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Persistent toxic substances in urban highway runoff in Shanghai

Zhang Haiping[1] Teng Junwei[1] Jiang Yue[2] Yin Qiuxiao[3]

([1] College of Environmental Science and Engineering, Tongji University, Shanghai 200092, China)

([2] Shenyang Urban Planning Design and Research Institute, Shenyang 110004, China)

([3] Shanghai Dongtan International Wetland Co., Ltd, Shanghai 202162, China)

Abstract: Urban highway runoff samples from seventeen rainfall events were collected in Shanghai in 2011. The concentrations of ten heavy metals and sixteen polycyclic aromatic hydrocarbons (PAHs) are analyzed. The results show that the heavy metal concentrations range within 0.50 to 51.80 (As), 0 to 20.80 (Se), 13.67 to 445.80 (Zn), 0 to 44.20 (Pb), 0 to 15.80 (Ni), 39.58 to 264.20 (Fe), 0 to 253.00 (Mn), 0 to 8.20 (Cr), 0 to 124.20 (Cu), and 159.83 to 536.40 μg/L (Al). Se, Pb, Mn and Al concentrations in most samples exceed their corresponding criterion continuous concentrations (CCCs), while Zn and Cu concentrations exceed their criterion maximum concentrations (CMCs). The concentrations of ΣPAHs range within 37.25 to 114.57 ng/L and concentrations of PAHs are all below their corresponding CCCs. Cu, Zn and ΣPAHs show the first flush phenomenon. Analysis results of the modified Nemerow index method (NIM) indicate that runoff from eight rainfall events may have very strong biological toxicity effects, four have strong effects, three have moderate effects and only two have insignificant effects. Therefore, it is concluded that urban highway runoff is a significant pollution source to aquatic ecosystems and needs immediate purification.

Key words: highway runoff; heavy metal; PAHs; Nemerow index method; toxicity

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Highway runoff has been considered as one of the major contributing sources that deteriorate the quality of receiving waters[1-2]. During wet weather periods, highway runoff carries many pollutants, the components of which are very complex, including many different xenobiotic compounds[3]. These compounds may threaten aquatic organisms and lead to the alternation of the freshwater ecosystems[4-5].

Much attention has been paid to heavy metals and polyaromatic hydrocarbons (PAHs) due to their frequent occurrence in highway runoff and their toxicological effects on the environment and human beings[6]. Studies showed that the toxicity of runoff samples was associated with heavy metals and PAHs which were related to tires and exhaust gas of vehicles on urban highways[7-10]. The contamination of aquatic systems by heavy metals and PAHs can be critical because of their persistence in the environment. Furthermore, they can gradually accumulate in some plants and animals, and interfere with human's normal metabolic activity when taken in through the food chain[11]. Due to their toxicity and carcinogenicity, sixteen PAHs have been classified as priority pollutants by the United State Environment Protection Agency (USEPA)[12].

In recent years, more and more urban infrastructures such as highways have been built in Shanghai, resulting in increasingly serious runoff pollution[13]. The mean concentrations of TSS, TN, TP and NH_3-N are 264, 7.51, 0.63 and 3.87 mg/L in the highway runoff in Shanghai, respectively, which are worse than the Environmental Quality Standards for Surface Water Grade V, and the COD load from the traffic areas in Shanghai is 1 399 kg/($hm^2 \cdot a$). Runoff pollution imposes significant adverse impacts on the receiving waters[14-15]. However, up to now there are few studies on heavy metal and PAHs contaminations in the highway runoff in Shanghai and the information is seldom available.

This study will investigate ten heavy metals (As, Se, Zn, Pb, Ni, Fe, Mn, Cr, Cu and Al) and sixteen PAHs in highway runoff as a preliminary work of a proposed rainwater harvesting project. The pollution level and biotoxicity effects of runoff samples will also be assessed using the modified Nemerow index method (NIM).

1 Materials and Methods

1.1 Sites and sampling

Runoff samples were collected from a highway in Shanghai downtown area during seventeen rainfall events from April 2011 to August 2011. The traffic volume of the highway ranges from 4 154 to 9 820 veh/h.

The runoff samples for analysis were collected in polyethylene bottles (1 L), placed at the bottom of stormdrains on both undersides of the highway. Both grab and composite samples were collected. The composite sam-

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ples were accomplished by taking a fixed amount of samples at fixed time intervals (15 min) during a storm. All samples were stored immediately in darkness at 4 ℃ until analyzed the following day, which were filtered through a 0.45 μm Millipore filter before testing.

1.2 Sample analysis

Metal analysis (As, Se, Zn, Pb, Ni, Fe, Mn, Cr, Cu and Al) was performed using the Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES, Perkin Elmer Optima 2100 DV). Sixteen PAHs classified as priority pollutants by USEPA were extracted and analyzed by the solid-phase extraction-gas chromatographic method with mass spectrometric detection.

2 Results and Discussion

2.1 Characteristics of heavy metals and PAHs

The concentrations of ten metals and PAHs in all the samples are listed in Figs. 1 and 2, respectively.

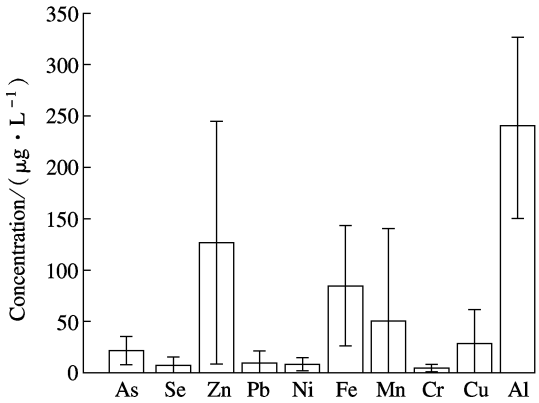

Fig. 1 Concentrations of heavy metals from seventeen rainfall events in the highway runoff

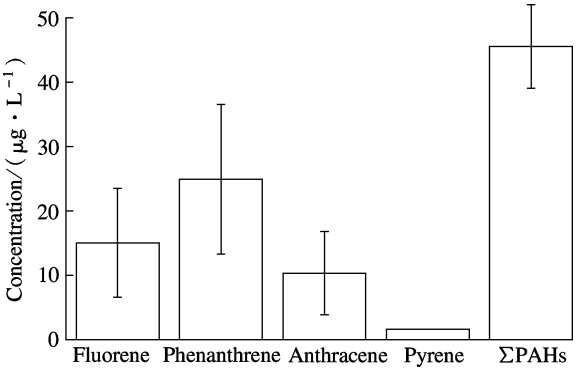

Fig. 2 Concentrations of LMW PAHs and Σ16PAHs in the highway runoff from seventeen rainfall events

The criterion maximum concentration (CMC) and criterion continuous concentration (CCC) from the National Recommended Water Quality Criteria are applied for the evaluation of contamination in urban stormwater runoff (see Tabs. 1 and 2). The CMC is known as the "acute" toxicity to aquatic life. The concentrations of these pollutants exceeding the value of CMC indicate that their adverse effects on living creatures will occur frequently in a short time. The CCC is equated with chronic toxicity. The concentrations of these pollutants exceeding the value of CCC indicate that their adverse effects on living creatures may increase in incidence from rare to occasional over a long time. The CMC and CCC values have been widely used to assess the water quality[16].

Tab. 1 CMC and CCC of heavy metals

Criterion	Concentration/(μg · L⁻¹)										
	As	Se	Zn	Pb	Cd	Ni	Fe	Mn	Cr	Cu	Al
CMC	340	13 to 186	120	65	2.0	470		2 300		13	750
CCC	150	5	120	2.5	0.25	52	1 000	80		9	87

Tab. 2 CMC and CCC of LMW PAHs

Criterion	Concentration/(ng · L⁻¹)				
	Naphthalene	Fluorene	Phenanthrene	Anthracene	Pyrene
CMC	190	70	30	13	
CCC	1.1	3.9	6.3	0.73	0.025

The heavy metal concentrations varied greatly and ranged within 0.50 to 51.80 (As), 0 to 20.80 (Se), 13.67 to 445.80 (Zn), 0 to 44.20 (Pb), 0 to 15.80 (Ni), 39.58 to 264.20 (Fe), 0 to 253.00 (Mn), 0 to 8.20 (Cr), 0 to 124.20 (Cu), and 159.83 to 536.40 μg/L (Al). Cd was not detected, while Se, Pb, Mn and Al concentrations in most samples exceed their corresponding CCCs. Zn and Cu concentrations in most samples exceed their corresponding CMCs. Therefore, Zn and Cu can be regarded as key metal pollutants in the highway runoff in Shanghai.

Of 16 analyzed PAHs, four low-molecular weight (LMW) PAHs were detected as primary pollutants: naphthalene, fluorine, phenanthrene and pyrene. This may result from the fact that high-molecular weight PAHs have low solubility and mainly concentrate in the particles, while LMW PAHs can easily dissolve in the rainwater and accumulate in the ground through wet deposition[17]. The concentrations of ΣPAHs ranged within 37.25 to 114.57 ng/L and the concentrations of LMW PAHs were all below their corresponding CCCs.

The concentration variations of main metals (Cu, Zn) and ΣPAHs during a single rainfall event were further investigated. The data from the rainfall event of June 4, 2011 were used as an example for analysis here. As shown in Fig. 3, for both heavy metals and ΣPAHs, the first flush phenomenon was quite obvious. The concentration reached the highest in 15 min after the runoff started. The heavy metal concentrations remained at a low and relatively constant level afterwards, while the ΣPAHs concentrations varied greatly. It is noted that there is a significantly positive correlation between the rainfall intensity and the ΣPAHs concentrations, while it is less significant between the rainfall intensity and the heavy metal concentrations.

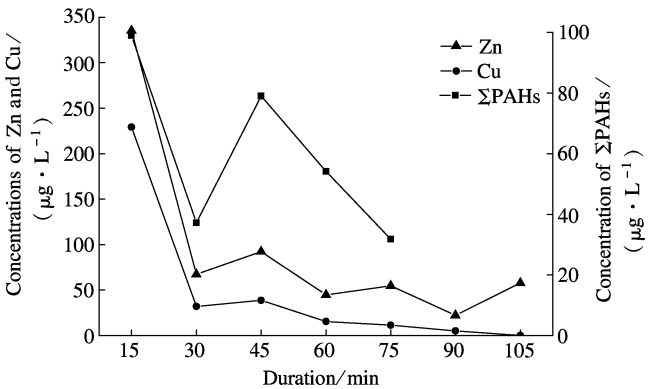

Fig. 3 Pollutographs for June 4, 2011 rainfall event

2.2 Evaluation of urban highway runoff

The modified Nemerow index method is applied to assess the water quality of highway runoff, which can be formulated as follows[18]:

$$F = \sqrt{\frac{F'^2_{\max} + F'^2_{\text{mean}}}{2}} \tag{1}$$

$$F'_{\max} = \frac{F_{\max} + F_{\text{w}}}{2} \tag{2}$$

$$W_i = \frac{R_i}{\sum_{i=1}^{n} R_i} \tag{3}$$

where F is the modified Nemerow index value; $F_{\max}$ is the maximum value of C_i/S_i; C_i is the measured concentration; S_i is the standard CMC value; F'_{mean} is the average of C_i/S_i; F_{w} is the ratio of maximum value C_i to S_i; $R_i = S_{\max}/S_i$; $S_{\max}$ is the maximum value of S_i. Water quality can be classified into five categories according to F values (see Tab. 3).

Tab. 3 Water quality classification

Category	Ⅰ	Ⅱ	Ⅲ	Ⅳ	Ⅴ
F	<0.8	0.81 to 2.50	2.50 to 4.25	4.25 to 7.20	>7.20

The weights are calculated on the basis of CMC standard levels and shown in Tab. 4. Tab. 5 presents the modified Nemerow index value and water quality classification of highway runoff samples. The analysis results of the modified NIM indicate that runoff from eight rainfall events (belonging to Ⅴ) may have very strong biological toxicity effects, four (belonging to Ⅳ) have strong effects, three (belonging to Ⅲ) have moderate effects and only two (belonging to Ⅱ) have insignificant effects. It shows that in the samples taken from seventeen rainfall events, 47% is very poor, 24% is poor, 18% is relatively good, and only 12% is good. Therefore, the urban highway runoff has varying degrees of biological toxicity, but is highly toxic in general.

Tab. 4 Weights of metals and PAHs of urban highway runoff

Metal	As	Se	Zn	Pb	Ni	Fe
Weight	1.97×10^{-2}	3.60×10^{-2}	5.58×10^{-2}	1.03×10^{-1}	1.43×10^{-2}	6.70×10^{-3}
Metal	Mn	Cr	Cu	Al	PAHs	
Weight	2.91×10^{-3}	1.14×10^{-2}	5.15×10^{-1}	8.93×10^{-3}	1.12×10^{-3}	

Tab. 5 Modified Nemerow index value and water quality classification of seventeen samples

Date	Nemerow index F	Water quality classification
2011-04-15	8.97 to 16.85	Ⅴ
2011-05-22	11.00 to 13.00	Ⅴ
2011-05-23	5.46 to 10.46	Ⅳ to Ⅴ
2011-06-04	6.33	Ⅳ
2011-06-06	3.49	Ⅲ
2011-06-10	8.10	Ⅴ
2011-06-14	3.27	Ⅲ
2011-06-15	1.88	Ⅱ
2011-06-17	3.78	Ⅲ
2011-06-18	1.73	Ⅱ
2011-06-21	6.66	Ⅳ
2011-07-04	7.45	Ⅴ
2011-07-14	12.89	Ⅴ
2011-07-31	9.16	Ⅴ
2011-08-03	15.96	Ⅴ
2011-08-04	7.05	Ⅳ
2011-08-14	9.77	Ⅴ

3 Conclusion

Urban highway runoff samples from seventeen rainfall events in Shanghai in 2011 were collected and analyzed. Cd was not detected. Se, Pb, Mn and Al concentrations in most samples exceed their corresponding CCCs, while Zn and Cu concentrations in most samples exceed their corresponding CMCs. Continuous monitoring of single rainfall events reveals that Zn and Cu has a typical first flush effect. The concentration peaks occurred immediately after the runoff started (around 15 min), and the concentration remained at a low and relatively constant level soon afterwards. Of 16 analyzed PAHs, four LMW PAHs were detected as primary pollutants: naphthalene, fluorine, phenanthrene and pyrene. The concentrations of ΣPAHs ranged within 37.25 to 114.57 ng/L, which were all below their corresponding CCCs. ΣPAHs also had first flush effects and the concentration was positively correlated to the rainfall intensity. The analysis results of the modified NIM show that runoff from eight rainfall events may have very strong biological toxicity effects, four have strong effects, three have moderate effects and only two have insignificant effects, indicating that urban highway runoff in Shanghai has varying levels of biological toxicity, but is highly toxic in general. Therefore, it is concluded that urban highway runoff is a significant pollution source to aquatic ecosystems and needs immediate purification.

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上海市高架道路径流持久性有毒物质研究

张海平[1] 滕俊伟[1] 姜 月[2] 尹秋晓[3]

([1] 同济大学环境科学与工程学院,上海 200092)

([2] 沈阳市规划设计研究院,沈阳 110004)

([3] 上海东滩国际湿地有限公司,上海 202162)

摘要:对上海市高架道路 17 场降雨径流进行收集监测,分析了降雨径流中 10 种重金属和 16 种多环芳烃(PAHs)的浓度. 结果表明:上海市高架道路径流中 10 种重金属 As, Se, Zn, Pb, Ni, Fe, Mn, Cr, Cu 和 Al 的浓度范围分别为 0.50 ~ 51.80, 0 ~ 20.80, 13.67 ~ 445.80, 0 ~ 44.20, 0 ~ 15.80, 39.58 ~ 264.20, 0 ~ 253.00, 0 ~ 8.20, 0 ~ 124.20, 159.83 ~ 536.40 μg/L. 其中,Se, Pb, Mn 和 Al 浓度值超过了其对应的基准连续浓度,而 Zn 和 Cu 则超过了其所对应的基准最大浓度. 径流中多环芳烃浓度值范围为 37.25 ~ 114.57 ng/L,均低于对应的基准连续浓度. Zn, Cu 和 PAHs 表现出明显的初期冲刷效应. 运用改进的内梅罗指数法对径流水质进行评价,发现 8 场降雨径流样品水质生物毒性极强,4 场生物毒性较强,3 场生物毒性一般,仅有 2 场生物毒性较弱. 因此,城市高架道路径流对水生态系统具有较高的生态风险,需对其进行净化处理.

关键词:高架道路径流;重金属;多环芳烃;内梅罗指数法;毒性

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