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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; King 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

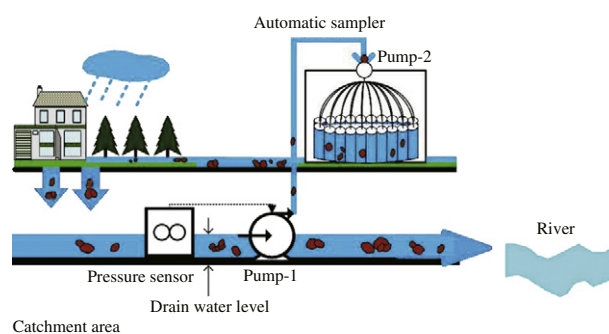


Fig. 1 – Schematic of the stormwater capturing system used for sequential sampling. (1) Pressure sensor: Placed in the drain to measure water level (m) in 5 min intervals and also send signal when drain water level changed (up and down) by 25 mm; (2) Pump-1: Installed in the drain to capture stormwater 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.

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