ISEIS

Journal of Environmental Informatics 23(1) 44-54 (2014)

Journal of Environmental Informatics

www.iseis.org/jei

Pollutant Flushing Characterizations of Stormwater Runoff and Their Correlation with Land Use in a Rapidly Urbanizing Watershed

L. Z. Wang[1], Y. F. Huang[1,*], L. Wang[1,2], and G. Q. Wang[2]

[1]*State Key Laboratory of Hydroscience and Engineering, Tsinghua University, Beijing 100084, China*
[2]*Tianjin Binhai New Area Construction and Investment Group Company Limited, Tianjin 300457, China*

Received 10 March 2012; revised 23 January 2013; accepted 21 March 2013; published online 24 March 2014

ABSTRACT. In this study, pollutant flushing characterizations of stormwater runoff were analyzed in a rapidly urbanizing area based on field monitoring. The results showed that both imperviousness and rainfall intensity have a positive impact on first flush effect. Significant end flush effect exists in rapidly urbanizing areas and it occurs more frequently than first flush effect under the condition of high proportion of agricultural land use and light rainfall intensity. Compared to urban areas, first flush effect is relatively weak and end flush effect is relatively strong in rapidly urbanizing areas. BMPs based on first flush concept should be carefully applied in watershed with strong end flush effect and weak first flush effect.

Keywords: end flush, first flush, nonpoint source pollution, rainfall-runoff, rapid urbanization

1. Introduction

Urbanization increases stormwater runoff quantity and degrades surface water quality (Shaw, 1994). The pollution from urban stormwater runoff can exceed that from secondary treated domestic sewage effluent (House et al., 1993). Typical pollutants found in urban stormwater runoff include suspended solids, fecal coliform, nutrients, chloride, and heavy metals such as aluminum, lead, copper, and zinc (Tsihrintzis and Hamid, 1997). These pollutants impose considerable physical, chemical, and biological stresses on receiving waters and therefore pose risks to aquatic life and human health (Field et al., 1998).

In order to prevent water quality deteriorated by pollutants in urban stormwater runoff, structural and non-structural best management practices (BMPs), such as wet ponds, storm wetlands, and sand filters, are employed to manage and treat stormwater runoff before it is discharged to receiving water bodies (Freni et al., 2010; Jefferies et al., 1999; Lee et al., 2010; Perez-Pedini et al., 2005; Sieker and Klein, 1998). Many BMPs are designed based on concept of first flush, which occurs when the majority of the pollutant load flushes in the initial portion of the event stormwater runoff (Bertrand-Krajewski et al., 1998).

The characterizations of stormwater runoff were studied in some urban areas and first flush effects were observed in some storm events and watersheds. Athanasiadis et al. (2010) identified the existence of the first flush effect of copper roof runoff and found that almost 40% of all sampled precipitation events exhibited a moderate first flush effect. Barrett et al. (1998) studied the characterization of highway stormwater runoff in Austin, Texas, Area and found that first flush effect was evident during small volume events. He et al. (2010) characterized physicochemical quality of stormwater runoff from an urban area in Calgary, Alberta and strong first flush effects for dissolved solids were observed. Lau et al. (2009) studied the characteristics of highway stormwater runoff in Los Angeles and found that the average first flush for 14 different water quality constituents was modest, with 30 to 35% of the load contained in the first 20% of the runoff.

However, some researchers found that some pollutants in some storm events didn't exhibit significant first flush and exhibited so-called "second flush" or "end flush", which means high pollutant concentrations in runoff towards end of the storm event. Francey et al. (2010) characterized the quality of stormwater runoff in seven urban catchments in South Eastern Australia and first flush effect was found not to be significant at all sites except the smallest catchment with the simplest drainage layout. Flint and Davis (2007) studied pollutant mass flushing characterization of highway stormwater runoff from an ultra-urban area and found that a significant amount of the pollutant load can be contained in later portions of the runoff volume. McCarthy (2009) studied the characterization of stormwater runoff from four urban catchments and found that first flush effect was not consistently in stormwaters and end flush effects occurred in stormwaters. If first flush effect is not predominant and second or end flush effect is significant, the performance of BMPs based on first flush theory for water quality

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[*] Corresponding author. Tel.: +86 10 62795303; fax: + 86 10 62772463.
E-mail address: yuefeihuang@tsinghua.edu.cn (Y. F. Huang).

ISSN: 1726-2135 print/1684-8799 online
doi:10.3808/jei.201400256

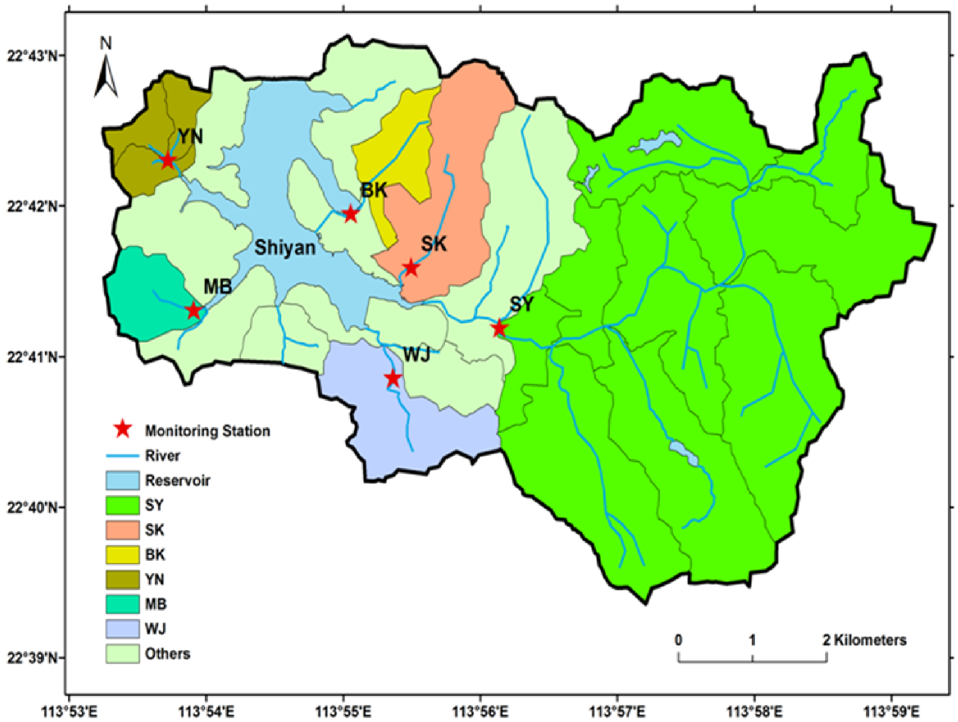

Figure 1. Map of Shiyan Reservoir and monitoring stations.

improvement may be compromised (Flint and Davis, 2007). Therefore, pollutant flushing characterizations are important for the management and treatment of stormwater runoff pollution.

Numerous efforts have been made to investigate the characterization of stormwater runoff in urban areas. All of these studies have made contributions to understanding pollutant flushing characterizations of stormwater runoff in urban areas. However, most of the studies were carried out in urban or ultra-urban areas (Lee and Bang, 2000; Lee et al., 2005; Li et al., 2007; Sansalone and Buchberger, 1997), while there are few studies reporting pollutant flushing characterizations in rapidly urbanizing catchments with highly mixed land uses in developing countries such as China. In addition, most of the studies focused on spatial variation of pollutant loads, runoff water quality and their correlation with land use (Fisher et al., 2000; Glick, 2009; Zampella et al., 2007), while few studies have been carried out to investigate the relationship between pollutant flushing characterizations and land use. Qin et al. (2010) analyzed the spatial variation of first flush effect and their correlation with land-use pattern, using a rapidly urbanizing Shiyan Reservoir catchment as a study area. The results indicate that: (1) impervious land use contributes significantly to first flush, whereas pervious land use has low or even zero first flush. (2) Residential land use has the greatest effects on first flush and other impervious land-use types (e.g. industrial land use or roads) also have some effects on first flush. Qin et al. (2010) concluded that: (1) different interception ratio of initial rainfall-runoff volume should be considered in different urbanizing catchment for runoff pollution control. (2) More attention should be paid to residential land-use type to effectively intercept runoff pollution, but industrial land use and roads cannot be neglected.

Based on the research of Qin et al. (2010), further studies were carried out to analyze pollutant flushing characterizations of stormwater runoff and their correlation with land use in four rapidly urbanizing subcatchments in the Shiyan Reservoir Watershed, Shenzhen, China. The objective of this paper is trying to answer these questions: (1) whether significant end flush effect exists in rapidly urbanizing areas? (2) If so, under what condition end flush effect is stronger than first flush effect? (3) Whether the performance of BMPs based on first flush effect in rapidly urbanizing areas is as well as that in urban areas for preventing stormwater runoff pollution?

2. Methods

2.1. Study Area

The study area is the Shiyan Reservoir Watershed, located in the Shenzhen City, in southeast China (Figure 1). The total drainage area of the watershed is 44.8 km^2. There are six main tributaries, including Shiyan (SY), Shenkeng (SK), Baikeng (BK), Yunniu (YN), Mabu (MB) and Wangjia (WJ) river/streams. The watershed has a mild, subtropical maritime climate with mean annual temperature of 22.4 °C and mean annual precipitation of 1,933 mm of which 85 to 90% falls from April to September.

The watershed has been undergoing rapid urbanization for the last 20 years. It has been regarded as rapidly urbaning watershed in terms of its population increasing rate and land use ch-

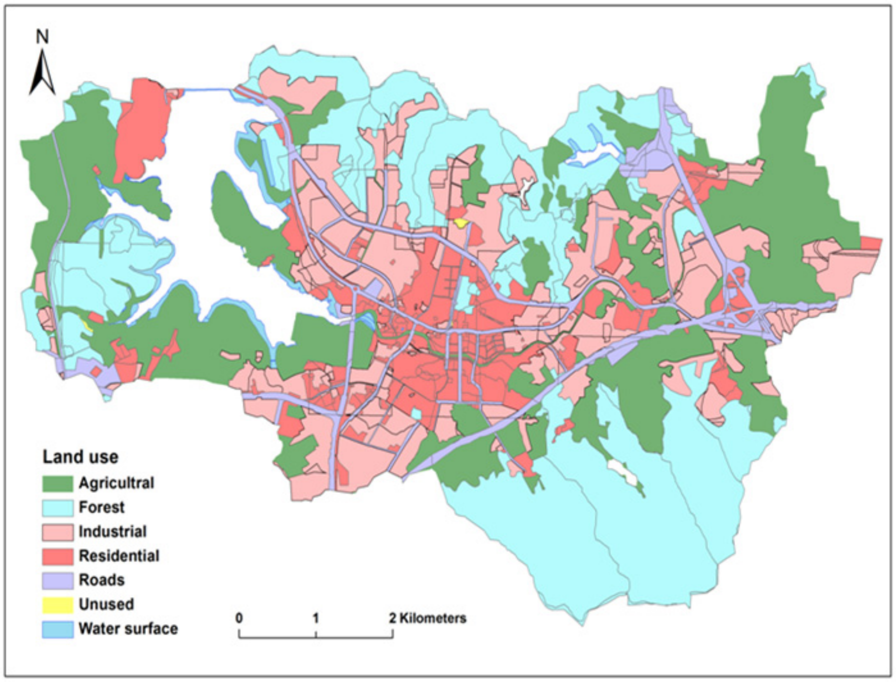

Figure 2. Land use map of Shiyan Reservoir.

Table 1. Features of Study Area Subcatchments

Subcatchment	Area (km^2)	Land use (%)							Impervious area (%)	Mean slope (%)
		Residential	Industrial	Agricultural	Transportation	Forest	Vacant	Water area		
SY	21.99	10.13	15.90	28.71	6.42	37.23	1.00	0.61	32.45	4.30
WJ	2.05	16.27	59.54	14.81	8.74	0.64	0.00	0.00	84.55	3.07
SK	2.71	9.03	33.73	1.30	5.52	35.73	11.45	3.24	48.28	4.17
MB	0.98	2.39	11.68	62.52	2.86	19.63	0.72	0.19	16.94	3.66

anges. The land use of the watershed is presented in Figure 2. Although the urbanization levels and land-use patterns of these subcatchments are different, they resulted in significant pollutant contribution to water quality deterioration in the Shiyan Reservoir. As one of four major drinking water sources, the Shiyan Reservoir Watershed requires effective measures to control nonpoint source pollution so that water quality in the reservoir could be improved. Therefore, it is necessary to carry out approaches on pollutant flushing characterizations in the watershed. In this paper, studies were undertaken to address pollutant flushing characterizations in four subcatchments, including SY, WJ, SK and MB since monitored data are not enough efficient for characteristic analysis in another two subcatchments of YN and BK. The features of the four subcatchments are summarized in Table 1. More information about the study area can be found in Qin et al. (2010).

2.2. Monitoring and Sampling

Since there is no hydrological monitoring station in the study area, temporary monitoring sites were set up at the outlets of each subcatchment to measure runoff flow and associated water quality before and during the rainfall events. Field observations were conducted synchronously at four subcatchments for four storm events during February to May 2007 and March to April 2009. These four storm events present four typical rainfall events which might reflect rainfall characteristics in the study area. Water sampling was started at the initiation of the storm event and ended when water flow receded to the dry weather water level. Generally, water samples were collected every 15 to 20 minutes when runoff flow was increasing and then every 30 to 60 minutes when runoff flow was receding. For each storm event, 9 to 12 samples were collected for water quality analysis. All water samples were collected manually at 10 cm depth from the water surface and stored in 1.0 L narrow-mouth plastic polyethylene with Teflon®-lined screw caps. Two identical water samples were taken at each sampling location to ensure precision and accuracy. Samples were transported to the laboratory immediately after the storm. The samples were refrigerated and analyzed within 8 hours after collection. Chemical oxygen demand (COD), 5-day biochemical oxygen demand (BOD_5), ammonia nitrogen (NH_3-N), total nitrogen (TN), total phosphorus (TP) and suspended solid (SS) concentrations were measured by using standard methods.

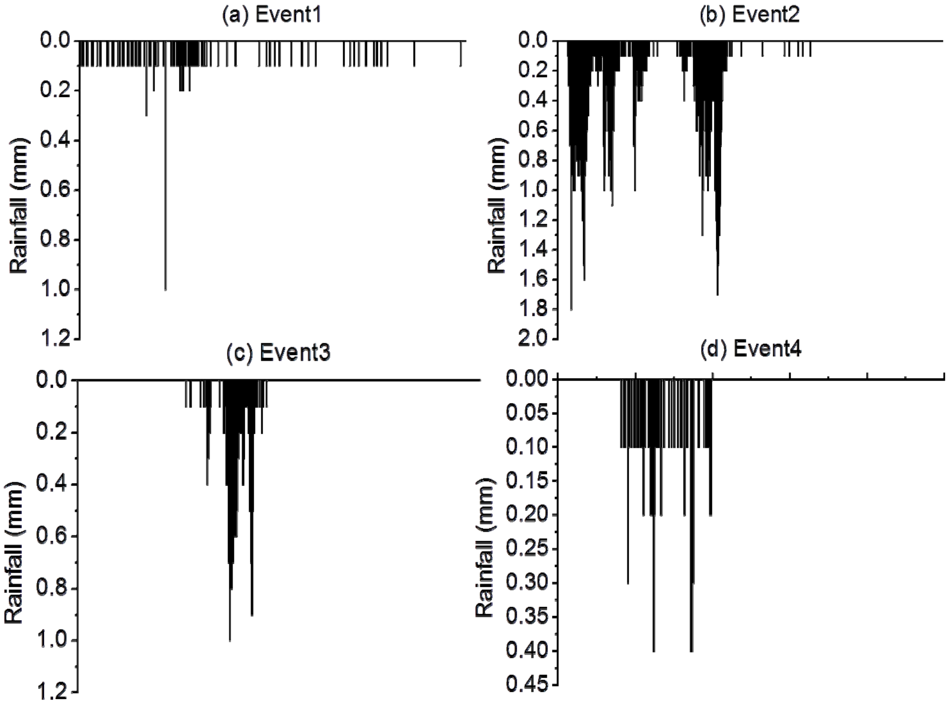

Figure 3. Observed data of four rainfall events.

Table 2. Characteristics of Four Storm Events

Date	Amount (mm)	Duration (h)	Average intensity (mm/h)	Max. intensity (mm/min)	Antecedent dry period (d)	Type
2007/03/19	10.00	5.92	1.69	1.00	27	Moderate
2007/04/02	73.30	3.73	19.65	1.80	14	Heavy
2009/03/24	14.70	1.20	12.25	1.00	10	Moderate
2009/04/13	6.30	1.17	2.38	0.40	6	Light

These water quality parameters including COD, BOD5, NH3-N, TN, TP and SS were the main pollutants that resulted in significant water quality deterioration in the Shiyan Reservoir. Therefore, these water quality parameters were selected in the management of nonpoint source pollution in the watershed and used in this study.

Accompanying with water sampling, runoff flow rate was also measured. At the outlets of the SY, SK and WJ subcatchments, flow rates were measured by propeller flow meters, while at the outlet of MB subcatchment, rectangular flow weirs were constructed on the 3-meter wide river channel for flow rate measurement. At all monitoring sites, water level was recorded with 5-minute interval. Rainfall data were recorded by an automated gauge at 1-minute interval at the Shiyan reservoir rainfall monitoring station. Table 2 and Figure 3 show the characteristics of the four storm events.

2.3. Normalized Pollutant Load and Runoff Volume Calculations

The pollutant flushing characterizations of stormwater runoff can be described by two curves: the hydrograph $Q(t)$ and pollutograph $C(t)$ for each considered pollutant (Alley 1981; Bertrand-Krajewski et al., 1998). Before producing these two curves, the cumulative pollutant load and runoff volume should be normalized by Equations (1) and (2), respectively:

$$M(t)=\frac{\int_0^t Q(t)C(t)dt}{M} \tag{1}$$

$$V(t)=\frac{\int_0^t Q(t)dt}{V} \tag{2}$$

where M is the total mass of emitted pollutant; V is the total runoff volume; $C(t)$ and $Q(t)$ are the pollutant concentration and runoff volume as functions of time.

2.4. Mass Flush Ratio

Mass first flush (MFF) ratio is a useful tool for quantifying the magnitude of first flush (Han et al., 2006; Barco et al., 2008). In order to describe the fractional mass of pollutant emitted at all stages of storm progress beyond just the initial stage of storm progress, mass flush (MF) ratio is defined as follows:

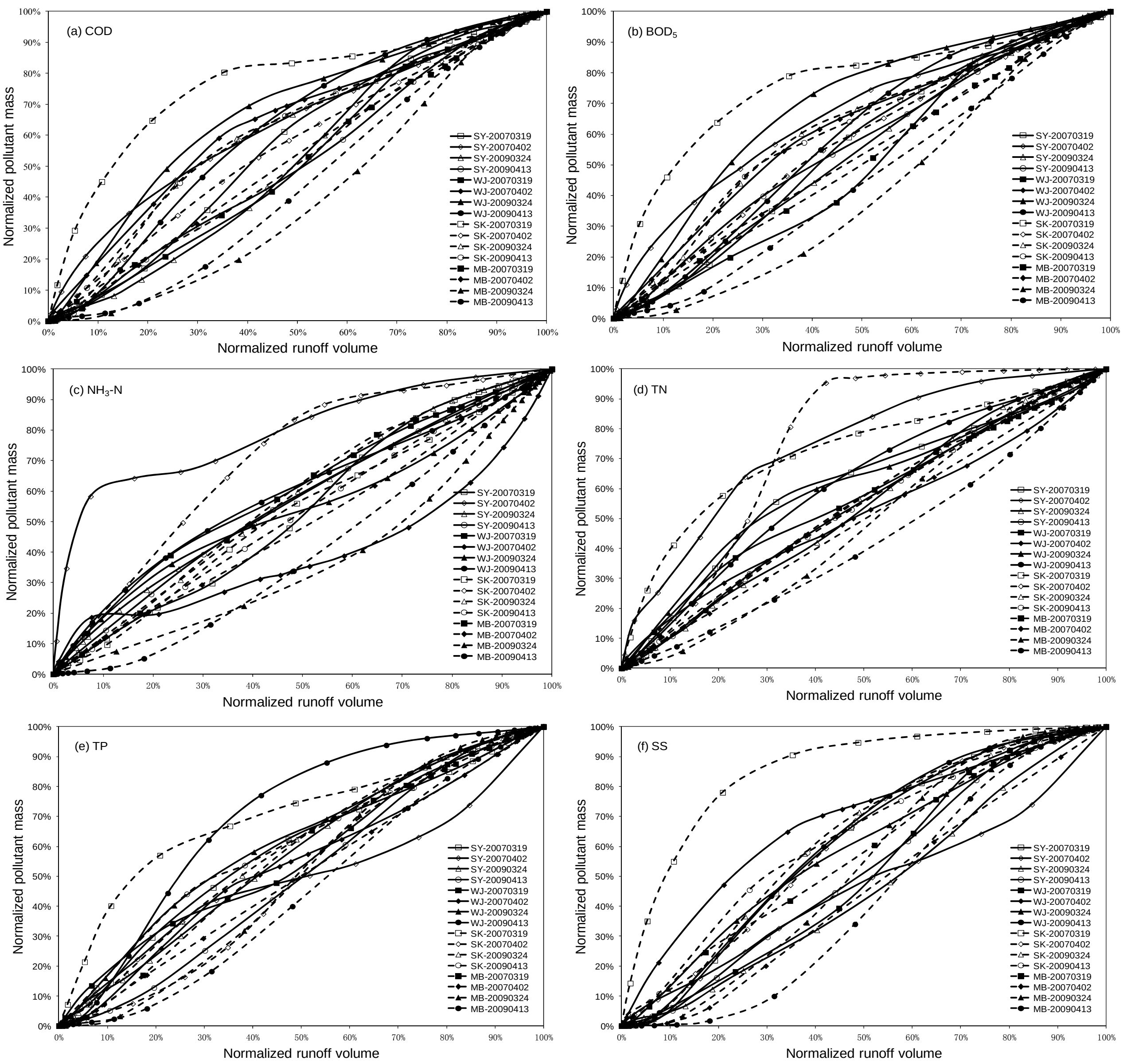

Figure 4. M(V) Curves of normalized pollutant load and runoff volume. SY-20070319 means storm event on March 19, 2007 at the SY subcatchment.

$$MF=\frac{\int_{t_1}^{t_2} Q(t)C(t)dt \div \mathrm{M}}{\int_{t_1}^{t_2} Q(t)dt \div \mathrm{M}} \tag{3}$$

where t_1 and t_2 are the start time and end time of the research stage. By definition, $MF > 1$ indicates the emission of pollutant mass is faster than that of runoff volume. If $MF > 1$ at the initial stage of stormwater runoff, first flush effect generally occurs. If $MF > 1$ at the late stage of stormwater runoff, end flush effect generally occurs. MF ratio was defined on the basis of Mass first flush (MFF) ratio. It is a useful tool for quantifying the magnitude of first flush and end flush. For example, first flush can be defined as flushing 50% of the total pollutant loads in the first 30% of stormwater runoff volume and end flush can be defined as flushing 50% of the total pollutant loads in the last 30% of stormwater runoff volume.

3. Results Analysis

3.1. The M(V) Curve of Normalized Pollutant Load and Runoff Volume

The M(V) curve of normalized pollutant load and runoff volume is usually used for pollutant flushing analysis. It is useful and helpful for analyzing variation of pollutant load accompanying with runoff volume during a storm event (Bertrand-Krajewski et al., 1998). The M(V) curves of six pollutants (in-

Table 3. Flushing Characterization Statistics of M(V) Curves

Subcatchment	Pollutant	Advanced	Mixed-I	Simultaneous	Mixed-II	Lagging
SY	COD	1 (H)	0	1 (L)	2 (M, M)	0
	BOD_5	1 (H)	0	1 (L)	2 (M, M)	0
	NH_3-N	3 (H, M, L)	0	0	1 (M)	0
	TN	2 (M, H)	0	2 (M, L)	0	0
	TP	2 (M, M)	1 (H)	0	1 (L)	0
	SS	1 (M)	1 (H)	0	1 (L)	1 (M)
WJ	COD	3 (H, M, L)	0	0	1 (M)	0
	BOD_5	3 (H, M, L)	0	0	1 (M)	0
	NH_3-N	2 (M, L)	2 (H, M)	0	0	0
	TN	3 (M, M, L)	1 (H)	0	0	0
	TP	4 (M, H, M, L)	0	0	0	0
	SS	3 (H, M, L)	0	0	1 (M)	0
SK	COD	4 (M, H, M, L)	0	0	0	0
	BOD_5	4 (M, H, M, L)	0	0	0	0
	NH_3-N	2 (H, M)	0	2 (M, L)	0	0
	TN	2 (M, H)	0	2 (M, L)	0	0
	TP	3 (M, M, L)	0	0	1 (H)	0
	SS	4 (M, H, M, L)	0	0	0	0
MB	COD	0	0	2 (M, H)	0	2 (M, L)
	BOD_5	0	0	2 (M, H)	0	2 (M, L)
	NH_3-N	1 (M)	0	1 (H)	0	2 (M, L)
	TN	1 (M)	0	1 (H)	1 (M)	1 (L)
	TP	1 (M)	0	1 (H)	2 (M, L)	0
	SS	1 (M)	0	0	2 (M, L)	1 (H)

* H-Heavy rain, M-Moderate rain, L-Light rain.

Table 4. Pearson Correlation Coefficients between Pollutant Flushing Type and Land-Use Pattern

	Residential	Industrial	Agricultural	Transportation	Forest
First flush	0.874	0.869	-0.942	0.843	-0.222
End flush	-0.724	-0.752	0.984*	-0.685	0.029

cluding COD, BOD_5, NH_3-N, TN, TP and SS) during four storm events at the studied four subcatchments are shown in Figure 4.

In Figure 4, pollutant flushing characterization varies in term of pollutant, subcatchment and storm event. In order to further analyze and summarize pollutant flushing characterizations in Figure 4, all M(V) curves are classified into five types, including advanced, mixed-I, simultaneous, mixed-II and lagging as shown in Figure 5. Alley (1981) classified the M(V) curves into four types, including advanced, simultaneous, mixed-II and lagging. Figure 4 shows that mixed-I M(V) curve is different from the other four M(V) curves and also exists in urban stormwater runoff. Therefore, M(V) curves are classified into five types in this study. It can be qualitatively inferred that advanced and mixed-I M(V) curves generally exhibit first flush effect and mixed-II and lagging M(V) curves generally exhibit end flush effect according to the definitions of first flush and end flush.

3.2. M(V) Curve Analysis

According to the classification definition, 96 M(V) curves of six pollutants in four storm events from four subcatchments

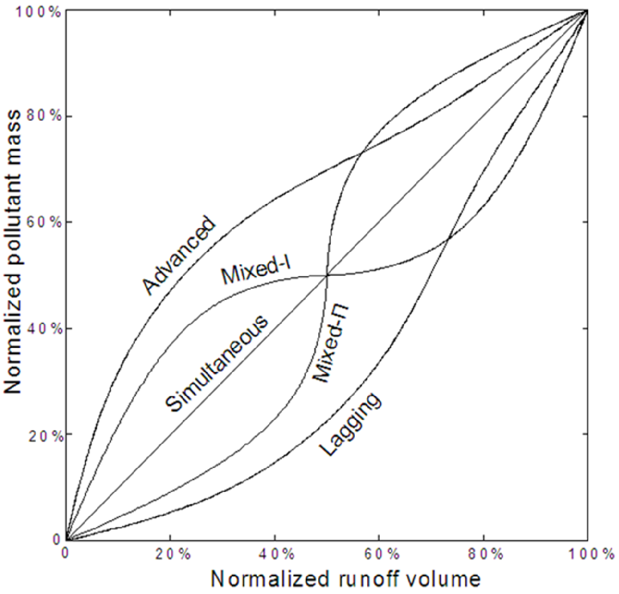

Figure 5. Typical types of M(V) curve.

Table 5. Mass Flush (MF) at Three Stages of Urban Storm Events

Subatchment	Pollutant	2007/03/19 (Moderate)			2007/04/02 (Heavy)			2009/03/24 (Moderate)			2009/04/13 (Light)			Average value		
		Prophase	Metaphase	Anaphase	Prophase	Metaphase	Anaphase	Prophase	Metaphase	Anaphase	Prophase	Metaphase	Anaphase	Prophase	Metaphase	Anaphase
SY	COD	1.1	1.25	0.57	1.67	0.75	0.67	0.83	1.48	0.53	1	1.08	0.9	1.15	1.14	0.67
	BOD_5	1.07	1.23	0.63	1.8	0.75	0.53	1.07	1.15	0.73	1.33	0.93	0.77	1.32	1.01	0.67
	NH_3-N	0.93	1.33	0.63	2.27	0.7	0.13	1.3	0.95	0.77	1.3	0.95	0.77	1.45	0.98	0.58
	TN	1.77	0.65	0.7	2.27	0.65	0.2	1.07	1.18	0.7	1.2	0.98	0.83	1.58	0.86	0.61
	TP	1.47	0.85	0.73	1.33	0.5	1.33	1.2	1.15	0.6	0.83	1.25	0.83	1.21	0.94	0.88
	SS	1.37	1.18	0.4	1	0.78	1.3	0.77	1.1	1.1	1	1.2	0.73	1.03	1.06	0.88
WJ	COD	0.9	1.33	0.67	1.73	0.73	0.63	1.93	0.7	0.47	1.5	1.08	0.4	1.52	0.96	0.54
	BOD_5	0.83	1.38	0.67	1.6	0.8	0.67	2	0.73	0.37	1.23	1.25	0.43	1.42	1.04	0.53
	NH_3-N	1.5	0.88	0.67	0.8	0.58	1.77	1.37	0.65	1.1	1.53	0.75	0.8	1.3	0.71	1.08
	TN	1.43	0.8	0.83	1.2	0.78	1.1	1.7	0.65	0.77	1.5	0.98	0.53	1.46	0.8	0.81
	TP	1.3	0.98	0.73	1.3	0.8	0.97	1.6	0.83	0.63	2	0.88	0.17	1.55	0.87	0.63
	SS	0.8	1.45	0.6	1.97	0.65	0.5	1.43	0.93	0.67	1.4	1.2	0.33	1.4	1.06	0.53
SK	COD	2.53	0.3	0.4	1.3	0.95	0.77	1.67	0.75	0.67	1.67	0.78	0.63	1.79	0.69	0.62
	BOD_5	2.47	0.33	0.43	1.33	0.98	0.7	1.7	0.75	0.63	1.7	0.73	0.67	1.8	0.69	0.61
	NH_3-N	1.13	0.95	0.93	1.87	0.93	0.23	1.2	1.15	0.6	1.07	1.05	0.87	1.32	1.02	0.66
	TN	2.23	0.48	0.47	2.1	0.9	0.03	1.17	1.05	0.77	1.17	1	0.83	1.67	0.86	0.53
	TP	2.13	0.5	0.53	0.67	1.48	0.7	1.37	1.05	0.57	1.6	0.78	0.7	1.44	0.95	0.63
	SS	2.9	0.28	0.07	1.27	1.28	0.37	1.5	1.05	0.43	1.67	0.85	0.53	1.83	0.86	0.35
MB	COD	1	1.13	0.83	1.07	1.08	0.83	0.43	1.2	1.3	0.53	1.33	1.03	0.76	1.18	1
	BOD_5	1.03	1.05	0.9	1.13	0.98	0.9	0.47	1.23	1.23	0.7	1.13	1.13	0.83	1.09	1.04
	NH_3-N	1.23	1.13	0.6	1	0.95	1.07	0.57	0.83	1.67	0.5	1.13	1.33	0.83	1.01	1.17
	TN	1.17	1.03	0.8	1	0.98	1.03	0.73	1.3	0.87	0.73	0.93	1.37	0.91	1.06	1.02
	TP	1.17	1.1	0.7	1	1	1	0.7	1.5	0.63	0.53	1.35	1	0.85	1.24	0.83
	SS	1.23	1.1	0.63	0.67	1.2	1.07	0.77	1.6	0.43	0.27	1.63	0.9	0.73	1.38	0.76

are classified into five types correspondingly (Table 3). In Table 3, the total number of advanced and mixed-I M(V) curves is 56, accounting 58.3% of total 96 curves. The total number of mixed-II and lagging M(V) curves is 25, accounting 26.0% of total 96 curves. The results indicate that 58.3% and 26.0% of M(V) curves exhibit first flush effect and end flush effect, respectively.

The total number of advanced and mixed-I M(V) curves in SY, WJ, SK and MB are 12, 21, 19 and 4, accounting 50.0%, 87.5%, 79.2% and 16.7% of 24 curves for each subcatchment, respectively. The total number of mixed-II and lagging M(V) curves in SY, WJ, SK and MB are 8, 3, 1 and 13, accounting 33.3%, 12.5%, 4.2% and 54.2% of 24 curves for each subcatchment, respectively. It indicates that in WJ and SK, most of M(V) curves exhibit first flush and only a few M(V) curves exhibit end flush. In SY, half of M(V) curves exhibit first flush and one third of M(V) curves exhibit end flush. In MB, a few of M(V) curves exhibit first flush and more than half of M(V) curves exhibit end flush.

In order to find the relationship between pollutant flushing characterizations and land use, Pearson correlation coefficients between the number of first flush curve, end flush curve and the proportions of five main land use were calculated as shown in Table 4. In Table 4, first flush is positively related to residential, industrial and transportation land use and negatively related to agricultural land use. End flush is positively related to agricultural land use and negatively related to residential, industrial and transportation land use.

The total number of advanced and mixed-I M(V) curves under light, moderate and heavy storm event are 11, 28 and 17, accounting 45.8, 58.3 and 70.8% of 24, 48 and 24 curves, respectively. The total number of mixed-II and lagging M(V) curves under light, moderate and heavy storm event are 8, 15 and 2, accounting 33.3, 31.3 and 8.3% of 24, 48 and 24 curves, respectively. It indicates that first flush is positively related to rainfall intensity and end flush is negatively related to rainfall intensity.

3.3. MF Ratio Analysis

In order to quantitatively analyze pollutant flushing characterizations, rainfall-runoff process is divided into three stages according to the percentage of total runoff volume, including prophase (0 ~ 30%), metaphase (30% ~ 70%) and anaphase (70% ~ 100%). The mass flush (MF) ratio in the prophase, metaphase and anaphase of rainfall-runoff process were calculated as shown in Table 5.

The average values of MF of six pollutants in SY, WJ, SK and MB at the prophase stage are 1.29, 1.44, 1.64 and 0.82, respectively. The average values of MF in SY, WJ, SK and MB at the metaphase stage are 1.00, 0.91, 0.85 and 1.16, respectively. The average values of MF in SY, WJ, SK and MB at the anaphase stage are 0.72, 0.69, 0.57 and 0.97, respectively. The results indicate that in SY, WJ and SK, pollutant loads were mostly discharged at the prophase and metaphase stages. While in MB, pollutant loads were mostly discharged at the metaphase and anaphase stages. The similar conclusion can be also drawn from Figure 6. In Figure 6, the MF decreases in the order of prophase, metaphase and anaphase for most of pollutants in SY, WJ and SK. However, the MF ratio decreeses in the order of metaphase, anaphase and prophase for most of pollutants in MB. The reason for the difference among four subcatchments may be their different land-use patterns. Table 6 presents the Pearson correlation coefficients between the average values of MF at three stages of rainfall-runoff process for five main land-use patterns.

In Table 6, MF in the prophase of rainfall-runoff process shows a positive correlation with residential, industrial and transportation land use and a significant negative correlation with agricultural land use. In contrast, MF in the metaphase and anaphase of rainfall-runoff process shows a negative correlation with residential, industrial and transportation land use and a significant positive correlation with agricultural land use.

4. Discussion

The relationship between pollutant flushing characterizations and rainfall intensity indicates that rainfall intensity has some impact on pollutant flushing characterizations. The larger the rainfall intensity is, the more easily first flush effect occurs. Both the results of M(V) curve and MF ratio analysis indicate that residential, transportation and industrial land use have great effect on first flush, while agricultural land use has great effect on end flush. The results are consistent with that of Qin et al. (2010). Noting that residential, transportation and industrial land use have high proportion of impervious surface while Agricultural land use has high proportion of pervious surface, it can be inferred that the imperviousness has an important impact on pollutant flushing characterizations. The greater the imperviousness is, the more easily first flush effect occurs.

Some results of studies carried out in urban areas can be used as references for comparing the pollutant flushing characterizations in urban and rapidly urbanizing areas. In the study of Sansalone et al. (2004), 34.6% of TDS loads were discharged in the first 20% of runoff volume from two small urban catchments. In the study of Li et al. (2007), 62.4, 59.4, 46.8 and 54.1% of TSS, COD, TN and TP were discharged in the first 30% of runoff volume from an urban catchment, respectively. In the study of Barco et al. (2008), 40% of pollutants were discharged in the first 20% of runoff volume from a combined sewer system. In these studies, the values of MF range from 1.56 to 2.08 in the first 20% or 30% of runoff volume. In this study, the values of MF range from 0.82 to 1.64 in the first 30% of runoff volume. It indicates that the first flush effect in study area is weaker than that in urban areas.

In addition, the end flush effect in study area is stronger than that in urban or ultra-urban areas. In the study of Flint and Davis (2007), second flush effects occur in 17% of the storm events for TSS, 11% for NO_3^-, 5% for Zn, and 4% for Pb and NO_2^- from an ultra-urban area. No second flush effect was noted for Cd, Cu, TKN, and TP. In this study, end flush effects occur in 31% of the storm events for COD, 19% for NH_3-N, 12% for TN, 25% for TP, 37% for SS, 31% for BOD_5. In MB, 46% of storm events exhibit end flush effect while 25% of storm events exhibit first flush effect. It indicates that

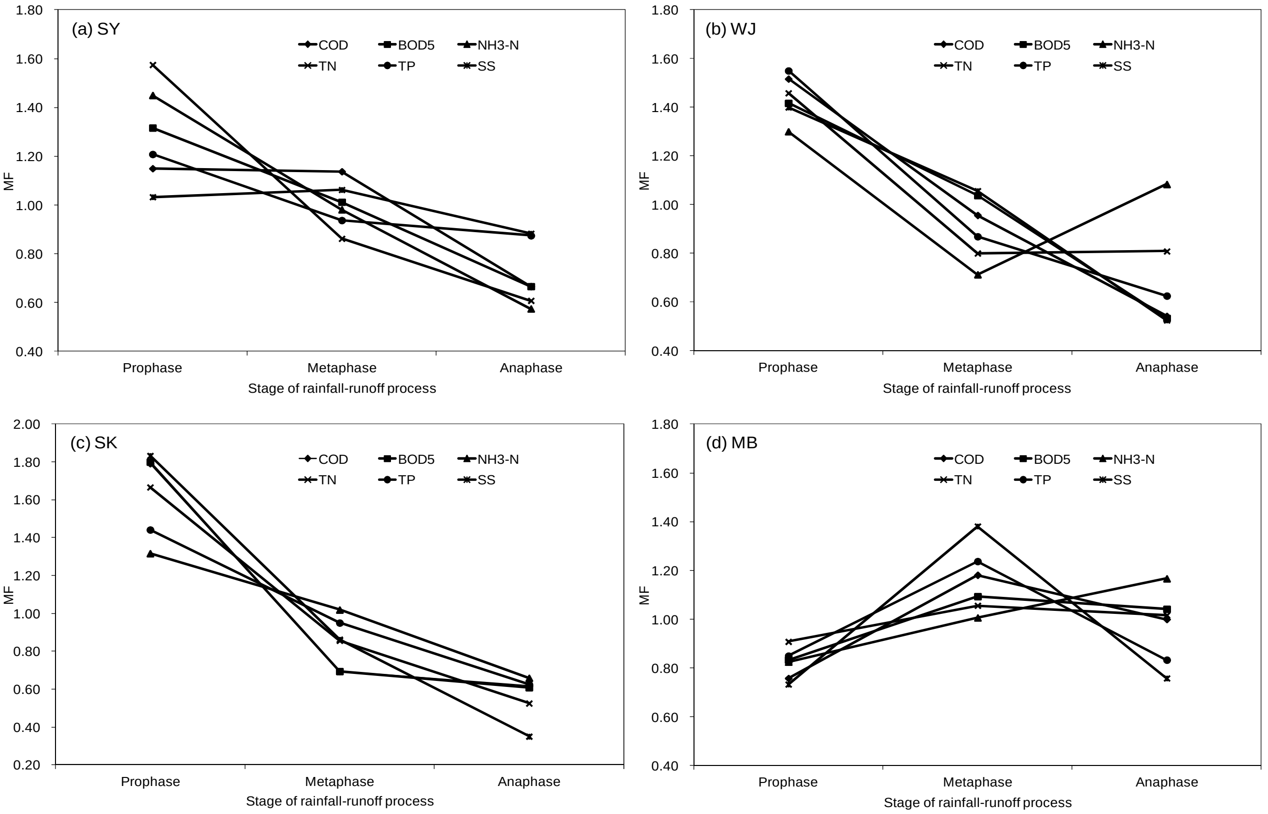

Figure 6. MF variation at three stages of rainfall-runoff process in 4 subcatchments.

Table 6. Pearson Correlation Coefficients between MF and Land-Use Pattern

	Residential	Industrial	Agricultural	Transportation	Forest
MF in prophase of rainfall-runoff process	0.704	0.629	-0.999^{**}	0.677	0.150
MF in metaphase of rainfall-runoff process	-0.730	-0.696	0.998^{**}	-0.698	-0.060
MF in anaphase of rainfall-runoff process	-0.652	-0.529	0.986^{*}	-0.630	-0.269

* Correlation is significant at the 0.05 level (2-tailed).
** Correlation is significant at the 0.01 level (2-tailed).

end flush effect is stronger than first flush effect in MB. Significant end flush effects were observed for some pollutants in some storm events, especially in the light rain event. For example, as showed in Figure 7, the peak concentration of NH_3-N appeared at anaphase of stormwater runoff stage and 50% of NH_3-N load was discharged in the last 30% of runoff volume in the 2009/03/24 event. Compared to SY, WJ and SK, MB has the greatest proportion of agricultural land use. In addition, all of the end flush effects occurred in moderate and light rain events except the flushing of SS in MB in the heavy rain event. Therefore, it can be concluded that end flush effect is stronger than first flush effect under the condition of high proportion of agricultural land use and light rainfall intensity.

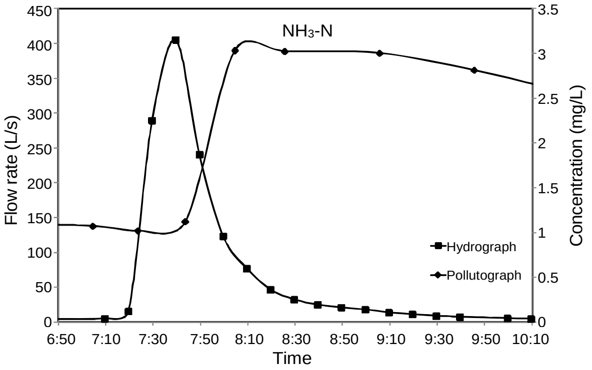

Figure 7. Hydrogragh and pollutogragh of NH_3-N in the 2009/03/24 event from MB.

In MB, the average ratios of pollutants loads being discharged in the first 30% of runoff volume are 23% for COD, 25% for NH_3-N, 27% for TN, 26% for TP, 22% for SS, 25% for BOD_5, while the average ratios of pollutants loads being discharged in the last 30% of runoff volume are 30% for COD, 35% for NH_3-N, 31% for TN, 25% for TP, 23% for SS, 31% for BOD_5. Therefore, the performance of BMPs based on first flush concept may be compromised in MB. However, compared to SY, WJ and SK, the area of MB is relatively small, so BMPs based on first flush concept could be applied in the Shiyan Reservoir Watershed, but the performance may not be as well as that in urban or ultra-urban areas.

5. Conclusions

This paper analyzes the pollutant flushing characterizations of stormwater runoff and their correlation with land use in a rapidly urbanizing catchment. The results indicate that:

(1) Pollutant flushing M(V) curves can be classified into five types: advanced, mixed-I, simultaneous, mixed-II and lagging. Advanced and mixed-I M(V) curves generally exhibit first flush effect whereas mixed-II and lagging M(V) curves generally exhibit end flush effect.

(2) The greater the imperviousness and rainfall intensity is, the higher the possibility is for first flush effect to occur. On the contrary, end flush will occur more frequently.

(3) Compared to urban areas, first flush effect is relatively weak and end flush effect is relatively strong in rapidly urbanizing areas.

(4) Significant end flush effect exists in rapidly urbanizing areas. End flush effect is stronger than first flush effect under the condition of high proportion of agricultural land use and light rainfall intensity.

(5) The performance of BMPs based on first flush effect for may be compromised in rapidly urbanizing areas. BMPs based on first flush concept should be carefully applied in watershed with strong end flush effect and weak first flush effect. range from 1.56 to 2.08 in the first 20% or 30% of runoff volume. In this study, the values of MF range from 0.82 to 1.64 in the first 30% of runoff volume. It indicates that the first flush effect in study area is weaker than that in urban areas.

Acknowledgments: This paper is financially supported by the National Natural Science Foundation of China (NO. 91125018) and the R&D Special Fund for Public Welfare Industry of the Ministry of Water Resources in China (No. 201001015&No. 201001080).

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