Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.21806

96 (2017) 231–236
November

Identifying the first flush in stormwater runoff using UV spectroscopy

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Received 20 March 2017; Accepted 15 December 2017

ABSTRACT

Stormwater often contains a wide range of chemical pollutants. In stormwater harvesting, separation of the polluted first flush is a significant but important challenge. Current practices are generally empirical and provide very approximate estimates of the finish of the first flush period. Since the first flush is significantly more expensive to treat, it is essential to accurately separate the first flush from the rest of the runoff in order to treat only the required volume. This is only possible when a real-time monitoring method is applied. This paper evaluates the feasibility of using UV spectroscopic methods to rapidly characterize stormwater pollutants over time in order to provide enough information to separate the first flush from the remaining volume to be harvested. Three stormwater events are used to demonstrate that relative comparison of UV spectra over time can be used to readily identify the end point of the first flush. The findings from this study will enable urban stormwater planners and engineers to more reliably and rapidly separate and treat stormwater for reuse in real-time.

Keywords: First flush; Stormwater pollutants; Urban drainage; UV spectra

1. Introduction

There is a shortage of potable water resources in most urbanized cities in Australia and this has prompted water authorities to refocus their attention on utilizing alternative water resources for both potable and non-potable end uses. The utilization of alternative water resources such as stormwater, graywater and wastewater can augment the availability of non-potable water supplies. However, the utilization of alternative water resources for potable augmentation comes at the expense of public health risks due to potential cross-connection problems. Recycled wastewater is generally considered as having relatively high risks for reuse purposes whereas harvested stormwater is considered as relatively clean and safe. In addition, harvesting and reusing stormwater will also contribute to the protection of natural aquatic environments from flooding, erosion and peak flows [1–3]. In order to effectively utilize stormwater as an alternative water resource, it is important to understand the associated health risks as well as designing appropriate fit-for-purpose stormwater treatment technologies for water pollutant control and abatement.

Stormwater quality is highly impacted by different catchment land uses as it carries pollutants deposited on the catchment surface along with its flow [4]. Some pollutants of concern in stormwater include heavy metals, polycyclic aromatic hydrocarbons (PAHs), pharmaceuticals and personal care products (PPCPs), biphenyl, phthalate esters, pesticides and natural organic matter and others [5–7]. The ability to characterize stormwater runoff quality with respect

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Presented at the 9th International Conference on Challenges in Environmental Science & Engineering (CESE-2016), 6–10 November 2016, Kaohsiung, Taiwan.

to catchment characteristics in a cost-effective manner has many important positive implications in the design and selection of stormwater treatment technologies for harvesting purposes [8]. Existing stormwater harvesting projects differ widely in design due to end-use purposes and local and national level requirements. According to the Australian Department of Environment and Conservation, the cost of treated stormwater is in the range of AUD 0.52 to AUD 42.0/kL in Australia [9]. The cost associated with stormwater treatment is one of the largest impediments to the widespread implementation of harvesting schemes. Therefore, the attractiveness of stormwater harvesting is dependent on the ability to develop a simple, rapid and economic method that can identify and quantify the pollutant portion that actually needs to be treated.

There are traditional empirical methods that have been applied for first flush volume identification. These include the first 20% of the flow [10], dimensionless curves, and normalized pollutants load vs. normalized runoff volume [11]. The first 20% of the flow neglects the rainfall intensity and pollutant concentration in water which is dependent on the antecedent dry weather period, whereas dimensionless curves (normalized pollutants load vs. normalized runoff volume) estimate the first flush volume arbitrarily. This arbitrary volume also depends on the past record [12]. This tells us that quantification of the first flush in real time with changing rainfall runoff dynamics and pollutant characteristics is a challenge.

Since each rainfall event is unique in terms of rainfall volume, intensity, duration, and antecedent dry weather period, stormwater runoff pollutant concentrations may vary from event to event [13–15]. Moreover, the profile of catchment pollution can change over time. As urbanization increases, land use and human behaviour change with time as do the nature of pollutants. These arbitrary definitions that have previously been adopted to quantify the first flush will not accurately estimate the true first flush phenomenon. There is a need to develop a straightforward method to quantify the first flush or the most polluted part of the runoff to avoid excessive and unnecessary treatment costs.

UV spectroscopy has been applied in previous studies to identify the nature of organic chemicals such as total organic carbon (TOC) and aromatics in water and wastewater [16–18]. Broad UV (200 to 400 nm) scanning of water samples of interest over time may provide extensive information on pollutants including relative changes in their concentrations over time. This method is simple, rapid and does not require any sample preparation. Moreover, it is cost-effective and has been widely adopted in the water industry. Recently, there have been a few examples of the application of UV spectral monitoring in wastewater membrane fouling prediction and reservoir water quality monitoring and river water quality monitoring [19–21]. A number of water treatment industries have recently adopted S::CAN technology (UV–Vis technology) that records the UV and visible spectra of water and provides information to plant operators to facilitate the choice and dosing of chemical treatment [22] (Fig. 1).

This study aimed to explore the role of UV spectroscopy to identify the first flush runoff volume by identifying changes in UV spectra over time by using a spectral comparison. It is anticipated that the developed UV spectroscopic methods will enable a more rapid and reliable characterization of stormwater organic pollution, in order to effectively plan and design fit-for-purpose treatment technologies for large-scale stormwater harvesting and reuse schemes.

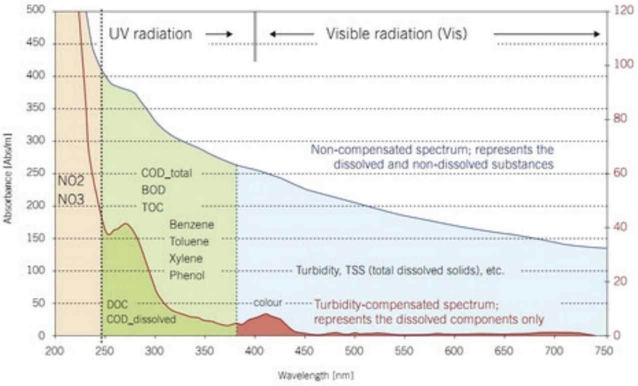

Fig. 1. Application of UV-visible spectroscopy for water quality monitoring (adopted from: http://www.interline.nl/EN/75/change.html) [22].

2. Material and methods

Stormwater samples were collected from a commercial district, a road and a parking lot for three wet weather events. These sub-catchments covered a total area of 0.11 km^2 (Fig. 2). The samples were collected using auto-samplers set for flow-weighted intervals (ISCO 6712 Autosampler, USA). The samples were collected when the flow depth exceeded a height of 0.06 m and stopped when the depth dropped below 0.04 m. The samples were collected at every 3 m^3 interval with a limit of 24 samples, each being 1 L in volume. Fig. 3(a) shows the surface characteristics of the area and Fig. 3(b) shows the hydrograph and sampling intervals in one of the captured events. The autosamplers were set to capture an entire event with a maximum of 24 samples. All the collected stormwater samples (i.e., individual and event mean samples) were filtered through a 0.45 μm filter (GF, Whatman) and the filtrates were analyzed by UV spectroscopy (Varian 50 Bio). The instrument was operated at a bandwidth of 1 nm, with quartz cell of 10 mm path length, wavelength of 190–400 nm and at a scanning speed of 190 nm/min (slow).

The UV spectra were normalized according to Vaillant et al. [16] by attributing the same area (norm) to all measured UV spectra to minimize concentration influence in the spectrum. In this instance, the sum of absorbance values over the chosen wavelength intervals was selected. For a given spectrum and acquisition step of 5 nm for UV spectroscopy, the area is given by:

$$\text{Area} = \sum\nolimits_{\lambda=190}^{400} A(\lambda) \tag{1}$$

where λ is the wavelength.

The absorbance value at the wavelength changes according to a given value of the norm N (100) into a normalized absorbance, Abs (λ_N):

$$\text{Abs}(\lambda_N) = \text{Abs}(\lambda)\frac{N}{\text{Area}} \tag{2}$$

Fig. 2. Catchment area.

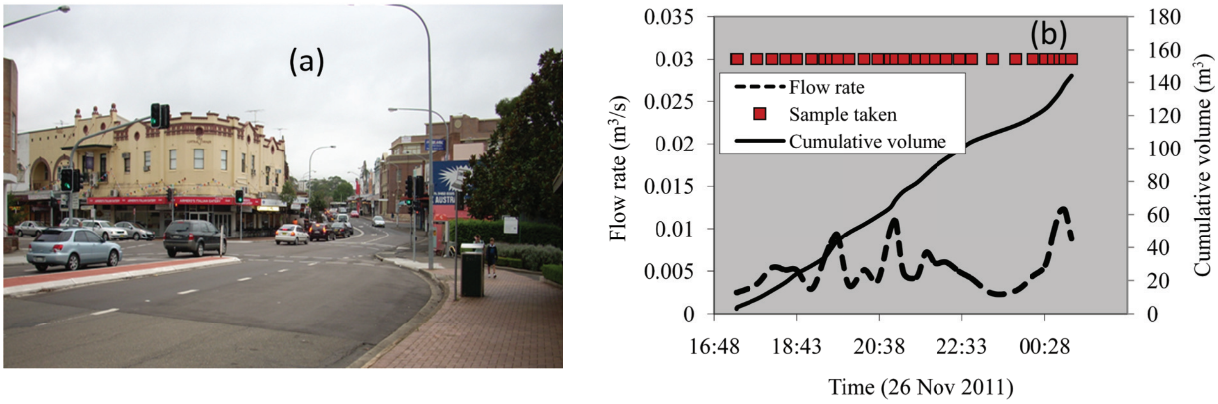

Fig. 3. (a) Catchment area (ground view) and (b) a sample captured on wet weather event 2.

Plotting of the normalized spectra enabled characterization of the concentration and chemical composition of the sample. Spectrum overlaps indicate similar chemical compositions whereas if an isosbestic point appears (crossing of the spectrum), this indicates that the chemical composition is different between the samples.

A statistical hierarchical cluster analysis using Ward's method was performed using the SPSS program (version 18). Ward's method uses an analysis of variance approach and specifies the distance between two clusters as the increase in the "error sum of squares" (ESS) after fusing two clusters into a single cluster in successive clustering steps. This was undertaken to minimize the increase in ESS at each step.

3. Results and discussion

Fig. 4 shows the UV spectra of stormwater samples collected for all three events. The UV spectra for the event mean stormwater samples collected from the catchment showed a broad shoulder characteristic peak in the wavelength range of 200–230 nm. Considering the land use types and traffic activities, the broad shoulder characteristic peak might arise from the influence of PAHs [23]. As the nature of stormwater is dynamic, the prevalence and concentration of chemical pollutants may vary from one event to another and also within the event itself.

In order to identify and differentiate the nature and concentration of organic chemical pollutants, data normalization was carried out based on the UV spectral area within the wavelength range 190–400 nm. Fig. 5 shows the normalized UV spectra of stormwater samples collected for the three events, which show the spectra crossing each other. The point of crossing is called the isosbestic point, which reflected that there is a difference in chemical constituents between the stormwater samples. In event 1, samples 1 and 2 showed a different pattern than the remaining samples 4 to 6 with an isosbestic point at 218 nm. This tells that samples 1 and 2 had different pollutant characteristics in the flux

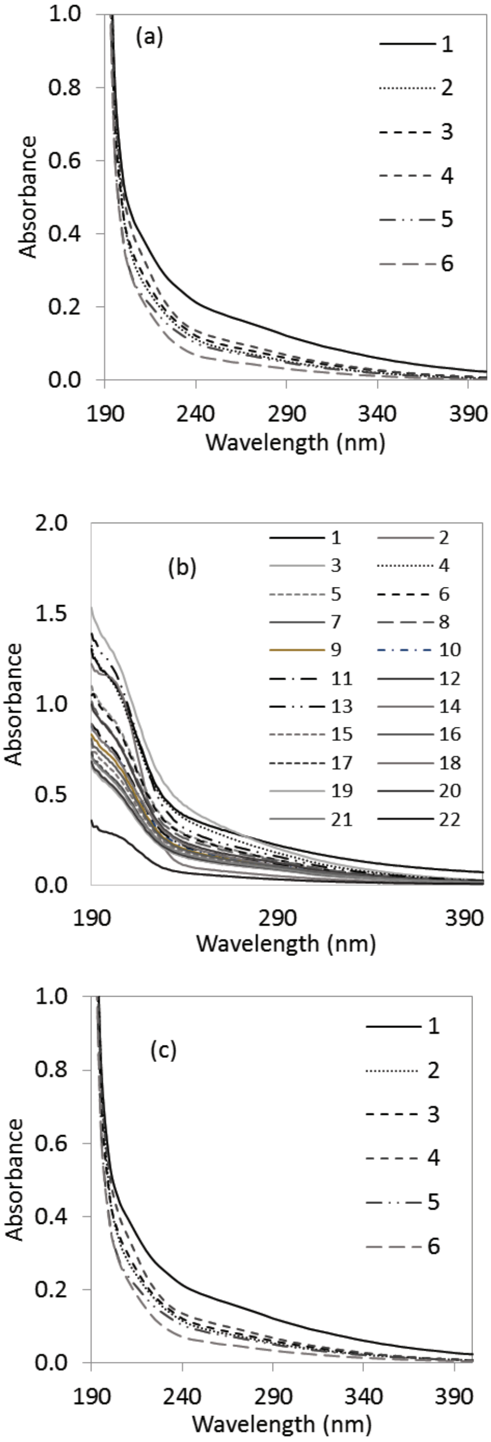

Fig. 4. UV spectra of stormwater samples in events 1(a), 2(b) and 3(c).

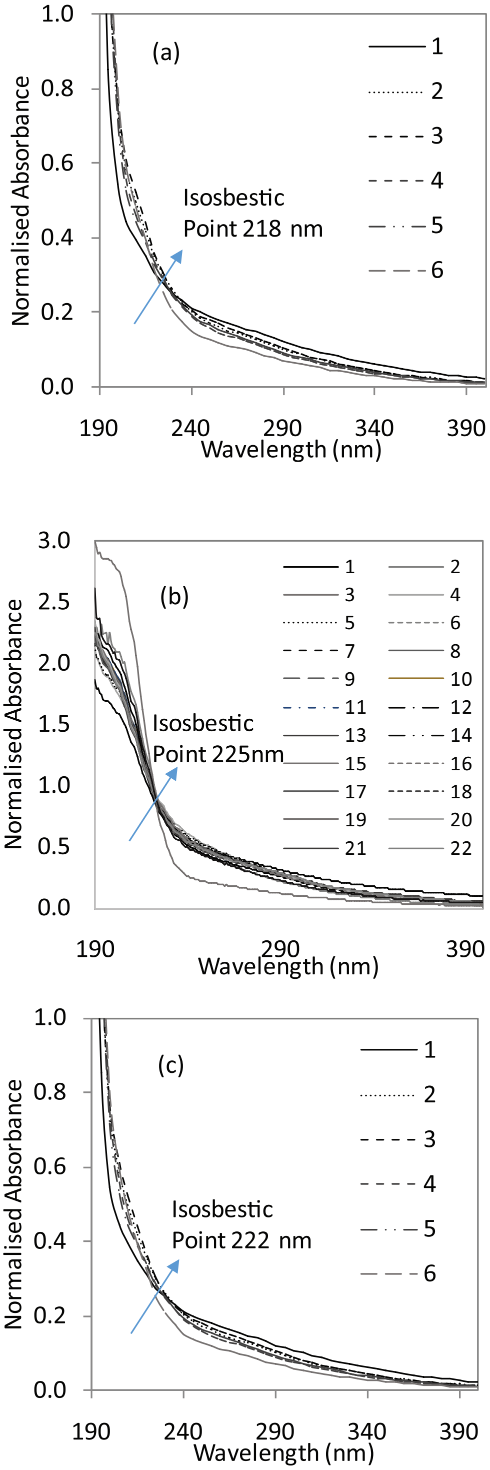

Fig. 5. Normalized UV spectra of stormwater samples in events 1(a), 2(b) and 3(c).

than samples 4–6. Similarly, in event 2, samples 1–3 overlapped and crossed with the remaining samples at 225 nm. This pointed out that the first three samples showed different chemical composition than the rest indicating the first flush phenomenon. In the third event, samples 1–3 overlapped and showed crossing of their spectra with the rest samples at 220 nm indicating that samples 1–3 carried the first flush. The appearance of an isosbestic point at different wavelengths (218, 225 and 222 nm) in three events indicates that the pollutant composition was different in those three events. This is supported by previous studies where pollutant composition was found to be different from event to event [13,24].

To verify the difference observed in normalized spectra and to identify the closeness among the samples in the event, a multivariate statistical cluster analysis was performed on all three samples. Fig. 6 shows the dendrogram (tree diagram) for all three events. The first event (Fig. 6(a)) shows three clusters and among these, the first sample is quite different while the second sample appears as an intermediate between the first and the remaining samples. This indicates that this first sample carried the majority of the first flush, which spilled over to the second sample as well. Similarly, Fig. 6(b) shows three clusters and of these, the first three samples separated themselves from the rest providing evidence that the first flush was limited to these three samples. The third event (Fig. 6(c)) also showed three clusters but the first two clusters were quite close, again indicating that the first flush was dominant in only the first three samples. The identified isosbestic points also supported the above statistical results. This further provides evidence that application of UV spectroscopy can be very useful for stormwater first flush identification.

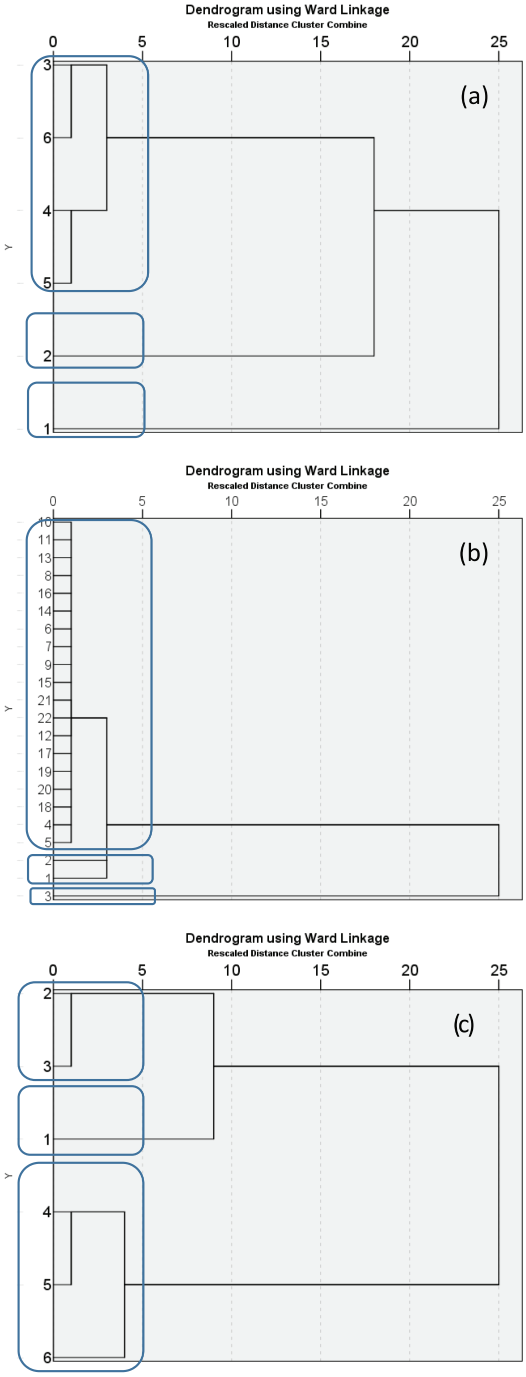

Fig. 6. Dendogram obtained from UV spectra of stormwater samples in events 1(a), 2(b) and 3(c).

The advantage of this proposed method over traditional first flush methods, such as mass first flush or event mean concentration (EMC), is that it is conducted in real time and provides information when the first flush is commences and ends irrespective of the volume and time. The mass first flush method usually captures the first 20% or so of the storm volume and often bypasses the remaining volume. This either results in an overestimation of the required treatment volume, leading to increased treatment costs, or underestimates the pollutant concentrations which can lead to downstream ecosystem damage. There is also the possibility of not recording the first flush for large catchments due to these occurring at later stages of the runoff [11,22]. Similarly, the EMC method takes an average of the discharged pollutants over the total volume. This method does not specifically predict the first flush period [23,24].

This UV method is independent of the time, volume and catchment size. The chemical signal is picked up once it appears in the runoff. The strength of the signal and the relative comparison of the signal with previous records indicates how pollutant concentrations and composition are changing over time. This information allows prediction of the presence of stormwater pollutants in real time, which in turn enables effective treatment of only the required volume. The UV spectra provides holistic information of organic chemicals in stormwater, but may not provide detailed characteristics of chemicals in the first flush and human/ecological health risk associated of those pollutants in stormwater.

4. Conclusion

Stormwater samples collected from three wet weather events falling over three different land uses were analyzed using UV spectroscopy. When compared, the UV spectra showed some differences indicating that the concentration and/or composition of chemicals in the samples may have changed from event to event. The normalized UV spectra displayed an isosbestic point in each event indicating that stormwater runoff chemical composition changed with time. The samples before and after these isosbestic points can provide evidence of when the first flush ends in real time. The appearance of isosbestic points at 218, 225 and 222 nm for events 1, 2 and 3, respectively, provided such evidence of changes in chemical composition in the three runoff events. This was further validated by applying a cluster analysis to the UV data. The separate cluster of UV data from early runoff samples demonstrates that UV spectroscopy can help to identify and quantify the first flush and thereby enables selective treatment of the required volume for each event.

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