The temporal changes in road stormwater runoff quality and the implications to first flush control in Chongqing, China

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Abstract This study investigates the quality of stormwater runoff from a driveway in the southwest mountainous urban area of Chongqing, China, from 2010 to 2011. The results showed that the mean concentrations of chemical oxygen demand (COD), total nitrogen (TN), and total phosphorus (TP) were 4.1, 2.4, and 2.2 times the grade V levels of the national surface water standard of China. The pollutant concentration peak preceded or synchronized with the rainfall intensity peak and occurred 10 min after the runoff started. The significant high pollutant concentration in the initial stage of the rainfall suggested that first flush control is necessary, especially for the most polluted constituents, such as total suspended solids, COD, and TN. Three potential pollution sources were

identified: the atmospheric dry and wet deposition (TN, NO_3^- -N, NH_4^+ -N, and DCu), the road sediment and materials (total suspended solids, COD, and TP), and the vehicle emissions (DPb and DZn). Therefore, this study indicates that reductions in road sediments and material pollution and dry and wet deposition should be the priority factors for pollution control of road stormwater runoff in mountainous urban areas.

Keywords Road runoff · Water quality · Event mean concentration (EMC) · First flush · Pollution sources

Introduction

Urban stormwater runoff was identified as one of the leading causes of degradation to the quality of receiving waters (US EPA 1998). Road surfaces accumulate significant quantities of pollutants including nutrients, heavy metals, organic compounds, and suspended solids (Ngabe et al. 2000; Farm 2002; Opher and Friedler 2010). Due to pavement impermeability, pollutant runoff from stormwater during wet weather enters streams via the urban drainage networks or is discharged directly into nearby waters or lands in rural areas, causing deterioration of the receiving waters and contamination of roadside soil.

Road runoff pollution has been widely investigated in many urban areas. For example, Legret and Pagotto

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(1999) found that the most common metals from highway runoff in France were copper, lead, and zinc; Lee et al. (2011) found that the concentration ranges of total suspended solids (TSS) and chemical oxygen demand (COD) were 15–370 and 10–360 mg/L and were the dominant pollutants from urban highways in South Korea with peak concentrations occurring 20 min after the runoff started.

Factors affecting the quality of urban road runoff include rainfall characteristics (volume, intensity, duration, and previous storm characteristics), traffic characteristics (volume, average daily traffic, vehicles during a storm, and the antecedent dry period), climatic factors, land use, and the road site environment (Opher and Friedler 2010). Kayhanian et al. (2007) and Gan et al. (2008) found that the event mean concentration (EMC) values of pollutants have a significant negative correlation with the rainfall volume. Some studies have found a positive correlation between the load or concentration of certain pollutants and rainfall intensity (Crabtree et al. 2008), while others show negative relationships (Crabtree et al. 2006; Kim et al. 2005). Han et al. (2006) found that the EMC of COD and total Kjeldahl nitrogen had a significant positive correlation with the antecedent dry period.

The first flush (FF) effect is often a noted phenomenon because of its importance in how to control road stormwater pollution. If a large portion of pollutant mass is contained in the first portion of the runoff, best management practices that are optimized to treat the first portion may be economically advantageous. Ma et al. (2004) found that most pollutants had medium mass FFs where 40 % of the total pollution masses were transported by the first 30 % of the total flow volume as was observed in 52 storms at nine highway sites. Han et al. (2006) reported that 30 to 35 % of the mass was contained in the first 20 % of the runoff. Deletic (1998) and Taebi and Droste (2004) concluded that the magnitude of FF is positively and significantly correlated to the maximum rainfall intensity.

The source partition is also a very important issue for pollution control; Sansalone and Buchberger (1997) found that zinc (Zn) and lead (Pb) were mainly sourced from vehicle exhaust; Davis et al. (2001) found that the most likely source of copper (Cu) was the wear of brake linings and moving engine parts; Huang et al. (2007) found that organic matter in road runoff mainly came from vehicle activities; and Drapper et al. (2000) found that total organic carbon (TOC) and COD concentration on asphaltum roads

were three to five times higher than on concrete roads. Recently, a multivariate technique has been developed for partitioning the source of water pollution. Huang et al. (2007) successfully applied the multivariate technique to identify the water pollution source from a watershed into two principal components (PCs): one was related to nutrient and soil losses and to organic pollutant discharge and another was from heavy metal losses.

In China, stormwater pollutions from roads have been investigated in the urban areas of Beijing, Hanyang of the Hubei Province, etc. These areas are located on plains with relatively flat roads. However, roads located in mountainous or hilly urban areas have not as yet been investigated. Chongqing is located in the southeastern of Sichuan Basin and is known as a mountainous city with steep roads. It belongs to an area with a subtropical monsoon climate, a mean annual temperature of 17.5–18.7 °C, and a mean annual precipitation of 1,100–1,300 mm, most of which occurs between April and September. The aims of this study are to: (1) investigate the characteristics of pollutants in runoff from a driveway during rainfall events and its relation to rainfall characteristics, (2) analyze the FF effect in the mountain city and its influencing factors, and (3) identify the main pollution sources for an urban driveway. The investigation of road stormwater pollution in Chongqing will provide valuable information for pollution control in a mountainous urban area.

Materials and methods

Study site

The road stormwater runoff that was monitored was located in Yubei District, Chongqing, China. The monitoring site was situated in the upper part of the road consisting of an area of 540 m², a slope of 10°, and is covered with asphalt with average daily traffic of ~10,000 vehicles. The sampling sites were surrounded by commercial buildings and residential housing with both sides of the road containing green belt and walking trails.

Sampling and analyses

Nine rainfalls between 2010 and 2011 were sampled (Table 1) at the road drainage pipes, beginning at the initiation of rain event and ending when the rainfall runoff had stopped. Sampling intervals were 5–10 min in the

Table 1 Rainfall characteristics for the nine investigated rain events

No.	Date	Rainfall (mm)	Runoff duration (min)	Average rainfall intensity (mm/min)	Maximum rainfall intensity (mm/min)	Antecedent dry weather period (day)	Time of maximum rainfall intensity (min)	Rainfall type
1	June 6, 2010	10.9	90	0.12	0.44	4	60	Low
2	June 19, 2010	23.6	465	0.054	0.16	8	125	Medium
3	July 4, 2010	21.2	150	0.14	0.62	6	5	Medium
4	July 9, 2010	59.4	90	0.66	1.78	3	15	High
5	September 13, 2010	2.1	55	0.04	0.14	7	10	Low
6	May 30, 2011	7.4	115	0.06	0.15	7	15	Low
7	June 5, 2011	6.1	150	0.04	0.08	4	20	Low
8	July 11, 2011	9.2	170	0.06	0.10	17	125	Low
9	August 4, 2011	3.4	65	0.05	0.14	1	30	Low

first 60 min and 15–30 min in the period of 60 to 120 min and then 60 min afterwards. The rain events were classified into three kinds of intensity: low (<15 mm), medium (15–50 mm), and high (>50 mm) according to the standard meteorological classification in China.

The samples were stored in 1-L polyethylene bottles in a container with ice and transported to the laboratory immediately. The major dissolved metals (DCu, DPb, and DZn) were analyzed using an inductively coupled plasma optical emission spectroscopy (ICP-MS 7500a, Agilent Technologies USA). The pH was analyzed using a pH meter (Hach, USA, SensionTM156). Following the National Standard Method of China (GB3838-2002a), COD was analyzed using the rapid digestion and spectrophotometric method; total nitrogen (TN) using the alkaline potassium persulfate digestion–UV spectrophotometric method; total phosphorus (TP) using the persulfate digestion spectrophotometric method; TSS using the filtering, drying, and weighing method; ammonium-nitrogen (NH₄⁺-N) using Nessler's reagent spectrophotometric method; and nitrate nitrogen (NO₃⁻-N) using the phenol disulfonic acid spectrophotometric method.

Data analyses

Event mean concentration

Due to the high variability in pollutant concentrations throughout a given stormwater runoff event, the EMC

was used as a measure to compare the pollution between rain events (Sansalone and Buchberger 1997; Lee and Bang 2000).

$$EMC = \frac{\sum C_i Q_i \Delta t_i}{\sum Q_i \Delta t_i} \quad (1)$$

$$Q_i = P \times \Psi \times A \quad (2)$$

Where EMC is event mean concentration (in milligrams per liter); C_i is pollutant concentration during any measured interval (in milligrams per liter); Q_i is runoff discharge during the period Δt_i (in cubic meters per minute); P is the total precipitation (in millimeter) during Δt_i and measured by an automated gauge nearby; Ψ is the runoff coefficient (0.9); A is the catchment area (in square meter); and Δt_i is time increment between successive measurements (in minute).

Pollutant loading

Annual pollutant load from road stormwater runoff was calculated as:

$$L_y = K \times P \times \Psi \times EMCs \quad (3)$$

where L_y is the annual pollutant loading (in grams per square meter per year); K is the conversion constant

(10^{-3}); P is the mean annual precipitation (in millimeter); Ψ is the runoff coefficient (0.9); and EMCs are the mean concentrations of the monitoring rainfall events (in milligrams per liter).

First flush effect

The definition of the FF is the initial period of stormwater runoff during which the concentration of pollutants is substantially higher than those observed during the latter stages of the storm event (Gupta and Saul 1996). The percentage of pollutant masses transported by the early runoff portion with 30 % of the total flow volume (FF_{30}) was used to assess the magnitude of the FF effects of different rain events and pollutants (Kim et al. 2005). Three levels of the FF were classified as high, medium, and non-FF and were designated as $FF_{30} \geq 50\%$, $30\% < FF_{30} < 50\%$, and $FF_{30} \leq 30\%$.

Statistical analysis

Because most of the parameters significantly deviated from a normal distribution, nonparametric Spearman rank-order correlation was used following the method of Mosley and Peake (2001). Only the correlations that were significant at $p < 0.05$ are reported in this study.

In order to identify the unobservable, latent pollution sources, principal component analysis (PCA) was applied to include correlated variables with the purpose of reducing the numbers of variables and explaining the same amount of variance with fewer variables (principal components) (Helena et al. 2000). In our study, PCA of the normalized variables (water quality dataset) was performed to extract the significant PCs and to further reduce the contribution of variables with minor significance; these PCs were subjected to varimax rotation (raw) generating original variables. The Kaiser–Meyer–Olkin (KMO) and Bartlett's sphericity tests were used to examine the validity of the PCA. Following Pekey et al. (2004), eigenvalues > 1 were selected as the new orthogonal variables. According to Liu et al. (2003) and Huang et al. (2010), the factor loadings indicated as strong, moderate, and weak corresponded to the absolute loading values of > 0.75 , 0.75 – 0.50 , and 0.50 – 0.30 , respectively.

The Spearman correlations and PCA were performed using SPSS 19.0 (SPSS Inc., USA).

Results and discussion

Runoff water quality and pollutant load

The minimum, maximum, mean concentrations and standard deviations of the pollutants in nine raining events are shown in Table 2. High variability was found for the runoff parameters COD, TN, and DCu. The pH value was the only parameter found to be stable over the study period with a mean value of 8.22. The average EMC values of COD, TN, and TP were 4.1, 2.4, and 2.2 times the corresponding values for the grade V surface water standard as formulated by China (GB3838-2002) (State Environment Protection Bureau of China 2002b).

The annual averages of EMC for COD, TN, TP, TSS, NH_4^+-N , NO_3^--N , DPb, DCu, and DZn were 163.17, 4.74, 0.89, 461.11, 1.56, 2.00, 0.0031, 0.0065, and 0.0058 mg/L, respectively. As the mean annual precipitation was 1,200 mm, the annual pollutant loads were 176.22, 5.12, 0.96, 498.00, 1.69, 2.16, 0.0033, 0.0070, and 0.0063 g/(m²·year), respectively.

Comparing the runoff quality between Chongqing, Macau, (Huang et al. 2007), and Guangzhou in China (Gan et al. 2008), Genoa, Italy (Gnecco et al. 2005), and Los Angeles, California (Han et al. 2006) and California in the USA (Kayhanian et al. 2007) (Table 3), the mean EMCs of TSS, TP, TN, and COD concentrations in urban road runoff in Chongqing were significantly higher than in Macau and Genoa. Compared with the highway sites, the mean EMC of TSS concentrations in Chongqing was significantly higher than the other urban sites. In addition, the mean EMCs of TP, TN, and COD concentrations were also higher. It is assumed that this is because of the high slope of the road in this study (10°), and therefore, the vehicle tire and road surface friction are greater than that in the other urban roads/highways. As a result, the mean EMC of the TSS concentrations was higher than the other urban sites, even though their traffic volume was greater than in Chongqing. Lau et al. (2005) found that greater runoff concentrations of polycyclic aromatic hydrocarbons in a slope site compared to two other nearby sites are due to more fuel being burnt when driving uphill. The mean EMCs for the concentrations of the dissolved metals (Cu, Pb, and Zn) in Chongqing were significantly lower than in the other urban areas, probably because the traffic volume in Chongqing was lesser than in the other areas. Göbel et

Table 2 Event mean concentrations (EMCs) of road stormwater runoff and rainwater

Date	pH	COD (mg/L)	TP (mg/L)	TN (mg/L)	NH ₄ ⁺ -N (mg/L)	NO ₃ ⁻ -N (mg/L)	TSS (mg/L)	DPb (mg/L)	DCu (mg/L)	DZn (mg/L)
June 7, 2010	7.91	91.2	0.79	7.07	1.31	0.95	314.2	0.0039	0.0047	0.0081
June 19, 2010	8.04	64.0	0.37	1.98	0.53	0.28	211.0	0.0031	0.0036	0.0020
July 4, 2010	8.01	208.0	1.01	5.00	1.40	1.04	874.0	0.0022	0.0047	0.0065
July 9, 2010	8.60	60.8	0.68	2.07	1.31	1.59	564.8	0.0022	0.0019	0.0101
September 13, 2010	7.67	142.4	3.14	6.36	0.31	3.08	120.1	0.0036	0.0065	0.0067
May 30, 2011	8.12	373.4	0.62	9.03	5.14	4.67	950.2	0.0041	0.0142	0.0057
June 5, 2011	8.46	125.1	0.36	2.09	0.75	1.04	377.2	0.0042	0.0049	0.0047
July 11, 2011	8.38	259.8	0.44	4.54	1.26	3.03	494.4	0.0017	0.0113	0.0029
August 4, 2011	8.76	143.8	0.58	4.50	2.07	2.31	244.2	0.0031	0.0067	0.0054
Mean	8.22	163.17	0.89	4.74	1.56	2.00	461.11	0.0031	0.0065	0.0058
Maximum	8.76	373.40	3.14	9.03	5.14	4.67	950.20	0.0042	0.0142	0.0101
Minimum	7.67	60.80	0.36	1.98	0.31	0.28	120.10	0.0017	0.0019	0.0020
Standard deviation	0.35	102.04	0.87	2.46	1.44	1.39	290.70	0.0009	0.0039	0.0025
Water quality standard ^a	6–9	≤40	≤0.4	≤2.0	≤2.0	–	–	≤0.1	≤1.0	≤2.0
Annual pollutant loading (g/(m ² ·year))	–	176.22	0.96	5.12	1.68	2.16	498.00	0.0033	0.0070	0.0063
Average pollutant concentrations of rainwater (n=9)	5.12	28.00	0.07	3.16	1.27	1.17	11.27	0.0112	0.0041	0.0518
Pollutant concentration ratio of rainwater to road runoff (%)	62.29	17.16	08.22	66.75	81.09	58.46	2.45	360.11	62.46	892.99

^a The standards are the grade V of surface water standard of China (GB3838-2002) (State Environment Protection Bureau of China 2002b)

al. (2007) concluded that the heavy metal concentrations were higher for traffic areas. The mean EMCs for the TSS concentrations in China were observed to be

significantly higher than those in the USA and Italy. This could indicate poor quality of either the atmosphere and/or the sanitary conditions in China.

Table 3 Comparison of the water quality of surface runoff in various locations

Parameters	This study (2012)	Huang et al. (2007)	Gan et al. (2008)	Gnecco et al. (2005)	Han et al. (2006)	Kayhanian et al. (2007)
Location	Chongqing China	Macau China	Guangzhou China	Genoa Italy	Los Angeles, California, USA	California USA
Road/highway	Road	Road	Highway	Road	Highway	Highway
Annual average daily traffic (vehicles/day)	8,000	30,000	22,170	–	260,000–328,000	1,800–320,000
COD (mg/L)	163.2	117.8	308.0	129.0	252.5	–
TP (mg/L)	0.89	0.24	0.39	–	0.90	0.29
TN (mg/L)	4.74	3.58	7.32	–	–	–
TSS (mg/L)	461.1	417.2	415.7	140.0	67.7	112.7
DPb (mg/L)	0.0031	–	–	0.0132	0.0049	0.0076
DCu (mg/L)	0.0065	–	–	0.0194	0.0659	0.0149
DZn (mg/L)	0.0058	–	–	0.0811	0.4153	0.0688

Table 4 Relations of both EMC and FF₃₀ of stormwater runoff pollutants to rainfall characteristics ($n=9$)

Item	Runoff duration (min)	Rainfall (mm)	Average rainfall intensity (mm/min)	Maximum rainfall intensity (mm/min)	Antecedent dry weather period (day)	Time of maximum rainfall intensity (min)
EMC pH	0.033	0.050	0.008	-0.201	-0.479	—
COD	-0.467	0.076	-0.101	-0.393	0.361	—
TP	-0.033	-0.622	0.353	0.527	-0.118	—
TN	-0.400	-0.378	0.084	-0.008	0.143	—
NH ₄ ⁺ -N	0.075	-0.160	0.481	0.311	-0.409	—
NO ₃ ⁻ -N	-0.569	-0.422	-0.181	-0.345	0.156	—
TSS	0.367	0.269	0.647	0.301	-0.025	—
DPb	-0.471	-0.229	-0.508	-0.316	-0.186	—
DCu	-0.728*	-0.118	-0.414	-0.672*	0.283	—
DZn	0.133	-0.706*	0.496	0.611	-0.513	—
FF ₃₀ COD	0.294	0.617	0.740*	0.552	0.328	0.067
TP	0.244	0.750*	0.765*	0.678*	0.084	-0.067
TN	0.210	0.517	0.655	0.251	-0.185	0.403
NH ₄ ⁺ -N	0.521	0.317	0.017	-0.184	0.571	0.563
NO ₃ ⁻ -N	0.681*	0.233	-0.134	-0.377	0.319	0.571
TSS	0.395	0.867**	0.924**	0.728*	-0.008	0.034
DPb	-0.588	-0.533	-0.261	-0.025	-0.235	-0.303
DCu	0.261	0.800**	0.798**	0.703*	0.210	0.042
DZn	0.681*	-0.033	-0.193	-0.351	0.908**	0.185

** p value <0.01; * p value <0.05

Correlation analysis of water quality parameters to rain characteristics

As shown in Table 4, there were no significant relationships between the EMC of pollutants from road runoff and rainfall, average rainfall intensity, maximum rainfall intensity, and antecedent dry weather period, except that there were significant negative correlations between DCu EMC and the runoff duration and maximum rainfall intensity ($p<0.05$) and between DZn EMC and the rainfall ($p<0.05$).

Temporal changes in pollution during raining

The pollutographs for COD, TN, TP, TSS, NH₄⁺-N, NO₃⁻-N, DPb, DCu, and DZn vary with rainfall density as represented by the rain events on July 9, 2010 (59.4 mm, high intensity), July 4, 2010 (21.2 mm, medium intensity), and May 30, 2011 (7.4 mm, low intensity) (Figs. 1, 2, and 3).

On July 9, 2010, the peak concentrations of the nine water quality parameters preceded the peak rainfall intensity and occurred at 10 min after the start of the runoff (Fig. 1). The pollutant concentration peak synchronized with the rainfall intensity peak and occurred at the beginning of runoff on July 4, 2010 (Fig. 2). On May 30, 2011, the pollutant concentration peak preceded or synchronized with the rainfall intensity peak (Fig. 3); however, the pollutant concentrations declined with time more slowly than that on July 9 (Fig. 1) and July 4 (Fig. 2).

In this study, the peak pollutant concentration often occurred 10 min after the start of rain. In another study, Lee et al. (2011) reported that the pollutant concentration peak occurred 20 min after the rain started. The reason for this difference is probably because of the quick convergence of runoff from the slope (10°) in our study. Chaplot and Le Bissonnais (2000) and Fang et al. (2008) found also that the larger slope gradient could lead to higher flow velocity and increased runoff generation capacity. Similar

Fig. 1 Temporal variation of pollutant concentrations of road stormwater runoff on July 9, 2010

temporal patterns were shown between TSS and TP. One explanation for this pattern is that the concentration of TSS and TP was susceptible to the impact of rainfall intensity. The concentration variation of TN was similar to $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ because they all come from the same source. The temporal variation of the DPb and DZn

concentrations had larger fluctuations in the later period of the three rain events. This fluctuation is thought to be the result of Pb and Zn originating principally from vehicle traffic, and the runoff sampling was at 14:45–17:15, 9:50–11:20 and 14:25–16:20 hours when heavy traffic was on the road to release more pollutants.

Fig. 2 Temporal variation of pollutant concentrations of road stormwater runoff on July 4, 2010

First flush effect

As shown in Table 5, the means of the FF_{30} values of COD, TN, TP, TSS, NH_4^+-N , NO_3^--N , DCu, and DZn were 57.0, 58.1, 50.4, 52.5, 52.9, 62.0, 65.1, and 57.2 %, respectively, indicating a high FF effect for

these parameters. The mean of the FF_{30} value of DPb was 38.3 %, indicating a medium FF effect. Similar results were reported in an earlier study by Ma et al. (2004) where they reported that most of the pollutants studied had medium mass FF at nine highway sites. Because of the high slope (10°) of the road in our

Fig. 3 Temporal variation of pollutant concentrations of road stormwater runoff on May 30, 2011

study, the FF occurred more often. Zhang et al. (2012) found also that the FF_{30} values of all pollutants from the tile roof with slope gradient of 25° were higher than from the concrete roof with slope gradient of 0° .

As shown in Table 4, the FF_{30} values of TP, TSS, and DCu were significantly positively related to rainfall, average rainfall intensity, and maximum rainfall intensity ($p < 0.05$), which are similar to previous

Table 5 Statistical summary of FF₃₀ values of TN, TP, TSS, NH₄⁺-N, NO₃⁻-N, DPb, DCu, and DZn

Date	COD (%)	TP (%)	TN (%)	NH ₄ ⁺ -N (%)	NO ₃ ⁻ -N (%)	TSS (%)	DPb (%)	DCu (%)	DZn (%)
June 7, 2010	65.0	63.5	60.7	41.2	48.9	72.3	60.1	60.0	49.4
June 19, 2010	57.4	45.5	53.3	75.3	77.2	41.9	34.3	69.1	76.5
July 4, 2010	76.9	76.8	60.7	32.5	58.0	80.9	41.1	82.7	57.3
July 9, 2010	60.8	66.8	68.0	54.7	58.4	75.2	29.6	95.0	23.1
September 13, 2010	49.9	44.8	42.0	45.1	49.1	29.6	32.1	50.7	47.0
May 30, 2011	46.3	37.8	51.1	51.8	58.1	41.0	37.1	54.5	61.5
June 5, 2011	41.7	38.9	54.5	51.1	65.4	40.6	35.7	47.9	53.6
July 11, 2011	70.5	52.1	73.1	83.7	84.8	57.2	33.8	73.8	96.7
August 4, 2011	44.8	27.7	59.8	40.8	58.3	33.6	41.2	51.8	49.7
Mean	57.0	50.4	58.1	52.9	62.0	52.5	38.3	65.1	57.2
Maximum	76.9	76.8	73.1	83.7	84.8	80.9	60.1	95.0	96.7
Minimum	41.7	27.7	42.0	32.5	48.9	29.6	29.6	47.9	23.1
Standard deviation	12.3	15.8	9.2	16.7	12.0	19.4	9.0	16.2	20.4

FF₃₀ the percentage of pollution load transported by the first 30 % of runoff volume

studies (Deletic 1998; Taebi and Droste 2004; Luo et al. 2012). However, the FF₃₀ values for all the parameters studied were not correlated with the time of maximum rainfall intensity, which differs from the previous study. Li et al. (2007) concluded that the maximum rainfall intensity appears earlier and would cause a more distinctive FF. The difference with our study was that the road with a high slope (10°) leads to higher runoff velocity and stronger flushing capacity to road; therefore, when the rainfall intensity is not large in the initial of rainfall, the first flush also occurred and the time of maximum rainfall intensity had less affect on the FF₃₀. The FF₃₀ values of NO₃⁻-N and DZn were positively correlated to runoff duration ($p < 0.05$), and the FF₃₀ value for DZn was also positively correlated to the antecedent dry weather period ($p < 0.01$). FF₃₀ value for COD was positively correlated to the average rainfall intensity ($p < 0.05$).

The first flush effect is an important phenomenon for selecting the best management practices (BMPs) by providing reasonable treatment criteria. In this study, stormwater runoff pollution showed high first flush effect in mountainous city roads. This suggests that BMPs that can capture or treat the first flush should be evaluated for their ability to remove the correlated pollutants because they will be present in the first flush. The concentrations of COD, TN, and TP were 4.1, 2.4, and 2.2 times the corresponding values of the grade V surface water standard as formulated by China (GB3838-2002) (State Environment

Protection Bureau of China 2002b), respectively, and the concentration of TSS was higher from the mountainous city road runoff. Therefore, the TSS, COD, TN, and TP were mainly water parameters for control road runoff pollution. First of all, suspended solid is considered as the major pollutant in runoff since many micro-pollutants are attached to them (Shinya et al. 2000). Previous study showed also that there were strong correlation among TSS and TP, TN, and COD (Vaze and Chiew 2002; Han et al. 2006), implying that the TSS, COD, and TP were come from same source. Therefore, the TSS is the most important parameter for control road runoff pollution. The physical methods, such as sedimentation and filtration, could be used for the initial stormwater runoff treatment. Davis and Birch (2006) found that the land treatment system, such as wetlands, could intercept effectively the pollutants in runoff. Zhang et al. (2010) concluded that 86.2–98.3 % of COD and 89.6–97.3 % of TSS were removed by the sedimentation and filtration systems. Secondly, the initial storm runoff can be transported to the wastewater treatment plant for treatment. Due to the different processing capability of each sewage treatment plant, thus, we need to further discuss the FF. As shown in Table 6, if the runoff of initial 10 min was treated, 38.5 % of COD, 22.6 % of TP, 29.5 % of TN, and 20.5 % of TSS could be reduced. If the runoff of initial 20 min was treated, 42.4 % of COD, 37.3 % of TP, 44.1 % of TN, and 38.6 % of TSS could be reduced. If the runoff of initial 30 min was treated, 56.6 % of COD, 51.4 % of TP, 59.2 % of TN,

Table 6 The mean (minimum–maximum) of the percentages of pollutant loads of COD, TP, TN, and TSS in the first 10 min (L_{10}), 20 min (L_{20}), and 30 min (L_{30}) of runoff

Parameters	COD (%)	TP (%)	TN (%)	TSS (%)
L_{10}	28.5 (10.2–67.0)	22.6 (6.0–64.3)	29.5 (11.3–45.1)	20.5 (3.1–62.7)
L_{20}	42.4 (16.3–81.5)	37.3 (8.6–81.8)	44.1 (16.4–68.0)	38.6 (4.6–85.6)
L_{30}	56.6 (23.4–88.1)	51.4 (10.5–88.1)	59.2 (19.9–89.3)	54.0 (6.2–90.2)

and 54.0 % of TSS could be reduced. Therefore, measures to treat the first flush of road stormwater should be completed for effectively controlling stormwater pollution in urban area.

Potential pollution sources

Multivariate statistical techniques can be used to reduce the number of variables into a smaller set of independent variables that capture the variance of the initial data set. In this study, the PCA reduced ten original variables into three key independent factors that make it easier to identify the unobservable, latent pollution sources (Helena et al. 2000). As shown in Table 7, the KMO and Bartlett's sphericity test were 0.742 and 839.577 ($p < 0.05$), respectively, indicating that the PCA is useful for providing significant reductions in dimensionality. On the basis of eigenvalues > 1 , PCA evolved three PCs comprising 80.89 % of the total variance.

The PC1, which accounted for 46.56 % of the total variance, had strong and positive loadings on TN, DCu, $\text{NH}_4^+\text{-N}$, and $\text{NO}_3^-\text{-N}$ and had a moderately negative loading on the pH. It was concerned with the nitrogen pollutants and may be caused by the atmospheric dry and wet deposition. As shown in Table 2, the TN, $\text{NO}_3^-\text{-N}$, and $\text{NH}_4^+\text{-N}$ in rainwater accounted for 66.75, 58.46, and 81.09 %, respectively, in the road runoff, indicating that rainwater may contribute a significant amount of N nutrients to the road runoff. Wu et al. (1998) found that 70–90 % of nitrogen loadings of road runoff originated from atmospheric dry and wet deposition. Thus, PC1 can be identified as the atmospheric dry and wet deposition pollution. The PC2 accounted for 21.60 % of the total variance and had strong and positive loadings on TSS, COD, and TP. These pollutants could be caused by the debris which was from vehicle tire and asphalt road. In general, the wear and weathering of vehicle tire and asphalt material road could bring mass street sediments, and the sediments often contain hydrocarbon and phosphate

matters (Opher and Friedler 2010). In a wet day, these sediments could be washed out and lead to SS, P, and organic contamination in road runoff. Huang et al. (2007) found that organic matter in road runoff mainly come from vehicle activities. Drapper et al. (2000) found that TOC and COD concentrations in asphalt road runoff were three to five times higher than that of concrete road. Therefore, the asphalt road is a source of organic contamination. Thus, PC2 can be identified as road sediment and road material pollution. For PC3, it accounted for 12.73 % of the total variance and had strong and positive loadings on DPb and a moderately positive loading on DZn. The Zn and Pb pollution was mainly sourced from vehicle exhaust (Sansalone and Buchberger 1997; Huang et al. 2007), but Mangani et al. (2005) reported tire wear as a significant source for Zn and Davis et al. (2001) and Ball et al. (1998) reported that Pb is sourced from lubrication oil and grease. Thus, PC3 mainly results from vehicle emission.

Table 7 Loadings of ten selected variables on varimax-rotated factors matrix for road runoff data set

Parameters	PC		
	PC1	PC2	PC3
TN	0.897	0.263	0.048
$\text{NH}_4^+\text{-N}$	0.836	0.161	0.169
$\text{NO}_3^-\text{-N}$	0.797	0.402	0.067
DCu	0.760	0.273	0.094
pH	−0.616	0.299	−0.080
TSS	0.230	0.930	−0.080
COD	0.351	0.865	−0.136
TP	0.187	0.860	−0.003
DPb	−0.075	−0.036	0.938
DZn	0.542	−0.054	0.671
Eigenvalue	4.66	2.16	1.27
% total variance	46.56	21.60	12.73
Cumulative %	46.56	68.16	80.89

Conclusion

Water quality parameters were monitored during 2010–2011 in runoff from a mountainous urban road. A summary of our results is as follows:

1. The major pollutants from the mountain city road runoff were COD, TN, and TP and their average EMC values were 4.1, 2.4, and 2.2 times the corresponding values of the grade V surface water standard, respectively. The annual unit pollutant loads for COD, TN, TP, TSS, $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$, DPb, DCu, and DZn were 176.22, 5.12, 0.96, 498.00, 1.69, 2.16, 0.0033, 0.0070, and 0.0063 $\text{g}/(\text{m}^2\cdot\text{year})$, respectively. The polluted rainfall runoff could pose serious threats to the water environment nearby.
2. The pollutant concentration peak preceded or synchronized with the rainfall intensity peak and occurred 10 min after the runoff started. The results indicate that the slope is an important factor affecting mountain city road runoff quality.
3. The high FF effects of stormwater runoff pollutants occurred in Chongqing. The means of the FF₃₀ values for COD, TN, TP, TSS, $\text{NH}_4^+\text{-N}$, $\text{NO}_3^-\text{-N}$, DCu, and DZn were 57.0, 58.1, 50.4, 52.5, 52.9, 62.0, 65.8, and 58.3 %, respectively. No correlation was found between FF₃₀ and the time of maximum rainfall intensity for all the parameters.
4. Three potential pollution sources were identified for mountain city road: atmospheric dry and wet deposition, road sediment and materials, and vehicle emissions.

Therefore, based on these results, it is suggested that the local government should immediately develop treatment measures to protect the receiving body of water.

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