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Distribution of polycyclic aromatic hydrocarbons in urban stormwater in Queensland, Australia

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The presence of organic carbon on impervious surfaces and rainfall duration plays a dominant role in the distribution of PAHs in urban stormwater.

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ABSTRACT

This paper reports the distribution of Polycyclic Aromatic Hydrocarbons (PAHs) in wash-off in urban stormwater in Gold Coast, Australia. Runoff samples collected from residential, industrial and commercial sites were separated into a dissolved fraction (<0.45 μm), and three particulate fractions (0.45–75 μm, 75–150 μm and >150 μm). Patterns in the distribution of PAHs in the fractions were investigated using Principal Component Analysis. Regardless of the land use and particle size fraction characteristics, the presence of organic carbon plays a dominant role in the distribution of PAHs. The PAHs concentrations were also found to decrease with rainfall duration. Generally, the 1- and 2-year average recurrence interval rainfall events were associated with the majority of the PAHs and the wash-off was a source limiting process. In the context of stormwater quality mitigation, targeting the initial part of the rainfall event is the most effective treatment strategy. The implications of the study results for urban stormwater quality management are also discussed.

1. Introduction

Many urban areas around the world are currently experiencing water scarcity due to population growth and industrialisation. In particular, parts of Australia have experienced acute water shortage in the past five years (Hurlimann and Dolnicar, 2010; Williams, 2010). Under these circumstances, stormwater runoff can be considered as a potential water source for potable and non-potable use in order to strengthen the long-term sustainability of urban areas. Unfortunately, urban stormwater runoff is a significant non-point pollutant source as it acts as the medium for the transport of a wide variety of pollutants and plays a key role in the degradation of aquatic environments in urban areas. Researchers such as Haiping and Yamada (1998) found that the pollution loading in urban stormwater can be appreciably higher than treated domestic sewage. Among the various pollutants, substances such as Polycyclic Aromatic Hydrocarbons (PAHs), which are detrimental to human and ecosystem health are commonly found in urban stormwater runoff (Estebe et al., 1997).

Therefore, it is important that strategies are implemented to remove hazardous substances such as PAHs in order to realise the full potential offered by stormwater runoff as an alternative water source in urban areas. This in turn requires an in-depth understanding of the distribution and transport of PAHs in urban stormwater runoff. PAHs in urban stormwater runoff are primarily associated with particulate matter (Gonzalez et al., 2000; Makepeace et al., 1995; Marsalek et al., 1997; Wang et al., 2001). Furthermore, it has also been shown that the particulate size is an important parameter in the adsorption of PAHs to solids in the stormwater.

This paper reports a study undertaken to investigate the distribution of PAHs in different particulate compartments in urban stormwater runoff generated from three typical urban land uses, namely: residential, industrial and commercial. The outcomes from this research study and the recommendations provided will contribute to the enhancement of the design of stormwater quality treatment strategies for the removal of PAHs.

2. Materials and methods

2.1. Study sites

The study sites were in the Gold Coast region, which is located south of the Queensland State capital, Brisbane, Australia. Site 1 was an access road (Millswyn Crescent) located in a typical urban residential area (Residential A) with detached

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family houses with small gardens. The site was chosen due to its typical suburban characteristics. The road system is primarily used by the residents for access, which was reflected in the good condition of the street surface.

Site 2 (Stevens Street) was located in a light industrial area. The site was chosen because of the diversity of industries located along the road. Industries at the site include a sheet metal works, a boat painter and a furniture manufacturer. Compared to the residential site, the street surface was significantly degraded. Site 3 was a parking lot in a suburban shopping centre. The shopping centre has 570 parking spaces and is considered to be one of the busiest in the region with 45 specialty retailers in the complex. The condition of the parking lot was found to be fair but with a coarse texture. The coarse texture suggested that large numbers of particles could be embedded within the voids.

2.2. Rainfall simulation

A specially designed rainfall simulator was used to replicate probabilistically different rainfall events. The use of rainfall simulation helped to eliminate the significant constraints usually experienced by researchers due to the random nature of occurrence and the high variability in the characteristics of natural rainfall events (Herngren et al., 2005a,b).

Care was taken to simulate the rainfall characteristics, including drop rates (14.2–14.4 L/min) and uniformity of distribution, as closely as possible to natural rainfall (Herngren et al., 2005b). Deionised water spiked to replicate the chemical quality of natural rainfall in the study region in relation to pH (6.40±0.52), electrical conductivity (51.71±4.26) and dissolved organic carbon (8.81±4.29) was used for the simulations. Research literature has confirmed that these parameters exert a significant influence on pollutant characteristics in stormwater runoff (Herngren et al., 2005a; Warren et al., 2003).

2.3 Sample collection

The wash-off sample collection from the road surfaces was confined to small plot areas of size 1.5 × 2 m which enabled the acquisition of more reliable data. For understanding the fundamental pollutant wash-off processes, the use of small plots provides a more suitable approach rather than catchment scale studies. It ensures the homogeneity of the study surfaces and thereby reduces the number of variables. This in turn helps to minimise the location specific nature of research outcomes commonly inherent in catchment scale studies with heterogeneous surfaces (Egodawatta and Goonetilleke, 2008). The plot size was specifically selected to ensure the uniform distribution of the simulated rainfall (Herngren et al., 2005a,b).

Four different plots equidistant between the kerb and the median strip of the road were selected at each study site. The amount of pollutant build-up in each plot for a specific road site was assumed to be uniform. Though Sartor and Boyd (1972) found that a relatively larger fraction of solids are accumulated near the kerb, the distribution pattern of PAHs was assumed to be the same across the road surfaces. The runoff samples were collected by positioning the rainfall simulator above each of the selected plots and simulating pre-determined rainfall intensities and durations. The simulated rainfall intensities ranged from 65 to 133 mm/hr and the durations ranged from 5 to 65 min to represent 1 year, 2 year, 5 year and 10 year ARI (average recurrence interval) design storm events for the study region.

The collected samples were transported to the laboratory on the same day, mixed thoroughly and the mixed samples were considered as representing the Event Mean Concentrations (EMC) of pollutants for that specific rainfall event. Sub-sampling was performed in the laboratory as early as possible and the samples were preserved and refrigerated as specified in Standard Methods for the Examination of Water and Waste Water (APHA, 2005). Deionised water and field water blanks were analysed as part of the standard quality control procedures as specified in Australia/New Zealand Standards (AS/NZS, 5667.1:1998).

2.4. Laboratory analysis

Initially, the particle size distribution of the suspended solids in the wash-off samples was determined using a Malvern Mastersizer Particle Size Analyzer. This was followed by wet sieving, which separated the samples into the following four particle size classes; >150 μm (corresponds to coarse to fine sands), 75–150 μm (very fine sands and silt), 0.45–75 μm (silt and clay) and <0.45 μm. The smallest size class (<0.45 μm) was defined as the dissolved fraction of the runoff samples. The research study used the results from the Mastersizer analysis to obtain the relative proportions of the different particle size ranges used in the study. This in turn acted as a means of cross-checking the weight of the different size ranges obtained after wet sieving. The different size classes were then individually analysed for pH, Electrical Conductivity (EC), Total Organic Carbon (TOC), Inorganic Carbon (IC), Dissolved Organic Carbon (DOC), Total Suspended Solids (TSS), and Total Dissolved Solids (TDS) according to standard methods (APHA, 2005).

The 16 priority PAHs (Table 1) listed by the US EPA (Manoli and Samara, 1999) were analysed in each particle size fraction. The dissolved fraction (<0.45 μm) was extracted using the liquid–liquid extraction method (US EPA method 610) as specified by the US EPA (1991). The particulate fractions (0.45–75 μm, 75–150 μm and >150 μm) were extracted using ultrasonication. Ultrasonication was chosen due to the reduced extraction time compared to methods such as Soxhlet extraction. The technique used is outlined in US EPA Method 3550 (US EPA, 1986). However, the method does not specify the preferred solvent or the extraction time. Guerin (1999) found that a mixture of dichloromethane (DCM) and acetone provided the most efficient extraction, and that 1 h was sufficient for the extraction of 2- and 3-ring PAHs. After this time, the recoveries decreased due to loss by volatilisation. Zhou and Maskaoui (2003) successfully extracted the 16 priority PAHs using two 30 min ultrasonication intervals. Therefore, in the current study, a DCM:acetone (3:1) mix was used as the solvent and three 20 min extractions by ultrasonication was employed.

Table 1
Priority PAHs as listed by US EPA together with their aqueous solubilities (adapted from Manoli and Samara, 1999).

PAH compound	Solubility [mg/L]
Naphthalene, NAP	32
Acenaphthene, ACE	3.4
Acenaphthylene, ACY	3.93
Fluorene, FLU	1.9
Anthracene, ANT	0.05–0.07
Phenanthrene, PHE	1.0–1.3
Fluoranthene, FLA	0.26
Benzo[a]anthracene, BaA	0.01
Benzo[b]fluoranthene, BbF	–
Benzo[k]fluoranthene, BkF	–
Chrysene, CHR	0.002
Pyrene, PYR	0.14
Benzo[a]pyrene, BaP	0.0038
Dibenzo[a,h]anthracene, DbA	0.0005
Benzo[ghi]perylene, BgP	0.00026
Indeno[1,2,3-cd]pyrene, IND	–

12 mL of DCM:acetone (3:1) were used in each extraction interval. After each extraction, the extract was transferred to a 100 mL glass beaker. The combined extract was filtered into a 50 mL glass beaker using a GF/C glass microfibre filter (Whatman) which was purified by column chromatography using activated silica gel and sodium sulphate (Na_2SO_4). The silica gel and Na_2SO_4 were activated in a furnace at 100 °C for 24 h and allowed to cool to room temperature in a vacuum desiccator prior to use. The clean-up process removed any interfering compounds. Following purification, the PAH extract was concentrated under vacuum to less than 5 mL using a rotary evaporator (35 °C temperature) and further concentrated to approximately 0.5 mL using a gentle stream of ultra pure nitrogen gas. The samples were then analysed using a HP5972 Gas Chromatograph – Mass Spectrometer (GC–MS) which was calibrated using deuterated PAH internal standards obtained from Sigma–Aldrich.

2.5. Data analysis

2.5.1. Descriptive statistics analysis

The mean and standard deviation of the primary water quality parameters obtained for the three study areas were estimated using descriptive statistics. These parameters provided an insight into the trends and patterns of variation in water quality with land use. Furthermore, the results derived also provided information that would underpin the outcomes from the more detailed data analysis.

2.5.2. Multivariate statistical analysis

Several recent studies (see for example Settle et al., 2007 and references therein) have shown that multivariate statistical techniques are useful tools for the analysis of data with large numbers of variables and objects. Consequently, Principal Component Analysis (PCA) was carried out on the data using MatLab software developed by Kramer (1993). This data analysis method for example has been successfully used for process identification in river water quality data (Petersen et al., 2001), identification of parameter relationships of lake polluted sediments (De Bartolomeo et al., 2004) and investigation of relationships between heavy metals and suspended solids in urban stormwater runoff (Herngren et al., 2005b). Nevertheless, its application to urban stormwater quality research has been limited.

Each object (wash-off samples in this research) has a score on each Principal Component (PC), and each variable is characterised by a loading or weighting on each PC. The PCs are extracted in such a way that the first PC (PC1) describes most of the data variance, and the second (PC2) describes the second highest amount of data variance and so on. The advantage of this method is that most of the data variance is usually described by the first few PCs. In this study, the appropriate number of principal components (PCs) were estimated from a Scree plot (Cattell, 1966), and the reduced data were presented as biplots, which show the relationships among the objects and the variables.