Distributions of typical contaminant species in urban short-term storm runoff and their fates during rain events: A case of Xiamen City

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Abstract

The pollutants in urban storm runoff, which lead to an non-point source contamination of water environment around cities, are of great concerns. The distributions of typical contaminants and the variations of their species in short term storm runoff from different land surfaces in Xiamen City were investigated. The concentrations of various contaminants, including organic matter, nutrients (i.e., N and P) and heavy metals, were significantly higher in parking lot and road runoff than those in roof and lawn runoff. The early runoff samples from traffic road and parking lot contained much high total nitrogen (TN 6–19 mg/L) and total phosphorus (TP 1–3 mg/L). A large proportion (around 60%) of TN existed as total dissolved nitrogen (TDN) species in most runoff. The percentage of TDN and the percentage of total dissolved phosphorus remained relatively stable during the rain events and did not decrease as dramatically as TN and TP. In addition, only parking lot and road runoff were contaminated by heavy metals, and both Pb (25–120 µg/L) and Zn (0.1–1.2 mg/L) were major heavy metals contaminating both runoff. Soluble Pb and Zn were predominantly existed as labile complex species (50%–99%), which may be adsorbed onto the surfaces of suspended particles and could be easily released out when pH decreased. This would have the great impact to the environment.

Key words: urban runoff; storm water; contamination; nutrient; heavy metal

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Introduction

Surface water quality is negatively impacted by urban development due to pollutant loads in storm runoff (Li et al., 2007; Brabec et al., 2002). The pollutants in urban storm runoff, which lead to an non-point source contamination of water environment around cities, are of great concerns (Kim et al., 2006). Rainfall in urban areas is typically more problematic than in rural areas, because of impervious surfaces such as roofs, parking lots and roads (Teemusk and Mander, 2007).

Great research effort has been concentrated to investigate the basic qualities and characteristics of organic or inorganic contaminants in runoff from different urban land surfaces. Due to the high level of pollutants in road runoff, worldwide studies on the road runoff have been carried out with topics including quantity and quality investigation (Gan et al., 2008; Drapper et al., 2000; Pagotto et al., 2000; Mangani et al., 2005), modeling (Kim et al., 2005a; Chen et al., 2007), pollutant load estimation (Legret and Pagotto, 1999; Kim et al., 2006), environmental impact assessment (Leitao, 2005) and pollution control development (Kim et al., 2005b), among which the quantity and quality investigation is the essential step and provides basic knowledge for others (Gan et al., 2008). Roof runoff is also known to be a potential source of non-point source pollution because the compounds contained in roof materials and debris deposited on roof surfaces can leach into the runoff (Ballo et al., 2009). However, although Förster (1995) demonstrated that roof runoff was a significant source of trace pollutants, Pazwash and Boswell (1995) reported that roof runoff was often nearly free of suspended matter and impurities found in runoff from other surfaces. Based on their results of roof runoff, Teemusk and Mander (2007) concluded that the quality of the runoff water varied depending on the character of the runoff and the pollutants accumulated on the roof. Other major urban land uses also include parking lot and lawns. Key source areas vary by pollutant within urban areas (Gilbert and Clausen, 2006). Therefore, it is important to compare the qualities of runoff water from various urban surfaces among different cities. In other words, more studies on qualities of runoff from various cities in different countries need to be conducted to get more basic data for better understanding of urban non-point source pollution.
There are many kinds of contaminants in urban runoff, including organic, inorganic and nutrient matters. Especially, most of these contaminants exist as different species, such as particulate and dissolved forms, in the runoff. For example, urban runoff contributes to the eutrophication of receiving waters around the world, and phosphorus and nitrogen were obviously the most concerned nutrient in surface waters (Lee and Bang, 2000). Whilst considerable data exist on the concentrations of nitrogen and phosphorus in urban runoff, there are less on its composition (Taylor et al., 2005). For example, dissolved inorganic nitrogen (DIN) includes ammonia (NH$_3$), nitrite (NO$_2^-$), and nitrate (NO$_3^-$). These constituents have the greatest impact on water bodies because they are readily available for uptake by simple organisms (Seitzinger et al., 2002), and may lead to eutrophication, hypoxia, and loss of biodiversity and habitat (Galloway et al., 2003). Nitrate is the common soluble species in aquatic systems and urban runoff (Galloway et al., 2003), and is not well retained by soil particles (Sakadevan and Bavor, 1998). While many data exist for DIN, less are available for total dissolved nitrogen (TDN) (Taylor et al., 2005), which is similar with that of phosphorus. However, the investigation of correlations between nitrogen species and other contaminants in various runoffs is still relatively few.

Heavy metals are also significant contaminants in certain kinds of runoff which are always concerned by many researchers. When considering heavy metal contaminants, speciation information is also important in runoff. Toxicities and bioavailabilities depend on heavy metal species, e.g., free ion and labile complexes are more toxic and bioavailable to aqueous organisms and plants (Rijstenbil and Poortvliet, 1992; Almas et al., 2006). The information on speciation of heavy metals is useful because removals of heavy metals in runoff by plant uptake are sometimes expected (Muthanna et al., 2007). Besides, transport of heavy metals is also related to their speciation (Murakami et al., 2009). In designing runoff treatment systems, it is also necessary to understand the composition of contaminants in urban runoff, then to maximize the removal of dominant contaminant forms in the runoff. Understanding pollutant composition in urban runoff will assist in proportioning and prioritizing the processes to be facilitated by treatment systems (Taylor et al., 2005). The forms of these contaminants may change and transfer during the rain events. Moreover, different contaminants with various forms would also interact with each others. The extremely complicated speciation and interaction among these pollutants give a great challenge to make efficient design and maintenance strategies of rainwater utilization systems.

This study provides a comprehensive assessment of the distributions and fates of typical contaminants (i.e., organic matter, nutrient, heavy metals) in short-term storm runoff from different urban surfaces. It also extends to reveal the variations of significant species of these typical contaminants during rain events. The short-term storm events were selectively investigated because the sampled runoff would be weakly affected by the runoff from longer distance catchments, therefore the pollution on micro urban catchments was revealed. These results will complement the world database about water qualities of urban storm runoff, and benefit the understanding and management of urban non-point source pollution in Xiamen City.

### 1 Materials and methods

#### 1.1 Sampling procedure

Water samples of storm runoff from four typical urban land surfaces (concrete roof, lawn, parking-lot and traffic road) in Xiamen City, Fujian Province, China were collected. Several samples (2–8) were obtained from each kind of harvesting surface in one rain event. Automatic water samplers (Pagotto et al., 2000) were used to take mean samples every 5 min, in proportion with the discharged volume of water. For example, the fist sample was taken between 0 and 5 min, then followed by the second sample (6 to 10 min). The number of total samples collected from each surface depends on the permeability of harvesting surface and the volume of rainfall. For instance, only two samples were taken successfully from lawn surface in the rain event on 30 July, 2008 because of the high permeability of water in lawn land. A maximum of six to eight samples taken from each surface in one rain event is considered to be enough for result interpretation, because of the short storm duration and the relatively stable quality of final runoff. The results of two typical rain events were shown here, one is in summer on 30 July, 2008 (rainfall 8.2 mm and duration about 1 hr, six samples were collected) and another is in autumn on 06 October, 2008 (rainfall 7.5 mm and duration about 45 min, eight samples were collected). The reason of selecting short-term storm event to be investigated is that the sampled runoff would be weakly affected by the runoff from other catchments.

The sampling sites are shown in Fig. 1. The sampling roof made by concrete material was on the top of a building with total five floors, which was built fifteen years ago. The studied driveway (at Dongdu road) is located in the westside of the Xiamen Island, a section of the G319 national main traffic road consists of four lanes in each direction.
with relatively high traffic volume (approximately 23,000 to 41,000 vehicles per day), and the driveway was made by asphalt. The automatic sampler was installed under the inlet of road runoff gutter (one gutter inlet for every 50 m). In addition, there were also approximately 3000 pedestrians walking through the pavement every day. The parking lot is one of public traffic bus stations, of which the surface is made by concrete and about 2500 m² (calculated using as-built map). There are about 2000 people using this station every day. A small building with several office rooms lies in this station and there are no more than 10 persons working here. The station ground is cleaned every day by cleaning workers. The studied lawn is located in the south side of the island close to the sea (not shown in Fig. 1). The watershed area of the lawn is about 200 m² and the slope is about 0.5. This lawn was fertilized just before collecting the runoff samples on 06 October, 2008 (rain event), and the results of these samples were dramatically interfered and cannot represent the real natural condition of the lawn during the most period in a year. Therefore, the results of lawn runoff on 06 October, 2008 rain event was not shown.

1.2 Chemical analyses

pH, total suspended solids (TSS), total dissolved solids (TDS), chemical oxygen demand (COD), total nitrogen (TN), TDN, total phosphorus (TP), total dissolved phosphorus (TDP) and some typical heavy metals (Cu, Pb, Cd, Zn) were all determined on all storm runoff samples. Reagent-grade chemicals and ultra-pure water (Milli-Q) were used. The analyses were generally carried out according to standard methods (CEPA, 2002a). TDS and pH were measured by using conductivity meter (ExStik EC400, USA) and pH meter (F-20, Qiyuan Technology, China) respectively, and the results were automatically corrected for temperature influence. One split of each sample was filtered through a membrane with pore size 0.45 µm and the total suspended solids (TSS) were retained on the membrane. The membrane was dried at 105°C before and after being used, then the content of TSS was determined by the mass difference. The filtered solution was analyzed for dissolved organic carbon (DOC) (TOC-VPCH, Shimadzu, Japan), TDN and TDP. Another split of each sample was not filtered and used directly for analyzing COD, TN and TP. COD was analyzed by a repaid COD measurement instrument (5B-3C, Lianhua Technology Co., Ltd., Lanzhou, China), in which organic matters were oxidized by potassium dichromate with sulfuric acid. TN and TDN were determined spectrophotometrically by measuring UV absorbance at 220 and 275 nm after decomposition with potassium persulphate; while, for TP and TDP the molybdenum blue-absorption method (at 700 nm) was applied in combination with decomposition by the same oxidant.

Heavy metals (Cu, Cd, Pb and Zn) were fractionated (e.g., free ion and labile complex) and measured in all runoff water samples. One split (10 mL) of raw sample was acidified to pH < 1 by concentrated HNO₃ and then centrifuged at 5000 r/min for 10 min (Waara and Farm, 2008). The total soluble metals (TSM) in the upper clarified solution (pH < 1) were determined directly with an atomic absorption spectrometry (M6 AA spectrometer, Thermo Electron Corporation, USA). The free ions (FI) of metals were measured in the filtrate of sample filtered by 0.45 µm membrane under ambient pH condition (around pH 7). The difference between TSM and FI is defined as labile complex of metal, which may be absorbed onto the surface of suspended solids under ambient pH condition. The stable metals which can only be digested out by concentrated acid under high temperature were not investigated in this study, because the stable metals that exist inside mineral or other similar matter would not be easily released out under natural condition in relative short time (e.g., several years or decades) and may have few impacts on the environment. This study focuses on the free ionic metals in the solution and labile complexes (adsorbed on suspended solid surface) because both parts would easily re-enter into water environment, and bring great challenge to the environmental pollution control and management.

2 Results and discussion

2.1 Distributions and variations of TSS and TDS in runoff from different surfaces

As shown in Fig. 2, the traffic road runoff had the highest TSS and TDS concentration, then followed by parking lot, lawn and roof in a decreasing order of pollutant concentra-

![Fig. 2 Distributions and variations of total suspended solids (TSS) (a) and total dissolved solids (TDS) (b) in runoff from different urban surfaces. Rf: roof; Lw: lawn; Pk: parking lot; Rd: road.](jesc.ac.cn)
tion. Especially, the median concentration of TSS or TDS in traffic road runoff was about 10–50 times higher than that in the runoff from other urban surfaces (i.e., parking lot, lawn and roof).

2.2 Organic contaminants in runoff from different urban surfaces

Figure 3a shows that the highest COD in the runoff samples were from traffic road during each rain event. The median values of COD in runoff from different surfaces clearly showed a decreasing order: road > parking lot > lawn > roof for both rain events. Moreover, the COD of most runoff samples from road and parking lot were much higher than class V surface water standard of 40 mg/L (CEPA, 2002b). The dissolved organic carbon (DOC) was also higher in the early runoff samples from road and parking lot than that from roof and lawn, which is consistent with the distribution of COD. However, the median DOC in runoff sample from road (around 20 mg/L) was almost the same as that in parking lot runoff (around 18 mg/L) in both rain events (Fig. 3b), which was different from COD. For example, the median COD in road runoff is around 400 mg/L, which was about two times the COD (around 200 mg/L) in parking lot runoff in October rain event. It indicates that the dissolved organic matter (DOM) was not the main component contributed to the COD in the runoff water (Fig. 3).

In addition, the COD concentration peak occurred before DOC peak for the runoff from road and parking lot, which demonstrates that the amount of DOC transported by runoff was originated from a location of further distance.

2.3 Distributions and variations of nitrogen and phosphorus species in runoff

The TN concentrations in most of runoff samples were higher than the class III surface water (1.0 mg/L), of which the quality is recommended as a low limit for drinking water source (CEPA, 2002b). Only the roof runoff collected in October 08 rain event contained low TN (< 1.0 mg/L) (Fig. 4a). The road and parking lot runoff contained very high TN, of which the median TN values were about 2 times higher than that of class V surface water (the worst surface water) (2.0 mg/L) (Fig. 4a). Similar to the distribution of TN in different runoff waters, TP was also high in most runoff samples from road and parking lot surfaces and low in roof and lawn runoff (Fig. 4b). Moreover, the early runoff samples from traffic road always contained the highest TN, which indicates the road was heavily contaminated by nitrogen and the concentration...
was higher than other urban lands. However, there is no great difference between TN (or TP) in the last few samples from road and parking lot. The low and stable content of TN or TP in roof and lawn runoff may be attributed to the light contamination of TN or TP on roof and the adsorption function of soil in lawn land, respectively.

The proportion of total dissolved nitrogen (TDN) or phosphorus (TDP) in runoff is shown as percentage of TN or TP in Fig. 4. The proportions of TDN (or TDP) in runoff from all the four surfaces (roof, lawn, parking lot and road) were relatively high and mostly around or higher than 50%, which was similar to the reported result (Taylor et al., 2005), in which TDN made up of the largest proportion of TN during storms. The TDN and TDP have the greatest potential impacts on water bodies because they are readily available for uptake by simple organisms (Seitzinger et al., 2002), and may lead to eutrophication, hypoxia, and loss of biodiversity and habitat (Galloway et al., 2003). The concentrations of TDN and TDP in roof or lawn runoff were not high due to the low TN and TP in these runoff. Therefore, the TDN and TDP in roof and lawn runoff could be negligible. However, more attention should be paid on controlling the contents of TDN and TDP when considering of the improvement of management and treatment of parking lot runoff water, because there were high TN and TP with relatively high TDN and TDP in runoff. On the contrary, there were high concentrations of TN and TP but relatively low TDN (Fig. 4a) and TDP (Fig. 4b) in the road runoff. It means most of N or P species in road runoff existed as particulate forms or insoluble forms adsorbed by particles.

It is interesting to note that the percentage of TDN or the percentage of TDP in the runoff did not change in the same way as the TN or TP did during the rain events. For example, TDN percentage of parking lot runoff did not decreased as dramatically as the TN did. The TDN percentage even increased in the last few samples collected from traffic road in the October 08 rain event, which was contrary to the variation of TN (Fig. 4a). Similarly, the difference between the variations of TDP percentage and TP can also be found based on the data of parking lot runoff in the July 08 rain event (Fig. 4b). If TDN or TDP percentage in a runoff remained stable, the content of DN or DP in the runoff would decrease consistently with the decreasing of TN or TP. However, the increasing of TDN or TDP percentage in a runoff during a rain event could be attributed to the sedimentation of some TSS containing particulate N or P from the runoff.

2.4 Distributions and variations of heavy metal in urban runoff

The total soluble metal can be separated into free ions and labile complexes (refer to Section 1.2). For the case of presenting the distributions and fates of heavy metals in runoff, July 08 rain event is presented in Fig. 5.

As shown in Fig. 5a, the content of free ionic Cu in all four urban land runoff was lower than 10 µg/L, the class I surface water (the best kind of surface water) limit and
the total soluble Cu was even lower than 1000 µg/L, TN the class III surface water limit. It demonstrates that the pollution of Cu was not significant and could be neglected.

Similarly, the total soluble Cd in each runoff was also lower than the limit value (5 µg/L) of class II surface water, and its contamination in the urban runoff could also be negligible (Fig. 5b). The content of Cr in each runoff was also very low, therefore the data is not shown here.

However, the concentration of total soluble Pb was significantly higher than other heavy metals (i.e., Cu, Cd) in each kind of runoff (Fig. 5c). The highest concentrations of free ion and labile complex Pb both appeared in the parking lot runoff. The highest free Pb in this runoff was around 30 µg/L and the highest labile complex Pb was about 120 µg/L, which was much higher than the value of class V surface water. The labile complex Pb concentration in most runoff samples from road and parking lot were higher than class III water standard (50 µg/L). Therefore, Pb should be considered as one of significant heavy metal contaminants in the road and parking lot runoff, and should be treated critically in water treatment system before the runoff water were to be reused.

Figure 5d shows the distribution and variation of Zn in the runoff from four urban lands. The concentrations of free Zn species in this runoff were all relatively low and around the class I surface water standard of 0.05 mg/L. The concentration of labile complex Zn was especially high in the traffic road runoff, and the highest labile Zn concentration was beyond the class III surface water standard (1.0 mg/L). It implies that Zn was another kind of significant heavy metal contaminant in the road runoff. It confirms the conclusion (Liu et al., 2008) that with rapid urbanization, sedimentary Pb and Zn concentrations increased.

Figure 5e, d shows that Pb and Zn dominantly existed as labile complexes in each runoff. This illuminates that most of Pb and Zn (50%–99%) was adsorbed on the surfaces of suspended particles and prone to being transported by particles in the runoff. This is consistent with the reported result (Zhao et al., 2009). The high concentration of TSS in the early runoff sample would contribute to the high concentrations of labile complex Pb and Zn. The labile species of Pb and Zn would have great impacts on the water bodies accepting the urban runoff, and would be released out when ambient condition (e.g., pH) changed.

### 3 Conclusions

The concentrations of various contaminants, including organic matter, nutrients (i.e., N and P) and heavy metals, were significantly higher in parking lot and road runoff than those in roof and lawn runoff. The early runoff samples from traffic road and parking lot contained much high total nitrogen (TN, 6–19 mg/L) and total phosphorus (TP, 1–3 mg/L). A large proportion (around 60%) of TN existed as total dissolved nitrogen (TDN) species in most runoff. TDN or TDP percentage remained relatively stable during rain event and did not decrease as dramatically as TN or TP. In addition, only parking lot and road runoff were contaminated by heavy metals, and both Pb (25–120 µg/L) and Zn (0.1–1.2 mg/L) were major heavy metals contaminating both runoff. Soluble Pb and Zn were predominantly existed as labile complex species (50%–99%), which may be adsorbed onto the surfaces of suspended particles and could be easily released out when pH decreased. This would have the largest impact to the environment.

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