Water Research 91 (2016) 264–276

Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate/watres

Influence of uncertainty inherent to heavy metal build-up and wash-off on stormwater quality

Buddhi Wijesiri, Prasanna Egodawatta, James McGree, Ashantha Goonetilleke*

Science and Engineering Faculty, Queensland University of Technology (QUT), GPO Box 2434, Brisbane, 4001, Queensland, Australia

ARTICLE INFO

Article history:
Received 11 August 2015
Received in revised form
10 January 2016
Accepted 12 January 2016
Available online 14 January 2016

Keywords:
Heavy metals
Pollutant build-up
Pollutant wash-off
Process uncertainty
Stormwater quality
Stormwater pollutant processes

ABSTRACT

Uncertainty inherent to heavy metal build-up and wash-off stems from process variability. This results in inaccurate interpretation of stormwater quality model predictions. The research study has characterised the variability in heavy metal build-up and wash-off processes based on the temporal variations in particle-bound heavy metals commonly found on urban roads. The study outcomes found that the distribution of Al, Cr, Mn, Fe, Ni, Cu, Zn, Cd and Pb were consistent over particle size fractions <150 μm and >150 μm, with most metals concentrated in the particle size fraction <150 μm. When build-up and wash-off are considered as independent processes, the temporal variations in these processes in relation to the heavy metals load are consistent with variations in the particulate load. However, the temporal variations in the load in build-up and wash-off of heavy metals and particulates are not consistent for consecutive build-up and wash-off events that occur on a continuous timeline. These inconsistencies are attributed to interactions between heavy metals and particulates <150 μm and >150 μm, which are influenced by particle characteristics such as organic matter content. The behavioural variability of particles determines the variations in the heavy metals load entrained in stormwater runoff. Accordingly, the variability in build-up and wash-off of particle-bound pollutants needs to be characterised in the description of pollutant attachment to particulates in stormwater quality modelling. This will ensure the accounting of process uncertainty, and thereby enhancing the interpretation of the outcomes derived from modelling studies.

1. Introduction

Heavy metals are common stormwater pollutants found in urban environments. The presence of different heavy metal species is attributed to specific sources, particularly automobile–use activities and industrial activities (Councell et al., 2004; Gunawardena et al., 2013; Mummullage et al., 2014). During dry weather periods, heavy metals build-up on urban impervious surfaces (e.g. roads, parking lots), and are subsequently washed-off during storms events. Stormwater runoff, which may carry significant amounts of heavy metals, is thus identified as a major non-point source of pollution to urban water bodies (Al Bakri et al., 2008).

The toxicity and the bioavailability of heavy metals discharged to urban waters exert significant impacts on ecosystem health (Beasley and Kneale, 2002; Islam et al., 2015). Consequently, urban water management recognises the importance of the mitigation of heavy metal pollution of stormwater as essential for safeguarding the urban aquatic environment (Barbosa et al., 2012; Niemczynowicz, 1999). However, the effectiveness of treatment strategies for removing specific pollutants such as heavy metals can be unreliable. This is due to decision making in relation to stormwater pollution mitigation relying on incomplete knowledge about the processes which these pollutants undergo (Li et al., 2006; Revitt et al., 2014; Stagge et al., 2012). In this context, the intrinsic variability of pollutant build-up and wash-off processes is one of the least investigated attributes of pollutant processes. This process variability creates uncertainty in relation to these processes. The process uncertainty constrains the accurate interpretation of stormwater quality predictions, which is the basis for management decision making (Haddad et al., 2013; Lee et al., 2012; Sun et al., 2012; Zoppou, 2001). Therefore, poor assessment of process uncertainty may significantly impact on the effectiveness of any stormwater pollution mitigation strategies implemented.

* Corresponding author.
E-mail addresses: b.mahappukankanamalage@qut.edu.au (B. Wijesiri), p.egodawatta@qut.edu.au (P. Egodawatta), james.mcgree@qut.edu.au (J. McGree), a.goonetilleke@qut.edu.au (A. Goonetilleke).

http://dx.doi.org/10.1016/j.watres.2016.01.028
0043-1354/

Fig. 1. Aerial and street views of the road study sites.

Table 1
Characteristics of the road study sites.

Suburb	Urban form			Road surface condition
	Housing type	Household density (households/km^2)[a]	Population density (residents/km^2)[a]	
Clearview Estate-Nerang	Detached housing	402.6	456.6	Asphalt paved Good condition Fair slope
Benowa	Detached and town housing, waterfront properties, warehouses, workshops	167.1	1173.4	Asphalt paved Poor condition Mild slope

[a] ABS (2011).

The common practice for predicting stormwater quality is the use of computer based models (Zoppou, 2001). However, current approaches in modelling do not enable the assessment of process uncertainty due to several limitations. Models which are widely used, for example, Stormwater Management Model-SWMM (Rossman, 2009) and Mike URBAN (MikeUrban, 2014a) are physically based, and capable of simulating key hydrologic and hydraulic processes and stormwater quality. However, the mathematical replication of pollutant processes in these models does not adequately describe the variations in pollutant load and composition during these processes. Moreover, a commonly used modelling approach, namely, Model for Urban Stormwater Improvement Conceptualisation-MUSIC (MUSIC, 2009) is recognised as primarily being suitable for conceptual level modelling. This is due to its limitations in modelling the complex behaviour of pollutants such as chemical interactions between different pollutants while undergoing pollutant processes (Elliott and Trowsdale, 2007). Similarly, the regression relationships of pollutant concentrations adopted in another commercially available modelling tool, SIMPLE KAREN, are found to poorly replicate the temporal variations of pollutant loads in stormwater runoff (Dotto et al., 2012; Rauch and Kinzel, 2007).

Understanding the sources of uncertainty is critical for its accurate assessment (Hvitved-Jacobsen et al., 2010; Zoppou, 2001). In regard to heavy metal build-up and wash-off, variations in heavy metal load and composition (mixture of the amounts of different heavy metal species) generates variability in these processes. These variations are predominantly influenced by the behaviour of particulates to which the heavy metals are attached, during build-up and wash-off (Kayhanian et al., 2012; Patra et al., 2008; Sansalone and Buchberger, 1997; Wijesiri et al., 2015a). Moreover, past studies have reported that different sized particles exhibit different behaviour while undergoing build-up and wash-off (Furumai et al., 2002; Vaze and Chiew, 2002), and the concentration of associated heavy metals vary among these particle size ranges (Herngren et al., 2006; McKenzie et al., 2008; Sansalone and Buchberger, 1997). As such, it is evident that the behaviour of different sized particles primarily determines the variability in heavy metal build-up and wash-off.

Specifically, Wijesiri et al. (2015a, b) suggested that the temporal variations of particles <150 μm and >150 μm during build-up and wash-off determine the variability in associated pollutant load and

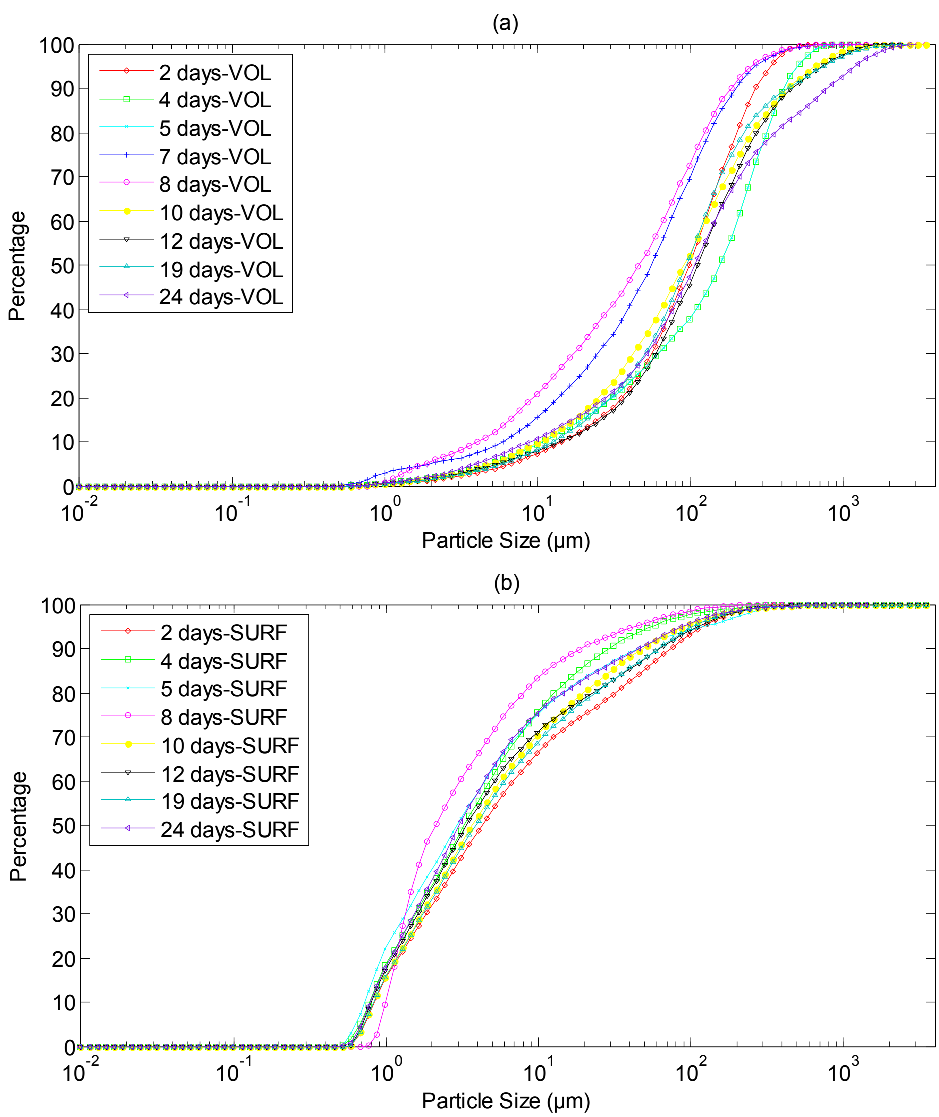

Fig. 2. Particle size distribution for particulate build-up at Mediterranean Drive: (a) Volume-based (VOL); (b) Surface area-based (SURF).

composition in built-up over the dry weather period and washed-off during a storm event. In the investigation of commonly available heavy metals associated with road deposited solids (Zn, Al, Fe, Mn, Cu, Cd, Cr and Pb), Herngren et al. (2006) concluded that these are primarily bound to particles <150 μm. Consequently, the importance of understanding pollutant build-up and wash-off process variability in terms of the behaviour of particle size fractions <150 μm and >150 μm has been highlighted in past research literature. In this context, it is also essential to investigate the affinity of heavy metals to these two particle size fractions during build-up and wash-off. This is necessitated by the fact that pollutant affinity for particulates is influenced by several physical and chemical characteristics of the particulates (Bradl, 2004; Gunawardana et al., 2013; Weber Jr et al., 1991). Gunawardana et al. (2013) identified the significance of the role played by particle characteristics such as surface area, organic matter content, clay content and metal (Fe, Mn, Al) oxide coatings in the association of heavy metals to different particle size ranges.

The primary objective of the current study was to characterise the variability in particle-bound heavy metal build-up and wash-off as the basis to assess process uncertainty. The research investigation was based on understanding the build-up and wash-off of heavy metals commonly associated with road deposited particles <150 μm and >150 μm. The study outcomes presented in this paper are expected to contribute to the more efficient design of stormwater pollution mitigation strategies.

2. Materials and methods

2.1. Study sites

Eight road sites were selected from two urban suburbs: Clearview Estate-Nerang and Benowa in Gold Coast, Australia. Both suburbs are located within the Nerang River catchment in Gold Coast. The aerial and street views of road sites are shown in Fig. 1. The four road sites in Clearview Estate-Nerang suburb have typical residential urban form, while residential and commercial land uses surround the road sites in Benowa suburb. Table 1 presents the details in relation to urban form and road surface condition at each suburb.

2.2. Build-up and wash-off sampling

Particulate build-up samples were collected from road surface plots at the eight road sites. The sampling was conducted using a wet and dry vacuum system, which consisted of a portable vacuum cleaner (Delonghi Aqualand Model) and a spraying unit (60L Swift Compact Sprayer), for nine antecedent dry periods: 2, 4, 5, 7, 8, 10, 12, 19 and 24 days. The antecedent dry periods were selected to encompass the rapid initial build-up rate which gradually declines with time (Ball et al., 1998; Egodawatta and Goonetilleke, 2006). The antecedent dry period was considered to commence immediately after a storm event in the study area. Moreover, in each sampling episode, the samples were collected from a plot adjacent to the plot where samples were collected for the previous antecedent dry period. Further details on the build-up sample collection procedure can be found in Wijesiri et al. (2015c).

Two road sites from each suburb (Yarrimbah Drive and De Haviland Avenue), where the highest particulate build-up was detected, were selected for wash-off sampling using rainfall simulation. This was to ensure that the heavy metal concentrations in the wash-off samples were within the instrument limits of detection. As wash-off is influenced by storm event characteristics, it was necessary to simulate events with different intensities and durations. Accordingly, storm events with intensities of 45 and 60 mm/h at Yarrimbah Drive and 30 and 70 mm/h at De Haviland Avenue were simulated using an artificial rainfall simulator. The performance of the simulator was verified prior to undertaking the field experiments. The storm event duration was fixed at 30 min, and six particulate wash-off samples were collected at 5 min intervals from each simulation. The design and operation procedures of the rainfall simulator are described in detail in Egodawatta et al. (2007). Additionally, the initially available particulate solids samples were also collected from the road sites prior to simulating the storm events.

2.3. Laboratory analysis

The context for the laboratory analysis was based on the fact that heavy metals are adsorbed by particles as a result of ionic and molecular interactions that take place on the particle surface. These interactions occur between different chemical forms of heavy metals and organic and inorganic molecular units protruding from the particle surface (surface functional groups), and thereby forming metal complexes (Bradl, 2004; Sposito, 2008). It has been reported in past studies that particles with larger surface area to volume ratio have higher adsorption capacity (amount of adsorbed substances) as they accommodate greater surface functional groups (Cristina et al., 2002; Thomson et al., 1997). Accordingly, the particulate build-up and wash-off samples were analysed for volume-based and surface area-based particle size distribution, suspended and dissolved solids, heavy metals, and organic matter content. Based on past research findings, organic matter content was selected as one of the influential factors in relation to heavy metal affinity for particles, and it was preferred over organic carbon content as organic matter encompasses a wide range of particle surface functional groups that bind with heavy metals (Gunawardana et al., 2013; McBride, 1994).

Firstly, particle size distributions of build-up and wash-off samples were determined using a Mastersizer 3000 analyser which incorporates a laser diffraction technique (Malvern Instrument Ltd., 2015). The instrument allows volume-based and surface area-based particle size distributions to be detected over a particle size range of 0.01–3500 μm.

Subsequently, particulate build-up and wash-off samples were wet sieved for separation into particle size fractions <150 μm and >150 μm. Gravimetric test methods, 2540C and 2540D (APHA, 2012) were adopted to determine particulate solids concentrations. For the analysis of heavy metals, each size fractionated sample was first subject to HNO_3 digestion using a hot block digester (SC154-Environmental Express) in order to extract particle-bound heavy metals into solution. The digested samples were then analysed for nine heavy metals: Al, Cr, Mn, Fe, Ni, Cu, Zn, Cd and Pb, which are commonly found in the urban environment, particularly in road deposited solids (Gunawardana et al., 2015). Inductively Coupled Plasma-Mass Spectrometry procedure as given in Method 200.8 (USEPA, 1994) was used employing an Agilent 8800 Triple Quadrupole instrument.

Organic matter content in particle size fractions <150 μm and >150 μm was determined using loss-on-ignition method (Rayment and Lyons, 2011) for particulate samples and by test method 5310C (APHA, 2012) for dissolved samples. A high temperature muffle furnace (set at 550 °C) was used to ignite particulate solids samples, and the dissolved organic matter was determined in the form of organic carbon, using an organic carbon analyser (Shimadzu TOC-V_{CSH}). The measured organic carbon was multiplied by a conversion factor of 1.72 in order to convert to organic matter (Baldock and Skjemstad, 1999).

3. Results and discussion

3.1. Influence of particle size on heavy metal build-up and wash-off

Fig. 2 shows the surface area-based and volume-based particle size distributions for build-up samples collected at Mediterranean Drive, while Fig. 3 shows the particle size distributions for wash-off samples collected during the 70 mm/h event at De Haviland Avenue. It is evident that the particle surface area to volume ratio increases with decreasing particle size. This observation is consistent with the particle size distributions corresponding to build-up and wash-off samples collected at other road sites as shown in Figures S1 and S2 in the Supplementary Information, suggesting that the fine particle size fraction contains the majority of heavy metals.

Fig. 4 shows the concentrations of the heavy metals associated with the build-up of particle size fractions <150 μm and >150 μm at Mediterranean Drive. It is evident that all nine heavy metal species are predominantly concentrated in the particle size fraction <150 μm except for a few anomalies in build-up events corresponding to antecedent dry periods of 7 and 8 days. This fact is further evident from the distribution of these heavy metal species in the build-up of the two particle size fractions at other road sites (Figs. S3 – S9 in the Supplementary Information). Moreover, in addition to the concentration, it was also evident from the comparison of heavy metal loads in the two particle size fractions (Fig. S10 in the Supplementary Information) that comparatively, particles <150 μm provides a more significant contribution to the total heavy metal load during build-up.

In the case of wash-off, the highest concentrations of most heavy metals were detected in particle size fraction <150 μm (Fig. 5 and Figs. S11 – S13 in the Supplementary Information), similar to the build-up. Additionally, Fig. S14 in the Supplementary Information, which shows the proportions of heavy metal load associated with the two particle size fractions, also confirms the significance of particles <150 μm during wash-off. However, the concentration of Cd and Pb was significantly higher in particle size fraction >150 μm during the 70 mm/h intensity storm event, which was simulated at De Haviland Avenue (Fig. 5). Specifically, Figs. S11 – S13 show that unlike Cd, the anomalous distribution of Pb in particle size fraction >150 μm is more common over different road sites and storm events. Additionally, Cr (Figs. S11 and S12) and Ni

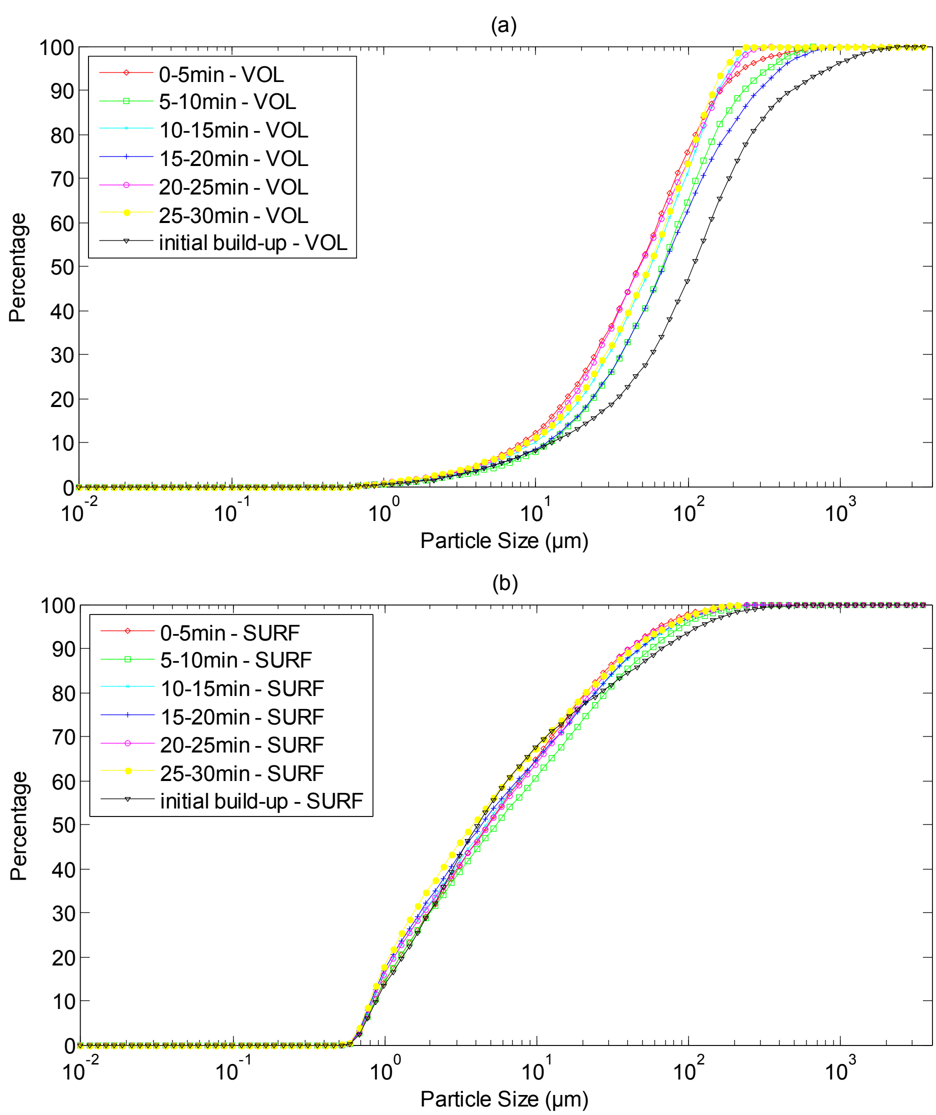

Fig. 3. Particle size distribution for particulate wash-off (70 mm/h event) at De Haviland Avenue: (a) Volume-based (VOL); (b) Surface area-based (SURF).

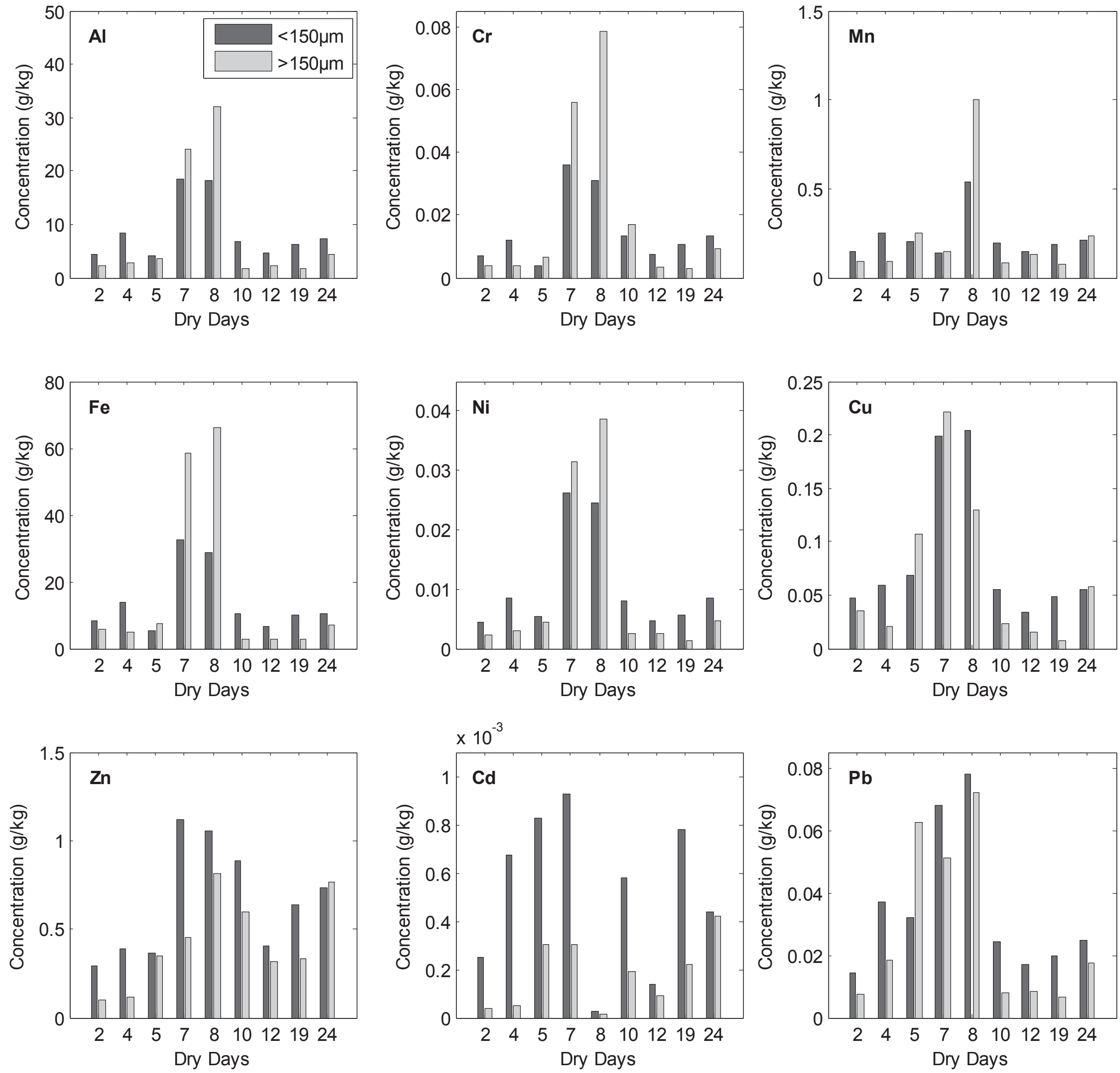

Fig. 4. Comparison of the concentrations of heavy metals associated with particle size fractions <150 μm and >150 μm during build-up – Mediterranean Drive. Note: horizontal axis is not to scale.

(Fig. S13) also exhibit higher concentrations in particle size fraction >150 μm. However, the anomalies in the distributions of Cr and Ni were limited for specific site and storm event conditions similar to the distribution of Cd.

The observed anomalies can be attributed to possible re-adsorption of heavy metals in the solution (runoff) by particles >150 μm, as discussed below. During wash-off, heavy metals associated with both particle size fractions, <150 μm and >150 μm can be released into solution. The release of heavy metals are governed by the effects of competitive adsorption by cations such as Zn, Fe and Mn (Bradl, 2004; Milberg et al., 1978; Rendell et al., 1980; Santillan-Medrano and Jurinak, 1975). The competition by metal cations for binding sites (surface functional groups) on particle surfaces can be related to the relative mobility of heavy metals, where the more preferred heavy metals for adsorption often have lower relative mobility than those heavy metals being released into solution (Sposito, 2008).

The relative mobility describes the mobility of specific particle-bound heavy metals relative to the particle mobility in solution, which implies that lower the relative mobility, stronger the affinity for particles. As such, the relative mobility of some heavy metals follows the order (decreasing mobility): Cd > Zn > Pb > Mn > Ni > Cu > Cr, as described in literature (Banerjee, 2003; Duong and Lee, 2009; Fernández et al., 2000; Li et al., 2001; Manno et al., 2006; Tokalıoğlu and Kartal, 2006). As such, the higher concentrations of Zn, Fe and Mn (Fig. 5 and Figs. S11–S13) in the particle size fraction <150 μm suggest that these heavy metals are preferentially adsorbed by particles <150 μm, while desorbing some other heavy metals.

The metal extraction experiments conducted by Rendell et al. (1980) suggested that heavy metals such as Pb and Cd released by one sediment component can be re-adsorbed by another sediment component. Accordingly, the higher concentrations of such heavy metals in the particle size fraction >150 μm in wash-off samples can be a consequence of this re-adsorption phenomenon. However, it was noted that Rendell's extraction experiments were conducted over durations longer than the durations of storm events simulated in the current investigation (i.e. 30 min). This implies that heavy metal re-adsorption by particles >150 μm can be constrained by the lack of sufficient time for the chemical interactions between heavy metals and particles. Consequently, in addition to re-adsorption, the anomalous distributions of Pb and Cd in particle size fractions <150 μm and >150 μm may also be influenced by several other factors (e.g. mineralogical composition of particulate solids) which need to be further investigated (Bradl, 2004; Reddy et al., 2014; Sangiumsak and Punrattanasin, 2014).

In fact, the adsorption of heavy metals which are released from particles <150 μm, by particles >150 μm is potentially stimulated by the particle-bound organic matter content which provides surface functional groups that form metal organic complexes. Fig. 6 shows the concentrations of organic matter associated with the two particle size fractions during wash-off. The organic matter concentrations are relatively high in the particle size fraction >150 μm compared to those in the particle size fraction <150 μm during the storm events simulated at De Haviland Avenue. However, opposite to the presence of organic matter at De Haviland Avenue, higher organic matter concentrations were detected in the particle size fraction <150 μm in the storm events simulated at Yarrimbah Drive. Accordingly, these findings are consistent with the fact regarding the anomalous distributions of heavy metals (i.e. higher concentrations in the particle size fraction >150 μm) are more common during the wash-off events at De Haviland Avenue compared to those at Yarrimbah Drive.

In summary, most heavy metals are distributed over particle size fractions <150 μm and >150 μm in a consistent pattern, such that highest heavy metal concentrations can be detected in particle size fraction <150 μm. Accordingly, the subsequent analyses were undertaken based on the hypothesis that temporal variations in build-up and wash-off of heavy metals are consistent with temporal variations in build-up and wash-off of particles <150 μm and >150 μm.

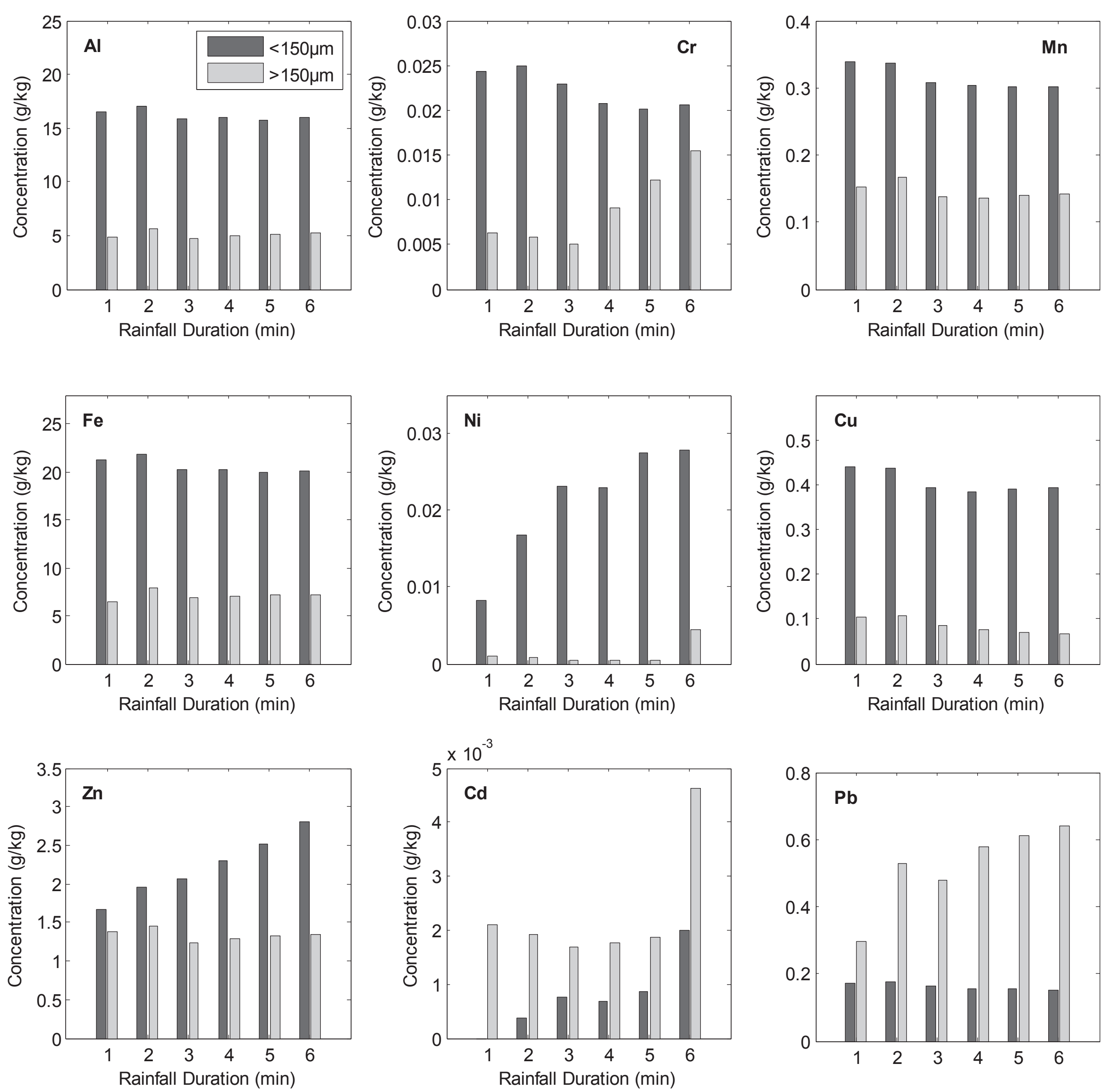

Fig. 5. Comparison of the concentrations of heavy metals associated with particle size fractions <150 μm and >150 μm during wash-off – 70 mm/h event at De Haviland Avenue.

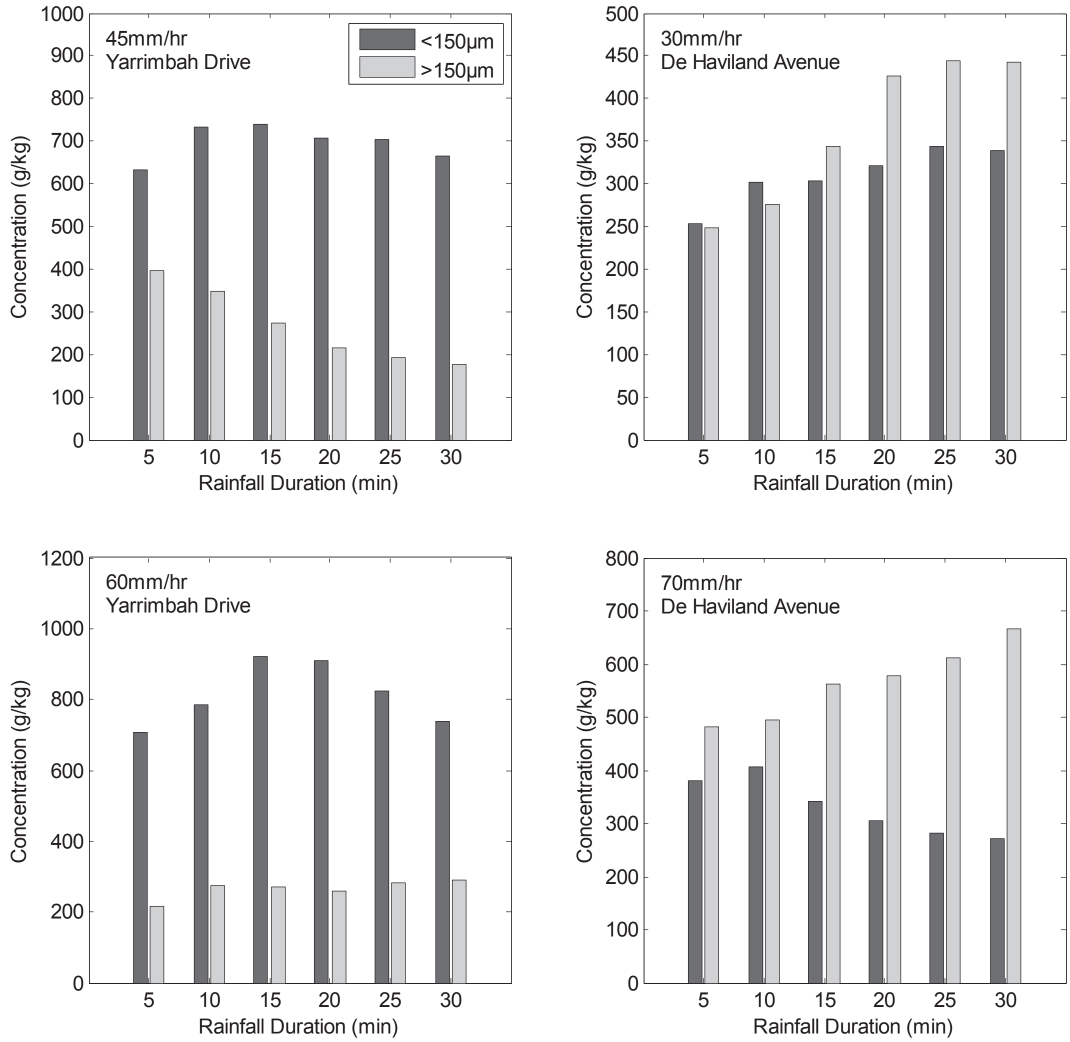

Fig. 6. Comparison of the concentrations of organic matter associated with particle size fractions <150 μm and >150 μm during wash-off.

3.2. Variability in particle-bound heavy metal build-up and wash-off

Particulate build-up/wash-off scenarios developed by Wijesiri et al. (2015c) are an effective way to explain the variations in particulate load and composition (mixture of the amounts of particles <150 μm and >150 μm) built-up over the antecedent dry period and during wash-off. These scenarios are combinations of particulate build-up and wash-off events that occur on a continuous timeline, and were developed based on the temporal variations of particle size fractions <150 μm and >150 μm over the antecedent dry period and the duration of the storm event. The three particulate build-up/wash-off scenarios shown in Fig. 7 were validated for replicating the characteristics of build-up and wash-off process variability under specific field conditions (e.g. weather, vehicular traffic, road surface conditions).

As evident from Fig. 7, in each scenario, the build-up event is depicted by a characteristic decreasing pattern of particles <150 μm and increasing patterns of particles >150 μm (Wijesiri et al., 2015a). Different combinations of these two build-up patterns distinguish between build-up/wash-off scenarios, such that a different particulate composition is generated during the build-up event corresponding to Dry period 2 in each scenario. Specifically, as evident from scenario 2 (Fig. 7b), the particulate composition generated during a build-up event could be significantly different from the composition generated during the preceding/following build-up events. This implies that two consecutive build-up events may exhibit different patterns. It is also evident from Fig. 7 that the composition of retained particulate solids after the wash-off event that occurs between two build-up events has significant influence on the build-up pattern. Accordingly, scenarios 1 and 2 (Fig. 7a and b) can be distinguished from scenario 3 (Fig. 7c) based on the composition of retained load of particles <150 μm and >150 μm. It is important to note that the patterns of particulate wash-off are not depicted in the build-up/wash-off scenarios as both particle size fractions <150 μm and >150 μm follow a similar pattern (increasing pattern) over the duration of the storm event (Sartor and Boyd, 1972; Wijesiri et al., 2015b).

Moreover, as build-up and wash-off events occur in a regular recurring order on a continuous timeline, the scenarios in Fig. 7 effectively depict how variations in particulate load and composition during a specific build-up/wash-off event influence these variations during the following build-up/wash-off event. This is particularly important for understanding wash-off process variability as the washed-off particulate load and composition vary proportionate to the load and composition of particulate build-up available at the beginning of the wash-off event (Wijesiri et al., 2015b).

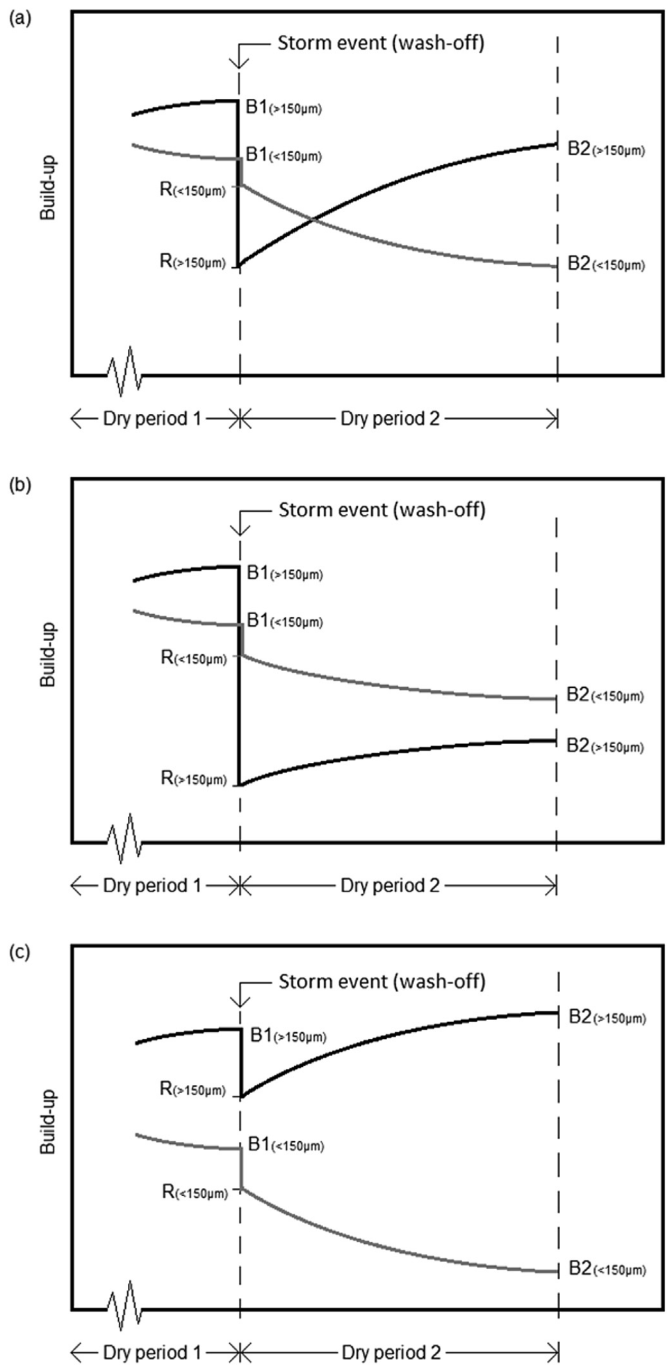

Fig. 7. Scenarios of particulate build-up and wash-off events: (a) Scenario 1; (b) Scenario 2; (c) Scenario 3; $B1_{(<150\mu m)}$, $B1_{(>150\mu m)}$ and $B2_{(<150\mu m)}$, $B2_{(>150\mu m)}$ are particulate build-up available at the end of Dry period 1 and Dry period 2, respectively; $R_{(<150\mu m)}$ and $R_{(>150\mu m)}$ are particulate loads retained after the storm event. Note: intense build-up that potentially occurs on wet road surface immediately after a storm event is not shown (adapted from (Wijesiri et al. (2015c)).

Accordingly, based on the hypothesis described in Section 3.1, the build-up/wash-off scenarios for heavy metals, which were considered equivalent to build-up/wash-off scenarios for particulates, were used to investigate the characteristics of process variability in heavy metal build-up and wash-off. Build-up/wash-off scenarios for heavy metals are combinations of build-up and wash-off events of heavy metals that take place on a continuous timeline. As such, nine possible scenarios were identified at each of the two road sites: Yarrimbah Drive from Clearview Estate-Nerang suburb and De Haviland Avenue from Benowa suburb. These scenarios correspond to the nine antecedent dry periods described in Section 2.2. In each scenario, the wash-off event precedes the build-up event similar to the order of events depicted in particulate build-up/wash-off scenarios shown in Fig. 7. As such, each of the nine antecedent dry periods is equivalent to dry period 2 in the scenarios in Fig. 7.

For each scenario, the data were collected only for the build-up event as the preceding wash-off event was the result of a natural storm. It is important to note that these natural storm events that occurred prior to each build-up event are different from the storm events simulated for wash-off sampling described in Section 2.2. Accordingly, the heavy metal build-up/wash-off scenarios are shown in Fig. 8 (Yarrimbah Drive) and Fig. S15 in the Supplementary Information (De Haviland Avenue) in terms of the build-up of heavy metals associated with particle size fractions <150 μm and >150 μm. This build-up load of heavy metals consists of both retained heavy metals from the previous wash-off event and heavy metals deposited during the antecedent dry period that follows the wash-off event. The retained heavy metals load is the difference between the load available prior to the storm event and heavy metals washed-off during the storm event. The typical patterns of wash-off of heavy metals at both road sites can be recognised from Fig. 9 and Fig. S16 in the Supplementary Information, which show the heavy metal loads retained after the simulated storm events. The retained heavy metals load was considered in order to investigate the relationship between the preceding wash-off event and the following build-up event.

As evident from Fig. 8 and Fig. S15, at both road sites, the built-up load of heavy metals associated with particle size fraction <150 μm is greater than that of heavy metals associated with particle size fraction >150 μm for all the scenarios except for some scenarios with antecedent dry periods of 7, 8 and 24 days. Accordingly, based on the hypothesis that temporal variations in heavy metal build-up are consistent with those of particulates <150 μm and >150 μm, it can be concluded that heavy metals exhibit build-up pattern similar to particulate build-up pattern as in the build-up/wash-off scenario 2 (Fig. 7b). In fact, this observation in relation to Yarrimbah Drive is consistent with the respective particulate build-up pattern reported in Wijesiri et al. (2015c). However, the particulate build-up patterns at De Haviland Avenue identified in the same study (as in build-up/wash-off scenario 1 or 3 in Fig. 7) do not comply with the respective build-up patterns of heavy metals. This was further investigated using the patterns of heavy metal wash-off at Yarrimbah Drive and De Haviland Avenue.

According to Fig. 9 and Fig. S16, at Yarrimbah Drive, the retained heavy metal load associated with particle size fraction <150 μm is greater than that associated with particle size fraction >150 μm, except for some cases of Mn and Zn. This implies that the wash-off pattern of most heavy metals at Yarrimbah Drive would be similar to the wash-off pattern in build-up/wash-off scenario 2 in Fig. 7b. However, this wash-off pattern of heavy metals is not consistent with that of particulates (i.e. the retained load of particle size fraction <150 μm is less than that of particle size fraction >150 μm as in build-up/wash-off scenario 3 in Fig. 7c) at the same road site (Wijesiri et al., 2015c).

On the other hand, at De Haviland Avenue, all heavy metals except for some cases of Ni, Cd and Pb exhibit similar wash-off patterns (Fig. 9 and S16). This means that the retained load of heavy metals associated with particle size fraction <150 μm was less than that of heavy metals associated with particle size fraction >150 μm. Moreover, Wijesiri et al. (2015c) noted similar particulate wash-off patterns at De Haviland Avenue (as in build-up/wash-off scenario 3 in Fig. 7c). This implies that unlike at Yarrimbah Drive,

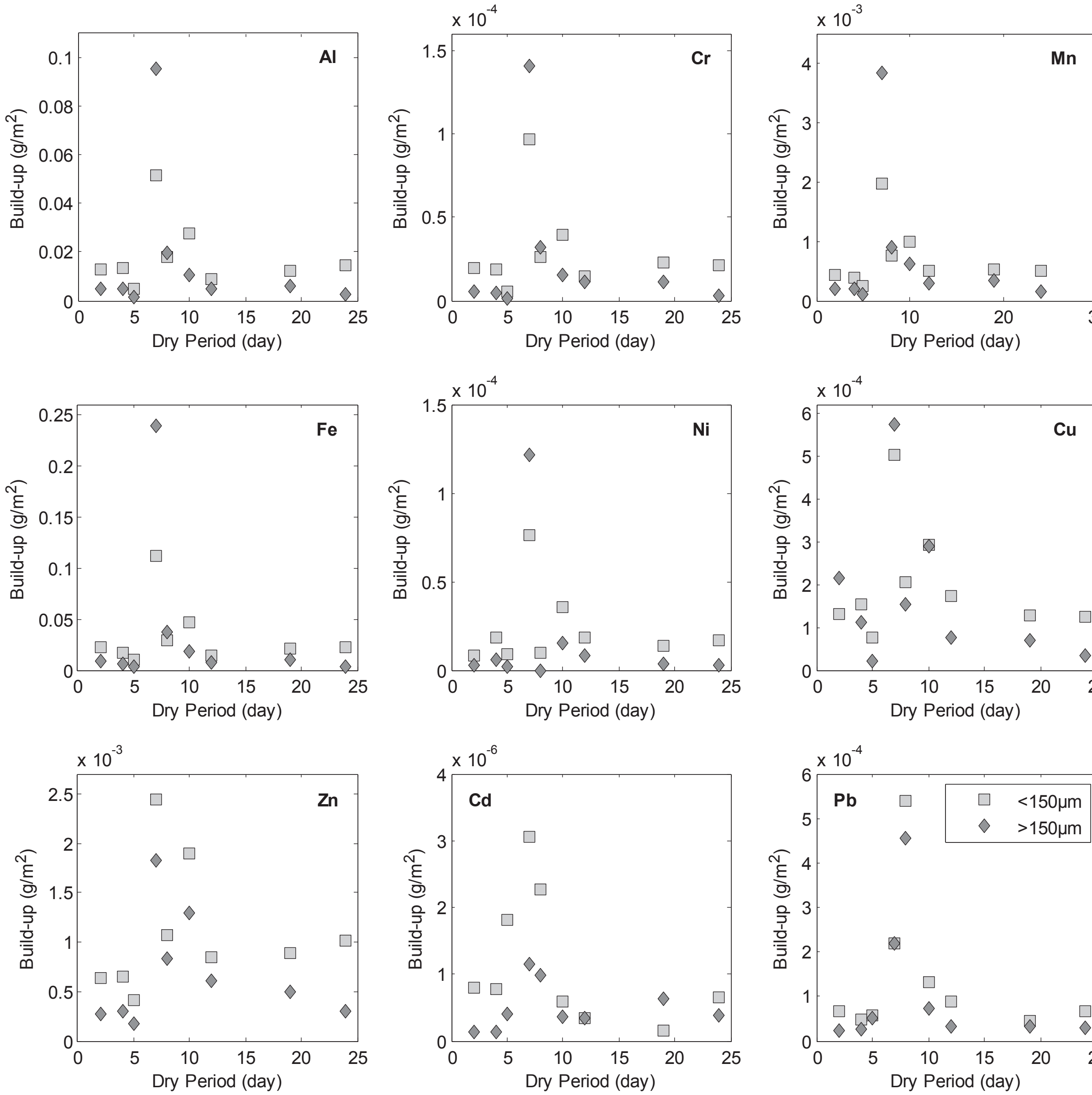

Fig. 8. Heavy metal build-up for scenarios of build-up and wash-off events at Yarrimbah Drive.

wash-off patterns for heavy metals and particulates are consistent at De Haviland Avenue.

Accordingly, it was found that the build-up of heavy metals are consistent with those of particulates at Yarrimbah Drive, while wash-off of heavy metals are consistent with those of particulates at De Haviland Avenue. Moreover, the inconsistencies observed between wash-off of heavy metals and particulates at Yarrimbah Drive, and build-up of heavy metals and particulates at De Haviland Avenue could be primarily attributed to interactions between heavy metals and particulates <150 μm and >150 μm such as re-adsorption, particularly during wash-off (under wet weather conditions). This implies that the potential changes in heavy metal affinity for particulates significantly influence the variations in heavy metal load and composition over consecutive build-up and wash-off events. In summary, the variability induced by the behaviour of different sized particles during build-up and wash-off can result in variations in load and composition of heavy metals entrained in stormwater runoff, and thereby influencing stormwater quality.

3.3. Potential implications of process uncertainty

Accounting for changes in heavy metal load and composition at a given point in time that result from build-up and wash-off process variability can be critical in the context of effective stormwater pollution mitigation. This can be achieved by assessing process uncertainty that arises from process variability. Wijesiri et al. (2015c) recommended that accounting for variability in pollutant build-up and wash-off in stormwater quality models, which provide critical information (stormwater quality predictions) for formulating pollution mitigation strategies (Loucks et al., 2005), enables the quantitative assessment of process uncertainty.

This means that incorporation of process variability into a currently available stormwater quality model (primary model) changes the mathematical formulation of build-up and wash-off, resulting in a revised model. In addition to the modelling

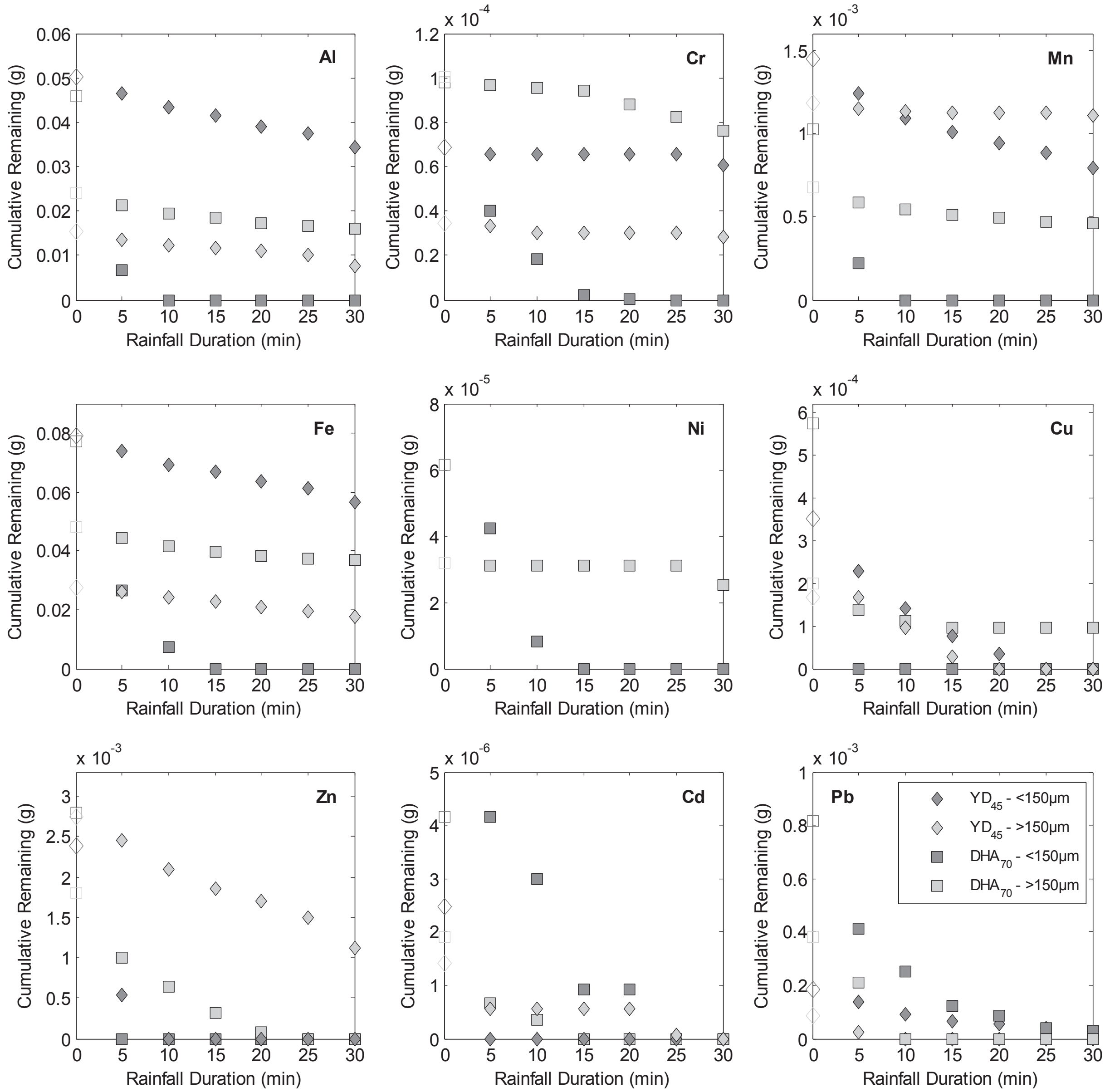

Fig. 9. Wash-off of heavy metals associated with particle size fractions <150 μm and >150 μm during 45 mm/h event at Yarrimbah Drive-YD_{45} and 70 mm/h event at De Haviland Avenue-DHA_{70} (given as retained heavy metals load after each storm event). Note: build-up of heavy metals available prior to simulating each storm event is shown in the vertical axis.

uncertainty that generally builds into model outcomes, the changes to the primary model will potentially generate uncertainty in the outcomes of the revised model. Moreover, the changes to the primary model may not significantly affect the model prediction performance. This is due to the approach proposed by Wijesiri et al. (2015c), which revised the mathematical form of the replication equations of build-up and wash-off, but does not lead to a different model structure which could affect the model prediction performance (Bertrand-Krajewski, 2007; Butts et al., 2004). Therefore, it is possible to conclude that the uncertainty resulting from the revised model, which can be statistically quantified, will reflect the inherent process uncertainty due to process variability.

Stormwater quality models are primarily based on the processes that particulates undergo. These models account for the effects of particle-bound pollutants by conceptualising pollutant attachment to particulates. For example, the surface runoff quality module in Mike URBAN considers pollutants attached to fine (<500 μm) and coarse (>500 μm) particles. However, such conceptualisations do not adequately address the variations in pollutant load and composition over the antecedent dry period and during storm events (MikeUrban, 2014b). This means that current tools (stormwater quality models) employed to create pollution mitigation strategies are deficient in addressing the variations in load and composition of heavy metals during build-up and wash-off, which are induced by the behaviour of particulates <150 μm and >150 μm, limiting the accounting of process uncertainty. Specifically, the potential inconsistencies identified between heavy metal and particulate build-up/wash-off events need to be characterised in the model description of pollutant attachment to particulates, in order to ensure the accurate accounting of the process uncertainty.

Moreover, the uncertainty assessment approaches need to be evidence based rather than relying on various subjective criteria in order to quantitatively assess uncertainty inherent to build-up and wash-off processes. However, current uncertainty assessment techniques used in stormwater quality modelling such as Generalized Likelihood Uncertainty Estimation (GLUE) (Beven and Binley, 1992) and Classical Bayesian Approach based on Markov Chain Monte Carlo (MCMC) method and the Metropolis–Hastings Sampler (Beven, 2009; Doherty, 2003) are found to have drawbacks that limit their application. Several past studies (e.g. Dotto et al., 2012; Freni et al., 2008, 2009; Freni and Mannina, 2010; Mannina and Viviani, 2010) have noted that these drawbacks constrain objective assessment of uncertainty. Although it is necessary to improve the current uncertainty assessment techniques, they can be effective in assessing process uncertainty when the characteristics of pollutant build-up and wash-off process variability identified in this study are incorporated into stormwater quality modelling.

4. Conclusions

The variability characteristics of heavy metal build-up and wash-off were investigated based on the temporal variations in build-up and wash-off of heavy metals associated with particulates <150 μm and >150 μm. The distribution of heavy metals between particle size fractions <150 μm and >150 μm during build-up and wash-off was found to be consistent over different field conditions. Most heavy metals are predominantly concentrated in the particle size fraction <150 μm. However, higher concentrations of some heavy metals such as Pb found in particle size fraction >150 μm during wash-off could be attributed to re-adsorption taking place in solution (runoff).

The temporal variations in heavy metal load were consistent with the variations in particles <150 μm and >150 μm, when build-up and wash-off are considered as independent occurrences. However, these variations are not consistent over consecutive build-up and wash-off events that occur on a continuous timeline. This is attributed to the interactions between heavy metals and particulates <150 μm and >150 μm such as re-adsorption, particularly under wet weather conditions.

The characteristics of process variability in heavy metal build-up and wash-off identified suggest that the behaviour of different sized particles during build-up and wash-off influences variations in load and composition of heavy metals. This implies that uncertainty inherent to heavy metal build-up and wash-off processes contributes to variations in stormwater quality in a catchment. The variations in stormwater quality need to be accounted for in the context of stormwater pollution mitigation. The quantitative accounting of process uncertainty will ensure the accurate interpretation of the outcomes derived from modelling studies, and thereby enhancing stormwater pollution mitigation strategies.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.watres.2016.01.028.

References

ABS, 2011. Australian Bureau of Statistics *Census-QuickStats*. Retrieved 15 April, 2015, from. http://www.abs.gov.au/websitedbs/censushome.nsf/home/quickstats?opendocument&navpos=220.

Al Bakri, D., Rahman, S., Bowling, L., 2008. Sources and management of urban stormwater pollution in rural catchments, Australia. J. Hydrol. 356 (3–4), 299–311.

APHA, 2012. In: Rice, E.W., Baird, R.B., Eaton, A.D., Clesceri, L.S. (Eds.), Standard Methods for Examination of Water and Wastewater, 22 ed. American Public Health Association, American Water Works Association, Water Environment Federation, Washington, D.C.

Baldock, J.A., Skjemstad, J.O., 1999. Soil organic carbon/soil organic matter. In: Peverill, K.I., Sparrow, L., Reuter, D.J. (Eds.), Soil Analysis: an Interpretation Manual. CSIRO Publishing, pp. 159–170.

Ball, J.E., Jenks, R., Aubourg, D., 1998. An assessment of the availability of pollutant constituents on road surfaces. Sci. Total Environ. 209 (2–3), 243–254.

Banerjee, A.D.K., 2003. Heavy metal levels and solid phase speciation in street dusts of Delhi, India. Environ. Pollut. 123 (1), 95–105.

Barbosa, A.E., Fernandes, J.N., David, L.M., 2012. Key issues for sustainable urban stormwater management. Water Res. 46 (20), 6787–6798.

Beasley, G., Kneale, P., 2002. Reviewing the impact of metals and PAHs on macroinvertebrates in urban watercourses. Prog. Phys. Geogr. 26 (2), 236–270.

Bertrand-Krajewski, J., 2007. Stormwater pollutant loads modelling: epistemological aspects and case studies on the influence of field data sets on calibration and verification. Water Sci. Technol. 55 (4), 1–17.

Beven, K., Binley, A., 1992. The future of distributed models: model calibration and uncertainty prediction. Hydrol. Process. 6 (3), 279–298.

Beven, K.J., 2009. Environmental Modelling: an Uncertain Future? Routledge, London, UK.

Bradl, H.B., 2004. Adsorption of heavy metal ions on soils and soils constituents. J. Colloid Interface Sci. 277 (1), 1–18.

Butts, M.B., Payne, J.T., Kristensen, M., Madsen, H., 2004. An evaluation of the impact of model structure on hydrological modelling uncertainty for streamflow simulation. J. Hydrol. 298 (1–4), 242–266.

Councell, T.B., Duckenfield, K.U., Landa, E.R., Callender, E., 2004. Tire-wear particles as a source of zinc to the environment. Environ. Sci. Technol. 38 (15), 4206–4214.

Cristina, C., Tramonte, J., Sansalone, J., 2002. A granulometry-based selection methodology for separation of traffic-generated particles in urban highway snowmelt runoff. Water, Air, Soil Pollut. 136 (1–4), 33–53.

Doherty, J., 2003. MICA: Model Independent Markov Chain Monte Carlo Analysis: Watermark Numerical Computing (Brisbane, Australia).

Dotto, C.B.S., Mannina, G., Kleidorfer, M., Vezzaro, L., Henrichs, M., McCarthy, D.T., Freni, G., Rauch, W., Deletic, A., 2012. Comparison of different uncertainty techniques in urban stormwater quantity and quality modelling. Water Res. 46 (8), 2545–2558.

Duong, T.T.T., Lee, B.-K., 2009. Partitioning and mobility behavior of metals in road dusts from National-scale industrial areas in Korea. Atmos. Environ. 43 (22–23), 3502–3509.

Egodawatta, P., Goonetilleke, A., 2006. Chracteristics of pollutants build-up on residential road surfaces. In: Proceedings of the 7th International Conference on HydroScience and Engineering, Philadelphia, USA. Available at: http://eprints.qut.edu.au/12660/.

Egodawatta, P., Thomas, E., Goonetilleke, A., 2007. Mathematical interpretation of pollutant wash-off from urban road surfaces using simulated rainfall. Water Res. 41 (13), 3025–3031.

Elliott, A.H., Trowsdale, S.A., 2007. A review of models for low impact urban stormwater drainage. Environ. Model. Softw. 22 (3), 394–405.

Fernández, A.J., Ternero, M., Barragán, F.J., Jiménez, J.C., 2000. An approach to characterization of sources of urban airborne particles through heavy metal speciation. Chemosphere - Glob. Change Sci. 2 (2), 123–136.

Freni, G., Mannina, G., 2010. Uncertainty in water quality modelling: the applicability of variance decomposition approach. J. Hydrol. 394 (3–4), 324–333.

Freni, G., Mannina, G., Viviani, G., 2008. Uncertainty in urban stormwater quality modelling: the effect of acceptability threshold in the glue methodology. Water Res. 42 (8–9), 2061–2072.

Freni, G., Mannina, G., Viviani, G., 2009. Uncertainty in urban stormwater quality modelling: the influence of likelihood measure formulation in the GLUE methodology. Sci. Total Environ. 408 (1), 138–145.

Furumai, H., Balmer, H., Boller, M., 2002. Dynamic behavior of suspended pollutants and particle size distribution in highway runoff. Water Sci. Technol. 46 (11–12), 413–418.

Gunawardana, C., Egodawatta, P., Goonetilleke, A., 2015. Adsorption and mobility of metals in build-up on road surfaces. Chemosphere 119 (0), 1391–1398.

Gunawardana, C., Goonetilleke, A., Egodawatta, P., 2013. Adsorption of heavy metals by road deposited solids. Water Sci. Technol. 67 (11), 2622–2629.

Gunawardena, J., Egodawatta, P., Ayoko, G.A., Goonetilleke, A., 2013. Atmospheric deposition as a source of heavy metals in urban stormwater. Atmos. Environ. 68 (0), 235–242.

Haddad, K., Egodawatta, P., Rahman, A., Goonetilleke, A., 2013. Uncertainty analysis of pollutant build-up modelling based on a bayesian weighted least squares approach. Sci. Total Environ. 449 (0), 410–417.

Herngren, L., Goonetilleke, A., Ayoko, G.A., 2006. Analysis of heavy metals in road-deposited sediments. Anal. Chim. Acta 571 (2), 270–278.

Hvitved-Jacobsen, T., Vollertsen, J., Nielsen, A.H., 2010. Urban and Highway Stormwater Pollution: Concepts and Engineering. CRC Press, Taylor and Francis Group.

Islam, M.S., Ahmed, M.K., Raknuzzaman, M., Habibullah-Al-Mamun, M., Islam, M.K., 2015. Heavy metal pollution in surface water and sediment: a preliminary assessment of an urban river in a developing country. Ecol. Indic. 48, 282–291.

Kayhanian, M., McKenzie, E.R., Leatherbarrow, J.E., Young, T.M., 2012. Characteristics of road sediment fractionated particles captured from paved surfaces, surface run-off and detention basins. Sci. Total Environ. 439 (0), 172–186.

Lee, J.G., Selvakumar, A., Alvi, K., Riverson, J., Zhen, J.X., Shoemaker, L., Lai, F.-h, 2012. A watershed-scale design optimization model for stormwater best management practices. Environ. Model. Softw. 37 (0), 6–18.

Li, X., Poon, C.-s., Liu, P.S., 2001. Heavy metal contamination of urban soils and street dusts in Hong Kong. Appl. Geochem. 16 (11–12), 1361–1368.
Li, Y., Lau, S.-L., Kayhanian, M., Stenstrom, M.K., 2006. Dynamic characteristics of particle size distribution in highway runoff: implications for settling tank design. J. Environ. Eng. 132 (8), 852–861.
Loucks, D.P., Van Beek, E., Stedinger, J.R., Dijkman, J.P., Villars, M.T., 2005. Water Resources Systems Planning and Management: an Introduction to Methods, Models and Applications. UNESCO, Paris.
Malvern Instrument Ltd, 2015. Mastersizer 3000 User Manual. MAN0474-04-EN-00, UK.
Mannina, G., Viviani, G., 2010. An urban drainage stormwater quality model: model development and uncertainty quantification. J. Hydrol. 381 (3), 248–265.
Manno, E., Varrica, D., Dongarrà, G., 2006. Metal distribution in road dust samples collected in an urban area close to a petrochemical plant at Gela, Sicily. Atmos. Environ. 40 (30), 5929–5941.
McBride, M.B., 1994. Environmental Chemistry of Soils. Oxford University Press, New York.
McKenzie, E.R., Wong, C.M., Green, P.G., Kayhanian, M., Young, T.M., 2008. Size dependent elemental composition of road-associated particles. Sci. Total Environ. 398 (1), 145–153.
MikeUrban, 2014a. Mike Urban Collection System - User Guide. Danish Hydraulic Institute.
MikeUrban, 2014b. Mouse Pollution Transport - Reference Manual. Danish Hydraulic Institue.
Milberg, R.P., Brower, D.L., Lagerwerff, J.V., 1978. Exchange adsorption of trace quantities of cadmium in soils treated with calcium and sodium: a reappraisal. Soil Sci. Soc. Am. J. 42 (6), 892–894.
Mummullage, S., Egodawatta, P., Goonetilleke, A., Ayoko, G.A., 2014. Variability of metal composition and concentrations in road dust in the urban environment. Int. J. Environ. Earth Sci. Eng. 8 (2), 54–59.
MUSIC, 2009. User Manual Version 4.0. Cooperative Research Centre for Catchment Hydrology, Australia.
Niemczynowicz, J., 1999. Urban hydrology and water management—present and future challenges. Urban Water 1 (1), 1–14.
Patra, A., Colvile, R., Arnold, S., Bowen, E., Shallcross, D., Martin, D., Price, C., Tate, J., ApSimon, H., Robins, A., 2008. On street observations of particulate matter movement and dispersion due to traffic on an urban road. Atmos. Environ. 42 (17), 3911–3926.
Rauch, W., Kinzel, H., 2007. KAREN - User Manual. hydro-IT GmbH, Innsbruck.
Rayment, G.E., Lyons, D.J., 2011. Soil Chemical Methods. CSIRO Publishing, Australasia.
Reddy, K.R., Xie, T., Dastgheibi, S., 2014. Removal of heavy metals from urban stormwater runoff using different filter materials. J. Environ. Chem. Eng. 2 (1), 282–292.
Rendell, P.S., Batley, G.E., Cameron, A.J., 1980. Adsorption as a control of metal concentrations in sediment extracts. Environ. Sci. Technol. 14 (3), 314–318.
Revitt, D.M., Lundy, L., Coulon, F., Fairley, M., 2014. The sources, impact and management of car park runoff pollution: a review. J. Environ. Manag. 146, 552–567.
Rossman, L.A., 2009. Stormwater Management Model User's Manual Version 5.0. EPA/600/R-05/040. U.S. Environmental Protection Agency, Washington, D.C.
Sangiumsak, N., Punrattanasin, P., 2014. Adsorption behavior of heavy metals on various soils. Pol. J. Environ. Stud. 23 (3), 853–865.
Sansalone, J.J., Buchberger, S.G., 1997. Partitioning and first flush of metals in urban roadway storm water. J. Environ. Eng. 123 (2), 134–143.
Santillan-Medrano, J., Jurinak, J.J., 1975. The chemistry of lead and cadmium in soil: solid phase formation. Soil Sci. Soc. Am. J. 39 (5), 851–856.
Sartor, J.D., Boyd, G.B., 1972. Water Pollution Aspects of Street Surface Contaminants. EPA-R2-72-081. U.S. Environmental Protection Agency, Washington, D.C.
Sposito, G., 2008. The Chemistry of Soils. Oxford University Press.
Stagge, J.H., Davis, A.P., Jamil, E., Kim, H., 2012. Performance of grass swales for improving water quality from highway runoff. Water Res. 46 (20), 6731–6742.
Sun, S., Fu, G., Djordjević, S., Khu, S.-T., 2012. Separating aleatory and epistemic uncertainties: probabilistic sewer flooding evaluation using probability box. J. Hydrol. 420–421 (0), 360–372.
Thomson, N.R., McBean, E.A., Snodgrass, W., Monstrenko, I.B., 1997. Highway stormwater runoff quality: development of surrogate parameter relationships. Water, Air, Soil Pollut. 94 (3–4), 307–347.
Tokalıoğlu, Ş., Kartal, Ş., 2006. Multivariate analysis of the data and speciation of heavy metals in street dust samples from the organized industrial district in Kayseri (Turkey). Atmos. Environ. 40 (16), 2797–2805.
USEPA, 1994. Method 200.8: Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma-mass Spectrometry. Revision 5.4.. U.S. Environmental Protection Agency, Ohio.
Vaze, J., Chiew, F.H.S., 2002. Experimental study of pollutant accumulation on an urban road surface. Urban Water 4 (4), 379–389.
Weber Jr., W.J., McGinley, P.M., Katz, L.E., 1991. Sorption phenomena in subsurface systems: concepts, models and effects on contaminant fate and transport. Water Res. 25 (5), 499–528.
Wijesiri, B., Egodawatta, P., McGree, J., Goonetilleke, A., 2015a. Process variability of pollutant build-up on urban road surfaces. Sci. Total Environ. 518–519 (0), 434–440.
Wijesiri, B., Egodawatta, P., McGree, J., Goonetilleke, A., 2015b. Influence of pollutant build-up on variability in wash-off from urban road surfaces. Sci. Total Environ. 527–528 (0), 344–350.
Wijesiri, B., Egodawatta, P., McGree, J., Goonetilleke, A., 2015c. Incorporating process variability into stormwater quality modelling. Sci. Total Environ. 533 (0), 454–461.
Zoppou, C., 2001. Review of urban storm water models. Environ. Model. Softw. 16 (3), 195–231.