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RESEARCH ARTICLE

Understanding dissolved organic matters in stormwater from different urban land uses: implications for reuse safety

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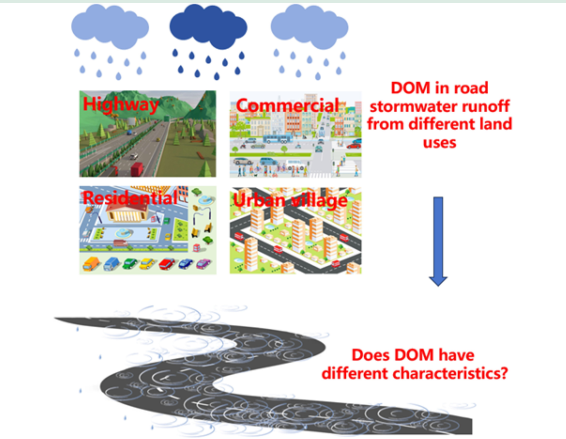
HIGHLIGHTS

- Dissolved organic matters (DOM) in stormwater from different land uses were compared.
- Surrounding environments significantly influenced DOM characteristics in stormwater.
- Commercial/highway stormwater had higher DOM concentrations with higher aromaticity.
- Stormwater/rainwater tended to be more hydrophilic than other water sources.
- All water sources included a very high fraction of low molecular weight DOM.



ABSTRACT: Chlorination plays a vital role in guaranteeing the safety of reused stormwater, but it must be carefully managed due to its potential to react with dissolved organic matter (DOM) in water, forming disinfection by-products (DBPs). This study investigated DOM characteristics in stormwater from different land uses. The results showed that surrounding environments significantly impacted DOM characteristics in stormwater. Commercial stormwater and highway stormwater showed higher DOM concentrations with higher aromaticity than urban village and residential areas. DOM in commercial stormwater and highway stormwater had a high humification while residential stormwater and urban village stormwater had a higher fraction of recently microbially-generated DOM. When compared to other water sources in China, stormwater (rainwater that reaches the ground and washes off pollutants)/rainwater (rainwater without reaching ground surfaces) exhibited higher humification and fewer extracellular substances produced by microorganisms. Stormwater/rainwater was also more hydrophilic, with percentages ranging from 50.77% to 93.73%. However, all water sources contained a significant fraction of low molecular weight DOM, such as < 1 kDa, with stormwater in this study containing 36.45% to 66.39% of DOM < 1 kDa. These findings provide valuable insights into the DOM characteristics of stormwater.

KEYWORDS: Dissolved organic matters, Stormwater reuse, Land use, Reuse safety

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1 Introduction

Stormwater reuse has received much attention since it is one of the most important alternative water sources (Wijesiri et al., 2020; Hong et al., 2022). To ensure stormwater reuse safety, proper treatment should be undertaken prior to their reuse (Furlong et al., 2017; Feng et al., 2022). One of the important treatment processes is disinfection. This is because stormwater generally contains pathogenic microorganisms. For example, Saifur and Gardner (2021) have found that stormwater significantly contributed fecal indicator bacteria into fresh and marine waters. Paule-Mercado et al. (2016) noted that stormwater runoff from urban land uses and land covers contained 3.33−7.39 $\log_{10}$MPN/100 mL *E. coli* and 3.30−7.36 $\log_{10}$MPN/100 mL *Fecal streptococci*. Hamilton et al. (2019) reported that more than 20 types of pathogens were found in stormwater reuse systems. Sidhu et al. (2012) noted that urban stormwater runoff in Australia contained a diversity of pathogenic microorganisms. The number of *E. coli* and *Enterococcus* spp. had reached 4.3×10^4 and 3×10^5 L^{-1}, respectively (Sidhu et al., 2012). Zhan et al. (2020) investigated urban road stormwater quality in Shenzhen, China and found that the number of *E. coli* and total bacteria reached 2200 and 7000 L^{-1}, individually. These observations implied that stormwater disinfection is essential before any purposes of reuse.

Chlorination disinfection is one of the most commonly used disinfection approaches during water and wastewater treatment processes. Although chlorination showed a good performance on disinfection efficiency and cost-effectiveness, a negative point is disinfection by-products (DBPs) formation (Zhu et al., 2024). A number of past studies have found that chlorine disinfectants can react with dissolved organic matters (DOM) present in water and form many types of DBPs such as trihalomethane and haloacetic acid (Yuan et al., 2019; Brinkmann et al., 2024; Czarnecki et al., 2024; Yang et al., 2024). For example, Chen et al. (2024) investigated source water in Tibetan Plateau, China and found a strong positive correlation between DBPs generation and DOM amounts. Huang et al. (2023) DOM characteristics had an important influence on DBPs formation and DBPs removal using UV irradiation and O_3 oxidation advanced treatment processes. Shakhawat et al. (2024) found that after continues rainfall, drinking water sources showed a higher DBPs formation potential. This was because rainfall input DOM into drinking water sources. They suggested that drinking water treatment should re-assess chlorine dosages during wet seasons. Muni-Morgan et al. (2023) reported that urban stormwater pond is a DOM pool, particularly including high concentrations of dissolved organic nitrogen (DON). This might lead to high nitrogenous DBPs formation. Therefore, DOM is a key precursor of DBPs formation. These DBPs had high toxicity such as ecological toxicity (Wang et al., 2022), reproductive toxicity (Zhang et al., 2023b), cytotoxicity (Qiu et al., 2024) and genotoxicity (Zhang et al., 2017). For instance, it is noted that when zebrafish were exposed to nitrogenous DBPs, a significant reduction in hatchability and an increase in mortality happened. This was because zebrafish heart function and neuronal function were inhibited (Lin et al., 2016). These seriously threaten stormwater reuse safety after chlorination disinfection is conducted to stormwater.

DBPs formation is significantly influenced by DOM characteristics. These characteristics generally include concentrations, aromaticity, molecular weight distribution, hydrophilicity/hydrophobicity and substances compositions. Different water sources might have different DOM characteristics. For example, Lin et al. (2022) noted that DOM in urban road stormwater is more hydrophilic while reclaimed water is more hydrophobic. He et al. (2020) noted that DOM present in atmospheric wet deposition primarily included proteins-like substances and soluble microbial products (SMPs), which are important precursors of halogenated acetamide (HAMs, one of highly toxic DBPs). Hu et al. (2016) compared DOM characteristics in drinking water and reclaimed water and found that DOM amounts in reclaimed water were higher than drinking water. This might lead to higher DBPs formation potential in reclaimed water than drinking water. Yuan et al. (2024) noted that DOM in rainwater had the most hydrophilic fraction, followed by hydrophobic acidic, hydrophobic bases and hydrophobic neutral fractions. Both hydrophobic acidic and hydrophobic neutral fractions were the primary precursors of trihalomethanes (THMs).

Stormwater has different water quality from traditional water sources because of different sources. For example, drinking water is primarily from reservoirs (Zhang et al., 2024); reclaimed water is recycled wastewater (Mancuso et al., 2023). However, stormwater is generated due to rainwater reaching and washing-off ground surfaces. In this context, pollutants present in the stormwater might come from the atmosphere and ground surfaces, where atmospheric environment and catchment characteristics such as land use significantly influence stormwater quality (Liu et al., 2018; Yan et al., 2024). This means that DOM characteristics of stormwater might differ from other water sources. Although past studies have investigated DOM characteristics in many water sources such as drinking water (Awad et al., 2018), reclaimed water (Zhang et al., 2022) and surface water (He et al., 2022), how DOM characteristics vary with stormwater from different land uses has not been fully understood, which is a knowledge gap. This has constrained effective stormwater reuse implementation and undermined reuse safety.

In this context, this study collected stormwater samples from urban roads in typical land uses, including highway, residential area, commercial area and urban village. A comprehensive investigation was undertaken to analyze DOM characteristics (concentrations, aromaticity, molecular weight distribution, hydrophilicity/hydrophobicity and substances compositions) among these stormwater samples. Additionally, a comparison analysis was also conducted to compare DOM characteristics in different water sources in China (stormwater/rainwater, drinking water, reclaimed water, wastewater, surface water and groundwater) by a comprehensive literature review. The novelty of this study was to investigate how DOM characteristics vary with stormwater from different land uses while past studies mainly focused on drinking water, reclaimed water and surface water. The research outcomes were expected to contribute a good understanding of DOM characteristics in urban stormwater and hence provide useful guidance to effective stormwater reuse strategy implementation.

2 Methods and materials

2.1 Study sites

The stormwater samples for this study were collected in Guangzhou, a highly developed city in China that serves as the capital of Guangdong province. With a population exceeding 18 million, Guangzhou is characterized by its warm climate, with an annual average temperature of around 22.2 °C and an annual average rainfall depth of approximately 1800 mm (sourced from baidu.com). To investigate DOM in stormwater from different land uses, four study sites were selected in Guangzhou. Each site represented a distinct land use type, providing a comprehensive data set for analysis. They were a highway (E113.358°, N23.133°), a commercial area (E113.358°, N23.013°), an urban village (E113.353°, N22.973°) and a residential area (E113.338°, N23.145°). The highway carried a very high traffic volume. Vehicles run on this highway at a very high speed. The commercial area is surrounded by shopping malls and office buildings. The traffic volume was also high. The urban village is a type of settlement that emerges when a former village, once surrounded by fertile land, becomes enveloped by urban development due to construction during urban expansion (Li et al., 2024). The majority of streets and roads within the urban village are narrow, accommodating a mix of vehicles, bicycles, and motorbikes, creating a challenging traffic environment. The residential area was quiet and clean, with many trees and plants. The traffic volume was low in this residential site. Figure 1 shows study sites.

2.2 Stormwater sampling

Stormwater sampling was conducted in September 2022 under specific meteorological conditions: a rainfall depth of 5.5 mm, with antecedent dry days totaling 12 d, and a rainfall duration of approximately 3.5 h. Road stormwater was chosen for sampling due to its potential for reuse in non-potable applications such as landscaping and cleaning. To collect the samples, a manual method was employed using acid-washed and deionized water-washed glass bottles (500 mL) placed at the drainage outlet on the road.

The importance of road stormwater as a resource for reuse is evident from the construction of underground stormwater storage tanks in many places, designed to collect runoff from roads and streets (Zhang et al., 2023a). By analyzing the collected stormwater samples, insights can be gained into the quality and characteristics of this resource, which can inform decisions on its appropriate reuse and management.

Prior to the collection of stormwater samples, any large rubbish and stones were manually removed from the drainage outlet to ensure the integrity and representativeness of the samples. Sampling began once runoff was generated and continued until sufficient volumes of stormwater, typically 3–5 L, were collected from each sampling point. Each sampling bottle was carefully labeled with the sampling time, location, and number to maintain accurate record-keeping. After the samples were collected, they were promptly transported to the laboratory and stored at 4 °C to preserve their quality for further testing. The study focused on a single rainfall event to minimize the influence of varying rainfall characteristics and to clearly demonstrate the impact of land uses on stormwater quality. By isolating the effects of a single rainfall event, the study aimed to provide a clearer understanding of how land uses influence DOM characteristics in stormwater. This approach allowed for more accurate insights into the

Fig. 1 Locations and photos of sampling sites.

relationship between land use and stormwater quality, facilitating informed decisions on stormwater management and reuse.

2.3 Sample testing

This study conducted a comprehensive investigation of DOM characteristics in stormwater from various land uses, focusing on parameters such as concentration, aromaticity, molecular weight distribution, hydrophilicity/hydrophobicity, and substance compositions. The following section discusses the testing methods employed to measure these parameters.

2.3.1 Basic water quality parameters

Before analyzing the stormwater samples, a preprocessing step was conducted where the samples were filtered through glass filter papers with a pore size of 0.45 μm to eliminate any larger particles. This ensured that the subsequent water quality tests were not influenced by these particles. The basic water quality parameters measured included total nitrogen (TN), total phosphorus (TP), dissolved organic carbon (DOC), UV absorbance at 254 nm (UV_{254}), and $SUVA_{254}$ (specific UV absorbance at 254 nm). TN and TP were tested according to the standards GB11894-89 and GB11893-89, respectively. DOC was analyzed using a TOC analyzer manufactured by Analytik Jena AG in Germany. UV_{254} was measured using a UV-vis spectrophotometer from Thermo Fisher Scientific in the United States. $SUVA_{254}$ was calculated by dividing the UV_{254} values by the DOC concentrations for all samples. Namely, $SUVA_{254}$ can yield an estimate for the quantitative aromatic content per unit concentration of organic carbon (Karanfil et al., 2005). Both UV_{254} and $SUVA_{254}$ are indicators of the amount of aromatic organic content in the water, as noted by Karanfil et al. (2005). For quality control purposes, each test was conducted in triplicate to ensure accuracy.

2.3.2 Molecular weights distribution testing

To obtain four distinct fractions based on molecular weight, a series of ultrafiltration membranes sourced from Amicon in Billerica, Massachusetts, were employed. These membranes allowed for the isolation of four molecular weight fractions: less than 1 kDa, from 1 to 3 kDa, from 3 to 10 kDa, and from 10 to100 kDa. The separation of stormwater samples into these fractions involved a methodical approach. Initially, a 5-L sample was filtered through the membranes in a specific order, beginning with the membrane possessing the largest pore size and progressively moving to the one with the smallest pore size. This sequential filtration process guaranteed that each fraction comprised molecules strictly within its designated molecular weight range. For a comprehensive understanding of the testing methodologies employed, Hua and Reckhow (2007) is recommended.

2.3.3 Hydrophobic/hydrophilic fraction testing

Prior to filtration through the ultrafiltration membranes, the stormwater samples underwent a preliminary treatment. They were first acidified to achieve a pH level of 2 using sulfuric acid. Following acidification, the samples were sequentially passed through two types of resin: XAD-8 and then XAD-4. The effluent that successfully passed through the XAD-4 resin was designated as the hydrophilic fraction (HPI). Conversely, the fraction that adhered to the XAD-8 resin was subsequently eluted using a sodium hydroxide solution maintained at a pH of 11. This eluted component was termed the hydrophobic fraction (HPO). Meanwhile, the organic compounds that were retained by the XAD-4 resin were classified as the transphilic fraction (TPI). These compounds were eluted using the same sodium hydroxide solution but in a reverse direction. For more detailed information on this separation method, it can refer to Hua and Reckhow (2007).

2.3.4 3D excitation-emission matrix fluorescence testing

A 3D excitation-emission matrix (3D-EEM) fluorescence test is a powerful analytical tool used to examine the composition of dissolved organic matter (DOM) in stormwater samples. This test was executed utilizing a fluorescence spectrophotometer manufactured by Thermo Scientific Lumina in the United States. The results of the 3D-EEM test typically reveal five distinct regions, each characterized by specific excitation (EX) and emission (EM) wavelengths. These regions are as follows:

- Region I (Tyrosine-like): Typically located with excitation wavelengths around 220–250 nm and emission wavelengths around 280–330 nm. This region is associated with aromatic amino acids such as tyrosine and tryptophan, which are common components of proteins;
- Region II (Tryptophan-like): Found with excitation wavelengths around 250–280 nm and emission wavelengths centered at around 330–380 nm. This region is also linked to tryptophan, another aromatic amino acid found in proteins;
- Region III (Fulvic acid-like): Characterized by excitation wavelengths spanning 250–400 nm and emission wavelengths ranging from 380 to 500 nm. This region is indicative of fulvic acids, which are low-molecular-weight components of natural organic matter (NOM) often found in surface waters;
- Region IV (Soluble microbial byproduct-like): Identified by excitation wavelengths around 250–290 nm and emission wavelengths centered at around 420–480 nm. This region is associated with soluble microbial byproducts (SMPs), which are organic compounds released by microbial activity in aquatic environments;
- Region V (Humic acid-like): Located with excitation wavelengths spanning 290–450 nm and emission wavelengths centered at around 420–600 nm. This region is indicative of humic acids, which are high-molecular-weight components of NOM typically derived from the decomposition of plant and animal.

In addition to the qualitative analysis, this study also performed regional integration calculations for each region in the 3D-EEM to obtain quantitative results. The region classification and integration calculation methods used in this study are based on the work of Chen et al. (2003).

Based on the 3D-EEM results, three indices were calculated for each sample: the fluorescence index (FI), humification index (HIX), and biological index (BIX). These indices provide additional insights into the characteristics of the dissolved organic matter (DOM) in the stormwater samples. The FI is used to identify the sources of DOM, distinguishing between terrestrial and microbial sources. Specifically, FI values between 1.7 and 2.0 suggest that microbial activities are the primary source of DOM, while FI values less than 1.4 indicate that terrestrial sources might be the main contributor (McKnight et al., 2001; Wickland et al., 2007). The HIX is used to assess the degree of humification of the DOM. A HIX value less than 4 is associated with autochthonous fresh DOM, while a HIX value greater than 4 is related to humified organic materials (Birdwell and Engel, 2010). The BIX is used to evaluate autotrophic productivity. When BIX values range from 0.8 to 1.0, it indicates freshly produced DOM of biological/microbial origin. Conversely, BIX values less than 0.6 suggest a limited amount of organic matter from autochthonous origin (Birdwell and Engel, 2010).

FI index was calculated as the ratio of the emission intensity at 450 nm to the emission intensity at 500 nm, both measured at an excitation wavelength of 370 nm. HIX index was calculated by dividing the sum of the emission intensities between 435 and 480 nm by the sum of the emission intensities between 300 and 345 nm, both measured at an excitation wavelength of 254 nm. BIX index was calculated as the ratio of the emission intensity at 380 nm to the emission intensity at 430 nm, both measured at an excitation wavelength of 310 nm. The calculation methods for these indices were based on the work of Zhang et al. (2019).

3 Results and discussion

3.1 Comparison of basic water quality

Table 1 shows basic water quality of stormwater runoff from different land uses. It was found that highway stormwater had the highest concentration of TN (11.667 ± 0.689 mg/L) and TP (0.144 ± 0.003 mg/L) while commercial stormwater showed the highest concentration of DOC (88.6 ± 0.680 mg/L) and UV_{254} value (1.78 ± 0.003 cm^{-1}). In terms of $SUVA_{254}$ values, the highway (2.324 ± 0.141 L/(mg·m)) and commercial (2.009 ± 0.012 L/(mg·m)) stormwater samples were relatively higher than urban village (0.971 ± 0.021 L/(mg·m)) and residential areas (0.966 ± 0.007 L/(mg·m)). These observations suggested that stormwater from highway and commercial areas contained more nutrients such as nitrogen, phosphorus and organic carbon. The significant difference of these parameters among different land uses can be also supported by *P*-values, which are less than 0.05 (*P*-value of TN, TP, DOC, UV_{254} and $SUVA_{254}$ were 6.8×10^{-5}, 1.1×10^{-5}, 7.2×10^{-8}, 1.5×10^{-11}, and 8.9×10^{-5}, respectively). This can be attributed to land use characteristics. The highway carries very high traffic volume, which leads to much vehicle emission, trye wear and road surface wear. This could generate many pollutants deposited on road surfaces during dry periods. Additionally, plants and trees such as green belts along the highway might also contribute to a high nutrient concentration as shown in Table 1. Vehicle emission generally contains many oxynitrides, which might contribute to nitrogen amounts in stormwater runoff. Bartlett et al. (2012) noted that nutrients of sediments and water in a stormwater management pond caused toxicity to *Hyalella Azteca.* They found that the stormwater management pond received stormwater runoff from a highway. This means that the highway can contribute a high nutrient level to stormwater runoff. Commercial areas generally have complex environments, including high population density, traffic volume, commercial shops and office buildings. These human activities can significantly contribute pollutants into stormwater runoff. Behrouz et al. (2024) also noted that high-density population areas such as commercial areas have higher pollutant concentrations such as suspended solids in stormwater. They attributed this to frequent human activities. These lead to high pollutant concentrations in commercial areas, especially DOC (Table 1). High DOC concentrations generally mean a high potential of forming DBPs after chlorination. This suggests a potential risk of reusing commercial road stormwater runoff. However, urban village and residential areas have relatively better daily maintenance such as frequent sweeping, even though there are also many human activities. This could mean that not many pollutants enter stormwater runoff because most of them are removed during daily maintenance.

It can be noted that the commercial area had the highest UV_{254} value, followed by highway, urban village and residential area. This means that commercial stormwater runoff could contain a high amount of aromatic organic substances with C–C double bonds and C–O double bonds as well as humic macromolecule organic substances. This implies that commercial stormwater might have higher DBPs formation potential than other land use stormwater samples since these unsaturated organic substances are one of the most important precursors of DBPs formation. In terms of $SUVA_{254}$ values, both highway and commercial stormwater samples were larger than 2 L/(mg·m). This further confirms that highway and commercial stormwater could include a high quantity of aromatic/humic macromolecule organic substances. However, the $SUVA_{254}$ values of urban village and residential area were less than 2 L/(mg·m). This means

Table 1 Basic water quality parameters

Land use	TN (mg/L)	TP (mg/L)	DOC (mg/L)	UV_{254} (cm^{-1})	$SUVA_{254}$ L/(mg·m)
Highway	11.667 ± 0.689	0.144 ± 0.003	13.923 ± 0.847	0.323 ± 0.000	2.324 ± 0.141
Commercial area	6.259 ± 0.199	0.121 ± 0.000	88.6 ± 0.680	1.78 ± 0.003	2.009 ± 0.012
Urban village	2.877 ± 0.054	0.085 ± 0.000	32.15 ± 0.544	0.312 ± 0.001	0.971 ± 0.021
Residential area	4.740 ± 0.076	0.072 ± 0.003	12.947 ± 0.095	0.125 ± 0.000	0.966 ± 0.007

that urban village and residential areas stormwater had low humification and aromatization and included many organic matters with low molecular weight and low hydrophobicity. These organic matters are relatively difficult to remove by the traditional coagulation-sedimentation treatment approach (Matilainen et al., 2010). Therefore, urban village and residential areas stormwater treatment for reuse needs to combine other approaches to enhance organic matter removal efficiency.

3.2 Comparison of molecular weight distribution

Figure 2 provides the comparison of molecular weight compositions of DOM in stormwater from different land uses, indicated by DOC. It is noted that < 1 kDa DOM accounted for the highest percentages for all land use stormwater samples, namely 52.28% for highway, 36.45% for commercial area, 66.39% for urban village and 60.10% for residential area, respectively. Except for commercial area, other three land use stormwater samples contained more than 50% of organic matters with < 1 kDa. This means that commercial stormwater contained organic matters with higher molecular weight than other three land uses. This result agrees with previous studies. Lin et al. (2022v found that both urban road stormwater and reclaimed water included the highest fraction of organic matters with < 1 kDa (43.0%–77.5%). Hu et al. (2016) investigated 234 reclaimed water samples and 117 drinking water source samples and found the average fractions of organic matters with < 1 kDa of these two water types were 45% and 57%, individually. Shi et al. (2020) reported that low molecular weight DOM such as < 1 kDa accounted for the highest percentage in both influent and secondary effluent of wastewater treatment plants. The lower molecular weight the organic matters had, the more difficult the organic matters were removed. He et al. (2023) also noted a high percentage of low molecular weight DOM in rivers. They attributed this to human input of wastewater DOM with low molecular weight and condensation degree.

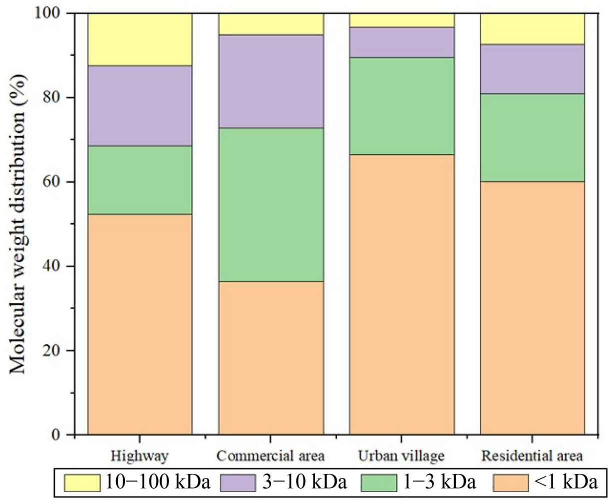

Fig. 2 Molecular weight distribution of DOM in stormwater samples.

These outcomes imply that DOM in urban stormwater was primarily small molecular organic matters such as < 1 kDa and this was regardless of land use types. However, these small molecular DOM is generally difficult to be removed by traditional water treatment approaches such as coagulation-sedimentation and sand filtration (Matilainen et al., 2010). These small molecular DOM is also easy to be absorbed by microorganisms, leading to their growth. In addition, advanced oxidation processes do not have a good performance on removing these small molecular DOM from water (Siddique et al., 2022). This is because advanced oxidation processes treat organic matters by breaking-down large molecular substances into small molecular substances (Siddique et al., 2022). In this context, a large amount of low molecular weight DOM present in urban stormwater as shown in Fig. 2 could lead to DBPs formation during chlorination.

3.3 Comparison of hydrophilicity/hydrophobicity

Figure 3 shows DOM fractions of hydrophilic/hydrophobic compositions. It can be noted that

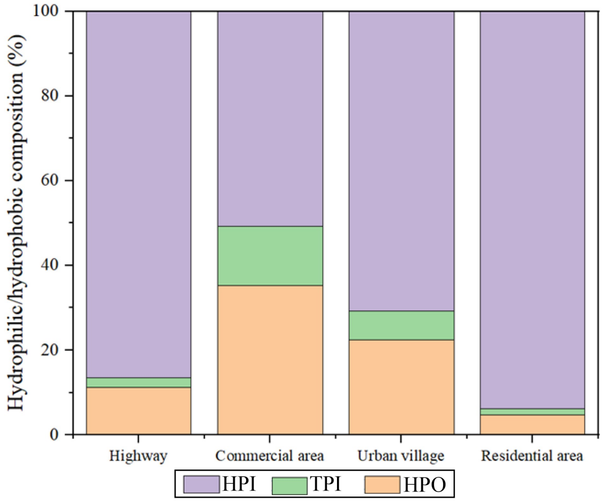

Fig. 3 DOM fractions of hydrophilic/hydrophobic compositions in stormwater samples (HPO: hydrophobic composition; TPI: transphilic composition; HPI: hydrophilic composition).

regardless of land use types, all urban stormwater samples contained the highest percentages of hydrophilic DOM, 86.45% for highway, 50.77% for commercial area, 70.72% for urban village and 93.73% for residential area, respectively. Especially, DOM in residential stormwater had a very high fraction of hydrophilic DOM (more than 90%). Since hydrophilic DOM primarily included aliphatic hydrocarbons such as amino acid and carbohydrate, these substances might be sourced from human life in residential area. In terms of hydrophobic DOM, commercial stormwater showed the highest fraction, 35.33%. This means that commercial stormwater could include a higher amount of humic acid and fulvic acid related organic matters.

These observations agree with past studies. Lin et al. (2022) investigated DOM characteristics in both urban road stormwater and reclaimed water. They found that there were higher fractions of hydrophilic compositions in urban road stormwater samples (70.4%–88.2%) than reclaimed water (30.9%–76.2%). He et al. (2020) analyzed DOM hydrophilic/hydrophobic compositions in artificial rainwater (mixing atmospheric dry deposition and ultrapure water) and noted a 47.9% of hydrophilic composition. These past outcomes further confirm that DOM in stormwater might tend to be hydrophilic. However, this means that DOM in stormwater is hard to be treated by traditional water treatment methods such as coagulation-sedimentation because of low octanol-water partition coefficient. Therefore, these hydrophilic DOM present in stormwater might lead to DBPs formation during chlorination.

3.4 Comparison of DOM substance compositions

Substance compositions of DOM were investigated by undertaking 3D-EEM spectra analysis. Figure 4 shows the 3D-EEM spectra of DOM in stormwater samples. It can be observed that main peaks of 3D-EEM spectra were in Region V for all stormwater samples while there were not obvious peaks in Region I, II and III. This means that all stormwater samples included a large quantity of humus related organic substances while aromatic proteins related substances and fluvic acid related substances were less. This can be also supported by spectra volumetric integration results (Fig. 5). All

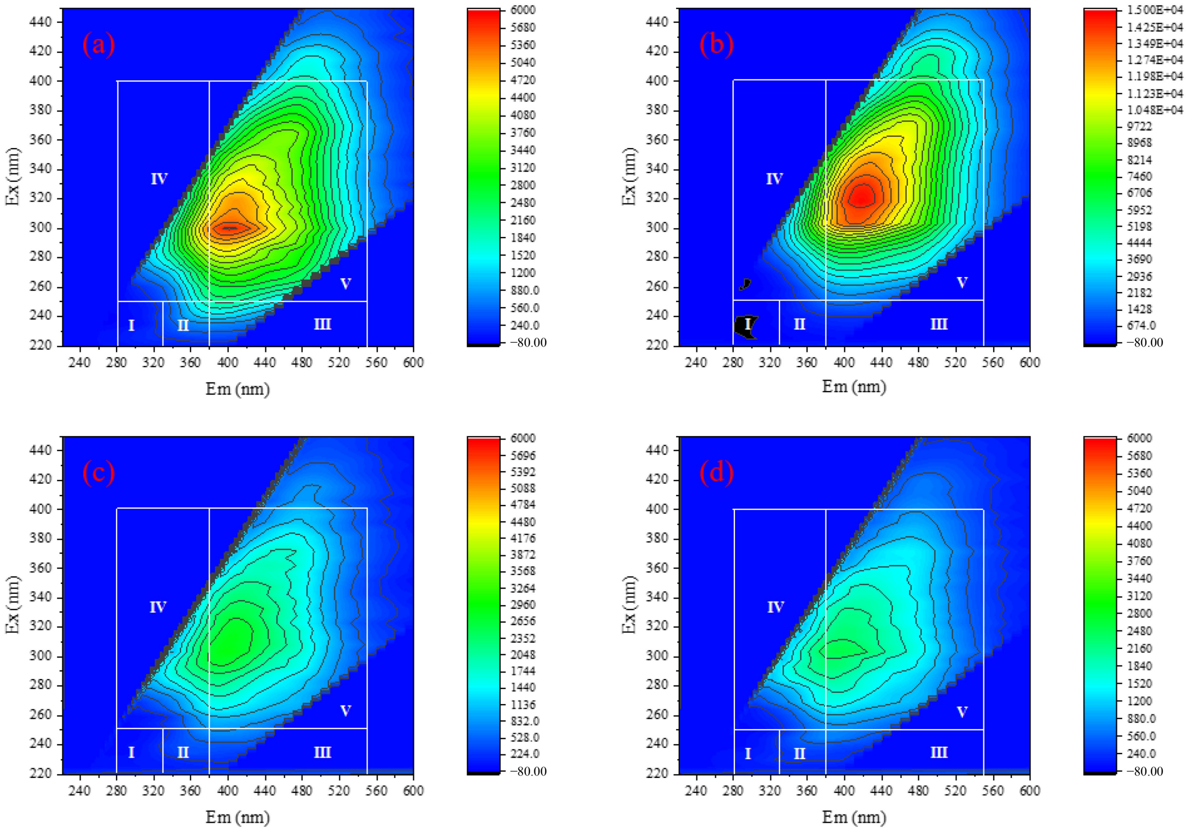

Fig. 4 3D-EEM of stormwater samples from different land uses: (a) highway, (b) commercial area, (c) urban village, (d) residential area

stormwater samples showed the highest volumetric integration percentages of Region V. They were 45.45% for highway, 53.55% for commercial area, 44.68% for urban village and 43.37% for residential area, respectively. In terms of fluorescence intensity, commercial stormwater was significantly higher than other three land uses. The order of fluorescence intensity followed commercial area > highway > urban village > residential area. These outcomes confirmed a high fraction of humus related organic substances in urban stormwater, particularly for commercial stormwater. This can be attributed to complex human activities, which emit many organic pollutants. These organic pollutants mixed with urban soil such as green belts and become humus related organic substances.

Table 2 shows FI index, HIX index and BIX index of all stormwater samples. For FI index, all stormwater samples were around 1.9. The order followed urban village (1.96) > residential area (1.83) > highway (1.82) = commercial area (1.82). This suggested that DOM in urban stormwater was primarily related to microorganic activities. The order of HIX index showed commercial area (6.34) > highway (4.02) > urban village (3.19) > residential area (2.67). This means that commercial stormwater contained a large amount of humus related organic substances, which mainly came from terrestrial sources. This result is similar to 3D-EEM analysis. Although highway stormwater also contained much humus related organic substances, they could be generated from authigenic sources. However, both urban village and residential stormwater had lower humification degrees than commercial and highway stormwater. In the case of BIX index, the order was residential area (1.05) > urban village (0.98) > highway (0.96) > commercial area (0.80). This suggested that these stormwater samples contained a higher fraction of DOM recently generated by microorganisms.

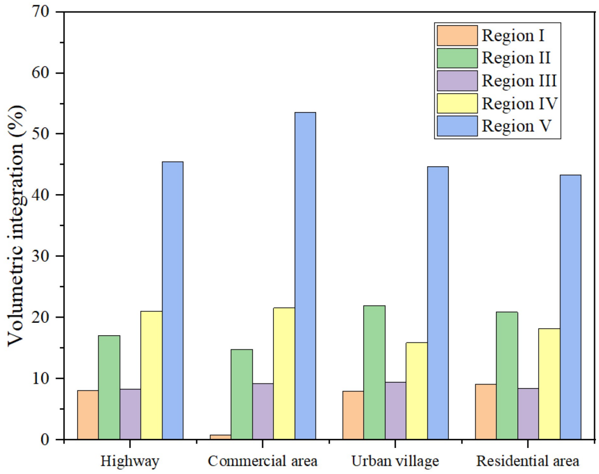

Fig. 5 Volumetric integration percentages of 3D-EEM.

Table 2 FI, HIX, and BIX values

Index	Highway	Commercial area	Urban village	Residential area
HIX	4.02	6.34	3.19	2.67
BIX	0.96	0.80	0.98	1.05
FI	1.82	1.82	1.96	1.83

These observations implied that DOM in stormwater from different land uses had different compositions. Commercial and highway stormwater samples included more humus related organic substances. Urban village and residential stormwater samples had lower humidification degrees and primarily included DOM from recent microorganism activities. This means that commercial stormwater and highway stormwater could have higher DBPs formation potential since humus related organic substances are one of the most important precursors. This observation is similar to a past study (Nguyen et al., 2013), which showed a strong correlation between humic-like DOM and DBPs formation potential for both large and small rainfall events. Therefore, collecting commercial stormwater and highway stormwater for reuse should be with a particular care after chlorination disinfection.

3.5 Comparison with other water sources in China

Figures 6 and 7 shows DOC, UV_{254} and $SUVA_{254}$ values as well as FI, HIX, and BIX values of different water sources, including stormwater/rainwater (including data in this study), drinking water, reclaimed water, wastewater, surface water and groundwater in the past studies (Supplementary Materials). These water sources were all located in China. Supporting Information also showed DOM molecular weights, hydrophobicity/hydrophilicity and compositions of these water sources. These data were collected by a comprehensive literature review, using keywords, “dissolved organic matters,” “water sources,” “stormwater,” “rainwater,” “reclaimed water,” “surface water,” “drinking water” and “groundwater.” For surface water, it included river water, lake water, coastal water and seawater. Two important criteria were used during literature review. One was that the water source is in China. Another one was that at least one parameter indicating DOM characteristics (DOC, UV_{254}, $SUVA_{254}$, FI, HIX, BIX, molecular weights, hydrophobicity/hydrophilicity and compositions) should be present in the literature. Eventually, 18 literature was identified (see Supplementary material).

In terms of DOC concentrations (Fig. 6(a)), surface

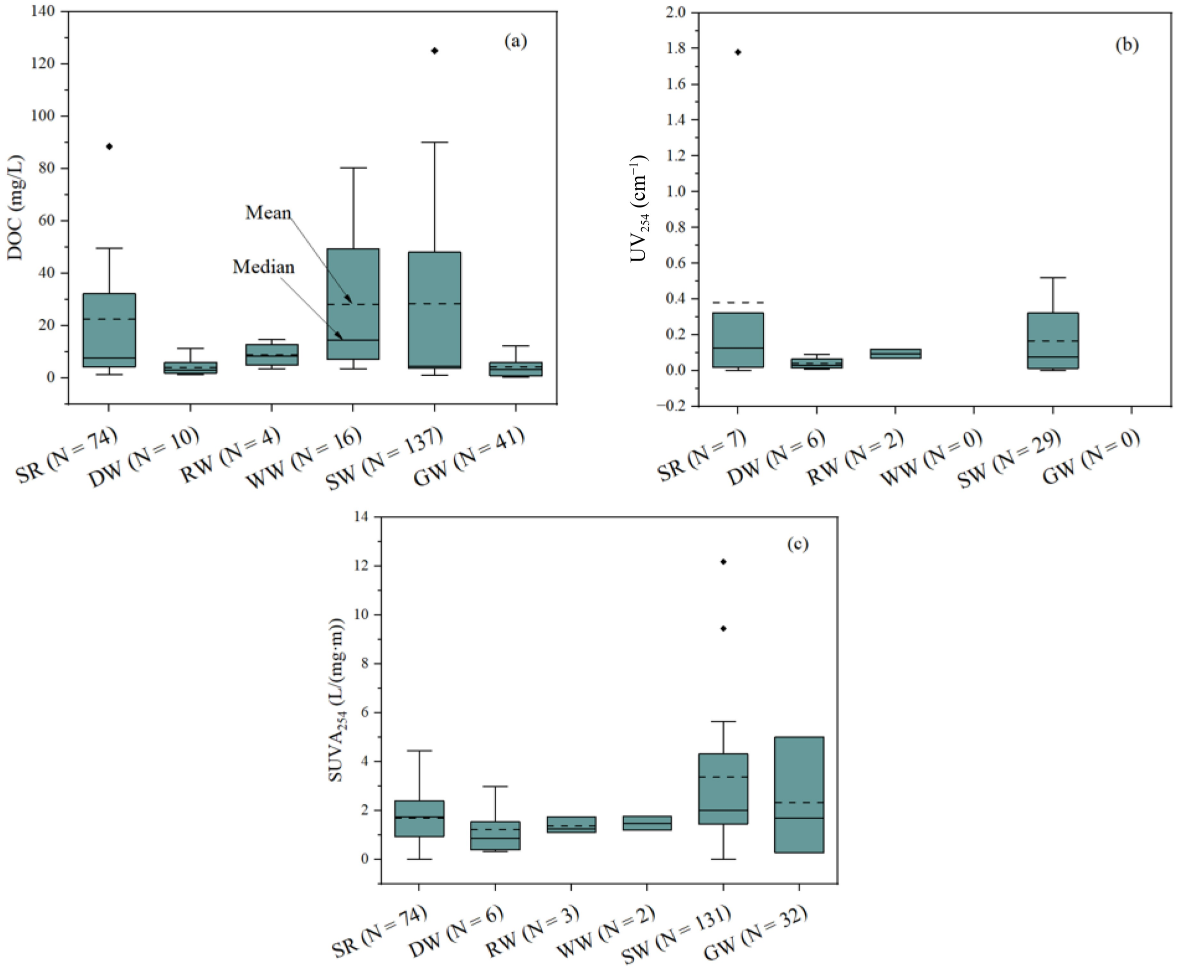

Fig. 6 DOC (a), UV_{254} (b) and $SUVA_{254}$ (c) values of different water sources (SR: stormwater/rainwater; DW: drinking water; RW: reclaimed water; WW: wastewater; SW: surface water; GW: groundwater).

water (mean value was 28.41 mg/L) and wastewater (mean value was 28.17 mg/L) had higher values, followed by stormwater/rainwater (mean value was 22.37 mg/L). However, reclaimed water (mean value was 8.76 mg/L), groundwater (mean value was 4.30 mg/L) and drinking water (mean value was 3.96 mg/L) showed much lower DOC concentrations. Additionally, compared to other water sources, stormwater/rainwater, wastewater and surface water had a higher variation of DOC concentrations since their DOC concentration ranges were wider than other water sources. This means that stormwater/rainwater, wastewater and surface water could be highly influenced by other factors such as human activities, climate and surrounding environments.

For UV_{254} values (Fig. 6(b)), although no data was found in past studies for wastewater and groundwater, it can be noted that stormwater/rainwater (mean value was 0.38 cm^{-1}) had the highest UV_{254} value, followed by surface water (mean value was 0.17 cm^{-1}) while drinking water (mean value was 0.04 cm^{-1}) and reclaimed water (mean value was 0.09 cm^{-1}) showed lower UV_{254} values. Additionally, stormwater/rainwater and surface water also showed higher variability of UV_{254} values than drinking water and reclaimed water. This means that compared to drinking water and reclaimed water, stormwater/rainwater and surface water could contain a high amount of aromatic organic substances with C-C double bonds and C-O double bonds as well as humic macromolecule organic substances.

In the case of $SUVA_{254}$ values (Fig. 6(c)), surface water (mean value was 3.37 L/(mg·m)) and groundwater (2.32 L/(mg·m)) showed higher $SUVA_{254}$ values while stormwater/rainwater, drinking water, reclaimed water and wastewater had a mean value of < 2 L/(mg·m). Generally, when $SUVA_{254}$ values are less than 2 L/(mg·m), DOM primarily included non-humics, high hydrophilicity, and low molecular weight compounds (Hu et al., 2016). This means that DOC removal by traditional approaches such as coagulation could be very difficult. Therefore, surface water and groundwater might be easy to remove DOC during traditional water treatment while stormwater/rainwater, drinking water, reclaimed water and wastewater could be hard.

According to the collected data in past studies (see Supporting Information), it is also found that most of water sources had a high fraction of low molecular weight DOM, such as < 1 kDa. Stormwater/rainwater tended to be more hydrophilic while reclaimed water and drinking water tended to be more hydrophobic. Surface water might be hydrophilic (such as Pearl River in Guangdong, China) (Zheng et al., 2016) or hydrophobic (such as Ganjiang River in Jiangxi, China) (Feng et al., 2021) according to water source characteristics. In terms of DOM compositions, most of stormwater/rainwater primarily contained humic acid-like substances while other water sources' DOM compositions were relatively complex. For example, Shen et al. (2016) found that drinking water in Shanghai, China contained much SMP-like DOM while Lin et al. (2022) noted that reclaimed water in Shenzhen, China had much SMP-like and humic acid-like substances. River water (Maozhou River, Shenzhen, China) included high abundances for tyrosine-like and tryptophan-like substances (Ye et al., 2019) while Pearl River, China contained much more humic-like, fulvic-like and protein-like DOM (Zheng et al., 2016).

Figure 7 compared FI, HIX and BIX index among different water sources. In terms of FI index (Fig. 7(a)),

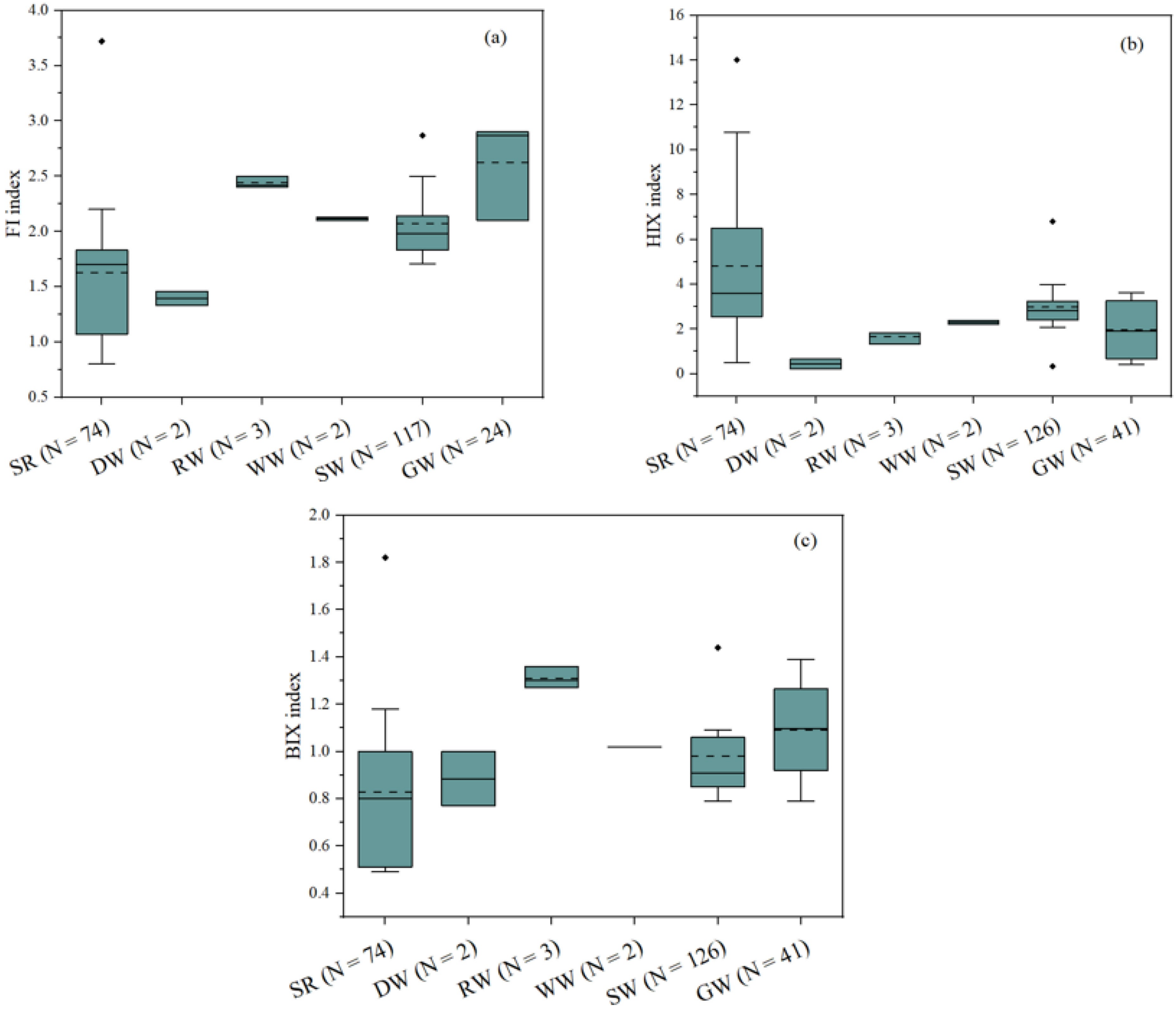

Fig. 7 FI (a), HIX (b) and BIX (c) values of different water sources (SR: stormwater/rainwater; DW: drinking water; RW: reclaimed water; WW: wastewater; SW: surface water; GW: groundwater).

stormwater/rainwater (mean value was 1.63) and drinking water (mean value was 1.39) showed relatively lower FI values than other water sources. Since Yuan et al. (2023) have noted, an FI value close to 1.4 means that the DOM primarily derives from terrestrial sources while an FI value close to 1.9 indicates autochthonous sources. This means that compared to other water sources, DOM in stormwater/rainwater and drinking water tended to be terrestrial sources. In terms of HIX index (Fig. 7(b)), stormwater/rainwater (mean value was 4.82) showed relatively higher values than other water sources. The mean HIX values of drinking water, reclaimed water, surface water, wastewater and groundwater were 0.44, 1.66, 2.30, 2.98, and 1.97, respectively. Huguet et al. (2009) reported that a HIX value larger than 4 indicates DOM with a relatively strong humification degree. This implies that compared to other water sources, DOM in stormwater/rainwater tended to be humic-like substances. For BIX index (Fig. 7(c)), stormwater/rainwater and drinking water showed a mean value of around 0.80 while other water sources had higher BIX values. This means that other water sources might include more extracellular substances excreted by microorganisms than stormwater/rainwater and drinking water (Birdwell and Engel, 2010).

3.6 Implications for stormwater reuse, limitations and future research

According to data analysis results, it is noted that surrounding environments can significantly influence DOM characteristics in stormwater. Commercial stormwater and highway stormwater showed higher DOC concentrations with higher aromaticity than urban village and residential areas. Additionally, commercial stormwater and highway stormwater contained a large amount of humus related organic substances, which means they had a high humification while residential stormwater and urban village stormwater had a higher fraction of DOM recently generated by microorganisms. The results also indicated that although stormwater was sourced from different land uses, they all had the highest percentage of DOM less than 1 kDa and tended to be hydrophilic. These characteristics mean that DOM in stormwater is hard to be treated by traditional water treatment methods such as coagulation-sedimentation because of low molecular weight and low octanol-water partition coefficient. This would lead to a high DBPs formation potential after chlorination disinfection during stormwater reuse. These outcomes implied that carefully selecting stormwater is highly needed to ensure reuse safety since DOM characteristics in stormwater are highly influenced by surrounding environments such as land uses, traffic characteristics and population density. Land uses with high traffic volume and population density could generate stormwater which contained high DOC concentrations with high aromaticity and hence could lead to high DBPs formation potential.

Furthermore, as shown in this study, DOM is widely present in the stormwater. To ensure its reuse safety, it is necessary to properly treat stormwater before its reuse, particularly effectively removing DOM and hence reduce DBPs formation potential. For example, low impact development systems (LID)/Sponge City facilities (commonly used in China) such as raingarden, swales, bioretention basins and constructed wetlands can be used to remove DOM in the stormwater. LID and Sponge City facilities are nature-based solutions, capable of removing various organic pollutants by soil infiltration and plant intake (Jia et al., 2017). This would benefit to reduce DOM amounts in stormwater runoff. When the stormwater enters drinking water sources and experiences following chlorination disinfection, DBPs formation would decrease.

Compared with other water sources in China, stormwater/rainwater showed different DOM characteristics such as higher humification and less extracellular substances generated by microorganisms. Stormwater/rainwater also showed higher hydrophilicity, compared to other water sources. However, all water sources investigated in this study had a high fraction of low molecular weight DOM, such as < 1 kDa. This means that most organic matter present in water sources are small molecular. These implied that appropriate treatment approach selection should consider DOM characteristics in these water sources. A “one-size-fits-all” treatment strategy could lead to failure and hence undermine water source utilization safety.

It is noteworthy that this study only focused on four different land uses and one rainfall event. Future research may look at more types of land uses and monitor more rainfall events with different characteristics such as various rainfall intensities and rainfall durations. Other influential factors such as temperature and vegetations are also recommended to consider in future research. This will provide a more comprehensive understanding of DOM characteristics of stormwater. Additionally, this study only focused on DOM characteristics of stormwater and has not investigated how these DOM characteristics influence DBPs formation. Therefore, chlorination disinfection is recommended to undertake for stormwater from different land uses and rainfall events in the future and

DBPs formation should be investigated as well. This can further provide useful insight to stormwater reuse strategy implementation. This study did not analyze the influence of DOM characteristics on their treatment efficiency, either. This can be one of future research directions since the relevant research results can guide an effective DOM removal and hence limit DBPs formation. Furthermore, this study focused on urban road stormwater. In fact, roof stormwater is also one of the most important alternative water sources. Roof stormwater primarily includes pollutants from the atmosphere and roof surfaces. This could lead to difference in DOM characteristics, compared to road stormwater. Therefore, investigating DOM characteristics in roof stormwater is also recommended for future research.

4 Conclusions

This study investigated DOM characteristics in stormwater from different urban land uses, namely highway, commercial area, urban village and residential area. DOM characteristics including concentrations, aromaticity, molecular weight distribution, hydrophilicity/hydrophobicity and substances compositions were investigated. The outcomes showed that stormwater from different land uses had different DOM characteristics. Commercial stormwater and highway stormwater showed higher DOC concentrations with higher aromaticity than urban village and residential areas. Additionally, commercial stormwater and highway stormwater contained a large amount of humus related organic substances while residential stormwater and urban village stormwater had a higher fraction of DOM recently generated by microorganisms. However, all stormwater samples showed the highest percentage of low molecular weight DOM (< 1 kDa) as well as tended to be hydrophilic. These DOM characteristics can influence DBPs formation after chlorination disinfection during stormwater reuse. Compared with other water sources in China, DOM in stormwater /rainwater showed higher humification and less extracellular substances generated by microorganisms. Stormwater/rainwater also tended to be more hydrophilic (hydrophilic percentages were 50.77%–93.73%) than other water sources. However, all water sources included a very high fraction of low molecular weight DOM. The research outcomes filled a knowledge gap on DOM characteristics of stormwater from different land uses, which is the novelty of this study. Results were expected to contribute a good understanding of DOM characteristics in urban stormwater and hence ensure stormwater reuse safety. It is also noteworthy that to minimize other influential factors' distraction, this study only collected stormwater runoff samples from one rainfall event. This might create a certain uncertainty of understanding this study's outcomes. Therefore, future research should focus on various rainfall characteristics to provide more comprehensive results.

Conflict of Interests The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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