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# Characterisation of dissolved organic matter in stormwater using high-performance size exclusion chromatography

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## ABSTRACT

Understanding the complexity of dissolved organic matter (DOM) in stormwater has drawn a lot of interest, since DOM from stormwater causes not only environmental impacts, but also worsens downstream aquatic quality associated with water supply and treatability. This study introduced and employed high-performance size exclusion chromatography (HPSEC) coupled with an ultraviolet–visible (UV–vis) diode array detector to assess changes in stormwater-associated DOM characteristics. Stormwater DOM was also analysed in relation to storm event characteristics, water quality and spectroscopic analysis. Statistical tools were used to determine the correlations within DOM and water quality measurements. Results showed that dissolved organic carbon (DOC) and UV absorbance at 254 nm ( $UV_{254}$ ) as conventional DOM parameters were found to be correlated well to the changes in stormwater quality during each of the three storm events studied. Both detector wavelengths (210 and 254 nm) and their ratio ( $A_{210}/A_{254}$ ) were found to provide additional information on the physiochemical properties of stormwater-associated DOM. This study indicated that  $A_{210}/A_{254}$  is an important parameter which could be used to estimate the DOM proportions of functional groups and conjugated carbon species. This study provided also an understanding of stormwater quality constituents through assessing variability and sensitivity for various parameters, and the additional information of rainfall characteristics on runoff quality data for a better understanding of parameter correlations and influences.

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## Introduction

Stormwater brings various inorganic and organic substances into the environments (Göbel et al., 2007; Al-Reasi et al., 2013). These chemical discharges can worsen downstream water quality if the stormwater is used as water source, as well as impacts on the ecosystem. Among these chemical substances, dissolved organic matter (DOM) has drawn a great interest as it can enter aquatic matrixes, thus affecting the composition and quality of surface

waters (Chong et al., 2013; McElmurry et al., 2013). DOM is also naturally present in the environment and has frequently been detected in source waters (Matilainen et al., 2011; Xing et al., 2012; Fabris et al., 2013). It can be responsible for the yellow-brownish colour, unpleasant taste and bad odour of natural waters. Hence the varying levels and compositions of DOM in stormwater sources need to be taken into account, since its chemical characteristics can be variable at any time depending on the local activities, climate conditions and rainfall influences. As

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a general concern in the course of drinking water treatment and/or wastewater recycling processes, DOM affects not only the performance of each treatment step, such as traditional coagulation–flocculation, adsorption and membrane filtration (Chow et al., 2004; Rosenberger et al., 2006; Fabris et al., 2008); but also more importantly, reacts with various disinfectants to produce harmful disinfection by-products (DBPs) (Richardson et al., 2007; Zhao et al., 2008).

Conventionally, pH, turbidity, colour and inorganics are the common parameters used to describe water quality, while dissolved organic carbon (DOC) determination, ultraviolet (UV) adsorption analysis, specific UV absorbance (SUVA) and specific colour are commonly used as parameters to measure DOM in water sources. They provide both quantitative and qualitative information. Along with substantial improvement in analytical techniques, compared to the earlier work in this field, current DOM analytical work has been shifted towards more advanced fractionation analysis. A series of advanced analytical techniques, including resin fractionation, fluorescence spectroscopy and size exclusion chromatography have been widely used in the water research field (Matilainen et al., 2011; Nebbioso and Piccolo, 2013). Hydrophobicity, molecular weight and aromaticity, provided by these techniques as indicators provide more insight into chemical qualitative and structural features of DOM and more informative outcomes, and either applied as a single technique or in combinations can generate additional values on DOM characterisation (Bazrafkan et al., 2012; Chong et al., 2013; Li et al., 2013; Wei et al., 2013).

Molecular weight distribution is an important physical property associated with DOM transport, reactivity and treatability. High-performance size exclusion chromatography (HPSEC) has been developed to characterise DOM predominantly for water treatment applications and also in various soil, aquatic and marine samples (Matilainen et al., 2011; Nebbioso and Piccolo, 2013). The principle of HPSEC is based on apparent molecular weight (AMW) separation. Additionally, it can couple with various detectors, such as DOC determination (Her et al., 2008), UV absorbance with a single or multiple wavelengths (Her et al., 2008; Korshin et al., 2009; Liu et al., 2010; Bazrafkan et al., 2012; Xing et al., 2012; Yan et al., 2012), excitation emission fluorescence detection (Li et al., 2013), and mass spectroscopy (Nebbioso and Piccolo, 2013).

An additional advantage of using HPSEC is the ability to separate inorganic constituents and minimise inorganic interferences, as these are generally in a range of molecular weights (MW) less than 0.25 kDa (Her et al., 2008). Several studies have also demonstrated that the HPSEC technique is informative and reliable when used to assess water treatability by comparison between raw and treated water based on the HPSEC profiles after coagulation in drinking water treatment (Chow et al., 2008; Fabris et al., 2008; Liu et al., 2010; Xing et al., 2012) or applying a peak-fitting model to predict treatability (Chow et al., 2008). Korshin et al. (2009) investigated the relationships between MW and DBP formation. HPSEC in conjunction with UV detector is particularly useful and informative. More than one wavelength and/or multi-wavelength absorbance detection have been introduced and applied by several researchers (Her et al., 2008; Korshin et al., 2009; Yan et al., 2012). The wavelengths at 210 nm and 254 nm have been used in previous work because the wavelength 210 nm allows the detection of DOM functional groups (hydroxyl,

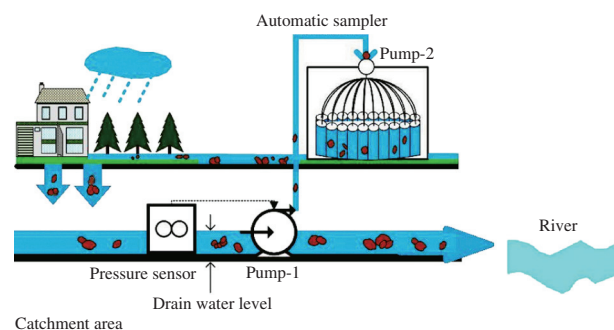
carboxyl, carbonyl, ester and nitrogen-containing compounds) and the wavelength at 254 nm is the recognisable absorbance for the conjugated aromatic substituents (Her et al., 2008). The wavelength around 210 nm has also been addressed to associate particularly with nitrate concentrations, which relates to nutrient content and microbial activities (Whitehead and Cole, 2006).

Elevated pollutant loadings, particularly of DOM, during a storm event can provide early notice of potential impacts of stormwater discharge on surface waters. Water quality and the potential risks of stormwater need to be assessed and controlled in order to improve watershed management. The aim of this study was to characterise DOM present in stormwater through extensive sampling of three representative storm events and develop some useful tools to understand stormwater DOM properties. The objectives were (1) to determine stormwater quality using a series of conventional measurement techniques and to describe their sensitivity and potential relationships, (2) to extend HPSEC with UV absorbance detection as a monitoring technique to characterise stormwater-associated DOM based on molecular weight distribution, (3) to determine DOM compositions using two UV wavelengths (210 and 254 nm) of the HPSEC and their ratio for further analysis, and (4) to estimate pollutant loadings using simple statistical methods, combining measured flow data with various water quality parameters.

## 1. Materials and methods

### 1.1. Sampling strategy

A semi-urban catchment, located at Mannum, South Australia, was selected to determine the impact of stormwater quality on surface water quality, since the stormwater in this area (study) could enter directly into the river and can impact on surface water quality. A sampling point located in the underground



**Fig. 1 – Schematic of the stormwater capturing system used for sequential sampling. (1) Pressure sensor:** Placed in the drain to measure water level (m) in 5 min intervals and also send signal when drain water level changed (up and down) by 25 mm; **(2) Pump-1:** Installed in the drain to capture stormwater after active by the signal from pressure sensor; **(3) Automatic sampler (24-bottle carousel):** Installed and housed in the cabinet; **(4) Pump-2:** Part of the automatic sampler assembly for pumping stormwater into the sampling bottles.

stormwater pipe was selected to capture stormwater downstream the stormwater drains. Fig. 1 shows the monitoring setup, including a pressure sensor as well as an automatic 24 bottle carousel sampler and their installation. The pressure sensor was used to measure water level in the stormwater drain continuously at 5 min intervals and to control the automatic sampling system. The automatic sampling system was triggered when water level was above a threshold (25 mm). The sampling strategy applied was based on flow condition and employed sequential (multi-bottle) sampling. Water level was also recorded corresponding to the sample (bottle) collection. As soon as the first sample was taken, a signal (SMS) was sent to the operator to initiate event control. Depending on the triggering time; usually a site visit was made the following morning to ensure a good capture of the event. However, if the trigger was in the early morning, the site visit would be in the afternoon. Samples were collected and transported back to our laboratory within 24 hr of the triggering time. The triggers of these three events all came at midnight, so all of the samples were collected the following morning and transported back to the laboratory for analysis.

### 1.2. Instrumental analysis

Turbidity was determined using a 2100AN Laboratory Turbidimeter (Hach, USA) with results given in nephelometric turbidity units (NTU). Samples for DOC, colour (456 nm) and UV absorbance at 254 nm ( $UV_{254}$ ) were filtered through a 0.45  $\mu$ m membrane. A 1 cm quartz cell and 5 cm cell were used for  $UV_{254}$  and true colour at 456 nm, respectively. Colour is expressed in Hazen Unit (HU) after calibration using a 50 HU cobalt platinum standard and  $UV_{254}$  is expressed in Abs/cm. DOC was measured using a Sievers 900 Total Organic Carbon Analyser (GE Analytical Instruments, USA). Specific UV absorbance ( $SUVA_{254}$ ) was calculated as  $UV_{254}$  divided by DOC multiplied by 100, and expressed in L/(mg·m). Similarly, specific colour at 456 nm was calculated as colour divided by DOC and expressed in HU L/mg.

Molecular weight profiles were determined using a Waters 2690 Alliance system (Waters Corporation, USA) with a Shodex KW802.5 glycol functionalized silica gel column, which was equilibrated at 30 °C. Samples were filtered through a 0.45  $\mu$ m membrane filter prior to analysis and 100  $\mu$ L samples were injected. The mobile phase was 0.02 mol/L phosphate buffer at pH 6.8 adjusted to an ionic strength of 0.1 mol/L with sodium chloride. The system was operated at isocratic conditions with an eluent flow rate of 1.0 mL/min. Polystyrene sulfonate standards (Polysciences, USA) with MW 4.6, 8, 18 and 35 kDa were used to calibrate the retention time response to AMW.

### 1.3. Statistical analysis

All statistical analysis was applied using R (version 3.1.0, R Development Core Team). R is a free and relatively well-

developed programming language and provides an effective environment to implement statistical techniques. The standard analysis of variance (ANOVA) was utilised to evaluate the significant influence of seasonal variation on DOM characteristics. Pearson's Product Moment Correlation (PPMC) was used to evaluate if correlations of various general and spectroscopic parameters existed. The correlations between colour evaluation and other parameters were the main purpose of PPMC analysis in the current study. Both correlation factor ( $R^2$ ) and probability ( $p$ ) values were used to determine significance.

## 2. Results and discussion

### 2.1. Storm event characteristics

This stormwater study was conducted in 2010, and three storm events spread over the year were agreed by the project team during the planning phase of the case study. For each event, the auto-sampler was triggered by the flow condition, and samples were taken for an approximately 25 mm change in the water level. According to a previous study provided by Leecaster et al. (2002), 12 samples in one event would be sufficient for efficient characterisation of a single storm event. Thus, event less than 12 samples were disregarded in this current study. All three storm events presented provided more than 12 samples per event. The first event (Event 1) was conducted over 7 hr on 29 July, 2010. The period of July–September is considered as the wet season in South Australia (supported by rainfall data in 2010 provided by the Bureau of Meteorology). If the sampling plan was just based on following rain events, the second event would have actually been in the same month. However, it was decided that the second event (Event 2) would be that which occurred on 18 August, 2010 (over 12 hr). This allowed a longer period after Event 1 (the auto-sampler was physically turned off). Event 2 had similar rainfall values compared to Event 1 which happened to be useful for comparison as this could minimise the rainfall interference factor. Event 3 was conducted on 25 November 2010 (over 11 hr). This last event was planned to capture the stormwater quality after a period of the dry season in order to study the impact of seasonal change. The three events reported in this study were thus carefully selected to obtain the maximum amount of information.

A summary of the meteorological data of the 3 storm events is given in Table 1. Data obtained from the Bureau of Meteorology, including total rainfall, rainfall duration, antecedent dry period and runoff samples. Event 1 was captured after a longer antecedent dry period (14 days), while Event 2 was captured after a shorter antecedent dry period (7 days) following a heavy rainfall event. Event 3 shared a similar antecedent dry period (7 days) with Event 2 but was captured during a warmer season. It was notable that the number of

**Table 1 – Summary of monitored storm events.**

Rainfall event (m/day)	Rainfall (mm)	Rainfall duration (min)	Antecedent dry period (days)	Number of samples (n)	Season
Event 1 (29/07)	10	420	14	18	Winter
Event 2 (19/08)	8	755	7	13	Winter
Event 3 (25/11)	14	655	7	24	Summer

samples captured across a storm event was proportional to the intensity of rainfall, and was linked to flow conditions but not rainfall duration. During Event 3, because of the highest rainfall (14 mm), 24 samples were collected, followed by Event –1 (10 mm) 18 samples and Event 2 (8 mm) 13 samples. Fig. 2 shows the relationship of water level and rainfall duration during each storm event when samples were collected. This duration graph illustrates that although Event 2 was in the longest rainfall period, it had relatively more stable and lower flow (low water level compared to the other two events) during the event, whereas Event 1 and Event 3 had larger dynamic changes of the flow condition during the runoff process. Based on the observed flow conditions, samples were collected more frequently at larger fluctuations of water level changes and less frequently at smaller fluctuations of water level changes, and as water level changed rapidly, the time between samples decreased. At the beginning of a heavy rain, 7 and 11 samples were collected within 100 min for Event 1 and Event 3, respectively, whereas only a couple of samples were triggered within a similar period time for Event 2. These observations imply the sampling method used in this case study could be sufficient to capture the characteristics of rainfall–runoff process in this catchment area. These sequential samples collected based on flow sampling were analysed to gain insight into the changes of stormwater quality and quantity during each storm event.

## 2.2. General stormwater quality analysis

Analytical data shown in Table 2 reveal that the characteristics of the dissolved components in the stormwater as determined by DOC and UV<sub>254</sub> varied significantly among events. The average DOC concentration from the samples collected in Event 3 was 14.7 mg/L which was found to be higher than those in Event 1 and Event 2, which were 13.5 mg/L and 9.9 mg/L, respectively. Both UV<sub>254</sub> and colour measurements showed similar trends as the DOC concentrations for all three events. The results of UV<sub>254</sub> for Events 1, 2 and 3 were 0.432 Abs/cm, 0.301 Abs/cm and 0.501 Abs/cm, respectively. Colour for Event 3 stormwater samples was detected with an average of 99 HU, which was also higher than those in Event 1 and Event 2, which were 77 HU and 41 HU, respectively. These analytical data might suggest that stormwater samples in Event 3 had relatively higher amounts of humic substances. A strong correlation between DOC and UV<sub>254</sub>

was also observed ( $R^2 = 0.99$ ,  $p < 0.001$ ) from all samples based on statistical PPMC analysis. These observations were predicted to indicate that the stormwater DOM from this site had aromatic structures in nature. Additionally, it was worth pointing out that Event 3 had the most scattered data of DOC, UV<sub>254</sub> and colour, resulting in the highest standard deviation values, followed by Event 1 and Event 2. A possible explanation for this observation could be due to dynamic flow variations during the event. The stormwater quality would additionally depend on rainfall intensity and environmental conditions. The other two potential factors, rainfall duration and antecedent dry period might be expected to have less influence on stormwater quality. The chemical loads in Event 3 stormwater were higher than those in Event 2 although their antecedent dry periods were similar. This could be explained by environmental conditions, since temperature has impacts on physicochemical and biological reactions (Chong et al., 2013; Tang et al., 2013; McElmurry et al., 2013). Event 1 had higher rainfall intensity and was likely to lead to higher pollutant loadings in stormwater compared to Event 2. However, the DOM character and water quality parameters were not correlated well, since stormwater runoff volume could be a potential factor influencing stormwater monitoring.

## 2.3. HPSEC profile analysis

A new combined profile based upon use of two wavelengths coupled with size exclusion chromatography (SEC) was introduced. These HPSEC profiles revealed that DOM in all samples had mostly similar AMW ranges, from 0.3 to 2 kDa. Both the first and last samples collected from each storm event were chosen for analysis in Fig. 3.

Similar HPSEC profiles were observed for both Event 1 and Event 2 but there was a difference obviously in Event 3. In all the HPSEC chromatograms obtained from Event 1 and Event 2, aside from the differences of DOM absorbance intensities, insignificant changes of peak patterns were observed across of each storm event under various flow conditions or water levels. It was also worth noticing that the stronger absorbance intensities were measured at the lower wavelength of 210 nm. A maximum absorbance at approximately 0.3–0.5 kDa was followed by weaker absorbance intensities at approximately 1–2 kDa. These high levels of absorbance intensity measured at 210 nm could be an indication of DOM enriched with various

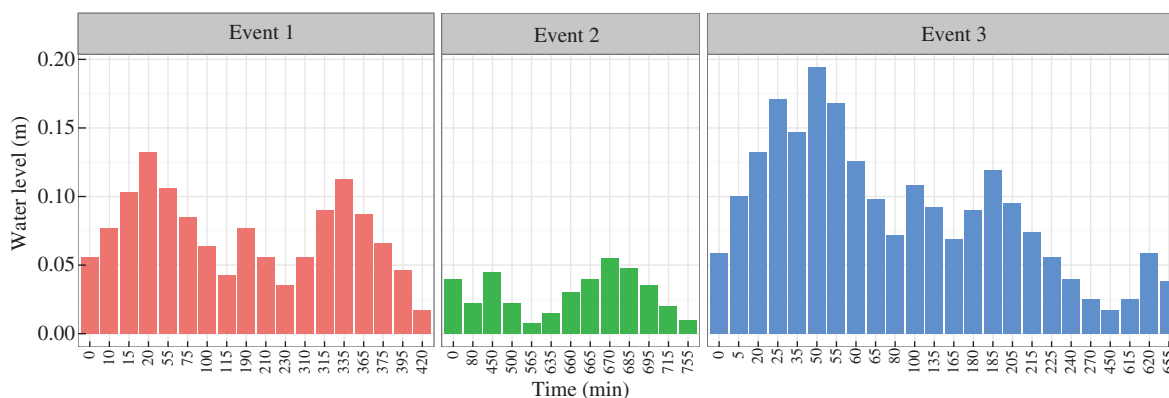


Fig. 2 – The relationship of water level and the corresponding storm event duration.



**Table 2 – Results of dissolved organic matter (DOM) characterisation of the stormwater samples.**

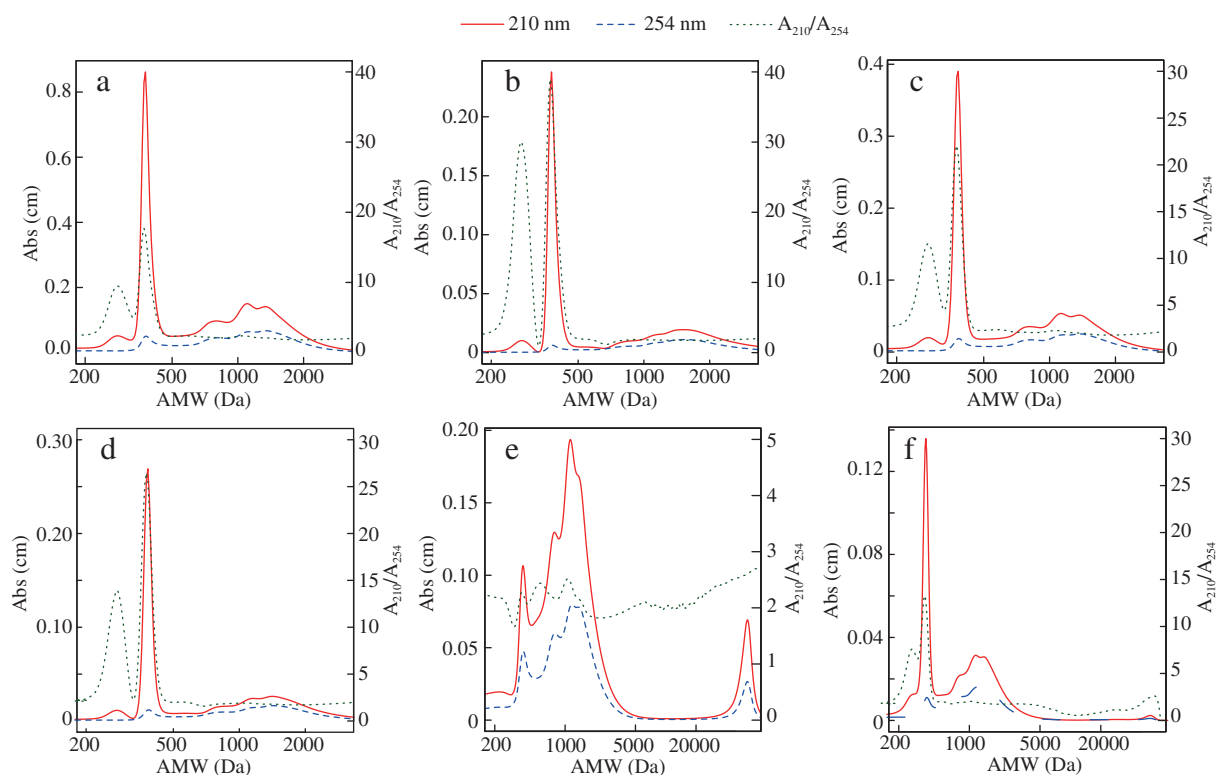
	Event 1		Event 2		Event 3	
	Range	Mean $\pm$ SD <sup>a</sup>	Range	Mean $\pm$ SD <sup>b</sup>	Range	Mean $\pm$ SD <sup>c</sup>
Turbidity (NTU)	47–580	172 $\pm$ 172	59–638	352 $\pm$ 214	14–431	175 $\pm$ 122
Colour (HU)	41–112	77 $\pm$ 22	34–57	41 $\pm$ 7	57–236	99 $\pm$ 44
UVA <sub>254</sub> (Abs/cm)	0.217–1.227	0.432 $\pm$ 0.267	0.198–0.497	0.301 $\pm$ 0.074	0.278–1.768	0.501 $\pm$ 0.378
DOC (mg/L)	6.7–47.2	13.5 $\pm$ 10.6	6.8–18.9	9.9 $\pm$ 2.9	7.3–67.5	14.7 $\pm$ 14.3
SUVA <sub>254</sub> (L/(mg·m))	2.6–3.9	3.4 $\pm$ 0.3	2.6–3.7	3.1 $\pm$ 0.3	2.6–4.1	3.7 $\pm$ 0.4
Specific colour (L HU/mg)	0.13–0.99	0.49 $\pm$ 0.24	0.04–0.23	0.13 $\pm$ 0.04	0.10–1.23	0.75 $\pm$ 0.46

n: number of samples. <sup>a</sup> n = 18, <sup>b</sup> n = 13, <sup>c</sup> n = 24.

non-aromatic functional groups (Her et al., 2008; Korshin et al., 2009). The absorbance intensity patterns at 254 nm, on the other hand, were likely to be stable for each sample. These observations support the hypothesis that stormwater DOM had a relatively high concentration of aromatic carbon and/or phenolic compounds, regardless of the levels of absorbance intensity (Xing et al., 2012). However, HPSEC profiles for Event 3 appeared much more complex and varied prominently through all samples. For instance, remarkable differences between the first and the last samples were exhibited in Fig. 3e and f. While the HPSEC profile for the last sample shared similar dominant peaks with those from Events 1 and 2, presenting totally different results. HPSEC profiles for the first sample demonstrated that the

DOM was comprised of relatively higher absorbing compounds with adsorption maxima at higher AMW fractions, ranging from 1 kDa to 5 kDa. Another identified difference was due to larger AMW absorbance, at approximately 50 kDa. This could be associated with the contribution of a large amount of plant and/or microorganism cell deaths, and vegetation decay under dry-weather conditions or comprise organic colloidal material (organometallic complexes) (Chow et al., 2008).

DOM fractions with higher AMW values were likely to have a higher absorbance at higher wavelengths (O' Loughlin and Chin, 2001). AMW above 1 kDa, for instance, had a stronger absorbance at wavelengths above 254 nm than AMW below 1 kDa. This observation could be explained by the fact that



**Fig. 3 – Comparison of A<sub>210</sub>/A<sub>254</sub> values and HPSEC-UV chromatograms obtained at 210 nm and 254 nm: (a) Event 1 first-sample, (b) Event 1 last-sample, (c) Event 2 first-sample, (d) Event 2 last-sample, (e) Event 3 first-sample, and (f) Event 3 last-sample. HPSEC: high-performance size exclusion chromatography; UV: ultraviolet.**

unsaturated compounds are more sensitive to a higher UV wavelength (254 nm), while functional groups including hydroxyl, carboxyl, carbonyl, ester and nitrogen-containing compounds, may be associated with a lower wavelength (210 nm) (Her et al., 2008).

#### 2.4. Interpretation of $A_{210}/A_{254}$ on HPSEC profiles

The absorbance ratio index (ARI) as a spectroscopic parameter has been widely reported associated with DOM characterisations. The ARI of  $A_{210}/A_{254}$  introduced by Her et al. (2008) was found to be able to provide information on the relative proportion of UV absorbance between the non-aromatic and aromatic components (Yan et al., 2012). The  $A_{210}/A_{254}$  was applied for DOM analysis in the current study in order to gain further insight into the composition of DOM in stormwater.  $A_{210}/A_{254}$  data were plotted in corresponding graphs (Fig. 3) for comparison.

In accordance with data shown in Fig. 3, the dominant fraction at 0.3–0.5 kDa was likely to give a couple of sharp peaks for  $A_{210}/A_{254}$  values which were in a range of 10–40. These high readings could imply that the corresponding DOM sources contained a higher functional group proportions which could be related to protein-like materials and/or simple amino acids associated with nutrient organic matter. Her et al. (2008) stated that  $A_{210}/A_{254}$  increases with the increase in microbiologically derived components that have a high functional group proportion. The unexpected peak exhibited below 0.3 kDa was considered due to the presence of inorganics, such as nitrate, sulfate and phosphate, as these inorganic species have UV absorbance at less than 230 nm wavelengths. The two-wavelength approach on the basis, one being in a range of 200–220 nm and the other being selected above 250 nm was previously applied to estimate nitrate concentration in various water sources (Edwards et al., 2001). Therefore, these peaks could be thought as a result of the presence of nitrate containing compounds. However,  $A_{210}/A_{254}$  ranging from 1 to 3 was observed in some samples in Event 3, such as the first-sample (Fig. 3e). These low  $A_{210}/A_{254}$  values could indicate that these DOM sources could be comprised of higher aromatic content, including a larger amount of both humic acid and fulvic acids. Her et al. (2008) have also confirmed that humic acids and fulvic acids with higher and intermediate aromaticity have the lower  $A_{210}/A_{254}$  values at 1.59 and 1.88, respectively. The  $A_{210}/A_{254}$  value below 5 for the AMW located at approximately 50 kDa, also suggested these constituents could have high aromatic characters. In agreement with the previous literatures (Her et al., 2008), our study has also illustrated  $A_{210}/A_{254}$  as a phenomenological parameter that can help characterise DOM in stormwater samples.

#### 2.5. Influence of stormwater runoff volume

Several researchers have attempted to model and understand rainfall–runoff processes, since it is a crucial factor to determine pollutant movement and to estimate contaminants' fate in environments. Many previous studies have emphasised stormwater rainfall–runoff transformation characterisation analysis, particularly of runoff process, since they act as a major pathway for transport of contaminants from urban areas into surface water bodies (Avellaneda et al., 2009). Pollutant

wash-off load has generally been assumed proportional to the rainfall intensity or runoff volume in previous studies. The pollutant wash-off load was assumed as a function of runoff volume, which increases would result in increase in pollutant loads. Runoff volume as a useful parameter allows the analysis of the variation of the pollutant mass during storm events and determines the total pollutant mass in relation to the total runoff volume (Chen and Adams, 2007). Following the rainfall–runoff model provided by Chen and Adams (2007), the corresponding water level measured in the drain (Fig. 1) was assumed as runoff volume, since surface area was consistent in the current study. It appears that the action of combining water level data and water quality parameter results can be also developed and employed as an essential and simple tool for stormwater character analysis.

On the basis of the flow condition sampling process, simple multiplications of values of general parameters and corresponding water levels could be applied to estimate the pollutant loadings in stormwater at a specific time period during a storm event. For instance, the DOC loading could be obtained by multiplying measured DOC concentration by the corresponding water level as expressed in  $\text{mg}/\text{m}^2$  (Fig. 4a). Other general water quality parameters, such as  $\text{UV}_{254}$ , colour and turbidity were also interpreted in conjunction with water level shown in Fig. 4b–d. This information could be used to evaluate the qualitative and quantitative removal of contaminants from the land surface across a runoff event (Avellaneda et al., 2009). An additional advantage of this multiplication appeared to minimise stormwater dilution factor and hence enabled to analyse pollutant mass distribution during storm events. Event 3 had the highest water levels across the storm event and these led to the highest DOM washed-off load compared to the other two events. This observation could be linked to the effects of rainfall intensity. It is also worth pointing out that higher pollutant loadings were observed at the beginning of each event.

Additionally, due to the conversion from concentration to mass-based values, the correlations between general DOM character parameters and general water quality parameters were improved. Strong statistical correlations ( $p < 0.001$ ) using PPMC analysis were found between colour evaluation and other parameter determinations, as summarised in Table 3. Similar trends in stormwater quality were observed in most parameter analysis based on combined water level analysis as illustrated in Fig. 4 and PPMC analysis (Table 3).  $R^2$  values above 0.80 were revealed between colour evaluations and DOM measurements, DOC,  $\text{UV}_{254}$  and  $\text{SUVA}_{254}$ . The highest  $R^2 = 0.92$  was obtained for the correlation between colour and  $\text{UV}_{254}$ . A relatively weak correlation was given between colour and turbidity ( $R^2 = 0.61$ ). Turbidity, an indication of the concentration of colloids and suspended particulates, was measured in an extremely high range for each storm event from 1 to 3. These relatively high turbidity results are an indication of the stormwater in this area containing high and stable portions of solid particles.

The above findings for stormwater quality assessment indicated that, although water level could be the main contributor to these phenomena, the stormwater colour appeared to respond proportionally to DOM characteristics. The higher DOC results tended to be positively correlated with higher  $\text{UV}_{254}$  measurements and higher colour observations, indicating higher pollutant concentrations in the runoff process. The outstanding definitive correlation ( $R^2 = 0.99$ ,  $p < 0.001$ ),



**Fig. 4 – The relationship between the results of general parameter values multiplied by water levels and the corresponding storm event duration, (a) DOC, (b) UV<sub>254</sub>, (c) colour, and (d) turbidity. DOC: dissolved organic carbon; UV: ultraviolet.**

between DOM and UV<sub>254</sub> indicates that UV<sub>254</sub> is also a good surrogate for DOM in the stormwater samples in this semi-urban catchment area. Moreover, as a result of this observation,

stormwater in this area could be considered as naturally high in aromatic content, regardless of the impacts of rainfall intensities. The statistical results revealed that there was a strong

**Table 3 – Correlations between colour measurements, other parameters and the influences of seasonal variation.**

	Colour PPMC ( $R^2$ , $p < 0.001$ )	Seasonal variation ANOVA ( $p$ )
Colour		<0.001
Turbidity	0.61	>0.05
UVA <sub>254</sub>	0.92	<0.05
DOC	0.85	<0.05
SUVA <sub>254</sub>	0.81	<0.001
Specific colour	0.74	<0.001
Averaged $A_{210}/A_{254}$ (1–2 kDa)	0.87	<0.001

relationship between rainfall intensity and the loads of pollutants across each storm event. Event 3 had the highest levels of rainfall intensity which led to the highest pollution. The stormwater quality of Event 2 was lower than that of Event 1 which followed also the rainfall intensity levels. The good distributions of samples throughout the flow variations proved that the protocol of an approximately 25 mm change in water level to trigger sample collection was valid and could represent effectively the character of stormwater flow events.

We also applied statistical analysis tools to evaluate the results generated from the HPSEC profiles and general water quality parameters. As a result of multiplying by the corresponding water level, the  $A_{210}/A_{254}$  values averaged over a 1–2 kDa range were found to be correlated strongly with the SUVA<sub>254</sub> ( $R^2 > 0.91$ ), and the  $A_{210}/A_{254}$  values averaged over the 0.3–2 kDa range were correlated with the specific colour ( $R^2 = 0.83$ ) (Fig. 5). Compared to Fig. 5b, all linear regressions represented in Fig. 5a were stronger on the basis of  $R^2$  values. These observations imply that the value of  $A_{210}/A_{254}$  averaged over 1–2 kDa range are affected by DOM aromaticity, whereas the specific colour values were not only dependent on aromatic contents associated with AMW 1–2 kDa range but were also a reflection of the non-aromatic content involved in AMW below 1 kDa. This finding indicates that  $A_{210}/A_{254}$  could be used to simplify complex HPSEC profiles and effectively represent DOM character changes during a storm event.

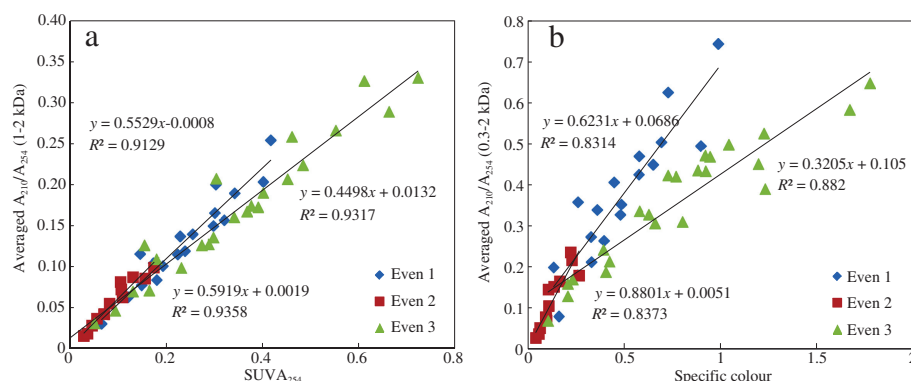
## 2.6. Influence of seasonal variation

In order to statistically determine the influences of seasonal variations on stormwater characteristics, we used the statistical tools PPMC and ANOVA to assess the correlations between colour measurements and those water quality parameters. Table 3 indicates that turbidity was the only parameter found to be unrelated to season related variables ( $p > 0.05$ ) when comparing the results of Event 3 and those of the combined Event 1 and Event 2. This could imply that the suspended substances entering into surface water bodies were independent of seasonal changes. Other general parameters and  $A_{210}/A_{254}$  averaged over the AMW range 1–2 kDa of DOM were found to be significant ( $p < 0.05$ ). Due to the limited rainfall and surface runoff in the warmer season, microbial processes could explain the associated increases in aromaticity and higher results of DOC, UV<sub>254</sub>, SUVA<sub>254</sub>, colour and specific colour.

Considering seasonal change influences as discussed above, both Event 1 and Event 2 occurred during rainy seasons, in which the stormwater samples may have had similar DOM characterisations, while Event 3 under hot summer conditions showed distinctively different DOM. Sharp et al. (2006) investigated the seasonal variation in surface water DOM in England and found that there was a significant change in DOM composition throughout the year. There was agreement between these observations and a similar study reported by Chong et al. (2013). These authors also found that the dry-weather storm event differed from another three wet-weather events. In addition, fulvic-like and humic acid-like compounds were mainly attributed to the dry-weather event. All wet-weather event samples had higher concentration of soluble microbial by-product-like substances than other regions.

## 3. Conclusions

DOC and UV<sub>254</sub>, as conventional DOM parameters, were found to be strongly correlated to the changes in stormwater quality during each storm event. Colour measurements of stormwater were indicative for both non-aromatic and aromatic compounds of DOM. The profile of HPSEC–UV could provide additional



**Fig. 5 – Correlation improved by runoff volume integration (a) between SUVA<sub>254</sub> and  $A_{210}/A_{254}$  averaged over AMW 1–2 kDa, (b) between specific colour and  $A_{210}/A_{254}$  averaged over AMW 0.3–2 kDa. SUVA: specific ultraviolet absorbance; A: absorbance.**



physiochemical characteristics of stormwater-associated DOM, molecular weight and size distribution, and also provide some interesting information on the influence of DOM character on UV absorbance measurements at 254 and 210 nm.  $A_{210}/A_{254}$  is an important parameter which could also be used to estimate the DOM proportions of functional groups and conjugated carbon species. The water quality results combined with the flow data could provide further insight on pollutant loadings and their characteristics during storm events. This implies that flow condition indeed plays an important role in affecting pollutant load in storm events. The correlation among various parameters associated with DOM properties and water qualities were explored using simple statistical methods. This study only provides limited data and did not fully indicate various factors influencing pollutant runoff and accumulation in stormwater, such as land use, seasonal changes and urban activities. The results from this study suggest, moreover, that specific treatment may be required to reduce contaminants from urban stormwater.

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