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Study on Mercury Distribution and Speciation in Urban Road Runoff in Nanjing City, China

Rajendra Prasad Singh [1,2,*], Jiaguo Wu [1,2], Alagarasan Jagadeesh Kumar [1,2] and Dafang Fu [1,*]

1 School of Civil Engineering, Southeast University, Sipai Lou 2#, Nanjing 210096, China; wujiaguo2017@163.com (J.W.); jaga.jagadeesh1987@gmail.com (A.J.K.)
2 Southeast University-Monash University Joint Research Centre for Water Sensitive Cities, Nanjing 210096, China
* Correspondence: rajupsc@seu.edu.cn (R.P.S.); fdf@seu.edu.cn (D.F.); Tel.: +86-13301580003 (D.F.)

Received: 7 September 2017; Accepted: 2 October 2017; Published: 12 October 2017

Abstract: The current study was aimed to investigate the mercury pollution in urban road runoff. A total of 34 rainfall events were monitored on 5 independent road catchments from 2015 to 2016 in Nanjing city, China. Events mean concentrations of mercury and the impact factors of mercury pollution in urban road runoff were also carried out in the current study. Results revealed that the concentration of various mercury species was very high. Total mercury, dissolved mercury and particulate mercury were found to be in the range of 0.173–8.254 μg/L, 0.069–6.823 μg/L, and 0.086–2.485 μg/L, respectively. The order of total mercury concentration among the five catchments was as follows: Longpan road > Xinjiekou > Jiulonghu > Zhujiang road > Maqun area. Results revealed the existence of different dominant species of mercury in different urban areas. Particularly, mercury in urban road runoff mainly existed in particulate form in Maqun area, and the concentrations of inactive mercury (0.250–2.821 μg/L) were far more than that of volatile mercury (0.023–0.215 μg/L) and active mercury (0.026–0.359 μg/L). The order of impact factors of rainfall characteristics on Hg pollution in runoff was dry periods > runoff time > duration of rainfall > storm intensity > rainfall. Analysis based on the first flush effect showed that the first flush phenomenon of mercury was not significant.

Keywords: mercury species; urban road runoff; events mean concentrations (EMCs); water pollution; first flush

1. Introduction:

Mercury (Hg) is a global pollutant which is accumulated in the long term through natural and anthropogenic activities in the environment in organic or inorganic form [1–3]. As a kind of non-biological metabolism of toxic heavy metals, Hg in low concentrations is still seriously harmful to the natural environment and human health [4]. There are two categories of the main sources of Hg, natural sources and anthropogenic sources. Natural sources mainly include volcanic, forest fire, soil and water Hg release [5], whereas anthropogenic sources include traffic activities, ore smelting, garbage incineration and fossil fuel combustion, etc. [6]. Along with the advancement of urbanization, industrialization and human activities intensifying, Hg pollution prevention is essential to reduce more serious pollution of mercury in the urban environment.

With acceleration of the urbanization process, polluted runoff as one of the major causes of water quality impairment in urban area has attracted more and more attention. In recent decades, researchers have investigated various contaminants in road runoff such as suspended solids, nutrients and common heavy metals like Cu, Zn, Pb and Cr [7–11], but there are few studies about Hg pollution in urban road runoff [12]. Mercury has drawn global attention due to its ability to contaminate entire water bodies from remote non-point source trace level inputs that bio-accumulate through the food chain [13]. It is reported that rivers flowing through urban areas have higher Hg concentrations compared to the rural areas [14,15], probably caused by pollution from expressway runoff. Hg in urban runoff mainly comes from direct anthropogenic activities such as mining, or indirectly through dry and wet deposition such as atmospheric deposition, vehicle sources, and the road surface wear. There are a variety of different forms of Hg in the environment which can be classified as particulate Hg (PHg) and dissolved Hg (DHg), according to their solubility. Furthermore, Hg can also be classified as organic mercury and inorganic mercury [12,16], in which the methyl Hg (MeHg) is best known due to its high toxicity and bioavailability. Because of the different hazards of various Hg species, investigation of each species in urban road runoff is highly significant to assess the pollution level of runoff and to determine the treatment process of Hg pollution.

In order to have a relatively accurate assessment of Hg pollution in urban road runoff in Nanjing city, the current study aimed to investigate the event mean concentrations (EMCs) of different Hg species during various rainfall events. The impact factors of the Hg pollution and the first flush in urban road runoff were also analyzed. Furthermore, the current study also aimed to assess the level of Hg pollution in urban road runoff, and meanwhile, to provide basic data and theoretical support for the treatment of Hg pollution and the reuse of stormwater.

2. Methods

2.1. Site Description

Nanjing is located in the middle and lower reaches of the Yangtze River Delta region in East China (Figure 1), with an average temperature of 15.3 °C. Annual average rainfall in Nanjing is 1106.05 mm, with most of the rainfall events occurring in summer time. Five urban road catchments divided according to the surrounding land use in Nanjing were selected for monitoring during the period of April 2015–May 2016 (Table 1).

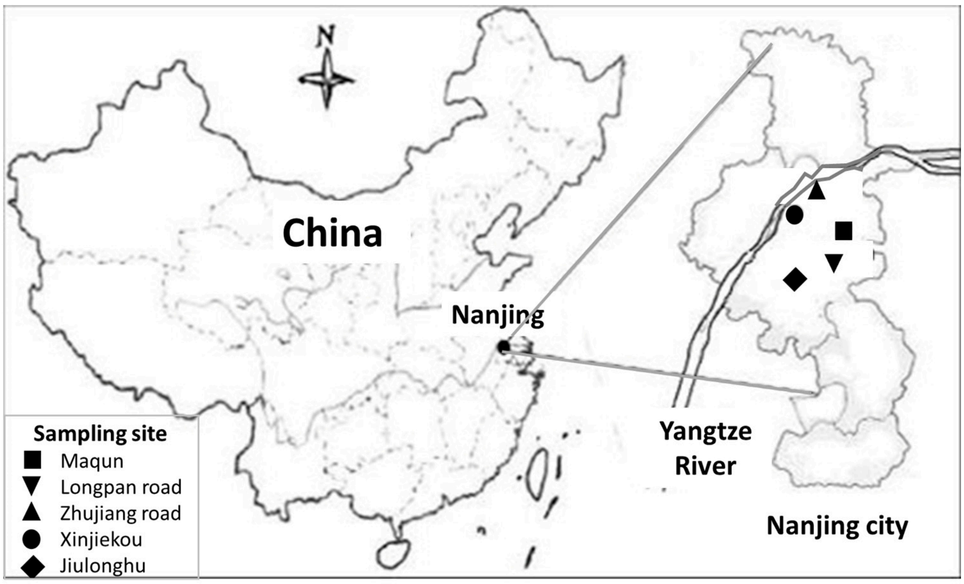


Figure 1. Sampling sites.

Table 1. Characteristics of studied catchments.

Catchment Identification	Area (m^2)	Surrounding Land Use	Road Material	Vehicle Flow Rate (/Day)
Maqun	1100	Transports	Pitch	38,400
Longpan road	1200	Transports	Pitch	39,200
Zhujiang road	1300	Electronic	Pitch, cement	30,000
Xinjiekou	1500	Commercial	Pitch, terrazzo	47,800
Jiulonghu	900	University campus, thermal power plant	Pitch	2000

The land use type in surroundings of the study area is mainly transportation. Maqun area of Nanjing city circle expressway is one of the main expressways into the city center situated on the east of Nanjing. Longpan road area has a vehicle flow rate of 39,200 vehicles/day, which was selected to represent the traffic load. Zhujiang road area is the largest distribution center for electronic products in East China. Xinjiekou area is a commercial area located in the center of Nanjing. It is a high-density population area. Jiulonghu area has Southeast University Jiulong lake campus, as well as a thermal power plant also located very close.

2.2. Rainfall Characteristics

A total of 34 effective rainfall events were monitored from April 2015 to May 2016. Rainfall runoff events data are presented in Table 2.

Samples of each rainfall event were manually collected from running water flowing out of the rainwater collection pipe (made of polyvinyl chloride material) below the pavement, for the purpose of investigating the level of Hg pollution in urban road runoff. 1 L polyethylene bottles were used to collect the runoff samples. In the first 30 min of the runoff formation, samples were collected at 5–10 min intervals. Samples were collected at 10–15 min intervals during 30 to 60 min. Following that, samples were collected at 30–60 min intervals to the end of the rainfall event. Samples were collected with precautions and immediately sent to the laboratory. Prior to analysis, a portion of each sample was extracted and filtered with a 0.45 µm filter membrane for dissolved mercury analysis. Then all of the samples except samples for total suspended solid (TSS) analysis were pretreated by adding HCl to adjust pH to less than 1 and then 0.5g K_2CrO_4 to keep the orange color of water, followed by shaking. All of the samples were kept at 0–4 °C temperature to minimize the loss of Hg. JS22 Siphon-hyetometer (Tianjin Meteorological Instrument Industry, China) can record the attributes of rainfall such as volume and intensity, which was placed at 1.5 m above the ground to collect the rainfall data.

Table 2. Rainfall characteristics in study areas.

Site	Date	Rainfall (mm)	Duration of Rainfall (min)	Runoff Time (min)	Max Storm Intensity (mm/min)	Average Storm Intensity (mm/min)	Min Storm Intensity (mm/min)	Dry Periods (h)
Maqun	12 June 2015	1.96	185	37	0.0238	0.0106	0.0060	32.0
	20 June 2015	7.15	450	65	0.0350	0.0159	0.0017	180.5
	24 June 2015	1.27	100	85	0.0267	0.0127	0.0011	83.8
	29 June 2015	22.01	385	15	0.2908	0.0572	0.0017	47.6
	14 July 2015	6.13	438	213	0.0189	0.0140	0.0012	240.5
	19 July 2015	4.40	450	26	0.0500	0.0098	0.0026	98.3
	8 August 2015	14.30	288	38	0.3497	0.0497	0.0031	120.7
	21 August 2015	9.40	158	8	0.4000	0.0595	0.0019	23.0
	25 August 2015	2.35	138	42	0.0400	0.0013	0.0124	59.0
	2 May 2016	4.80	267	21	0.0800	0.0400	0.0188	72.4
	7 May 2016	0.91	121	52	0.0200	0.0075	0.0031	88.3

Table 2. *Cont.*

Site	Date	Rainfall (mm)	Duration of Rainfall (min)	Runoff Time (min)	Max Storm Intensity (mm/min)	Average Storm Intensity (mm/min)	Min Storm Intensity (mm/min)	Dry Periods (h)
Longpan road	21 April 2015	12.00	480	58	0.2500	0.0921	0.0042	192.0
	29 April 2015	58.00	90	30	3.7000	0.6443	0.0073	84.1
	7 May 2015	100.00	180	47	2.0000	0.5884	0.0023	156.0
	14 May 2015	23.50	204	29	0.2000	0.1966	0.0038	27.2
	18 May 2015	18.00	210	64	0.3900	0.1210	0.0083	82.3
	2 May 2016	4.80	267	21	0.0800	0.0400	0.0188	72.4
	7 May 2016	0.91	121	52	0.0200	0.0075	0.0031	88.3
Zhujiang road	29 April 2015	58.00	90	30	3.7000	0.6443	0.0073	84.1
	7 May 2015	100.00	180	47	2.0000	0.5884	0.0023	156.0
	14 May 2015	23.50	204	29	0.2000	0.1966	0.0038	27.2
	18 May 2015	18.00	210	64	0.3900	0.1210	0.0083	82.3
	2 May 2016	4.80	267	21	0.0800	0.0400	0.0188	72.4
	7 May 2016	0.91	121	52	0.0200	0.0075	0.0031	88.3
Xinjiekou	7 May 2015	100.00	180	47	2.0000	0.5884	0.0023	156.0
	14 May 2015	23.50	204	29	0.2000	0.1966	0.0038	27.2
	18 May 2015	18.00	210	64	0.3900	0.1210	0.0083	82.3
	2 May 2016	4.80	267	21	0.0800	0.0400	0.0188	72.4
	7 May 2016	0.91	121	52	0.0200	0.0075	0.0031	88.3
Jiulonghu	7 May 2015	100.00	180	47	2.0000	0.5884	0.0023	156.0
	14 May 2015	23.50	204	29	0.2000	0.1966	0.0038	27.2
	18 May 2015	18.00	210	64	0.3900	0.1210	0.0083	82.3
	2 May 2016	4.80	267	21	0.0800	0.0400	0.0188	72.4
	7 May 2016	0.91	121	52	0.0200	0.0075	0.0031	88.3

2.3. Hg Analysis

Parameters such as total suspended solid (TSS), total Hg (THg), dissolved Hg (DHg), particulate Hg (PHg), volatile Hg (Hg^0, also often referred to as dissolved gaseous mercury), active Hg (which can be considered to mainly correspond to Hg^{2+} [17]), and inactive Hg (Hg^{re}, which is also referred to as residual Hg) were analyzed in the current study.

Total Hg and DHg were determined by Hydra II A Mercury Vapourmeter (Teledyne Leeman Labs, Hudson, NH, USA), while Hg at various valence states was detected by Hydra II C Mercury Vapourmeter (Teledyne Leeman Labs, Hudson, NH, USA). Experimental methods for analyzing various Hg forms are presented in Table 3.

Table 3. Analytical methods of different Hg species.

Hg	Methods
THg	50 μL stormwater, taken by pipette, was placed in a nickel boat, and Hydra II A mercury analyzer was utilized to measure the absolute values of Hg concentrations directly.
DHg	Stormwater samples were filtered through a 0.45 μm filter membrane, and 50 μL sample was analyzed by the method of THg.
PHg	PHg = THg-DHg [18,19]
Hg^0	Concentrated sulfuric acid by sub-boiling distillation was used to acidify 100 mL stormwater; then, N_2 was used to blow the samples at a rate of 350 to 400 mL/min for 30 min, and Hg^0 was captured onto the gold tube. Finally, samples were analyzed by Hydra IIC mercury analyzer.
Hg^{2+}	Stormwater samples, which have been measured for Hg^0, continue to be used to analysis Hg^{2+}. Hg^{2+} in water samples was reduced to Hg^0 by 5 mL of 20% $SnCl_2$. N_2 was used to blow the samples at a rate of 350 to 400 mL/min for 30 min, and Hg^0 as a redox product was captured onto the gold tube. Finally, samples were analyzed by Hydra IIC mercury analyzer.
Hg^{re}	Hg^{re} = THg-Hg^{0-}-Hg^{2+}

2.4. Events Mean Concentrations (EMCs)

Event mean concentration is a generally accepted index to assess the pollution levels in road runoff, which was represented by the ratio of total pollution loads and the total volume of runoff (USEPA) [20]. The formulation of EMCs is as follows:

$$\mathrm{EMC} = \overline{C} = \frac{M}{V} = \frac{\int C(t)Q(t)dt}{\int Q(t)dt} \approx \frac{\sum_{t=1}^{t=T} C(t)Q(t)}{\sum_{t=1}^{t=T} Q(t)} \tag{1}$$

M: total mass of the contaminant;
V: total volume of runoff;
$C(t)$: concentrations of the contaminant at different times;
$Q(t)$: flow of runoff;
t: runoff time.

The total runoff volume was not monitored in the current work due to the limitation of equipment, which was alternated by rainfalls. Similarly, the flow of runoff for a certain period was alternated by the product of rainfall intensity in that period and catchment area, for which the total mass of contaminant can be calculated. The beginning of rainfall and the formation time of runoff was monitored to reduce errors. In addition, the evaporation and infiltration of runoff during the rainfall were limited, which could be neglected.

2.5. Measurement of First Flush

First flush (FF) is the phenomenon in which the concentration of pollutants is substantially higher in stormwater runoff in the initial period of of a storm event compared to those obtained during the later stages [21–24]. The phenomenon is described as the relationship of dimensionless cumulative pollutant mass and dimensionless cumulative runoff volume which is calculated by the following formulas.

$$m'(t) = \frac{m(t)}{M} = \frac{\int_0^t c(t)q(t)dt}{\int_0^{t_r} c(t)q(t)dt} \tag{2}$$

$$v'(t) = \frac{v(t)}{V} = \frac{\int_0^t q(t)dt}{\int_0^{t_r} q(t)dt} \tag{3}$$

M: total mass of the contaminant;
V: total volume of runoff;
$m(t)$: Cumulative mass of the contaminant at time t;
$v(t)$: Cumulative volume of runoff at time t;
$c(t)$: concentrations of the contaminant at different times;
$q(t)$: flow of runoff;
t: runoff time;
t_r: runoff total duration.

There are differences in the determination of the first flush phenomenon in different studies. Earlier findings indicated that a first flush occurs at time t if the $m'(t)$ exceeds the $\nu'(t)$ at all instances during the storm events [25]. Bertrand-Karajewski et al. believed that first flush phenomenon occurs when at least 80% of the pollution load is transferred in the first 30% of the runoff volume [26].

When we define FF_n as the quotient of $m'(t)$ and $v'(t)$, the previous two standards are equivalent to $FF_n > 1$ and $FF_{30} \geq 2.7$.

$$FF_n = \frac{m'(t)}{v'(t)} \quad (4)$$

where n: the proportion of the runoff volume that has been generated to the total runoff volume.

In the current study, FF_{30} was calculated to determine if the first flush phenomenon exists in the various Hg species in urban road runoff.

3. Results and Discussion

3.1. EMCs of Various Hg Species

Event mean concentrations of Hg in stormwater runoff events in 5 sampling point are presented in Table 4. The data revealed that the concentrations of Hg in different forms varied greatly over 34 rainfall events, ranging from 0.173 to 8.254 μg/L for THg, from 0.069 to 6.823 μg/L for DHg, and from 0.086 to 2.485 μg/L for PHg, respectively. The EMCs of THg in 22 stormwater runoff events and also the average value of all rainfall events far exceeded 1.0 μg/L. The relationship of THg mean concentration among five regions was as follows: Longpan road (4.243 μg/L) > Xinjiekou (2.332 μg/L) > Jiulonghu (1.686 μg/L) > Zhujiang road (1.185 μg/L) > Maqun (1.120 μg/L). This phenomenon indicated that Hg concentration in urban road runoff is independent of the traffic flow. The high concentrations of Hg in urban road runoff, therefore, would cause severe pollution once entering water bodies.

Table 4. Event mean concentrations (EMCs) of Hg pollution in urban storm water runoff.

Site	Date	Hg (μg/L)			DHg/PHg	log K_d	TSS (mg/L)
		THg	DHg	PHg			
Maqun	12 June 2015	0.335	0.085	0.250	0.34	4.49	95
	20 June 2015	2.760	0.786	1.974	0.40	4.16	174
	24 June 2015	0.437	0.175	0.262	0.67	4.49	48
	29 June 2015	0.337	0.102	0.235	0.43	4.44	84
	14 July 2015	3.347	0.862	2.485	0.35	4.05	256
	19 July 2015	0.667	0.236	0.431	0.55	4.30	92
	8 August 2015	3.001	0.778	2.223	0.35	3.77	484
	21 August 2015	0.439	0.215	0.224	0.96	4.51	32
	25 August 2015	0.173	0.069	0.104	0.66	4.20	96
	2 May 2016	0.373	0.127	0.246	0.52	4.45	68
	7 May 2016	0.455	0.136	0.319	0.43	4.28	123
	Mean	1.120	0.234	0.796	0.515	4.38	141
	Median	0.439	0.136	0.262	0.43	4.31	95
	Range	0.173~3.347	0.069~0.862	0.104~2.485	0.34~0.96	3.77~4.51	32~484
Longpan road	21 April 2015	4.311	3.300	1.011	3.26	—	—
	29 April 2015	8.254	6.823	1.431	4.77	—	—
	7 May 2015	5.241	4.872	0.369	13.20	—	—
	14 May 2015	2.892	0.491	2.401	0.20	—	—
	18 May 2015	0.519	0.267	0.252	1.06	—	—
	2 May 2016	3.256	2.431	0.825	2.95	—	—
	7 May 2016	5.230	3.767	1.463	2.57	—	—
	Mean	4.243	3.151	1.092	4.00	—	—
	Median	4.311	3.300	1.011	2.95	—	—
	Range	0.519~8.254	0.267~6.823	0.252~2.401	0.20~13.20	—	—
Zhujiang road	29 April 2015	0.813	0.318	0.495	0.64	—	—
	7 May 2015	1.332	0.953	0.379	2.51	—	—
	14 May 2015	1.882	0.745	1.137	0.66	—	—
	18 May 2015	0.711	0.498	0.214	2.33	—	—
	2 May 2016	1.345	0.917	0.428	2.14	—	—
	7 May 2016	1.025	0.782	0.243	3.22	—	—
	Mean	1.185	0.702	0.483	1.92	—	—
	Median	1.179	0.622	0.355	2.24	—	—
	Range	0.711~1.882	0.318~0.953	0.214~1.137	0.64~3.22	—	—

Table 4. *Cont.*

Site	Date	Hg (μg/L)			DHg/PHg	log K_d	TSS (mg/L)
		THg	DHg	PHg			
Xinjiekou	7 May 2015	3.862	2.171	1.691	1.28	—	—
	14 May 2015	1.892	0.873	1.019	0.86	—	—
	18 May 2015	1.243	0.531	0.712	0.75	—	—
	2 May 2016	2.659	1.528	1.131	1.35	—	—
	7 May 2016	2.005	1.229	0.776	1.58	—	—
	Mean	2.332	1.351	1.432	1.16	—	—
	Median	2.005	0.531	1.691	1.28	—	—
	Range	1.243~3.862	0.531~2.171	0.712~1.691	0.75~1.58	—	—
Jiulonghu	7 May 2015	2.027	1.464	0.563	2.60	—	—
	14 May 2015	0.986	0.663	0.323	2.05	—	—
	18 May 2015	2.045	1.096	0.949	1.15	—	—
	2 May 2016	1.962	1.593	0.369	4.32	—	—
	7 May 2016	1.410	0.972	0.438	2.22	—	—
	Mean	1.686	1.074	0.612	2.47	—	—
	Median	1.962	1.096	0.623	2.22	—	—
	Range	0.986~2.045	0.663~1.593	0.323~0.949	1.15~4.32	—	—

Table 5 shows the relevant studies carried out by other researchers around the world. Data revealed that Hg pollution in urban road runoff in Nanjing has a higher level than other cities. Hg in urban road runoff mainly comes from the wet and dry deposition processes which include the discharge of automobile, the wear degree of the road materials, and some other human activities. It is hypothesized that land uses and weather conditions caused the differences.

Various forms of Hg can be reflected by the proportion of PHg and DHg (Table 4). In Maqun area, the average EMCs of PHg was 0.796 μg/L, which is much higher than the concentration of DHg. The DHg/PHg ratio of runoff in the 11 rainfall events was less than 1 (Table 3), illustrating that Hg concentrations were predominantly in particulate form. The partition coefficient K_d was calculated to explain the distribution for Hg between dissolved and particulate phases (K_d = [ng of Hg (kg of sediment)$^{-1}$]/[μg of Hg (L of rain water)$^{-1}$]) [27,28]. The log K_d values ranged from 3.77 to 4.51, showing that the Hg is associated with the particulate phase. While the DHg/PHg ratio of runoff in Xinjiekou fluctuated at 1, which shows that two Hg forms existed at an equal level. Therefore, it can be concluded that Hg in the urban road runoff of Longpan road, Zhujiang road and Jiulonghu areas was mainly in the dissolved state.

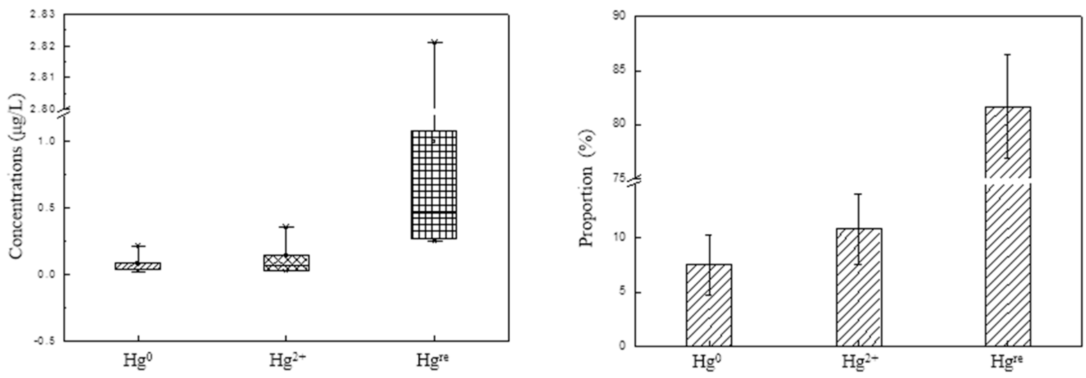
Table 5. EMCs of Hg pollution in different regions (average values).

Sites		Land Using Type	EMCs (μg/L)	Reference
			THg	
near Ontario lake in Canada		Urban	0.015	[12]
Beijing, China		Urban	0.1075	[16]
Shanghai, China		Urban	0.510	[29]
Tianjin, China	City road A	Urban	0.520 (0.412–2.76)	[30]
	City road B	Urban	0.730 (0.174–1.223)	
	Industrial district	Industry	0.660 (0.104–1.182)	
Nanjing, China		Urban	2.036 (0.173–8.254)	Current study

An earlier study by Eckleya and Branfireuna [12] has reported that PHg accounted for 84% of total Hg. Dissolved Hg can be easily absorbed by aquatic organisms, followed by accumulation in the human body through the food chain; while PHg would be adsorbed by sediments over a long time, and transfer to DHg in suitable conditions. The current study revealed different results because the samples analyzed were all collected from urban road runoff, where the biological absorption and accumulation are not obvious. This is the reason for the occurrence of different dominant Hg species in different regions.

3.2. EMCs of Hg in Different Valence States

It is well known that the toxicity of Hg in different states of Hg is different. In addition to methyl mercury (MeHg), highly active divalent mercury is one of the most toxic pollutants. Investigation of different Hg species in urban road runoff is highly significant to assess the Hg pollution level. The concentrations of Hg in different valence states (Hg^0, Hg^{2+}, and Hg^{re}) in urban road runoff in Maqun area were monitored for 6 rainfall events, and the results are provided in Figure 2.



(**a**) (**b**)

Figure 2. Distribution of Hg in different valence states: (**a**) Concentrations of Hg^0, Hg^{2+} and Hg^{re}, and (**b**) proportions of Hg^0, Hg^{2+} and Hg^{re}.

The concentrations of EMCs of Hg^0, Hg^{2+}, and Hg^{re} changed greatly, with 0.023–0.215 μg/L, 0.026-0.359 μg/L, and 0.250–2.821 μg/L, respectively (Figure 2a). The average concentration of Hg^{re} was 1.080 μg/L, which was much higher than of the concentrations of Hg^0 (0.090 μg/L) and Hg^{2+} (0.150 μg/L). Wang et al. [16] investigated the EMCs of Hg in different species in a farmland near Beijing and found the EMCs of Hg^0, Hg^{2+} and Hg^{re} were 0.011 μg/L, 0.0429 μg/L and 0.0536 μg/L, respectively, which were all lower than the results of the current study, indicating that Hg pollution of urban road runoff was much more serious, and also demonstrating different occurrence regularity in different regions.

Figure 2 shows the event mean concentrations (EMCs) (Figure 2a) and proportions (Figure 2b) of different Hg species in urban road runoff. The average percentage of Hg^{re} was 81.66%, which is more than 10 times of Hg^0 (7.51%). Hg^{re} is relatively stable and has the least hazard compared to other species. The proportion of Hg^{2+} was 10.85%, which is relatively activated and transforms easily to MeHg.

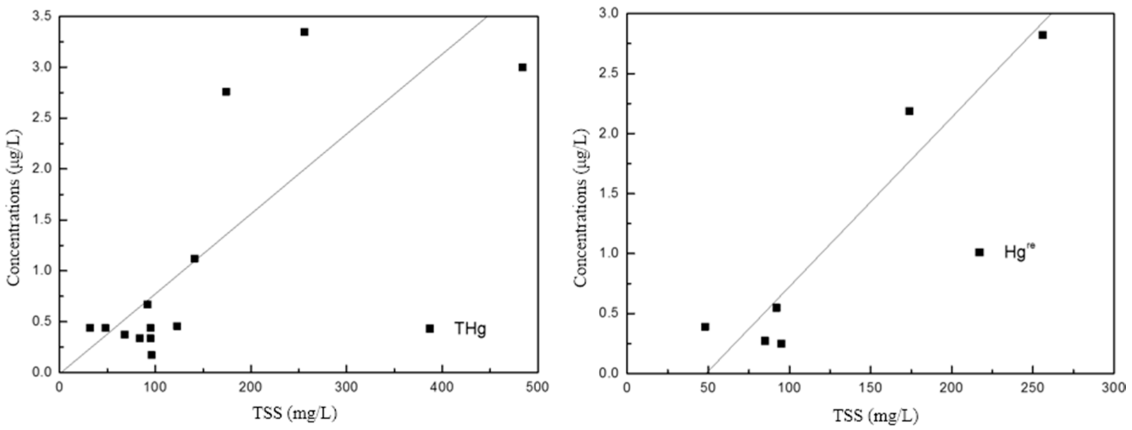
Earlier findings of a study carried out in Beijing by Liu et al. revealed that the concentration of Hg^{re} (0.171 $\mu g \cdot L^{-1}$) was much higher than the concentrations of Hg^0 (0.039 $\mu g \cdot L^{-1}$) and Hg^{2+} (0.066 $\mu g \cdot L^{-1}$) [31], which is similar to the current study. Whereas, Zhang et al. reported that the concentration of Hg^{re} was at the same level with Hg^{2+}, both of which were about 4 to 5 times higher than the concentration of Hg^0 in Shanghai [29]. Therefore, it is assumed that the presence of Hg species in urban road runoff greatly depends on the sources of Hg in the environment.

3.3. Relationship between EMCs of Hg and TSS

Pearson correlation coefficient data of various Hg species and TSS is presented in Table 6. Results revealed that all of the Hg species are positively correlated with TSS ($p < 0.01$) except Hg^0 ($p < 0.05$ levels) in the current study and the Pearson correlation coefficients ranged from 0.768 to 0.954. For Hg in different occurrence forms in urban road runoff, the Pearson correlation coefficient of PHg was highest, which can also illustrate that Hg mainly existed in particulate form in Maqun area. It was reported that there was a significant TSS/THg relationship (r^2 = 0.67, $p < 0.01$) in Toronto near Lake Ontario [12], which is similar with the current study (r^2 = 0.657, Figure 3a). The Pearson correlation coefficient of Hg^{re} was highest for Hg in various valence states. Furthermore, the concentrations of Hg^{re} and TSS have liner correlation (r^2 = 0.9105, Figure 3b), illustrating that most of Hg^{re} adsorbed on particles in urban road runoff [32].

Table 6. Pearson correlation coefficients of different Hg species and total suspended solid (TSS).

Hg	TSS	Significance Level
THg	0.807	0.01
DHg	0.768	0.01
PHg	0.819	0.01
Hg°	0.850	0.05
Hg^{2+}	0.923	0.01
Hg^{re}	0.954	0.01



(**a**) (**b**)

Figure 3. Correlation between TSS and Hg: (**a**) total Hg vs. TSS; and (**b**) residual Hg vs. TSS.

3.4. Influence of Rainfall Characteristics

Cluster analysis is a general method to reveal the relationship among multiple variables and adopted to reveal the different characteristics of rainfalls effect to EMCs of Hg species [33]. The similarity between different variables in tree diagrams of cluster analysis was depicted by Mini tab to represent the impact levels. The length and the correlation are inversely proportional; therefore it can be taken to assess the influence levels of characteristics of rainfall to Hg pollution in urban road runoff.

Nanjing city expressway was chosen to find out that some impact factors, including road materials, land use types, vehicle flow rate, atmospheric sedimentation, and the methods of road cleaning were relatively stable. Dry periods, runoff time, rainfall, rainfall duration, and rainfall intensity (including max. rainfall intensity and average rainfall intensity) were considered as the main influence factors. The cluster analysis of these factors and Hg in different occurrences is shown in Figure 4. The influence factors of rainfall characteristics on different Hg species were found to be similar. Results revealed a notable correlation between dry periods and concentration of all forms of Hg, indicating that Hg pollution in road runoff mainly comes from the accumulation of particle contaminants in dry periods. Results are consistent with an earlier study which reported that pollutants accumulate on urban surfaces mainly from dry atmospheric deposition as well as from vehicle sources during dry periods [34]. The order for impact factors on Hg deposition is as follows: dry periods > runoff time > rainfall duration > rainfall intensity > rainfall.

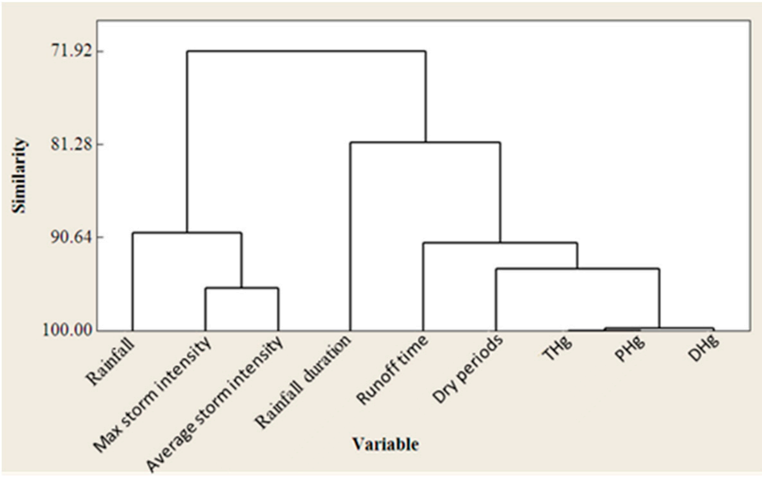


Figure 4. Cluster analysis of different Hg species and characteristics of rainfalls.

3.5. First Flush Effect (FF_{30})

The FF_{30} of various forms of Hg in urban road runoff at 4 different sites are presented in Table 7. Findings revealed that in over 23 rainfall events, the FF_{30} of Hg in different occurrence forms ranges from 0.132 to 0.570 for THg, from 0.036 to 0.793 for DHg, and from 0.177 to 0.907 for PHg, respectively. All of the FF_{30} values were lower than 2.7, means that none of the rainfall events were fulfilling the criteria of 80% of pollution load in the first 30% of the volume. These results are consistent if the relatively weak standard ($FF_n > 1$) is adopted. Therefore, there is no first flush of Hg but there is a significant dilution effect in the urban road runoff.

Table 7. First Flush effect (FF_{30}) of THg, DHg and PHg in different rainfall events.

Site	Date	FF_{30} of Hg		
		THg	**DHg**	**PHg**
Longpan road	21 April 2015	0.479	0.485	0.508
	29 April 2015	0.471	0.489	0.384
	7 May 2015	0.378	0.337	0.907
	14 May 2015	0.276	0.636	0.195
	18 May 2015	0.535	0.233	0.372
	2 May 2016	0.523	0.638	0.583
	7 May 2016	0.492	0.448	0.473
Zhujiang road	29 April 2015	0.132	0.793	0.217
	7 May 2015	0.179	0.205	0.181
	14 May 2015	0.496	0.102	0.332
	18 May 2015	0.319	0.284	0.177
	2 May 2016	0.255	0.639	0.291
	7 May 2016	0.364	0.584	0.195
Xinjiekou	7 May 2015	0.287	0.305	0.287
	14 May 2015	0.483	0.402	0.483
	18 May 2015	0.373	0.356	0.386
	2 May 2016	0.404	0.399	0.329
	7 May 2016	0.378	0.428	0.372
Jiulonghu	7 May 2015	0.570	0.160	0.355
	14 May 2015	0.450	0.036	0.692
	18 May 2015	0.407	0.282	0.482
	2 May 2016	0.529	0.183	0.622
	7 May 2016	0.358	0.157	0.475
	Range	0.132~0.570	0.036~0.793	0.177~0.907

4. Conclusions

Results from this study revealed that the Hg concentrations of different forms in urban road runoff varied greatly and ranged from 0.173 to 8.254 μg/L for THg, 0.069 to 6.823 μg/L for DHg, and 0.086 to 2.485 μg/L for PHg. Results also showed the existence of different dominant forms of Hg in different studied regions. The range of EMCs of Hg in different valence states was 0.023–0.215 μg/L for Hg^0, 0.026–0.359 μg/L for Hg^{2+}, and 0.250–2.821 μg/L for Hg^{re}. The concentration of Hg^{re} was higher than the concentration of Hg^0 and Hg^{2+}. Different Hg species in runoff were positively correlated with TSS, indicating that Hg mainly existed as particle type in Maqun area, and most of the Hg can be removed by precipitation. The order of impact factors on Hg pollution was as follows: dry periods > runoff time > duration of rainfall > storm intensity > rainfall. Current results are highly significant for understanding the Hg concentrations in urban road runoff. Outcomes of the current study will also be helpful in carrying out further research aiming to investigate the fate and transformation behavior of Hg during various treatment processes.

Acknowledgments: This research was supported by the National Natural Science foundation of China NSFC Grants No. 51550110231, 51650410657).

Author Contributions: Dafang Fu and Rajendra Prasad Singh conceived and designed the experiments; Jiaguo Wu performed the experiments and analyzed the data with Rajendra Prasad Singh; Alagarasan Jagadeesh Kumar contributed reagents/materials/analysis tools; and Rajendra Prasad Singh wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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