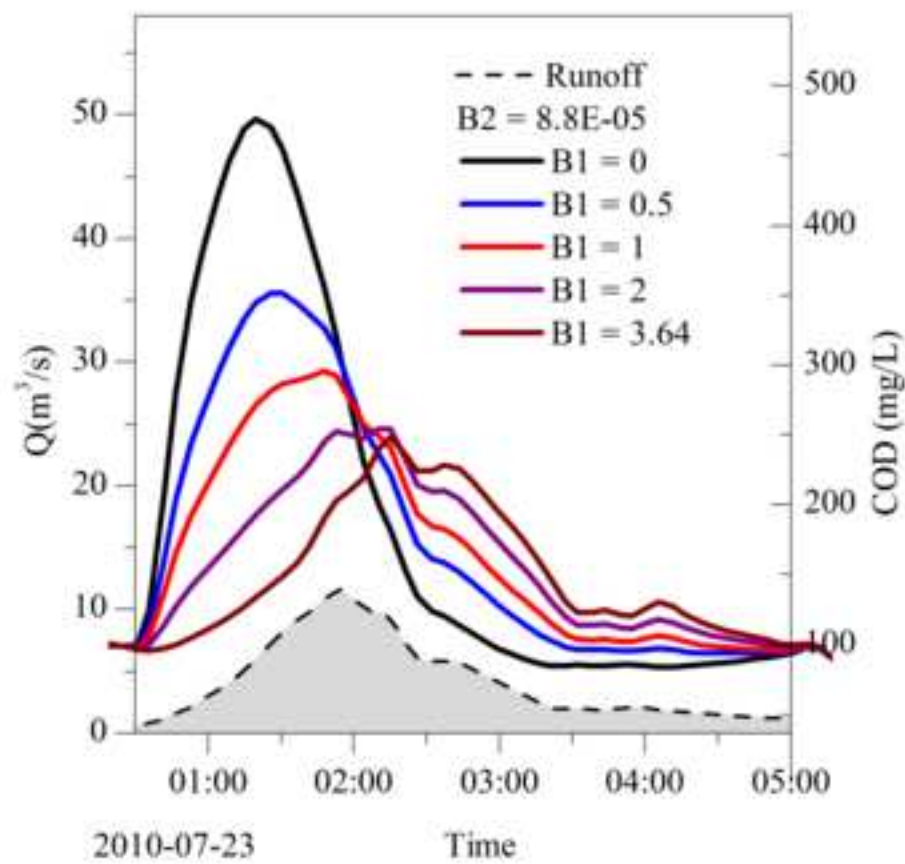
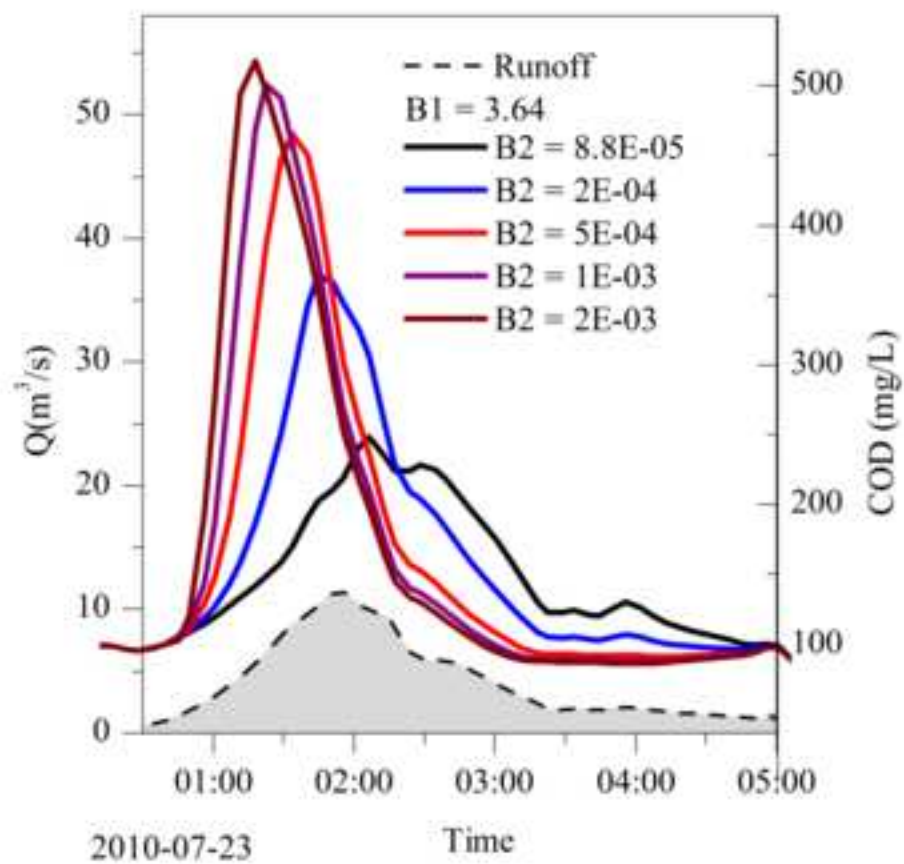


Fig.8 One-at-a-time sensitivity analysis
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(a)



(b)

Fig.9 Sobol's sensitivity analysis for new model
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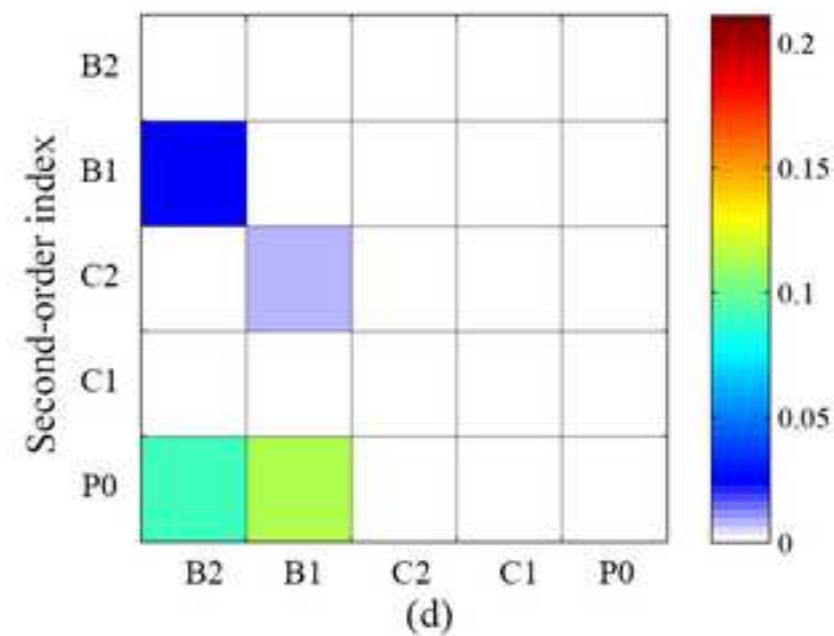
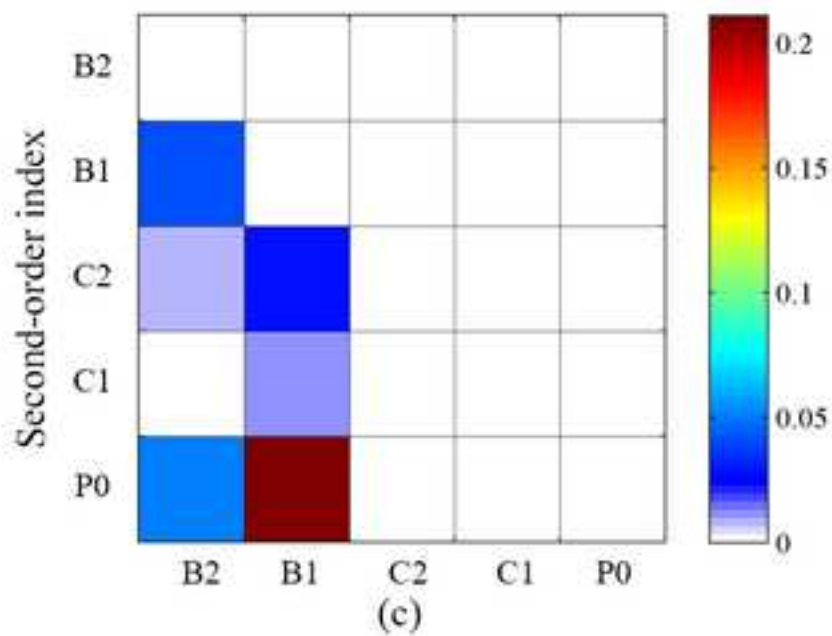
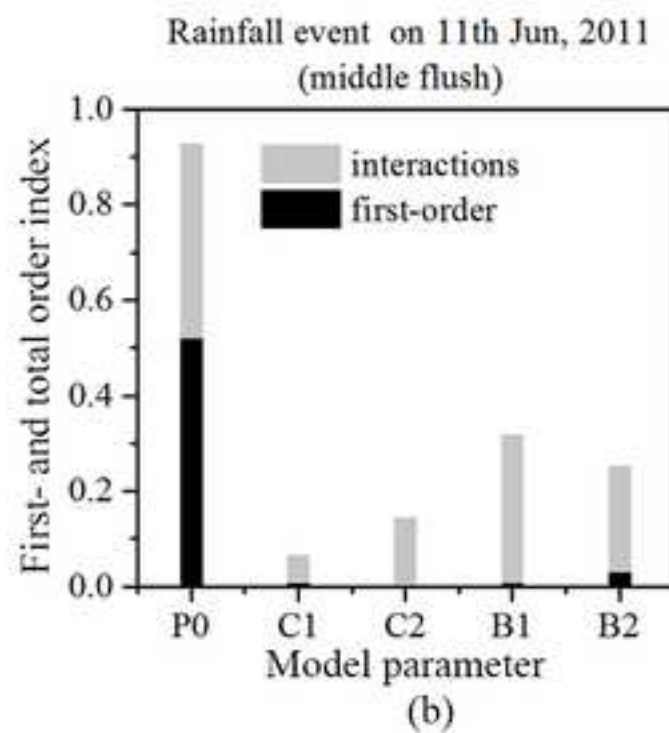
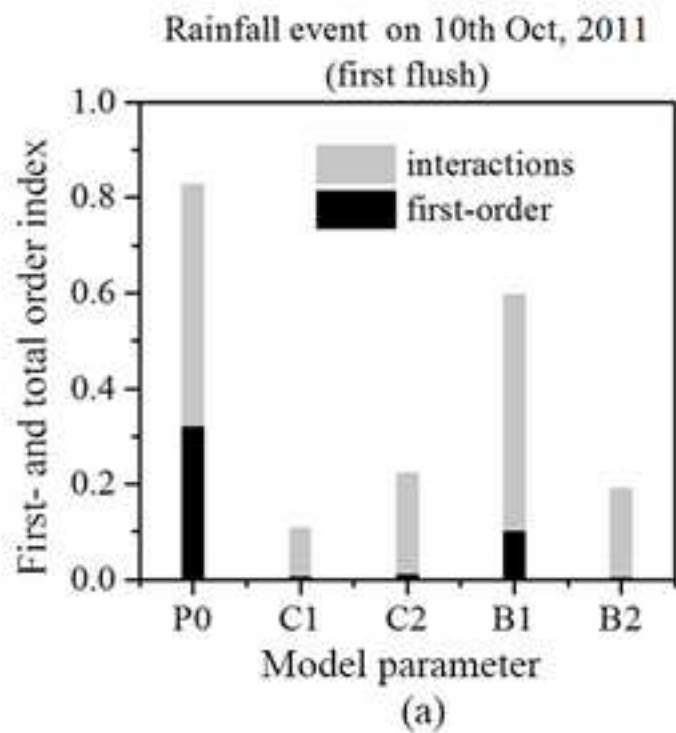


Table 1 Main characteristics of observed storms

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}